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Spis treści

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Prof. dr hab. inż.
CZESŁAW SZAFRAŃSKI
07.02.1953–17.01.2015

Z głębokim żalem pożegnaliśmy zmarłego 17 stycznia 2015 roku Prorektora ds. Kadr i Rozwoju Uniwersytetu Przyrodniczego w Poznaniu Prof. zw. dr. hab. inż. Czesława Szafrańskiego.

Był wybitnym specjalistą w zakresie kształtowania środowiska. Głównym obszarem jego działalności naukowej były melioracje i gospodarka wodna gleb – bardzo liczne publikacje m.in. w Roczniku Ochrona Środowiska.

Pełnił funkcję Dziekana Wydziału Melioracji i Inżynierii Środowiska Uniwersytetu Przyrodniczego w Poznaniu (2002–2008), Kierownika Katedry, Dyrektora Instytutu Melioracji, Kształtowania Środowiska i Geodezji (1994–2015).

Był aktywnym członkiem m.in. Polskiego Towarzystwa Melioracyjnego, Komitetu Melioracji i Inżynierii Środowiska Rolniczego PAN, Komisji Badań Czwartorzędu „Oddziału Poznańskiego” PAN.

Za wybitne osiągnięcia naukowe, organizacyjne i dydaktyczne Profesor Czesław Szafrański został odznaczony Krzyżem Kawalerskim Orderu Odrodzenia Polski, Złotym Krzyżem Zasługi oraz Medalem Komisji Edukacji Narodowej.

Był dobrym i bardzo życzliwym człowiekiem. Nauka polska poniosła ogromną stratę. Cześć Jego pamięci.

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Where Is the World Heading? Social Crisis Created by Promotion of Biofuels and Nowadays Liberal Capitalism

Lucjan Pawłowski
Lublin University of Technology

Introduction

The starting point for our discussion is the statement that rapid technical and technological development gave the modern man immense power, which enables him to transform the world virtually to an unlimited degree, including its destruction. Therefore, the reasons of escalating ecological (as well as social) crisis should be sought in the dominant socio-economic model [1–5].

Conferences organized since 2005 by Professor Tadeusz Piecuch (Annual Set The Environmental Protection 2005–2014) focus on environmental engineering, which creates technical devices for shaping and protecting the environment. I believe that the development of this science provides ever-improving tools for preventing the degradation of environment and undoing harm done by people. However, it turns out that modern man does not always take advantage of these abilities appropriately [6–10].

In Poland, the beginnings of environmental engineering in its present understanding can be traced back to the 1980s, while its predecessor – sanitary engineering – to the 19th century. Some actions associated with the modern environmental engineering can already be found in the ancient times. Sanskrit – scripture of ancient Hindu – prescribes filtration of water through gravel and heating in the Sun's rays in order to make it suitable for drinking. The Ancient Chinese added ash from dried leaves to water and invented tea through experimentation. In our culture, a well-known description is found in the Book of Exodus (march from the Red Sea to Mt. Sinai). It recounts the story of Moses leading Jews through a desert, who encountered springs of undrinkable water on his way. Moses cut the branches of a shrub and tossed them into water, thus purifying it. Recently conducted research showed that on Sinai desert, there is a shrub containing oxalic acid. The acid from the sap of cut branches caused precipitation of calcium and magnesium ions, resulting in partial desalination of water. Hence, Moses was the first person to employ water desalination for the purpose of consumption.

By and large, up until the 15th century epidemic outbreaks ravaged Europe, e.g. plague, which broke out in the 14th century killed over 30% of population.

It is commonly assumed that the advances in health protection are due to the development in medicine. Few people realize that the greatest breakthrough in that field was made by sanitary engineers who introduced covered sanitary sewers and supplied clean drinking water.

Removal of pollutants and water supply is well-established from the technical point of view. Therefore, if so many people suffer from the shortage of clean water, it is not due to insufficient technical knowledge, but rather from the lack of adequate socio-economic solutions.

In his book, Professor T. Piecuch, along with minister Gawłowski [11], showed that energy supply will be the main problem in the next several dozen years. On the one hand, modern world will not be able to function without sufficient supply of energy; on the other hand, all the major issues concerning both the natural and social environment occur during the gathering, processing and use of energy.

Energy versus climatic changes

One of the greatest dangers connected with the gathering and processing of primal energy sources is the CO_2 emission from the combustion of fossil fuels and its impact on the climatic changes. The greenhouse gases emitted to the atmosphere, mainly CO_2 and CH_4, as well as steam, retain heat radiated from the surface of Earth. This phenomenon is not negative on its own, as without it the average temperature on Earth would amount to –14.5 C°.

The problem is that the CO_2 emission caused by the combustion of fossil fuels is constantly on the rise since the times of Industrial Revolution. While the CO_2 concentration equaled 278 ± 5 ppm in 1759 m, it reached 390 ± 0.1 ppm in 2011 [12].

IPCC reports [11,12] unequivocally indicate CO_2 as the main factor of increasing temperature on Earth to the point of threatening the stability of planet's ecosystem. It is worth noting that Lindzen, an outstanding American climatologist [13] does not question the impact of CO_2 concentration on the temperature increase; however, he points out that this influence is an order of magnitude lower than assumed. This statement is important because the preventive measures employed in order to mitigate the greenhouse effect, especially in the European Union, are relatively expensive and may negatively impact the economy of member states, as they mainly focus on significant changes in energy policy.

It should be noted that the global anthropogenic CO_2 emission in 2013 amounted to 9.5±0.8 billion tons of CO_2 per year [12], whereas the combined breathing emission of people, animals and plants was many times greater and equalled 119±1 billion tons of CCO_2/year in 2013. These values are significantly higher and therefore, focusing solely on the energy policy seems to be irrational, especially as some of the actions recommended in that field raise concerns.

Characteristic of energy sources

While the greenhouse effect is a commonly known phenomenon, fewer people realize that the main fossil fuels and non-renewable Earth resources are rapidly depleted, which constitutes greater danger for the existence of our civilization. A few examples include: with the current rate of consumption, the reserves of crude oil will suffice for 40–50 years, natural gas: for 60–70 years, coal: 140–150 years, uranium: probably for 140–150 years. While analyzing the supply of primal energy source materials it must be stated that in Poland, it is impossible to cease using coal in the nearest 20–30 years without major social consequences.

Nuclear power is an important source of primal energy in the world scale. With the current use of conventional reactors the known deposits of uranium will suffice for approximately 140 years. If the breeder reactors were used, availability of uranium for electric energy production would lengthen to hundreds of years. The problem is that breeder reactors produce plutonium, which can easily be used in the construction of an atomic bomb. That is why breeder reactors are used nowadays only for military purposes.

High hopes are put into the travelling-wave reactor developed by an American company TerraPower. In this type of reactor, breeding nuclear reaction is initiated in the core, then the energy-generating fission-zone advances steadily through the core for as long as several dozen years. Such solution enables enclosing the fuel rods in a sealed reactor for the period of several dozen years, which significantly limits the availability of fission materials. TerraPower informed that the first reactor of this type, with the output of 100 MW will be launched in 2015. It seems that the developments in nuclear power may provide sufficient energy supply. A lot of attention is drawn into so called renewable energy sources, such as: solar energy (thermal, photovoltaic) [14,15], Earth internal energy (geothermal), falling water and tidal energy, energy from waste [16,16] and widely-advertised biomass energy. However, utilizing biomass as a source of energy becomes problematic due to environmental and social issues connected with its application.

Consequences of bio-fuel application

While discussing the environmental protection, we usually think about the natural environment and that is where the protective actions aim at. The human environment, with its important component – socio-economic conditions – is usually forgotten about. The afore-mentioned bio-fuel utilization is an example of overlooking the socio-economic conditions.

Focusing of energy policy only on counter-acting the CO_2 emission threatens the sustainable development of the world. One of the most essential sustainable development paradigms is the intra-generational justice, which prescribes equal access to basic resources, including food, to all people. Despite appeals, almost 1 billion people in the world still suffer from starvation. It turns out that the directive signed by European Union in 2009, which enforces 10% share of biofuels in transportation by 2020, might threaten the sustainable development paradigm of intra-generational justice without having a significant effect on mitigating CO_2 emission, as the production of biofuels both increases prices of food and lowers its production.

Competition with food production industry

The food demand will continue to increase for two reasons: growing human population and greater number of better-fed people. Meanwhile, 250 thousand people starve to death each day, while 780 million people in developing countries and 27 million people in developed countries are malnourished. With this status quo, devoting large areas of land for the biomass used in fuel production raises moral concerns. This is especially relevant in the context of biofuels from agriculture. According to the European Commission decision from 2009, as much as 10% of energy used in transportation should be obtained from biofuels made from food crops. In order to make biofuels a viable solution, European governments subsidize powerful industrial and agricultural lobbies. For instance, by 2020 each person in Great Britain will pay approximately £35 per year (£1-2 billion in total) for biofuel subsidies, while in Germany – roughly €30 (€1.4–2.2 billion in total).

Also in the United States, the production of ethanol (mainly from corn) which is used as fuel additive developed rapidly thanks to subsidies. In 2011, as much as 127 million tons of corn, i.e. 40% of annual production was devoted for bioethanol production. Allocating such a great amount of corn for ethanol production in 2007–2012 caused a 100% increase in the prices of corn. Large import of crops for biofuels by the European Union caused a dramatic 2.5-fold increase in the food price index. The increase in food prices is especially severely felt by poor people, who spend most of their income on this basic commodity.

In the light of the above-mentioned statements, utilizing biomass from agricultural crops as a source of energy endangers the implementation of sustainable development, as it violates the intra-generational justice paradigm by limiting the access to food for the poor.

Effect of biofuels on the greenhouse gases emission

The promotion of biofuels is based on an erroneous assumption that their combustion releases equal amount of CO_2 to the one absorbed earlier by plants. This oversimplification does not take into consideration the entire biofuel production cycle. The effects of land use and energy outlays for the cultivation and processing of biomass used in fuel production are omitted in the calculations.

A lot of pressure put on the usage of biofuel in transportation, exerted especially by the European Union policy, resulted in the deforestation of tropical forests and cultivation of biofuel plants – especially in the developing countries. According to the research conducted by Danielsen et al., the absorption of CO_2 by tropical forests is much greater than the one of plants grown in their place. Consequently, the biofuel production decreases CO_2 absorption on the lands of felled tropical forests. Transforming tropical forests and moors for the cultivation of biofuel plants leads to an additional emission of 55 Mg CO_2 annually per hectare for the period of 120 years. Therefore, the usage of agricultural biofuels usually does not mitigate CO_2 emission.

Moreover, in order to produce biofuel, e.g. corn bioethanol, it is necessary to provide power for the cultivation, fertilizer production, plant collection, as well as fuel processing through fermentation and distillation. By using the life cycle assessment technique, it was shown that the amount of the emitted CO_2 per unit of energy obtained from corn ethanol is 60% greater in relation to the CO_2 amount emitted in combustion of the equivalent petroleum-based fuels. Even in the case of sugar cane ethanol produced in Brazil, where the industry is most advanced and where the leftover biomass is entirely used, e.g. sugar cane stalks are burned for heat energy; it was not possible to decrease CO_2 to a lower level than the one of oil-based liquid fuels.

However, in the case of Brazil, the development in sugar cane ethanol helped to create approximately 700 thousand new jobs, which can be considered a positive effect increasing the social sustainability. It allowed Brazil to become independent from the liquid fuels import, and the price of ethanol is competitive to the one of petrol. In Brazil, it was possible to achieve sustainable access to liquid fuels in transportation; still, the emission of CO_2 did not decrease. However, this case is exceptional.

The full analysis of production cycle showed that cultivation of some plants for biofuel production, such as rape, requires application of large amount of fertilizers which increase the emission of another greenhouse gas; namely, nitrous oxide, thus contributing to the greenhouse effect. In the case of rape, the nitrous oxide may increase the greenhouse effect by as much as 70%.

Assessment of biofuels in the aspect energy efficiency

According to the research by Professor Piementel from Cornell University [18], the amount of energy consumed in bioethanol production is greater than the one obtained by combustion in car engines.

In the process of corn ethanol production, 29% more energy is consumed than obtained, in the case of grass ethanol – 45%, wood ethanol – 57%.

The situation is similar in the case of biodiesel, which is produced from soybeans. Here, 27% more energy is consumed than generated, and when biodiesel is produced from sunflower seeds, this value increases up to 118%. The data presented above shows that in the United States (and probably other developed countries as well), utilizing plants in liquid fuel production is not sustainable, because – conversely – it increases both the consumption of fossil fuels and CO_2 emission.

Impact of biofuels on the environment

The development of biofuel plant cultivation destroys habitats and biological diversity.

More than half of land animal species live in tropical forests. The forests in south-eastern Asia, which provide habitats for a plethora of various organisms, are the most endangered by the biofuel plant plantations. The tropical forests absorb roughly 46% of carbon dioxide found in the atmosphere. Their destruction may increase the carbon dioxide concentration by 25%.

Hence, there is an internal contradiction in devoting tropical forests for the cultivation of plants for so called low-carbon fuels. It is estimated that the number of species living in the area decreases fivefold when forests are cut and turned into biofuel plantations.

Production of liquid biofuels for the transportation also has a negative impact on the aquatic environment due to a high consumption of water both for watering plants and during processing to biofuels. Moreover, the processing involves production of large quantities of hazardous wastewater, e.g. production of 1 litre of ethanol is tantamount to 6–12 litres of highly contaminated sewage. Meanwhile, water shortage is already negatively influencing food production.

Generally, approximately 2500 litres of water are used in order to obtain 1 litre of biofuel. Such amount of water is enough to produce food for one person. In order to irrigate 30,000,000 hectares of land for biofuel cultivation, roughly 180km^3 of fresh water will need to be used. One must bear in mind that due to the growth of population to 8.3 billion in 2030 (from 7.2 billion in 2012), food, water and energy demand will increase by 35%, 40% and 50%, respectively.

Large monocultures, which are usually employed in the case of biofuel plants, require wide application of herbicides and pesticides, which then infiltrate to ground waters – contaminating them. Soybean farming in Brazil is an example of a negative effect of pesticides. Along with herbicides, they are used on a large scale in the Pantanal wetland, which constitutes one of the most important habitats for hundreds of birds, mammals and reptiles. Another example includes 20,000 hectare sugar cane plantation, intended for ethanol production, which is located in the delta of Tana River in Kenia. With the planned water uptake of 1680 m^3 water/min, which equals 30% of river flow rate, it seriously threatens the local ecosystem which is a habitat to 345 species of water and marsh birds.

Socio-economic conditions of the present crisis

Advancements in the energy supply is commonly associated with the technical and technological development. Problems related with the utilization of biofuels indicate however that the increasing lack of balance in the development of the modern world is caused by the prevailing socioeconomic system which assumes unlimited domination of free market that degrades human and his needs to the level of mere tools for its development. According to this widely-held doctrine, it is human who should serve economy, not the other way around, thus making it some kind of supreme entity.

Evolution of socioeconomic environment in present times

From a practical point of view the quality of life is determined by the availability of basic goods necessary for life, the quality of the natural environment, and human relationships determined by the sociopolitical system. The problem is that, since the times of President Ronald Reagan, there has been a gradual deterioration of socioeconomic relations, whilst the difference in living standards and incomes has risen sharply. Undoubtedly, the rise of capitalism caused an accelerated development of production. Initially, an enormous diversity in society was observed. Employees, particularly manual workers were deprived of any rights, even the right to a guaranteed minimum living wage. In response to this, movements arose, calling for a fairer distribution of wealth. The encyclical *Rerum Novarum*, issued by Pope Leo XIII was a notable voice, due to the importance of the institution. At the same time, socialist movements also arose calling for equality and social justice. Consequently, this led to the rise of trade unions in the first half of the nineteenth century which, with their increasing power, significantly influenced the transformation of the state's role in the direction of a national welfare state, towards the end of the first half of the twentieth century. These *changes* – because it is difficult to call them Reforms (as reforms have a positive connotation) – whose creators were President Ronald Reagan and Prime Minister Margaret Thatcher, reduced the role of traditional unions, which led to a recurrence of unjustified inequalities and to a direct rise in large groups of people thrown onto the side-line. As intra-generational justice is one of the basic paradigms of sustainable development, it is worth looking at modern civilization of liberal capitalism from this viewpoint. This issue has been repeatedly raised in the journal entitled Problemy Ekorozwoju/Problems of Sustainable Development.

The cause of this state of affairs was seen as the inadequate development of social sciences and humanities [13–21].

In my assessment, today's (rising inequalities) and future threats (the overexploitation of the rapidly depleting natural resources, progressive degradation of the environment) indicate that modern civilization is developing in an unsustainable way. In the next section I will attempt to point out the causes.

Causes of unsustainability

The paradigm of modern liberal capitalism is the immense greed of the elite financial to accumulate wealth at all cost, through the principle of *grow or die*. Capital can be accumulated by using the Earth's resources and human labour. I have already mentioned the trade unions which, by the mid twentieth century, led to a balance in society between capital and the workers on the one hand, and also – through the strong role of the state – imposed the high standards of environmental protection on the other. This was possible because the power of the capital was offset by the power of the state where trade unions represented the workers [1–19].

The state began its withdrawal, from the time of Ronald Reagan and Margaret Thatcher, in line with the *less state* slogan, which was also propagated in Poland. The weakened trade unions were not able to oppose this trend in many countries. The withdrawal of the state and the rise of multinational corporations have meant the loss not only of the element protecting workers, but also of such issues as environmental protection, protection of working rights, the rationalised consumption of the Earth's non-renewable resources.

Basically, there is no sufficiently powerful partner who could play a regulatory role in relation to the international corporations, whose sole purpose is profit. That is why production is so easily transferred from countries with greater social and environmental safeguards to countries where these regulations are more liberal. Consequently, despite huge increases in productivity, poverty in the world has not been reduced, whilst the number of excluded people continues to grow. Thus, it follows that for a global economy there is also a need for a powerful transnational partner, who would have the instruments to control and enforce pro-social and pro-environmental behaviours in accordance with the principle of sustainable development. Deregulation of the financial markets and large-scale privatisation of banks, as initiated by Ronald Reagan and Margaret Thatcher, is an even worse evil. This allowed for financial speculation and its detachment from production, unprecedented in human history. In the recent years, it was mainly the financial markets which caused the appropriation of most of the revenues as a result of speculation – prof. Brunnhuber from Club of Rome showed that as much as 98% money translations are pure speculations. Yet, these missing vast sums have been transferred somewhere. It is even more outrageous that as a result of these massive transfers, no added value has been created as opposed to production processes.

The deregulation of financial markets, allowing for speculation of money on an unprecedented scale in the history of mankind, is the main cause of inequalities. A new class has emerged, managing corporations and financial institutions on an international scale, with exorbitant incomes, which through links with the political elite does not bear any responsibility. An example in Poland are the notorious pension funds (OFE), so eagerly introduced by the Jerzy Buzek's government, whose boards receive generous rewards regardless of the results. Insomuch, voices are being heard, calling for a return of the welfare state [19–22], all the more, as the Scandinavian countries were not submissive to the Reagan-Thatcherite ideology and function quite satisfactorily as countries with a developed social policy.

Is globalisation compatible with sustainable development?

The creators of modern liberal capitalism extol globalisation, pointing out the positives arising from the creation of an international (borderless) market economy. Meanwhile, as demonstrated by Fotopolous [23], the opening and liberalisation of the markets was carried out in the interests of the world's financial elite, who control the market economies. Its purpose was, and is, to minimize social control over the market, particularly of those who, like the trade unions, are trying to safeguard workers' interests and environmental protection. This in turn becomes an obstacle to increasing economic efficiency and increased profits. Free movement of capital and goods across borders required the liberalisation of all the markets in order to minimise the role of the states, which are capable of effective control, protecting workers and the environment on their territory. However, on an international scale, corporations do not have a sufficiently powerful controller.

Consequently, according to a report by the International Labour Organisation (ILO), globalisation repeatedly leads to fast growing inequalities, creating a superrich elite, and side-lining increasingly larger groups of people.

This phenomenon occurs particularly strongly after 1990. This way, socialist ideas created in the East, or the social democratic ideas created in the West (equality and social justice) are pushed out of the modern civilization.

Conclusions

Modern civilization is developing in an unbalanced way. Without proper control, free market and liberalisation associated with globalisation lead to a fast, if not an exponential, rise in inequality. This is facilitated by the lack of sufficiently strong employee representation on an international forum, thus causing a direct increase in poverty. Simultaneously, the lack of proper control of international corporations causes an irrationally rapid depletion of Earth's non-renewable resources and degradation of the environment.

The financial markets are a big threat to the world's stability, where speculation leads to acquiring vast sums of money without creating any added value. The slogan *less state* only serves big international capital, leaving most citizens without adequate safeguards. It is essential to work on replacing the gross national product with a newly defined indicator, as a measure of development, which will determine the quality of life, taking into account the sustainability of the socioeconomic system: permitting full compliance of environmental quality, and the degree of consumption of the Earth's resources on the one hand, and the welfare of all citizens on the other. Just as in the nineteenth century, the spectre of unemployment is beginning to appear. This requires studies to be performed on how to change the organisation of socioeconomic systems. An unemployment rate of 20–30% among young people is practically a humanitarian disaster. It acts degradingly on people affected by it, even more so than living in a degraded environment.

References

1. **Ikerd J.:** *Sustainable Capitalism: A matter of ethics and morality.* Problemy Ekorozowju/Problems of Sustainable development. 3(1), 13–22 (2008).
2. **Habermas J.:** *What does a crisis mean today? Legitimation problems in late capitalism.* Social Research. 40(4), 643–667 (1973).
3. **Spychalski G.:** *Wyzwania kryzysowe na tle ewolucji kapitalizmu z uwzględnieniem uwarunkowań środowiskowych.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 780–792 (2013).
4. **Deluga W.:** *Grupa Energetyczna Energa na krajowym rynku energii.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 944–965 (2013).
5. **Borkowski P., Borkowski, J., Bielecki, M.:** *Production of ecological fuel from charcoal using high pressure water jet.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 167–180 (2013).

6. **Michnowski L.:** *Renewed EU Sustainable Development Strategy: what does it mean for Poland?* Problemy Ekorozwoju/Problems of Sustainable Development. 3(2), 1–13 (2008).
7. **Wagner P.:** *The democratic crisis of capitalism: refelctions on political and economic modernity in Europe.* London School of Economic. 44 (2011).
8. **Meadowcroft J.:** *Environmental and Political Theory: Toward an Ecocentric Approach*. Robyn Eckersley Albany: State University of New York Press. Canadian Journal of Political Science. 26(2), 420–421 (1993).
9. **Piecuch I., Hewelt G.:** *Environmental Education – first knowledge and then the habit of environment protection.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 136–150 (2013).
10. **Piecuch I., Piecuch T.:** *Environmental education and its social effects.* Rocznik ochrony Środowiska (Annual Set the Environment Protection). 15, 192–212 (2013).
11. **Gawłowski L., Listowska-Gawłowska R., Piecuch T.:** *Bezpieczeństwo Energetyczne Kraju*. Monografia nr 1787, Wydział Budownictwa i Inżynierii Środowiska, Koszalin 2011.
12. **IPCC 2013**, Fifth Assessment Report – Climate Change 2013.
13. **Lindzen R.:** *Global Warming: The origin and nature of the alleged scientific consensus?* Problemy Ekorozwoju/Problems of Sustainable Development. 5(2), 13–28 (2010).
14. **Żelazna A.:** *The influence of collector type on emission indicators in solar systems life cycle assessment.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 258–271 (2013).
15. **Gułkowski S., Olchowik J. M.:** *Computer modeling in cost-efficient solar cell production technology.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 436–447 (2013).
16. **Wystalska K., Sobik-Szołtysek J., Bień J. B.:** *Vitrification and devitrification of ash after sewage sludge combustion.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 181–191 (2013).
17. **Czechowska-Kosacka A.:** *Sewage sludge as a source of renewable energy.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 314–323 (2013).
18. **Piementel D.:** *Energy Production from Maize.* Problemy Ekorozwoju/Problems of Sustainable Development. 7(2), 15–22 (2012).
19. **Gawor L.:** *Filozofia zrównoważonego rozwoju – preliminaria.* Problemy Ekorozwoju/Problems of Sustainable Development. 5(2), 69–76 (2010).
20. **Tuziak A.:** *Socio-Economic Aspects of Sustainable Development on Global and Local Level.* Problemy Ekorozwoju/Problems of Sustainable Development. 5(2), 39–49 (2010).

21. **Hueting R.:** *Ekologicznie zrównoważony dochód narodowy i inne sposoby metody poprawy jakości informacji na temat wzrostu gospodarczego*. Problemy Ekorozwoju/Problems of Sustainable Development. 6(1), 31–46 (2011).
22. **Liszewski D.:** *Etyczne podstawy rozwoju zrównoważonego.* Problemy Ekorozwoju/Problems of Sustainable Development. 2(1), 27–33 (2007).
23. **Fotopoulous T.:** *Is Growth Compatabile with a Market Economy.* International Journal of Inclusive Democracy. 3(1), 13–28 (2007).

Dokąd zmierza świat? Kryzys społeczny stworzony przez promocję biopaliw i współczesny liberalny kapitalizm

Streszczenie

Człowiek współczesny dzięki rozwojowi techniki i technologii jest zdolny praktycznie do dowolnego przekształcania świata, nie wyłączając jego zagłady. Jeśli zatem obserwuje się narastający kryzys ekologiczny to jego przyczyny należy doszukiwać się w dominującym obecnie modelu społeczno-ekonomicznym opartym na idei liberalnego kapitalizmu, w którym dominującą pozycje zajęły międzynarodowe korporacje. Osłabione przez Prezydenta R. Regana i premier M. Thatcher związki zawodowe nie są w stanie równoważyć siły tych korporacji. W konsekwencji w większości krajów lawinowo rosną nierówności. Zachodzące przemiany zostały zilustrowane na przykładzie zaopatrzenie w energie. Rozwój niekontrolowanego rynku biopaliw doprowadził do 2,5-krotnego wzrostu cen żywności w sytuacji kiedy ponad 1 mld ludzi głoduje. Zakładane wielkoobszarowe plantacje roślin przeznaczonych na biopaliwa, przyczyniają się do poważnych negatywnych zmian w środowisku w krajach rozwijających się. Co gorsze ich stosowanie w większości przypadków nie przyczynia się do redukcji emisji CO_2.

Słowa kluczowe:
zrównoważony rozwój, kryzys ekologiczny, kryzys społeczny, polityka energetyczna, efekt cieplarniany

Keywords:
sustainable development, ecological crisis, social crisis, energetical policy, greenhouse effect.

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Application of Cluster Analysis in Defining the Meteorological Conditions Shaping the Variability of PM10 Concentration

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1. Introduction

Particulate matter is a complex mixture of solid, liquid and gaseous particles which, due to high degree of dispersion, can linger suspended in atmosphere for a long time. Two main fractions of particulate matter are commonly distinguished: PM10 – with a diameter of particles less than10 µm, and PM 2.5 – with a diameter of particles less than 2.5 µm. The fractions differ not only in particle diameter, but also in the process of its origin, chemical composition and half life time.

The concentrations of both fractions they are being closely monitored in Poland as well in Europe due to negative health effects they may cause. The results of air quality monitoring serve as a basis for assessing air quality and spatial variability of air quality [22, 26, 28, 29]. According to recommendations of the Directive of the European Parliament and of the Council CAFÉ [8], the numerical methods for modelling of air pollution dispersion [17] are also used in order to research into the reasons behind violation of admissible standards of particulate matter concentration, including identification of individual sources or sectors of emission responsible for excessive concentrations.

Recent Report of the Inspection of Environment [26] indicates that excessive concentrations of PM10 are recorded in many regions of the country. It results from still high share of solid fuels in the structure of basic primary energy carriers in Poland, as well as the high share of ground level emission. Because of better ventilation conditions in the northern and central part of Poland smog episodes are not problematic yet in the southern part of Poland, particularly in not-easily ventilated basins and well-developed river valleys, smog episodes occur with greater frequency [25].

Apart from emission, air quality is additionally determined by meteorological factors [4, 7, 18, 27, 31]. The effect of weather can be seen in the formation of the dispersion of pollutants and in the rate of disposition. The level of pollutants dispersion depends on, among other things, the dynamics of air movement which is governed by anemometric conditions and thermal stratification within the atmospheric boundary layer. Concentration is also determined by the types of air mass [12] and type of circulation – as has been demonstrated in Małopolska and Górny Śląsk [19, 20, 30]. Precipitation also plays a significant role in the shaping of aerosanitary conditions. According to Czarnecka and Nidzgorska-Lencewicz [5], in the period of 2005–2007, mean concentration of PM10 particulate matter recorded in a series of hours and days with precipitation were, depending on a season and day, by 10–35% smaller than concentrations recorded before the precipitation occurred.

The research on the relationship between air quality and meteorological conditions makes use of various statistical methods such as: correlation, regression, cluster analysis and principal components analysis [4, 6, 9, 11, 16, 23, 31, 33]. The aim of the present paper is to single out the set of meteorological elements which affect the variability of PM10 concentration in the area of Tricity agglomeration in six winter seasons from 2004/2005 to 2009/2010, with the use of cluster analysis.

Only PM10 fraction is taken into consideration in this paper as the obligatory monitoring of PM2.5 particulate matter, as regulated by the Directive 2008/50/WE [8] of 21 May 2008, was introduced in Poland as late as at the beginning of 2010.

2. Materials and methods

Maritime industry is the basis for development but also the main source of pollution in Tricity. The metropolitan area is polluted by shipbuilding industry comprising seven shipyards, including the two largest located in Gdańsk and Gdynia, as well as seaports with ongoing production and services business. Air quality is additionally greatly affected by electrochemical and petrochemical plants, as well as food industry. Additionally, as in every metropolitan area, road transport and power and heat facilities represent important sources of air pollution.

The materials used in this study comprise measurements of immission and basic meteorological elements including air temperature, relative humidity, atmospheric pressure as well as wind speed and direction recorded during the calendar winters (December–February) in the period of 2004/2005–2009/2010. Data was obtained from five automatic air quality measuring stations located in the Tricity agglomeration and was provided by the Agency of Regional Air Quality Monitoring in the Gdańsk Metropolitan Area (**ARMAAG**). The locations of the measuring stations are shown in Fig. 5. Detailed information regarding the methodology of the measurements and elaboration of data is given at http://armaag.gda.pl/. The project of the ARMAAG monitoring network was developed under supervision of Jerzy Trapp, PhD. from the University of Gdańsk and based on longstanding research on meteorological conditions, population density and data on emission from point and surface sources. Monet software obtained by courtesy of the Politecnico di Milano and positively assessed by the Institute of Environmental Protection [34] was used in the project. All the stations located in five districts of Tricity are defined as urban background stations. However, two of them (Gdańsk Wrzeszcz and Gdynia Pogórze) are located in residential areas, and the station in Gdańsk Jasień is located in the vicinity of scattered, low-building housing developments next to the Tricity ring road. Sopot station is located in allotment area, and the station in Gdynia Śródmieście – on the harbour waterfront.

The cluster analysis method was used to estimate the amount and variability of PM10 particulate matter immission with respect to meteorological conditions. Prior to the analysis, all baseline data was standardised according to the formula [21]:

$$z = \frac{x - \bar{x}}{s} \tag{1}$$

where:
x – non-standardised variable,
$\bar{x}$ – arithmetic mean,
s – standard deviation.

Such transformation allows for comparison of values of many variables, regardless of their original distribution and units of measurement. As a result of standardisation all variables were in the range of 0 to 1.

Hierarchical clustering is used most commonly in studies on air quality [2, 6, 31, 33]. However, in this paper we use the *k*-means clustering (Euclidean distance), which belongs to a group of non-hierarchical cluster analysis methods. The mechanism implemented in STATISTICA software is based on the v-fold cross-validation, and allowed for identification of the optimal number of segments which are combinations of immission and meteorological elements. However, wind directions based on octagonal compass rose constituted a qualitative change in this analysis. K-mean clustering consisted in transferring the observations from one cluster to another in order to maximise the variations between individual clusters and at the same time minimise the variations within the analysed clusters. The significance of differences between singled out clusters was calculated with the use of analysis of variance – Fisher's test, at the level of $p \leq 0.05$.

The complex influence of meteorological conditions on the variability of particulate matter concentration in selected clusters was determined by linear multiple regression, using a stepwise procedure, at the significance level $p \leq 0.05$. The contributions of individual weather elements in explaining the size of the concentrations were determined using the partial regression coefficients. All calculations were performed using the STATISTICA 10 software.

3. Results and discussion

The winter seasons in the years 2004–2010 were characterized by contrastive thermal conditions (Fig. 1). Only in two of the winter periods, namely in 2005/2006 and 2009/2010, mean temperature of the three winter months (December–February) was below 0°C and amounted to -1.7 and -2.5°C respectively. Moreover, it was well below the average. The temperature in the remaining winter seasons was above 0°C, and two winter seasons (2006/2007 and 2007/2008) were particular ly warm with mean temperature over 3°C. The variability of mean temperature recorded in Tricity metropolitan area during the three winter months amounted to approximately 2°C – Sopot being the warmest district and Gdańsk

Jasień the coldest. The distribution of PM10 concentration in the six analysed winter periods markedly indicates the influence of heating on the variability of pollutants concentration. In two cold winter periods mean concentrations of PM10 exceeded 40 µg·m^{-3}, whereas in the overly warm winter periods the concentration was two times lower (Fig. 1).

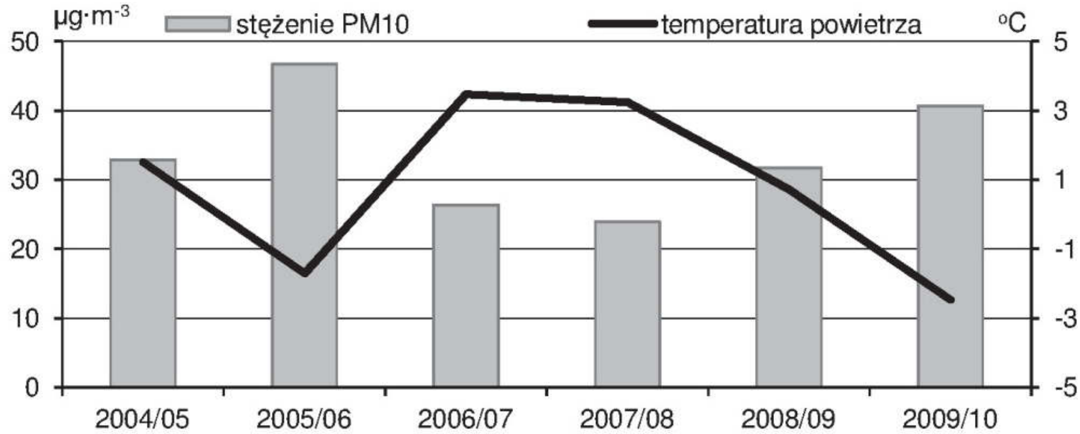

Fig. 1. Average seasonal (December-February) the concentration of PM10 and the air temperature in the Tricity urban area
Rys. 1. Średnie sezonowe (grudzień–luty) stężenia pyłu zawieszonego PM10 oraz temperatury powietrza w Trójmieście

As shown in Fig. 2, in almost all winter seasons the daily limit of PM10 concentration was exceeded. Violation of air quality standards due to abnormal concentrations of PM10 is a problem not only in Poland. According to the *Air Quality in Europe* Report [10], Poland is located in a region where high concentrations of PM10 are recorded more often than in Western Europe.

The highest number of the violations of the standard daily PM10 concentrations were recorded in the two coldest winters, that is in the winter of 2005/2006 and 2009/2010. In the winter of 2005/2006 the standard PM10 concentration was exceeded in approximately 20–40% of cases, and in the winter of 2009/2010 in 20 to almost 50% of winter days, depending on the district of Tricity. In the winter of 2005/2006 the PM10 concentrations standards were exceeded in all districts in January, whereas in the winter of 2009/2010 in various months. Gdynia Śródmieście was the district in which PM10 concentrations standards were exceeded most often. In comparison with the other districts, the winter of

2008/2009 was marked with frequent violation of PM10 concentration standards and even in relatively warm seasons, namely 2006/2007 and 2007/2008, the standards were violated on more than 20 days. The only instance when the PM10 concentration did not exceed the standard was in the winter of 2008/2009 in Gdańsk Wrzeszcz district.

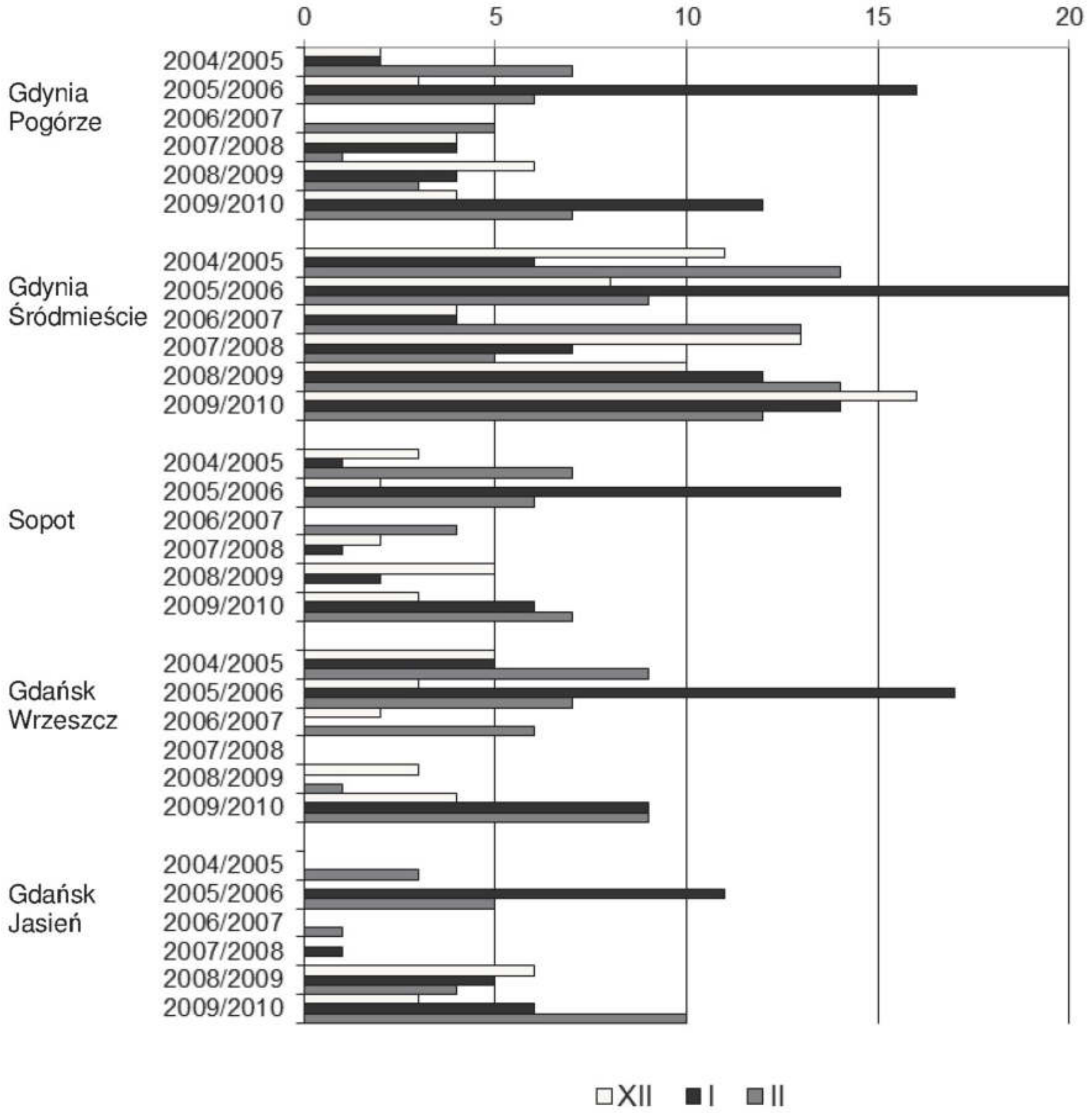

Fig. 2. Number of days with violations of the acceptable mean daily particulate matter (PM10) concentration (50 µg· m^{-3}) during December-February in years 2004/05–2009/10
Rys. 2. Liczba dni z ponadnormatywnymi dobowymi stężeniami (50 µg·m^{-3}) pyłu zawieszonego PM10 w okresie XII–II w latach 2004/05–2009/10

The factor which definitely contributes to the spatial variability of air quality is the wind which causes pollutants transport in the atmosphere. Directional compass roses presented in Fig. 3 show the wind field deformation caused by local factors such as the height of the buildings, distribution, exposure and distance between buildings, transport network or green areas [32]. Only in two districts of Tricity, i.e. Gdynia-Śródmieście and Gdańsk-Jasień, located respectively at the northernmost and south-westernmost outskirts of the agglomeration, W and SW winds prevailed. This is a characteristic feature of the open terrain of the entire region of Pomerania [1]. Due to the specific location of the station in Sopot, among low-building, densely developed, detached-house areas, on the west side of the city, and single health-resort buildings and sports facilities, to the east, the most frequently recorded winds were S-SW-SE. In Gdańsk Wrzeszcz, SE winds were predominant, and N and SE winds were reported with a similar frequency in Gdynia Pogórze. On average, the winds reached higher speeds in the districts where west winds prevailed. The coldest and the warmest parts of Tricity also exhibited contrasting wind speeds. By far the highest average winter wind speed, namely 3.3 m $s^{-1,}$ (with the lowest frequency of calms) was noted in Gdańsk Jasień, while the lowest, i.e. 2.1 m·s^{-1}, in Sopot. Calm weather usually occurred in Gdynia, with a frequency of 3.7% in both districts, while in the other parts of Tricity calms were recorded more than twice less often.

The basic values classified according to the spatial clustering method included sets of hourly measurements of PM10 concentration and meteorological data with the qualitative variable of wind direction. The results of the adopted cluster analysis are presented in Tab. 1, 2, and Fig. 4. The applied algorithm has identified, depending on the area, from 4 to 8 optimal clusters. On average, individual clusters were characterized by different wind directions, occurring with greater and even dominating frequency in comparison to other wind directions recorded in a given district (Tab. 1). Variable wind directions occurring with greatest frequency were characteristic for all identified clusters in Sopot and Gdańsk Wrzeszcz districts. In the remaining three districts of Tricity the cases with the same and most frequent wind directions were included as parts of some clusters. In Gdynia Pogórze NE winds were included into two different clusters (2 and 6); in Gdynia Śródmieście SW winds were included into clusters 3 and 7, and in Gdańsk Jasień W winds to clusters 1 and 4. In almost all identified clusters other wind directions were also observed apart from the main wind directions, yet in most districts the wind direction which was included into other clusters was N wind and additionally NW wind in Sopot and Gdańsk Wrzeszcz. The greatest variation of wind direction in all clusters was observed in Gdańsk Jasień. Winds from N-SE sectors and SW winds were included in every cluster in that district. In Gdynia Pogórze, each of the six clusters included additional E, SW and W winds. The only cluster which grouped conditions connected with S winds, was found in Gdynia Śródmieście.

The characteristics of particulate matter concentrations and meteorological factors in selected clusters are shown in Table 2. The volume of the analyzed meteorological elements in particular clusters generally reflect their well-known role in the shaping of variability of PM10 concentrations. Clusters grouping the highest or elevated particulate matter concentrations in Tricity districts were characterized, in most cases, by the lowest air temperature and lower wind speed, the greatest share of calm – conditions characteristic for a high-pressure weather. Low air temperature contributes to the intensification of district heating based on the use of traditional energy carriers, and to an increase in the emission of the conventional fuels combustion products from local coal-burning heating plants and household furnaces. Moreover, calms, mild winds and frequent inversion layers characteristic for anticyclonic weather limit the vertical and horizontal air ventilation. The increase in pollution concentration in high-pressure weather was demonstrated by Kukkonen et al. (2005), Czarnecka, Nidzgorska-Lencewicz [4], Juda-Rezler et al. [15] Unal et al. [31].

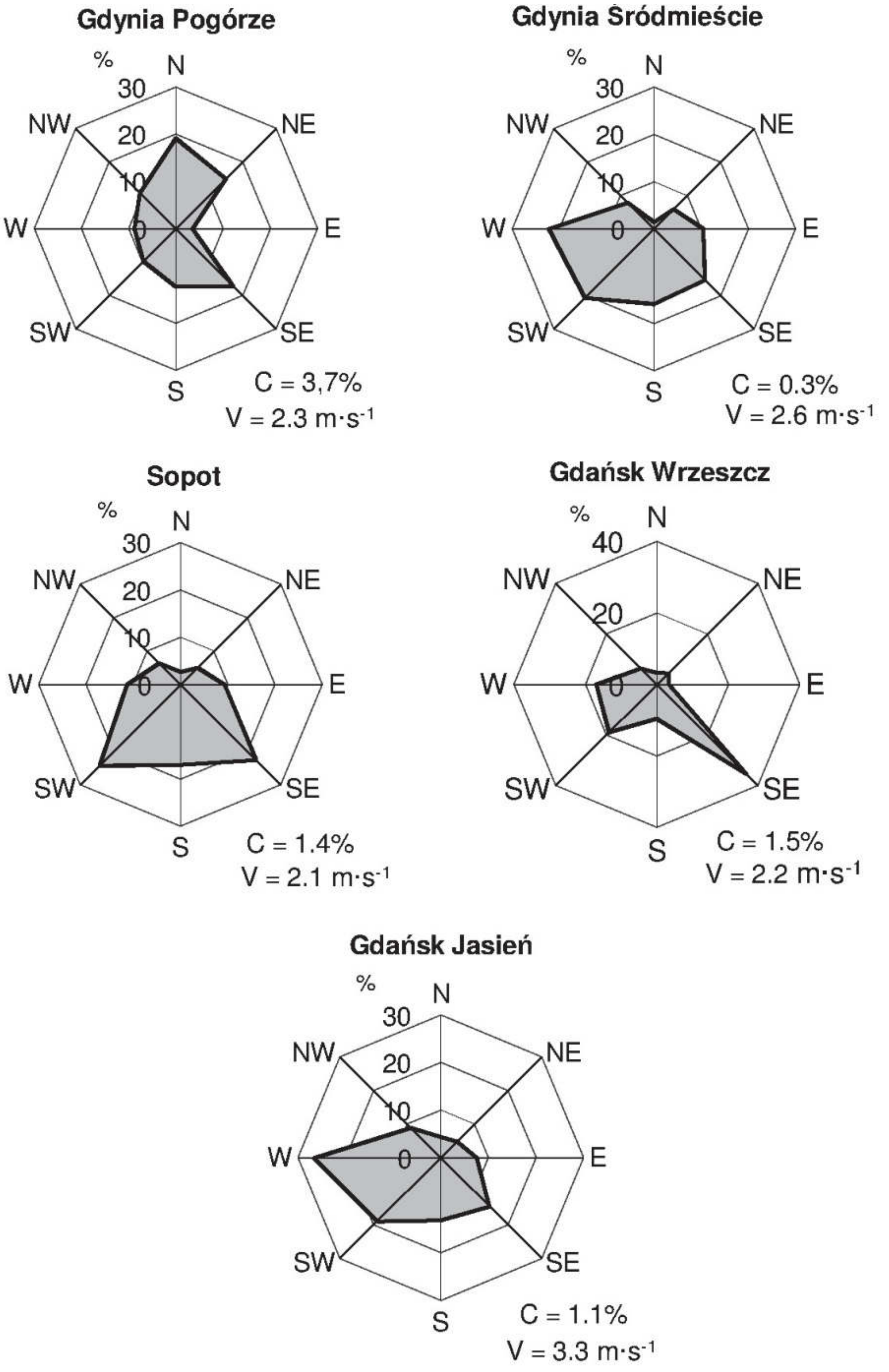

Fig. 3. Characteristics of anemometric conditions in the Tricity urban area during calendar winters (December-February). Years 2004/05–2009/10
Rys. 3. Charakterystyka warunków anemometrycznych w aglomeracji trójmiejskiej w okresie kalendarzowej zimy (XII-II). Lata 2004/05–2009/10

Table 1. Frequency (%) of wind directions and calms in distinct clusters
Tabela 1. Częstość występowania (%) kierunków wiatru i cisz atmosferycznych w wyróżnionych skupieniach

station	cluster	wind directions								calm
		N	NE	E	SE	S	SW	W	NW	
Gdynia Pogórze	1	·	·	0.3	·	·	2.3	1.4	10.8	·
	2	·	9.9	0.8	·	·	3.3	2.4	·	2.6
	3	·	·	0.7	17.3	·	0.1	0.3	·	·
	4	19.0	·	1.0	·	·	0.9	2.2	·	0.2
	5	·	·	0.8	·	12.3	2.0	1.7	·	1.0
	6	·	5.1	0.1	·	·	1.2	0.8	·	·
Gdynia Śródmieście	1	0.2	·	·	·	·	·	23.1	·	·
	2	0.2	6.0	·	·	·	·	·	·	·
	3	·	·	·	·	·	11.2	·	·	·
	4	0.1	·	·	·	14.9	·	·	·	·
	5	·	·	11.7	·	·	·	·	·	·
	6	0.1	·	·	·	·	·	·	8.0	·
	7	0.5	·	·	·	·	8.1	·	·	0.2
	8	0.1	·	·	15.5	·	·		·	0.1
Sopot	1	0.3	0.9	9.3	·	·	·	·	0.4	·
	2	0.2	0.3	·	·	16.9	·	·	0.7	0.1
	3	0.4	0.6	·	22.5	·	·	·	0.6	1.2
	4	0.5	0.8	·	·	·	·	·	1.7	0.1
	5	1.3	2.5	·	·	·	24.3	·	3.0	·
Gdańsk Wrzeszcz	1	0.5	·	·	35.4	·	·	·	0.3	·
	2	1.2	·	3.5	·	·	·	·	1.3	1.2
	3	0.1	·	·	·	·	18.9	·	0.7	·
	4	0.8	4.5	·	·	·	·	·	2.4	0.1
	5	0.1	·	·	·	·	·	17.0	0.5	·
	6	0.6	·	·	·	9.6	·	·	1.2	0.2
Gdańsk Jasień	1	0.6	1.1	2.6	3.5	·	2.0	10.8	·	0.7
	2	1.4	2.0	2.5	3.7	12.5	2.7	·	·	·
	3	1.6	1.2	2.6	5.6	·	4.6	·	9.0	0.4
	4	0.7	0.7	0.2	1.7	·	9.0	16.4	·	·

· not occur

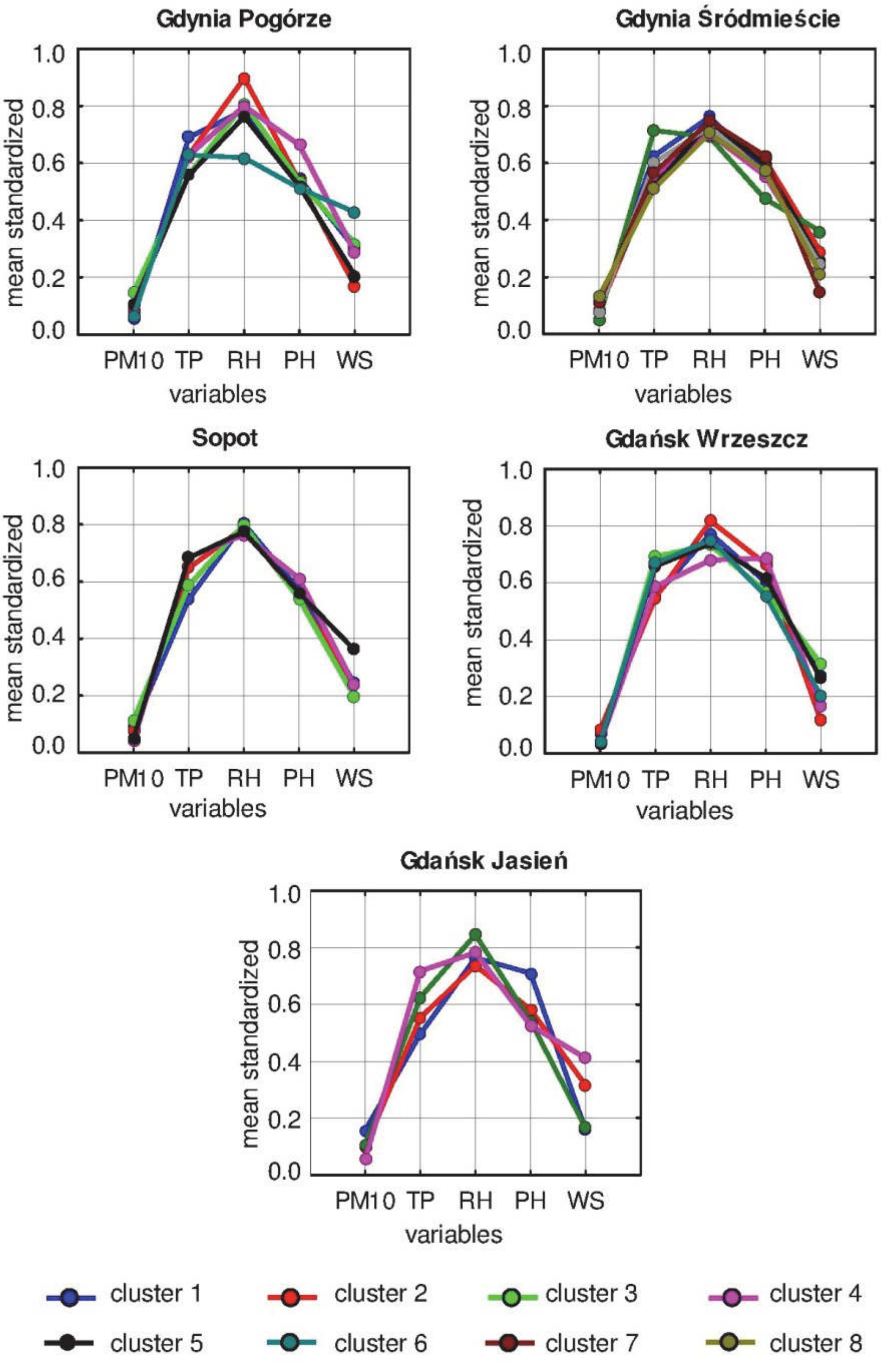

Fig. 4. Mean standardized values of particulate matter PM10 concentrations and meteorological elements for each recognized cluster

Rys. 4. Średnie standaryzowane wartości stężeń PM10 i elementów meteorologicznych dla wydzielonych skupień

Table 2. Characteristics of particulate matter (PM10) concentrations and meteorological factors in distinct clusters
Tabela 2. Charakterystyka stężeń pyłu zawieszonego PM10 i elementów meteorologicznych w wyróżnionych skupieniach

station	cluster	PM10 [$\mu g \cdot m^{-3}$]	AT [°C]	RH [%]	PH [hPa]	WS [$m \cdot s^{-1}$]	cases [%]
Gdynia Pogórze	1	19.8	4.1	85.9	1016.9	2.6	14.8
	2	27.8	2.1	93.2	1016.0	1.5	18.8
	3	48.3	-0.1	87.2	1015.9	2.8	18.3
	4	23.6	2.0	86.8	1027.3	2.5	23.1
	5	34.6	-0.2	84.3	1014.6	1.8	17.8
	6	22.4	2.2	74.8	1013.9	3.7	7.3
Gdynia Śródmieście	1	42.3	1.8	81.9	1015.6	2.7	23.3
	2	43.0	-0.7	77.7	1018.5	3.0	6.2
	3	27.4	4.6	76.7	1007.2	3.7	11.2
	4	57.5	-0.4	77.6	1013.8	2.5	15.0
	5	59.9	-1.6	80.5	1017.1	2.7	11.7
	6	39.9	1.1	79.3	1014.6	2.6	8.1
	7	57.6	-0.1	80.8	1019.4	1.6	8.8
	8	67.6	-1.8	77.6	1015.1	2.3	15.7
Sopot	1	34.1	-1.9	86.7	1011.2	1.9	10.9
	2	30.3	2.0	85.7	1008.9	1.8	18.2
	3	42.9	-0.2	86.4	1008.7	1.6	25.2
	4	16.0	3.4	84.0	1014.5	1.8	14.6
	5	19.5	3.3	84.8	1010.4	2.8	31.0

AT – air temperature; RH – relative humidity; PH – normalized pressure; WS – wind speed

Table 2. cont.
Tabela 2. cd.

station	cluster	PM10 [$\mu g \cdot m^{-3}$]	AT [°C]	RH [%]	PH [hPa]	WS [$m \cdot s^{-1}$]	cases [%]
Gdańsk Wrzeszcz	1	44.1	-1.2	86.0	1014.7	2.4	36.1
	2	50.6	-1.4	88.7	1019.8	1.1	7.1
	3	20.6	3.4	83.6	1012.2	2.8	19.7
	4	22.2	-0.1	80.4	1021.3	1.5	7.9
	5	22.1	2.3	83.9	1016.0	2.3	17.6
	6	24.5	2.7	84.7	1011.2	1.8	11.5
Gdańsk Jasień	1	43.1	-4.4	83.7	1026.4	1.9	21.4
	2	27.6	-2.3	82.1	1016.3	3.8	24.8
	3	29.9	0.2	88.7	1013.2	2.0	25.1
	4	15.6	3.4	84.9	1012.0	4.9	28.8

AT – air temperature; RH – relative humidity; PH – normalized pressure; WS – wind speed

The negative effect of winter weather conditions in high pressure systems was most prominent in Gdańsk Jasień. The greatest concentrations of particulate matter, approximately 43 $\mu g \cdot m^{-3}$, were recorded at the lowest air temperature that is -4.4°C, the lowest wind speed of 1.9 $m \cdot s^{-1}$ and highest pressure – over 1026 hPa (cluster 1). In the conditions of high, positive temperature over 3°C with twice as high wind speed and significantly lower pressure, PM10 concentration was almost 2.5 times lower (cluster 4). Also in Gdańsk Wrzeszcz the highest concentration of particulate matter was connected with the lowest air temperature and the lowest wind speed accompanied by increased, yet not the highest, pressure (cluster 2). In the remaining districts of Tricity high concentrations were recorded either in connection with great decrease in air temperature (Gdynia Śródmieście – cluster 8) or with relatively low wind speed (Sopot – cluster 3), occurring both in conditions of elevated as well as decreased pressure. The results were inconsistent mainly regarding humidity accompanying low and high concentration of PM10. For example, in Gdynia Pogórze the highest concentration of particulate matter (cluster 3) occurred at relatively high relative humidity, approximately 87%, and was lower by almost a half at relative humidity approximately 75% (cluster 6.)

The results of the regression analysis indicate that winter meteorological conditions had a statistically significant influence on the variability of particular matter concentration – Tab. 3. The total coefficients of determination proved to be statistically significant, yet ranged widely from below 2 to about 36%, depending on the district and cluster. In general, the accuracy of correlation was determined by the concentration of particulate matter in individual clusters. For every district of Tricity the weakest influence of meteorological conditions on immission was found in clusters grouping the average lowest concentrations of particulate matter. The strongest influence of weather on variability of greatest average particulate matter concentrations was found in Gdynia Pogórze and in both districts of Gdańsk. In the most polluted district of Tricity, that is Gdynia Śródmieście, the extreme values of the coefficients of total determination were calculated for cluster 7 involving the elevated, yet not the highest, hourly PM10 concentrations. The least variable values of the total determination coefficient was calculated for Gdańsk Wrzeszcz despite the fact that individual clusters grouped (individual) different (prevailing) wind directions.

Meteorological conditions which explain the variability of PM10 concentrations usually included 3–4 elements (Tab. 3). However, the development of the variability of PM10 concentration – expressed as coefficients of partial determination (r^2), was mainly due to air temperature and the wind speed. The positive influence of the meteorological elements on developing variability of immission was reflected by negative directional coefficients. The fundamental role of thermal and anemometric conditions in providing explanation for the concentration and variability of pollutants was shown in numerous research [3, 13, 14, 24].

Strong correlation between air temperature and particulate matter concentration in winter season in Tricity was found mainly in clusters grouping instances of high, yet not always highest, PM10 concentration. For example in Gdynia Śródmieście, the greatest values of the partial determination coefficient (25%), which reflect the significance of thermal conditions, were calculated for cluster 7. In this cluster, the average PM10 concentrations occurring mainly at SW winds was by 10 $\mu g \cdot m^{-3}$ lower than the highest concentration recorded in the same district – occurring mainly at SE circulation and classified as cluster 8.

Table 3. Coefficients of total determination (R^2) and coefficients of partial determination (r^2). in %. for the relationships between particulate matter(PM10) concentrations and meteorological elements in distinct clusters

Tabela 3. Współczynniki determinacji zupełnej (R^2) oraz determinacji cząstkowej (r^2). w %. dla zależności stężeń pyłu zawieszonego PM10 od elementów meteorologicznych w wyróżnionych skupieniach

station	cluster	R^2	r^2 element of meteorology			
			AT	RH	PH	WS
Gdynia Pogórze	1	9.8	0.6	·	1.8	3.9
	2	8.4	0.6	1.1	·	7.1
	3	23.0	12.1	5.1	·	7.9
	4	7.8	3.2	·	2.6	6.0
	5	23.0	12.5	0.3	3.2	0.3
	6	14.6	·	·	4.9	11.7
Gdynia Śródmieście	1	25.9	12.3	·	1.0	3.0
	2	11.8	·	1.9	1.1	6.1
	3	6.4	1.0	1.6	2.9	·
	4	17.4	10.2	·	0.5	1.4
	5	14.1	5.6	0.5	0.6	11.3
	6	14.9	2.1	1.0	1.9	3.2
	7	36.3	25.0	1.7	3.0	10.3
	8	16.2	8.3	·	0.3	9.8
Sopot	1	18.0	1.3	·	0.5	16.5
	2	28.3	14.3	·	2.9	1.4
	3	14.1	8.6	0.2	0.1	2.8
	4	1.6	·	·	0.3	1.7
	5	15.8	8.4	0.1	0.7	3.0
Gdańsk Wrzeszcz	1	16.9	11.8	0.3	·	4.3
	2	23.6	18.2	·	·	10.8
	3	16.7	6.1	·	1.3	2.6
	4	22.9	10.0	6.1	1.1	4.2
	5	17.0	11.1	0.3	0.2	0.5
	6	19.9	8.5	·	0.3	4.6
Gdańsk Jasień	1	22.7	12.3	0.7	0.4	8.0
	2	15.1	6.5	0.4	·	9.3
	3	20.9	8.3	1.0	2.9	9.4
	4	4.4	1.3	0.9	·	2.9

· not significant at p ≤0,05; 0.2 – underlined value indicates a positive; AT – air temperature; RH – relative humidity; PH – normalized pressure; WS – wind speed

Wind which is the main pollution transport agent in the lower part of the atmosphere, not only contributes to the dispersion of pollution, but also to its inflow from other emission sources which in urban areas are mostly local sources. The results of wind direction analysis at which the average highest one-hour concentrations of PM10 were recorded, are presented in Fig. 5. In the greatest part of Tricity, that is in the northern and central part of the agglomeration, the risk of occurrence of the highest PM10 concentrations was connected with SE winds. In Gdańsk Wrzeszcz the increased concentrations of PM10 were recorded at E winds, whereas in Gdańsk Jasień at W winds.

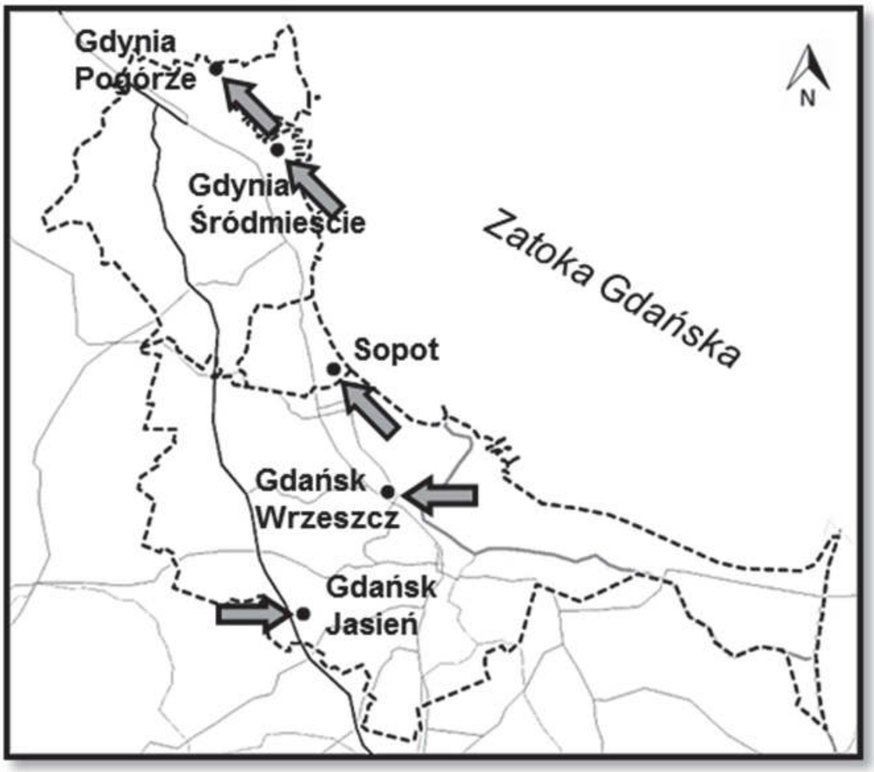

Fig. 5. Wind directions posing the greatest risk of high concentrations of particulate matter PM10 in Tricity urban area
Rys. 5. Kierunki wiatru stwarzające w okresie kalendarzowej zimy ryzyko wystąpienia w aglomeracji trójmiejskiej wysokich stężeń pyłu zawieszonego PM10

The influence of wind speed on the variability of PM10 concentrations proved to be smaller than that of air temperature (Tab.3). Only in two districts (Gdynia Pogórze and Gdańsk Wrzeszcz) the highest determination coefficients, thus the role of wind, were calculated for clusters grouping the highest PM10 concentrations. In other districts, the strong influence of wind was found in connection with much lower concentration of particulate matter. Wind served mostly as a ventilation factor in Tricity, and an increase in wind speed resulted in a decrease in particulate matter concentrations. The only case of negative effect of wind on particulate matter immission was found in Gdynia Pogórze, in cluster 6. Despite the fact that this cluster grouped concentrations recorded during meteorological conditions connected with NE circulation, that is the same as in the case of cluster 2, the increase in wind speed of this direction and also of SW and W winds was markedly correlated with an increase of particulate matter concentration. NE winds which were recorded more often in cluster 2, similarly to SW and W winds, contributed to the dispersion of particulate matter pollution. The complex and opposite role of winds of the same direction in the northern part of Tricity agglomeration can be attributed to the fact that it was found during different thermal and humidity conditions – positive at temperatures above 0°C (around 2°C) and high relative humidity but with low frequency of calms; and negative at temperatures below 0°C and low humidity (Tab. 2).

The comparison of data shown in Tab. 3 and 1 indicates that in Tricity agglomeration none of the predominant (in a cluster) wind direction was characterized by the strongest relationship between particulate matter concentrations and air temperature, not to mention wind speed. In every district the highest share of the elements mentioned above in the variability of PM10 particulate matter concentration was connected with different wind direction. Moreover, even within individual districts the greatest values of determination coefficients for both elements were calculated for different directions. Only in Gdańsk Wrzeszcz the strongest influence, both of temperature as well as wind speed, was found during prevailing winds of the same direction, namely E winds (cluster 2).

The share of relative humidity and atmospheric pressure in explaining the variability of particulate matter concentration proved to be incomparably lower, even statistically insignificant in some clusters, and ambiguous as for its direction. In most clusters, concentrations of PM10 showed a positive relationship with pressure, yet in some clusters the correlation was negative. The increase in relative humidity which is characteristic for cyclonic weather contributed both to an increase as well as decrease in particulate matter concentration in clusters including instances recorded at positive and negative air temperature. Therefore, the not so strong correlation between particulate matter and this element is not surprising. Relative humidity is not a coefficient which would characterize the concentration of water vapour in air well and definitely plays more important role in chemical changes of gaseous pollutants, mainly catalytic oxidation of sulfur dioxide. The correlation between immission of pollutants and relative humidity was demonstrated by Elminir [9], Freitas et al. [11], Pires et al. [27], yet with different directions depending on the type of pollutant, climatic conditions, season and local topography.

4. Conclusions

During the calendar winter (December - February), the northern part of Tricity which borders the waterfront areas and administratively belongs to Gdynia Śródmieście, is the most strongly PM10 polluted area of the urban agglomeration. Mean seasonal concentrations are by approximately 40% higher than in other districts and are marked by greatest variability.

The cluster analysis adopted in this study showed that average highest or increased hourly concentration of PM10 was recorded in Tricity on general during weather conditions of the lowest air temperature and smaller wind speed, as well as the greatest occurrence of atmospheric calms – that is in the conditions of anticyclonic weather. In much of the area of the agglomeration, in the districts Gdynia Pogórze and Śródmieście as well as in Sopot, the highest risk of high and excessive concentration of PM10 was connected with SE circulation. In the southern districts, the greatest risk was connected with E wind (Gdańsk Wrzeszcz) or W winds (Gdańsk Jasień), as is presented in Fig. 5.

Main meteorological elements affecting the variability of PM10 particulate matter concentration are air temperature, speed and direction of wind. The increase in air temperature and consequently lower emission, mostly connected with ineffective, scattered, local and individual heating systems, markedly contribute to the decrease in particulate matter concentration. Though directions of wind reflect inflow emission which originated locally as well as that coming from the outside of the agglomeration, in all districts of Tricity the increase in wind speed results in decrease of PM10 concentrations.

References

1. **Atlas of climatic resources and hazards in Pomerania** pod red. C. Koźmiński, B. Michalska. Szczecin 2004.
2. **Beaver S., Palazoglu A.:** *Cluster analysis of hourly wind measurements to reveal synoptic regimes affecting air quality.* Journal of Applied Meteorology and Climatology. 45, 1710–1726 (2006).
3. **Cuhudaroglu B., Demirci E.:** *Influence of some meteorological factors on air pollution in Trabzon city.* Energy and Buildings. 25, 179–184 (1997).
4. **Czarnecka M., Nidzgorska-Lencewicz J.:** *Impact of weather conditions on winter and summer air quality*. International Agrophysics. 25(1), 7–12 (2011).
5. **Czarnecka M., Nidzgorska-Lencewicz J.:** *The influence of precipitation conditions on the concentration of suspended particulates PM10*. Meteorology and Climatology Research. red. J. Leśny. Acta Agrophysica. Rozprawy i Monografie. 184, 132–147 (2010).
6. **Darby L.S.:** *Cluster analysis of surface winds in Houston, Texas, and the impact of wind patterns on ozone*. Journal of Applied Meteorology. 44, 1788–1806 (2005).
7. **Demuzere M., Trigo R. M., Vila-Guerau de Arellano J., van Lipzig N.P.M.:** *The impact of weather and atmospheric circulation on O3 and PM10 levels at a rural mid-latitude site*. Atmos. Chem. Phys. 9, 2695–2714 (2009).
8. Dyrektywa 2008/50/WE Parlamentu Europejskiego i Rady z dnia 21 maja 2008 r. w sprawie jakości powietrza i czystszego powietrza dla Europy.
9. **Elminir H.K.:** *Dependence of urban air pollutants on meteorology*. Science of the Total Environment. 350, 225–237 (2005).
10. **European Environment Agency:** *Air quality in Europe*. Report 2012. No 4. 2012.
11. **Freitas M.C., Pacheco A.M.G., Verburg T.G., Wolterbeek H.T.:** *Effect of particulate matter, atmospheric gases, temperature, and humidity on respiratory and circulatory diseases' trends in Lisbon, Portugal*. Environ. Monit. Assess. 162, 113–121 (2010).

12. **Godłowska J.:** *The particulate matter PM10 air pollution in Cracow.* Wiadomości IMGW. XXVII(XLVIII), 1, 79–90 (2004).
13. **Grivas G., Chaloulakou A., Samara C., Spyrellis N.:** *Spatial and temporal variation of PM10 mass concentrations within the greater area of Athens, Greece*. Water, Air, and Soil Pollution. 158, 357–371 (2004).
14. **İçağa Y., Sabah E.:** *Statistical analysis of air pollutants and meteorological parameters in Afyon, Turkey*. Environ. Model. Asses. 14, 259–266 (2009).
15. **Juda-Rezler K., Reizer M., Oudinet J.P.:** *Determination and analysis of PM $_{10}$ source apportionment during episodes of air pollution in Central Eastern European urban areas: The case of wintertime 2006.* Atmospheric Environment. 45(36), 6557–6566 (2011).
16. **Kalbarczyk R., Kalbarczyk E.:** *Assessment of the value of tropospheric ozone concentration depending on meteorological conditions as exemplified by the Widuchowa station (North-West Poland)*. Ekologia (Bratislava). 29(4), 398–411 (2010).
17. **Kryza M., Werner M., Dore A.J., Błaś M., Sobik M.:** *Zastosowanie modelu FRAME do określania średniorocznych stężeń PM10 i wtórnych aerozoli nieorganicznych w Polsce 2010.* Ochrona powietrza w teorii i praktyce pod red. Jana Konieczyńskiego, Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk w Zabrzu. 2, 33–50 (2010).
18. **Kukkonen J., Pohjola M., Sokhi R.S., Luhana L., Kitwiroon N., Fragkou L., Rantamäki M., Berge E., Ødegaard V., Slørdal L.H., Denby B., Finardi S.:** *Analysis and evaluation of selected local-scale PM10 air pollution episodes in four European cities: Helsinki, London, Milan and Oslo*. Atmospheric Environment. 39, 2759–2773 (2005).
19. **Leśniok M., Caputa Z.:** *The role of atmospheric circulation in air pollution distribution in Katowice Region (Southern Poland).* Int. Journal of Environment and Waste Management. 4(1–2), 62–74 (2009).
20. **Leśniok M., Małarzewski Ł., Niedźwiedź T.:** *Classification of circulation types for Southern Poland with an application to air pollution concentration in Upper Silesia*. Physics and Chemistry of the Earth. 35(9–12), 516–522 (2009).
21. **Łomnicki A.:** *Wprowadzenie do statystyki dla przyrodników*. Wydawnictwo Naukowe PWN, Warszawa 2005.
22. **Majewski G., Kleniewska M., Brandyk A.:** *Seasonal variation of particulate matter mass concentration and content of metals.* Polish J. of Environ. Stud. 20(2), 417–427 (2011).

23. **Nidzgorska-Lencewicz J., Czarnecka M.:** *Winter weather conditions vs. air quality in Tricity, Poland.* Theoretical and Applied Climatology. 115, DOI 10.1007/s00704-014-1129-8 (2015).
24. **Ocak S., Turalioglu F.S.:** *Relationship Between Air Pollutants and Some Meteorological Parameters in Erzurum, Turkey*. Dincer et al. (eds.), Global Warming, Green Energy and Technology. 485–499 (2010).
25. **Ośródka L., Krajny E., Klejnowski K., Rogula-Kozłowska W., Błaszczyk J., Kobus D., Wypych A.:** *Indeks jakości powietrza jako miara zanieczyszczenia powietrza w Polsce.* Nauka Przyroda Technologie. 5(4), 1–11 (2011).
26. **Państwowy Monitoring Środowiska (PMŚ), Inspekcja Ochrony Środowiska**: *Ocena jakości powietrza w strefach w Polsce za rok 2011*. Warszawa 2011.
27. **Pires J. C. M., Martins F. G., Sousa S. I. V., Alvim-Ferraz M. C. M., Pereira M. C.:** *Prediction of the daily mean PM10 concentrations using linear models*. American Journal of Environmental Sciences. 4(5), 445–453 (2008).
28. **Podawca K., Rutkowska G.:** *Analiza przestrzennego rozkładu typów zanieczyszczeń powietrza w układzie dzielnic m. st. Warszawy*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2090–2107 (2013).
29. **Sówka I., Łągiewka A., Zwoździak A., Skrętowicz M., Nych A., Zwoździak J.:** *Zastosowanie GIS do analizy przestrzennej stężeń pyłu PM2.5 oraz PM10 na terenie województwa dolnośląskiego*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 1667–1678 (2011).
30. **Tomaszewska A.:** *Analiza zależności występowania wysokich stężeń PM10 od typów cyrkulacji Lityńskiego.* Ochrona powietrza w teorii i praktyce pod red. Jana Konieczyńskiego, Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk w Zabrzu. 2, 375–388 (2010).
31. **Unal Y. S., Toros H., Deniz A., Incecik S.:** *Influence of meteorological factors and emission sources on spatial and temporal variations of PM10 concentrations in Istanbul metropolitan area*. Atmospheric Environment. 45, 5504–5513 (2011).
32. **Xie X., Huang Z., Wang J.:** *Impact of building configuration on air quality in street canyon.* Atmospheric Environment. 39, 4519–4530 (2005).
33. **Yoo H-J., Kim J., Yi S-M., Zoh K-D.:** *Analysis of black carbon, particulate matter, and gaseous pollutants in an industrial area in Korea*. Atmospheric Environment. 45, 7698–7704 (2011).
34. http://armaag.gda.pl/

Zastosowanie analizy skupień do wytypowania warunków meteorologicznych kształtujących zmienność stężeń pyłu zawieszonego PM10

Streszczenie

W pracy wykorzystano godzinne wyniki pomiarów stężeń pyłu zawieszonego PM10 oraz podstawowych elementów meteorologicznych rejestrowanych automatycznie w pięciu stacjach funkcjonujących w sieci pomiarowej Agencji Regionalnego Monitoringu Atmosfery Aglomeracji Gdańskiej (ARMAAG). Opracowaniem objęto okres kalendarzowej zimy (grudzień–luty) w latach 2004/2005–2009/2010. Zmienność stężeń zanieczyszczeń w warunkach pogodowych opisanych temperaturą i wilgotnością względną powietrza, ciśnieniem atmosferycznym oraz prędkością i kierunkiem wiatru, oceniono przy zastosowaniu analizy skupień, w tym metody k-średnich, z grupy metod niehierarchicznych. Kompleksowy wpływ warunków meteorologicznych na zmienność imisji pyłu PM10 w wyodrębnionych segmentach określono metodą liniowej regresji wielokrotnej, przy zastosowaniu procedury krokowej postępującej, na poziomie istotności $p \leq 0,05$. Udział poszczególnych elementów pogody w kształtowaniu wielkości stężeń określono za pomocą współczynników regresji cząstkowej. Zastosowany algorytm wyodrębnił, w zależności od dzielnicy Trójmiasta, od 4 do 8 optymalnych skupień najwięcej – w Gdyni, odznaczającej się największą imisją pyłu zawieszonego. W większości przypadków głównym czynnikiem zróżnicowania pomiędzy wyodrębnionymi skupieniami był kierunek wiatru. W przeważającej części aglomeracji trójmiejskiej, w Gdyni i w Sopocie, największą imisję pyłu zawieszonego PM10 notowano przy wiatrach SE, podczas gdy w części południowej, w Gdańsku, podwyższone stężenia pyłu notowano przy wiatrach E we Wrzeszczu oraz W w Jasieniu. Skupienia grupujące największe stężenie PM10 charakteryzowały się w większości przypadków najniższą temperaturą powietrza i mniejszą prędkością wiatru, a ponadto często wyższym ciśnieniem i niekiedy nieco mniejszą wilgotnością względną powietrza, czyli warunkami panującymi przy pogodzie antycyklonalnej. Warunki meteorologiczne miały statystycznie istotny wpływ na stężenia PM10 we wszystkich skupieniach, ale zasadniczą rolę odgrywały temperatura powietrza oraz prędkość wiatru. Wiatr, niezależnie od kierunku, był na ogół efektywnym czynnikiem wentylacji przyczyniając się przede wszystkim do zmniejszenia zapylenia powietrza.

Słowa kluczowe:
analiza skupień, regresja, PM_{10}, warunki meteorologiczne

Keywords:
cluster analysis, regression, PM_{10}, meteorological conditions

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Laboratory Studies on the Effectiveness of Thermal Treatment of Selected Compositions of Waste from Organic Chemistry Industry

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1. Introduction

Thermal processing is one of the methods of disposal of industrial waste. This process reduces volume and weight of those waste, and also allows to avoid their landfilling. However, by-products of thermal processing are: volatile components (flue gas and fly ash) and solids (slag, ash also called furnace waste), which are a source of contamination of the environment [2,4,12,13].

During development of the project of thermal processing of particular waste, various aspects of efficiency of the process should be considered, which should meet, among others, technological and economic conditions [19,20]. The aim of waste utilisation is recovery of their usable energy, maximum possible reduction of harmful substances produced during this process and decrease of their volume. It is connected with the pre-selection of waste.

Laboratory installation for thermal treatment of waste was designed and made at the Department of Water and Sludge Technology and Waste Utilisation of Koszalin University of Technology. It was used for studies on incineration process of pre-selected industrial and municipal waste. Also studies on the process of co-incineration of sewage sludge in mixtures with different types of waste were conducted [5,11,18]. Studied waste also included waste from organic chemistry industry such as plastics, rubber and petrochemical waste, which include paints and varnishes.

The paper presents the results of laboratory studies on the efficiency of incineration of different compositions of mixtures of waste from organic chemistry industry in terms of percentage reduction of their weight. Studies were conducted using different percentages of each waste in mixtures with sewage sludge, as the possibility of co-incineration of sewage sludge and studied waste.

2. Methodology of studies

2.1. Materials

The following materials were selected for the studies:

- polymer waste
  - rubber waste (waste tires) – industrial waste,
  - paint waste – industrial waste,
  - plastic waste – industrial waste, municipal waste,
- sewage sludge – municipal waste.

Waste tires were used as rubber waste. During studies only an external layer of tires was used, which is made of natural or artificial vulcanized caoutchouc – polymer (elastomer) [8,16]. In the case of paint waste, residues of oil-alkyd enamel, that is solvent alkyd-oil paint, one of the most common paints used for decoration and protection of surfaces, was used in the studies. Such waste may be classified as coating type polymers (polymer suspension). Plastomers, commonly recognized as representative sample of plastic materials in municipal waste, were plastics during studies. Sewage sludge used in the studies was taken from "Jamno" Wastewater Treatment Plant, which is an object operated by the local water supply and sewage treatment company in Koszalin. Sewage sludge has been dried to a water content of about 10% because the hydrated sewage sludge was characterized by high value of this parameter (W^r = ~50%), which negatively affects the efficiency of combustion process.

Materials, before incineration were ground to particle diameter < 1,25 mm in order to unify their size.

Technical analysis of the materials used for studies was conducted as a initial stage. It consisted of: determination of combustible parts (u,% – organic matter) and non-combustible (n,% – minerals and water).

The basic parameters characterizing solid fuels are: water content (W), ash content (A), volatiles content (V), and the heat of combustion (Q_s). The sum combustible organic matter, ash and water content is 100% [10]. Analysis was performer according to following standards: PN-ISO 1213-2:1999; PN-80/G-04511; PN-ISO 1171:2002; PN-80/G-04512; PN-G-04516:1998; PN-ISO 1928:2002.

Additionally, qualitative analysis of the studied materials was conducted using MiniPal PW4025 XRF spectrometer, which uses X-ray fluorescence for identification of elements.

2.2. Study range

Studies on the of effectiveness of weight reduction of waste mass in the process of their thermal processing were conducted on laboratory installation. The main element of that installation is a laboratory, single zone, tube furnace with horizontal heating system of a maximum continuous operating temperature 1473K. The combustion process was carried out in atmospheric air, which was fed into the furnace using diaphragm pump, through a table rotameter, which measures the air flow intensity within the range of 0.5–8.5 $dm^3 \cdot min^{-1}$.

Process studies were conducted under following constant parameters of incineration:

T – temperature in the incineration zone of the furnace, °K – 1173.15 (900°C),
λ – excess air coefficient – 1.1 (air flow rate 4 $dm^3 \cdot min^{-1}$),
m – index of the sample material mass in relation to the volume of the furnace chamber, $kg \cdot m^{-3}$ – 1.3 (sample mass – 0.03 g).

Constants values of those parameters were determined on the base of previous studies of incineration process of various materials (municipal waste, sewage sludge and dust coal), using the same installation and also analysis of the influence of changes of mentioned parameters on concentration of pollutants in flue gases [5,11,18].

Studies presented in this work were divided into 4 stages:

I. Combustion of individual waste materials selected for the studies, as a comparative basis for the subsequent stages;
II. Combustion of 1st composition of waste – individual waste mixed with another, one type of waste;

III. Combustion of 2nd composition of waste – individual waste mixed with other two types of waste,
IV. Combustion of 3rd composition of waste – individual waste mixed with other three types of waste.

All compositions of waste selected for the given stages of studies are presented in the Table 1. Table 2 presents mass proportions of mixtures compositions of waste in each stage (at the constant sample mass – 0.03 g).

Table 1. Compositions of waste in individual stages of studies
Tabela 1. Kompozycje odpadów w poszczególnych etapach badań

Stage	Studied waste	Additional waste	
I	paint	–	
	rubber	–	
	plastics	–	
	sewage sludge	–	
II	paint	rubber	
		sewage sludge	
		plastics	
	rubber	sewage sludge	
		plastics	
	plastics	sewage sludge	
III	paint	rubber	sewage sludge
		rubber	plastics
		sewage sludge	plastics
	rubber	paint	sewage sludge
		paint	plastics
		sewage sludge	plastics
	plastics	rubber	sewage sludge
		rubber	paint
		sewage sludge	paint
	sewage sludge	rubber	paint
		rubber	plastics
		paint	plastics

Table 1. cont.
Tabela 1. cd.

Stage	Studied waste	Additional waste		
IV	paint	rubber	sewage sludge	plastics
	rubber	paint	sewage sludge	plastics
	plastics	paint	rubber	sewage sludge
	sewage sludge	paint	rubber	plastics

Table 2. Percentage and mass proportions of waste mixtures in individual stages of studies at fixed sample mass – 0.03 g
Tabela 2. Procentowe i masowe proporcje mieszanin odpadów w poszczególnych etapach badań przy założeniu stałej masy próby – 0,03 g

Percentage and mass share in a sample				
Stage	Studied waste	Additional waste		
I	100%, 0.03 g	–		
II	50%, 0.015 g	50%, 0.015 g		
III	50%, 0.015 g	25%, 0.0075 g	25%, 0.0075 g	
IV	50%, 0.015 g	16,7%, 0.005 g	16,7%, 0.005 g	16,7%, 0.005 g

Output parameter in each stage of studies was a percentage index Δm, % – sample loss of mass during combustion process of the selected compositions of waste. This parameter was calculated using following formula $\Delta m = \frac{m^0 - m}{m^0} \cdot 100\%$, where:
m^0, m – are, respectively, mass of the sample before and after incineration of waste.

However, attention cannot be paid only on the effectiveness of thermal processing in terms of reduction of their volume, because in the case of such type of installation, emissions of environmentally harmful flue gases, which are produced during combustion of waste, must be also taken into account.

Therefore, during all stages of studies described in this paper, the stream of exhaust gases from the furnace reactor was subjected to the analysis with exhaust gas analyzer MADUR GA-21 *plus*. Following gases were measured:

c_{SO2} –concentration of sulfur oxide (IV), mg · m^{-3},
c_{NOx} –concentration of nitrogen oxides, mg · m^{-3},
c_{CO} –concentration of carbon oxide (II), mg · m^{-3}.

In order to facilitate orientation and ability to compare the results, all concentrations of pollutants in exhaust gas were converted to standard contractual conditions of combustion at 11% of O_2 content in the exhaust.

3. Description and analysis of results

3.1. Technical analysis of the materials used for studies

Results of full technical analysis are presented in Table 3. According to standards, values of parameters characterizing the materials are specified for the analytic state (a) when the moisture is in equilibrium with the ambient humidity.

Analysis of the results in Table 3 shows much lower ash content A^a in waste plastic, as compared to other tested materials. It is connected with the content of mineral (non-combustible) substances in the fuel. Results of volatile V^a and combustible substances contents in the analyzed materials show that studied waste paints had the lowest values of those parameters, even in comparison with waste rubber and plastics, although they are also polymers.

This comparative analysis is mainly connected with the content of organic matter in discussed materials, that is analysis of elementary elements, such as carbon, hydrogen, nitrogen and sulfur. On the basis of literature data concerning the qualitative analysis of fuels (waste fuels) [9,14,17], it may be concluded that the waste plastics, despite low content of nitrogen n^a and sulfur s^a, contain significant amounts of elemental carbon c^a, which causes much higher organic matter content, which are also volatile. This amount is comparable eg. with sewage sludge. Low content of organic elements in the waste paint clearly shows a much lower content of volatile substances in that material.

Table 3. Results of technical analysis of materials used in laboratory studies
Tabela 3. Zestawienie zbiorcze wyników analizy technicznej materiałów wykorzystanych do badań laboratoryjnych

Granulation, mm	Volatiles content V^a, %	Water content W^a, %	Ash content A^a, %	Combustible parts u, %	Non-combustible parts n, %	Heat of combustion Q_s^a, MJ · kg^{-1}
Waste paints						
0.35–1.25	17.0	0.8	59.4	39.8	60.2	24.91
Waste rubber						
0.35–1.25	56.2	6.2	16.2	77.6	22.4	31.84
Waste plastics						
0.5–1.25	60.2	0.5	5.8	93.7	6.3	42.02
Sewage sludge (dry)						
0.125–1.25	54.3	10.6	32.0	57.4	42.6	13.57

On the other hand sewage sludge contains a much bigger amounts of volatile substances only due to a significant percentage of elementary elements: sulfur s^a and nitrogen n^a [21]. Energetic properties of waste (heat of combustion Q_s) also result from the content of organic matter. The low content of the elemental carbon c^a in the sewage sludge [21] causes much lower calorific value, in comparison with waste polymer – Table 3. This is confirmed by Bień and Wystalska [3]. According to their studies heat of combustion of the digested sludge, containing 50% of combustible parts, is about 11 MJ · kg^{-1}.

Analysis of water content in the waste polymer shows the comparability of those materials, because most plastics are water resistant. This is the reason of low value of W^a in such waste.

3.2. Studies on reduction of waste mass

Figures 1 and 2 show a graphical interpretation of average values of *Δm* parameter for each studied waste in certain compositions. Tables 4 and 5, however, present basic descriptive statistics calculated for that parameter.

Analysis of the results at first allows to observe that values of mass loss of waste samples vary considerably, although all studied waste, apart from sewage sludge, are by-products of organic chemistry industry. *Δm* parameter changes its value from 42% in the case of waste paint to observed 96% during incineration of waste plastic.

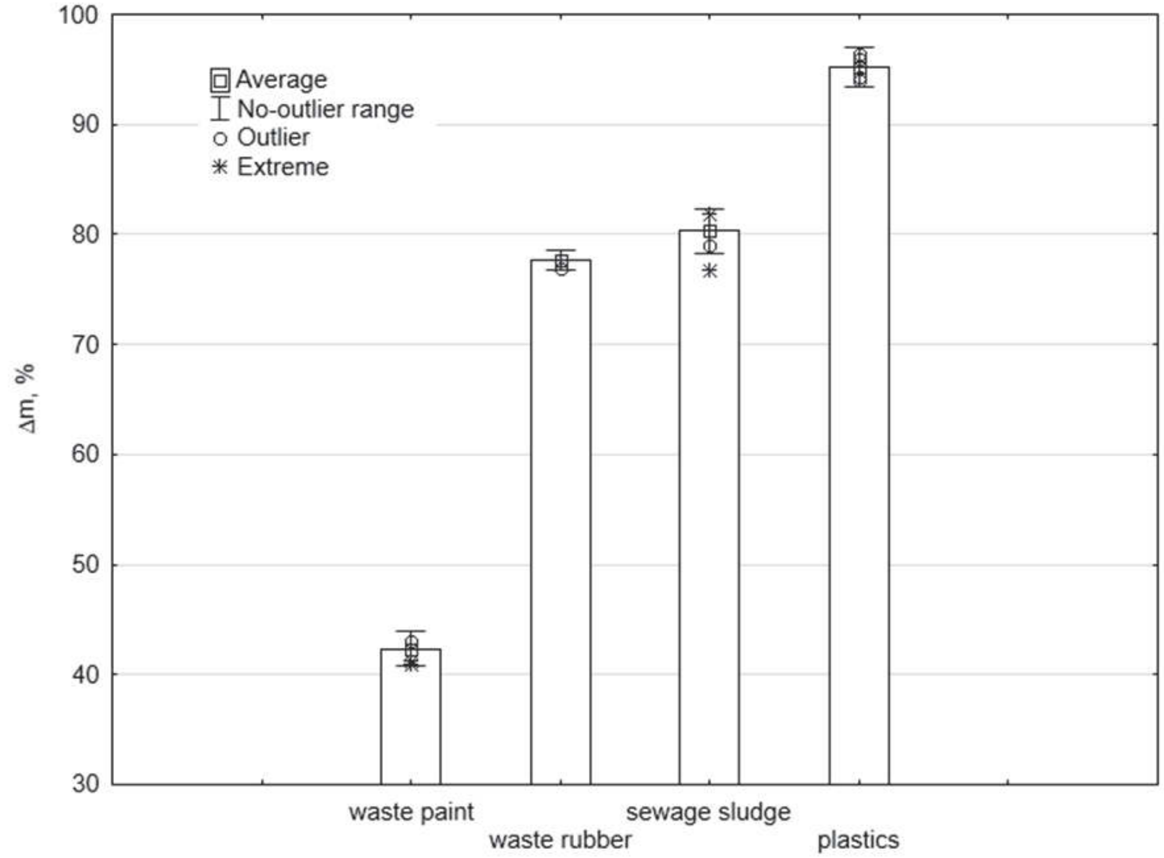


Fig. 1. Values of *Δm* parameter during incineration of studied waste (stage I)
Rys. 1. Wartości parametru *Δm* w procesie spalania badanych odpadów (I etap badań)

Table 4. Basic descriptive statistics calculated for Δm parameter after incineration of studied waste (stage I)

Tabela 4. Podstawowe statystyki opisowe parametru Δm dot. procesu spalania badanych odpadów (I etap)

	N of valid	% of valid	Average	Median	Minimum	Maximum	Standard deviation.
waste paint	25	100,0	42,3	42,6	41,0	43,0	0,8
waste rubber	25	100,0	77,6	78,0	77,0	78,0	0,5
sewage sludge	25	100,0	80,3	80,0	76,8	81,9	1,0
waste plastics	25	100,0	95,2	96,0	94,0	96,3	0,9

Due to the fact that waste plastics are characterized by the highest mass loss in the combustion process (which is directly related to the low value of the ash content index A^a – about 6% for waste plastics),their addition to studied compositions resulted in an increase of Δm index for all studied mixtures. Of course, the highest values of mass loss index were observed at the highest (50%) share of plastic waste in the mixture – the second stage of studies. In this case, addition of waste plastic to waste paint (very high residue after combustion of such waste) caused as much as approx. 60% increase in the value of Δm index, while the same addition to composition with rubber waste and sewage sludge caused much lower (approximately 20%) increase of the value of the Δm parameter, which in the case of incineration of only waste rubber and sewage sludge (I stage of the study) was similar and amounted to respectively 78% and 80% – Figure 1.

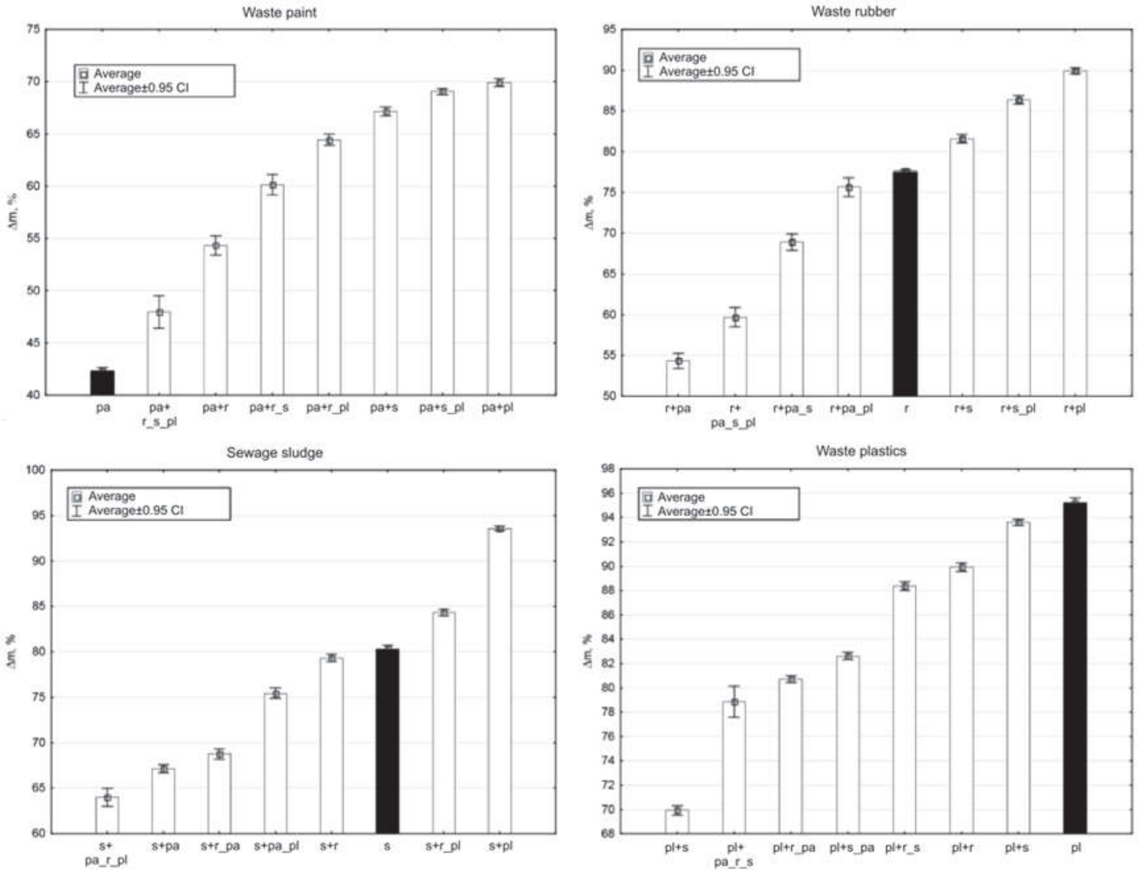


Fig. 2. Variability of *Δm* parameter during incineration of studied waste compositions; pa – waste paint, r – waste rubber; pl – waste plastics, s – sewage sludge

Rys. 2. Zmienność parametru *Δm* w procesie spalania badanych kompozycji odpadów; pa – odpady farbiarskie, r – odpady gumowe, pl – odpady z tworzyw sztucznych, s – osady ściekowe

The fact that a much lower value of mass loss of waste paint during combustion process compared to other studied materials was also the cause of low values of that parameter in the cases when waste paint was added to mixture compositions. It may be evidently observed in Figure 2. The addition of 50% of paint waste to studied mixtures caused following *Δm* parameter values: about 55% of the mixture with waste rubber (30% drop) and more than 65% in the composition with waste plastic and sewage sludge (respectively 27% and 17% drop).

Table 5. Basic descriptive statistics calculated for Δm parameter after incineration of studied compositions of waste (stage II–IV)

Tabela 5. Podstawowe statystyki opisowe parametru Δm dot. procesu spalania badanych kompozycji odpadów (etapy II–IV)

Waste compositions	N of valid	% of valid	Average	Median	Minimum	Maximum	Standard deviation.
f+g	25	100.0	54.3	55.0	46.1	59.5	2.3
f+o	25	100.0	67.1	67.0	65.0	68.1	1.0
f+tsz	25	100.0	69.9	70.0	69.0	71.0	0.9
g+f	25	100.0	54.3	55.0	46.1	59.5	2.3
g+o	25	100.0	81.6	82.0	78.5	83.0	1.3
g+tsz	25	100.0	89.9	90.0	89.0	91.0	0.9
o+f	25	100.0	67.1	67.0	65.0	68.1	1.0
o+g	25	100.0	79.3	79.0	78.0	81.0	1.0
o+tsz	25	100.0	93.6	94.0	93.0	95.0	0.6
tsz+f	25	100.0	69.9	70.0	69.0	71.0	0.9
tsz+g	25	100.0	89.9	90.0	89.0	91.0	0.9
tsz+o	25	100.0	93.6	94.0	93.0	95.0	0.6
f+g_o	25	100.0	60.1	61.0	55.1	63.7	2.4
f+g_tsz	25	100.0	64.4	65.0	62.0	66.0	1.3
f+o_tsz	25	100.0	69.1	69.0	68.0	70.0	0.8
g+f_o	25	100.0	68.9	69.6	64.5	72.1	2.4
g+f_tsz	25	100.0	75.6	75.0	73.0	83.0	2.8
g+o_tsz	25	100.0	86.4	86.0	85.0	88.0	1.2
o+g_f	25	100.0	68.8	69.0	66.0	70.5	1.4
o+g_tsz	25	100.0	84.3	85.0	83.0	85.2	0.8
o+f_tsz	25	100.0	75.4	76.0	73.0	77.0	1.4
tsz+g_o	25	100.0	88.4	89.0	87.0	89.0	0.9
tsz+g_f	25	100.0	80.7	81.0	80.0	82.0	0.7
tsz+o_f	25	100.0	82.6	82.0	82.0	84.0	0.7
f+g_o_tsz	25	100.0	48.0	47.0	44.0	58.2	3.8
g+f_o_tsz	25	100.0	59.7	60.0	56.0	64.1	2.8
o+f_g_tsz	25	100.0	64.0	64.0	59.3	67.0	2.4
tsz+f_g_o	25	100.0	78.9	78.0	75.0	84.1	3.1

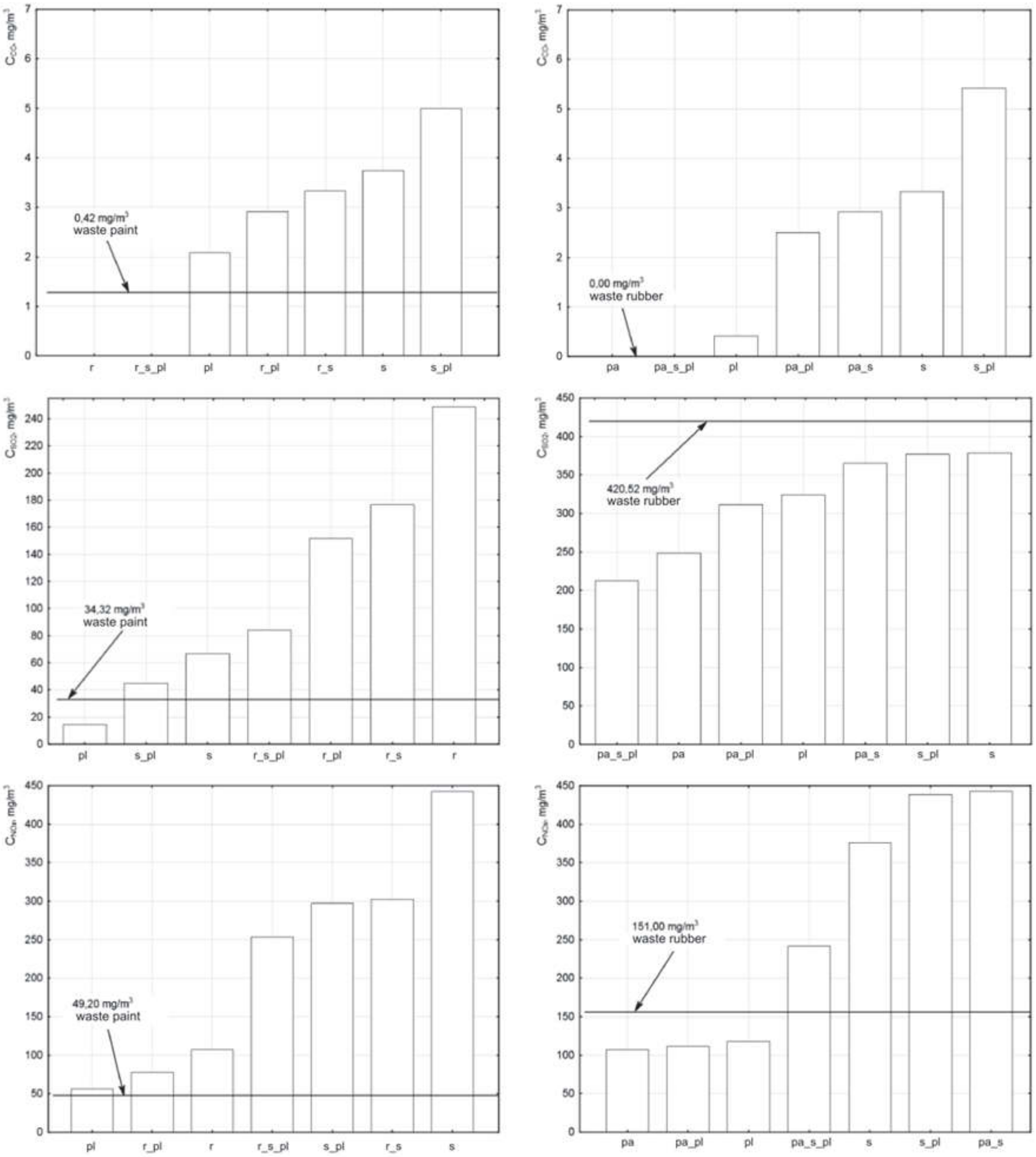
Similar values were achieved for the decrease of efficiency of the combustion of mixtures, when waste paint was added in the III and IV stage of the study. Addition of those waste was respectively 25% and 16%. For example, in such case a decrease of incineration efficiency was 17% for 25% of waste paint added to the mixture with plastic waste and sewage sludge and mixtures with sewage sludge and waste rubber, and a 25% decrease of the Δm parameter when 16.7% of waste paint was added to composition with sewage sludge, waste rubber and waste plastic products. Considering the elemental analysis of waste paint (content of non-combustible parts was much higher than value of that parameter, for example in sewage sludge), such low mass loss during incineration process of those waste is not surprising.

Analyzing the results of the incineration process of compositions of selected waste with sewage sludge, slight changes of mass loss after the combustion process in the case of a mixture of waste rubber with sewage sludge should be noted. The average value of Δm parameter of those mixtures is about 80%, and only addition of waste plastics caused an increase in the combustion mass efficiency to approximately 86%.

To sum up analysis of results of laboratory studies on the effectiveness of waste disposal, it should be noted that the biggest reduction was found for thermal processing of plastic waste and its composition with sewage sludge and waste rubber. However the least preferred is addition of waste paint into mixtures of incinerated waste.

3.3. Studies on changes of pollutants concentration in exhaust gases

The results of the measurement of concentrations of selected exhaust gases produced during incineration of investigated waste compositions are shown in Figures 3 and 4.



a) b)

Fig. 3. Variability of the concentrations of selected exhaust gases produced during incineration of examined compositions: a) waste paint, b) waste rubber; additional waste: pa – waste paint, r – waste rubber, pl – waste plastic, s – sludge

Rys. 3. Zmienność stężeń wybranych gazów spalinowych powstałych w procesie spalania badanych kompozycji: a) odpadów farbiarskich, b) odpadów gumowych; dodatkowe odpady: pa – odpady farbiarskie, r – odpady gumowe, pl – odpady z tworzyw sztucznych, s – osady ściekowe

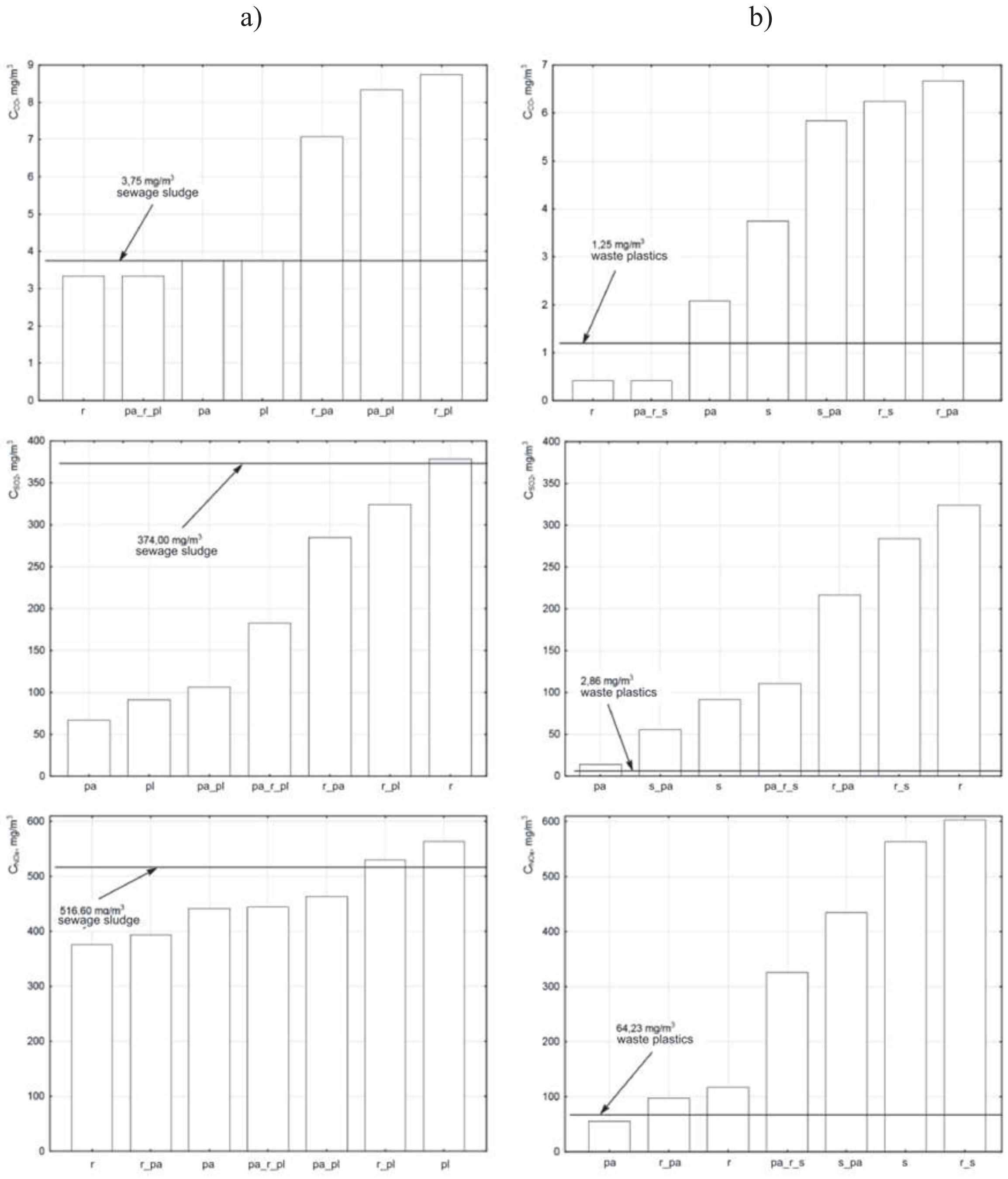


Fig. 4. Variability of the concentrations of selected exhaust gases produced during incineration of examined compositions: a) sewage sludge, b) waste plastics; additional waste: pa – waste paint, r – waste rubber, pl – waste plastic, s – sludge

Rys. 4. Zmienność stężeń wybranych gazów spalinowych powstałych w procesie spalania badanych kompozycji: a) osadów ściekowych, b) odpadów z tworzyw sztucznych; dodatkowe odpady: pa – odpady farbiarskie, r – odpady gumowe, pl – odpady z tworzyw sztucznych, s – osady ściekowe

Analysis of the results shows that high temperature of incineration process of studied waste compositions and sufficient excess air during the process resulted in minimal concentrations of carbon monoxide in all stages of research. In contrast, the negative effect of the thermal processing of examined mixtures of waste are: high concentrations of sulfur dioxide in case of incineration of waste rubber (400 mg · m^{-3}) and high concentrations of nitrogen oxides observed during sewage sludge incineration (500 mg · m^{-3}). Addition of those materials to mixtures with other waste caused a significant increase in the concentrations of SO_2 and NO_x. For example, the lowest value of c_{SO2} was observed in the case of incineration of plastic waste only. Addition of 50% of waste rubber and sewage sludge mixture to the composition with waste plastic caused increase of SO_2 concentration up to 280 mg · m^{-3}.

Of course such dependence is a result of significant content of fuel sulfur in the waste rubber and sewage sludge. This is confirmed by a qualitative analysis of the examined test materials which were performed using MiniPal PW4025 XRF spectrometer. Sample spectra obtained from XRF spectrograph with clearly labeled sulfur energy lines are shown in Figure 5. Spectra clearly show that rubber and sewage sludge contain significantly more elemental sulfur than waste plastics.

Significant differences in concentrations of sulfur and nitrogen oxides during incineration process of selected materials, observed during experiments, are caused mainly by the type of combusted material. Presence of SO_2 in the flue gases is almost entirely caused by oxidation of sulfur contained in fuel, admixtures and additives. Similar situation is in the case of NO_x, but here we have additional source, along with nitrogen contained in the fuel, also the nitrogen from the air is oxidized. Incineration of waste plastic was associated with production of relatively low values of c_{NOx} (mainly thermal oxides), as "pure" polymer does not contain elemental nitrogen. Nevertheless, fuel NO_x may be produced, due to application of antistatics to plastics. Those additional substances contain elemental nitrogen and are added in order to eliminate the phenomenon of electrification of surface of the plastic [22]. Chemicals which improve the properties of plastics usually significantly hinder their disposal and especially their thermal decomposition, causing an increase in the emission of harmful gases, eg. NO_x.

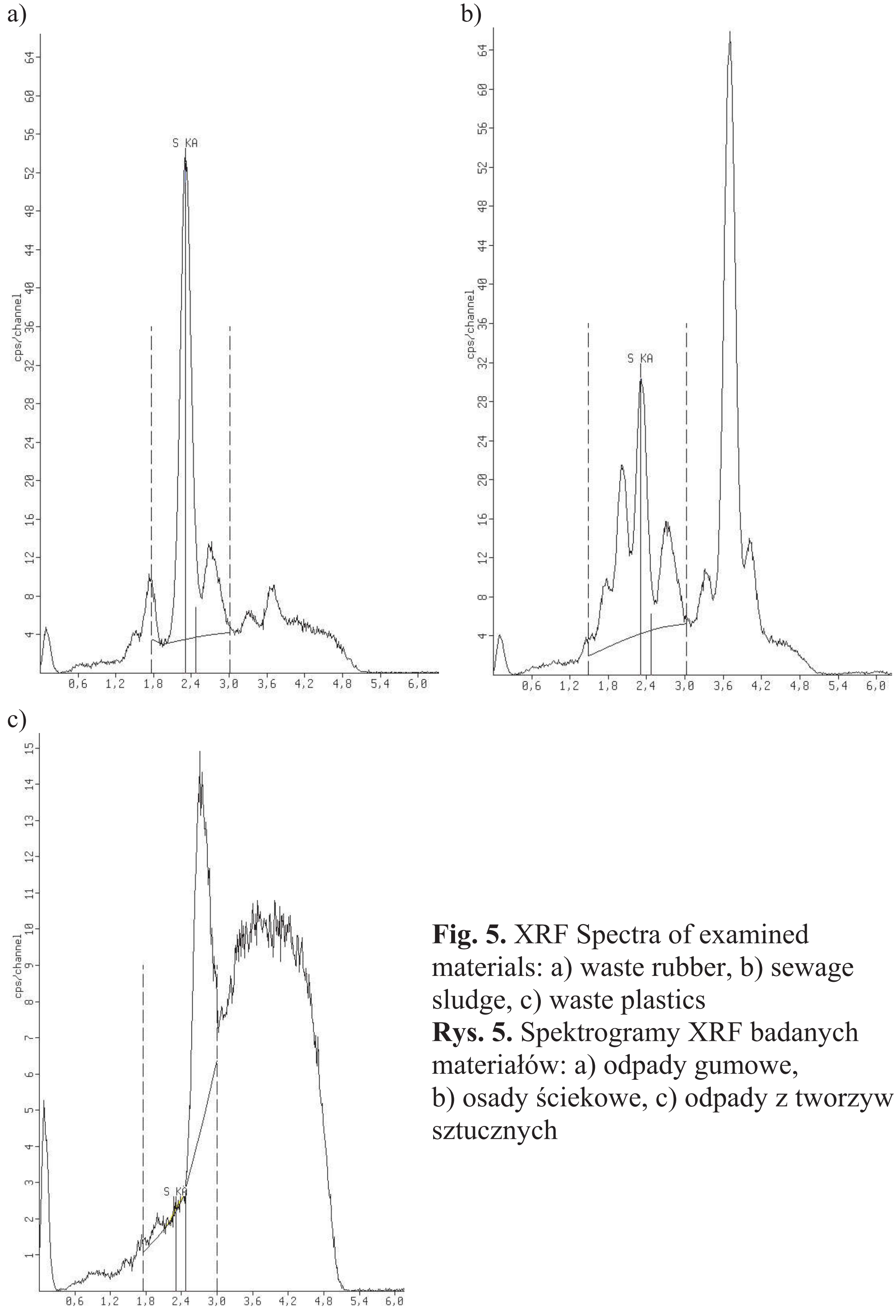


Fig. 5. XRF Spectra of examined materials: a) waste rubber, b) sewage sludge, c) waste plastics
Rys. 5. Spektrogramy XRF badanych materiałów: a) odpady gumowe, b) osady ściekowe, c) odpady z tworzyw sztucznych

Studies on literature results of elementary analysis of fuels clearly show, that sewage sludge is characterized by high content of fuel sulfur (approx. 1,4%) [1,3,5]. Authors of many publications [16,23] also indicate that in the case of waste rubber high concentrations of sulfur and nitrogen as fuel elements are determined. Average content of elemental sulfur in rubber waste can be up to 1.5%. Rubber is a product of vulcanization of natural or synthetic cautchuc with addition of 1–5% of sulfur to accelerators. It also contains plasticizers, fillers, pigments and other additives [8,23].

4. Conclusions

The final analysis of all laboratory studies presented in this paper has shown that waste plastics which have the biggest mass loss and lowest values of concentrations of exhaust gases produced during incineration of those waste, are characterized by the highest degree of efficiency of thermal decomposition process. But also other aspect must be taken into account – the fact that during the thermal treatment of such type of waste other toxic products (PCDDs, PCDFs, hydrogen cyanide, ammonia) may be produced [15,19,20,22]. Their analysis was not included within the range of studies presented in this paper. Therefore, it is necessary to design waste incineration installations which will include complex nodes of flue gases treatment [6,7,10,25]. Such type of installations should be designed on the base of the morphology of municipal waste, energy balance of incinerator feed, in order to make the process efficient and proper, not only for energetical, but also ecological reasons [19]. This will require a certain composition of waste feed into the furnace of thermal waste processing plant.

References

1. **Barz M.:** *Sewage sludge from wastewater treatment as energy source*. International Journal of Renewable Energy. 4(1) (2009).
2. **Bielińska E.J., Futa B., Baran S., Pawłowski L.:** *Eco-energy anthropopressure in the agricultural landscape*. Problemy Ekorozwoju – Problems of Sustainable Development. 9(2), 99–111 (2014).
3. **Bień J.B., Wystalska K.:** *Przekształcanie osadów ściekowych w procesach termicznych*. Wydawnictwo Seidel-Przywecki. Warszawa 2009.

4. **Czop M., Kajda-Szcześniak M.:** *Environemental impact of straw based fuel combustion*. Archives of Environmental Protection. 39(4), 71–80 (2013).
5. **Dąbrowski J., Piecuch T.:** *Badania laboratoryjne nad możliwością współspalania osadów ściekowych wraz z odpadami gumowymi*. Inżynieria Ekologiczna. 25, 55–66 (2011).
6. **Gomez-Garcia M.A., Pitchon V., Kiennemann A.:** *Pollution by nitrogen oxides: an approach to NO_x abatement by using sorbing catalytic materials*. Environment International. 31, 445–467 (2005).
7. **Goo J.H., Irfan M.F., Kim S.D., Hong S.Ch.:** *Effects of NO_2 and SO_2 on selective catalytic reduction of nitrogen oxides by ammonia*. Chemosphere. 67, 718–723 (2007).
8. **Jasiewicz M.:** *Sposoby granulowania i recyklingu zużytych opon. Kompleksowe zarządzanie gospodarką odpadami.* Praca zbiorowa pod red. T. Marcinkowskiego. Wydawnictwo PZITS Oddz. Wielkopolski. Poznań 2009.
9. **Kijo-Kleczkowska A., Otwinowski H., Środa K.:** *Specificity combustion of sewage sludge.* Archives of Waste Management Environmental Protection. 16(4), 93–102 (2014).
10. **Kordylewski W., Jakubiak M., Hardy T.:** *Pilot Plant Studies on NO_x Removal Via NO Ozonation and Absorption.* Archives of Environmental Protection. 39(3), 93–106 (2013).
11. **Lis J.:** *Badania efektywności spalania wybranych kompozycji mieszanin odpadów*. Praca magisterska. Promotor: prof. dr hab. inż. Tadeusz Piecuch. Politechnika Koszalińska. Koszalin 2013.
12. **Liu H.:** *Biofuel's Sustainable Development under the Trilemma of Energy, Environment and Economy*. Problemy Ekorozwoju – Problems of Sustainable Development. 10(1), 55–59 (2015).
13. **Lorenz U.:** *Skutki spalania węgla kamiennego dla środowiska przyrodniczego i możliwości ich ograniczenia*. Mat. Szkoły Eksploatacji Podziemnej. Sympozja i Konferencje nr 64. Wydawnictwo Instytutu GSMiE PAN. Kraków 2005.
14. **Marcisz M.:** *Zawartość siarki całkowitej w złożach monokliny Zofiówki (SW część Górnośląskiego Zagłębia Węglowego)*. Gospodarka Surowcami Mineralnymi – Mineral Resources Management. 29(3), 61–77 (2013).
15. **McKay G.:** *Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review.* Chemical Engineering Journal. 86(3), 343–368 (2002).
16. **Mianowski A., Radko T., Koszorek A.:** *Współspalanie miału węglowego i zużytych opon*. Zeszyty Naukowe Wydziału Budownictwa i Inżynierii Środowiska Politechniki Koszalińskiej. Koszalin 2007.

17. **Misiak J.:** *Jakość węgla eksploatowanych pokładów w LW „Bogdanka" S.A. (Lubelskie Zagłębie Węglowe)***.** Gospodarka Surowcami Mineralnymi – Mineral Resources Management. 28(4), 137–149 (2012).
18. **Piecuch T., Dąbrowski J., Dąbrowski T.:** *Laboratory Investigations on Possibility of Thermal Utilisation of Post-production Waste Polyester.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection). 11, 87–101 (2009).
19. **Piecuch T., Dąbrowski J.:** *Projekt koncepcyjno-technologiczny Zakładu Termicznego Przekształcania Odpadów Komunalnych dla Regionu Środkowopomorskiego.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection). 16, Monografia, 136 (2014).
20. **Piecuch T., Dąbrowski J.:** *Projekt koncepcyjny budowy Zakładu Termicznej Utylizacji Odpadów dla Gminy Połczyn-Zdrój*. Rocznik Ochrona Środowiska (Annual Set The Environment Protection). 16, 196–222 (2014).
21. **Rajczyk R., Bień J., Palka H., Pogodziński A., Smorąg H.:** *Co-Combustion of Municipal Sewage Sludge and Hard Coal on Fluidized Bed Boiler WF-6.* Archives of Environmental Protection. 40(3), 101–113 (2014).
22. **Saechtling H.:** *Tworzywa sztuczne. Poradnik*. Wydawnictwa Naukowo-Techniczne. Warszawa 2007.
23. **Skalmowski K.:** *Poradnik gospodarowania odpadami*. Wyd. Verlag-Dashöfer, Warszawa, 2007.
24. **Sobiecki M.:** *Rozwój systemu gospodarki odpadami po oponach samochodowych w Polsce.* Kompleksowe zarządzanie gospodarką odpadami. Praca zbiorowa pod red. T. Marcinkowskiego. Wydawnictwo PZITS Oddz. Wielkopolski. Poznań 2009.
25. **Wielgosiński G.:** *Instalacje Termicznego Przekształcania Odpadów Komunalnych w kontekście RIPOK – wybór technologii i koncepcji Rozwiązania problemu*. Wydawnictwo Nowa Energia. 1(37), 17–24 (2014).

Laboratoryjne badania nad skutecznością termicznego przekształcania wybranych kompozycji odpadów przemysłu chemii organicznej

Streszczenie

W pracy przedstawiono wyniki badań laboratoryjnych nad skutecznością spalania różnych kompozycji mieszanin odpadów przemysłu chemii organicznej w aspekcie procentowej obniżki ich masy. Badania te przeprowadzono przy założeniu różnych procentowych udziałów poszczególnych odpadów w mieszankach wraz z osadami ściekowymi jako możliwość współspalania ich z tymi odpadami.

Do badań wyodrębniono następujące materiały:

- odpady polimerowe
  - odpady gumowe (zużyte opony) – odpadowe przemysłowe.
  - odpady farbiarskie – odpady przemysłowe,
  - odpady z tworzyw sztucznych – odpady przemysłowe, komunalne,
- osady ściekowe – odpady komunalne,

Podsumowując analizę wyników laboratoryjnych badań nad efektywnością termicznego przekształcania badanych odpadów, należy stwierdzić, że największą skutecznością związaną z redukcją pozostałości po tej utylizacji charakteryzowało się termiczne przekształcenie odpadów z tworzyw sztucznych oraz ich kompozycji z osadami ściekowymi i odpadami gumowymi. Natomiast najmniej korzystny jest udział w spalanych mieszankach odpadów farbiarskich.

W trakcie wszystkich etapów badań opisanych w niniejszej pracy, równocześnie strumień gazów spalinowych wydostający się z reaktora pieca, poddawany był analizie za pomocą analizatora spalin typu MADUR GA-21 *plus*. Mierzonymi parametrami były stężenia tlenku siarki(IV), tlenków azotu i tlenku węgla(II).

Ostateczna analiza wszystkich opisanych badań pozwoliła stwierdzić, że odpady z tworzyw sztucznych posiadając największy masowy ubytek i najmniejsze wartości stężeń gazów spalinowych powstałych w procesie spalania tych odpadów, charakteryzują się największym stopniem efektywności tego procesu. Ale dodatkowo należy brać pod uwagę to, że w czasie termicznego przekształcania tego rodzaju odpadów powstają dodatkowe produkty toksyczne, zarówno gazowe, ciekłe jak i stałe, których analizy nie założono w zakresie badań niniejszej pracy.

Dlatego niezbędne jest projektowanie instalacji termicznej utylizacji odpadów (wraz z kompleksowymi węzłami oczyszczania spalin). Tego rodzaju instalacje należy projektować w oparciu o morfologie odpadów komunalnych oraz bilans energetyczny wsadu do pieca spalarni, tak aby proces ten był efektywny i właściwy, nie tylko ze względów energetycznych, ale i ekologicznych. Będzie to wymagało określonej kompozycji wsadu do komory pieca zakładu termicznego przekształcania odpadów.

Słowa kluczowe:
odpady, osady ściekowe, termiczne przekształcanie, skuteczność spalania

Keywords:
waste, sewage sludge, thermal processing, effectiveness of incineration

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Influence of Axial Heat Conduction in the Wall on Convective Heat Transfer in the Microchannel

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1. Introduction

In literature there are reported many experimental results revealed significantly lower value of heat transfer coefficients for fully developed laminar flow. Some of the authors are trying to explain this phenomenon due to scale, aspect ratio of micro channels in micro heat exchanger, roughness of the wall or axial heat conduction. The importance of axial heat conduction increases with increasing ratio of channel thickness to channel length, and wall to fluid thermal conductivity ratio. The fluid temperature along the channel length in uniformly heated channel did not increase linearly, according to many researchers. This evidence is due to axial conduction. Davis and Gill [2] numerically investigated the effect of axial heat conduction. According to survey of literature clearly exhibit the effect of axial conduction on heat transfer. Herwig and Hausner [3] compared their numerical simulation with experimental data of Tso and Mahulikar [6] for water flow in an aluminium plate with 25 circular microchannels. Experimental evidence as well as extensive numerical studies confirm this effect.

Many authors present their results both on theoretical and experimental investigation concerning usage of mini- and microchannel heat exchangers used in environmentally friendly distributed energy installations based on ORC ([1]). However, proper design of microchannel heat exchangers have to take into account many additional effects, for example axial heat conduction in microchannel heat exchanger walls.

In the present work a new analytical model is developed based on the axial conduction effects on the local fluid temperature and on the local wall temperature. This model is compared with available similar theoretical models and experimental data for single-phase liquid flow.

2. Theoretical Model

Consider laminar developed flow in micro channel subjected to constant heat flux. In this work, the analysis is oriented at evaluating the local fluid and wall temperatures at any section of the channel in the fully developed flow region. The model is intended to determine heat transfer coefficient in the fully developed region taking into account conduction in the wall. The sketch of the problem is shown in Fig. 1. Fluid is flowing in the channel and the wall is subjected to constant heat flux on the outside surface. Additionally, in the model the following assumptions were made: steady state, fluid properties are constant, fluid flow is thermally and hydro dynamically fully developed.

Fluid in the channel is warmed or cooled by convective heat flux q_k which has lower value then heat flux q on the outside surface of the wall. This is the reason that that convective heat transfer coefficient on the inner surface of the wall is lower than heat transfer coefficient calculated on the basis of heat flux on outer surface of the wall.

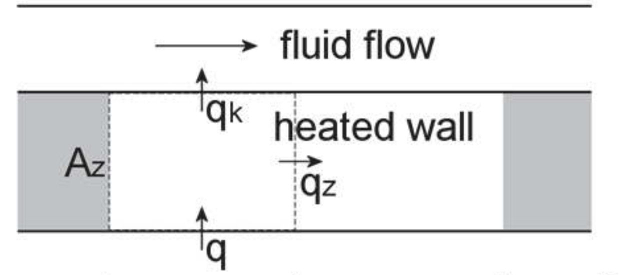

Fig. 1. The sketch of the problem of axial conduction in the wall
Rys. 1. Przedstawienie zagadnienia wzdłużnego przewodzenia ciepła w ściance

Considering the energy balance for:

1. the wall:

$$qU = q_k U + q_z A_z \tag{1}$$

Rewriting in details (1) we have;

$$qU = h_e U(T_w - T_f) - \lambda A_z \frac{d^2 T_w}{dz^2} \tag{2}$$

2. the fluid:

$$\dot{m} c_p dT_f = h_e U (T_w - T_f) dz$$

or

$$\dot{m} c_p \frac{dT_f}{dz} = h_e U(T_w - T_f) \tag{3}$$

Assuming that for constant heat fluxes:

$$\frac{dT_f}{dz} \cong \frac{dT_w}{dz} \tag{4}$$

we can obtain differential equation for the wall by introducing (3) and (4) to (2):

$$qU = \dot{m} c_p \frac{dT_w}{dz} - \lambda_z A_z \frac{d^2 T_w}{dz^2} \tag{5}$$

Solving (5) with boundary conditions $\frac{dT_w}{dz} = 0$ for z=L we get:

$$\frac{dT_w}{dz} = \frac{qU}{\dot{m} c_p}(1 - e^{-M(l-x)}) \tag{6}$$

where: $M = \frac{\dot{m} c_p}{\lambda_z A_z}$ (7)

Adiabatic boundary condition assumed for z=L is not exactly satisfied in the reality, but it simplifies mathematical calculation.

Introducing Reynolds Number $\mathrm{Re} = \frac{d_h G}{\mu}$ and Prandtl Number $\mathrm{Pr} = \frac{c_p \rho \gamma}{\lambda}$ we obtain dimensionless form of number M^+:

$$M^+ = \frac{\mathrm{Re}}{\mathrm{Pr}} \frac{\lambda_f}{\lambda_w} \frac{Ul}{A} \tag{8}$$

In the case when we neglect axial conduction in (2) we have heat transfer from wall to the fluid only through convection:

$$qU = h\,U(T_{wz} - T_{fz}) = \dot{m}c_p \frac{dT_{fz}}{dz} \tag{9}$$

where: h – nominal heat transfer coefficient for laminar developed heat transfer.

Assuming for constant heat flux that:

$$\frac{dT_{fz}}{dz} \cong \frac{dT_{wz}}{dz} \tag{10}$$

Introducing (10) to (9), we obtain constant gradient of temperature distribution in the wall.

$$\frac{dT_{wz}}{dz} = \frac{qU}{\dot{m}c_p} \tag{11}$$

Comparing (6) with (11) we can see that axial gradient temperature in the wall in case of taking into account axial conduction is less than in the case when we neglect axial conduction except of beginning conduction in the wall. Convective term in (2) is:

$$q_{con} = h_e(T_w - T_f) = \frac{\dot{m}c_p}{U}\frac{dT_f}{dz} \cong \frac{\dot{m}c_p}{U}\frac{dT_w}{dz} \tag{12}$$

Introducing (6) into (12) we get:

$$\frac{q_{con}}{q} = 1 - \exp(-M^+(1 - x^+)) \tag{13}$$

In the same relation are heat transfer coefficients. The ratio of the two heat transfer coefficients may be written as:

$$\frac{h_e}{h} = 1 - \exp(-M^+(1 - x^+)) \tag{14}$$

or

$$\frac{Nu_e}{Nu} = 1 - \exp(-M^+(1 - x^+)) \tag{15}$$

Relation (14) for $M^+=1$ is shown in Fig. 2.

Average value of equivalent heat transfer coefficient is:

$$\frac{h_e}{h} = \frac{1}{l}\int_0^1 \frac{h_e(x^+)}{h}dx^+ = 1 - \frac{1}{M^+}(1 - \exp(-M^+)) \tag{16}$$

or

$$\frac{Nu_e}{Nu} = 1 - \frac{1}{M^+}(1 - \exp(-M^+) \tag{17}$$

Dependence of $\frac{h_e}{h}$ against M^+ is presented in Fig. 3

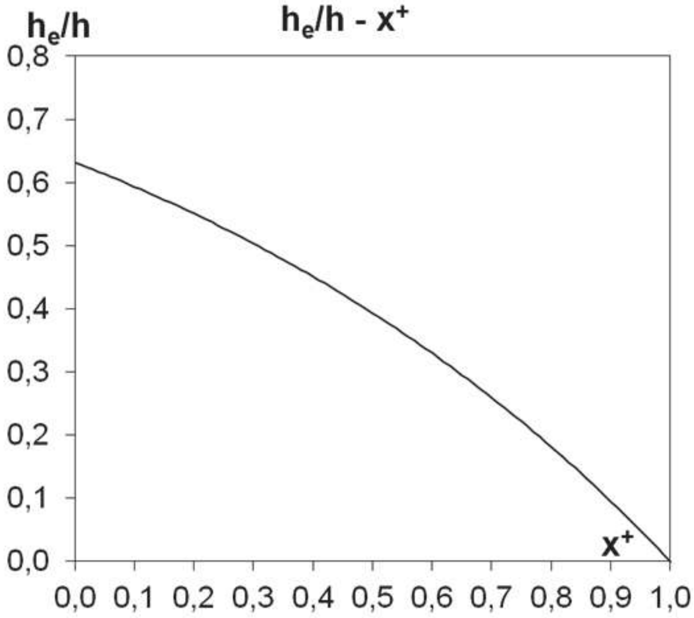

Fig. 2. Local ratio $\frac{h_e}{h}$ against reduced heated part's length x^+

Rys. 2. Lokalna iloraz $\frac{h_e}{h}$ w zależności od zredukowanej długości x^+

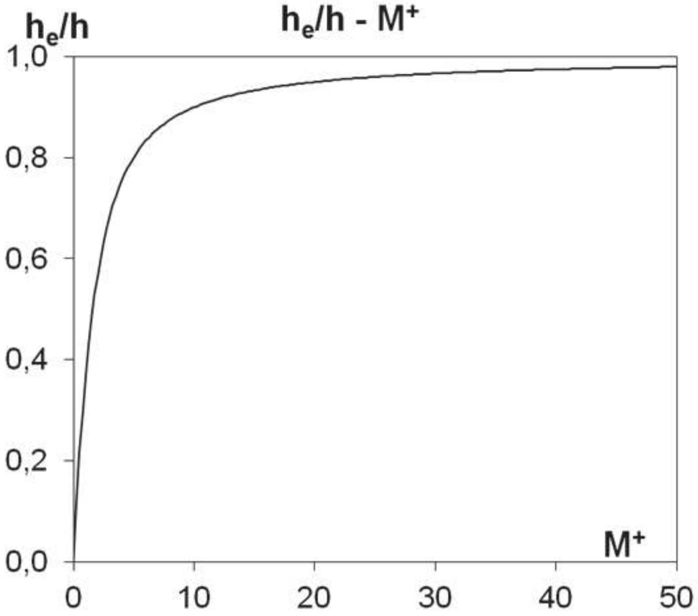

Fig. 3. Dependence of $\frac{h_e}{h}$ against M^+

Rys. 3. Zależność $\frac{h_e}{h}$ od M^+

3. Validation of the Model

Lin and Kandlikar [4] compared their model with numerical simulation of Maranzana et al [5] for water flow in a 100 μm channel formed by two 10 mm long and 500 μm thick silicon blocks. The channel was heated by 30 kW/m^2 uniform heat flux on one wall and the other wall was applied an adiabatic boundary condition. Fig. 4 shows the numerical simulation results by Maranzana et al [5] and Lin and Kandlikar [5]. The present model, Eq. (17) is also plotted in Fig.4 for comparison with simulation results.

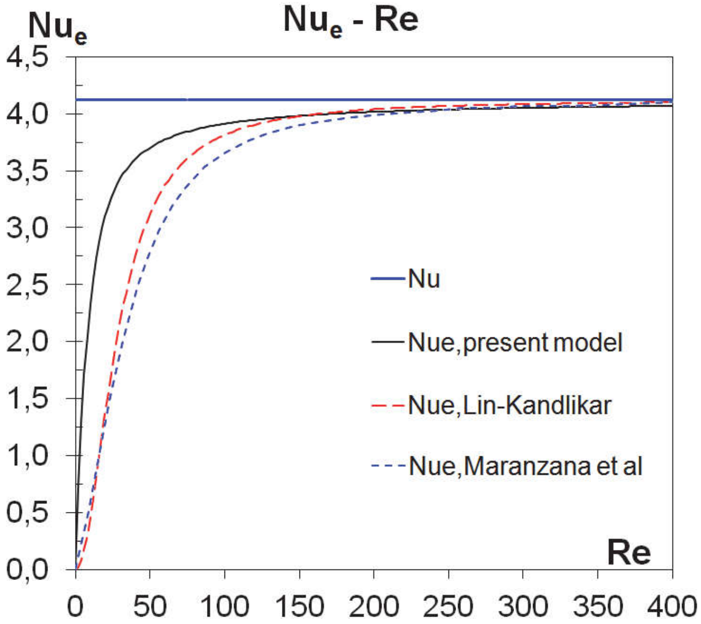

Fig. 4. Results of numerical simulations by Lin and Kandlikar [4] and Maranzana et al [5] with comparison to the present analytical model
Rys. 4. Wyniki porównania numerycznych symulacji wg Lin i Kandlikar [4] oraz Maranzana et al [5] z prezentowanym modelem analitycznym

4. Conclusions

The effect of axial conduction is important, while reducing the experimental data. A new model is developed to account for this effect. The effect of axial heat conduction in the fluid is shown to be negligible for air and water flow in microchannels for conditions generally encountered in cooling electronic equipment. The paper presents that the new model results are in agreement with numerical simulations and experimental evidences. The model shows that the axial conduction effect in the wall are important for gas flow in any wall material and is negligible for water flow in metal tubes.

Nomenclature

A – channel wall cross-sectional area for axial conduction, m^2
c_p – heat capacity, J/kgK
d_h – hydraulic diameter of the channel, m
h – heat transfer coefficient, W/m^2K
L – length of the heated part, m
M – nondimensional parameter
m – mass flow rate, kg/s
Nu – Nusselt number
Pr – Prandtl number
q – heat flux, W/m^2
Re – Reynolds number
U – perimeter, m
T – temperature, K
x – distance from the entrance of the heated part, m
z – axial coordinate, m

Greek letters

λ – thermal conductivity, W/mK

Subscripts

conv – convection
e – with conduction
f – fluid
w – wall
z – conduction
+ – dimensionless (reduced)

References

1. **Bohdal T.:** *Investigations of environmental friendly refrigerants' phase changes in minichannels.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection). 15, 107–126 (2013).
2. **Davis E. J., Gill W. N.:** *The effects of axial conduction in the wall on heat transfer with laminar flow.* Int. J. Heat Mass Transfer. 3(13), 459–470 (1970).
3. **Herwig H., Hausner O.:** *Critical view on "new results in micro-fluid mechanics": an example.* Int. J. Heat Mass Transfer. 5(46), 935–937 (2003).
4. **Lin T-Y., Kandlikar S. G.:** *A theoretical model for axial heat conduction effects during single-phase flow in microchannels.* J. Heat Transfer. 2(134) (2012).
5. **Maranzana G., Perry I., Maillet D.:** *Mini- and micro-channels: influence of axial conduction in the walls.* Int. J. Heat Mass Transfer. 17–18(47), 3993–4004 (2004).
6. **Tso C. P., Mahulikar S. P.:** *Experimental verification of the role of Brinkman number in microchannels using local parameters.* Int. J. Heat Mass Transfer. 10(43), 1837–1849 (2000).

Wpływ podłużnego przewodzenia ciepła w ściance na konwekcyjną wymianę ciepła w mikrokanale

Streszczenie

Opracowany został nowy model umożliwiający obliczenie wpływu podłużnego przewodzenia ciepła w ściance kanalika na wymianę ciepła pomiędzy ścianką a przepływającym czynnikiem w mikrokanale. Zbadany został przypadek ustalonej wymiany ciepła. Znaleziono bezwymiarowe kryterium umożliwiające ocenę ważności wzdłużnego przewodzenia ciepła w ściance. W publikacji przedstawiono porównanie wyników modelu z wynikami przy zaniedbaniu podłużnego przewodzenia ciepła oraz z wynikami innego modelu opracowanego przez Kandlikara. Dodatkowo wykonano porównanie nowego modelu z wynikami eksperymentalnymi innych autorów. Osiągnięto zadawalające rezultaty.

Słowa kluczowe:
podłużne przewodzenie w ściance, konwekcyjna wymiana ciepła, mikrokanał

Keywords:
axial conduction in the wall, convective heat transfer, microchannel

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Application of FEM and Vision-Based Methods to Analysis of Shearing Processes in the Aspect of Scrap Reduction

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1. Introduction

Metal cutting plays a very important role in mechanical manufacturing area, the nature of this process being concerned with many related subjects of technology and industry. Modern manufacturing cutting techniques are rife with problems related to ensuring the quality of manufactured products while minimising the cost of production and increasing process efficiency. In the 21st century, the production of new products must be subject to "*eco-design production*," which involves limiting negative impacts on the surrounding natural environment. The dominant components of this activity include the rational use of energy and environmental protection [4–8]. In this regard, it is important to correctly design and realise technological processes. In cutting process mechanism of material separation is often very hard to accomplish in the production cycle due to the difficulties encountered in precision process parameter settings [1–3]. As a result, such defects can appear after processing in workpiece (e.g., deformation, twisting, bowing, and defects of the sheared edge such as burrs and slivers). The accumulation of burrs and slivers on the knife, die and the work piece's sheared edge can result in an unacceptable surface finish and increases scrap (Fig. 1).

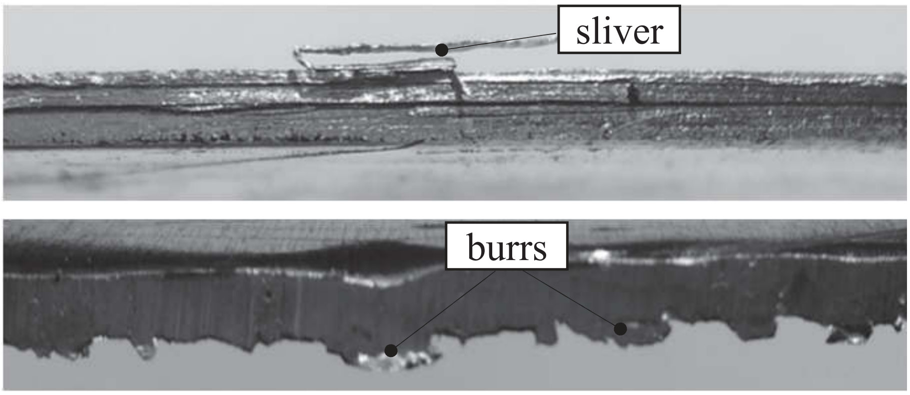

Fig. 1. A typical defects of the workpiece's sheared edge
Rys. 1. Typowe defekty napotykane na powierzchni przecięcia wyrobu

Finite element analysis (FEA) is a powerful and economical method that has been used widely for engineering design purpose [12–21, 23]. Whilst significant progress has been made in enhanced understanding of ductile fracture mechanisms in shearing process and developing advanced computational capabilities for detailed process simulation, application of FEM and vision-based methods is challenging [10, 11, 22]. A main difficulty in modelling of shearing process is that only a limited number of FEM models are currently capable of describing the complete shearing process, including the complete separation of the material parts through ductile fracturing. In experimental analysis a main problem is large and irregular deformations in tool - workpiece contact zone which is difficult to analysis [31]. For a long period of time, the method used for the analysis of displacements in contact zone was that of visioplasticity. Vision-based methods are ideally suited to the task of non-contact/non-intrusive deformation and strain measurement in cutting process. Using this methods an analysis of state of material displacements and deformation at any moment of process can be possible.

The present paper presents an application of FEM and vision-based methods to analysis of cutting process in the aspect of scrap reduction. The proposed methodology enabling the realization of measurements and calculations in a quick and precise manner for the shearing processes. This allows the analysis of the cutting process at any time during the process. This makes it possible to observe the formation of surface defects and then develop recommendations for their minimization.

2. Finite Element modeling

The description of the nonlinearity of the material was conducted using an incremental model that takes into account the influence of the history of strains and strain rate. The object (the metal sheet that is being cut) is treated as a body in which elastic strains may occur (in the scope of reversible strains) together with viscous and plastic strains (in the scope of irreversible strains) with nonlinear strengthening. For the purpose of constructing the material model, the following was used: Huber-Mises-Hencky's nonlinear plasticity condition, the associated flow law and combined strengthening (i.e., isotropic and kinematic). The state of the material after the aforementioned processing was taken into account by introducing the following initial states: displacement, stresses, strains and their rate. The states of strains and strain rate were described with nonlinear dependences and no linearization. In this description, adequate measures were used for an increment of strains and for an increment of stresses (i.e., an increment of Green-Lagrange strain tensor and an increment of the second symmetric stress tensor of Pioli-Kirchhoff). The incremental contact model covered the contact forces, the contact rigidity, the contact boundary conditions and the friction coefficients in this area. The mathematical model was supplemented with incremental equations of the object's motion and the uniqueness conditions. An incremental function of the total energy of the system was introduced. From the stationary condition of this function, it is possible to derive a variational nonlinear equation to describe the motion and deformation of the object for a typical incremental step. This equation was untangled with spatial discretization using the finite element method, which resulted in discrete systems of equations for the motion and deformation of the object in the guillotining process.

2.1. Basic relationships

Components of the Green-Lagrange's strain tensor increment, for a typical time step Δt, for the non-linear isotropic material with mixed hardening, were calculated from the formula [2, 24, 25]:

$$\Delta\varepsilon_{ij} = \frac{1}{1-\widetilde{S}^{**}} \cdot \left(D^{(E)}_{ijkl} \cdot \Delta\sigma_{kl} - \frac{\frac{2}{3} \cdot [\sigma_Y(\cdot)] \cdot \dot{E}_T \cdot \Delta\dot{\varepsilon}_e \cdot \widetilde{S}_{ij}}{\widetilde{S}_{ij} \cdot C^{(E)}_{ijkl} \cdot \widetilde{S}_{kl} + \frac{2}{3} \cdot \sigma_Y^2(\cdot) \cdot \left(\widetilde{C}(\cdot) + \frac{2}{3} \cdot E_T \right)} \right) \tag{1}$$

Components of the Pioli-Kirchhoff's stress tensor increment, for a typical time step Δt, for the non-linear material with mixed hardening, were calculated using the formula:

$$\Delta\sigma_{ij} = C^{(E)}_{ijkl} \cdot \left(\Delta\varepsilon_{kl} - \psi \frac{\widetilde{S}_{kl} \cdot \left\{ \widetilde{S}_{ij} \cdot C^{(E)}_{ijkl} \cdot \Delta\varepsilon_{kl} - \frac{2}{3} \cdot \sigma_Y(\cdot) \cdot \dot{E}_T^{(VP)} \cdot \Delta\dot{\varepsilon}_z^{(VP)} \right\}}{\widetilde{S}_{ij} \cdot C^{(E)}_{ijkl} \cdot \widetilde{S}_{kl} + \frac{2}{3} \cdot \sigma_Y^2(\cdot) \cdot \left(\widetilde{C}(\cdot) + \frac{2}{3} \cdot E_T \right)} \right) \tag{2}$$

Where ψ is the load factor and is $\psi = 1$ for loading and $\psi = 0$ for unloading processes, $\widetilde{S}^{**} = \widetilde{S}^{*}_{ij} \cdot C^{(E)}_{ijmn} \cdot \widetilde{S}_{mn}$ is a positive scalar variable, $\widetilde{S}_{ij} = S_{ij} - \alpha_{ij}\ (i, j = 1 \div 3)$ are the stress deviator component, $\widetilde{\mathbf{D}}_\sigma$ and $D^{(E)}_{ijkl}$ are the components for the tensor $\mathbf{D}^{(E)} = \mathbf{C}^{(E)^{-1}}$ in time t, $C^{(E)}_{ijkl}$ are the elastic constitutive tensor components $\mathbf{C}^{(E)}$, $\widetilde{C}(\cdot) = \widetilde{C}(\varepsilon_e^{(VP)}, \dot{\varepsilon}_e^{(VP)})$ is the temporary translation hardening parameter in time t. $\sigma_Y(\cdot) = \sigma_Y(\varepsilon_e^{(VP)}, \dot{\varepsilon}_e^{(VP)})$ is the accumulated material yield stress, which depends on the history of the viscoplastic strain and strain rate, $\varepsilon_e^{(VP)}$ and $\dot{\varepsilon}_e^{(VP)}$ are the cumulative effective viscoplastic strain and strain rate, respectively, E_T - is the strain hardening modulus at time t, $\dot{E}_T$ - is the strain rate hardening modulus at time t [26, 27]. The instantaneous value of the yield stress σ_Y can be calculated from patterns present in the ANSYS program database, such as the Johnson-Cook material law [28] or Cowper–Symonds model [2].

2.2. Application to the shearing processes

A numerical example is shown for guillotining and shear-slitting processes. A three-dimensional finite element models were constructed using explicit finite element software package ANSYS/LS-DYNA.

During the first part of the guillotining process, the upper and lower knives indent the sheet, pulling down some surface material. This causes the sheet to bend over the cutting tools, creating the rollover of material. After some knives movement, shear deformation will take over from the indentation, forming the sheared edge of the product. This is generally a smooth surface, which shows some wear due to the contact with the cutting tools. At some point in the shearing phase, ductile material failure will occur in the vicinity of the cutting edge of the tools. This fracture propagates through the sheet in the direction of the opposite cutting tool, forming the fractured zone of the product. In guillotining process is important to obtain products without twisting and bowing (Fig. 2). These defects give rise to waste after cutting. Analysis of the degree of deformation of the sheet during cutting is possible by measuring the displacements of the various areas of the sheet. Then it is possible to investigate the cause of the formation of twisting and bowing defects. Fig. 2 shows the contours of the equivalent stresses during guillotining. The greatest stresses occur in the cutting zone adjacent the cutting edges of tools.

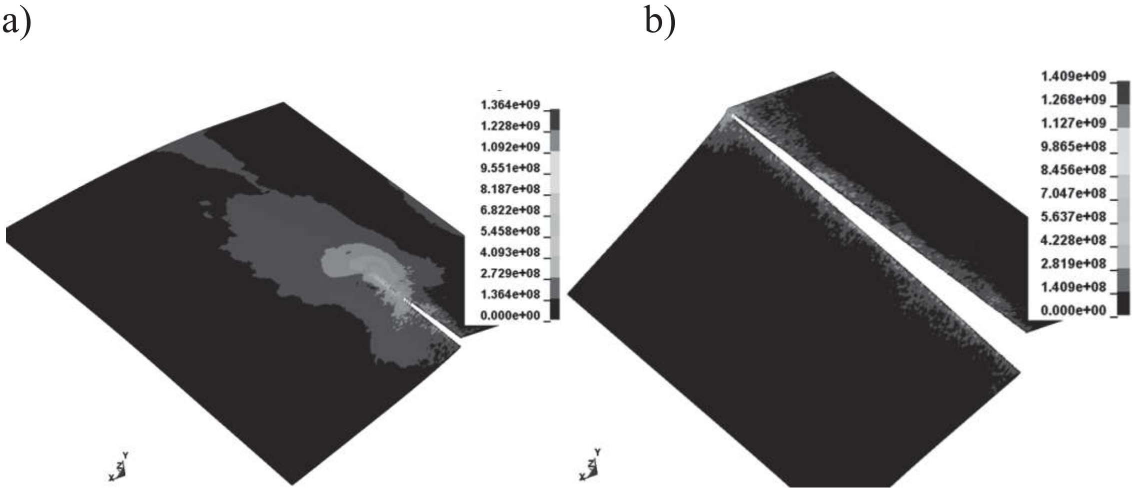

Fig. 2. Contours of the equivalent stress during guillotining of DC01 steel: a) 30% step time, b) 100% step time

Rys. 2. Rozkład naprężeń zastępczych podczas cięcia na gilotynie stali DC01: a) 30% zaawansowania procesu, b) 100% zaawansowania procesu

In shearing process in many cases a scrap formation is a result of fracture process because less steady and progresses in a nonuniform manner. A dramatic transition of the fracture mode from the "shear mode" to the "shear and tear mode" on cut surface can be observed

(Fig. 3). This result suggests that shearing under specific conditions is a three-dimensional rather than two-dimensional problem. The fracture process is unsteady and progressed in a nonuniform manner because of the stress and strain states created by the macroscopic cutting conditions.

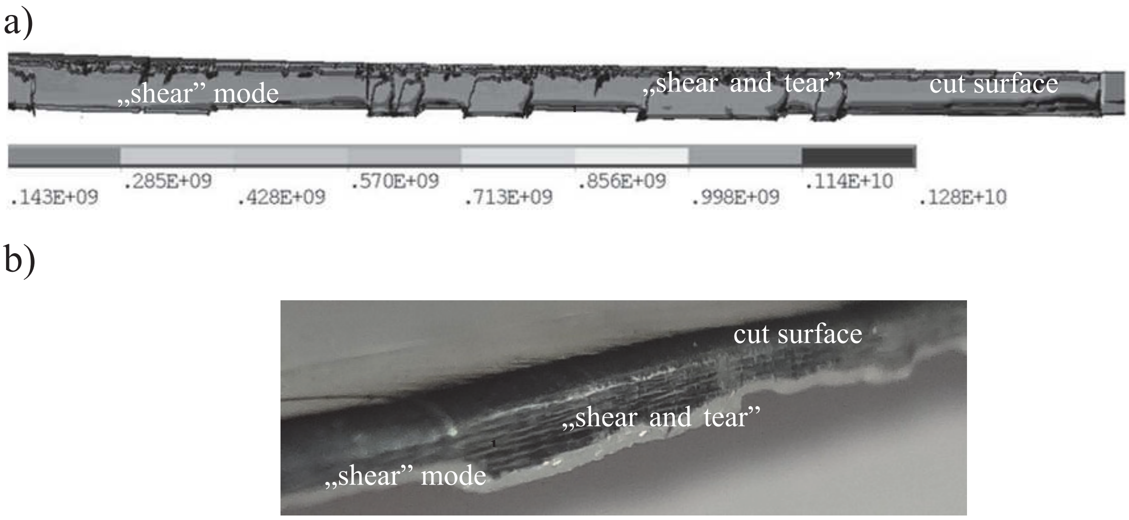

Fig. 3. Transition of the material fracture mode from the "shear" to the "shear and tear" mode during guillotining of aluminium alloy AA6111-T4:
a) simulation, b) experiment

Rys. 3. Zmiana charakteru pękania materiału podczas cięcia stopu aluminium AA6111-T4: a) symulacja, b) eksperyment

In slitting processes as the sheet slits, it moves tangentially to the blade. This causes the area of contact with the knive blade on the sheet to be inclined to the horizontal at an angle. The normal compressive stress is thus split into two components in the direction of the axes Z and Y contributing to the two normal stresses. The shear stress shows high values in the region where the sheet is expected to slit and the values drop down as the knives moves away from the region (Fig. 4). The high shear stress is caused by the shearing action of the two blades on either side of the sheet.

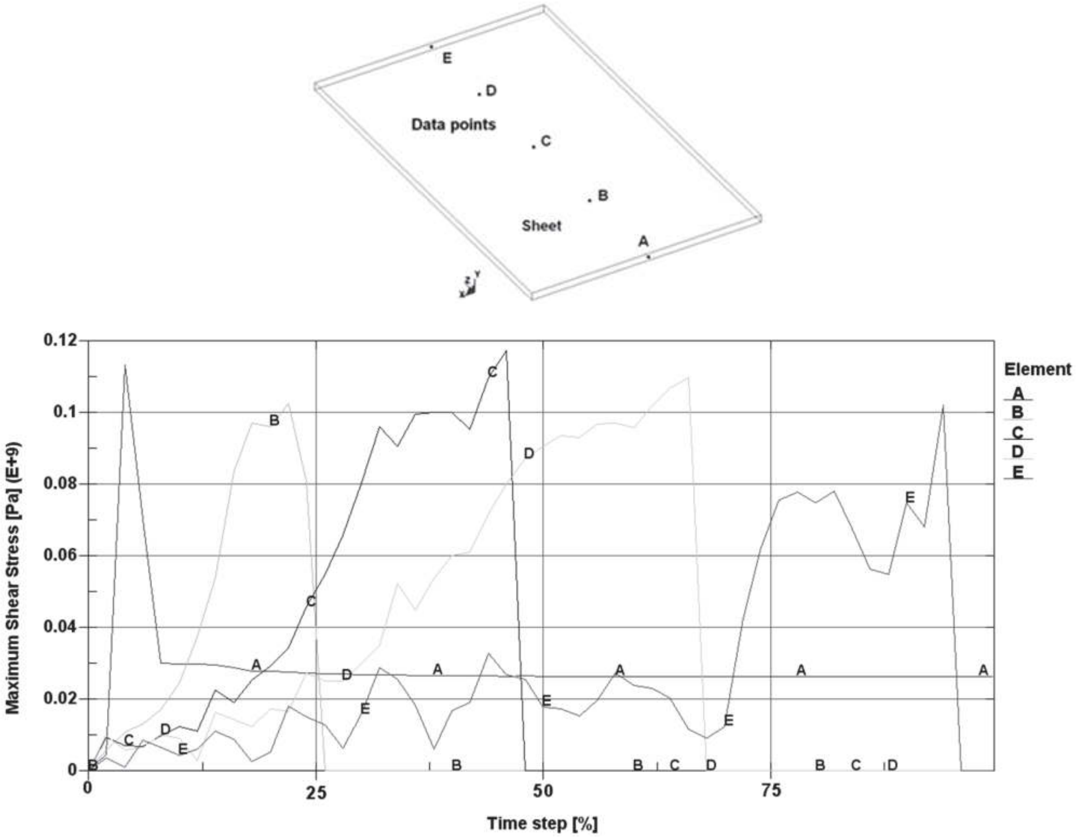

Fig. 4. Values of the maximum shear stresses measured in shearing region during slitting
Rys. 4. Wartości maksymalnych naprężeń ścinających mierzonych w strefie cięcia

The quality of the edge produced from the slitting of the sheet would depend upon the damage caused to the edge and the extent of the damage around the edge (Fig. 5). Measure the degree of damage can be done by the stress and strains analysis in the cut surface. Figs. 5 and 6 show the effective plastic strain distribution after process. The effective plastic strain is highest on the cut surface and decreases within the depth of the material and appear to stabilize at a depth of approximately 1.5 mm (Fig. 6). Obtained results can be used in analysis of size of degraded area.

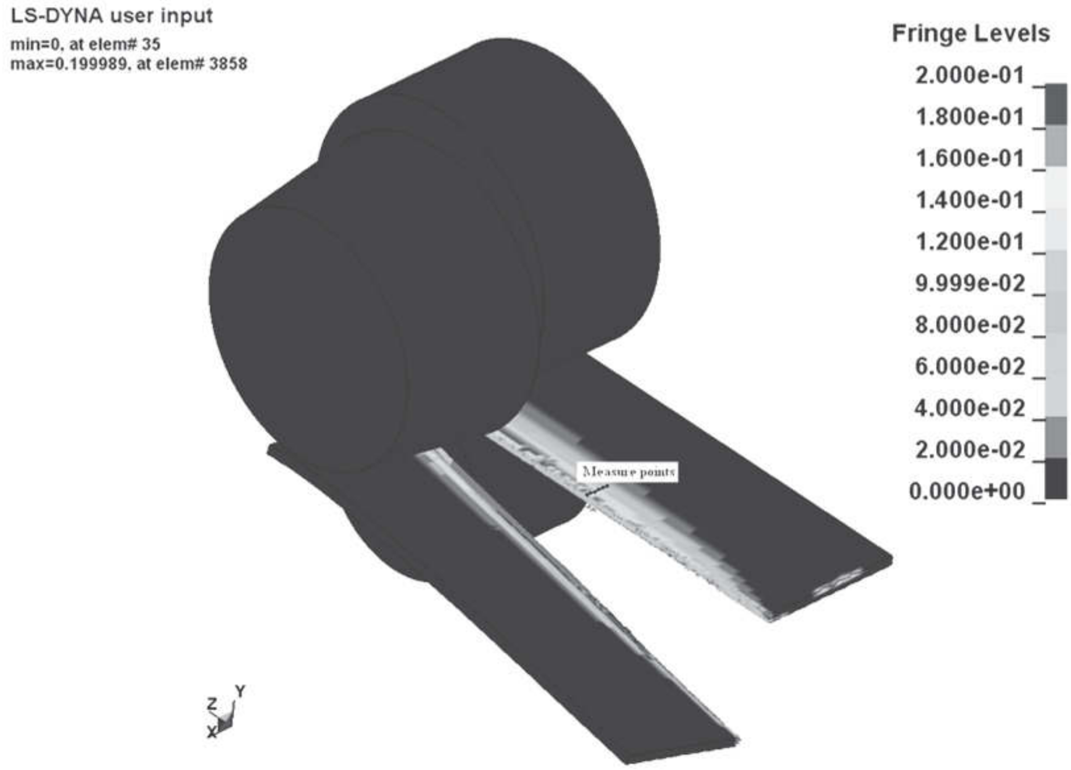

Fig. 5. The effective plastic strain distribution after process of slitting aluminum alloy AA6111-T4 (1.5 mm thick)
Rys. 5. Rozkład odkształceń zastępczych po procesie cięcia stopu aluminium AA6111-T4 o grubości 1,5 mm

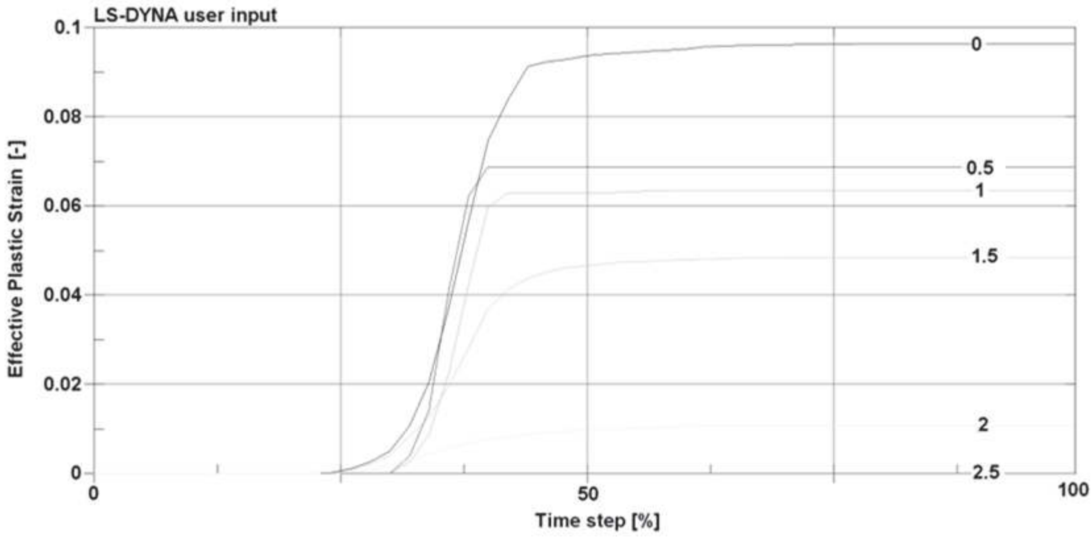

Fig. 6. Dependence of effective plastic strain on distance [mm] from the cut edge during slitting aluminum alloy AA6111-T4 (1.5 mm thick)
Fig. 6. Zależność odkształceń zastępczych od odległości [mm] od krawędzi cięcia stopu aluminium AA6111-T4 o grubości 1,5 mm

3. Vision-based measurement system

Full field displacement measurement methods have gained significant attention the last two decades, due to the great impact of the evolution of the digital imaging [9, 29, 30]. Modern digital cameras provide a cost-effective and highly reliable tool for recording and processing the images of an experiment with a personal computer. Image-based displacement and strain measurements are non-invasive. During the slitting process, a high-speed camera together with a computer controlled framegrabber can record a set of consecutive images of the sample surface (Fig. 7). A zoom lens is mounted on the high speed camera to focus on the small deformation zone. The optically track surface markers on the specimen during deformation is used to calculate the displacements and strains (Fig. 8d).

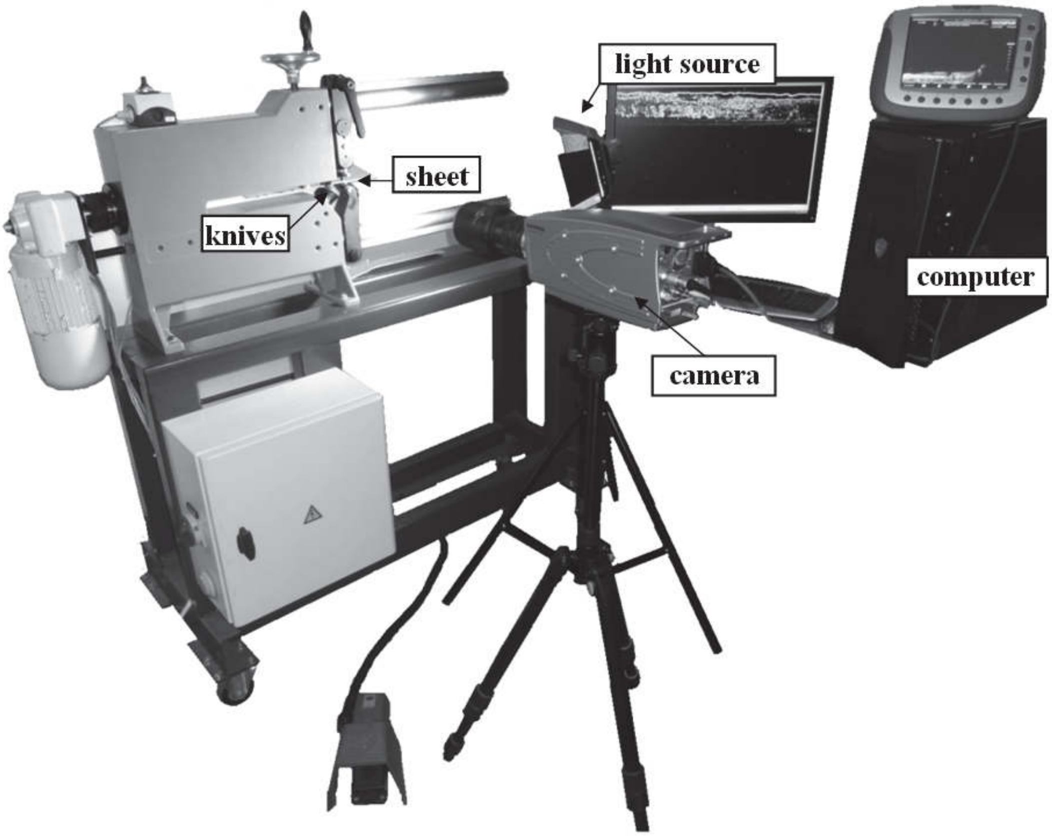

Fig. 7. Vison-based measurement system
Fig. 7. System wizyjny do monitorowania procesu cięcia

Vison-based measurement system allow for observation of the process of formation of defects in the form of burrs and bendings of the cut edges. Figure 8 show moment of final separation of sheet and a process of burr formation on the cut surface during slitting aluminum alloy AA6111-T4. It was found that this is caused by too much clearance between the knives. An interesting phenomenon is observed at final stage of process. Rapid crack propagation occurred after crack initiation with the burr closely following the shape of the upper knive. Analysis of displacements of markers allows to determine the deformation of the material being cut.

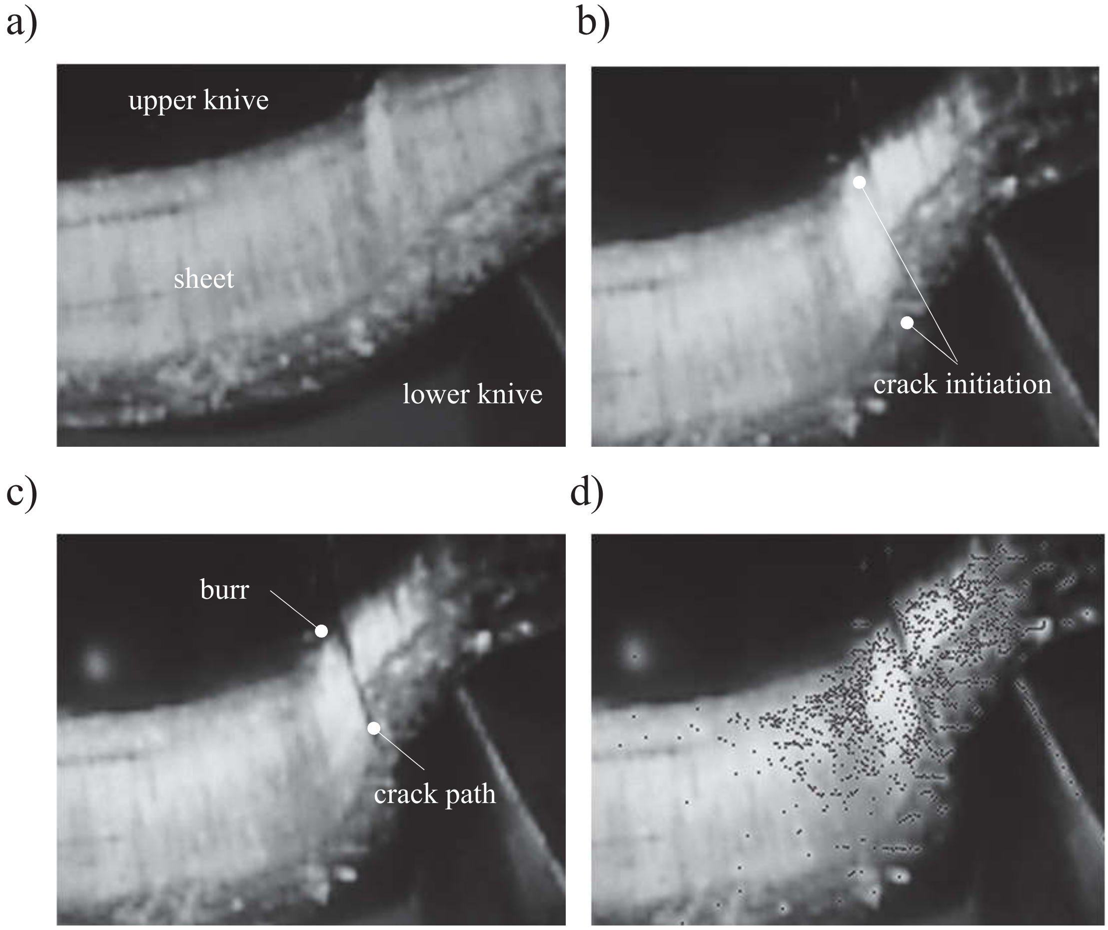

Fig. 8. Moment of final separation of sheet during slitting
Fig. 8. Moment całkowitego rozdzielenia materiału podczas cięcia na nożycach krążkowych

4. Conclusions

The paper presents the possibility of using FEM and vision-based techniques in the design of the cutting process. Using FEM and vision-based techniques allow for a detailed analysis of the physical phenomena occurring during the cutting and making developing of recommendations on the selection process conditions in terms of energy and scrap minimization. Vision-based techniques are a valuable tool for the validation of numerical models. The results obtained can be a great significance to the control of the properties of materials sheared and offer a possibility of an effective interference with the designing of the technological process and an adaptation of the technological quality is the adequate functional requirements and operating conditions. This will reduce energy consumption and negative impact of this process on the natural environment.

References

1. **Bohdal Ł.:** *Finite element simulation of 3D sheet metal guillotining using elastic/visco-plastic damage model.* Steel Research International. Special Edition: 14th International Conference on Metal Forming, 1419–1422 (2012).
2. **Bohdal L, Kukielka L.:** *Application of variational and FEM methods to the modelling and numerical analysis of guillotining process for geometrical and physical nonlinearity.* Mechanika, 20(2), 197–204 (2014).
3. **Bohdal Ł., Walczak P.:** *Eco-modeling of metal sheet cutting with disc shears,* Rocznik Ochrona Srodowiska (Annual Set the Environment Protection), 15, 863–872 (2013).
4. **Bohdal Ł., Kulakowska A., Patyk R.:** *Analysis of slitting of aluminum body panels in the aspect of scrap reduction.* Rocznik Ochrona Srodowiska (Annual Set the Environment Protection), 16, 105–114 (2014).
5. **Chodor J., Kukielka L.:** *Numerical analysis of chip formation during machining for different value of failure strain*, GAMM 78th Annual Meeting of the Gesellschaft für Angewandte Mathematik und Mechanik, 16, July, Zürich. Journal PAMM, 7/1, 4030031-4030032, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 12 Dec 2008.
6. **Florianowicz M., Bohdal Ł.:** *Modeling of the refrigerants condensation in the superheated vapor area*. Rocznik Ochrona Srodowiska (Annual Set the Environment Protection), 14, 393–406 (2012).
7. **Gontarz S., Radkowski S.:** *Impact of various factors on relationships between stress and eigen magnetic field in a steel specimen*. Magnetics, IEEE Transactions on 48 (3), 1143–1154 (2012).

8. **Iwaniec M., Witoś M., Roskosz M., Gontarz S.:** *Diagnosis of supporting structures of HV lines using magneto-mechanical effects.* Solid State Phenomena 208, 70–85 (2014).
9. **Gałęzia A., Gontarz S., Jasiński M., Mączak J., Radkowski S., Seńko J.:** *Distributed system for monitoring of the large scale infrastructure structures based on analysis of changes of its static and dynamic properties*. Key Engineering Materials 518, 106–118 (2012).
10. **Golovashchenko S.F.:** *A study on trimming of aluminum autobody sheet and development of a new robust process eliminating burrs and slivers*. International Journal of Mechanical Sciences, 48, 1384–1400 (2006).
11. **Hilditch T.B., Hodgson P.D.:** *Development of the sheared edge in the trimming of steel and light metal sheet. Part 1 – Experimental observations.* Journal of Materials Processing Technology, 169, 184–191 (2005).
12. **Kukielka L., Kulakowska A., Patyk R.**: *Numerical analysis of embossing process of regular inequalities with triangular outline on cylindrical semi product*, Journal of Systemics, Cybernetics and Informatics. 8/3, 36–41 (2010).
13. **Kukielka L., Geleta K., Kukielka K.:** *Modelling and Analysis of Nonlinear Physical Phenomena in the Burnishing Rolling Operation with Electrical Current,* Steel Research International Special Edition on Metal Forming, 1379–1382 (2012).
14. **Kukielka L., Kukielka K.:** *Numerical analysis of the process of trapezoidal thread rolling*, in: C.A. Brebbia (Eds.), High Performance Structures and Materials III, WIT*PRESS*, 663–672, Southampton-Boston 2006.
15. **Kukielka L., Kukielka K.:** *Numerical analysis of the physical phenomena in the working zone in the rolling process of the round thread*, in: J.T.M. de Hosson, C.A. Brebbia, S-I Nishida (Eds.), Computer Methods and Experimental Measurements for Surface Effects and Contact Mechanics VIII, WIT*PRESS*, 125–124, Southampton-Boston 2007.
16. **Kukielka L., Chodor J.:** *Numerical analysis of the influence of abrasive grain geometry and cutting angle on states of strain and stress in the surface layer of object*, Eighth International Conference On Computer Methods and Experimental Measurements for Surface Effects and Contact Mechanics "Contact and Surface 2007". Wessex Institute, Ashurst Lodge, Ashurst, Southampton, UK. Editors: J.T.M. De Hosson, C.A. Brebbia, S-I Nishida. WITPRESS, 183–193, Southampton, Boston 2007.
17. **Kukielka L., Chodor J., Storch B.:** *New method of determination of tool rake angle on the basis of crack angle of specimen in tensile test and numerical simulations*, Ninth International Conference on Surface Effects and Contact Mechanics: Computational Methods and Experiments "Contact and Surface 2009", 9–11 June 2009, Algarve, Portugal. Editors: J.T.M. De Hosson, C.A. Brebbia. WITPRESS, 207–216, Southampton, Boston 2009.

18. **Kulakowska A., Kukielka L.:** *Numerical analysis and experimental researches of burnishing rolling process with taking into account deviations in the surface asperities outline after previous treatment.* Steel Research International, 2, 42–48 (2008).
19. **Kulakowska A.:** *Problems of surface preparation under burnishing rolling in aspect of product quality.* Steel Research International, 81/9, 218–221 (2010).
20. **Kulakowska A.:** *Experimental researches of burnishing rolling process of regular surface asperities prepared in turning process*. Steel Research International. Special Edition: 14th International Conference on Metal Forming, 127–131 (2012).
21. **Kułakowska A., Patyk R., Bohdal L.:** *Zastosowanie obróbki nagniataniem w tworzeniu ekologicznego produktu.* Annual Set The Environment Protection (in press).
22. **Li M.:** *Micromechanisms of deformation and fracture in shearing aluminum alloy sheet,* International Journal of Mechanical Sciences 2000, Vol . 42., 907–923.
23. **Orłowska M., Czapp M.:** *Numerical analysis of heat efficiency of the convective heat exchanger build with horizontal plates*, Rocznik Ochrona Srodowiska (Annual Set The Environment Protection), 14, 582–586 (2012).
24. **R. Patyk, L. Kukielka:** *Optimization of geometrical parameters of regular triangular asperities of surface put to smooth burnishing.* Steel Research International, 2, 642–647 (2008).
25. **Patyk R.:** *Theoretical and experimental basis of regular asperities about triangular outline embossing technology*, Steel Research International, 81 (9), 190–193 (2010).
26. **Patyk R.:** *New method of technological surface layer shaping of machine parts during duplex burnishing rolling process.* Steel Research International, Special Edition: 14th International Conference on Metal Forming, 115–117 (2012).
27. **Patyk R., Kułakowska A., Bohdal L.:** *Ekologiczne, ekonomiczne i eksploatacyjne aspekty stosowania obróbki nagniataniem.* Annual Set The Environment Protection (in press).
28. **Salvatore F., Mabrouki T., Hamdi H.:** *Elaboration of analytical thermomechanical cutting model matched by numerical and experimental results.* Mechanika, 18 (6), 705–712 (2012).
29. **Świłło S.:** *Experimental apparatus for sheet metal hemming analysis.* Computer Methods in Materials Science, 13 (2), 326–332 (2013).

30. **Świłło S, Czyżewski P.:** *An experimental and numerical study of material deformation of a blanking process.* Computer Methods in Materials Science, 13 (2), 333–338 (2013).
31. **Zilinskaite A., Ziliukas A.:** *General deformation flow theory*. Mechanika**,** 2 (70), 11–15 (2008).

Zastosowanie metody elementów skończonych i technik wizyjnych do analizy procesów cięcia w aspekcie redukcji odpadu

Streszczenie

Współczesne techniki wytwarzania nie są pozbawione problemów związanych z zapewnieniem odpowiedniej jakości wytwarzanych elementów przy jednoczesnej minimalizacji kosztów ich produkcji jak i wzroście wydajności procesu. W pracy przedstawiono możliwości zastosowania Metody Elementów Skończonych i technik wizyjnych do analizy zjawisk fizycznych zachodzących podczas procesów cięcia. Jednym z czynników ograniczających prawidłowy przebieg procesu cięcia są defekty na powierzchni przecięcia w postaci zadziorów i wiórów. Powoduje to niedokładne przyleganie blach, a w przypadku konieczności składania ich w pakiecie stanowi przeszkodę w prawidłowym montowaniu elementów ciętych w układach mechanicznych lub elektrycznych. Rozwiązanie tego problemu jest jednym z kluczowych zadań tej technologii, a jednym ze stosowanych sposobów jest analiza symulacyjna i doświadczalna poszczególnych faz procesu cięcia. Wyniki analiz mogą być wykorzystane do projektowania procesu cięcia, a także być podstawą doboru parametrów procesu w aspekcie jakości technologicznej wyrobu. Pozwoli to na podniesienie ich jakości i zmniejszenie odpadów materiałowych. Spowoduje to bezpośrednio zmniejszenie zużycia energii i przyczyni się do ograniczenia negatywnego wpływu tego procesu na otaczające środowisko.

Słowa kluczowe:
cięcie, stop aluminium, odpad, Metoda Elementów Skończonych,
techniki wizyjne

Keywords:
cutting, aluminum alloy, scrap, Finite Element Method, vision based solutions

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Dust Features Used to Calculate Dust Removal Performance in Cyclones

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1. Introduction

Almost all the manufacturing processes connected with air pollution with the industrial dust. This pollution has a huge impact to the health of people working at the factories. That's ways the air purification of the industrial gas is a very actual problems nowadays. It is highly important to specify properties of suspended solids, i.e. dust to be removed from air and fluids, in order to determine dust removal performance and state whether it is rational to use one or another type of a deduster.

It is necessary to consider features of dust particles and their interaction with fluids to develop a mathematical method supposed to evaluate dust collecting performance. Provided filters are used as dust collectors geometric dimensions of a particle (diameter) can be essential when choosing an appropriate filter. When cyclones are used the following features are more often considered: density of particles, their geometric dimensions (diameter) and shapes.

2. Literature background

When a shape of an article differs from a spherical one an equivalent diameter d_{ekv}, which is determined by various researchers in different ways, is normally taken to carry out calculation. For instance, [11], take the distance between two the most remote particles for d_{ekv}. In this case the value of the diameter is initially overestimated. Shilyaev offer to consider the equivalent diameter d_{ekv} equal to the diameter of a sphere, the mass equal to the mass of the given particle or the density equal to the material density [8].

Use of an effective diameter as a basic feature of particles, in the case of the mathematical simulation of particles settling in a cyclone, is related to a possibility to apply the Stokes' formula [1]. Whereas the following discrepancies and inaccuracy may arise:

- When using the equivalent diameter of the particles their shapes, which affect hydraulic resistance, are not considered;
- Use of the effective diameter with the aim to apply the Stokes' formula may only be essential in the case of small particles, which movement is ensured by the Reynolds number Re<1. There is no point to use an effective diameter in the case of the large-size particles;
- A possible interaction of particles with fluids is not taken into account;
- the density of the material should be considered to take into account interaction of particles with fluids and determine their relaxation time. This may create tolerances due to the difference between the material density and the effective density of particles since the mass of fluid involved in movement should be also considered in the case of the particles with complicated shapes.

3. Materials and methods

When developing a mathematical model to compute the dust removal performance a calculation practice applied in hydrology with regard to particles settling is suggested to be used. It is also suggested to take a hydraulic size w – hydraulic size under action of the gravity force of each participle in quite large volumes of fluid at rest (gas) as a basic feature of a particle. This value ensures that different factors such as size and shape of particles, fluid (gas) viscosity, relative density of particles and others are considered integrally. Settling of particles under action of the gravity force is considered in hydrology. For this reason let us denominate this value as a gravity settling wg. There is also such a name as an aerodynamic diameter in literature [2, 3, 10].

When computing gravity clarifiers the following is assumed: the hydraulic size of a suspended particle in moving fluid in relation to the volume of this fluid for both the fluid at rest and turbulent flow is equal to the gravity settling w_g. The same assumption is used to compute performance of cyclones.

The value of the gravity settling can be determined in theoretical and empirical ways.

In theory the gravity settling of particles can be obtained by making difference between the gravity force and Archimedes' buoyant force equal to the value of the force of any frontal resistance of a particle falling uniformly with the velocity w:

$$\rho_p \cdot \frac{\pi d^3}{6} g - \rho_f \cdot \frac{\pi d^3}{6} g = c_r \frac{\rho_{ж} w^2}{2} \frac{\pi d^2}{4}, \tag{1}$$

where: $\rho_ч$ – particie density; ρ_f – fluid density; d – particle diameter; c_r – drag coefficient (resistance force);

$$w = \frac{4}{3} \frac{\rho_ч - \rho_{ж}}{\rho_{ж}} \frac{g d^2}{c_x \operatorname{Re}_d \nu}, \tag{2}$$

where: $\operatorname{Re}_d = \frac{wd}{\nu}$.

In the case of small particles (Re$_d$<1) when the Stokes' formula is true and has the following form: $c_x = \frac{24}{\operatorname{Re}_d}$, we can obtain:

$$w = \frac{1}{18} \frac{\rho_p - \rho_f}{\rho_f} \frac{d^2}{\nu} g, \tag{3}$$

In the case of large-size particles (Red>100) we may take $c_r = 0{,}47$ and obtain:

$$w = \sqrt{\frac{\frac{4}{3} \frac{\rho_p - \rho_f}{\rho_f} g d}{c_r}}, \tag{4}$$

As to the model of a particle movement in a cyclone let's introduce the notion of a centrifugal hydraulic size w_c, which is the velocity of the quasi-uniform motion of a particle in relation to the fluid volume moving this particle under action of the centrifugal force caused by its curvilinear motion path. Evidently, when it comes to the centrifugal field we obtain an analogical ratio of the centrifugal hydraulic size w_c, to the centrifugal acceleration u_ε^2/r on the grounds of the same assumptions.

Let's express the hydraulic size in terms of the gravity one with the help of the following ratio; consequently, we obtain the following for small particles:

$$w_c = \frac{u_\varepsilon^2}{gr} w,$$

for large-size particles:

$$w_c = w\sqrt{\frac{u_\varepsilon^2 g}{r}}.$$

When conveying the gravity settling w into the centrifugal hydraulic size wцб it is necessary to ensure that the numbers Red, to be determined for the values w and wцб, are related to the same field of resistance (quadratic and Stokes' one). From the practical point of view it can be accepted that the boundary between these fields is equal to Re_d=10 [5, 9]. The median radial velocity of the particle motion towards a wall of the cyclone under action of the centrifugal force, which is entered into the mathematical model, is considered to be equal to the value of the centrifugal settling velocity.

There is a comprehensive way to determine the gravity settling of particles which is empirical measurement.

In this case the velocity of falling particles of different types due to the gravity force should be measured, i.e. it is easier to state the time within which a certain particle (evolved from a source of pollution) due to its dead-weight can pass through a fixed distance vertically. This can be named as a basis of experimental arrangement.

An initially motionless particle falls with acceleration until environmental resistance put the gravity force in equilibrium – according to [7]. The time, within which the particle moves uniformly, is known as the relaxation time of the particle [5, 6]:

$$t_r = k\frac{w}{g}, \tag{5}$$

where k=1 – for small particles when the Reynolds' number Red is related to the Stokes' resistance for large-size particles, and k=1,8 when the Reynolds' number Red is related to the quadratic resistance.

When carrying out experiments the distance lr, to be passed by the particle appears to be a more accessible way for the particle to move uniformly. This value can be named as the relaxation length. The minimum value l_r is as follows:

$$l_r = w \cdot t_r = k \frac{w^2}{g}. \tag{6}$$

The top point of the basis should be lower by the value lr comparing with the point at which the particles enter the area given; consequently, it is necessary to set the basis with the height 1–2 m. The length of the basis is to be determined in relation to the type of the dust so an acceptable accuracy in measuring the time, within which the particle passes through the basis, is ensured. The required condition is that the particle must move from the top point of the basis up to the lowest one with the velocity equal to the gravity settling w. In relation to the type of dust it is necessary to identify fixation techniques of the particle passing through the top and the lowest points of the basis if there is the uniform motion of the particle.

4. Experimental methods and results

When carrying out the experiment the basis of 1,5m has been given. A stopwatch and camera shooting have been used to determine the time when the particle passes a certain distance moving uniformly. A subsequent computer processing has been executed.

The particles of flour, powder and caster sugar have been taken as full-size particles. The results obtained for the hydraulic size are given in the Table 1.

The research on solid particles recovery from air in welding industry is considered to be an up-to-date one. A part of these particles may continue moving at constant high temperature resulting in oxidation (combustion), another part represents the ‘cold’ metal dust. There is no point of measuring diameter or density for the particles under combustion. It is impossible since the particle under combustion has a solid and fluid component, and the only way to identify the features of the particles is to measure the gravity settling.

In this case as in the case of other dust types the most accurate findings can be obtained by carrying out a full-scale experiment. Welding industry has been used as a source of pollution; metal particles evolved while electric welding have been taken as an alloy. As an outcome of this experiment the gravity settling of the particles under combustion has been determined being nearly equal to 1–4 m/s, and, consequently, the relaxation length of the particles l_r, approximately amounts to 0,5–1,5 m (fig. 1).

The results of measuring the hydraulic size w for the metal particles evolved while welding have been obtained when carrying out the full-scale experiment, and are given in the Table 2 [2, 4, 9].

Table 1. Hydraulic size for model particles
Tabela 1. Wymiar hydrauliczny modelowanych cząstek

w, m/s					
meas	powder particles	meas	flour particles	meas	semolina particles
1	0.25	1	0.47	1	0.94
2	0.13	2	0.64	2	1.64
3	0.19	3	0.70	3	1.09
4	0.14	4	0.29	4	0.99
5	0.18	5	0.46	5	0.90
6	0.17	6	0.70	6	1.16
7	0.18	7	0.64	7	1.79
8	0.14	8	0.39	8	0.94
9	0.15	9	0.47	9	1.64
w_{av}	0.15	w_{av}	0.51	w_{av}	1.5

Fig. 1. Measuring the hydraulic size of the dust particles evolved while welding
Rys. 1. Pomiar hydraulicznego wymiaru cząstek pyłu podczas spawania

Table 2. Hydraulic size for nature particles
Tabela 2. Wymiar hydrauliczny rzeczywistych cząstek

meas	w, m/s	meas	w, m/s	meas	w, m/s	meas	w, m/s
1	6.25	1	4.38	1	4.00	1	3.83
2	3.75	2	5.50	2	4.69	2	4.25
3	6.00	3	4.00	3	5.00	3	5.00
4	4.50	4	3.75	4	5.08	4	4.75
5	3.50	5	4.25	5	4.64	5	4.25
6	3.61	6	4.25	6	5.17	6	4.75
7	5.42	7	4.00	7	4.06	7	3.50
8	4.06	8	3.75	8	3.38	8	5.75
9	3.75	9	4.00	9	3.45	9	4.25
10	3.89	10	4.25	10	3.30	10	3.75
w_{av}	4.41	w_{av}	4.21	w_{av}	4.41	w_{av}	4.57

In this case fractional composition can be neglected since the particles act following no particular pattern.

It should be considered that the features of particles may differ in the context of different industries in relation to individual special aspects of the welding machinery, technologies and materials.

The experiments have proved this method to be quite simple. The findings have been obtained privately and given as an example.

The methods used to measure and calculate the gravity settling w make it possible to eliminate the tolerances related to determination of the effective diameter and effective density when computing dust collecting performance in a cyclone. This improves estimation accuracy with reference to the technical performance of the equipment.

5. Conclusion

The notion of the hydraulic size is widely used in hydrology what can be explained by a simplified expression for the hydraulic size of suspended particles in various environments. For instance, in the case of sand pumps the water features are constant; the density and viscosity of water do not change (at the temperature of 200ºC); the shape of suspended sand particles is close to spherical; the gravity settling for the sand particles in fluid only depends on the particle diameter. It would be sufficient to state the ratio of the hydraulic density to the diameter of the particles and enter the result data into the table sheet.

The case of dust is more complicated. First and foremost, the gravity settling depends on the material density (from 500 kg/m^3 (for wood) to 7000 kg/m^3 (for metal)), and in the case of the «non-spherical» particles – on the effective density. Besides, the air viscosity may change to a large extent in relation to the temperature; and fractional composition of the dust is more varied. For this reason the hydraulic size should be determined empirically for each type of the particles.

The method to determine the hydraulic size w described above can be feasible in working environment without using special equipment and well-trained specialists to carry out this experiment.

References

1. **Szkarowski A., Janta-Lipińska S.:** *Examination of boiler operation energy-ecological indicators during fuel burning with controlled residual chemical underburn.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 981–995 (2013).
2. **Vatin N., Chechevichkin V., Chechevichkin A., Shilova Y., Yakunin L.:** *Application of natural zeolites for aquatic and air medium purification.* Applied Mechanics and Materials. 587–589, 565–572 (2014).
3. **Petrochenko M., Yavtushenko E.:** *Diffused structure of drained and back-ventilated rainscreen claddings*. Advanced Materials Research. 945–949, 1015–1022 (2014).
4. **Strelets K., Kitain M., Petrochenko M.:** *Welding spark parameters determination for cyclone removal calculation*. Advanced Materials Research. 941–944, 2098–2103 (2014).
5. **Girgidov A.:** *Deposition of Solid Particles from a Concentrated Suspension.* Power Technology and Engineering. 48 (1), 29–33 (2014).
6. **Dąbrowski J., Piecuch T.:** *Mathematical Description of Combustion Process of Selected Groups of Waste*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 253–268 (2011).
7. **Girgidov A., Vatin, N., Strelets K.:** *Numerical modelling in three dimension velocity field in cyclone.* Magazine of Civil Engineering. 5, 5–9 (2011).
8. **Shiljaev M.I.:** *Hydrodynamics, heat and mass exchange in sprayer sprinkling chambers.* Thermophysics and Aeromechanics. 18(1), 13–24 (2011).

9. **Girgidov A.:** *Mekhanika zhidkosti i gaza (gidravlika) (Fluid Mechanics).* SPBSPU, Saint-Petersburg 2002.
10. **Zhongchao T.:** *Mechanism or particle separation in aerodynamic air cleaning.* for the degree of PhD, Urbana, Illinois 2004.
11. **Shtokman E.A.:** *Ochistka vozduha.* Izdatel'stvo ASV. 62–64 (1998).

Właściwości pyłów wykorzystywane w obliczeniach sprawności odpylania w cyklonach

Streszczenie

Praca poświęcona została badaniom właściwości cząstek pyłów podlegających usuwaniu w odśrodkowych odpylaczach – cyklonach. Podczas oczyszczania powietrza ważne znaczenie maja właściwości zawiesin, czyli pyłów podlegających usuwaniu ze strumienia gazowego. W celu opracowania modelów matematycznych do oceny efektywności odpylania należy uwzględniać charakterystyki cząstek pyłów oraz ich współdziałanie ze strumieniem gazu. Jeśli do odpylania stosuje się filtry, to głównym wskaźnikiem do ich dobory są geometryczna charakterystyka cząstki (srednica). W przypadku zastosowania cyklonów najczęściej wykorzystywane są następujące charakterystyki: gęstość substancji, wymiary geometryczne cząstek (średnica). W literaturze jako główna charakterystykę cząstek pyłów najczęściej stosuje się ich średnicę lub średnicę efektywną, w przypadku kształtu nie sferycznego. To powoduje szereg niedokładności podczas obliczeń sprawności odpylania. Autorzy proponują jako główna charakterystykę cząstek pyłów wprowadzaną do obliczeń sprawności systemów odpylania, stosować ich hydrauliczny wymiar zamiast wymiaru geometrycznego, korzystając z doświadczenia obliczeń osadzania się cząstek wykorzystywanych w hydrologii. Ta wielkość fizyczna w sposób zintegrowany uwzględnia różne czynniki, takie jak wymiary i kształt cząstek, lepkość płynu (gazu), względna gęstość i inne. Zaproponowano sposoby określenia wymiaru hydraulicznego dla cząstek pyłów powstających podczas spawania, jak pokazano na rysunku 1, a także dla innych rodzajów pyłów. Wyniki badań przedstawiono w tabeli 1 i 2. Opracowano możliwość wykorzystania tej charakterystyki w obliczeniach sprawności odpylania w cyklonie.

Słowa kluczowe:
cyklon, grawitacyjny wymiar hydrauliczny, odśrodkowy wymiar hydrauliczny cząstek

Keywords:
cyclone, gravitation hydraulic size, centrifugal hydraulic size

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Phenol Oxidation in the Photo-Fenton Process Catalyzed by Clinoptylolite Modified with Co

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1. Introduction

In view of deepening problem of access to clean water and a steady increase of concentration of difficult to remove industrial pollutants in natural waters, advanced oxidation methods (AOPs) gain increasing importance. Their high effectiveness results from the generation of very reactive hydroxyl radicals ($OH^{\bullet}$), which non-selectively oxidize most organic contaminants to simple forms, easily degradable in biological processes, or in case of full mineralization – to CO_2, H_2O and nitrogen and sulphur compounds. Heterogeneous photo-Fenton process is one of the AOPs methods. Catalysts used in this process, have active compound of iron or other transition metal (Mn, Cu, Ni, Co), present in the form of metal organic complexes, its oxides or hydroxyoxides, immobilized on a solid support. The most common supports are: pillared clays [5, 10], zeolites [1,4,8,13], ion exchange resins [9], active Al_2O_3 [7], granulated activated carbon [17] and multiwalled carbon nanotubes [16].

Heterogeneous catalysts are characterized by high catalytic activity, small amount of generated sludge (compared to homogeneous Fenton process), possibility of multiple use and extension of pH at which effective oxidation of pollutants takes place.

Zeolites are particularly noteworthy of mentioned supports. They are aluminosilicates with a unique crystal structure with channels of diameter slightly bigger than a water molecule. Cations present in those channels may be exchanged for other ions from the environment. In this way zeolites gain ion exchange and adsorption properties. In the process of oxidation adsorption of organic substances on the catalyst surface may increase the degree of their removal [3].

Activity of the catalyst is determined by a number of factors, which include modification method and type and form of active substance. Studies of Rajič et al. [12] have shown that microcrystals of Cu_2O, ZnO and NiO with diameter of 2–5 nm were formed by dehydration in clinoptilolite (modified with ions of Cu, Zn or Ni using ion exchange method) heated at temperature of 550°C. Their size, much bigger than diameter of channels in clinoptilolite (approx. 0.4 nm) indicates surface type of crystallization. Presumably during the dehydration metal ions migrate to the surface of zeolite, where they react with atmospheric oxygen. However, in the case of Mn-clinoptilolite formation of manganese oxides crystals was not observed and clinoptilolite passed into an amorphous form [12].

It was also found that during photo-Fenton process crystalline iron (III) oxides on the surface of the catalyst elute into solution in smaller degree than its amorphous form [2,11]. Martinez et al. explain high catalytic activity of Fe_2O_3 crystalline forms immobilized on SBA-15 synthetic zeolite with high light absorption and high quantum efficiency in excitation of compounds and generation of radical forms which are responsible for the decomposition of organic matter [11].

Furthermore, in order to gain high activity of catalyst good dispersion of crystals of oxides of active metal is required [17]. Structure of zeolites favours that, where chambers and channels effectively prevent aggregation of nanoparticles [12].

Aim of this study was to evaluate the possibility of application of heterogeneous catalyst (clinoptilolite modified with Co ions) for oxidation of organic pollutants in the process of photo-Fenton. Phenol was used as a model substance. It is one of the most commons anthropogenic pollutants. It is widely used in the industry, including synthesis of resins, dyes, pharmaceuticals and pesticides, and its annual world production is over 3 million tonnes [15].

The effect of dose of the catalyst on efficiency of phenol oxidation and type of generated intermediate products of degradation was investigated. Efficiencies of photo-Fenton process carried out with heterogeneous catalyst, homogeneous catalyst and without catalyst were compared in order to determine the mechanism of degradation of phenol.

2. Research methodology

2.1. Preparation of catalyst

The studies used Slovak natural zeolite containing more than 80% of clinoptilolite was used in the investigations. Zeolite of granulation of 0.25–0.5 mm was transformed into the hydrogen form with 5% HCl, according to methodology described in the work [14]. Next it was subjected to modification with Co(II) ions using ion exchange method. One cycle of modification was conducted using following procedure. Zeolite was added into a 0.05 M solution of $Co(NO_3)_2$ using ratio of 1:10 and stirred for 5 hours at temperature 50°C. Then decanted zeolite was rinsed with three portions of deionised water and dried at temperature of 105°C. Such cycle was repeated three times in order to increase cobalt content in the zeolite. Modified zeolite (Co-Clin) was calcined for 2 hours at 450°C.

2.2. Photo-Fenton process

The oxidation of phenol in the photo-Fenton process was carried out in the UV-reactor (Fig. 1) equipped with a 150W of power Heraeus TQ 150 Z1 lamp which is placed in glass tube and stopping radiation below 300 nm. A model solution of phenol (PhOH) with concentration of 200 mg/l was fed into the reactor from bottom with peristaltic pump.

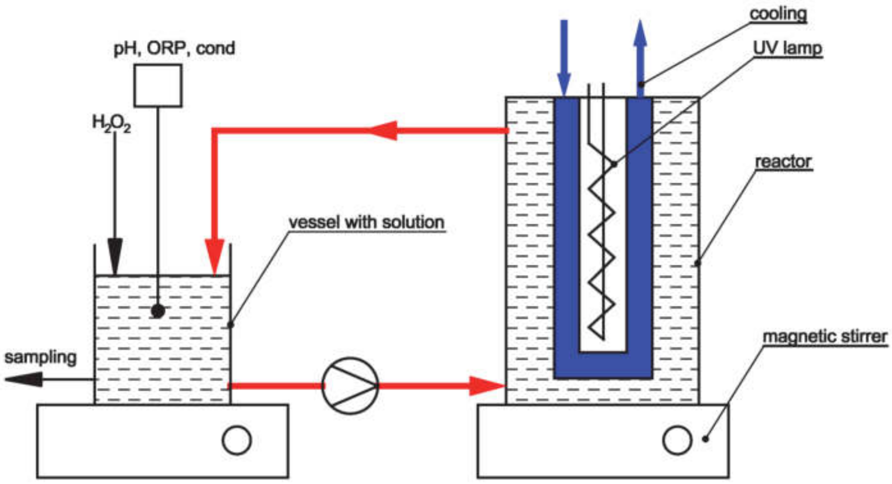

Fig. 1. Scheme of laboratory set-up for phenol oxidation in photo-Fenton process
Rys. 1. Schemat stanowiska badawczego do utleniania fenolu
w procesie foto-Fentona

That provided proper aeration of solution and stirring of the catalyst, dozed in the amount of 2 g/l or 5 g/l. After 15 minutes of UV lamp heating 30% H_2O_2 (dose of 1 g/l) was fed into the reactor, thereby initiating the process of oxidation (t = 0). The process was carried out for 4 hours. During that time following solution parameters were monitored: pH, conductivity, oxygen and Co ions concentrations, content of total organic carbon (TOC) and inorganic carbon (IC), type and amount of intermediate oxidation products.

2.3. Analytical determinations

Examinations of elution of the zeolite were carried out for 24 hours at three different pH of deionised water: 3, 6 and 9 (pH adjustment with 0.1 M NaOH or 0.1 M HNO_3). Zeolite (1 g/100 ml) was stirred on a shaker, observing changes of pH, conductivity, turbidity and concentration of Co ions in solution after a certain period.

Concentration of Co ions was determined with atomic absorption spectrometer Varian Spectr AA 20 plus.

Microstructure of the zeolite surface and its qualitative composition was examined with a scanning electron microscope JSM 5500 LV, equipped with an adapter for EDS analysis.

TOC and IC content in oxidized phenol solution was determined using Shimadzu TOC/VCPH.

Concentrations of phenol and intermediate oxidation products (hydroquinone, pyrocatechol, o-quinone, glyoxylic acid and formic acid) were determined on a Varian liquid chromatograph (HPLC) using a RP 18 column.

3. Description and analysis of results

3.1. Characteristics of Co-Clin catalyst

Content of cobalt in clinoptilolite increased significantly in subsequent cycles of modification, from 3.66 mg/g after first cycle to 6.42 mg/g after the second and to 8.45 mg/g of dry zeolite after the third, which is 0.85% of zeolite weight.

The modification process was carried in acidic solution – pH of approx. 4. At this pH 100% of Co occurs in the form of aquaions of Co(II), which facilitates exchange of Co(II) ions for ions from the zeolite structure. Another factor increasing the degree of Co(II) ions exchange was higher temperature of modification (T = 50°C). Some of these ions which occupy spaces inside the zeolite, remain in the zeolite matrix during elution conducted at room temperature. The reason for this is an increase of the radius of ions Co at lower temperature.

During calcinations of the zeolite at temperature of 450°C cobalt oxides (Co_3O_4) may arise from hydrated compounds of Co(II), forming more stable connections with the zeolite matrix than hydrated forms. Presence of oxides on the surface of the zeolite was confirmed by tests of its microstructure using SEM with an EDS analysis (Fig. 2). Crystallites are unevenly distributed on the surface of the zeolite – more of them are placed along the crystal structure, characterized by a higher content of Co (approx. 1.4% wt.) in comparison with the rest of the surface.

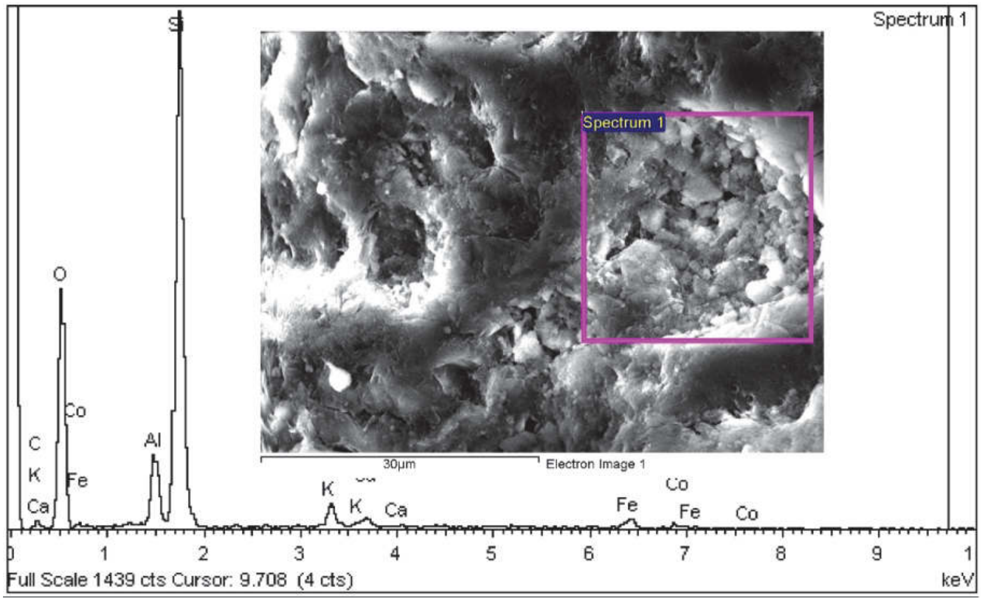

Fig. 2. Qualitative characteristics of Co-Clin
Rys. 2. Charakterystyka jakościowa zeolitu Clin-Co

Cobalt compounds may elute from the surface of the zeolite to the solution. This phenomenon is highly depends on the initial pH of the solution. Examinations of elution have shown that the most intense leaching of Co from the zeolite occurs in acidic solution ($pH_o = 3$), gradually decreasing along with increasing pH (Fig. 3A). After 24 hours of shaking, 3.72% of Co contained in the zeolite was eluted to the solution.

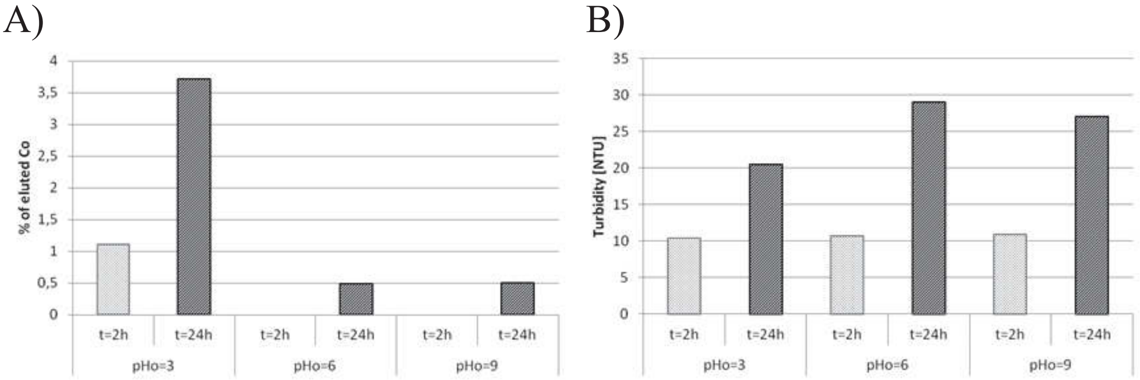

Fig. 3. Effect of initial pH of solution on: (A) % amount of eluted Co to solution, (B) solution turbidity after 2 and 24 hours of contact. Doze of Co-Clin 10 g/l
Rys. 3. Wpływ początkowego pH roztworu na: (A) % ilość eluowanego Co do roztworu, (B) mętność roztworu po 2 i 24 godzinach kontaktu. Dawka Clin-Co 10 g/l

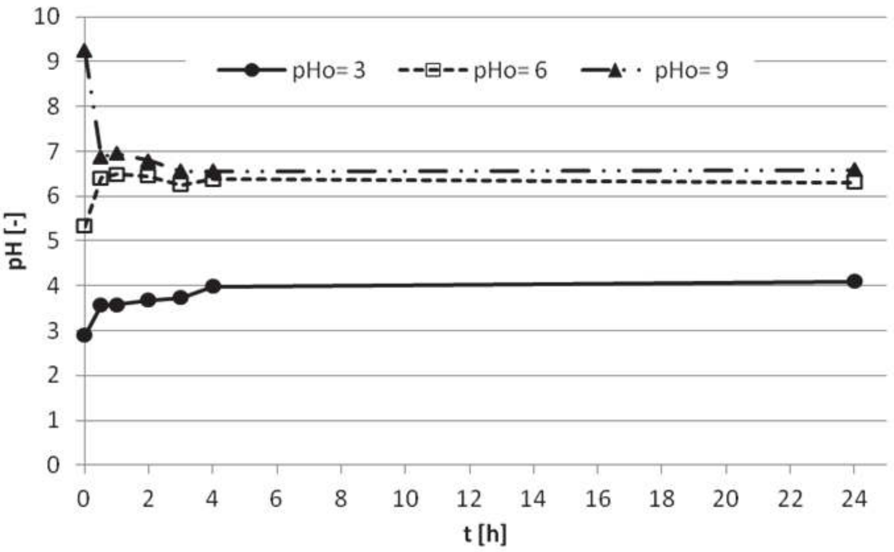

Fig. 4. Effect of initial pH of solution on pH change after 24 hours of contact. Doze of Co-Clin 10 g/l
Rys. 4. Wpływ początkowego pH roztworu na zmianę odczynu po 24 godzinach kontaktu. Dawka Clin-Co 10 g/l

At the same time for this pH the lowest turbidity was observed – soluble Co(II) aquaions were present in the solution. At higher pH hardly soluble cobalt compounds could form causing an increase of turbidity of the solution (Fig. 3B). For the initial $pH_o = 6$ and $pH_o = 9$ comparable turbidity values were obtained after 24 hours test of elution (29 and

27.1 NTU). This was caused by buffering properties of the zeolite, which kept relatively constant pH of the solution, regardless of its initial pH – Fig. 4.

3.2. Oxidation of phenol in the photo-Fenton process

During the photo-Fenton process catalysed with Co-Clin (dose of 2 g/l), decrease of phenol and TOC concentrations are noted – Fig. 5. After 210 minutes of oxidation reaction, phenol concentration decreased from approx. 200 mg/l to 172 mg/l, that is from approx. 155 mg C/l to approx. 132 mg C/l. At the same time, a decrease of TOC from approx. 155 mg C/l to approx. 143 mg C/l was observed. Conducted chemical analyses showed that oxidation of phenol caused decrease of its concentration and only hydroquinone is formed as an intermediate product. After 210 minutes of oxidation, its concentration was 1.12 mg/l. Concentrations of simpler intermediates is on trace level.

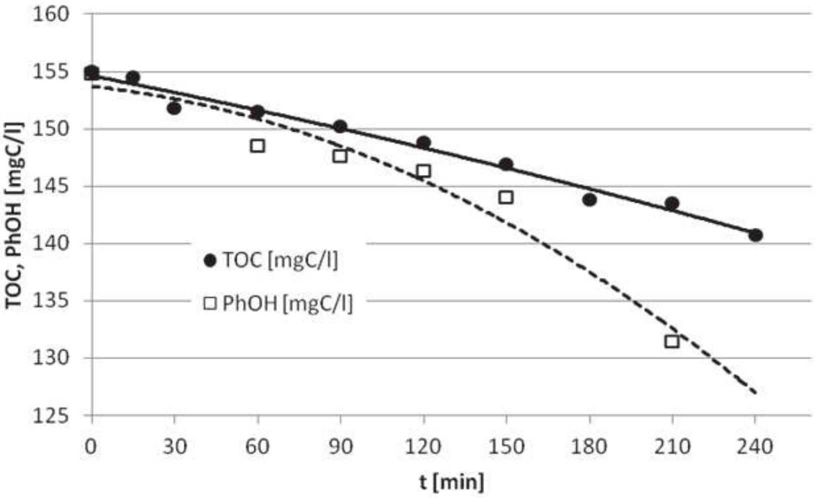

Fig. 5. Comparison of changes of phenol concentration and value of TOC in time, in the presence of Co-zeolite 2 g/l and H_2O_2 1 g/l
Rys. 5. Porównanie zmiany stężenia fenolu oraz wartości wskaźnika TOC w czasie, w obecności Clin-Co 2g/l i H_2O_2 1g/l

During oxidation of phenol pH of solution was changing. Studies have shown that with increasing contact time of Co-Clin with phenol aqueous solution from 0 to 240 minutes, pH decreases after the process – Fig. 6. Only after 60 minutes of contact of Co-Clin zeolite with solution of phenol of an initial pH of approx. 5.4 its value decreases to approx. 3.8. Extension of the contact time of the zeolite with solution does not result in a further significant decrease of pH.

Examinations results shown in Fig. 6 prove that addition of active Co-Clin zeolite significantly decreases pH of the solution, while increasing concentration of Co in the solution caused by ion exchange and, in smaller degree, by abrasion of the zeolite and migration of the suspension to the solution. After reaction time of 240 minutes, cobalt content in the solution is approx. 0.5 mg/l.

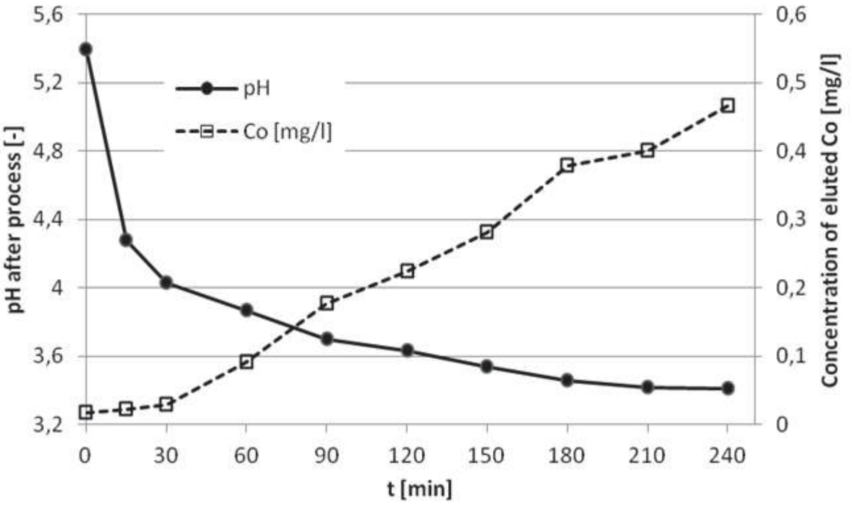

Fig. 6. Change of solution pH and concentration of eluted Co during reaction of phenol oxidation in the presence of Co-Clin 2 g/l and H_2O_2 1 g/l
Rys. 6. Zmiana odczynu roztworu oraz stężenia eluowanego Co w czasie reakcji utleniania fenolu w obecności Clin-Co 2 g/l i H_2O_2 1 g/l

Additional factor, in addition to migration of protons from the zeolite matrix, which contributes to the decrease of pH are reactions (1) and (2):

$$\text{Z-Co}^{2+} + H_2O = \text{Z-CoOH}^{+} + H^{+} \quad (1)$$

$$\text{2Z-OH} + \text{Co}^{2+} = (\text{Z-O})_2\text{-Co} + 2H^{+} \quad (2)$$

At pH<4 migration of cobalt compounds is the biggest. Then there are only the dissociated ions of Co (II) in the solution.

Not enough confirmed investigations on UV-Fenton reaction with application of modified zeolite with cobalt ions are published, therefore, evaluative studies on effect of a given dose of cobalt on the efficiency of phenol oxidation were conducted. Homogeneous catalyst was used – cobalt (II) nitrate at concentration of 1 mg/l, twice as big as maximum concentration of eluted Co. Within the whole range of duration the photo-Fenton reaction, no intermediate oxidation products were formed and removal of TOC was comparable with the system without a catalyst, that is H_2O_2 + UV and did not exceed 4%. Therefore it may be concluded that the efficiency of phenol oxidation using Co-Clin zeolite is not affect by migration of cobalt compounds from the matrix into the solution.

Low efficiency of the system: H_2O_2 + UV results from the type of radiation source, which intensity in the range of 200–300 nm is reduced, while after Herney-Ramirez et al. [6] photolysis of hydrogen peroxide occurs more effectively at shorter wavelengths and photocatalytic reactions are promoted at wavelengths longer than 350 nm.

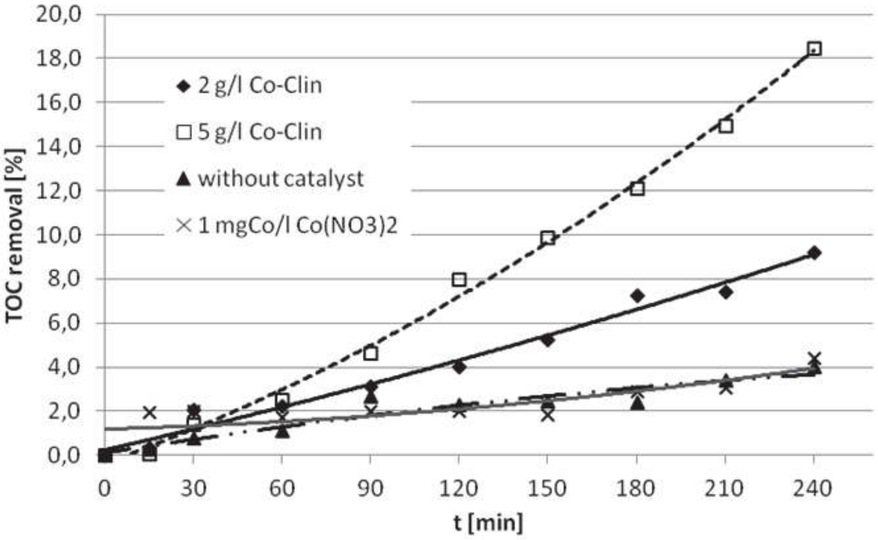

Fig. 7. Comparison of efficiencies of phenol oxidation depending on the type and amount of catalyst added into the solution at a constant dose of H_2O_2 1 g/l
Rys. 7. Porównanie efektywności utleniania fenolu w zależności od rodzaju i ilości wprowadzonego do roztworu katalizatora przy stałej dawce H_2O_2 1 g/l

Assessment of influence of catalyst dose allows to conclude that along with increasing doses of Co-Clin from 2 g/l to 5 g/l degree of removal of TOC doubled. After 210 minutes of oxidation phenol concentration decreased by 18% to value of 164 mg/l. Products of phenol degradation with application of Co-Clin were: primarily hydroquinone (2 mg/l) and in smaller amount resorcinol – 0.08 mg/l. This proves that phenol is oxidised in heterogeneous photo-Fenton process, although its effectiveness is low, which precludes the use of Co-Clin catalyst in technical scale.

4. Conclusion

Basing on the carried out investigations it may be concluded that the clinoptilolite modified with Co(II) ions is not very efficient, heterogeneous catalyst of photo-Fenton reaction. At higher examined dose of the zeolite 5 g/l, containing approx. 43 mg of Co, only 20% of TOC was removed. At the same time investigations have shown that concentration of phenol decreases as a result of oxidation, and is mainly hydroquinone is formed as an intermediate product.

During oxidation along with decreasing pH of the solution, ions of Co(II) are eluted from the surface of the zeolite, which however do not affect significantly the efficiency of photo-Fenton process. Only 4% of TOC was removed applying homogeneous catalyst, and such reduction level is comparable with effect obtained in the system without catalyst: H_2O_2 + UV.

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References

1. **Aleksić M., Kušić H., Koprivanac N., Leszczynska D., Lončarić Božić A.:** *Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water – The application of zeolite assisted AOPs*. Desalination. 257(1–3), 22–29 (2010).
2. **Calleja G., Melero J.A., Martínez F. and Molina R.:** *Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol*. Water Research 39. 1741–1750 (2005).
3. **Gonzalez-Olmos R., Kopinke F.-D., Mackenzie K., Georgi A.:** *Hydrophobic Fe-zeolites for removal of MTBE from water by combination of adsorption and oxidation*. Environ. Sci. Technol. 47, 2353–2360 (2013).
4. **Gonzalez-Olmos R., Martin M.J., Georgi A., Kopinke F-D., Oller I., Malato S.:** *Fe-zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH*. Applied Catalysis B: Environmental. 125, 51–58 (2012).
5. **Hadjltaief H., Costa P., Beaunier P., Gálvez M.E., Zina M.:** *Fe-clay-plate as a heterogeneous catalyst in photo-Fenton oxidation of phenol as probe molecule for water treatment*. Applied Clay Science. 91–92, 46–54 (2014).

6. **Herney-Ramirez J., Vicente M.A. and Madeira L.M.:** *Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review*. Applied Catalysis B: Environmental. 98, 10–26, (2010).
7. **Hsueh Ch.-L., Huang Y.-H., Wang Ch.-Ch. and Chen Ch.-Y.:** *Photoassisted Fenton degradation of nonbiodegradable azo-dye (Reactive Black 5) over a novel supported iron oxide catalyst at neutral pH*. J. Mol. Catal. A. 245(1–2), 78–86 (2006).
8. **Kasiri M. B., Aleboyeh A., Aleboyeh H.:** *Investigation of the solution initial pH effects on the performance of UV/Fe-ZSM5/H2O2 process.* Water Science & Technology. 61(8), 2143–2149 (2010).
9. **Lv X., Xu Y., Lv K., Zhang G.:** *Photo-assisted degradation of anionic and cationic dyes over iron(III)-loaded resin in the presence of hydrogen peroxide*. J. Photochem. Photobiol. A. 173(2), 121–127 (2009).
10. **Martin del Campo E., Romero R., Roa G., Peralta-Reyes E., Espino-Valencia J., Natividad R.:** *Photo-Fenton oxidation of phenolic compounds catalyzed by iron-PILC.* Fuel. 138, 149–155 (2014).
11. **Martinez F., Calleja G., Melero J.A., Molina R.:** *Iron species incorporated over different supports for the heterogeneous photo-Fenton oxidation of phenol*. Applied Catalisis B: Environmental. 70, 452–460 (2007).
12. **Rajic N., Stojakovic D., Daneu N., Recnik A.:** *The formation of oxide nanoparticles on the surface of natural clinoptilolite.* Journal of Physics and Chemistry of Solids. 72, 800–803 (2011).
13. **Shahbazi A., Gonzalez-Olmos R., Kopinke F-D., Zarabadi-Poor P., Georgi A.:** *Natural and synthetic zeolites in adsorption/oxidation processes to remove surfactant molecules from water.* Separation and Purification Technology. 127, 1–9 (2014).
14. **Świderska-Dąbrowska R., Schmidt R.:** *Zastosowanie katalizatora homogenicznego ZCu w procesie Fentona.* Gaz, Woda i Technika Sanitarna. 7, 279–283 (2014).
15. **Taketa L.Y, Ignachewski F., Villalba J.C., Anaissi F.J., Fujiwara S.T.:** *Phenol degradation using the mixed material clay/Fe immobilized on glass slides.* Environmental Science and Pollution Research. 22, 894–902 (2015).
16. **Variava M.F., Church T.L., Harris A.T.:** *Magnetically recoverable* Fe_xO_y*–MWNT Fenton's catalysts that show enhanced activity at neutral pH*. Applied Catalysis B: Environmental. 123–124, 200–207 (2012).
17. **Wang Y., Zhao H., Zhao G.:** *Iron-copper bimetallic nanoparticles embedded within ordered mesoporous carbon as effective and stable heterogeneous Fenton catalyst for the degradation of organic contaminants*. Applied Catalysis B: Environmental. 164, 396–406 (2015).

Utlenianie fenolu w procesie foto-Fentona katalizowanym przez klinoptylolit modyfikowany Co

Streszczenie

W pracy przedstawiono wyniki badań utleniania fenolu w procesie foto-Fentona z zastosowaniem heterogenicznego katalizatora Co-Clin (naturalny klinoptylolit, modyfikowany jonami Co(II)). Analiza widm EDS mikroskopem skaningowym wykazała, że modyfikacja ma charakter powierzchniowy i wewnątrzkanałowy, a krystality Co_3O_4 są nierównomiernie rozproszone na powierzchni zeolitu – więcej jest ich wzdłuż struktury krystalicznej i charakteryzują się większą zawartością Co (ok. 1,4% wag.).

Przy wyższej z badanych, dawce zeolitu 5 g/l (zawierającej ok. 43 mg Co) po 4 godzinach procesu utleniania, usunięto zaledwie 20% TOC. Jednocześnie badania wykazały, że w wyniku rozkładu zmniejsza się stężenie fenolu, a powstaje jako produkt pośredni głównie hydrochinon i w śladowej ilości rezorcyna. W badanym zakresie czasu trwania reakcji utleniania nie powstawały kolejne jej produkty.

Podczas reakcji utleniania, wraz z obniżaniem się pH roztworu, z powierzchni zeolitu wymywane są jony Co(II), które nie wpływają jednak znacząco na efektywność procesu foto-Fentona. Przy udziale homogenicznego katalizatora uzyskano zaledwie 4% usunięcie TOC, które było porównywalne z efektem uzyskanym w układzie bez katalizatora: H_2O_2+UV. Świadczy to, że utlenianie fenolu zachodzi przede wszystkim w heterogenicznym procesie foto-Fentona, aczkolwiek jego niewielka efektywność wyklucza zastosowanie katalizatora Co-Clin w skali technicznej do utleniania zanieczyszczeń przemysłowych.

Słowa kluczowe:
klinoptylolit modyfikowany jonami kobaltu, katalizator heterogeniczny, foto-Fenton, rozkład fenolu

Keywords:
cobalt-clinoptilolite, heterogeneous catalyst, photo-Fenton, phenol degradation

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Drug-Resistant Bacteria in Soils Fertilized with Sewage Sludge

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Introduction

Apart from chemical contaminants such as heavy metals or organic compounds, sewage sludge might also contain substantial amounts of bacteria, fungi, viruses and helminth eggs. The scientific literature has reported that sewage sludge is also characterized by high contamination with pathogenic microorganisms [6,7]. Microorganisms which are particularly dangerous to humans are often found in sewage sludge, including bacilli of typhoid fever (*Salmonella*) dysentery (*Shigella*), tetanus (*Clostridium tetani*) gas gangrene (*Clostridium perfringens*) and bacilli that cause foodborne disease (*Clostridium botulinum*). Examinations of microbiological composition of sewage sludge reveal also tuberculosis bacterial species (*Mycobacterium tuberculosis*) and anthrax bacilli (*Bacillus anthracis*). These microorganisms cause serious diseases in both cattle and in humans [4]. The properties of sewage sludge (physical, chemical and biological) are significantly affected by the way it is processed [8,19,20,21]. The uncontrolled use of antibiotics in medical care of humans and animals also contributes to the threat connected with development of new drug-resistant forms of microorganisms in sewage and sewage sludge. Despite numerous studies that have investigated the problems of the use of sewage sludge in nature and agriculture, no sufficient information has been provided to date about certain parasitic and pathogenic forms that are resistant to the drugs used which can survive in sludge and soils fertilized with sludge and in the plants grown in these soils. The effects of introduction of sewage sludge to the soil might be observed even many years after fertilization [14,15]. There are few reports on the presence of drug-resistant bacteria in sludge in the literature concerning sludge fertilization [9,10]. In both sludge and a conventional organic fertilizer provided by manure, numerous pathogenic forms have been found while they acquired or developed resistance patterns with respect to a number of antibiotic available in health care [2]. This problem is connected with excessive and often needless overuse of antibiotics in health prevention and health care. Antibiotics have also been popular in animal farming, not only for medical purposes, but often used with small doses for a longer period of time in order to increase animals' weight. One example is the United States of America, where some 40% of the antibiotics production is used for such purposes. In some countries, antibacterial drugs are used in farming and horticulture. It should also be noted that consumption of food that contains antibiotics with small contents prepares bacteria (e.g. those contained in the intestinal flora) for development of resistance patterns if the appropriate conditions occur [5]. These practices lead to selection of microflora that is resistant to antibiotics. Drug-resistant bacteria present in sludge accumulate in sewage sludge during processing and become a real threat to the environment. Few studies on the problems of drug-resistant bacteria in sewage and sewage sludge and the results obtained by the authors of the present paper point to the probability of a substantial survival of these particularly dangerous microorganisms in sewage sludge and in the soils fertilized with the sludge [10,14].

Experimental

Sewage sludge from the wastewater treatment plant in Myszków, Poland, was used in the experiments. The sludge was sampled after biological processes of sewage treatment, without fermentation. Stabilization occurred through anaerobic pathways. After dehydration (with addition of polyelectrolytes) in presses, part of the samples were subjected to liming and stored in a storage area for 6 months. Other samples were dried after liming in a solar dryer. After this process, sludge was also stored for the period of six months. One type of soil was fertilized. This was sandy soil and its characterization (similar to sewage sludge and manure) is provided in Tables 1 and 2. Properties of the fertilized soil were consistent with the recommendations for the use of sewage sludge [17,18]. For comparison purposes, the authors used straw-based cattle manure, which was also stored before the evaluation. The examinations were carried out under field experiment conditions (small beds with the surface area of 10 m^2). The doses of fertilizers used were 10, 20, 30 and 40 Mg d.m.·ha^{-1}, added in spring to arable layer at the thickness of 30 cm. The duration of the experiment was one vegetation season. White mustard (*Sinapis alba*) was planted in the fertilized soils. In autumn, after harvest of the plants, biological analyses of the fertilized soils were carried out. The experiments were carried out with 3 repetitions. The results obtained are represented by the means from these repetitions.

Table 1. Physical and chemical properties of soil, sewage sludge and manure used in the experiments
Tabela 1. Właściwości fizyczne i chemiczne gleby, osadów ściekowych i obornika stosowanych w badaniach

Parameter	Unit	Soil	Sewage Sludge		Manure
			Myszków (after natural drying)	Myszków (after solar drying)	
		Contents			
Organic substance	[% d.m.]	0.29	42.2	39.0	61.0
Reaction (pH$_{H2O}$)	-	6.87	7.01	7.2	8.01
Organic carbon	[g·kg^{-1} d.m.]	13.40	218.4	215.0	246.6
Total nitrogen		0.64	39.1	35.0	39.8
Available P	[mg·kg^{-1} d.m.]	34.0	616.70	601.0	470.0
Available K		21.8	238.6	219.6	2260.0
Available Mg		55.6	893.6	901.0	994.3
Cr		10.4	17	19	2.1
Zn		75.0	908	913	132
Pb		17.8	21	23	7.3
Cu		12.6	139	142	21
Cd		0.4	2.1	2.3	1.2
Ni		10.3	102.5	120.0	2.2
Hg		0.003	1.6	1.82	0.11

The contents of 7 standard heavy metals (Cd, Cu, Ni, Pb, Zn, Hg, Cr) in the sewage sludge used for the experiments and in the manure did not exceed the permissible values that are a prerequisite for their use in nature. The contents of heavy metals found in the sewage sludge allowed even for their agricultural use and soil reclamation for agricultural purposes. Furthermore, the contents of heavy metals in the soils used in the experiments did not exceed permissible values for the use in agriculture and for reclamation of soil [17,18].

Biological conditions of research materials used in the field experiments are presented in Table 2.

Table 2. Biological properties of soil, sewage sludge and manure used in the experiments

Tabela 2. Własności biologiczne gleby, osadów ściekowych i obornika stosowanych w badaniach

Parameter	Unit	Soil	Sewage Sludge		Manure
			Myszków (after natural drying)	Myszków (after solar drying)	
		Contents			
Escherichia coli	Coliform index	10^{-1}	10^{-5}	10^{-5}	10^{-5}
Proteus vulgaris		10^{-2}	10^{-5}	10^{-4}	10^{-5}
Clostridium perfringens		n.s.	10^{-5}	10^{-4}	10^{-4}
Salmonella species bacteria	[JTK/g d.m.]	n.s.	n.s.	n.s.	n.s.
Total bacterial count		$5.2*10^{5}$	$21*10^{9}$	$31*10^{8}$	$29*10^{10}$
Total fungi count		$2.5*10^{4}$	$25*10^{6}$	$31*10^{3}$	$51*10^{6}$
Total actinobacteria count		$1.4*10^{3}$	$43*10^{6}$	$49*10^{6}$	$55*10^{6}$
Total count of *Fusarium* fungi species		n.s.	$21*10^{3}$	$21*10^{1}$	$23*10^{10}$
ATT index		n.s.	n.s.	n.s.	n.s.

n.s. – no presence was found

The sanitary state of the sewage sludge determined before the experiments (Tab. 2) allowed for its use in agriculture. No *Salmonella* bacteria (detected on the medium SS) were isolated and no helminths' eggs (detected by Wasilkowa flotation method), which are the main sanitary indicator that determines possibility of the use of sewage sludge in nature, were found in the sludge.

Laboratory tests methodology

The fertilized soils were evaluated with respect to bacterial count concerning the bacteria that exhibited resistance to first-line antibiotics. After obtaining the positive results of the first determinations, the authors analysed the resistance of conditional pathogens to the final antibiotic (vancomycin).

Biological tests methodology

Determination of total count of pathogenic bacteria resistant to first-line antibiotics

Quantitative and qualitative analysis of individual groups of microorganisms was carried out using the Koch's dish method in agar plates. In order to determine drug resistance of the microorganisms, the authors used blood agar plates and MacConkey agar plates. After 18-hour incubation at 37 degrees Celsius, the authors evaluated growth and isolation of individual strains. Biochemical examinations aimed at identification of individual bacteria species from the family *Enterobacteriaceae,* employed Enterotest and non-fermenting gram-negative bacilli test (Nefermtest, Lachema). Simultaneous tests of drug resistance were also carried out. Drug resistance tests used Mueller-Hinton plates.

Furthermore, the plates with the following antibiotics were added:

• ampicillin	10 mg,
• gentamicin	10 mg,
• amikacin	10 mg,
• ceftazidime	30 mg,
• amoxicillin with clavulanic acid	20/10 mg,
• cefotaxime	30 mg.

The tests were carried out at the temperature of 37 degree Celsius for 18 hours. Antibiotics were chosen so that they were consistent with the basic antibiogram (first-line antibiotics) according to the recommendations for test selection of the National Reference Centre for Microbial Drug Sensitivity [3].

Determination of total vancomycin-resistant mesophilic bacteria count

Determination was carried out using Koch's dish method with agar plate which was added the appropriate dose of the antibiotic (6mg/l according to the guidelines of KORLD) [3]. Then, the plates were inoculated with the suspension of bacteria from dilutions while using spread plate method. Incubations were carried out for 24 hours at 37˚C. After 24 hours, the authors enumerated the colonies that had grown and the results of the determination were given as vancomycin-resistant mesophilic (conditional pathogen) bacteria count per 1g of soil, mixtures of soil with sewage sludge and those with manure. The experiments were carried out with 3 repetitions. The results obtained are represented by the means from these repetitions. The results obtained were analysed statistically using the Kruskal-Wallis test.

Results

The results obtained for qualitative determinations and drug-resistance (compared to first-line antibiotics) of conditionally pathogenic microorganisms in the sandy soils fertilized with sewage sludge and manure after a year from fertilizing under conditions of field experiment are presented in Tables 3–5. Figure 1–4 presents a comparison of mean susceptibility or resistance of pathogenic microorganisms to these drugs in the fertilized soils (collectively for all the doses).

Figure 5 presents mean bacteria count for conditionally-pathogenic vancomycin-resistant bacteria for all the doses determined in the soils fertilized with sewage sludge and manure.

Table 3. Results obtained for determination of drug resistance of conditionally pathogenic microorganisms in sandy soils fertilizedwith sewage sludge from Myszkow wastewater treatment plant after natural drying
Tabela 3. Wyniki lekooporności drobnoustrojów warunkowo chorobotwórczych w glebie piaszczystej nawożonej osadami ściekowymi z oczyszczalni ścieków w Myszkowie po naturalnym suszeniu

Fertilizer dose [Mg d.m.·ha^{-1}]	Type of isolated microorganisms	Susceptibility of the microorganisms to the antibiotic used					
		Amikacin	Amoxicillin with clavulanic acid	Ceftazidime	Cefotaxime	Gentamicin	Ampicillin
10	*Enterobacter sp*	s	r	s	s	s	r
	Photorhabdus luminescens	s	s	s	s	s	r
	Escherichia coli	s	s	S	s	s	r
	Proteus vulgaris	s	s	S	s	s	ms
20	*Enterobacter sp*	s	r	S	s	s	r
	Photorhabdus luminescens	s	s	S	s	s	r
	Escherichia coli	s	s	S	s	s	r
	Proteus vulgaris	s	s	S	s	s	ms
	Klebsiella oxytoca	ms	r	S	r	s	r
30	*Enterobacter sp*	ms	r	S	s	s	r
	Photorhabdus luminescens	s	s	S	s	s	r
	Escherichia coli	s	ms	S	s	s	r
	Proteus vulgaris	s	s	S	s	s	r
	Klebsiella oxytoca	ms	r	S	r	s	r
	Enterobacter kobei	ms	s	S	s	s	r
40	*Enterobacter sp*	r	r	S	s	s	r
	Photorhabdus luminescens	s	s	S	s	s	r
	Escherichia coli	s	r	S	s	s	r
	Proteus vulgaris	s	s	S	s	s	r
	Klebsiella oxytoca	r	r	S	r	s	r
	Enterobacter kobei	r	s	S	s	s	r

s – susceptible, ms – medium susceptible, r – resistant

Table 4. Results obtained for determination of drug resistance of conditionally-pathogenic microorganisms present in sandy soil fertilized with sewage sludge from Myszków wastewater treatment plant after solar drying

Tabela 4. Wyniki lekooporności warunkowo chorobotwórczych mikroorganizmów obecnych w glebie piaszczystej nawożonej osadami ściekowymi z oczyszczalni ścieków w Myszkowie po solarnym suszeniu

Fertilizer dose [Mg d.m.·ha^{-1}]	Type of isolated microorganisms	Susceptibility of the microorganisms to the antibiotic used					
		Amikacin	Amoxicillin with clavulanic acid	Ceftazidime	Cefotaxime	Gentamicin	Ampicillin
10	*Alcaligenes faecalis*	s	s	S	s	s	s
20	*Alcaligenes faecalis*	s	s	S	s	s	s
	Achromobacer piechandii	s	s	S	s	s	s
30	*Alcaligenes faecalis*	s	s	S	s	s	s
	Achromobacer piechandii	s	s	S	s	s	s
	Pseudomonas alcaligenes	s	s	S	s	s	r
40	*Alcaligenes faecalis*	s	s	S	s	s	s
	Achromobacer piechandii	s	s	S	s	s	ms
	Pseudomonas alcaligenes	s	s	S	s	s	r

s – susceptible, ms – medium susceptible, r – resistant

Table 5. Results obtained for determination of drug resistance of conditionally-pathogenic microorganisms in the sandy soil fertilized with manure
Tabela 5. Wyniki lekooporności warunkowo-patogennych drobnoustrojów w piaszczystej glebie nawożonej obornikiem

Fertilizer dose [Mg d.m.·ha^{-1}]	Type of isolated microorganisms	Susceptibility of the microorganisms to the antibiotic used					
		Amikacin	Amoxicillin with clavulanic acid	Ceftazidime	Cefotaxime	Gentamicin	Ampicillin
10	*Enterobacter sp*	s	s	S	s	s	r
	Serratia fonticola	s	ms	S	ms	s	r
	Yersinia rodhei	s	r	S	ms	s	r
20	*Enterobacter sp*	s	s	S	s	s	r
	Serratia fonticola	s	ms	S	ms	s	r
	Yersinia rodhei	s	ms	S	ms	s	r
	Photorhabdus luminescens	s	r	S	r	s	r
	Enterobacter kobei	s	ms	S	s	s	r
30	*Enterobacter sp*	s	s	S	s	s	r
	Serratia fonticola	s	r	S	r	s	r
	Yersinia rodhei	s	r	S	r	s	r
	Photorhabdus luminescens	s	r	S	r	s	r
	Enterobacter kobei	s	ms	S	s	s	r
	Citrobacter brakii	s	r	S	ms	s	r
40	*Enterobacter sp*	s	r	S	s	s	r
	Serratia fonticola	s	r	S	r	s	r
	Yersinia rodhei	s	r	S	ms	s	r
	Photorhabdus luminescens	s	r	S	r	s	r
	Enterobacter kobei	s	r	S	r	s	r
	Citrobacter brakii	s	r	S	s	s	r

s – susceptible, ms – medium susceptible, r – resistant

Statistical analysis of the results obtained in the field experiment based on Kruskal-Wallis test revealed that the resistance to the antibiotics used differed between the samples. In the case of fertilization with the sludge after natural drying, amikacin-resistance bacteria were found. They were not present after fertilization with manure and the sludge after solar drying. With regard to amoxicillin with clavulanic acid in the soil after the use of the solar-dried sludge, all the bacteria exhibited susceptibility. After fertilization with manure and the sludge after natural drying, the cases of medium susceptibility and resistance to the drug were observed. Susceptibility to cefotaxime was found in all the potentially pathogenic bacteria isolated from sandy soil fertilized with the sludge after solar drying. In the soils after fertilization with manure and the sludge after natural drying, the cases of medium susceptibility and resistance to the drug were observed. With regard to amipicilin, the most of the bacteria in the soils fertilized with the sludge after solar drying were susceptible. Furthermore, fertilization of the soil with manure and the sludge after natural drying caused, in the most of the cases, the development of pathogenic forms of bacteria which were resistant to this antibiotic. In the case of ceftazidime and gentamicin, all the analyses revealed the sensibility of the isolated conditionally pathogen forms to these antibiotics. Furthermore, it was found in the field experiment that the increase in the fertilizer dose contributed significantly to the increase in resistance of pathogenic forms in the soils studied.

All the sludge and manure samples and the samples of soils fertilized with them contained vancomycin-resistant microorganisms. Presence of insignificant number of bacteria that exhibited resistance to vancomycin was observed in the non-fertilized control soil. The most of these forms ($22*10^4$) were found in manure and soils fertilized with manure. Sewage sludge after solar drying contained the more of vancomycin-resistant bacteria compared to the sludge after natural drying.

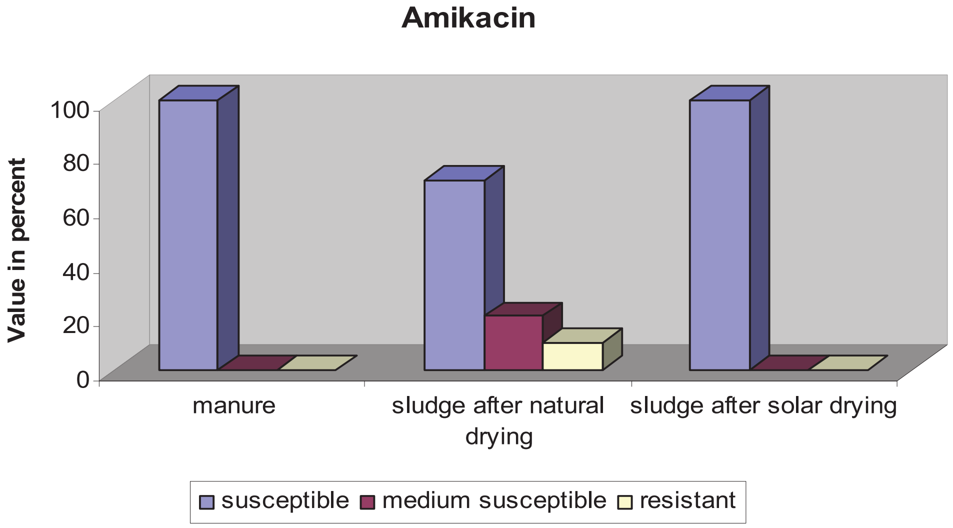

Fig. 1. Mean overall sensitivity to selected first-line antibiotics in drug-resistant conditionally-pathogenic to Amikacin microorganisms after fertilization of sandy soil with sewage sludge and manure [%]
Rys. 1. Średnia wrażliwość na wybrane antybiotyki pierwszego wyboru wśród lekoopornych warunkowo chorobotwórczych mikroorganizmów na Amikacynę po nawożeniu gleby piaszczystej osadami ściekowymi i obornikiem [%]

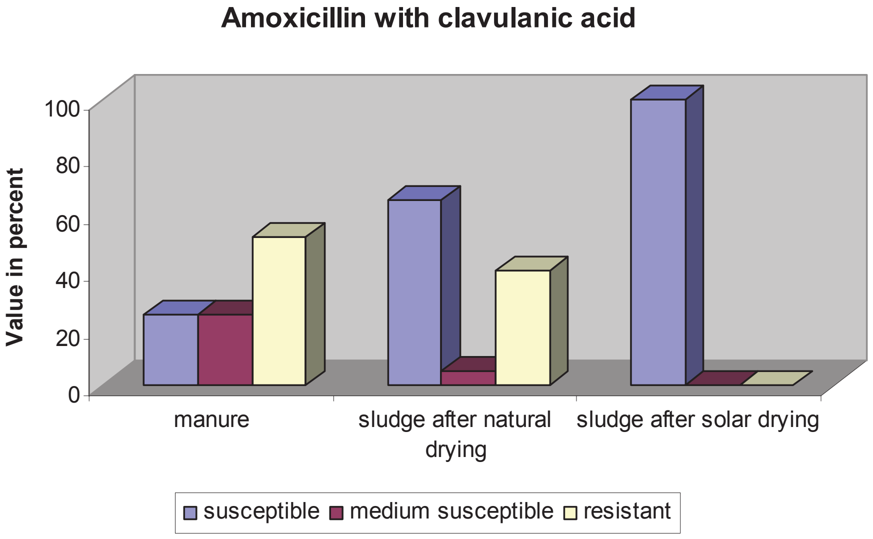

Fig. 2. Mean overall sensitivity to selected first-line antibiotics in drug-resistant conditionally-pathogenic to Amoxicilin with clavulanic acid microorganisms after fertilization of sandy soil with sewage sludge and manure [%]
Rys. 2. Średnia wrażliwość na wybrane antybiotyki pierwszego wyboru wśród lekoopornych warunkowo chorobotwórczych mikroorganizmów na Amoksycylinę z kwasem klawulanowym po nawożeniu gleby piaszczystej osadami ściekowymi i obornikiem [%]

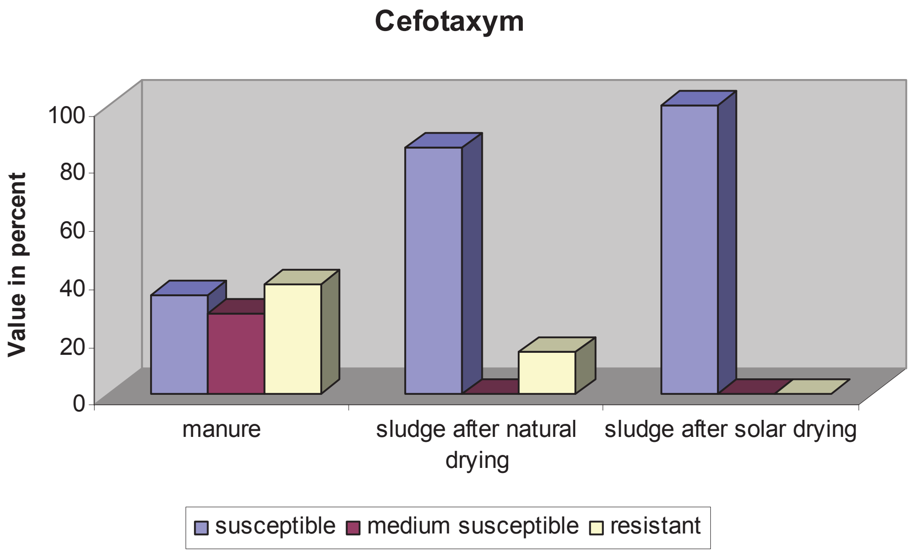

Fig. 3. Mean overall sensitivity to selected first-line antibiotics in drug-resistant conditionally-pathogenic to Cefotaxym microorganisms after fertilization of sandy soil with sewage sludge and manure [%]
Rys. 3. Średnia wrażliwość na wybrane antybiotyki pierwszego wyboru wśród lekoopornych warunkowo chorobotwórczych mikroorganizmów na Cefotaksym po nawożeniu gleby piaszczystej osadami ściekowymi i obornikiem [%]

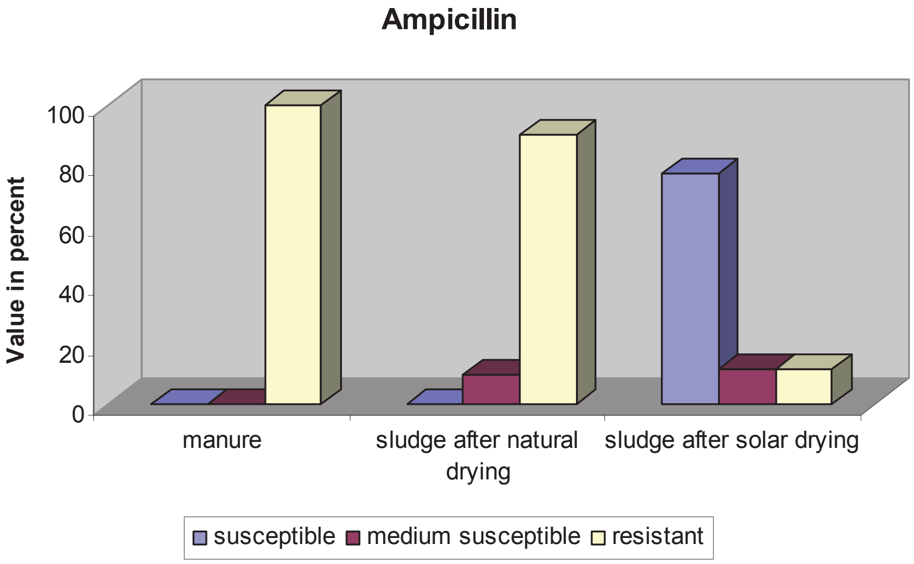

Fig. 4. Mean overall sensitivity to selected first-line antibiotics in drug-resistant conditionally-pathogenic to Ampicilin microorganisms after fertilization of sandy soil with sewage sludge and manure [%]
Rys. 4. Średnia wrażliwość na wybrane antybiotyki pierwszego wyboru wśród lekoopornych warunkowo chorobotwórczych mikroorganizmów na Ampicilinę po nawożeniu gleby piaszczystej osadami ściekowymi i obornikiem [%]

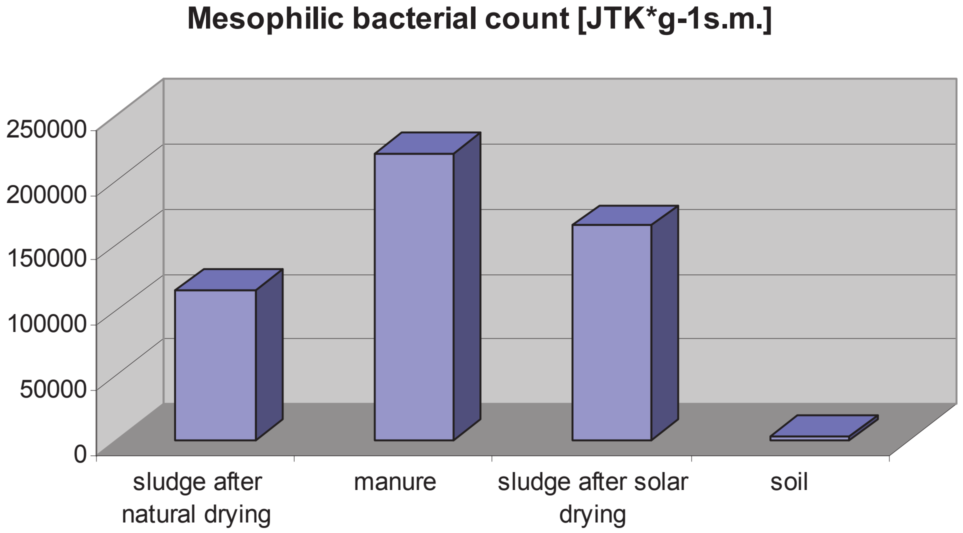

Fig. 5. Mean total bacterial count of conditionally pathogenic vancomycin-resistant bacteria in the soils fertilized with sewage sludge and manure
Rys. 5. Średnia całkowita liczba warunkowo patogennych bakterii odpornych na wankomycynę w glebach nawożonych osadami ściekowymi i obornikiem

Discussion

The attention should be paid to the risk of the use of sewage sludge in nature (and manure according to the available literature reports) which is caused by the presence of conditionally-pathogenic microorganisms which are dangerous to both people and animals. They often acquire resistance to popular drugs [2]. The sewage might contain a variety of residual contents of drugs, which then accumulate in the products of treatment i.e. sewage sludge, causing development of resistance patterns during the contact with microorganisms [11]. Substantial concentrations of Tamiflu (Oseltamiwir) [16] which is used for fighting viral infections were found in the sludge. The residual parts of drugs contained in sewage sludge used for fertilization might be transported to the soil profile. They might also cause resistance to drugs in soil autochthonous and allochthonous microorganisms. The study found that the use of sewage sludge and manure for fertilization of sandy soils caused development of conditionally-pathogenic microorganisms. A number of isolated microorganisms were characterized by drug resistance to first-line antibiotics. Some microorganism counts were similar to those isolated by Goyal and Adams [1]. The authors cited found in the sewage sludge stored in the Atlantic

Ocean, after 30 months from the drop to the water (which was one of the treatment methods): *Enterobacter cloacea, Klebsiella pneumoniae, Citrobacter freundii, Proteus vulgaris, Aeromonas hydrophila, Escherichia coli, Enterobacter agglomerans. Escherichia coli* turned out to be susceptible to all the antibiotics used, including ampicilin and gentamicin. *Klebsiella pneumoniae* exhibited resistance only with respect to ampicilin. *Citrobacter freundii* showed resistance to ampicilin and cephalosporins. *Klebsiella oxytoca*, apart from the resistance to the above two antibiotics, was also resistant to biseptol (sulfamethoxazol and trimethoprim). *Proteus vulgaris* was resistant to 6 of 13 antibiotics used, including ampicilin, cephalosporins and chloramphenicol. The authors found much higher resistance of the isolated forms of pathogenic forms with respect to the basic antibiotics compared to the findings published by Goyal and Adams [1]. A particularly worrying phenomenon is long survival rate of potentially pathogenic forms with resistance to basic antibiotics in the soils fertilized with sewage sludge and manure which was found by the authors of the study that was carried out for several years. One method of elimination or reduction in the content of these forms in organic fertilizers, mainly in the sewage sludge, might be provided by drying process, e.g. solar drying [12]. The field experiment demonstrated that this method of drying causes a significant decline in the content of drug-resistant pathogens in the sludge and the soil fertilized with the sludge. However, it is not always effective. This phenomenon was observed through determination of the vancomycin-resistant bacteria count (fig.5). The number of forms which were resistant to this antibiotic was significantly higher in the sludge after solar drying and the soils fertilized with this sludge compared to the use of the sludge after natural drying. The study found that the increase in the dose of sewage sludge and manure caused an increase in drug-resistant bacterial count. Similar findings were presented by Stańczyk-Mazanek et al. [13] and Stańczyk-Mazanek [14] in studies on the resistant pathogenic forms in the soils fertilized with sewage sludge. The increase in the dose of sewage sludge in the present study caused an increase in resistance of individual isolated pathogenic microorganisms. Higher resistance to the antibiotics used was found in allochthonous soil bacteria. It was found under conditions of field experiment that the manure used in the study also caused development of higher count of drug-resistant forms in the soils fertilized with manure. 100% of the bacteria from the soils fertilized with manure and ca. 90% of conditional pathogens from soils fertilized with sewage sludge were resistant to ampicilin (fig. 4). The study demonstrated that, similar to sewage sludge, manure can also be the source of drug-resistant bacteria in soil. These observations were also made by Holzel et al [2]. Solar drying of the sludge reduced the number of resistant forms to 10% in the soils where this type of sludge was introduced. The process of solar drying turned out to be an effective method that reduced the count of potential pathogens, including the forms resistant to first-line antibiotics in the sludge and then in the soil fertilized with them. However, this process was less effective with respect to vancomycin-resistant bacteria. This drug is used during serious infections with gram-positive bacteria which are resistant to other anti-bacteria drugs and in the patients with hypersensitivity to penicilin and cephalosporins. It is used for treatment of bacterial diseases such as infective endocarditis, sepsis, osteomyelitis, central nervous system infections, lower respiratory tract infections (pneumonia), skin infections and soft tissue infections.

Conclusions

Fertilizing of sandy soils with municipal sewage sludge and with manure caused development of conditionally pathogenic microorganisms with acquired resistance to popular antibiotics. A number of isolated microorganisms (mostly from sewage sludge compared to manure) were characterized by considerable resistance to popular antibiotics i.e. first-line antibiotics. The highest resistance in bacteria isolated from soils fertilized with sewage sludge and manure was found for ampicilin (ca. 100% drug-resistant forms). The highest sensitivity of the most of conditional pathogens was found for ceftazidime. A very worrying finding is the presence of vancomycin-resistant microorganisms in both sewage sludge and manure (vancomycin is an antibiotic used for treatment of serious bacterial diseases. The contact with so contaminated soil after fertilization might represent the serious threat to the environment, including animals and humans. It seems essential to emphasize the effectiveness of stabilization and hygienization of sewage sludge in destruction of pathogenic microorganisms which might exhibit drug resistance. The process of solar drying of municipal sewage sludge was not always effective method of its processing in terms of reduction in the count of potential pathogens, including drug-resistant forms.

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References

1. **Goyal S.M., Adams W.N.:** *Drug-resistant bacteria in continental shelf sediments.* Environmental Microbiology. 48(4), 861–862 (1984).
2. **Holzel C.S., Schwaiger K., Harms K., Kuchenhoff H., Kunz A., Meyer K., Muller C., Bauer J.:** *Sewage sludge and liquid pig manure as possible sources of antibiotic resistant bacteria.* Environmental Research. 110, 318–326 (2010).
3. **Hryniewicz W., Sulikowska A.:** *Recommendations for selection of tests for determination of bacterial sensitivity to antibiotics and chemical therapeutics.* Recommendations of the National Institute for Public Health, Warsaw 2006.
4. **Marcinkowski T.:** *Effect of stabilization of secondary sludge with calcium hydroxide on its biological composition.* Environmental Protection. 2, 49–55 (2003).
5. **Markiewicz Z., Kwiatkowski Z.A.:** *Bacteria, antibiotics and drug resistance*. Wydawnictwo Naukowe PWN, Warszawa 2008.
6. **Ngole V., Mpuchane S., Totolo O.:** *Survival of faecal coliforms in four different types of sludge-amended soils in Botswana*. European Journal of Soil Biology. 42, 208–218 (2006).
7. **Pourcher A.M., Francoise P.B., Ferre V., Gosinska A., Stan V., Moguedet G.:** *Survival of faecal indicators and enteroviruses in soil after land-spreading of municipal sewage sludge*. Applied Soil Ecology. 35, 473–479 (2007).
8. **Placha I., Venglovsky J., Makova Z., Martinez J.:** *The elimination of Salmonella typhimurium in sewage sludge by aerobic mesophilic stabilization and lime hydrated stabilization*. Bioresource Technology. 99, 4269–4274 (2008).
9. **Reinthaler F.F., Feierl G., Galler H., Haas D., Leitner E., Mascher F., Melkes A., Posch J., Winter I., Zarfel G., Marth E.:** *ESBL-producing E. coli in Austrian sewage sludge*. Water Research. 44, 1981–1985 (2010).

10. **Reinthaler F.F., Posch J., Feierl G., Wust G., Haas D., Ruckenbauer G., Mascher F., Marth E.:** *Antibiotic resistance of E. coli in sewage and sludge*. Water Research. 37, 1685–1690 (2003).
11. **Rogers H.R.:** *Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges*. The Science of the Total Environment. 185, 3–26 (1996).
12. **Salihoglu N.K., Pinarli V., Salihoglu G.:** *Solar drying in sludge management in Turkey*. Renewable Energy. 32, 1661–1675 (2007).
13. **Stańczyk-Mazanek E.:** *Environmental threats in the processes of the use of sewage sludge in nature*. Publishing by Czestochowa University of Technology, Monograph 246, Częstochowa 2012.
14. **Stańczyk-Mazanek E., Nalewajek T., Zabochnicka M.:** *Drug-Resistant microorganisms in soils fertilized with sewage sludge.* Archives of Environmental Protection. 38(1), 97–102 (2012).
15. **Stańczyk-Mazanek E., Piątek M., Kępa U.:** *Wpływ następczy osadów ściekowych stosowanych na glebach piaszczystych na właściwości kompleksu sorpcyjnego.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2437–2451 (2013).
16. **Straub J.O.:** *An environmental risk assessment for oseltamivir (Tamiflus) for sewage works and surface waters under seasonal-influenza-and pandemic-use conditions*. Ecotoxicology and Environmental Safety. 72, 1625–1634 (2009).
17. The Ordinance of the Minister of Environment as of 13 July 2010 on municipal sewage sludge. Journal of Laws No. 137, pos. 924.
18. The Ordinance of the Minister of the Environment as of 9 September 2002 on standards of soil quality and standards of ground quality. Journal of Laws No. 165, Pos. 1358 and 1359.
19. **Wolski P., Wolny L.:** *Wpływ dezintegracji i fermentacji na podatność osadów ściekowych do odwadniania*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 1697–1706 (2011).
20. **Wolski P., Zawieja I.:** *Analiza parametrów reologicznych wstępnie kondycjonowanych osadów ściekowych poddanych fermentacji.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1645–1657 (2013).
21. **Zawieja I., Wolski P.:** *Wpływ chemiczno-termicznej modyfikacji osadów nadmiernych na generowanie lotnych kwasów tłuszczowych w procesie fermentacji metanowej.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2054–2070 (2013).

Obecność bakterii lekoopornych w glebach nawożonych osadami ściekowymi

Streszczenie

Oczyszczaniu ścieków zawsze towarzyszy wydzielanie osadów ściekowych. Jedną z metod utylizacji, wykorzystującą własności nawozowe osadów jest ich przyrodnicze m.in. rolnicze użytkowanie (jeśli tylko spełniają dopuszczalne normy). Wraz z wprowadzanymi osadami do gleb mogą się też przemieszczać metale ciężkie, mikroorganizmy patogenne, powodując skażenie podłoży i pogorszenie się warunków rozwojowych dla organizmów autochtonicznych. Szczególne niebezpieczeństwo związane jest z występowaniem w osadach ściekowych drobnoustrojów lekoopornych. Problematyka ta nie jest jeszcze szczegółowo zbadana.

Celem badań autorek pracy było określenie zmian jakościowych i ilościowych drobnoustrojów lekoopornych w glebie piaszczystej nawożonej wybranymi osadami ściekowymi i obornikiem. Badania prowadzono w warunkach doświadczenia polowego. Zastosowano następujące dawki nawozów organicznych: 0, 10, 20, 30 i 40 $Mg \cdot ha^{-1}$. Do zdegradowanej piaszczystej gleby wprowadzono osady po różnych procesach suszenia (naturalnie i solarnie). Badano wpływ metod suszenia osadów ściekowych na obecność mikroorganizmów lekoopornych w nawożonej nimi glebie. Porównywano również ilość bakterii lekoopornych po zastosowaniu osadów i obornika. Badania prowadzono przez jeden sezon wegetacyjny.

Słowa kluczowe:
osady ściekowe, obornik, nawożenie, gleba, mikroorganizmy lekooporne, przeżywalność

Keywords:
sewage sludge, manure, fertilization, soil, drug-resistant microorganisms, bacteria survival

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Sustainable Development and Tourism. Example of Investments Connected with the Installation of Solar Collectors in Seaside Lodging Facilities

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1. Introduction

Tourism is one of the most dynamically developing sectors of economy, particularly in those states and regions which possess such values that are essential for its development. This concerns seaside areas among others, where almost 25 per cent of lodging facilities in Poland are concentrated. Tourism brings about notable economic benefits both to the local population and to local governments by supplying local budgets with incomes from taxes and local charges. The economic significance for the development of regions has on many occasions been the subject of research by various authors, who demonstrated a multifaceted favourable influence both on economic and social changes. However, tourism also means an exploitation of natural values. A high intensity of the tourist movement exerts an influence on a degradation of these values, and thus it considerably lowers their original value. As a consequence, there arises a question about a sustainable development of those tourism destinations where tourism constitutes an essential economic factor. The intention to balance the dynamic development of lodging facilities and the infrastructure that accompanies local tourist product necessitates search for those solutions which will limit the negative external effects to the environment and will contribute to sustainable development.

As a result of the climate and energy package that was approved in March 2007 by the European Parliament and the leaders of the EU Member States, attention was paid to three main areas owing to which the idea of sustainable development can be pursued. In the package, three basic objectives were presented which refer to a reduction of the emission of greenhouse gases by at least 20% by the year 2020 in comparison with the base year 1990, an increase of the participation of energy from renewable resources in the consumption of final energy up to 20% by the year 2020, including a 10 per cent share of biofuels in the consumption of propellant fuels as compared with the fuel and energy demand forecast. The approval of this policy makes the EU Member States undertake activities aimed an application of new solutions in the area of energy production and management. Renewable energy resources constitute one of those solutions with the aid of which two of the abovementioned goals can be realized.

In connection with the above, the authors of this study accepted as their main objective an analysis of the possibilities to use solar power by those facilities that provide lodging services located in the seaside strip. A hypothesis was accepted according to which an application of zero-emission solutions in the form of solar collectors especially in tourist facilities can be an important factor in the pursuit of the idea of the sustainable development of tourism. An attempt was made to provide answers to a number of questions concerning sustainable development in tourism, the intensity level of tourism movement in seaside communes, the emission of greenhouses gases by tourist facilities and also possibilities to use such energy generating equipment as solar collectors.

2. Idea of sustainable development in tourism

2.1. Sustainable development

The notion of sustainable tourism refers directly to the idea of eco-development or sustainable development. Sustainable development was defined for the first time in a declaration issued by the UN Convention in Stockholm in the year 1972, while the principles of sustainable development were formulated in the year 1987 by the World Commission on Environment and Development in the report entitled “Our Common Future”. In the year 1992 in Rio de Janeiro, during the “Environment and Development" conference, the majority of the participating states signed a declaration which expressed an obligation to implement the rules of a new social and economic development [45].

Writers generally trace the origins of the term 'sustainable development' back to a 1987 World Commission on Environment and Development report entitled Our Common Future (also known as the Brundtland Report, after the chair of the group commissioned to prepare it), where the term was first used to bring together the apparently disparate concepts of economic development and environmental conservation [14].

The Brundtland Commission Report [44] stated that 'Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. M.B. Ekinci stattes that Sustainable development can be defined as; 'sustaining the existence of all living creatures together in harmony and without any threat to each other [12].

The concept of sustainable development is based on four basic principles, namely:

- The principle of environmental sustainability, which provides development to be compatible with the maintenance of vital ecological processes, biological diversity and biological resources,
- Principle of social sustainability, providing development be compatible by traditional values of a community, while adding strengthening of their identity and providing cultural development to be compatible with the cultural values of human community, which also has an impact on the strengthening of their identity,
- The principle of sustainability – economic development to provide a cost effective and resource to be managed in a way they can use and future generations [1].

Sustainable development is determined by four major parameters, as follows: technology development, capital development (development of the banks), social development and protection of the natural environment. Of course, the issue is that all of those 4 parameters must develop in accordance with certain proportions because if one of them dominates over the others, it automatically delays and stops the development (in this case, the general value increase) of the other parameters [29].

The problem of sustainable development translates into a widely understood tourism economy. According to B. Garrod and A. Fyall, the term 'sustainable tourism' is derived from the more general concept of 'sustainable development', the former being a specific term used to denote the application of the latter to the particular context of tourism [14].

Although definitions of both sustainable development and sustainable tourism vary according to the different perspectives of the stakeholders concerned there is now considered to be general agreement on the key principles of sustainable tourism [2].

2.2. Sustainable tourism

The broad concepts of sustainability and sustainable development have been applied to specific sectors of the economy (e.g., tourism) [7]. According to J.M. Rempel, the concept of sustainable development, as applied to tourism, is about an evolving understanding of the complex and dynamic relationships between various parts of the social-ecological system [30].

"Tourism should be developed in a way so that it benefits the local communities, strengthens the local economy, employs the local workforce, and wherever ecologically sustainable, uses local materials, local agricultural products, and traditional skills. Mechanisms, including policies and legislation should be introduced to ensure the flow of benefits to local communities" [16].

The problem of sustainable tourism became the subject of many discussions in the 1990s. Recently, scholars have placed greater focus on the contradictions between the three aspects of sustainable tourism: economic, environmental, and social [34]. As with other subfields of the sustainable development literature, sustainable tourism is an area where the list of existing analyses is long and impressive [5].

Environment-friendly rules including a definition of sustainable tourism were formulated in the year 1996 in the document entitled Agenda 21 for travel and tourism industries: towards environmentally friendly and sustainable development, which was jointly prepared by the World Council of Tourism and the Earth Council. In this document, the sustainable development of tourism is defined as "development which allows the pursuit of the needs of present-day tourists and tourist regions, and at the same time it protects and strengthens the possibilities of future consumers and producers" [25].

The World Tourism Organisation defines sustainable tourism as "Tourism that takes full account of its current and future economic, social and environmental impacts, addressing the needs of visitors, the industry, the environment, and host communities [40]. This definition addresses the three main elements of Sustainability: Economic, Environmental and Social. Thereby, 'Sustainable tourism' signifies a condition of tourism based on the principles of sustainable development, taking "full account of its current and future economic, social and environmental impacts" [39]. Moreover, "Sustainable tourism development meets the needs of present tourists and host regions while protecting and enhancing opportunities for the future. It is envisaged as leading to management of all resources in such away that economic, social and esthetic needs can be fulfilled while maintaining cultural integrity, essential ecological processes, biological diversity and life support systems" [5]. B. Bramwell and B. Lane say that sustainable tourism is a positive approach aimed at reducing the tensions caused by the complex interaction of the tourism industry; tourists, the environment, and the hosts catering for holidaymakers [4]. A wide review of the definitions of sustainable tourism can be found among others in the study by H. Kiryluk, M. Borkowska-Niszczota [21].

According to J. Swarbrooke, sustainable tourism means a maximization of the economic, social, and environmental benefits of tourism, with a simultaneous minimization of costs [35]. B. Bramwell and B. Lane state that sustainable tourism is a positive approach that aims to reduce the tensions between the different elements in a complex tourist system: the tourism industry, the tourists, the environment, and the destination [4].

A review of scientific literature serves to prove that the notion of sustainable tourism is not only essential but it is also compound. This is explained among others by B. Mc Kercher, according to whom: sustainable tourism depends on: (a) meeting the needs of the host population in terms of improved standards of living in the short and long term (b) satisfying the demands of increasing tourist numbers and continuing the attract them to achieve this (c) safeguarding the environment to achieve the two foregoing aims [26].

It can be assumed that sustainable tourism is becoming a conscious and important element of present-day issues connected with tourist travels. Generally speaking, this notion is connected with a number of more and more popular forms of tourist travels. This concerns the phenomenon of the so-called nature-based tourism. Approximately 10–20% of all international travel is related to nature experiences globally [38]. According to R.J.G. Van den Born, R.H.J. Lenders, W.T. de Groot, and E. Huijsman, 70–90% of people in Western countries claim to value nature-friendly practices [42]. A detailed analysis of the individual forms of sustainable tourism was carried out by F. Kilipiris, S. Zardava, who distinguished the following forms, i.e.: green tourism, alternetive tourism and responsible tourism [20]. The notion of ecotourism is related to the development of sustainable tourism, while ecotourism constitutes the "core" of sustainable tourism [45]. Ecotourism refers to the harmony of ecosystems and the cultural identity of residents. Through its activities, ecotourism provides funds for an effective protection of the values of the cultural and natural heritage. Ecotourism is a form of sustainable tourism, yet not every form of sustainable tourism is equivalent with ecotourism. This is the result of a wide context of sustainable tourism, which is not restricted to ecological objectives only but also includes the economic and social goals of those areas that host tourists, which correspond to the concept of sustainable development [27].

2.3. Indicators of sustainable tourism

In view of the development of research into sustainable tourism, apart from strictly theoretical studies (including discussions concerning basic notions), the issue of proper indicators (meters) that depict the level of the development of sustainable tourism (the so-called sustainable tourism indicators) began to draw more attention on the part of scientists. In recent years there has indeed been significant progress in the definition of indicators for the sustainable management of firms and tourism destinations [10, 11, 23]. The indicators of sustainable tourism are variables that could be measured and monitored for detecting the changing status of a particular phenomenon, and represent tools for gathering new information through which existing information can be filtered. This new body of compressed necessary information facilitates the identification of trends and threats and allows for undertaking the appropriate actions [1].

In spite of such a significant progress in the research into sustainable tourism, „(…) the method of delivering sustainable tourism is not fully explored and although the concept has been widely endorsed, routes and directions for its practical application remain unclear" [31].

2.4. Negative influence of tourism on natural environment. Example of CO_2 emissions

The current development of tourism is a serious challenge for global climate change mitigation [9]. The tourism industry brings economic benefits to the country, but there are usually energy consumption and carbon dioxide emission associated with it [8]. A tourist not only uses direct energy in the form of petrol, gas and coal, but he (she) also uses indirect energy embodied in consumer goods such as services, food and products [43].

However, it is also likely that tourism development might have indirect effects on climate change through economic growth and energy capacity expansion. For example, an increase of tourism activities creates increased demand for energy at various functions such as transportation, catering, accommodation, and the management of tourist attractions [24].

This problem is very important because as stated by J.W. Lee, T. Brahmasrene, there has not been a time series approach to analyze the relationship among tourism, CO_2 emissions and economic growth for EU countries. This research questions whether tourism induces an increase in the CO_2 emissions and economic growth of the region. The questions are vital to disentangle the effect of tourism on both environment and economic growth in the region, where governments often make legislative responses to current environmental issues [22].

A study commissioned by the United Nations World Tourism Organization (UNWTO, 2008) estimated global tourism-related CO_2 emissions to be roughly 5% of total global emissions [40]. Most of these emissions are generated by the transport of tourists, in particular, air travel. Thus, the contribution of the tourism sector to climate change is on a global level and is substantial [22]. D. Scott et al. (2010) reported that the tourism sector could become a leading global source of greenhouse gases in the future [33]. While 5% of global emissions may appear insignificant when compared to other sectors such as agriculture, tourism is characterized by rapid growth. International tourist arrivals increased from 25 million in 1950 to 534 million in 1995, and 803 million in 2005. In the 2005–2007 period alone, international tourist arrivals grew by 100 million, reaching the 903 million mark. If this trend continues, tourism emissions will increase by over 150% by 2035 [UNWTO, 2008]. This growth in emissions must be considered in the context of emissions reduction targets as outlined by the IPCC (2008), which recommends to reduce global emissions by 50–80% by 2050 [33].

The problem of CO_2 emission emphasized above obviously is not only aspect of the negative environmental impact of tourism. To a significantly greater extent, this sector causes a number of changes, including those in the context of the abuse of water resources or excessive waste emissions [8].

3. Methodology

The research purpose accepted requires in the first order to have the intensity of the tourist movement examined. Seasonal tourist facilities located in those communes that border with the Baltic Sea were selected for purpose of the research. In the next order, an analysis was performed of the level of CO_2 emissions and the consumption of energy and hot water. Those indices which are available in literature were used at this stage. Numerical data concerning the number of lodging places in the seaside communes were obtained from the Bank of Local Data of the Central Statistical Office. In order to determine the consumption of water in the lodging facilities, values were accepted that are compliant with the water consumption standard in Poland, the Ordinance by the Minister of Infrastructure of 14 January 2002 on the determination of average water consumption standards (Journal of Laws No. 8 Item 70); it was accepted that 90% of water consumed is hot water above 40^0C.

The assessment of the determinants of the use of solar energy in tourist facilities was performed based on the average values of daily radiation in the individual months in the Middle and East Europe and the demand for hot water.

4. Lodging facilities in seaside communes

Seaside communes are the most counting tourist destinations in Poland. In the year 2012, the total number of lodging places in those communes was 168.6 thousand. This constitutes 25% of total lodging places in Poland. The communes possess 6.6 thousand of annual lodging places, which constitutes 15% of total annual lodging places in Poland. In the year 2012, in the communes analyzed, over 14.5 million accommodations (23% on the national scale) were given. The seasonal nature of the tourist movement has an influence on the nature of lodging facilities, which in seaside communes function in the majority of cases in the summer period only. The total number of seasonal lodging places in these communes is ca. 90.1 thousand (cf. Table 1).

Table 1. Characteristics of seasonal lodging facilities in coastal communes
Tabela 1. Charakterystyka sezonowej bazy noclegowej gmin nadmorskich

No.	Type of lodging facilities	Number of seasonal lodging places
1.	Hotels	331
2.	Boarding pensions	1192
3.	Other hotel facilities	1074
4.	Youth hostels	125
5.	School youth hostels	539
6.	Holiday centres	47794
7.	Summer camp centres	6916
8.	Training and holiday centres	4316
9.	Hotels	19
10.	Houses of creative work	135
11.	Complexes of tourist cottage houses	6600
12.	Campsites	10595
13.	Camping grounds	4256
14.	Spa works	778
15.	Remaining non-classified facilities	5477
16.	**Total**	**90147**

From among the tourist facilities analyzed, holiday centres (over 47 thousand places) are characterized by the highest number of seasonal lodging places. Campsites possess a four times smaller number, i.e. over 10 thousand places, and summer camp centres possess almost 7 thousand. There is a low degree of the seasonal nature of accommodation in the case of hotels and spa works, which in the majority of cases function over the whole calendar year.

5. Assessment of CO_2 emissions from tourist facilities

The functioning of lodging facilities requires an involvement of considerable expenditures of energy (Fig. 1). The majority of this energy (61%) is used in the processes of heating, ventilation or air-conditioning. In the further order, energy is used in 21% to heat water and to operate lightning and electric devices (12%). The smallest amount of energy is consumed during the preparation of meals (6%).

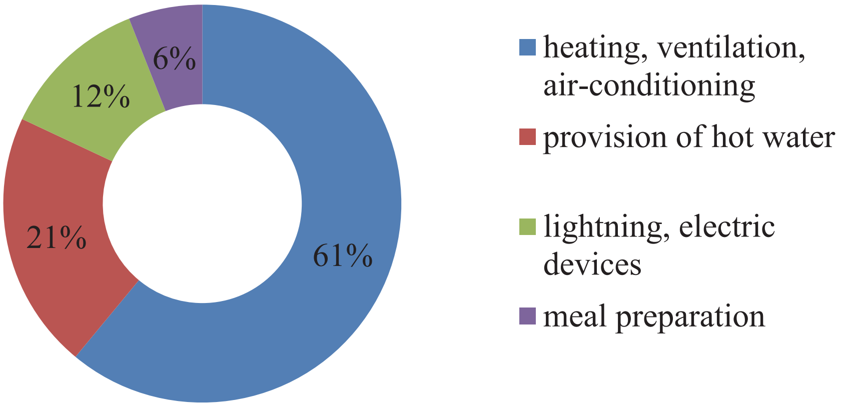

Fig. 1. Structure of energy consumption in hotels [28]
Rys. 1. Struktura zużycia energii w hotelach [28]

Depending on the type of accommodation, different levels are observed of the consumption of energy and CO_2 emissions. The energy consumption values presented by Gössling were accepted for the needs of the analyzes [15]. It results from these that hotels and, in the further order, cottage houses require the highest amounts energy in order to function (cf. Table 2).

The lowest demand occurs in the case of boarding pensions and camping grounds. The values provided here serve the purpose of the determination of CO_2 emissions from lodging facilities located in the seaside communes.

The high consumption of energy occurs as a result of the provision of lodging and gastronomic services. It is estimated that those tourists that visit developing countries consume daily eight times more water than local residents. In the case of hotels, there is a very high demand for electricity, which in connection with a high consumption of water causes that hotels have the highest negative environmental impact in the group of commercial and service buildings (Table 3).

Table 2. Assessment of average energy consumption and CO_2 emissions by type of accommodation [15]
Tabela 2. Ocena średniego zużycia energii oraz emisji CO_2 według typu bazy noclegowej [15]

No.	Type of lodging facilities	Consumption of energy for one visiting person per day [MJ]	CO_2 emissions for one visiting person [kg CO^2]
1.	Hotels	130	20,6
2.	Camping grounds	50	7,9
3.	Boarding pensions	25	4
4.	Accommodation offered without meals	120	19
5.	Holiday centres	90	14,3
6.	Cottage houses	100	15,9
7.	**Average**	**98**	**15,6**

Table 3. Estimated CO_2 emissions from selected tourist facilities
Tabela 3. Szacowana wielkość emisji CO_2 przez wybrane obiekty turystyczne

No.	Type of lodging facilities	Number of accommodations given within a year	CO_2 emissions per one visiting person [kg/person]	CO_2 emissions within a year [t/year]
1.	Hotel facilities	2339694	20,6	48198
2.	Camping grounds and camping sites	343596	7,9	2714
3.	Complexes of tourist cottage houses	236383	15,9	3758
4.	Other lodging facilities	8593619	15,6	134060
5.	**Total**	**11513292**	**-**	**188731**

The analysis carried out has demonstrated that seaside tourist facilities contribute to CO_2 emissions approximately on the level of 188.7 thousand t/year, out of which hotel facilities emit the smallest amounts, i.e. 2.7 thousand t/year, and the complexes of tourist cottage houses: 3.8 thousand t/year. Considering the seasonal nature of seaside accommodation, emissions take place mainly in summer months with an intensive tourist movement.

6. Determinants of the use of solar energy in tourist facilities

In the opinion of the Institute for Eco-development, the realization of the guidelines of sustainable development can occur in three ways, i.e.:

- through the greening of travel agencies and other institutions that provide tourist services, which in practice means a change of their image in such a way that they become an evidence of tourism being environment friendly,
- through the greening of the tourist product, which means control of the tourist movement in a given region in such a way so not to abuse natural environment values and resources,
- through the greening of the creation process of the tourist product by orienting it onto sustainable development in the scope of all its segments and elements, starting from transport, accommodation, catering to various additional services [19].

In the last case, the methods can be used of the reduction of environmental pollution, which is generated as a result of the creation and consumption of the tourist product. In a holistic model of sustainable tourism, on the level of tourist reception, environment friendly energy economy is mentioned [37]. This includes typical activities connected with the operation of the tourist movement, such as the provision of lodging, catering or transport services. Connections need to be considered of tourism with the other fields of the regional economy including farming, forestry, public utilities and communication, where solutions from the scope of renewable energy resources are also used.

A renewable energy source is a source that utilizes the energy of wind, solar radiation, geothermal, marine waves, currents and outflows, river gradients and energy acquired from biomass, landfill biogas and also biogas generated in the processes of sewage discharge or purification waste, or decomposition of plant and animal remnants stored

[41].The basic feature of renewable energy resources is that energy is acquired from natural and permanently repeated natural processes [13]. This is the primary difference in relation to traditional non-renewable energy sources in the form of fossil fuels, such as hard bituminous coal, brown coal or petroleum, which in the process of combustion provide large quantities of greenhouse gases that are released into the atmosphere. In sustainable development, particular attention is paid to the accumulation of pollutants, which are mainly generated in highly urbanized and industrialized areas. This also concerns those tourist regions which accept large numbers of visiting people over a short period of time, which involves a high energy demand.

One of the possibilities in the area of renewable energy resources is the use of solar energy mainly by tourist facilities that provide their services in the summer season. According to Tańczuk and Zając, the annual density of solar radiation in Poland on a horizontal surface fluctuates within the range of 950–1250 kWh/m^2 (Table 4), while the average insolation is 1.6 thousand of hours per year [36]. Moreover, in the calendar year, meteorological conditions are characterized by a very uneven annual layout of insolation (Fig. 2). The highest insolation (80%) coincides with six months of the spring and summer season from the beginning of April to the end of September. The time of solar operation lengthens up to 16 hours/day in summer, while in winter it shortens to 8 hours/day. These conditions are favourable for the installation of solar systems in those seaside tourist facilities where the highest numbers of visitors are observed in summer months.

Solar radiation is characterized by a spatial diversification. In this respect, it also diversifies Polish regions. Its highest values occur in the seaside strip and in the eastern part of Poland. When accepting the average annual density of solar radiation, 1.07 thousand kWh with no heat losses can be theoretically obtained from one square meter in the seaside strip. The average operational efficiency of flat solar collectors is an annual average of 55 per cent (the maximum is ca. 80%), which to a certain extent will reduce this amount of energy to the level of 592 kWh. Therefore, it can be accepted that 1 m^2 of a solar collector allows a saving of 592 kWh of energy. Depending on the technology used, the installation of solar collectors involves savings.

Table 4. Potential useful energy of solar radiation in kWh/m^2 per annum in selected regions in Poland [36]
Tabela 4. Potencjalna energia użyteczna promieniowania słonecznego w kWh/m^2/rok w wyróżnionych rejonach Polski [36]

No.	Region	Year (I–XII)	Summer half year	Summer season	Winter half year
1.	Seaside strip	1076	881	497	195
2.	Eastern part of Poland	1081	821	461	260
3.	Central part of Poland	985	785	449	200
4.	Western part of Poland with the upper drainage basin of the Odra River	985	785	438	204
5.	Southern part of Poland	962	682	373	280
6.	South-west part of Poland including Sudety with Tuchowo	950	712	393	238

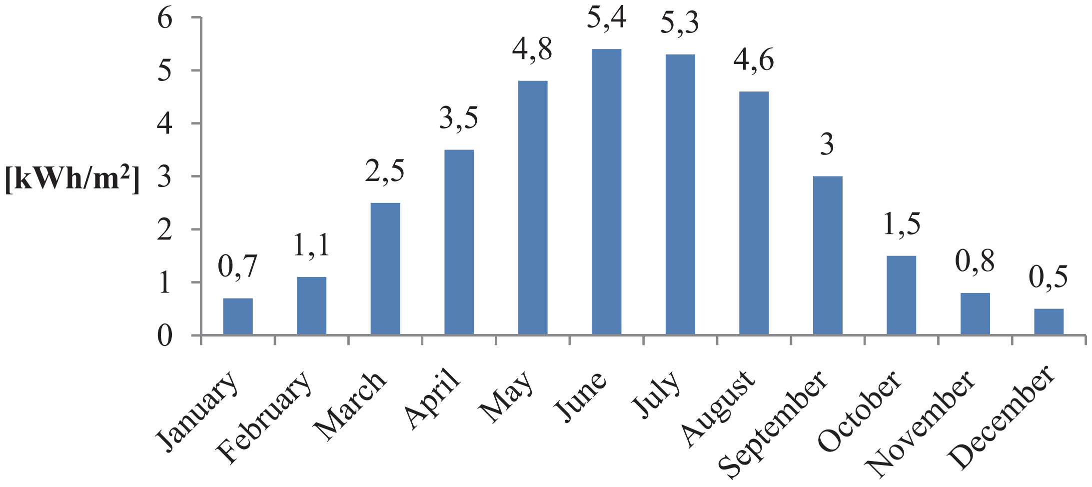

Fig. 2. Daily radiation in individual months in Central and Eastern Europe [18]
Rys. 2. Promieniowanie dzienne w poszczególnych miesiącach w Europie Środkowo-Wschodniej [18]

Due to the spatially and temporarily diversified level of solar radiation, different productivity of liquid collectors (cf. Table 5) is obtained. The density of solar radiation on the surface of the collector is decisive for the possibility to heat water. For example, with the radiation density of 6kWh/m^2, 1.02 thousand dm^3 of hot water with the temperature of 40^{0}C can be obtained. If we wish to obtain a higher temperature with the same radiation intensity, we will heat a smaller quantity of water.

Table 5. Efficiency of liquid collectors according to the daily dose of solar radiation [6]
Tabela 5. Wydajność kolektorów cieczowych w zależności od dziennej dawki napromieniowania słonecznego [6]

No.	Temperature of heated water in ^{o}C	Quantity of water in dm^3 within a day from 10 m^2 of collectors with daytime solar radiation dose being		
		3,0 kWh/m^2	4,5kWh/m^2	6,0 kWh/m^2
1.	40	330	660	1020
2.	50	150	340	550
3.	60	60	170	330
4.	70	20	80	190

The determinants concerning the use of solar energy in tourist facilities can be referred to the intensity of radiation in the individual months and in connection with the seasonal nature of tourism. The abovementioned phenomena are coincident as regards values. The highest solar radiation occurs simultaneously with a high energy demand, which results from the tourist movement intensity. Taking into consideration only the aspect of the reduction of CO_2 emissions without an analysis of the economic profitability of the investment, collectors can be used in seasonal tourist facilities to heat water.

The seasonal nature of the tourist movement may result in a diversification of the costs of energy producing installations. With variable solar radiation, in order to obtain the same energy production effectiveness in March as in June, July or August, the surface of collectors needs to be increased from 10 m^2 to 30 m^2. This involves a significant increase of the costs of the installation. Hence, the use of collectors in seasonal facilities will enable a decrease of the investment costs.

To assess the quantity of water which is consumed in lodging facilities situated in the seaside communes, Polish water consumption standards were used [32]. According to these standards, the consumption of water for one lodging place in a hotel is an average of 150 dm^3, while for camping sites and complexes of cottage houses this is 100 dm^3.

Table 6. Estimated area of solar collectors in relation to energy demand in summer months

Tabela 6. Szacunkowa powierzchnia kolektorów słonecznych względem zapotrzebowania na energię w miesiącach letnich

No.	Type of lodging facilities	Number of seasonal lodging places	Consumption of hot water[a]		Surface of collectors in m^2 [b]	
			dm^3/one person per day	m^3/day	July	August
1.	Hotels	331	150	45	50	66
2.	Boarding pensions	1192	150	161	179	239
3.	Other hotel facilities	1074	150	145	161	215
4.	Youth hostels	125	110	12	14	18
5.	School youth hostels	539	110	53	59	79
6.	Holiday centres	47794	150	6452	7161	9564
7.	Summer camp centres	6916	150	933	1036	1384
8.	Training and holiday centres	4316	150	582	647	864
9.	Hostels	19	110	2	2	3
10.	Houses of creative work	135	150	18	20	27
11.	Complexes of tourist cottage houses	6600	100	594	659	880
12.	Camping sites	10595	100	954	1058	1413
13.	Camping grounds	4256	33	126	140	187
14.	Spa works	778	150	105	117	156

[a] Values were accepted in accordance with the Polish water consumption standards, the Ordinance by the Minister of Infrastructure of 14 January 2002 on the determination of average water consumption standards (Journal of Laws No. 8 Item 70); it was accepted that hot water above 40^0C constitutes 90% of water consumed.

[b] Total daily radiation was accepted in July to be 5.3 kWh/m^2 and in August on the level of 4.6 kWh/m^2 [6]

The highest daily consumption of water in seaside communes occurs in holiday centres (6.4 thousand m^3) in the further order in camping sites (954 m^3), summer camp centres (954 m^3) and also in the complexes of tourist cottage houses (594 m^3) and training and holiday centres (582 m^3); cf. Table 6.

Assuming that the seaside tourist facilities analyzed function in summer months, i.e. in July and August (months with a great density of solar radiation) and are fully booked, the daily demand for hot water will be 10.2 thousand m^3. The highest daily consumption of hot water will be in holiday centres (6.4 thousand m^3), camping sites (954 m^3) and summer camp centres (933 m^3).

To heat this quantity of water (i.e. 10.2 thousand m^3) in July, with the daily radiation of 5.3 kWh/m^2, ca. 113 thousand m^2 of collectors is needed; in March, with the solar radiation of 2.5 kWh/m^2, the area of 308.6 thousand m^2 is required, that is almost three times as much. Tourist facilities have an opportunity to participate in sustainable development through the use of solar collectors, which will allow to acquire 21% of energy required for them to function, and to heat water.

7. Summary

1. The sustainable tourism is direct linked with the idea of eco-development or sustainable development; hence, apart from economic and social issues, it is equally focused on the problems of environmental protection including the emission of greenhouse gases. Those living services which are offered by lodging facilities require a high involvement of energy; thus, search for innovative solutions oriented onto low emissions of greenhouse gases in connection with energy production is important.
2. Accommodation facilities in Poland are characterized by a great concentration of lodging services. This particularly concerns the seaside strip, where 25% of lodging places are located on the national scale. Apart from this, seaside regions are mainly visited in summer months, i.e. in July and August. This causes a high intensity of the tourist movement and an energy demand over a relatively short period of time.
3. The use of energy in tourist facilities is diversified in relation to the facility type and the type of the services provided. The highest consumption of energy occurs in hotel facilities, while the smallest consumption is in the case of camping sites and camping grounds. This translates into CO_2 emissions related to the production of energy for the needs of tourists. It was estimated that the total CO_2 emissions in lodging facilities in seaside communes within a year amount to 188.7 thousand tones.
4. Hot water is one of the main factors that determine energy demand in lodging facilities. Solar collectors can be used to heat this water. The analysis carried out has demonstrated that in the case of seasonal facilities, the highest efficiency of the equipment and the greatest effectiveness of heat production is obtained in relation to the surface of collectors.

5. Investments connected with the installation of solar collectors may have a good impact on energy savings and they will contribute to reductions of CO_2 emissions in tourist regions. This constitutes an essential contribution to the sustainable development of tourism and also to the sustainable development of the region.

The analysis included in this article may constitute an introduction to wider research to take into consideration national and international aspects, for an example aspects all the Baltic countries. In the first case, research could cover comprehensive effects of the phenomenon analyzed, also in the context of the energy balance of Poland.

References

1. **Angelevska-Najdeska K., Rakicevik G.:** *Planning of sustainable tourism development*. Procedia – Social and Behavioral Sciences. 44 (2012).
2. **Ayuso A.:** *Comparing voluntary policy instruments for sustainable tourism: The experience of the Spanish hotel sector*. Journal of Sustainable Tourism. *15* (2007).
3. **Bohdanowicz P.:** *Turystyka a świadomość ekologiczna*. Wydawnictwo Adam Marszałek. Toruń 2006.
4. **Bramwell B., Lane, B.:** Sustainable tourism: an evolving global approach. Journal of Sustainable Tourism. 1(1) (1993).
5. **Cernat L., Gourdon J.:** *Paths to success: Benchmarking cross-country sustainable tourism*. Tourism Management. 33 (2012).
6. **Chochowski A.:** *Energia słoneczna, w: Zarządzanie w energetyce*. (red.) A. Chochowski, F. Krawiec. DIFIN. Warszawa 2008.
7. **Cottrell S.P., Vaske J.J., Roemer J.M.:** *Resident satisfaction with sustainable tourism: The case of Frankenwald Nature Park, Germany*. Tourism Management Perspectives. 8 (2013).
8. **Davenport J., Davenport J.L.:** *The impact of tourism and personal leisure transport on coastal environments: a review*. Estuarine Coastal and Shelf Science. 67(2) 2006.
9. **Dubois G., Peeters P., Ceron J.-P., Gössling S.:** *The future tourism mobility of the world population: Emission growth versus climate policy*. Transportation Research Part A. 45 (2011).
10. **Dwyer L., Forsyth P., Rao P.:** *The price competitiveness of travel and tourism: a comparison of 19 destinations.* Tourism Management. 21 (2000).
11. **Dwyer L., Forsyth P., Spurr, R.:** *Evaluating tourism's economic effects: New and old approaches*. Tourism Management. 25 (2004).

12. **Ekinci M.B.:** *The Cittaslow philosophy in the context of sustainable tourism development; the case of Turkey*. Tourism Management. 41 (2014).
13. *Energia ze źródeł odnawialnych w 2011 roku*. GUS. Warszawa 2012.
14. **Garrod B., Fyall A.:** *Beyond the rhetoric of sustainable tourism?* Tourism Management. 19(3) (1998).
15. **Gössling S.:** *Ecological footprint analysis as a tool to assess tourism sustainability*. Ecological Economics. 43(2–3) (2002).
16. International Conference of Environment Ministers on Biodiversity and Tourism. *The Berlin declaration on biological diversity and sustainable tourism*. Berlin. Germany. United Nations 1997.
17. IPCC.: *Climate change 2007: mitigation of climate change*. IPCC fourth assessment report, working group III. International Panel on Climate Change. Geneva 2008.
18. **Jabłoński W., Wnuk J.:** *Zarządzanie odnawialnymi źródłami energii. Aspekty ekonomiczno-techniczne*. Wyższa Szkoła Humanitas, Sosnowiec 2009.
19. **Kamieniecka J.:** *Ekopolityka w turystyce, Raport o zmianach możliwych i potrzebnych*. Warszawa 1998.
20. **Kilipiris F., Zardava S.:** *Developing sustainable tourism in a changing environment: issues for the tourism enterprises (travel agencies and hospitality enterprises)*. Procedia – Social and Behavioral Sciences. 44 (2012).
21. **Kiryluk H., Borkowska-Niszczota M.:** *Turystyka zrównoważona w: Zarządzanie turystyką na obszarach przyrodniczo cennych*. (red) B. Poskrobko. Wyższa Szkoła Ekonomiczna w Białymstoku 2005.
22. **Lee J.W., Brahmasrene T.:** *Investigating the influence of tourism on economic growth and carbon emissions: Evidence from panel analysis of the European Union*. Tourism Management. 38 (2013).
23. **Liu Z.H.:** *Sustainable tourism development: a critique.* Journal of Sustainable Tourism. 11(6) (2003).
24. **Liu J., Feng T., Yang X.:** *The energy requirements and carbon dioxide emissions of tourism industry of Western China: a case of Chengdu city*. Renewable& Sustainable Energy Reviews. 15 (2011).
25. **Majewski J.:** *Agenda 21*. Polska Gazeta Turystyczna. 10, 12 (1999).
26. **McKercher B.:** *The unrecognized threat to tourism: can tourism survive 'sustainability'?* Tourism Management (1993).
27. **Niezgoda A.:** *Rola różnych koncepcji i form rozwoju turystyki w dążeniu do celów rozwoju zrównoważonego*. Turyzm. 18/2 (2008).
28. **Ogrodniczuk J., Węglarz A., Kamieniecka J.:** *Energia w obiekcie turystycznym*. Fundacja Instytut na rzecz Ekorozwoju. Warszawa 2010.
29. **Piecuch I**., **Piecuch T.:** *Environmental Education and Its Social Effects.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection). 15, 192–212 (2013).

30. **Rempel J.M.:** *Sustainability in coastal tourism: pursuing the causal nexus*. TILTAI, Klaipeda 2009.
31. **Robson J., Robson I.:** *From shareholders to stakeholders: critical issues for tourism marketers.* Tourism Management. 17(7) (1996).
32. Rozporządzenie Ministra Infrastruktury z dnia 14 stycznia 2002 r. w sprawie określenia przeciętnych norm zużycia wody. (Dz. U. Nr 8, poz. 70).
33. **Scott D., Peeters P., Gössling S.:** *Can tourism deliver its "aspirational" greenhouse gas emissions reduction targets?* Journal of Sustainable Tourism. 18(3) (2010).
34. **Sörensson A., Friedrichs Y.:** *An importance-performance analysis of sustainable tourism: A comparison between international and national tourists*. Journal of Destination Marketing & Management. 2 (2013).
35. **Swarbrooke J.:** *Distribution channels: ethics and sustainability.* In: D. Buhalis, & E. Laws (Eds.), Tourism Distribution Channels Practice, Issues and Transformations. London: Continuum 2001.
36. **Tańczuk M., Zając D.:** *Ocena możliwości wykorzystania odnawialnych źródeł energii w gospodarce energetycznej Gminy Miasta Sopotu, ze szczególnym uwzględnieniem możliwości wykorzystania energii odnawialnej pozyskiwanej na bazie biomasy glonowej*. Opole 2011.
37. Tourism and Environment. Council of Europe. Strasbourg 1997.
38. **Tyrväinen L., Uusitalo M., Silvennoinen H., Hasu E.:** *Towards sustainable growth in nature-based tourism destinations: Clients' views of land use options in Finnish Lapland*. Landscape and Urban Planning. 122 (2014).
39. United Nations Environment Programme (UNEP) and World Tourism Organisation (WTO). Making tourism more sustainable: A guide for policymakers 2005.
40. UNWTO.: *Climate change and tourism: Responding to global challenges*. Madrid, Spain 2008.
41. Ustawa z dnia 10 kwietnia 1997 r. Prawo energetyczne. Dz. U. z 2012, poz. 1059.
42. **Van den Born R.J.G., Lenders R.H.J., de Groot W.T., Huijsman, E.:** *The new biophilia: An exploration of visions of nature in Western countries*. Environmental Conservation. 28 (2001).
43. **Van Engelenburg B.C.W., Van Rossum T.F.M., Blok K., Vringer K.:** *Calculating the energy requirements of household purchases: a practical step-by-step method*. Energy Policy. 21(8) (1994).
44. WCED.: *Our Common Future, ed. Gro Harlem Brundtland*. Nairobi. United Nations Environment Programme 1987.
45. **Zaręba D.:** *Ekoturystyka. Wyzwania i nadzieje*. Wydawnictwo Naukowe PWN. Warszawa 2000.

Rozwój zrównoważony a turystyka. Przykład inwestycji związanych z instalacją kolektorów słonecznych w nadmorskich obiektach noclegowych

Streszczenie

Autorzy niniejszego opracowania przyjęli za cel główny analizę możliwości wykorzystania energii słonecznej przez obiekty świadczące usługi noclegowe zlokalizowane w pasie nadmorskim. Przyjęto hipotezę, która zakłada, iż zastosowanie bezemisyjnych rozwiązań w postaci kolektorów słonecznych szczególnie w obiektach turystycznych może być ważnym czynnikiem realizacji idei rozwoju zrównoważonego turystyki. Na potrzeby weryfikacji hipotezy podjęto próbę odpowiedzi na szereg pytań dotyczących istoty zrównoważonego rozwoju w turystyce, poziomu natężenia ruchu turystycznego w gminach nadmorskich, emisji gazów cieplarnianych przez obiekty turystyczne, a także możliwości wykorzystania urządzeń do produkcji energii takich, jak kolektory słoneczne.

Przyjęty cel badawczy wymagał w pierwszej kolejności zbadania natężenia ruchu turystycznego. Do badań wybrano turystyczne obiekty sezonowe zlokalizowane w gminach graniczących z Morzem Bałtyckim. W następnej kolejności wykonano analizę wielkość emisji CO_2 oraz zużycia energii i ciepłej wody. Na tym etapie wykorzystano wskaźniki dostępne w literaturze. Dane liczbowe dotyczące liczby miejsc noclegowych w gminach nadmorskich pozyskano z Banku Danych Lokalnych Głównego Urzędu Statystycznego. Do określenia zużycia wody w obiektach noclegowych przyjęto wartości zgodnie normą zużycia wody w Polsce, Rozporządzenie Ministra Infrastruktury z dnia 14 stycznia 2002 r. w sprawie określenia przeciętnych norm zużycia wody (Dz. U. Nr 8, poz. 70); przyjęto, iż 90% zużytej wody, to woda ciepła powyżej 40°C.

Ocenę uwarunkowań wykorzystania energii słonecznej w obiektach turystycznych wykonano w oparciu o średnie wartości promieniowania dziennego w poszczególnych miesiącach w Europie Środkowo-Wschodniej oraz zapotrzebowania na ciepłą wodę użytkową.

Przeprowadzone badania pozwoliły na sformułowanie następujących wniosków.

1. Turystyka zrównoważona nawiązuje bezpośrednio do idei ekorozwoju lub rozwoju zrównoważonego stąd koncentruje się równorzędnie obok spraw gospodarczych i społecznych również na problemach ochrony środowiska, w tym emisji gazów cieplarnianych. Usługi bytowe, które oferują obiekty noclegowe wymagają dużego zaangażowania energii stąd ważnym jest poszukiwanie innowacyjnych rozwiązań ukierunkowanych na niskoemisyjność gazów cieplarnianych przy produkcji energii.

2. Baza noclegowa w Polsce charakteryzuje się dużą koncentracją usług noclegowych, co szczególnie dotyczy pasa nadmorskiego, w którym zlokalizowane jest 25% miejsc noclegowych w skali kraju. Dodatkowo regiony nadmorskie są głównie odwiedzane w miesiącach letnich, tj. lipcu oraz sierpniu, co powoduje duże natężenie ruchu turystycznego i zapotrzebowania na energię w relatywnie krótkim czasie.
3. Wykorzystanie energii w obiektach turystycznych jest zróżnicowane ze względu na typ obiektu i rodzaj świadczonych usług. Najwyższe zużycie energii występuje w obiektach hotelarskich, natomiast najmniejsze w przypadku kempingów i pól namiotowych. Przekłada się to na emisję CO_2, która powstaje przy produkcji energii na potrzeby obsługi turystów. Oszacowano, iż łączna emisja CO_2 w obiektach noclegowych gmin nadmorskich w przeciągu roku wynosi 188,7 tys. ton.
4. Jednym z głównych czynników determinujących zapotrzebowanie na energię o obiektach noclegowych jest ciepła woda użytkowa. Do podgrzewania tej wody można zastosować kolektory słoneczne. Przeprowadzona analiza wykazała, iż w przypadku obiektów sezonowych uzyskuje się najwyższą sprawność urządzenia i efektywność produkcji ciepła w stosunku do powierzchni kolektorów.
5. Inwestycje związane z instalacją kolektorów słonecznych mogą wpłynąć na oszczędności energii oraz ograniczą emisję CO_2 w regionach turystycznych, co stanowi istotny wkład w rozwój zrównoważony turystyki, jak również rozwój zrównoważony regionu.

Zawarta w niniejszym artykule analiza może stanowić wstęp do szerszych badań, uwzględniających aspekt krajowy oraz międzynarodowy, przykładowo odnoszący się do wszystkich krajów bałtyckich. W przypadku tego pierwszego, badania mogłyby się odnosić do kompleksowych następstw analizowanego zjawiska, m.in. w kontekście bilansu energetycznego Polski.

Słowa kluczowe:
turystyka, rozwój zrównoważony, turystyka zrównoważona, kolektory słoneczne

Keywords:
tourism, sustainable development, sustainable tourism, solar collectors

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Sorption of Acid Green 16 from Aqueous Solution onto Low-moor Peat and Smectite Clay Co-occurring in Lignite of Belchatow Mine Field

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1. Introduction

The consumption lifestyle and an increased demand on various colored textile, paper, cosmetic and food products contributes to creation of larger and larger amounts of wastewater containing dyes. Presently over 100,000 industry dyes are used and its annual production is estimated to be $7x10^5$ Mg. Approximately 10–15% of dyes used in coloring processes seeps into the natural environment becoming a serious threat for surface water, because even minor concentrations of dyes in water suppress oxygen diffusion, which blocks and prevents light from getting to autotrophs. Because of these, designing effective methods of dye containing wastewater treatment becomes an object of wide research. Such treatment, besides being efficient, should enable multiple reuse of treated water in technological processes [5,14,33].

Among the most popular processes of wastewater treatments are: adsorption, coagulation, oxidation, precipitation, ozonation, ultrafiltration, reversed osmosis and biological techniques [6,7,13,24]. Nevertheless, chemical methods of removing dyes from wastewater create sewage sludge, the disposal of which could be problematic.

Among the methods of water and wastewater treatment, adsorption is a highly efficient one, considering its high effectiveness at relatively low costs.

A sorbent commonly used to remove metal and metaloid ions, as well as organic pollutions (e.g. dyes), from water and wastewater is an activated carbon [3,27,30]. Its physical and chemical properties, including specific surface area, porosity and high surface reactivity, make it a popular component of adsorption treatment methods. On the other hand, the high costs of its production and the necessity of its regeneration force a search for new, low cost, though equally effective sorption materials. Due to this fact, mineral and organogenic materials of both natural and waste origin, characterized by high sorption capacity and wide availability, become objects of numerous research studies in the recent years. Among such sorbents are clay and clay minerals (smectites, illites, kaolnites and bentonites clays), zeolites, biolites (peats, lignites), biosorbents (composts, biomass) and waste materials (fly ashes) [1,8,15, 18,22,25,29].

Smectites are part of phyllosilicates group of 2:1 ratio, which means that between two tetrahedral sheets there is an octahedral sheet. The tetrahedral sheets, built of T_2O_5 units, normally contain Si, Al or Fe as the central atom. Two types of octahedral sheets occur in smectites: the *dioctahedral* type, where two-third s of the octahedral sites are occupied mainly by trivalent cations (Al^{3+} or Fe^{3+}), and the *trioctahedral* type, with most of the sites occupied by divalent cations (Mg^{2+}). The negative charge of the layers is balanced by hydrated exchangeable cations in the inter layers (mostly Ca^{2+}, Mg^{2+}, Na^{+}) [34]. They are an important material for ceramic, rubber, paper, pharmaceutical, chemical and food industries. Sometimes they are used as components of mineral fertilizers and drilling fluids. They are also used as sealing layers, stockpiles, vertical clay barriers, ash stabilizers and rock mass sealers in coal mines [23]. Due to the high surface area and high cation exchange capacity (CEC) they can also be used as sorbents. The main centers of sorption in the smectite minerals are silanol groups (–Si–OH) and aluminol groups ($–Al_2–OH$) created by breaking Si–O–Si and Al–O–Al bonds. In contrast, the interlayer cations, weakly bound to the mineral structure, are responsible for the ion-exchange sorption.

Peat is an organogenic sedimentary rock and a product of the earliest stage of plants coalification. It belongs to the rocks widespread in northern Europe (Scotland, Ireland, Sweden, Germany, Denmark, Poland, Finland, Iceland, and Russia), Asia (Siberia, Russia) and North America (Canada, USA). In Poland, about 70% of peatlands are located in the northern part of the country and the overwhelming number, i.e. 95.5%, belong to the low type. Peats are used for fuel, fertilization (horticultural and agricultural), medicine and sanitary purposes. They are used in the chemical and foundry industries as both an extender and insulating material. Due to its characteristics and availability they can also be used as an adsorbent to remove pollutants from water and wastewater [16,21,32]. The main centers of sorption in peats are –COOH and –OH fulvic and humic acids in which the H^+ ions may be substituted by alkaline earth metal ions, especially Ca^{2+}.

The aim of this study was to determine the sorption capacity of smectite clay (natural and thermally activated at 250°C) and the low-moor peat co-occurring with lignite of Belchatow mine field (Central Poland) for the cationic acid dye – Acid Green 16 (AG–16), as well as determining the effect of the clay thermal activation on its sorption capacity. In addition, the article presents the results concerning the applicability of three isotherm equations (e.g. Freundlich, Langmuir, and Dubinin-Radushkevich) to describe sorption as well as determine the rate of the sorption process and to estimate parameters in the kinetic equations.

2. Research materials

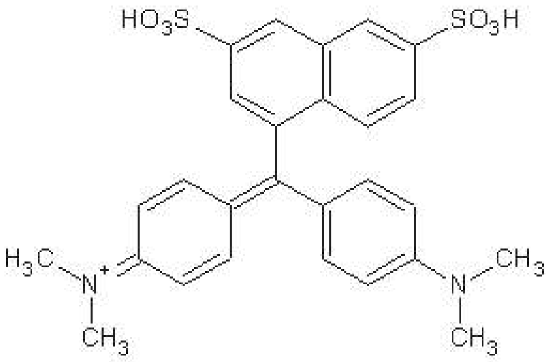
2.1. Acid Green dye 16 (AG–16)

The dye Acid Green 16 (AG–16), belonging to the acid dyes, was used. It came from Zaklad Boruta–Zachem Kolor Sp. z o.o. – the biggest producer of dyes and pigments in Poland.

AG-16 dye is used to color wool and fibers of animal origin, as well as paper and ink.

Figure 1 shows the structural formula of the dye and its characteristics, i.e. Colour Index – CI, CAS number, molecular weight – M, the cation diameter – d_d, as well as the wavelength – λ at which the measurements of the concentration and pH were performed, in the water, 1000 mg/dm^3 dye concentration.

The dye belongs to the arylmethane group of acid dyes. In its structure one can notice a naphthalene ring, two aryl-amino-dimethyl groups, and two sulfonic groups (–SO_3H). The molecule has a cationic structure and –SO_3H groups can act as proton acceptors in a hydrogen bond. However, the dye is characterized by a lack of donor groups. Due to the small size of the dye particle (diameter of the cation dye – 1.51 nm) and its relatively low molecular weight (539 g/mol) it shows a tendency to form bonds and interact with the surface of the adsorbent. Furthermore, it is not affected by steric effects, due to the lack of a branched structure of the molecule.



ACID GREEN 16
C.I. 44025
CAS 12768-78-4
C27-H27-N2-O6-S2
M 539 g/mol
λ=426 nm
pH 5.67
d_d 1.51 nm

Fig. 1. Characteristic of dye AG–16
Rys. 1. Charakterystyka barwnika AG–16

2.2. Sorbents and their physical and chemical properties

Sorbents applied in these studies were lignite co-occurring rocks from "Belchatow" field mine:
- smectite clay (BC) neogen age,
- low-moor peat (BP) holocen age.

In order to enhance the sorption capacity of smectite clay it was subjected to thermal activation at 250°C for 8 h (BC 250), which led to the removal of water from the structure of the smectite as a result of the dehydration process.

The chemical composition of the studied sorbents and their physicochemical properties, i.e. porosity (n), an average pore diameter (d) and their distribution, total (SSA H_2O) and external (SSA N_2) surface area, pH, and the point of zero charge (pH_{PZC}), defined by pH at which the charge of the particle is zero, as well as the cation exchange capacity (CEC) are all marked by methods described in other publications [22,35] and are shown in Tables 1–3.

Table 1. Chemical composition of natural and temperature activation smectite clay and low–moor peat, (%)
Tabela 1. Skład chemiczny termicznie iłu smektytowego – naturalnego i aktywowanego termicznie oraz torfu, (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
BC	55.81	15.25	6.45	2.82	1.74	0.042	0.57
BC 250°C	56.65	16.57	7.65	3.23	2.32	1.11	1.32
BP	8.26	2.32	2.31	4.57	0.33	0.067	0.213

Table 2. Physicochemical properties of natural and temperature activation smectite clays and low–moor peat
Tabela 2. Właściwości fizykochemiczne iłu smektytowego – naturalnego i aktywowanego termicznie oraz torfu

Samples	Porosity, n	Average pore diameter, d (μm)	Surface area (m^2/g)		pH	pH_{PZC}	CEC ($cmol_+$/kg)
			SSA (H_2O)	SSA (N_2)			
BC	0.0682	0.0186	141.8	41.38	7.85	7.40	82.39
BC 250°C	0.1113	0.0322	150.2	70.94	7.83	7.20	80.40
BP	0.5211	2.1503	218.9	11.38	5.62	5.77	125.0

The main clay building mineral was Ca-smectite and apart from this the presence of quartz, calcite and kaolinite was also indicated. Its chemical composition reflected the mineral one. The high content of CaO was an effect of the occurrence of Ca-smectite, described by Kaczynski and Grabowska-Olszewska as Ca-beidellite [19]. Iron was bound in the structure of the smectite, substituting clay in the octahedral layer, or silicon in the tetrahedral layer and approx. 0.091% of it was present in a form of free anamorphic oxides. The low Na_2O content was a result of the lack of feldspars in the examined clay [22].

Thermal activation of clay at 250°C and smectite dehydration did not cause significant changes in its chemical composition [35].

Table 3. Distribution of pores in studied samples
Tabela 3. Rozkład porów w badanych próbkach

Samples	Distribution of pores(%)		
	Macropores d > 30 μm	Mesopores 30 μm > d > 0,2 μm	Micropores d < 0,2 μm
BC	11.45	12.43	76.12
BC 250°C	12.11	15.23	72.66
BP	35.65	62.37	1.98

Low-moor peat was characterized by a high decomposition degree (70%) and amorphous structure. Ash content was 20.88%. The dominant mineral constituent in a peat sample was SiO_2 (8.26%), coming mainly from the sand deposited by water and wind. CaO content amounted 4.57%, it came from peat-forming plant incineration and was a result of the presence of calcite and gypsum minerals in the samples. MgO content was approximately one order lower (0.33%), similarly to K_2O content (0.213%). Iron occurred mainly in the form of amorphous oxides (1.39%). Main functional groups of humic acids contained in the peat are carboxyl groups (–COOH) and hydroxyl phenols (–OH) respectively in the amount of 90.0 $cmol_+$/kg and 115.3 $cmol_+$/kg [22].

The examined smectite clay was characterized by a high total surface area (141.83 m^2/g), while the external surface area was 41.38 m^2/g (Tab. 2). The porosity was 0.0682 and it was dominated by micropores of a diameter <2 μm (Tab. 3). Cation exchange capacity (CEC) was 82.39 $cmol_+$/kg; exchangeable cations were dominated by Ca^{2+} (72.5 $cmol_+$/kg) and Mg^{2+} (8.56 $cmol_+$/kg).

As a result of clay thermal activated, an approximately 60% increase in porosity to the value of 0.1113, an approximately 70% increase in size of the external surface to 70.94 m^2/g and a slight increase in total surface area occurred. Thermal activated did not affect the pore distribution in the clay (Table 3).

On the other hand, the studied peat was characterized by a high total surface area (218.98 m^2/g) and a high porosity level of 0.5211, dominated by mesopores and macropores (Table 3). Cation exchange capacity was 125 $cmol_+$/kg; main exchangeable ions were Ca^{2+} (95.18 $cmol_+$/kg), H^+ (21.8 $cmol_+$/kg) and Mg^{2+} (7.14 $cmol_+$/kg).

The pH of clay samples in water was weakly alkaline (pH 7.85 and 7.83), while of peat – acidic (pH 5.62).

3. Methods

3.1. Determination of sorbents' sorption capacity

Sorption capacity of the studied sorbents for dye AG–16 as well as the percentage removal of dye in the aqueous solutions was determined in static contact mode of a solid and a solution phases using the "batch" method. The basic dye solution was prepared through dissolution of 1000 mg of dye powder in 1 dm^3 of distilled water; then the pH was measured. Next, through appropriate dilutions, the basic solution was turned into working solutions of the dye, which were used in laboratory studies; their concentrations were 1, 10, 25, 50, 100, 150, 250, 500, 750 mg/dm^3.

Tests were carried out with a ratio solid phase:solution 1:20 (1 g of sorbent + 20 ml of solution of dye AG–16, having the appropriate concentration in the concentration range 1–1000 mg/dm^3) during 24 hours contact. Next the liquid phase was separated from the solid one by centrifugation at 4000 rpm for 20 minutes. Then, using the UV-VIS spectroscopy (Varian Cary 50 Scan UV-VIS) both initial (C_0) and equilibrium (C_{eq}) dye AG-16 concentrations in a solution were indicated. The wavelength at which the absorbance of the dye was measured was 426 nm. Tests were carried out at room temperature of $25 \pm 2^{o}C$.

In all the equilibrium solutions values of pH was measured and also, using flame photometry (photometer BWB-XP), the concentration of Ca^{2+} ions for dye concentrations C_0 50 and 500 mg/dm^3 was indicated and converted to load (mg/g).

An adsorbed amount of dye (q) by the sorbents was calculated from the formula:

$$q = \left(C_0 - C_{eq}\right)\frac{V}{m} \quad (mg/g) \tag{1}$$

and a percentage dye removal (R) from the formula:

$$R = \frac{C_0 - C_{eq}}{C_0} \cdot 100\% \tag{2}$$

where:

q – dye adsorbed per unit mass solid (mg/g),

R – a percentage dye removal (%),

C_0 – initial concentration of a dye in a solution (mg/dm^3),

C_{eq} – dye concentration in an equilibrium solution (mg/dm^3),
m – a sorbent mass (g),
V – a solution volume (dm^3).

3.2. The equations of adsorption isotherms.

In order to estimate the theoretical maximum sorption capacity of the sorbent and in order to determine the mechanism of the binding of the dye three 2-parameter isotherm equations were used: Freundlich, Langmuir and Dubinin-Radushkevich [11,20,25]. Constants in the equations were estimated by linear regression. Table 4 shows the formulas used in equations as well as their linear forms.

Table 4. Sorption isotherms and their linear forms
Tabela 4. Równania izoterm sorpcji i ich formy liniowe

Isotherm	Equation	Linear form	Plot	No Eq.
Freundlich	$q = K_F \cdot C_{eq}^{1/n}$	$\log q = \frac{1}{n} \log C_{eq} + \log K_F$	log q *vs.* log C_{eq}	3
Langmuir-1	$q = \frac{q_L K_L C_{eq}}{1 + K_L C_{eq}}$	$\frac{C_{eq}}{q} = \frac{C_{eq}}{q_L} + \frac{1}{K_L q_L}$	C_{eq}/q *vs.* C_{eq}	4.1
Langmuir-2		$\frac{1}{q} = (\frac{1}{K_L q_L}) \frac{1}{C_{eq}} + \frac{1}{q_L}$	1/q *vs.* 1/C_{eq}	4.2
Langmuir-3		$q = q_L - (\frac{1}{K_L}) \frac{q}{C_{eq}}$	q *vs.* 1/C_{eq}	4.3
Langmuir-4		$\frac{q}{C_{eq}} = K_L q_L - K_L q$	q/C_{eq} *vs.* q	4.4
Dubinin-Radushkevich	$q = q_D \cdot \exp(-\beta\varepsilon^2)$	$\ln q = \ln q_D - \beta\varepsilon^2$	ln q vs. ε^2	5

where: K_F – Freundlich isotherm constant (dm^3/g) and it is an approximate indicator of adsorption capacity, 1/n – a function of the strength of adsorption in the adsorption process, q_L – maximum monolayer coverage capacity (mg/g), K_L – Langmuir isotherm constant related to the affinity of binding sited (dm^3/mg), q_D – the sorption capacity of studied materials (mol/g), β – the constant (mol^2/J^2), ε – the Polanyi potential (J/mol) which is equal to $\varepsilon = RT\ln(1+\frac{1}{C_{eq}})$, R – the gas constant (8.314 J/molK), T – absolute temperature (K).

Furthermore, considering the isotherms course, they were classified to an appropriate type using the classification of Brauner and Giles [2,12]. According to Brauner [2] type I isotherm is characterized by monolayer filling of an adsorbent surface and describes a chemical adsorption and, rarely, a physical one; type II describes a physical adsorption with a multilayer filling of an adsorbent surface, the type III occurs when a heat of adsorption is equal or less than the heat of condensation of a pure component. This describes the case when the interaction of adsorbate and adsorbent particles is much smaller than the intermolecular interactions of adsorbate molecules. Types IV and V correspond to curves II and III and differ from them in the fact that at a certain section they run parallel to the OX axis, because in the adsorbent pores, due to the pore diameter, only a limited number of adsorption layers is formed. Giles [12], on the other hand, distinguished four main groups of adsorption isotherms: S, L, H and C, differing in course in low concentrations, which is connected to the competitive nature of the interaction of both solute and solvent with the surface of an adsorbent. Type S isotherm shows that in low concentrations of an adsorbate, a surface has a low affinity to it, which increases with an increase of its concentration in a solution. To this type belong isotherms, which strongly adsorb a solvent. For the L type (Langmuir) characteristic is a decreasing slope of an isotherm along with increasing concentrations of an adsorbate in a solution. In low concentrations of an adsorbate in a basic solution it indicates a high affinity of an adsorbate and adsorbent sorption centers, which decreases along with an increase in solution concentration. To the H-type belong isotherms for systems with a strong interaction between an adsorbate and an adsorbent. Type C is characteristic for isotherms of linear progress, which indicates a proportional distribution of a substance between a solid phase and a solution [31].

3.3. Kinetics of sorption process

The rate of the sorption process is controlled by a mass transfer in a solution, adsorbate diffusion through a liquid layer surrounding a particle, a process of adsorption equilibrium and diffusion within pores. Intraparticle diffusion is a process significantly affecting the overall rate of an adsorption [28].

Kinetics studies were carried out at an initial dye concentration in the solution i.e. 250 mg/dm^3. Measurements of the dye concentration in the solution were made after 2.5, 5, 15, 30, 60, 120, 300, 720, 1080 and 1440 minutes.

To interpret the results and to determine the relationship between an adsorbed amount of dye and reaction time, as well as to determine the kinetic constants, i.e. the amount of adsorbed dye per q_t and the constant adsorption rate k, the linear forms of kinetic equation of pseudo-first and pseudo-second order were used [26] (Table 5).

Table 5. Kinetic equations of sorption process
Tabela 5. Równań kinetyczne opisujące proces sorpcji

Equation	Formula	Linear form	No eq.
Pseudo-first order sorption	$\frac{dq_t}{dt}=k_1(q_{e1}-q_t)$	$\ln(q_{e1}-q_t)=\ln(q_{e1})-k_1 t$	7
Pseudo-second order sorption	$\frac{dq_t}{dt}=k_2(q_{e2}-q_t)^2$	$\frac{t}{q}=\frac{1}{k_2\cdot q_e^2}+\frac{t}{q_e}$	8

where: k_1 – the rate constant of the pseudo-first-order sorption (min^{-1}), q_t – the amount of sorption at time (mg/g), q_e – the amount of sorption at equilibrium (mg/g), k_2 – rate constant of pseudo-second-order sorption (g/mg/min).

On the other hand, to determine the role of diffusion within the particle during the sorption process the Boyle formula was used:

$$q=K\cdot t^{1/2} \tag{6}$$

where:
K – intraparticle diffusion rate constant (mg/kg·min).

4. Study results and discussion

4.1. Sorption of AG–16 dye by natural and thermally modified clays and peat

Experimental sorption isotherms of AG–16 dye on natural and temperature activated clays and peat were shown in the Figure 2, the percentage dye removal – in the Figure 3, while the pH in the equilibrium solutions – in the Figure 4.

AG–16 dye was bound to the minerals building smectite clay in an amount from 0.016 to 12.070 mg/g, depending on the initial concentration varying in the range 1–1000 mg/dm^3 (Fig. 2). This indicates that the percentage dye removal from the solution was respectively between 88.89 to 61.21% (Fig. 3). It was found that the percentage removal decreased along with increasing the initial concentration of the dye [17].

Sorption proceeded with minor changes of the pH in the range between 8.14–8.23 (Fig. 4). Despite the acidic condition of the dye solution (pH 5.67), after sorption in the equilibrium solutions their pH was similar to the pH of the clay, which proves the good buffer capacity of clay.

As a result of the thermal activation, there occurred an increase in the sorption capacity of the clay in all concentrations to a value within the range of 0.017 to 13.10 mg/g. It means a maximum increase in the sorption capacity of 8%. The percentage dye removal was 90–66.43% (Fig. 3). The dye sorption on the grains of the natural and activated clay proceeded at similar pH (Fig. 4), because the thermal activation did not affect the chemical properties of the clay, including its buffer property.

According to Giles classification, the experimental sorption isotherm of AG–16 dye on the natural clay belong to the S type, which means that in the low initial concentration of 250 mg/dm^3 impact of dye molecules on the surface of the sorbent was much weaker than the interaction of water molecules with the surface. The affinity of the dye molecules and the surface increased along with the increase in concentration of the solution. Thermal activation of the clay did not cause an alteration of the type of isotherm.

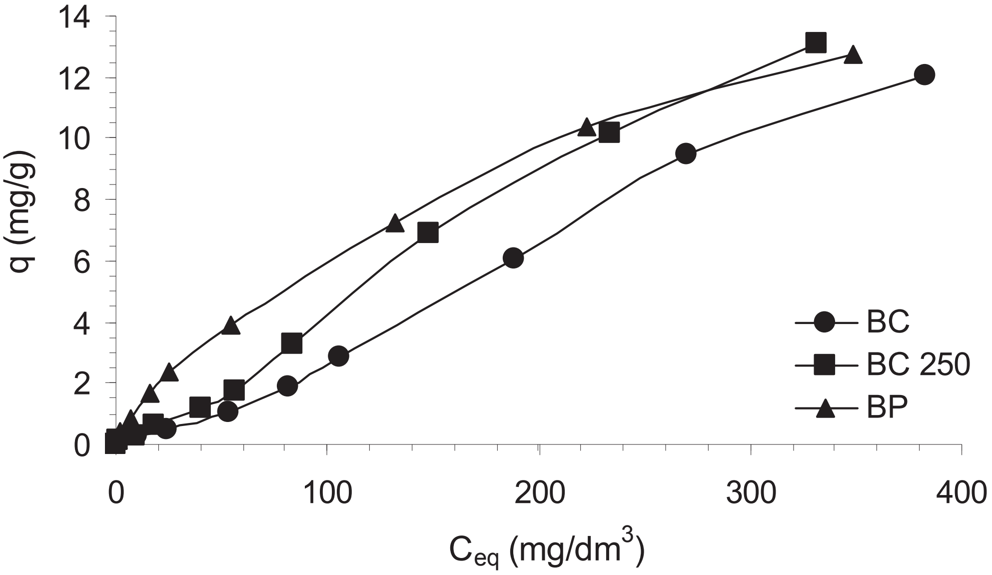


Fig. 2. Experimental sorption isotherms of dye AG–16 onto natural and temperature activation clays and peat
Rys. 2. Doświadczalne izotermy sorpcji barwnika AG–16 przez ił naturalny i aktywowany termicznie oraz torf

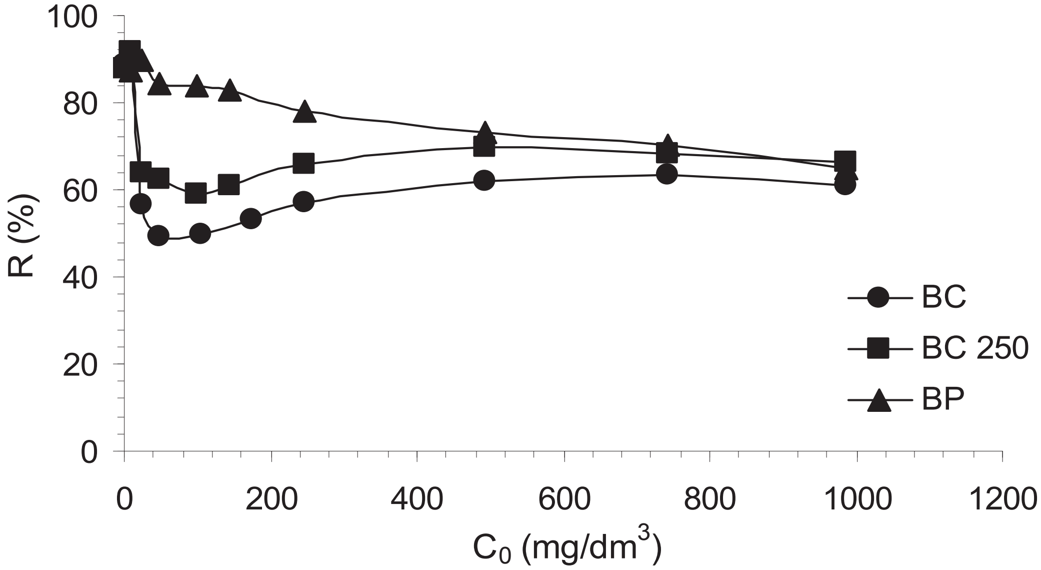


Fig. 3. Percentage removal of AG–16 dye from solutions
Rys. 3. Stopień usunięcia AG–16 z roztworów wodnych

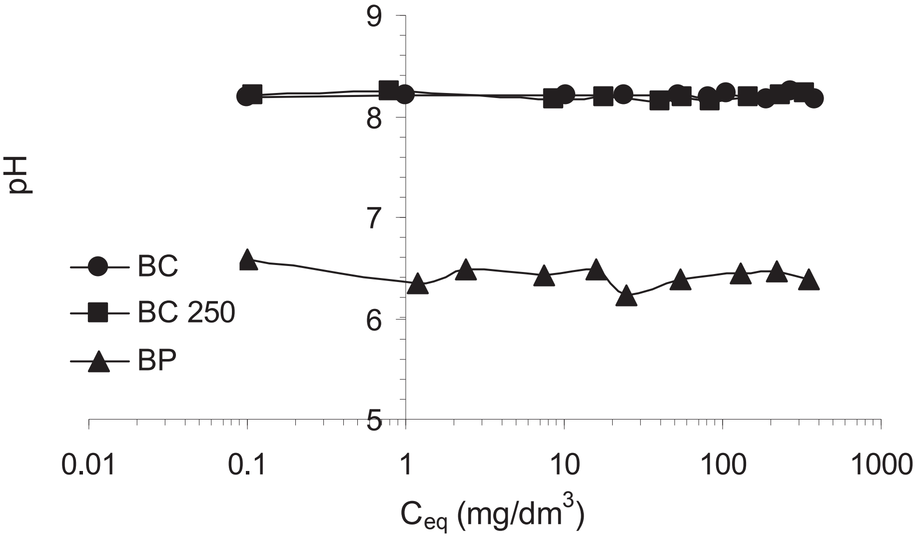


Fig. 4. Values of pH in equilibrium solution after sorption
Rys. 4. pH w roztworach równowagowych po sorpcji

According to Brauner classification, dye sorption isotherm of AG–16 belongs to a V-type. It depicts, on the one hand, stronger interactions between the dye molecules themselves than between them and the surface of the sorbent. On the other hand, it is a result of a domination of micropores in the examined clay, limiting formation of multiple layers. Despite the increase in total porosity at the time of activation of clays, neither the percentage share of micropores in the total porosity nor the isotherm type changed.

In contrast to the peat the AG–16 dye was bound to the amount of 0.018 mg/g at the initial concentration of 1 mg/dm^3 to 12.752 mg/g at the concentration of 1000 mg/dm^3. The percentage removal of dye from the solution varied between 90 and 64.67%; it decreased along with an increasing concentration of the dye in a solution.

Sorption on the peat also proceeded with minor changes of pH and with higher values than the sorbent pH (between 6.23 and 6.59).

Despite the similar maximum experimental sorption capacity of the peat in comparison to the activated clay, the course of the sorption of the AG–16 dye onto these materials varied significantly, especially at low concentrations.

Considering the shape of the experimental sorption isotherm of the AG–16 dye on the studied peat, it was found that according to the

Giles classification it belonged to L type, which indicates that it is much stronger than the impact of the dye molecules on the surface than the one of the water in all concentrations. According to the Brauner classification the isotherm belongs to the I type, characteristic for the monolayer sorption.

Thus, these results show that the clay, which is of an organic nature, having higher surface area and porosity, is an effective sorbent for the removal of cationic dye in the whole initial concentration range. Another very important parameter, except porosity, determining the effectiveness of the sorbent is a high contribution of macro and mesopores in pore distribution.

Moreover the surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent for dye ions. As a result, peat was more effective in the adsorption of basic dyes than anionic dyes [32].

Giving the pH in the equilibrium solutions after sorption of the AG–16 dye on the examined sorbents, it was found that in all cases the pH was higher than the pH at which the surface of the colloidal particles of the sorbent is of zero charge (pH_{PZC}), i.e. $pH > pH_{PZC}$.

The surface of clays and peat becomes negatively charged according the mechanisms:

$$-SiOH + -OH^- \rightarrow -SiO^- + H_2O \text{ or}$$
$$R-COOH \rightarrow R-COO^- + H^+\text{, respectively.}$$

It indicates that in all cases the sorption took place along with the negatively charged surface of the sorbent. It can therefore be concluded that one of the mechanisms binding the AG-16 dye of cationic nature by the natural and modified smectite clay and the peat are electrostatic interactions.

$$-SiO^- + dye^+ \rightarrow -Si-O^-dye^+ \text{ or}$$
$$R-COO^- + dye^+ \rightarrow R-COO^-dye^+.$$

Fill et al [10] indicated that at the sorption of cationic dyes the pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to the final pH. An increasing solution pH increases the number of hydroxyl groups thus, it increases the number of negatively charged sites and enlarges the attraction between cationic dye and adsorbent surface.

The results show that except the pH of the dye solutions, an important parameter for determining the pH of the equilibrium solution is the buffer capacity of the sorbent. In this study, despite the acidic dye AG–16 (pH 5.67), the pH of the equilibrium solutions clay-dye was > 8 (Figure 4) due to the high buffering capacity of the clay.

Another mechanism of dye binding on the tested sorbents could be ion exchange. Determined in equilibrium solutions ion load Ca^{2+} for the clay-dye system were suitable for the concentration of the dye in solution C_0 50 and 500 mg/dm^3 18 and 112 mg/kg which was 0.12 and 0.77% of the exchangeable calcium and it indicates that in the process of sorption of the AG–16 dye on the grains of clay, this type of binding was unimportant.

But for the peat-dye system calcium load indicated in the equilibrium solution were respectively 1550 and 1684 mg/kg which was 6.18 and 8.40% of the exchangeable calcium. It indicates that the dye could be bound by ion exchange with exchangeable Ca^{2+} cations substituting H^+ ions in the fulvic and humic acids of the peat. Moreover, the presence of sulfonic groups in the dye molecule suggests its potential binding with the peat via hydrogen bonding, where in the proton donors were H^+ ions derived from the iron hydroxide FeO (OH), which pH_{PZC} is set at pH 8.5–8.8 [4].

4.2. Freundlich, Langmuir and Dubinin–Radushkevich isotherm equations

Estimated sorption parameters and corresponding values of the determination R^2 coefficient of the linear forms of Freundlich, Langmuir and Dubinin-Radushkevich equations on natural and modified clay and peat are shown in table 6.

Based on the estimated values of sorption (Tab. 6) and the value of determination coefficient indicating that the theoretical curve fit the experimental data, it was found that the process of sorption of the AG–16 dye onto natural and modified clay may be, with high probability, described by the Freundlich equation. The values of R^2 coefficient were > 0.92. An even better fitting of the Freundlich isotherm was obtained for the sorption of the AG–16 dye on peat where R^2 was 0.9892. The estimated values of 1/n were less than 1, which indicates a favorable sorption process.

Table 6. Isotherm parameters for the sorption of AG–16 dye onto studied sorbents
Tabela 6. Parametry w równaniach izoterm opisujących sorpcję AG–16 na badanych sorbentach

Isotherm	Sorption parameters	BC	BC 250	BP
Freundlich	K_F (dm^3/g)	0.08115	0.09519	0.1475
	1/n [-]	0.7518	0.7943	0.8090
	R^2 [-]	0.9299	0.9567	0.9892
Langmuir-1	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	19.23	66.66	16.92
	K_L (dm^3/mg)	0.000015	0.000688	0.00726
	R^2 [-]	0.0000115	0.02818	0.9418
Langmuir-2	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	1.272	3.086	12.99
	K_L (dm^3/mg)	0.1268	0.04696	0.0271
	R^2 [-]	0.9972	0.9953	0.9998
Langmuir-3	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	45.67	53.89	12.18
	K_L (dm^3/mg)	0.0437	0.0400	0.0121
	R^2 [-]	0.0966	0.1133	0.7557
Langmuir-4	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	16.07	18.40	14.77
	K_L (dm^3/mg)	0.0042	0.0045	0.0092
	R^2 [-]	0.0966	0.1133	0.7557
Dubinin-Radushkevich	β(mol^2·kJ^{-2})	0.0102	0.0097	0.0059
	q_D (mmol/g)	0.4779	0.5590	0.224
	R^2 [-]	0.9648	0.9817	0,9978
	E (kJ/mol)	7.14	7.18	9.13

In the case of the Langmuir isotherm, it was observed that coefficient of determination values for all the four linearized form of Langmuir isotherm equations were different (Tab. 6). Similar results were obtained by K. Vasanth Kumar and S. Sivanesan [20] in studies of sorption Bismarck brown onto rice husk particles.

From the Table 6, based on R^2 values, type 2 Langmuir isotherms showed the best fit for AG–16 onto smectite clays and peat. Whereas type 1 of Langmuir isotherm shows a poor fit towards the experimental data for clays and good – for peat. Types 3 and 4 forms have the same R^2 values and show a poor fit towards the experimental data of the dye onto all studied sorbents.

This indicates that the sorption of the AG–16 dye on natural and modified clay samples can only be thermally described by the type 2 of the Langmuir equation (eq. 4.2). R^2 coefficient at 0.9972 indicates a very good fit of the theoretical curve to the experimental data. However, the estimated value of the q_L constant indicates the maximum sorption capacity approximately one order lower than the maximum experimental sorption. It suggests that it may not be appropriate to use this model in representing the equilibrium uptake of AG–16 onto smectite clay particles.

In contrast, the value of determination R^2 coefficient indicates a very good sorption fitting of the AG–16 dye on peat molecules through type 1 and 2 of Langmuir equation. The estimated at linear 4.1 and 4.2 forms of the Langmuir equation, q_L values were close to the maximum value of experimental sorption (Tab. 6).

Moreover the value of determination coefficient (R^2=0.9648–0.9978) indicates that there is a strong positive relationship for the data and that sorption data of the AG–16 onto clays and peat follows the Dubinin–Radushkevich isotherm.

On the basis of the estimated value of the parameter β free energy (E) per molecule of the adsorbate was determined from the formula:

$$E = \frac{1}{(2\beta)^{1/2}} \tag{9}$$

The E value distinguishes physical adsorption (E<8 J/mol) from ion exchange (8<E<16 J/mol).

The estimated values of the E parameter indicated that the sorption of the examined dye on the natural and modified clay is of a physical nature (E<8 kJ/mol) and the sorption on the peat – of the ion exchange nature (E>8 kJ/mol). These results confirmed the earlier theory of the ion exchange ability to participate in the binding of the dye on peat.

4.3. Sorption kinetics

The curves depicting the amount of dye adsorbed by clay and peat particles during time are shown in the Figure 5. While analyzing the amount of the AG–16 dye sorbed onto the natural clay and after thermal activation in time it was found that after 5 minutes of contacting the solid phase: solution amount of dye adsorbed was approximately 50% of the amount adsorbed in the equilibrium conditions, and on peat – approximately 40%. After 1 hour the clay sorbed approx. 78%, and the peat approx. 70%, after 5 hours the clay – 90%, the peat 75%.

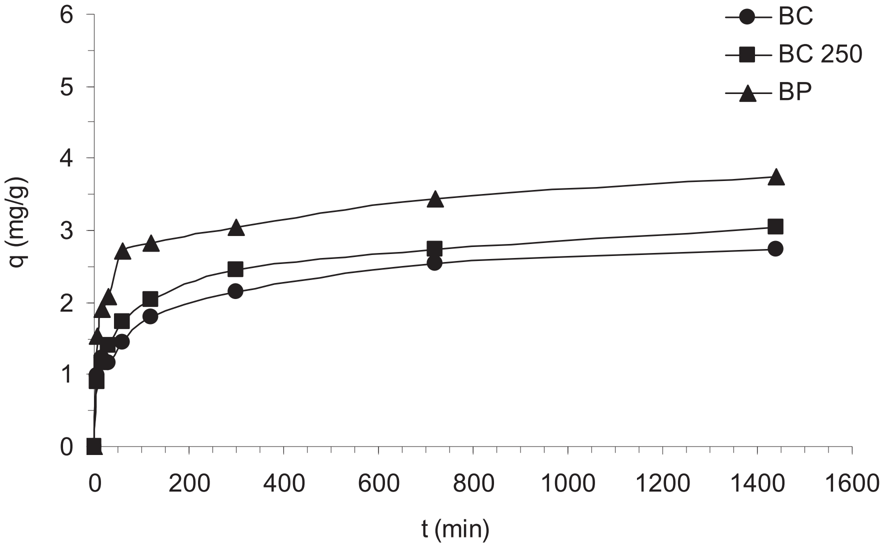


Fig. 5. Amount of dye adsorbed by clay and peat during time
Rys. 5. Adsorpcja barwnika przez iły i torf w czasie

Parameters estimated from the pseudo-first and pseudo-second order equations are shown in Table 7. On the basis of kinetic parameters and coefficients of determination R^2, it was found that the adsorption process occurred according to the pseudo-second order equation, as proved by the high values of the determination coefficient $R^2>0.99$. In addition, the estimated values of the q_{e2} parameter were at the level of the values determined experimentally. Research conducted by Ho and McKay [16] also shows that the process of sorption of the cationic dyes is better described by the pseudo-second order equation.

It was found that the rate constant k_2 of sorption of the AG–16 dye on the activated clay was higher than on the natural one, which indicates that the thermal activated affected not only the increase in the sorption capacity of the clay, but also the rate of the sorption process. This is because increasing the external surface area of the clay particle exposes more active sites to AG–16 ions. Erdem et al [9] found that with the decrease of particle size of diatomite adsorbent from 300 to 60 μm external surface area and the adsorption rate of dye increased.

Table 7. Kinetics parameter for sorption process of AG–16 dye onto studied sorbents
Tabela 7. Wartości parametrów w równaniach kinetycznych opisujących sorpcję barwnika AG–16

Sorbent		BC	BC 250	BP
Sorption capacity	q (mg/g)	2.826	3.266	3.866
Pseudo-first order sorption	q_{e1} (mg/g)	1.751	1.893	1.845
	k_1 (1/min)	0.00315	0.00283	0.00209
	R^2 [-]	0.9350	0.9026	0.6512
Pseudo-second order sorption	q_{e2} (mg/g)	2.778	3.058	3.704
	k_2 (g/mg·min)	0.008608	0.009082	0.010049
	R^2 [-]	0.9961	0.9962	0.9940
Intraparticle diffusion	K (mg/g·min)	0.0773	0.1025	0.0918
	R^2 [-]	0.9719	0.9571	0.7846

Using Boyle model, a significant role of the of intraparticle diffusion in the process of the AG–16 dye sorption on clay, and much less in the dye on peat sorption, was indicated.

The kinetics of the sorption process of AG–16 dye onto peat was found to follow a pseudo-second order rate and equilibrium data agrees well with the Langmuir isotherm. The determination coefficient R^2 for the pseudo–second order kinetic model are greater than the determination coefficient R^2 for the intraparticle diffusion coefficients for the sorption of AG–16 onto peat. This strongly suggests an activated sorption mechanism which could occur because of the chemical character of peat [15].

5. Summary

The present study showed that low–moor peat was an effective adsorbent for the removal of AG-16 from water and wastewater in a wide initial concentration and smectite clay – at a high initial concentration. As a result of thermal activation of the clay, the sorption capacity for the dye increased. The process of sorption proceeded with the negatively charged surface of the sorbents and indicated that one of the mechanisms of binding the cationic AG–16 dye were electrostatic interactions. In addition, the dye was also bound by peat as a result of ion exchange with exchangeable Ca^{2+} ions. The results fitted the equilibrium data of Freundlich, Langmuir and Dubinin–Radushkevich isotherms for smectite clay – the dye system has been best described by the Freudlich and Dubinin–Radushkevich isotherm model and the peat–dye system – by all of the isotherm models. The estimation of the E parameter from the Dubinin-Radushkevich equation indicated that the sorption test of the dye on the natural and modified clay is of a physical nature (E<8 kJ/mol) and the sorption on peat – of the nature of an ion exchange (E>8 kJ/mol). The sorption process of the AG–16 dye sorbents proceeded according to the equation of pseudo-second order and an important role of the intraparticle diffusion in the dye sorption on natural and modified clay molecules was observed.

Acknowledgements

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References

1. **Ansone l., Eglite L., Klavins M.:** *Removal of Arsenic compounds with peat, peat-based and synthetic sorbents.* Ecology and Chemical Engineering Science. 4(19), 513–531 (2012).
2. **Brauner S., Deming N.S., Deming W.E., Teller E.:** *On the theory of van der Waals adsorption of gases*. Journal of the American Chemical Society. 62, 1723–1732 (1940).
3. **Choma J., Jarowiec M., Burakiewicz-Mortka W., Gwizdalski M.:** *Adsorpcja związków organicznych z roztworów wodnych na węglach aktywnych*. Ochrona Środowiska. 1(56), 11–17 (1995).
4. **Cornell R.M., Schwertmann U.:** *The iron oxides. Structure, properties, reaction, occurrences and uses*. Wiley-VCH, Weinheim 2003.
5. **Crini G.:** *Non-conventional low-cost adsorbents for dye removal: A review*. Bioresource Technology. 97, 1061–1085 (2006).
6. **Czaplicka M., Chmielarz A.:** *Application of biosurfactants and non-ionic surfactants for removal of organic matter from metallurgical lead-bearing slime.* Journal of Hazardous Materiale. 2–3(163), 645–649 (2009).
7. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Badania nad usuwaniem barwnych związków organicznych ze ścieków z przemysłu włókienniczego*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1164–1176 (2013).

8. **Djordjevic D., Stojiljkovic D., Smelcerovic M.:** *Adsorption Kinetics of Reactive Dyes on Ash From Town Heating Plant.* Archives of Environmental Protection. 3(40), 123–135 (2014).
9. **Erdem E., Colgecen G., Donat R.**: *The removal of textile dyes by diatomite earth.* Journal of Colloid and Interface Science. 2(282), 314–319 (2005).
10. **Fil B. A., Özmetin C., Korkmaz M.:** *Cationic Dye (Methylene Blue) Removal from Aqueous Solution by Montmorillonite.* Bulletin of the Korean Chemical Society. 33, 3184–3190 (2012).
11. **Foo K.Y., Hameed B.H.:** *Insights into the modeling of adsorption isotherm systems.* Chemical Engineering Journal. 1(156), 2–10 (2010).
12. **Giles C.H., Smith D., Huitson A.:** *A general treatment and classification of the solute adsorption isotherm. I. Theoretical.* Journal of Colloids and Interface Science. 47, 755–765 (1974).
13. **Guibal, E., Roussy J.:** *Coagulation and Flocculation of Dye Containing Solutions Using a Biopolymer (Chitosan)*. Reactive and Functional Polymers. 67, 33–42 (2007).
14. **Gupta V.K., Suhas:** *Application of low-cost sorbents for dye removal – A review*. Journal of Environmental Management. 90, 2313–2342 (2009).
15. **Ho Y.S., McKay G.:** *Pseudo-second order model for sorption processes*. Process Biochemistry. 34, 451–465 (1999).
16. **Ho Y.S., McKay G.:** *Sorption of dye from aqueous solution by peat*. Chemical Engineering Journal. 2(70), 115–124 (1998).
17. **Hoda Roushdy Guendy:** *Treatment and Reuse of Wastewater in the Textile Industry by Means of Coagulation and Adsorption Techniques*. Journal of Applied Sciences Research. 6(8), 964–972 (2010).
18. **Jóźwiak T., Filipkowska U., Rodziewicz J., Mielcarek A., Owczarkowska D.:** *Zastosowanie kompostu jako taniego sorbentu do usuwania barwników z roztworów wodnych.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2398–2411 (2013).
19. **Kaczyński R., Grabowska-Olszewska B.:** *Soil mechanics of the potentially expansive clays in Poland*. Applied Clay Science. 11, 337–355 (1997).
20. **Kumar K.V., Sivanesan S.:** *Prediction of optimum sorption isotherm: Comparison of linear and non-linear method.* Journal of Hazardous Materials. 126, 198–201 (2005).
21. **Kyzioł J., Twardowska I., Schmitt-Kopplin Ph.:** *The role of humic substances in chromium sorption onto natural organic matter (peat).* Chemosphere. 63, 1974–1982 (2006).
22. **Kyzioł-Komosińska J., Barba F., Callejas P., Rosik-Dulewska C.:** *Beidellite and other natural low-cost sorbents to remove chromium and cadmium from water and wastewater*. Boletín de la Sociedad Española de Cerámica y Vidrio. 2(49), 121–128 (2010).

23. **Majer E.:** *Zastosowanie iłów beidelitowych z nadkładu w KWB Bełchatów S.A. jako materiału do budowy składowisk odpadów.* Górnictwo Odkrywkowe. 6(45), 56–61 (2003).
24. **Mo J.H., Lee Y.H., Kim J., Jeong J.Y.:** *Treatment of Dye Aqueous Solutions Using Nanofiltration Polyamide Composite Membrane for the Dye Wastewater Reuse*. Dyes and Pigments. 76, 429–434 (2008).
25. **Özcan A., Öncü E.M., Özcan A.S.:** *Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite*. Colloids and Surfaces A:Physicochemical and Engineering Aspects. 227, 90–97 (2006).
26. **Özcan A.S., Özcan A.:** *Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite.* Journal of Colloid And Interface Science. 1(276), 39–46 (2004).
27. **Pereira M.F.R., Soares S.F., Órfão J.J.M., Figueiredo J.L.:** *Adsorption of dyes on activated carbon: influence of surface chemical groups*. Carbon. 41, 811–821 (2003).
28. **Płaziński W., Rudziński W.:** *Kinetyka adsorpcji na granicy faz roztwór/ciało stałe. Znaczenie równań pseudo-first order oraz pseudo-second order*. Wiadomości Chemiczne. 29, 479–486 (2011).
29. **Qiao S., Hu Q., Haghseresht F., Hu X., Lu G.Q.:** *An investigation on the adsorption of acid dyes on bentonite based composite adsorbent*. Separation and Purification Technology. 67, 218–225 (2009).
30. **Sankar M., Sekaran G., Sadulla S., Ramasami T.:** *Removal of diazo and triphenylmethane dyes from aqueous solutions through an adsorption process*. Journal of Chemical Technology and Biotechnology. 74, 337–344 (1999).
31. **Sarbak Z.:** *Adsorpcja i adsorbenty. Teoria i zastosowanie.* Wydawnictwo Naukowe UAM, Poznań 2000.
32. **Sepúlveda L, Fernández K, Contreras E, Palma C.:** *Adsorption of dyes using peat: equilibrium and kinetic studies.* Environmental Technology. 9(25), 987–996 (2004).
33. **Shen D., Fan J., Zhou W., Gao B., Yue Q., Kang Q.:** *Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multi-solute systems.* Journal of Hazardous Materials. 172, 99–107 (2009).
34. **Stoch L.:** *Minerały ilaste*. PWN, Warszawa 1974.
35. **Tamayo A., Kyziol-Komosinska J., Sánchez MªJ., Callejas P., Rubio J., Barba MªF.:** *Characterization and properties of treated smectites*. Journal of the European Ceramic Society. 11(32), 2831–2841 (2012).

Sorpcja barwnika Acid Green 16 z roztworów wodnych na torfach niskich i iłach smektytowych towarzyszących złożom węgli brunatnych w polu Bełchatów

Abstrakt

Celem badań było wyznaczenie pojemności sorpcyjnej iłu smektytowego i torfu niskiego towarzyszących pokładom złóż węgli brunatnych w stosunku do barwnika Acid Green 16 (AG–16) oraz określenie mechanizmu jego wiązania.

Wyniki wskazały, że badany torf niski był skutecznym sorbentem barwnika AG-16 w całym zakresie stężeń początkowych (1–1000 mg/dm^3), natomiast ił smektytowy – jedynie z zakresie stężeń wysokich (> 250 mg/dm^3). W wyniku aktywacji termicznej iłu nastąpił wzrost jego pojemności sorpcyjnej w stosunku do badanego barwnika. Proces sorpcji barwnika przebiegał przy ujemnie naładowanej powierzchni sorbentów i wskazywał, że jednym z mechanizmów wiązania barwnika AG–16 były oddziaływania elektrostatyczne. Ponadto barwnik ten był wiązany przez torf również w wyniku wymiany jonowej z jonami Ca^{2+} występującymi w jego kompleksie sorpcyjnym. Stwierdzono, że sorpcję barwnika AG-16 na iłach najlepiej opisuje izoterma Freundlicha i Dubinina-Raduszkiewicza, a na torfie – wszystkie 3 izotermy. Sorpcja barwnika na iłach miała charakter fizyczny a na torfie była to chemisorpcja. Proces sorpcji przebiegał według równania pseudo-drugiego rzędu. Istotną rolę dyfuzji wewnątrz cząsteczkowej stwierdzono jedynie dla sorpcji barwnika na cząstkach iłu naturalnego i modyfikowanego.

Słowa kluczowe:
sorpcja, barwniki, iły smektytowe, torf, izotermy sorpcji

Keywords:
sorption, dyes, smectite clay, peat, sorption isotherms

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Long-term Study on Fibre Reinforced Fine Aggregate Concrete Beams Based on Waste Sand

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1. Introduction

Continuously enlarging waste sand dumps in northern Poland (Fig. 1) cause more and more interest of various communities (entrepreneurs, ecologists and scientists).

Fig. 1. Waste sand dump – northern Poland
Rys. 1. Hałda piasku odpadowego – północna część Polski

The solution that would please them all is to use these dumps for industrial production. For a few decades there has been carried out research on application of waste sand as a basic component of a concrete mix [15, 19]. Application of sand being a residue from aggregate hydroclasification is rather marginal and mainly involves production of industrial floors. [13]. There has also been conducted continual research on how to use waste sand for statically or/and dynamically loaded structure elements [4, 5, 21, 22]. Equally relevant, or maybe the most important, is study on using waste sand for long-term loaded elements. Such loads reflect real conditions in which the elements work in a structure. Also particularly important is long-term research on structure elements in which are used atypical components of a concrete mix. This is why in this article the author presents study on fine aggregate concrete beams containing steel fibres, which are long-term loaded in conditions of constant humidity and temperature.

2. Used Materials and Mix Proportions

Basic component of the fine aggregate concrete mix in the research programme was waste sand from aggregate mine located in Sępólno Wielkie (region of west Pomerania). This sand does not meet the standards of norms EN 206-1 [7] and EN 12620 [10] in relation to aggregate for plain concretes. Figure 2 presents grading curve of harnessed waste sand in comparison with grading curves obtained by other researches. Sand used in this study (Fig. 2) has shown to have the best granulometric properties. Fineness modulus and median grain was the best from presented curves and respectively amounted to: 98.4 % and 0.57 mm.

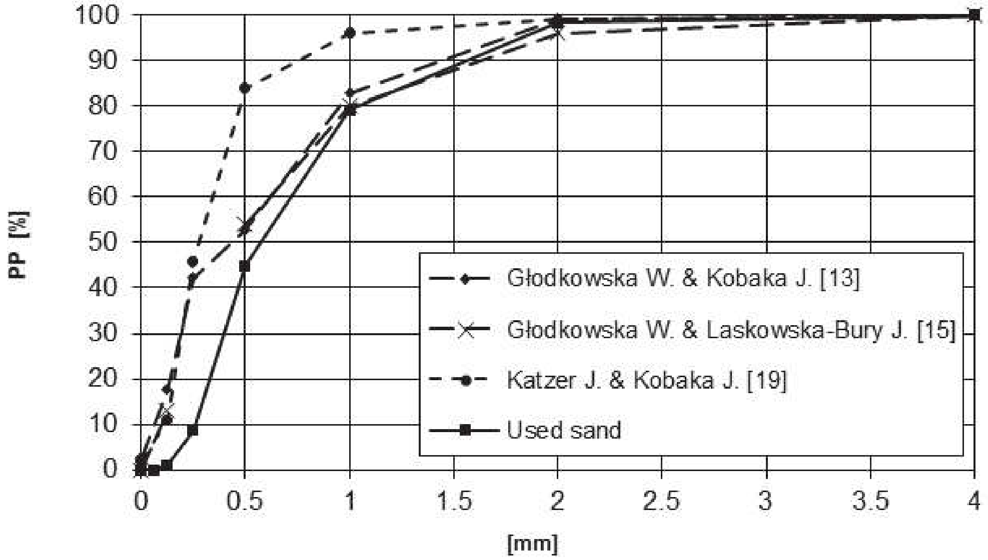

Fig. 2. Grading curve of harnessed waste sand
Rys. 2. Krzywa uziarnienia zastosowanego piasku odpadowego

Another component of the concrete mix was the Portland cement CEM II/B-V 32.5 R, which after 28 days reached 40.8 MPa strength and met the requirements of EN 197-1 [6]. According to EN 1008 [9] the author used drinking water. In order to obtain required consistence in compliance with ACI [1] the author also applied superplasticizer FM 34. Last components of the concrete mix were hooked steel fibres characterized by diameter 0.55 and 0.8 mm or length 30 and 50 mm (accordingly to EN 14889-1 [11]). The fibres were protected against corrosion and were produced using cutting method (analyzed in [2]). Properties of used fibres are presented in paper [18]. Final composition of fine aggregate concrete mix containing steel fibres is presented in Table 1.

Table 1. Mix proportions of one cubic meter
Tabela 1. Proporcje składników mieszanki na 1 m^3

Concrete / Series	Components					
	Sand [kg]	Cement [kg]	Water [dm^3]	FM 34 [dm^3]	Steel fibres [kg]	
					30/0.55	50/0.8
B9	1835	374	150	3,47	–	33
B10	1855	378	140	3,51	34	–

Additionally, in some specimens the author used ribbed reinforcement steel bars (ϕ 8 and 10 mm) made from steel 34GS and smooth reinforcing steel bars (ϕ 4.5 mm) made from steel St3SX-b.

3. Curing and Casting

The specimens were produced in series (in autumn- winter season in a room of approximately 25°C temperature) maintaining equal technological regime. There were two series of specimens produced (B9 and B10), which differ in terms of used steel fibres. Each series of specimens consists of a beam (150×200×3300 mm), a cylinder (150×300 mm) and 9 cubes (150×150×150 mm). In beam elements the author used longitudinal reinforcement (in tension zone: 3#10 mm; in compression zone 2#8 mm) and transverse reinforcement in the form of bars (diameter of 4.5 mm), placed every 13 cm (Fig. 3).

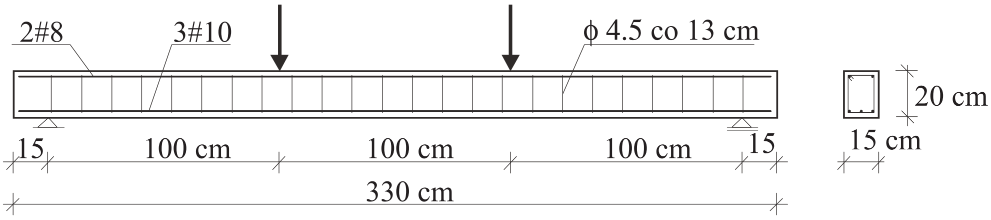

Fig. 3. Beam geometry and location of reinforced steel bars
Rys. 3. Geometria belek i rozmieszczenie prętów zbrojeniowych

For the first 24 hours (until the moment of demolding) and next six days the specimens ripen in the conditions of increased humidity, i.e. tightly covered with foil. After these seven days of growing, the specimens were transported to an air-conditioned room, where they were kept until the end of the study. The conditions in the room were as follows: temperature of 20 ± 2°C; humidity at 50 ± 3%. Humidity and temperature measurement was taken using EBI-2 register, programmed to record every 30 minutes.

4. Methodology and Programme of Research

The tests on small sized elements (cylinders and cubes) were conducted in accordance with valid norms and recommendations. Concrete compression strength, concrete tension strength during splitting and modulus of elasticity were tested after 28 days of curing. The shrinkage phenomenon was recorded from the moment of demolding cylinders until the end of studies. Creep analysis started after 28 days from the moment of making the specimens (cylinders) and lasted for over a year. In Fig. 4 there are presented small sized specimens from B9 series.

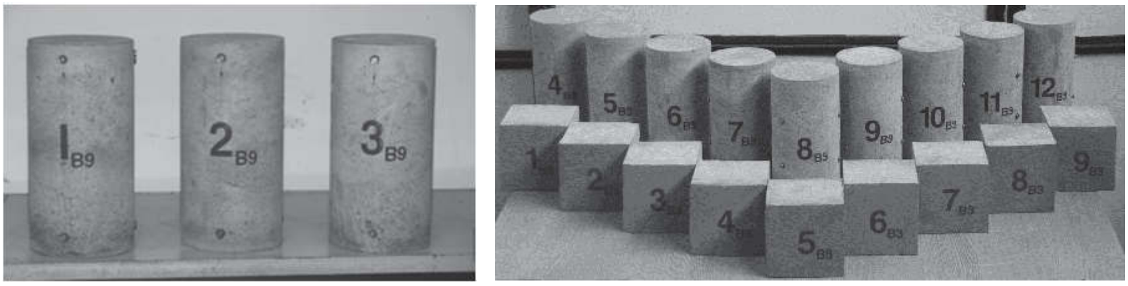

Fig. 4. Small-sized specimen elements of B9 series
Rys. 4. Drobnowymiarowe elementy próbne serii B9

The work-stand, where long-term tests on beam elements were conducted, consisted of steel channel sections along with lever system attached (Fig. 5). Static scheme for the analyzed elements is a single-span beam loaded with two concentrated forces imposed in one third of a span between the axes of supports. There were situated two supports on a stand: a roller support and a pinned support. The forces were imposed by a steel beam loaded with compound lever with disc weights. The weight of loads was chosen precisely so that during the study the bending moment for both beams would be on a level of 6 kN·m.

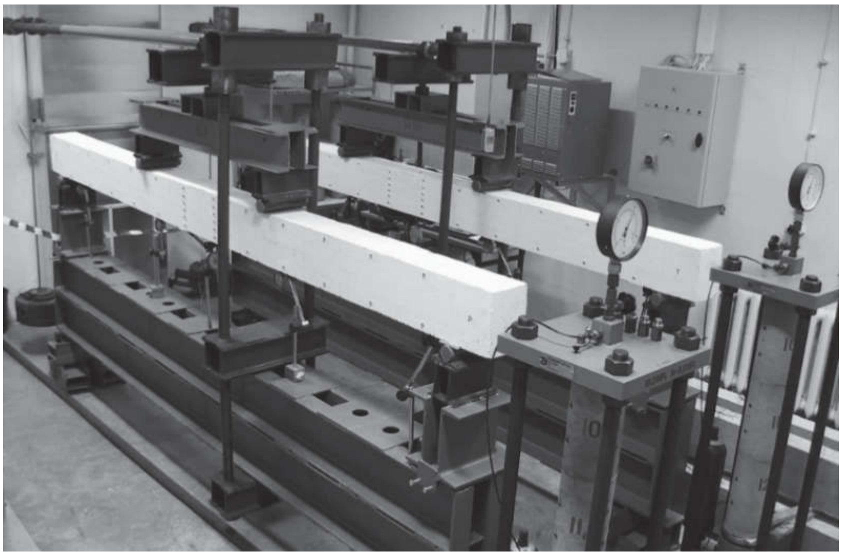

Fig. 5. The work-stand for long term research (beams and cylinders)
Rys. 5. Stanowiska do badań długotrwałych (belek i walców)

Measurement of beam vertical displacement (deflection) was conducted on its lower surface in 5 places (in the span center of beams, in the place of application of concentrated forces and at the distance of 100 mm from the axes of support) using dial gauges of a 500 and 100 mm range and of 0.01 mm accuracy (Fig. 5).

Crack widths measurement was done using a microscope of 0.02 mm accuracy with 36- fold enlargement.

Readings of long-term properties of researched elements were taken in the following days: 0 (day of loading) 3, 7, 14, 28, 56, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 365.

5. Results and Discussion

The results of strength properties of composites in question were determined on cylinders and cubes specimens after 28 and 365 days of curing, and are presented in table 2. Comparing both analyzed specimens series, there is a significant difference in strength, what is most likely caused by the size of used steel fibres and their special distribution in the elements [14, 21]. Moreover, in series B10 larger amount of shorter fibres was used, what certainly had an impact on the obtained values.

Table 2. Strength properties of analyzed composites with fibres
Tabela 2. Cechy wytrzymałościowe badanych fibrokompozytów

Concrete / Series	Certain material properties					
	$f_{cm,28}$ [MPa]	$f_{c,cube,28}$ [MPa]	$f_{ct,sp,28}$ [MPa]	$E_{cm,28}$ [GPa]	$f_{cm,365}$ [MPa]	$E_{cm,365}$ [GPa]
B9	31.0	39.5	3.6	29.3	38.0	30.1
B10	45.8	46.3	4.3	29.4	49.6	31.7

The results of the rheological strains determined on cylindrical samples are presented in fig. 6 and 7.

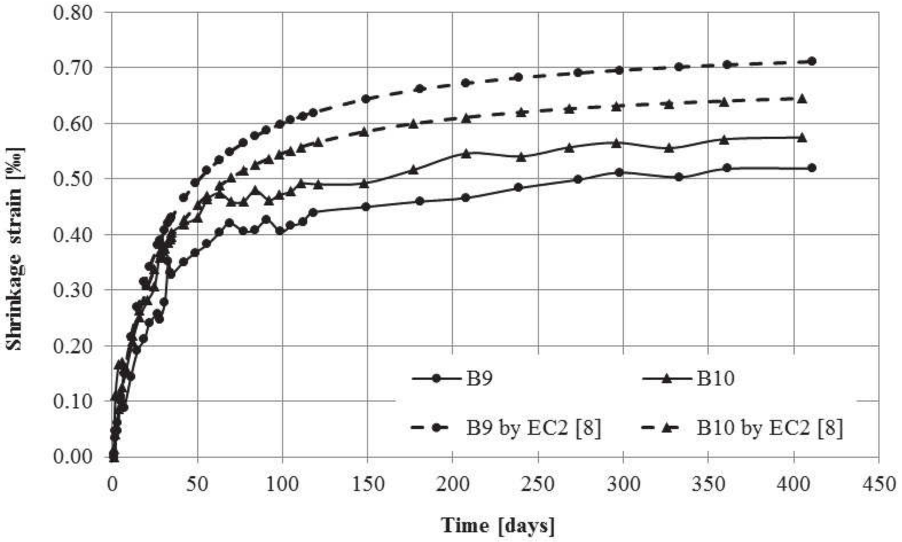

Fig. 6. Shrinkage strains measured and calculated in accordance with EC2 [8]
Rys. 6. Odkształcenia skurczowe pomierzone i obliczone wg EC2 [8]

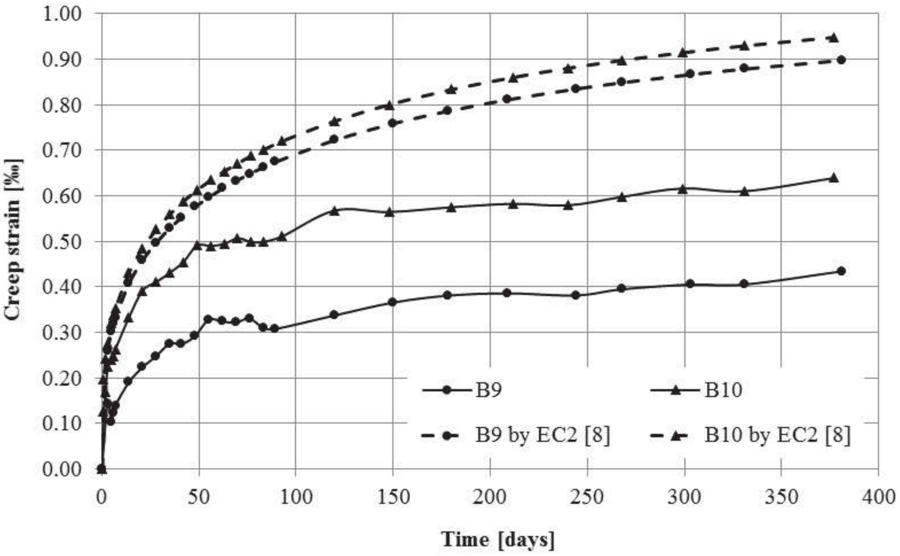

Fig. 7. Creep strains reduced by the value of shrinkage strain, calculated in accordance with EC2 [8].
Rys. 7. Odkształcenia pełzania, skorygowane (pomniejszone) o wartość odkształceń skurczowych oraz obliczone wg EC2 [8]

Additionally, in these graphs the author presents curves calculated according to EC2 [8], with regard to the strength qualities of analyzed composites with fibres. Both shrinkage and creep strains defined by EC2 [8] highly differ from values obtained from the tests. It confirms that adding steel fibres to the concrete mix reduces the level of shrinkage and creep strains [13, 23]. These differences are also caused by maladjustment of the normalization methodology to fine aggregate concrete containing steel fibres. The values of creep coefficient for both composites, which were obtained from the study, amount to 1.19 and 1.31 (respectively for B9 and B10 series). The average of these values is twice as low than calculated according to EC2 [8].

The analysis of serviceability limit state (i.e. deflection and cracking), induced by a long-term load, was conducted using beams measuring 150×200×3300 mm. In fig. 8 and 9 there is presented an increase in the value of beam deflection (B9 and B10) from day “0” to day 365. Comparing the results obtained from the study it is clear that differences between beam deflections are yet visible on the day of the load and last until the day 365 (B9 – 5,27 mm, B10 – 4,21 mm). The relation between deflections results obtained from the study and calculated according to EC2 [8] has shown large differences. The deflection rate calculated according to EC2 is higher approximately by 35%. This could be caused by the fact that calculation method applied accordingly to EC2 [8] is not adopted to the analyzed fine aggregate concrete beams containing steel fibres [3, 23].

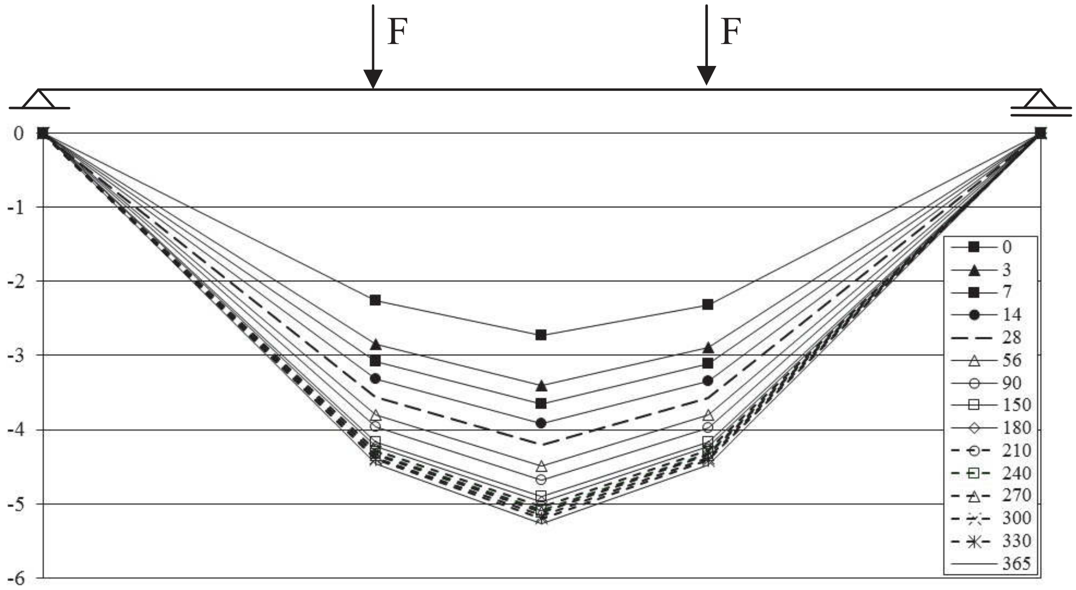

Fig. 8. Deflection of B9 beam [mm] during the time of load
Rys. 8. Ugięcie [mm] belki B9 w kolejnych dniach obciążenia

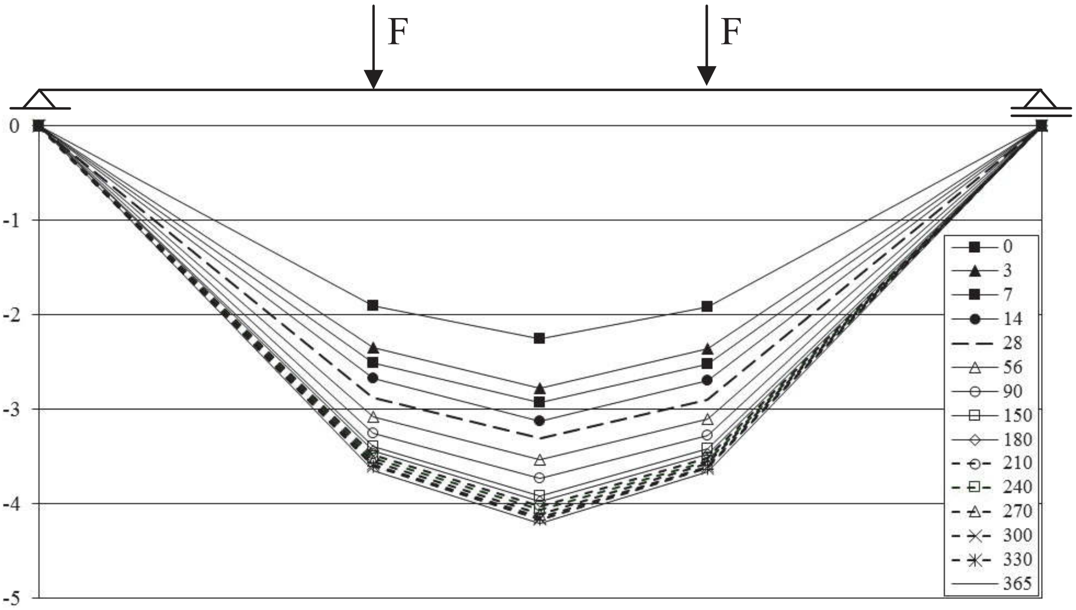

Fig. 9. Deflection of B10 beam [mm] during the time of load
Rys. 9. Ugięcie [mm] belki B10 w kolejnych dniach obciążenia

Cracking of beams was another analyzed serviceability limit state. Cracking moment of both beams (B9 and B10) was measured and was amounted respectively to 3,7 and 3,6 kN·m. The cracking was observed along the entire length of beam specimens, from both sides (Fig. 5). However, the analysis was limited to the area between forces (section loaded only with the bending moment – Fig. 10 and 11, left side "L" and right side "R" of the beams).

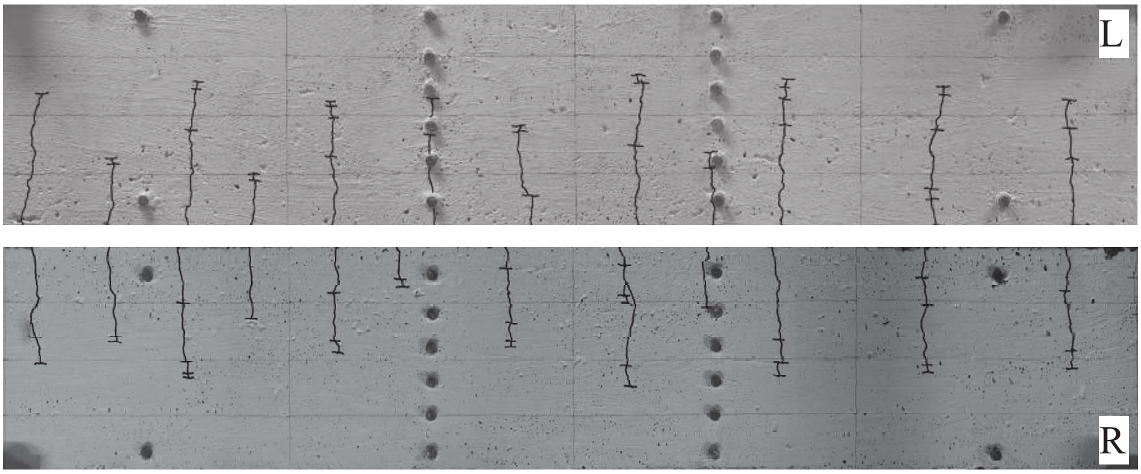

Fig. 10. Cracks distribution for beam B9 in section between forces
Rys. 10. Zarysowanie belki B9 na odcinku pomiędzy siłami

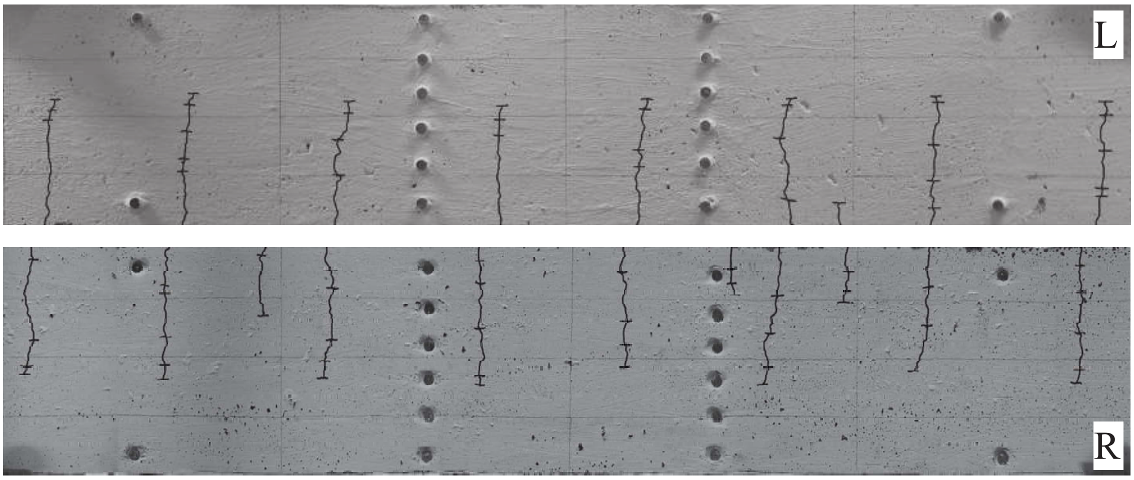

Fig. 11. Cracks distribution for beam B10 in section between forces
Rys. 11. Zarysowanie belki B10 na odcinku pomiędzy siłami

The level of stabilized cracking (lack of more cracks until the end of the study) was reached on the day of loading with the bending moment value on the level of 6 kN·m. Mean crack spacing was 83 and 102 mm, respectively for B9 and B10 beams. On the other hand the maximum crack width was 0.05 and 0.06 mm for B9 and B10 beams, which are the values allowed by EC2 [8].

6. Conclusion

Type of chosen aggregate is a very important component for well-designed concrete. Quality and ingredients of this aggregate depend on many variables [12]. Unfortunately, in the Central Pomerania, the granulometric composition of aggregate deposits, in about 70%, corresponds to sand [19]. This is why the attempts of using fine sand have been present since 1970's [13, 15]. Using steel fibres in sand concretes allows to reduce enormous waste sand dumps. Fine aggregate concretes containing steel fibres, are characterized by limited shrinkage value, in relation to elements made from both fine aggregate concrete and plain concrete. Creep rate for analyzed fine aggregate concretes containing steel fibres is also lower than for plain concretes having similar strength parameters [3].

Deflections of fine aggregate beams containing steel fibres obtained from the research significantly differ from values determined by EC2 [8]. Experimental crack width values are on the maximum level of 0.1 mm, what is acceptable under EC2 [8]. Analyzing these serviceability limit states of beams one should remember that the amount of of used fibres did not exceed 0.5%. This may indicate that such a small amount of fibres in fine aggregate concrete beams may cause real improvement of their functional properties [17, 22].

Undoubtedly using composite materials in construction elements is becoming more and more popular [16, 17]. The idea of using steel fibres in concrete mix based on waste aggregate seems to be a good idea [5] corresponding to the, so called, environmental sustainability. Lack of normalized methods enabling to analyze construction elements prepared from composite materials yet still remains a problem. Of course there exist studies on this matter [3, 20, 23] which, however, are not yet included in EC2 [8]. It could probably change after Model Code 2010 [20] is taken into account.

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References

1. **ACI 544.3R-93** Guide for specifying, proportioning, mixing, placing and finishing steel fiber reinforced concrete" (1998).
2. **Bohdal L., Kukiełka L.:** *Application of variational and FEM methods to the modelling and numerical analysis of guillotining process for geometrical and physical nonlinearity.* Mechanika. 20, 197–204 (2014).
3. **Bywalski Cz., Kamiński M.:** *Estimation of the bending stiffness of rectangular reinforced concrete beams made of steel fibre reinforced concrete.* Archives of Civil and Mechanical Engineering. 11, 553–571 (2011).
4. **Cichocki K., Ruchwa M.:** *Propagation of damage in structures under blast load*. Proceedings of 57th annual conference on scientific problems of civil engineering, Krynica-Rzeszow 18–22 September 2011, 98–99.
5. **Domski J., Katzer J., Fajto D.:** *Load-CMOD characteristics of FRCC based on waste ceramic aggregate*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 14, 69–80 (2012).
6. **EN 197-1:** *Cement. Composition, specifications and conformity criteria for common cements.*
7. **EN 206-1:** *Concrete. Specification, performance, production and conformity.*
8. **EN 1992-1-1:** *Design of concrete structures - Part 1-1: General rules and rules for buildings*.
9. **EN 1008:** *Mixing water for concrete. Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete.*
10. **EN 12620:** *Aggregates for concrete.*
11. **EN 14889-1:** *Fibres for concrete. Steel fibres. Definitions, specifications and conformity.*
12. **Gawenda T.:** *The influence of rock raw materials comminution in various crushers and crushing stages on the quality of mineral aggregates.* Mineral Resources Management. 29, 53–65 (2013).
13. **Głodkowska W., Kobaka J.:** *Application of waste sands for making industrial floors.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 11, 193–206 (2009) – in Polish.
14. **Głodkowska W., Kobaka J.:** *Modelling of properties and distribution of steel fibres within a fine aggregate concrete*. Construction and Building Materials. 44, 645–653 (2013).
15. **Głodkowska W., Laskowska-Bury J.:** *Piaski odpadowe jako wartościowe kruszywo do fibrokompozytów.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 17, (2015) – in press.

16. **Hendriks C.F., Janssen G.M.T.:** *Use of recycled materials in construction*. Materials and Structures. 36, 604–608 (2003).
17. **Karwowska J., Łapko A.:** *The usefulness of modern fiber-reinforced concrete in building structures*. Civil and Environmental Engineering. 2, 41–46 (2011) – in Polish.
18. **Katzer J., Domski J.:** *Quality and mechanical properties of engineered steel fibres used as reinforcement for concrete*. Construction and Building Materials, 34, 243–248 (2012).
19. **Katzer J., Kobaka, J.:** *Harnessing Waste Fine Aggregate for Sustainable Production of Concrete Precast Elements*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 12, 33–45 (2010).
20. **Model Code 2010,** *First complete draft*. International Federation tor Structural Concrete (*fib*), Bulletin 55 (2010).
21. **Ponikiewski T., Katzer J., Bugdol M., Rudzki M.:** *Determination of 3D porosity in steel fibre reinforced SCC beams using X-ray computed tomography*. Construction and Building Materials, 68, 333–340 (2014).
22. **Seitl, S., Keršner, Z., Bílek, V., Knésl, Z.:** *Fatigue parameters of cement-based composites with various types of fibers*. Key Engineering Materials, 417, 129–132 (2010).
23. **Tan K.H., Paramsivam P., Tan K.C.:** *Creep and shrinkage deflections of RC beams with steel fibers*. Journal of Materials in Civil Engineering, 6, 474–494 (1994).

Badania długotrwałe belek fibropiaskobetonowych na bazie kruszywa odpadowego

Streszczenie

W artykule opisano badania fibropiaskobetonów na bazie kruszywa odpadowego. Jako zbrojenie rozproszone zastosowano dwa rodzaje włókien stalowych w ilość nieprzekraczającej 0,5% objętościowo. W badaniach określono podstawowe właściwości zaproponowanych fibrobetonów takie jak: wytrzymałość na ściskanie, rozciąganie przy rozłupywaniu czy też moduł sprężystości. Jednak główny nacisk badawczy położono na określenie stanów granicznych użytkowalności badanych belek z uwzględnieniem cech relogicznych (tj. skurczu i pełzania) użytych fibrokompozytów.

Słowa kluczowe:
piasek odpadowy, włókna

Keywords:
waste sand, fibres

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Energy Saving Technologies with the Use of Heat Pumps

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Introduction

Price rise for energy carriers inevitably brings about the price rise for heat energy and finally the price rise for stuffs, which makes it necessary for a manufacturer to look for the new alternative sources and ways of saving traditional energy sources, effective use of secondary energy resources, including natural low temperature sources of heat. That is the reason why the use of energy saving technologies, heat pumps being one of them, acquires an ever increasing significance [2].

The use and manufacture of heat pumps (HP) in this country is being carried out with the great delay. The 90^s were characterized by the cut of demand for such innovative energy equipment as heat pumps. The reasons for that are well known. So a lot of machines and new developments which were already mastered proved to be out of usage.

The recent years gave real economic impetus for energy saving, which is determined by the increase of price for energy carries as well as by the changes in relation of electricity tariffs and prices for different kinds of fuel.

Heat pump units are effective in technological processes of processing and storing food raw materials here law temperature heat sources and secondary heat resources are used. Of self – sustained meaning is the use of heat pumps in the systems of heating and air conditioning of the food stuffs enterprises premises [8].

In many cases the requirements of ecological cleanness for methods of getting heat energy step forward.

Traditional systems of heat supply by using boiler – houses operating on various kinds of natural fuel are characterized by considerable irreversible losses. By using high quality organic fuel (gas, oil, coal) the combustion temperature exceeds 1000°C, while the customer weds low temperature heat – 70°–130°C [1].

From the thermodynamic point of view the most rational fuel consumption is attained at thermoelectric plants where high temperature heat of combustion is maximally used for producing electrical energy, and for heat supply – the heat carrier with temperature necessary for heating production premises and residential houses.

But the use of heat electric power plant (HEPP) may be irrational in many cases due to large losses at heat transfer for large distances or lack of need for such volumes of heat. For example, when the heat users are dispersed and at a large distance from each other or when the natural conditions do not allow it. In such areas the boiler – houses remain the main source of heat being the main reason of air pollution with sulfur oxides and other harmful substances for people.

The world dynamics of rising prices for sources and energy itself is of stable character. Of considerable importance is the fact that Russia's entering the WTO is followed by the price rise at the internal market which is connected will energy power engineering at the level of world prices. So saving of fuel and energy resources is an urgent task for Russia. It is even of greater importance for the Kaliningrad region due to its geographic separation from the vest of Russia, lack of necessary resources, rise of electricity consumption and necessity to provide its energy self sufficiency [3].

Research

The Kaliningrad state technical university has been carrying at research for using heat pumps (HP) in technological processes of fish processing for a number of years [9].

The research has been performed along the following lines:

1. The use of heat pumps in the systems of preparing air in cold smoking, drying and fish.
2. The use of HP for heating water in the closed aquacultures systems (CAS).

3. The use of HP in the autoclave water preparation systems (sterilization and pasteurization of hermetically packed products).

In the 90-s two experimental units for cold smoking of fish were made at two fish processing enterprises of the Kaliningrad region. The modernized unit H10-ИВЦ-1-03 produced 120 tons of products for the term of this unit was characterized by a better quality. The shore based fish processing complex in Pionersky town saw modernization of unit for continuous cold smoking of fish. For the term of one year it produced 4640 tons of product marked by a better quality. The economic effect owing to modernizations amounted to more than 95000 USD [6, 7].

The use of HP in autoclave water preparation systems (sterilization and pasteurization) is associated with energy saving in these processes. Thus documents regulating this process do not allow secondary use of water after autoclave. So, by using HP it is possible to return the warmth for heating water going into autoclave, which gives considerable economy of heat energy and cats environment pollution.

Cutting volumes of commercial fisheries brought about intensive development of aquaculture in many countries which made it possible to meet the fish products demands of population. The leading countries in this field, such as China, India, Japan, Norway and Chili supply their products not only the internal market but are also active on the world market. Having a great potential, Russia lags behinds by aquaculture indexes. In recent years the necessity of developing Russian enterprises that could have supplied the population with not expensive and fresh products has attained a State scale [10].

The overwhelming majority of methods used for running aquacultures farms prove to be useful in social sphere, providing foodstuff products with little or no harm for environment.

The closed water supply units (CWSU) prove to be the highest form of industrial fish culture, allowing to creating the optimal conditions for fish breeding all the year round both for supplying fish fry and commercial fish. It is the CWSU that provide the highest output of fish products per the square unit. Expediency of large development of this trend of industrial fish culture is based on the economy of water taken from under earth and other sources (daily water feedings is 5…25 % of the total volume), ecological cleanness, because it gives an opportunity for full or partial utilization of fish metabolism and organisms, residing in biofilters and avoiding their coming into open water systems.

Within CWSU the block for thermal water preparation is not only one of the most important but also one of the most energy consuming ones. Taking into consideration variety of hydrobionts bred in industrial fish culture, it is necessary to point out a broad range of temperature modes for their optimal growth even within one life cycle. Thus low temperature is necessary for ripening and it is to rise gradually from fry to marketable fish. There are optimal temperature modes for growing marketable fish to facilitate their growth. This 14–18°C is optimal for trout, 23–28°C – for carp, 18–23°C – for sturgeon, 25–30°C – for sheat-fish, 25–32°C – for tilaphia. So aquacultures farms with heat, but also to cool water supplied to system. And it is also to be taken into account that technology presumes 5–20% change of the whole water volume, circulating in CWSU. It is obvious that development of aquacultures farms using heat pumps for water preparation may facilitate appearance of new possibilities for rising effectiveness of fish culture from ripening roe to growing marketable fish. This will result in obtaining competitive product in both internal and foreign market. Taking into account the high cost of breeding fish in CWSU at the present stage of aquacultures development, it is used for breeding expensive fish species (eel, sturgeon) and fish capable of maximum gaining weight for the shortest period of time (tilaphia, sheat-fish) [4,5].

The use of plant for thermal water regulation of CWSU for fish culture makes it possible to solve this task but with taking into account large volumes of water for circulation and supply of fresh water.

To investigate operation of cheat pump within the system of water preparation of CWSU n experimental unit was made. Its chart is presented on fig.1; fish cultural part of CWSU is presented on fig.2.

HP unit MSR-J072WLC was mounted and tested in the international aquacultures center of the KSTU (Svetly). The Tests were carried out in summer and winter seasons. The technical water from well was used as a source of low-potential warmth. The change of water temperature was not large – 8°–10°C.

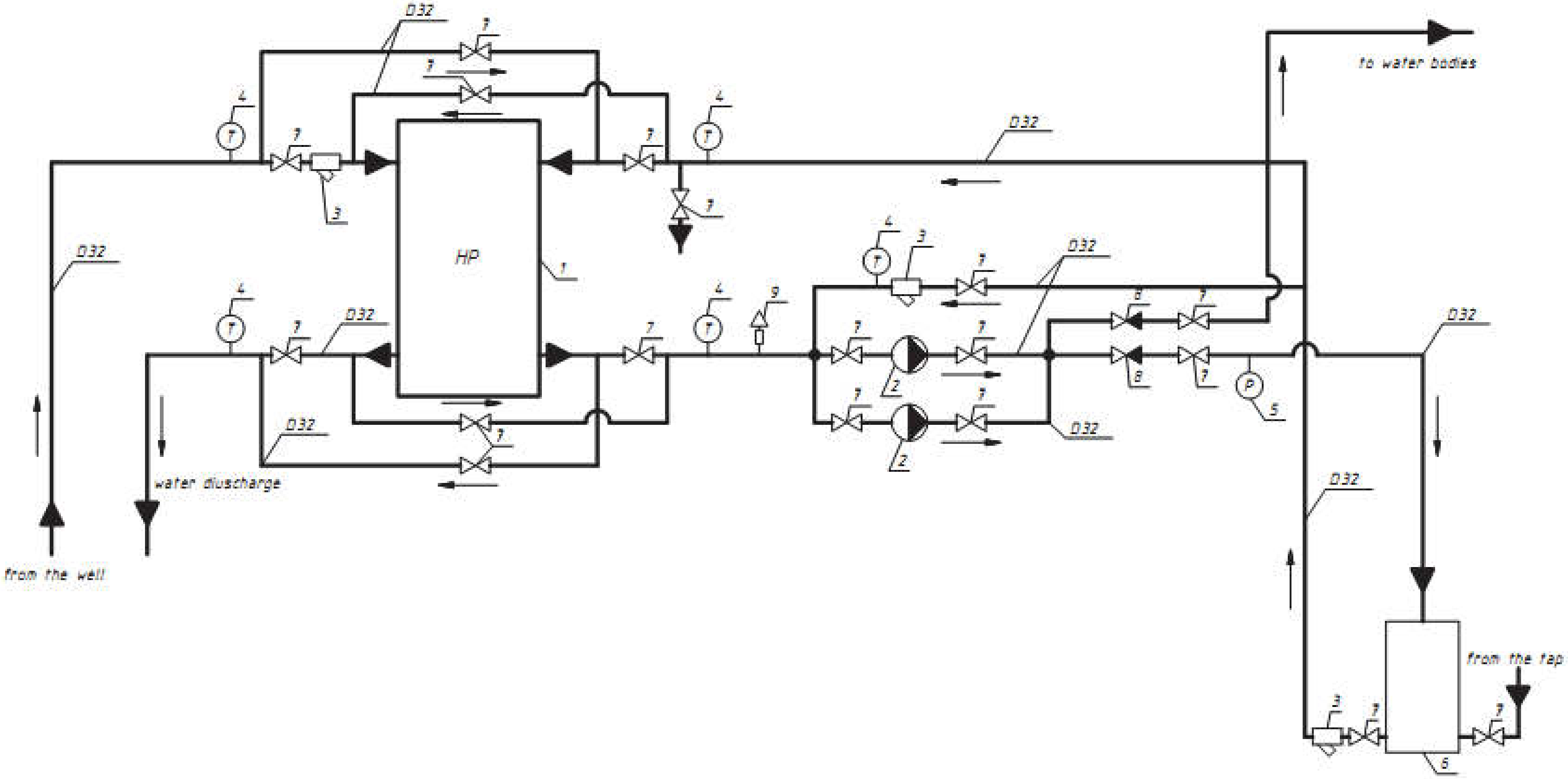

Fig. 1. The chart of experimental HP unit for thermal preparation of water; 1 – HP unit, 2 – water pumps, 3 – filter, 4 – thermometer, 5 – pressure-gauges, 6 – accumulator tank, 7 – valves, 8 – check valves
Rys. 1. Plan eksperymentalnej instalacji pompy ciepła do przygotowania wody; 1 – pompa ciepła, 2 – pompy wody, 3 – filtr, 4 – termometr, 5 – czujniki ciśnienia, 6 – zbiornik akumulacyjny, 7 – zawory, 8 – zawory zwrotne

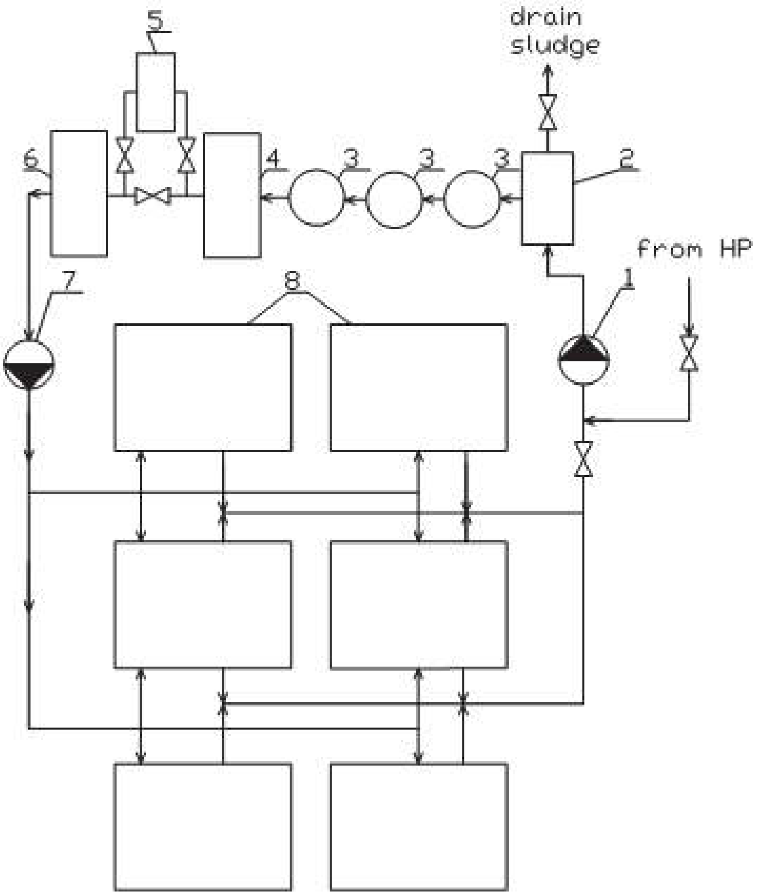

Fig. 2. Fish culture portion of closed water supply; 1 – water pump, 2 – mechanical filter, 3 – biofilters, 4 – bactericidal lamp, 5 – oxygenator, 6 – consumption tank, 7 – water pump, 8 – fish culture water bodies
Rys. 2. Zamknięty obieg zaopatrzenia w wodę w farmie rybnej; 1 – pompa wody, 2 – filtr mechaniczny, 3 – biofiltry, 4 – lampa bakteriobójcza, 5 – natlenianie, 6 – zbiornik zasilający, 7 – pompa wody, 8 – stawy rybne

Fig. 3, 4 show the dependence graph of electric power used by heat pump engine and energy transformation ratio on time of operation in heating up mode of water for feeding the system.

It is clear from graph (fig.3) that power used by 1 kWt at constant temperature and pressure in evaporator of HPU for 35 min of operation, which is accounted for by constantly increasing temperature and pressure in condensate of HPU, corresponding increase of pressure relation P_k/P_0, decrease of feeding ratio of HP.

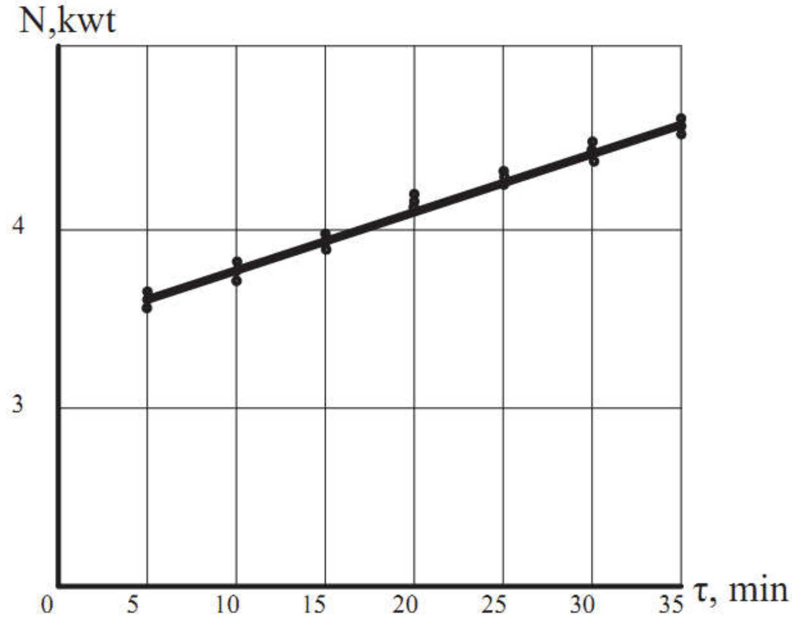

Fig. 3. Dependence of electric power used by HP engine on time
Rys. 3. Zależność zużycia energii elektrycznej przez silnik pompy ciepła od czasu

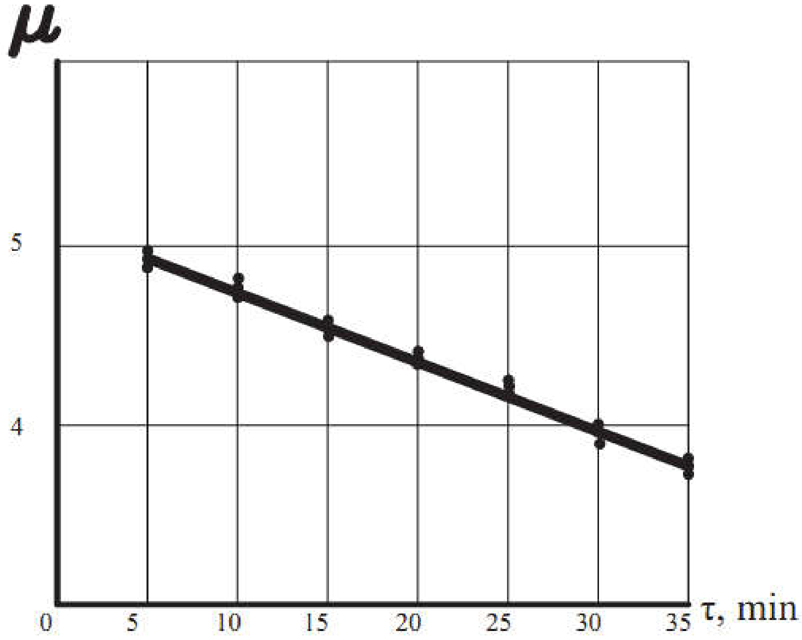

Fig. 4. Dependence of transformation energy ratio on time used by HP engine on time
Rys. 4. Zależność współczynnika przemiany energii od czasu pracy silnika pompy ciepła

At the same time the energy transformation ratio of HPU (fig.4) drops from 4.94 to 3.83, which is explained by the same reasons. The cost of water heating preparation after mounting a heat pump was cut by 3 times compared to the electric heating system which was earlier operated.

Considering prospects and possible field of use for heat pumps in fish culture it necessary to point out that because of the traditional structure and practice of designing heating and refrigeration systems for food production technological processes the use of heat pumps is unreasonably undervalued. Taking into account the present trend for sharp increase of investments for the production purposes the ample use of heat pumps on the food-staff enterprises seems quite expedient and promising.

Conclusions

An experimental heat pump unit for water thermal preparation in the CWSU was developed. Experimental data supporting its energy saving effectiveness were obtained. Effectiveness of using unit for thermal water regulation is confirmed by netting electrical energy consumption at condensing water, which is 3 times less than by conventional modes.

Maintaining set water parameters in conditions of daily feeding 20% water to CWSU from thermoregulation unit at the stage of keeping producers, 50% – at incubation and growing larval, 10–20% – at growing fry and marketable fish, made it possible:

- to obtain high quality and timely spawn products,
- to solve growth potential and health at all stage of biotechnical process,
- to make effective use of advantages of polycyclic technologies of fish culture in CWSU.

References

1. **Aerlichman V., Fatychov J., Suslov A.:** *Energy saving in technological processes in the agroindustrial complex with the use of heat pump installations.* Monograph, KGTU, Kaliningrad, 236 (2007).
2. **Chernishov V.:** *The role of the fishery industry in ensuring food security of the Russian Federation*. Refrigiration. 3, 7–8 (2010).
3. **Fatychov J., Aerlichman V., Suslov A.:** *Prospects of application of heat pumps in the food industry of the region.* Economics and management. International scientific conference. Kaunas 2007.
4. **Proskurenko I.:** *Closed fishery installation.* M.: VNIRO, 152 (2003).

5. **Rudenko M.:** *Heat pump systems for the fish farms.* Refrigiration. 1, 43–46 (1990).
6. **Suslov A.A., Ionov A.G.:** *Experimental-industrial unit with heat pump for cold smoking and dry-curing fish*. Refrigiration. 11, 35–37 (1988).
7. **Suslov A., Fatychov J., Aerlichman V.:** *The kinetics of drying fish in the equipped with a heat pump.* JPS. 1, 31–34 (2012).
8. **Suslov A., Fatychov J., Aerlichman V.:** *About expediency of application of heat pumps in heat supply systems.* Refrigiration. 12, 12–14 (2008).
9. **Suslov A.:** *Prospects of application of heat pumps in the fishing industry*. “Industry of cold for food, energy and environmental security”, International scientific and technical conference, Chillventa Rossija, Moscow, M.: DoMira Ltd, 41–43 (2013).
10. *The strategy of developing acquaculture in RF for the period of up to 2020*. The Ministry of Agriculture of RF. – M. 2007.

Energooszczędne technologie wykorzystujące pompy ciepła

Streszczenie

Wzrost cen nośników energii w sposób nieunikniony powoduje wzrost cen energii cieplnej i ostatecznie wzrost cen artykułów spożywczych. Powoduje to konieczność poszukiwania przez producentów nowych, alternatywnych źródeł i sposobów oszczędzania tradycyjnych źródeł energii, efektywnego wykorzystania zasobów energii wtórnej, w tym naturalnych, niskotemperaturowych źródeł ciepła. To jest powód, dla którego stosowanie energooszczędnych technologii, pompy ciepła są jedną z nich, nabiera coraz większego znaczenia.

W pracy przedstawiono eksperymentalną instalację pompy ciepła do przygotowania cieplnej wody w zamkniętym obiegu zasilania w wodę. Dane eksperymentalne pokazują skuteczność w oszczędzaniu energii. Wydajność przy zastosowaniu urządzenia do regulacji temperatury ciepłej wody potwierdza zużycie energii elektrycznej dla wody kondensacyjnej, która jest trzy razy mniejsza niż w tradycyjnych rozwiązaniach.

Słowa kluczowe:
pompa ciepła, oszczędność energii, akwakultura, eksperymentalna jednostka pompy ciepła

Keywords:
heat pump, energy saving, aquaculture, experimental heat pump unit

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Antibacterial and Antifungal Activity of Plant Extracts

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1. Introduction

Spices and herbs have been used for thousands of years by many cultures to enhance the flavor and aroma of foods. Early cultures also recognized the value of using spices and herbs in preserving foods. The numerous experiments since the late 19th century have documented the antimicrobial properties of some spices, herbs, and their components [59, 69]. Many herbs and spice are known to exert antioxidant activity and are useful for preventing lipid oxidation in living organisms as well as in foods [22].

The study of the effects which have natural chemicals compounds released from plants or microorganisms on the growth and spread of plants and microorganisms in natural communities is now engaged in a new field - chemical ecology. It oscillates around allelopathy issues, which so far have the greatest dealt with interaction between weeds, and various species of cereals. Currently, the literature reports, indicate the high bactericidal and fungistatic efficiency of extracts and essential oils prepared from different plant species [21, 39].

The family *Lamiaceae* consists of about 252 genera and more than 6700 species [28]. Some of *Lamiaceae* species are frequently used in cooked dishes and are recognized as important preventive factor of many diseases [5, 13, 39]. Essential oils and extracts of these plants are known to possess antiseptic, antiinflammatory and antimicrobial activities [8, 9, 63]. *Pogostemon cablin*, *Lavandula angustifolia*, *Melissa officinalis*, and *Salvia officinalis* are underutilized species of *Lamiaceae* [30].

Most of the *Pinus* species are trees or shrubs with specific morphological characteristics of leaves (needles) rich in terpene aromatic essential oil. Pine needle essential oils are mainly used in folk medicine for the treatment of respiratory [18]. Up to now, there has been an increased interest in studying chemical composition as well as biological activity of the essentials oils isolated from different pine species [41].

Plant extracts and essential oils are considered to be one of the potential sources of substances with anticancer, antimicrobial and antioxidant properties, and source of free radical scavenging agents [31, 38, 58].

The increasing recognition and importance of bacterial and fungal infections, the difficulties encountered in their treatment and the increase in resistance to antibacterial and antifungal agents have stimulated the search for therapeutic alternatives [50]. The essential oils (EO) and products of plant secondary metabolism have application in folk medicine, fragrance industries, food flavouring and preservation but only in recent years they have started to be recognized for their potential antimicrobial role [40]. Although numerous studies have documented the plant extracts antibacterial and anticandidal effect [9, 14, 24, 36, 49, 27]. There have been few comprehensive *in vitro* studies of the effects exerted by EO on filamentous fungi, probably due to the difficulties encountered in standardized susceptibility methods for these mycetes [27, 35, 37, 43, 61].

In many research centers are conducted intensive *in vitro* studies on the mechanism of action and safety of plant extracts and their individual components. The obtained results encourage to further investigations on the usefulness of the macerates, infusions, decoctions and plant oils in combating a particularly dangerous antibiotic-resistant microorganisms.

The aim of this work was to evaluate the antimicrobial activity of extracts from 3 plant species, obtained by various methods, collected in Poland against Gram-positive and Gram-negative bacteria and fungi. Some spice plants previously examined for biological activity by other investigators were included in this study because different methods and microorganisms or strains were used in the study, which provided a comparison base.

2. Materials and methods

2.1. Plant material

Fresh, free from disease, leaves, flowers and young sprouts of three different plants *Lavandula vera* L. – flowers and leaves, *Melissa officinalis* L. – leaves, *Pinus sylvestris* L. – young sprouts were collected in July 2014 from the area of Koszalin and surrounding areas (Poland). The parts of plants were washed thoroughly 2–3 times with running water and once with sterile distilled water and air-dried at room temperature on sterile blotter under shade for two weeks.

2.2. Preparation of the plant extracts

Used in *in vitro* investigations plant preparations were made in the form of aqueous extracts, as macerates, brews and decoctions. Macerate, brew and decoction were prepared according to the recipe given by Sas-Piotrowska et al. (2005) [55]. Macerate (cold method) – 5 g of dried plant poured over 100 ml of cold water and left for 24 h at 20°C, then filtered; brew (hot method) – 5 g of dried plant poured of 250 ml of boiling water and left covered for 30 minutes, after cooling the extract was filtered. The decoction was prepared according to the recipe given by Tyszyńska-Kownacka and Starek (1989) [68]. For this purpose, weighed 8.75 g of each dried herbs and poured over 1 liter of distilled water. The suspension was mixed thoroughly, allowed to stand for 24 hours and then boiled for 15 minutes. Boiled extracts were sieved through a sieve lined with gauze to glass containers, and after cooling, used for the investigations.

2.3. Essential oil isolation

Essential oil isolation was made by hydrodestillationin all-glass Clevenger apparatus (Ph. Eur 7, 2.8.12.). For that purpose, 20 g of minced plants were distilled for 4 hours. For purification purpose, anhydrous sodium sulfate was added to the isolated essential oil to remove residual water.

2.3. Test microorganisms

The antibacterial activity of the plant extracts were tested *in vitro* against the Gram-positive bacteria: *Bacillus subtilis, Listeria monocy-*

togenes, Micrococcus luteus, Staphylococcus aureus; and the Gram-negative bacteria: *Escherichia coli*. The antifungal activity of plant extracts was studied against 12 different microorganisms, including: *Alternaria alternata* (Fr.) Keissler, *Aspergillus glaucus* (L.) Link, *Aspergillus niger* (Tiegh.), *Botritis cinerea* (Pers), *Cladosporium herbarum* (Pers.) Link ex Fr*.*, *Fusarium culmorum* (Sacc.), *Fusarium oxysporum* (E.F.Sm.),W.C. Snyder & H.N.Hansen, *Fusarium poae* (Peck), *Fusarium sambucinum* (Fuckel f.6 Wollenweber), *Fusarium solani* (Mart.), *Penicillium chrysogenum* (Thom), *Sclerotinia sclerotiorum* (de Bary).

All microorganisms were obtained from the stock cultures of the Microbiology Laboratory (Division of Biological Agriculture Foundations, Koszalin University of Technology).

2.4. Preparation of Inoculum

The inoculum was prepared according to methodology given by Mahesh and Satish (2008) [45]. The Gram-positive and Gram-negative bacteria were pre-cultured in nutrient broth overnight in a rotary shaker in 37°C, centrifuged at 10,000 rpm for 5 min, pellet was suspended in double distilled water and the cell density was standardized spectrophotometrically (A_{610} nm). The fungal inoculum was prepared from 5 day old culture grown on potato dextrose agar medium. The Petri dishes were flooded with 8 to 10 ml of distilled water and the conidia were scraped using sterile spatula. The spore density of each fungus was adjusted with spectrophotometer (A_{595} nm) to obtain a final concentration of approximately 10^5 spores/ml.

2.5. Antimicrobial screening

The antibacterial activity of extracts was determined by diffusion method in Petri dishes (ø 10 cm) with a solid medium Müller - Hinton. Applied to a substrate prepared using a densitometer suspension of 0.5 McFarland units in (10^6jtk / ml), which was uniformly distributed on the surface, and after dried, placed a paper disk (ø 6 mm) soaked botanical extract. The measure of the extracts activity was the size of the zone of inhibition of growth colonies (in millimeters) after 24 hours of incubation in 37°C. The antifungal activity of extracts was determined by diffusion method in Petri dishes (ø 10 cm) with a solid medium PDA. On each substrate 4 drops of an aqueous suspension of spores and mycelial fragments was applied, next uniformly distributed on the surface, then they were dried and placed on a paper disk (ø 6 mm) soaked with botanical extract. The measure of the extracts activity was the size of the zone of inhibition of growth colonies (in millimeters) measured after 5 days incubation in 22°C.

The experiment was established in 6 replicates for each plant, method of extract preparation and the pathogen. Each repetition consisted of four Petri dishes. Results were analyzed using analysis of variance and correlation account.

2.6. Statistical analyses

The results were analyzed statistically by analysis of variance with a single classification ($P = 95\%$), separately for each plant, method of preparation and specific pathogens. The results presented in tables 1–6, were calculated relative to the control sample (the paper discs treated with sterile water). The Fisher's least significant difference ($LSD_{0.05}$) was applied to test the differences between samples at 5% significance level. Additionally, a comparison of averages was made using the correlation coefficient (the limit value of $r = 0.195$ for $\alpha = 0.05$ and $r = 0.254$ for $\alpha = 0.01$). Statistical analysis was performed using the programs ANW (Variance Analysis of Experiments) and ANK (Correlation Analysis of Experiments).

3. Results and discussion

Analysis of variance showed significant differences in the examined factors and their interaction. The reaction of the investigated bacteria on modified environment conditions, depended on the plant species from which the extract was prepared (Table 1) and the method of its preparation (Table 2). The growth of pathogens was most inhibited by extracts from *Lavandula vera* (mean value of inhibition zone ø 10.30 mm). The highest sensitivity to this extract showed *Staphylococcus aureus* (ø 12.08 mm). The most active extracts was applied to the bacterium *Listeria monocytogenes* (ø 12.08 mm). The highest antimicrobial activity was observed for oil from *Lavandula vera*. Among the bacteria the most resistant on the investigated species of plants was *Escherichia coli* (ø 8.22 mm).

Generally, Gram-positive bacteria were more susceptible than Gram-negative bacteria. *Listeria monocytogenes* was the most sensitive, while *Escherichia coli* was the most resistant strain (against all plant extracts). Our results are in good agreement with the finding of Cantore et al. (2004) [10].˙ Antibacterial properties of plants extracts depend not only on its chemical characteristics, but also on type of bacteria. Gram-negative bacteria are less susceptible because their membrane contains hydrophilic lipopolysaccharides (LPS), which create a barrier toward macromolecules and hydrophobic compounds [9, 33].

Table 1. Antibacterial activity of plant extracts (1.0 μg Ml $^{-1}$) in disc-diffusion method, inhibition zones (mm)
Tabela 1. Aktywność przeciwbakteryjna wyciągów roślinnych (1.0 μg Ml $^{-1}$) w metodzie dyfuzyjnej, strefa zahamowania wzrostu (mm)

Bacteria	*Lavandula vera*	*Melissa officinalis*	*Pinus sylvestris*
Bacillus subtilis	6.75	10.08	8.28
Eshcerichia coli	9.42	6.5	8.22
Listeria monocytogenes	13.5	9.67	12.08
Micrococcus luteus	9.75	10.25	10.5
Staphylococcus aureus	12.08	9.50	10.19
Mean value	10.30	9.20	10.07
LSD_{plant} = 0.1867	$LSD_{bacteria}$ =0.2410	LSD_{plant} x $LSD_{bacteria}$ =0.4174	

The data show the diameter of inhibition zone growth in mm. The diameter of paper disc was 6 mm. LSD – the least significant difference. When significant (P < 0.05), the value of LSD is indicated.

The growth of bacteria on the surface (Table 2) was the most limited by essential oils. Among the studied bacteria most sensitive to the applied extracts were: *Listeria monocytogenes* (ø 12,08 mm), *Micrococcus luteus* (ø 10,5 mm) and *Staphylococcus aureus* (ø 10,19 mm). The highest resistance was observed for *Escherichia coli* (ø 8.22 mm). The weakest effect on the pathogens growth showed applied macerates (ø 6,60 mm), and bacteria resistant to its use were *Bacillus subtilis* and *Listeria monocytogenes* (ø 6,00 mm).

Many researchers evaluated the antimicrobial activity of plant oils [1, 15, 44, 60, 64]. Analyzing the average values of the zones of growth inhibition of bacteria and fungi by lavender oils, it was found that they differ in the various species. Draws attention to the fact that the Gram-positive bacteria were more sensitive to applied lavender essential oils than Gram-negative bacteria. This is confirmed by the findings of other authors [1, 3, 6, 15, 16]. *Staphylococcus aureus* species is currently one of the major causes of nosocomial infections [23]. Recent studies show that bacteria do not yet have an adequate defense mechanism to tested oils. Other authors have shown inhibition zone for *S. aureus* in the range of 0,0-18,0 mm [19, 20, 25, 29, 51, 56, 64]. Serban (2011) and Cavanagh et al. (2002) investigations show that the antimicrobial properties depend on the composition of the oil, and also on the species or type of microorganism [1, 11, 56].

Table 2. The reaction of bacteria depending on the method of a plant extract preparation (mean value of diameter inhibition zone growth in mm)
Tabela 2. Reakcja bakterii w zależności od metody przygotowania ekstraktu roślinnego (wartość średnia średnicy zahamowania wzrostu w mm)

Bacteria	Macerate	Brew	Decoction	Oil	Mean value
Bacillus subtilis	6.00	6.00	6.00	15.11	8.28
Escherichia coli	6.67	6.78	7.78	11.68	8.22
Listeria monocytogenes	6.00	15.78	7.44	19.11	12.08
Micrococcus luteus	8.00	7.56	7.00	19.44	10.5
Staphylococcus aureus	6.33	7.11	7.44	19.89	10.19
LSD$_{bacteria}$ =0.2410	LSD$_{preparation}$ =0.2155		LSD$_{bacteria}$x LSD$_{preparation}$ =0.4820		LSD$_{plant}$x LSD$_{preparation}$ =0.3733

The data show the diameter of inhibition zone growth in mm. The diameter of paper disc was 6 mm. LSD – the least significant difference. When significant (P < 0.05), the value of LSD is indicated

Synthesis of the obtained results showed that the activity of the extracts dependent on the species of plants, a method of preparing plant extracts and the sensitivity of bacteria selected for the test (Table 3). It also showed significantly different response of tested pathogens to the applied extracts of various plant species.

To evaluate the antimicrobial properties of essential oils against strains of bacteria oils of lavender and melissa was examined. *Lavandula vera* and *Melissa officinalis* belong to the family *Lamiaceae*, whose representatives have a particularly valuable therapeutic properties. Lavender oil was the most active against bacteria, which is confirmed by obtained experimental results and it is also well know fact from the literature.

Table 3. Variation and correlation coefficients for the reaction of tested bacteria on plant extracts and methods of their preparation

Tabela 3. Współczynniki zmienności i korelacji dla reakcji badanych bakterii na wyciągi roślinne i sposoby ich przygotowania

Bacteria	$\bar{x}$	Range	V %	Correlation coefficient (r)				
				B. subtilis	*E. coli*	*L. monocytogenes*	*M. luteus*	*S. aureus*
Bacillus subtilis	8.28	6 – 22.33	60.67	–	–	–	–	–
Eshcerichia coli	8.22	6 –16.33	36.27	0.19	–	–	–	–
Listeria monocytogenes	12.08	6 – 21.67	56.75	0.56	0.41	–	–	–
Micrococcus luteus	10.50	6 – 23.00	55.27	0.88**	0.57	0.65*	–	–
Staphylococcus aureus	10.19	6 – 26.67	63.11	0.61*	0.84**	0.59**	0.84**	–

$\bar{x}$ – mean value of the diameter of inhibition zone growth in mm; V – coefficient of variation;

***, * – significant compatibility of bacteria response on tested plant extracts*

In the composition of this essential oil predominates compounds such as: pulegone – 40%, menthone – 13%, and menthol – 18%, responsible for inhibiting the growth of reference strains of *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* [4].

Lemon balm and raw material obtained from the essential oil are well known products with wide range of application, because of its valuable antimicrobial activity [47]. Highest activity exhibit monoterpene aldehydes and ketones (neral/geranial, citronellal, menthone and isomenthone) and sesquiterpene hydrocarbons (E-caryophyllene) [47]. In the presented investigations, the highest antibacterial activity showed melissa oil against the strains of *Microccocus luteus* and *Bacillus subtilis* and antifungial - against the *Sclerotinia sclerotiorum.* Comparison of the antimicrobial activity of the essential oil obtained from melissa and streptomycin against some human pathogenic bacteria, showed that *Melissa officinalis* has a strong antibacterial potential and can be used as a natural protective and fungicide [52]. Very strong protective activity of the essential oil in the process of lipid peroxidation, especially against hydroxyl radical [47], indicates that it can be used not only as a aromatic factor aromatic, but also as a safe dietary antioxidant and antiseptic in health foods and pharmaceuticals. The results of our investigations are reflected in the work of other authors, who confirms that apart from essential oil, also raw materials and extracts of rosemary acid (an important active ingredient *Melissa officinalis L*) exhibit antimicrobial properties [48, 65, 67].

The reaction of tested fungi depended on the plant species from which the extract was prepared (Table 4) and the method of its preparation (Table 4). The growth of pathogens was the most strongly limited by extracts from *Pinus sylvestris* (ø 10,29 mm), and the greatest sensitivity to this extract was observed for fungus *Scleroinia sclerotiorum* (ø 26,33 mm). Simultaneously the use of the aqueous extracts (macerate, infusion, decoction and oils) from *Lavandula vera* not significantly inhibited the growth of microorganisms (ø 8,55 mm). The most resistant fungus on the investigated plant species turned out to be *Aspergillus niger* (ø 7,00 mm) and *Fusarium sambucinum* (ø 7,00 mm).

Fungal growth on PDA medium (Table 4) was the most strongly limited by essentials oils (ø 13.83 mm). Among the analyzed fungi most sensitive to the applied extracts and essential oils have proven to be: *Sclerotinia sclerotiorum* (ø 17,56 mm) and *Fusarium poae* (ø 10,42 mm).

Additionally the weakest effect at the pathogens growth showed decoction (ø 7,20 mm), and fungus particularly resistant to the use of such kind of plant extract was *Aspergillus niger, Botritis cinerea, Fusarium sambucinum, Fusarium solani, Penicillum chrysogenum* (ø 6,00 mm).

Table 4. Antifungal activity of plant extracts (1.0 µg Ml $^{-1}$) in disc-diffusion method, inhibition zones (mm)
Tabela 4. Aktywność przeciwgrzybowa wyciągów roślinnych (1.0 µg Ml $^{-1}$) w metodzie dyfuzyjnej, strefa zahamowania (mm)

Fungi	*Lavandula vera*	*Melissa officinalis*	*Pinus sylvestris*
Alternaria alternata	12.92	9.25	8.67
Aspergillus glaucus	6.68	6.00	9.08
Aspergillus niger	6.68	6.00	8.33
Botritis cinerea	6.75	8.92	9.50
Cladosporium herbarum	7.42	11.75	7.00
Fusarium culmorum	10.5	8.50	8.83
Fusarium oxysporum	9.00	13.33	7.50
Fusarium poae	7.25	10.83	13.17
Fusarium sambucinum	6.58	6.00	8.42
Fusarium solani	6.67	6.33	9.58
Penicillium chrysogenum	11.17	8.08	7.17
Sclerotinia sclerotiorum	11.00	15.33	26.33
Mean value	8.55	9.19	10.29
LSD_{plant} = 0.1186	LSD_{fungi} =0.2372	LSD_{plant}xLSD_{fungi}=0.4108	

The data show the diameter of inhibition zone growth in mm. The diameter of paper disc was 6 mm. LSD – the least significant difference. When significant (P < 0.05), the value of LSD is indicated.

According to the findings of Sas-Piotrowska and Piotrowski (2003), the biological activity of plant extracts depends on several factors, and first of all on content of specific chemical compounds and on their ability to diffuse. Besides that, some those compounds may stimulate a pathogen development and increase a degree of contamination and the others can act as inhibition factors Differences between action of brew, macerate, decoction and oils probably resulting from possible losses caused by evaporation of the solvent during preparation and the difference in the solubility of the extracted compounds [54].

Table 5. The reaction of fungi depending on the method of a plant extract preparation (mean value of diameter inhibition zone growth in mm)

Tabela 5. Reakcja grzybów w zależności od metody przygotowania wyciągów roślinnych (średnia wartość średnicy strefy zahamowania wzrost w mm)

Fungi	Macerate	Brew	Decoction	Oil	Mean value
Alternaria alternata	9.56	11.78	6.56	13.22	10.28
Aspergillus glaucus	6.00	6.00	6.33	10.67	7.25
Aspergillus niger	6.00	6.00	6.00	10.00	7.00
Botritis cinerea	8.89	7.00	6.00	11.68	8.39
Cladosporium herbarum	9.67	10.44	7.33	7.44	8.72
Fusarium culmorum	6.00	6.00	6.00	19.11	9.28
Fusarium oxysporum	8.22	6.00	8.33	17.22	9.94
Fusarium poae	7.44	7.67	8.56	18.00	10.42
Fusarium sambucinum	6.00	6.33	6.00	9.67	7.00
Fusarium solani	7.00	7.11	6.00	10.00	7.53
Penicillium chrysogenum	8.78	6.00	6.00	14.44	8.81
Sclerotinia sclerotiorum	14.22	18.11	13.33	24.56	17.56
$\text{LSD}_{\text{fungi}} = 0.2372$	$\text{LSD}_{\text{preparation}} = 0.1369$		$\text{LSD}_{\text{fungi}}$ x $\text{LSD}_{\text{preparation}} = 0.8215$	$\text{LSD}_{\text{plant}}$ x $\text{LSD}_{\text{preparation}} = 0.2372$	

The data show the diameter of inhibition zone growth in mm. The diameter of paper disc was 6 mm. LSD – the least significant difference. When significant (P < 0.05), the value of LSD is indicated.

Table 6. Variation and correlation coefficients for the reaction of tested fungi on plant extracts and methods of their preparation

Tabela 6. Współczynniki zmienności i korelacji dla reakcji badanych grzybów na wyciągi roślinne i sposoby ich przygotowania

Fungi	$\bar{x}$	Range	V %	Correlation coefficient (r)											
				Aa	*Ag*	*An*	*Bc*	*Ch*	*Fc*	*Fo*	*Fp*	*Fsa*	*Fso*	*Pch*	*Ss*
Aa	10.28	6-27.67	59.41	-	-	-	-	-	-	-	-	-	-	-	-
Ag	7.25	6-18.33	48.69	-0.12	-	-	-	-	-	-	-	-	-	-	-
An	7.00	6-15.33	39.05	0.04	0.99**	-	-	-	-	-	-	-	-	-	-
Bc	8.39	6-20.00	53.39	0.02	0.82**	0.82**	-	-	-	-	-	-	-	-	-
Ch	8.72	6-18.00	50.41	0.31	-0.20	-0.16	0.31	-	-	-	-	-	-	-	-
Fc	9.28	6-24.00	66.88	0.53	0.50	0.61*	0.39	-0.10	-	-	-	-	-	-	-
Fo	9.95	6-21.67	55.27	0.28	0.16	0.25	0.24	-0.01	0.76**	-	-	-	-	-	-
Fp	10.42	6-22.33	54.79	-0.22	0.64*	0.64*	0.42	-0.30	0.62*	0.57	-	-	-	-	-
Fsa	7.00	6-14.67	35.93	0.03	0.98**	0.99**	0.80**	-0.19	0.59*	0.22	0.635*	-	-	-	-
Fso	7.53	6-16.33	38.47	-0.07	0.95**	0.95**	0.77**	-0.19	0.44	0.06	0.605*	0.96*	-	-	-
Pch	8.81	6-26.67	70.50	0.84**	0.21	0.35	0.39	0.30	0.74**	0.53	0.026	0.32	0.16	-	-
Ss	17.56	6-28.00	57.03	0.26	0.14	0.20	0.03	0.01	0.41	0.20	0.528	0.24	0.28	0.18	-

$\bar{x}$ – mean value of the diameter of inhibition zone growth in mm; V – coefficient of variation;
***, * – significant compatibility of fungi response on tested plant extracts.*
Aa – Alternaria alternata, Ag – Aspergillus glaucus, An – Aspergillus niger, Bc – Botritis cinerea,
Ch – Cladosporium herbarum, Fc – Fusarium culmorum, Fo – Fusarium oxysporum,
Fp – Fusarium poae, Fsa – Fusarium sambucinum, Fso – Fusarium solani, Pch – Penicillium chrysogenum,
Ss – Sclerotinia sclerotiorum

Synthesis of the obtained results (Table 6) showed that the activity of the extracts depended on the species of plants, a method of preparing plant extracts and the sensitivity of fungi selected for the test. It also showed significantly different response of tested pathogens to the applied extracts of various plant species.

Some plant extract have demonstrated a broad range of natural fungicidal effects against post-harvest pathogens. The antifungal activities of essential oils could be applied in the vapor phase for food storage. However, more study is required for vapor-phase application because possible deterioration of the food material could still occur [57].

4. Summary

The obtained results showed that the activity of extracts depend on the plant species, method of preparation and the sensitivity of bacteria and fungi selected for testing.

The results of carried investigations showed that the antimicrobial activity of the plant extracts was more effective against bacteria than fungi, similar to the results of Avato et al. (1997) and Zavala et al. (1997) and Erturk (2006) [2, 22, 70].

The macerate, brew, decoction and essential oils were inhibitory to the growth of all the bacteria and fungi under test. It can be concluded that tested extracts were the source of active substances, which (in varying degree) inhibited the growth of selected strains of bacteria and fungi. Additionally in this study the strongest antibacterial and antifungal activity was manifested by the essential oils. The greatest impact on the antimicrobial activity of extracts could have used raw material, the effectiveness of process of plant extracts preparation, as well as the content the active ingredients characterized by antimicrobial activity against bacteria and fungi.

All the tested essential oils showed the antibacterial and antifungal activity. The highest antibacterial activity was observed with the essential oils of *Lavendula vera,* with larger values of inhibition zone. Essentials oil obtained from *Melissa officinalis* exhibited comparatively weaker antibacterial activity. It is generally accepted that essential oils having higher contents of oxygenated terpenes exhibit potent antibacterial potential [32]. There is evidence in the literature that the essential oils of some *Lamiaceae* plants possess considerable antibacterial activities [7, 12, 17, 26, 34, 42, 46, 47, 53, 66]. However, carried studies have shown that oil of *Lavandula vera*, which most strongly inhibited the growth of bacteria, exhibited the lowest antifungal activity. Among all tested essentials, oil obtained from *Pinus sylvestris* showed the highest antifungal activity.

The most sensitive bacteria against tested plant extracts were *Listeria monocytogenes* and *Micrococcus luteus* (Gram-positive bacteria were more susceptible than Gram-negative bacteria). The tested plant extracts also showed antifungal activity against a wide range of fungi. It strongly inhibited the growth of *Sclerotinia sclerotiorum* and *Fusarium poae*.

In recent years, although technology and medicine have developed extensively, some countries have made it obligatory to use natural products for many different purposes due to decrease in natural richness and drawbacks. Like in many other countries, the plants known by people with health benefits are picked up and used for the treatment of various diseases.

In summary, it can be concluded that the essential oils of different varieties of plants have different spectrum of promising biological properties, which include antibacterial and antifungal properties. The current expansion of research on antimicrobial agents raises hopes that the well-known essential oils, as well as those from new plant varieties may become important class of therapeutically substances.

Due to the apparent increasing resistance of many species of bacteria to antibiotics, the results of the study indicate that it is possible to use plant extracts including essential oils, both in the protection of crop and preservation of food products obtained therefrom.

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References

1. **Adaszyńska M., Swarcewicz M., Markowska-Szczupak A.:** *Comparison of chemical composition and antimicrobial activity of lavender varieties from Poland*. Post. Fitoter, 2, 90–96. (In polish), 2013.
2. **Avato P., Vitali C., Mongelli P., Tava A.:** *Antimicrobial activity of polyacetylenes from Bellis perennis and synthetic derivatives*. Planta Med. 63: 503–507 (1997).
3. **Bakkali F., Averbeck S., Averbeck D., Idaomar M.:** *Biological effects of essential oils – A review*, Food and Chemical Toxicology 46, 446–475 (2008).
4. **Banthorpe D.V., Bates M.J., Ireland M.J.:** *Stimulation of accumulation of terpenoids by cell suspensions of Lavandula angustifolia following pre-treatment of parent cells*. Phytochem. 40, 83–87 (1995).
5. **Baser K.H.C., Demirci B., Kurkcuoglu M., Satil F., Tumen G.:** *Comparative moropholigical and phytochemical characterization of Salvia cadmia and S. smyrnaea*. Pakistan Journal of Botany, 41: 1545–1555 (2009).
6. **Boelens M.H.:** *Chemical and sensory evaluation of Lavandula oils*. Perf Flav. 20, 23–51 (1995).
7. **Bošković M., Baltić Ž.M., Ivanović J., Đurić J., Lončina J., Dokmanović M., Marković R.:** *Use of essential oils in order to prevent foodborne illnesses caused by pathogens in meat*. Tehnologija mesa 54 (1), 14–20 (2013).
8. **Bozin B., Mimica-Dukic N., Simin N., Anackov G.:** *Characterization of the volatile composition of essential oils of some Lamiaceae species and the antimicrobial and antioxidant activities of the entire oils*. Journal of Agriculture and Food Chemistry, 54: 1822–1828 (2006).
9. **Burt S.:** *Essential oils: their antimicrobial properties and potential application in foods-a review*. International Journal of Food Microbiology, 94: 223–253 (2004).
10. **Cantore P.L., Iacobellis N.S., Marco A.D., Capasso F., Senatore F.:** *Antioxidant activity of Coriandrum sativum L. and Foeniculum vulgare Miller Var. vulgare (Miller) essential oils*. Journal of Agricultural and Food Chemistry, 52,7862–7866 (2004).
11. **Cavanagh M.M.A., Wilkinson J.M.:** *Biological activity of Lavender essential oil*. Phytother Res; 16, 301–308 (2002).
12. **Celiktas O.Y., Kocabas E.E.H., Bedir E., Sukan F.V., Ozek T., Baser K.H.C.:** *Antimicrobial activities of methanol extracts and essential oils of Rosmarinus officinalis, depending on location and seasonal variations*. Food Chemistry,100, 553–559 (2007).

13. **Chalchat J.C. Ozcan M.M.:** *Comparative essential oil composition of flowers, leaves and stems of basil (Ocimum basilicum L.) used as herb*. Food Chemistry, 110: 501–503 (2008).
14. **Chami F., Chami N., Tennis S., Trouillas J., Remmal A.:** *Evaluation of carvacrol and eugenol as prophylaxis and treatment of vaginal candidiasis in an immunosuppressed rat model*. J Antimicrob Chemother 54, 909–914 (2004).
15. **Chao S., Young G., Oberg C., Nakaoka K.:** *Inhibition of methicillin-resistant Staphylococcus aureus (MRSA) by essential oils*. Flav Fragr J 2008; 23 (6), 444–449 (2008).
16. **Cong Y., Abulizi P., Zhi L., Wang X., Mirensha M.:** *Chemical composition of the essential oil from Lavandula angustifolia from Xinjiang*, China. Chem Nat Comp. 44, 810–815 (2008).
17. **Delmare A.P.L., Moschen-Pistorello I.T., Artico L., Atti-Serafini L., Exheverrigaray S.:** *Antibacterial activity of the essential oils of Salvia officinalis L. and Salvia triloba L. cultivated in South Brazil*. Food Chemistry, 100, 603–608 (2007).
18. **Dervendzi V.:** *Sovremeno lekuvanje so lekoviti bilki*, Tabernakul, Skopje. 81–83 (1992).
19. **Dorman H.J.D., Deans S.G.:** *Antimicrobial agents from plants: Antibacterial activity of plant volatile oils*. J Appl Microbiol. 88, 308–316 (2000).
20. **Dorman H.J.D.:** *Phytochemistry and bioactive properties of plant volatile oils: Antibacterial, antifungal and antioxidant activities*. PhD thesis. Strathclyde Inst Biomed Sci, University of Strathclyde, Glasgow 1999.
21. **Einhellig F.:** *Allelopathy: Current Status and Future Goals*. Am. Chem. Soc. Symp. Series 582, 1–24 (1995).
22. **Ertürk O.:** *Antibacterial and antifungal activity of ethanolic extracts from eleven spice plants*, Biologia, Bratislava, 61/3: 275–278 (2006).
23. **Exner M.:** *Divergent opinions on surface disinfection: myths or prevention? A review of the literature*. GMS Krankenhaushygiene Interdisziplinar; 2: 1–7 (2007).
24. **Friedman M., Henika P.R., Levin C.E., Mandrell R.E.:** *Antibacterial activities of plant essential oils and their components against Escherichia coli O157:H7 and Salmonella enterica in apple juice*. J. Agr. Food Chem., 52: 6042–6048 (2004).
25. **Ghardi T.A., Mousavi S.L., Sharafi S.M., Alipour Astaneh S.D., Rezaee M.B.:** *Antimicrobial, antioxidant, hematologic and cytotoxic properties of Lavandula angustifolia essential oil*. Modares J Med Sci. 12, 54–58 (2010).

26. **Gören A.C., Topçu G., Bilsel G., Bilsel M., Aydogmus Z., Pezzuto J.M.:** *The chemical constituents and biological activity of essential oil of Lavandula stoechas ssp. stoechas*. Zeitschrift für Naturforschung, 57, 797–800 (2002).
27. **Hammer K.A., Carson C.F., Riley T.V.:** *Antifungal effects of Melaleuca alternifolia (tea tree) oil and its components on Candida albicans, Candida glabrata and Saccharomyces cerevisiae*. J Antimicrob Chemother 53, 1081–1085 (2004).
28. **Hedge C.:** *A global survey of the biogeography of the Labiatae. In Harley RM & Reynolds T(eds) Advances in Labiatae Science*. Royal Botanic Gardens, Kew 7–17 (1992).
29. **Horváth G., Jámbor N., Végh A., Böszörményi A., Lemberkovics E., Héthelyi E., Kovács K., Kocsis B.:** *Antimicrobial activity of essential oils: the possibilities of TLC-bioautography*. Flav Fragr. 25, 178–82 (2010).
30. **Hussain A.I., Anwar F., Rao J.R., Mazumdar A.:** *Antibacterial activity of some Lamiaceae essential oils using resazurin as an indicator of cell growth*, LWT – Food Science and Technology, Volume 44, Issue 4, Pages 1199–1206 (2011).
31. **Hussain A.I., Anwar F., Sherazi S.T.H., Przybylski R.:** *Chemical composition. Antioxidant and antimicrobial activities of basil (Ocimum basilicum) essential oils depends on seasonal variations*. Food Chemistry, 108: 986–995 (2008).
32. **Hussain A.I., Anwar F., Iqbal T., Bhatti I.A.:** *Antioxidant attributes of four Lamiaceae Essential oils*, Pak. J. Bot., 43(2): 1315–1321 (2011).
33. **Hyldgaard M., Mygind T., Meyer R.L.:** *Essential oils in food preservation: mode of action, synergies, and interactions with food matrix components*. Front Microbiogy, 3,12. doi: 10.3389/fmicb.2012.00012, 2012.
34. **Imelouane B., Elbachiri A., Ankit M., Benzeid H., Khedid K.:** *Physicochemical compositions and antimicrobial activity of essential oil of Eastern Moroccan Lavandula dentata*. Int J Agric Biol. 11,113–118 (2009).
35. **Inouye S., Tsuruoka T., Watanabe M., Takeo K., Akao M., Nishiyama Y., Yamaguchi, H.:** *Inhibitory effect of essential oils on apical growth of Aspergillus fumigatus by vapour contact*. Mycoses 43, 17–23 (2000).
36. **Inouye S., Takizawa T., Yamaguchi H.:** *Antibacterial activity of essential oils and their major constituents against respiratory tract pathogen by gaseous contact*. J. Antimicrob. Chemoth., 47: 565–573 (2001).
37. **Inouye S., Uchida K., Yamaguchi H.:** *In-vitro and in-vivo anti-Trichophyton activity of essential oils by vapour contact*. Mycoses 44, 99–107 (2001b).

38. **Jie H., Tao S., Jun H., Shuangyang C., Xiaoqiang C., Guolin Z.:** *Chemical composition, cytotoxic and antioxidant activity of the leaf essential oil of Photinia serrulata*. Food Chemistry, 103: 355–358 (2008).
39. **Jezierska – Domaradzka A., Kuźniewski E.:** *Allelopathic effect of water extracts of Capsella bursa-pastoris (L.) Medik and Stellaria media (L.) Vill on germination and juvenile stages of Ocimum basilicum L. and Origanum majorana L.*, Agricultura, Annales Universitatis Mariae Curie-Skłodowska Vol. LXII (2) Sectio E, 10–16 (2007).
40. **Kalemba D., Kunicka A.:** *Antibacterial and antifungal properties of essential oils*. Curr. Med. Chem., 10: 813–829 (2003).
41. **Karapandzova M., Stefkov G., Trajkovska-Dokic E,. Kaftandzieva A., Kulevanova S.:** *Antimicrobial activity of needle essential oil of Pinus peuce Griseb. (Pinaceae) from Macedonian flora*, Macedonian pharmaceutical bulletin, 57 (1, 2) 25–36 (2011).
42. **Kelen M., Tepe B.:** *Chemical composition, antioxidant and antimicrobial properties of the essential oils of three Salvia species from Turkish flora*. Bioresour. Technol. 99 (10), 4096–4104 (2008).
43. **Koc A.N., Silici S., Ayangil D., Ferahbas A., Cankaya S.:** *Comparison of in vitro activities of antifungal drugs and ethanolic extract of propolis against Trichophyton rubrum and T. mentagrophytes by using a microdilution assay*. Mycoses 48, 205–210 (2005).
44. **Lis-Balchin M.:** *Lavender. The genus Lavandula*. Taylor & Francis, London 2002.
45. **Mahesh B., Satish S.:** *Antimicrobial activity of some important medicinal plant against plant and human pathogens*, World Journal of Agricultural Sciences 4 (S): 839–843 (2008).
46. **Mencherini T., Cau A., Bianco G., Della Loggia R., Aquino R.P., Autore G.:** *An extract of Apium graveolens vardulce leaves: structure of the major constituent, apiin, and its anti-inflammatory properties*. J Pharm Pharmacol 59:891–897 (2007).
47. **Mimica-Dukic N., Bozin B., Sokovic M., Simin N.:** *Antimicrobial and antioxidant activities of Melissa officinalis L. (Lamiaceae) essential oil*. Journal of Agriculture and Food Chemistry, 52: 2485–2489, 2004.
48. **Nurzyńska-Wierdak R.:** *Lemon balm (Melissa officinalis L.) – chemical compositiona and biological activity*. Annales Universitatis Mariae Curie-Skłodowska Lublin – Polonia vol. XXIII (1), 25–35. (In polish), 2013.
49. **Oliva B., Piccirilli E., Ceddia T., Pontieri E., Aureli P., Ferrini A.M.:** *Antimycotic activity of Melaleuca alternifolia essential oil and its components*. Lett Appl Microbiol 37, 185–187 (2003).

50. **Pina-Vaz C., Rodrigues A.G., Pinto E., Costa-de-Oliveira S., Tavares C., Salgueiro L.R., Cavaleiro C., Goncalves, M.J., Martinez-de-Oliveira J.:** *Antifungal activity of Thymus oils and their major compounds*. J Eur Acad Dermatol 18, 73–78 (2004).
51. **Roller S., Ernest N., Buckle J.:** *The antimicrobial activity of high-necrodane and other lavender oils on methicillin-sensitive and -resistant Staphylococcus aureus (MSSA and MRSA)*. J Altern Complement Med. 15, 275–279 (2009).
52. **Rostami H., Kazemi M., Shafiei S.:** *Antibacterial activity of Lavandula officinalis and Melissa officinalis against some human pathogenic bacteria*. Asian J. Biochem. 7 (3), 133–142 (2012).
53. **Rota M.C., Herrera A., Martinez R.M., Sotomayor J.A., Jordan M.J.:** Antimicrobial activity and chemical composition of *Thymus vulgaris*,*Thymus zygis* and *Thymus hyemalis* essential oils. Food Control, 19, 681–687 (2008).
54. **Sas-Piotrowska B., Piotrowski W.:** *Impact of plant extracts on vitality and root healthiness of Leguminous plants inoculated by Fusarium oxysporum (Schl.)*, Middle Pomeranian Scientific Society of the Environment Protection, 191–202 (2003).
55. **Sas-Piotrowska B., Piotrowski W., Kaczmarek-Cichosz R.:** *Longevity and healthiness of oat (Avena sativa L.) seeds treated with plant extracts.* J. Plant Protection Res. 45 (3): 181–194 (2005).
56. **Serban E.S., Ionescu M., Matinca D., Maier C.S.,Bojita M.T.:** *Screening of the antibacterial and antifungal activity of eight volatile essential oils*. Farmacia. 59, 440–446 (2011).
57. **Shaaban H.A.E., El-Ghorab A. H., Shibamoto T.:** *Bioactivity of essential oils and their volatile aroma components*. Review, The Journal of Essential Oil Research, 24(2), 203–212 (2012).
58. **Shabbir M. K., Nadeem R., Mukhtar H., Anwar F., Mumtaz M.W.:** *Physico-chemical analysis and determination of various chemical constituents of essential oil in Rosa centifolia*. Pakistan Journal of Botany, 41(2): 615–620 (2009).
59. **Shelef L.A.:** *Antimicrobial effects of spice*s. J. Food Safety 6: 29–44 (1983).
60. **Sienkiewicz M., Denys P., Kowalczyk E.:** *Antibacterial and immune-stimulatory effect of essential oils.* Int Rev Allergol Clin Immunol. 17, 40–44 (2011).
61. **Silva M.R.R., Oliveira J.G. Jr, Fernandes O.F.L., Passos X.S., Costa C.R., Souza L.K.H., Lemos J.A., Paula J.R.:** *Antifungal activity of Ocimum gratissimum towards dermatophytes*. Mycoses 48, 172–175 (2005).

62. **Sivropoulou A., Kokkini S., Lanaras T., Arsenakis M.:** Antimicrobial *activity of mint essential oils*. Journal of Agricultural and Food Chemistry, 43, 2384–2388 (1995).
63. **Skocibusic M., Bezic N., Dunkic V.:** *Phytochemical composition and antimicrobial activity of the essential oils from Satureja subspicata Vis. Growing in Croatia*. Food Chemistry, 96: 20–28 (2006).
64. **Soković M., Griensvbeni J.L.D.:** *Antimicrobial activity of essential oils and their components against the three major pathogens of the cultivated button mushroom, Agaricus bisporus*. Eur J Plant Pathol 116, 211–224 (2006).
65. **Stanojević D., Čomić L.J., Stefanović O., Solujić Sukdolak S.:** *In vitro synergistic antibacterial activity of Melissa officinalis L. and some preservatives*. Span. J. Agric. Res. 8 (1), 109–115 (2010).
66. **Tepe B., Akpulat H.A., Sokmen M., Daferera D., Yumrutas O., Aydin E.:** *Screening of the antioxidative and antimicrobial properties of the essential oils of Pimpinella anisetum and Pimpinella flabellifolia from Turkey*, Food Chemistry, 97, 719–724 (2006).
67. **Tóth J., Mrlianová M., Tekel'ová D, Koreňová M.:** *Rosmarinic acid – an important phenolic active compound of lemon balm (Melissa officinalis L.)*. Acta Facult. Pharm. Univ. Comenianae 50 (1), 139–146 (2003).
68. **Tyszyńska-Kownacka D., Starek T.:** *Herbs in polish house*. Wydawnictwo Warta, Warsaw. (In polish), 1989.
69. **Zaika L.L.:** *Spices and herbs: their antimicrobial activity and its determination*. J. Food Safety 9, 97–118 (1988).
70. **Zavala M.A., Perez S., Perez R.M.:** *Antimicrobial screening of some medicinal plants*. Phytother. Res. 11: 368–371 (1997).

Przeciwbakteryjna i przeciwgrzybowa aktywność wyciągów roślinnych

Streszczenie

W doświadczeniach laboratoryjnych oceniono aktywność przeciwdrobnoustrojową wodnych wyciągów roślinnych (wywar, napar, macerat) oraz olejków eterycznych na zahamowanie wzrostu chorobotwórczych kolonii bakterii i grzybów. Do przygotowania ekstraktów i olejków wykorzystano różne części następujących roślin: lawenda wąskolistna (*Lavandula vera* L.), melisa lekarska (*Melissa officinalis* L.), sosna zwyczajna (*Pinus sylvestris* L.). Przeciwdrobnoustrojowe właściwości wyciągów i olejków eterycznych testowano na bakteriach: *Bacillus subtilis, Escherichia coli, Listeria monocytogenes, Micrococcus luteus, Staphylococcus aureus* i grzybach: *Alternaria alternata*, *Aspergillus*

glaucus, *Aspergillus niger*, *Botritis cinerea*, *Cladosporium herbarum, Fusarium culmorum*, *Fusarium oxysporum*, *Fusarium poae, Fusarium sambucinum*, *Fusarium solani*, *Penicillium chrysogenum*, *Sclerotinia sclerotiorum*.

Analiza uzyskanych wyników wykazała, że aktywność wyciągów zależała od gatunku rośliny, sposobu przygotowania wyciągów oraz wrażliwości mikroorganizmów wybranych do badań. Wykazano istotnie różną reakcję testowanych patogenów na wyciągi z poszczególnych gatunków roślin.

Zarówno ekstrakty jak i olejki eteryczne były źródłem substancji aktywnych, które w różnym stopniu hamowały wzrost i rozwój wybranych szczepów bakterii oraz grzybów. Na aktywność przeciwdrobnoustrojową ekstraktów i olejków mogły wpływać: użyty surowiec, efektywność procesów otrzymania wyciągów, a także zawartość składników aktywnych o działaniu antybakteryjnym i przeciwgrzybowym. Działanie hamujące wzrost drobnoustrojów przez ekstrakty roślinne zależało od sposobu przygotowania wyciągów, który prawdopodobnie wpłynął na kształtowanie się różnych profili związków chemicznych.

Olejki eteryczne charakteryzowała największa aktywność przeciwdrobnoustrojowa wobec większości badanych mikroorganizmów, aniżeli wodnych wyciągów roślinnych. Najwyższą aktywnością przeciwbakteryjną, a najniższą przeciwgrzybową wyróżniał się olejek pozyskany z lawendy wąskolistnej. Natomiast najlepszymi właściwościami przeciwgrzybowymi charakteryzował się olejek uzyskany z sosny zwyczajnej.

Spośród badanych mikroorganizmów najwyższą wrażliwość na zastosowane ekstrakty roślinne wykazały szczepy z rodzajów: *Listeria monocytogenes, Micrococcus luteus* oraz *Sclerotinia sclerotiorum*, *Fusarium poae.*

Słowa kluczowe:
aktywność przeciwdrobnoustrojowa, wyciągi roślinne, olejki eteryczne, metoda dyfuzyjna

Keywords:
antimicrobial activity, plant extracts, essential oils, disc diffusion method

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Problems of the Integrated Urban Water Management. The Case of the Poznań Metropolitan Area (Poland)

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1. Introduction

The European water policy was based on the principles of Integrated Water Resources Management (IWRM), assuming e.g. that a hydrographic catchment constituted of the primary area for all planning and decision-making activities. In turn, the system of spatial planning in Europe was based on administrative boundaries, hindering a holistic approach to water resources management within the limits of catchments. Carter [1] indicated that frequently there is a lack of cooperation in terms of water resources management between communes or regions within one catchment.

To change the water management towards a more integrated management system a comprehensive revision of water policy at all planning level is required. This is currently on-going in many countries, e.g. Poland, where among others the rules of Water Framework Directive (WFD) [4] and Floods Directive [5] were introduced into Polish law and implemented [12, 14, 17]. Conventional water management policy needs to be modified including through introducing integrated approaches, developing the laws, regulations and institutions, and also interventions across sectors and scales to manage water resources in a more economically productive, socially acceptable and environmentally sustainable fashion [8]. Hoff [9] as crucial measures mentioned: inclusion of the full water resource management (containing also green water) instead of only blue water management, climate change mitigation measures in each region must take into account water resources availability, more sustainable trade strategy must be developed and implemented to reduce its negative impacts on water systems.

Integrated Urban Water Management (IUWM), nested within the broader framework of Integrated Water Resouces Management (IWRM) is one of the potential solutions, but it can be achieved only with political will, governance and a good coherent water policy [2, 3].

This study focused on the water resources management problems of one CEE city region – Poznań Metropolitan Area (PMA) (Poland). The objective of the study was to analyse the strategic and planning documents to verify their completeness in terms of the main problems of integrated urban water management in PMA.

2. Methods

Analyses were conducted on planning and strategic documents in spatial planning and water resources management at three planning levels: local, regional and national, based on the Poznań Metropolitan Area (PMA) (Poland). The study focused on local spatial development plans, which were local legal acts and determined land functions and land management. Based on the provisions of the acts the range of the biologically active area index was specified as indicated in individual documents.

PMA is located in Odra river basin, in the water region of the Warta administered by the Regional Water Management Board (RZGW) in Poznań (Fig. 1 and 2). (Only a small part of the Kościan commune is located in the water region in the Central Odra administered by RZGW in Wrocław). Delimitation of the PMA was performed by regional planning office Wielkopolskie Biuro Planowania Przestrzennego (WBPP). The final boundaries of the PMA take into account among others the water economic area of the Poznań Warta Catchment. The delimited PMA comprises 45 communes together with Poznań. It includes 10 cities – centers of district and 15 other small towns . The PMA area (6.2 thousand km^2) accounts for approx. 21% area of the Wielkopolska province, while the PMA population (1.3 million) – 39% province population.

Fig. 1. Poznań Metropolitan Area on the background of polish administrative division (województwa – provinces) and water regions (RZGW – Regional Water Management Boards)

Rys. 1. Położenie Poznańskiego Obszaru Metropolitalnego na tle podziału administracyjnego na województwa i regionalne zarządy gospodarki wodnej (RZGW)

It needs to be stressed that currently the PMA is only the functional area of Poznań (area of a special spatial management policy) and not a metropolitan area. Thus, the boundaries of the metropolitan area should be first specified in the concept of national spatial management.

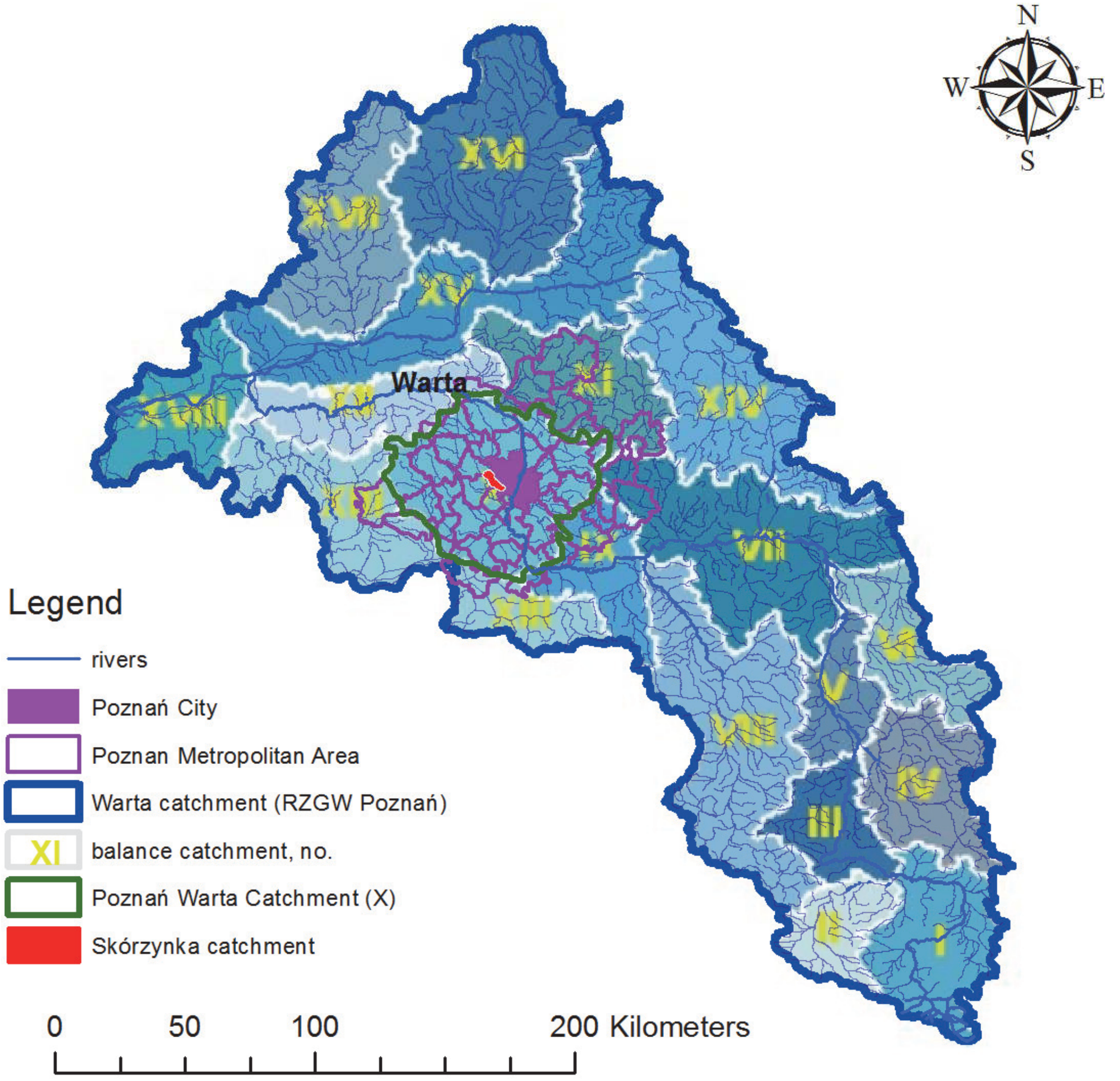

Fig. 2. Poznań Metropolitan Area and Skórzynka catchment on the background of Warta cachment (Regional Water Management Board – RZGW Poznań)
Rys. 2. Położenie Poznańskiego Obszaru Metropolitalnego i zlewni Skórzynki na tle zlewni bilansowych w zlewni Warty (RZGW Poznań)

The main issue was detailed analysis based on the Skorzynka river catchment covering about 10 km^2. The Skórzynka catchment is located within the rural communes of Tarnowo Podgórne, Dopiewo, and the city of Poznań, covering 21% area of its recipient – the Junikowski Stream. The Junikowski Stream as an uniform water body is a part of the consolidated surface water body No. W1007 – the Warta river from the Kopla to the Różany Potok. The Junikowski Stream was defined as a strongly altered water body and it was threatened with failure to reach environmental objectives. Due to the strong morphological changes temporal derogations were forecasted due to a lack of technical facilities and disproportional costs connected with watercourse renaturation (a strongly urbanized area). In the past the Skórzynka channel in the non-urbanized area was artificially deepened and it constituted a part of the land improvement system. At present the watercourse constitutes a recipient of rainwater from the catchment area.

The climate in PMA is characterized by variability of rainfall in time and space. Based on the climatic data provided by the climatic station of Poznań Ławica from 2000 to 2010, annual precipitation varied from 345 (2003) to 586 (2010) mm with an average value of 520 mm per year, which corresponds to the most arid regions of Europe. PMA is a region with the highest needs of developing water retention and the greatest need for irrigation. On the other hand, floodings are common natural disaster. The analysed area is found in the zone of lowest runoff in Poland. Mean unit surface flow for the Warta in Poznań is 4.1 $dm^3/s \cdot km^2$, with extreme values of 0.5–33.1 $dm^3/s \cdot km^2$. Low runoff values result both from low precipitation levels and low water retaining capacity of this area. It is also characterized by high values of flow irregularity rates, measured by the ratio of maximum to minimum flows. On average water stages and flows higher than the annual means are observed from December to May. The local water resources of the Regional Water Management Board in Poznan per capita amount to 0.86 thousand m^3 (Poland – 1.59) [7, 10, 16].

3. Results and discussion

3.1. The issue of natural and administrative boundaries

The primary problem in water resources management is connected with the natural catchment system, which is not the administrative division. For the needs of management of integrated water resources of surface and underground waters in the catchment system in the Warta region 18 balance catchments of. PMA were incorporated in catchments no.:

- X – Poznańska Zlewnia Warty (Poznań Warta Catchment) (the Poznań Region);
- XI – Wełna (the Wągrowiec and Gniezno Region);

- XII – Warta from Obrzycko to Noteć (the Szamotuły Region);
- XIII – Obra (the Grodzisk Wielkopolski, Nowy Tomyśl and Kościan Region);
- IX – Warta from Prosna to Kanał Mosiński (the Środa Wielkopolska and Śrem Region);
- VII – Warta from Ner to Prosna (the Września Region) (Fig. 2).

PMA is located within 31 consolidated[1] bodies of surface water, which are divided into 139 uniform bodies of surface water, defined in WFD (art. 2 item. 10) while only 7 consolidated bodies of surface water are found whole within the limits of PMA. The preliminary evaluation of anthropogenic impact for uniform water bodies, comprising pressures connected with water intakes, morphological as well as point and area, showed that catchments within PMA are threatened with failure to reach environmental objectives (mentioned in art. 4 of WFD), which resulted mostly from the threat to morphological and quality status, and partly the hydrological status. In the National water and environmental program [15] a vast majority – 121 (87%) – was considered as threatened uniform bodies of surface water.

3.2. Cost of planned measures action to achieve environmental objectives of WFD

In the National Water and Environmental Program [15] for each consolidated body of surface water there were planned measures to achieve environmental objective of WFD divided into 3 groups: part A (listed in Annex VI of WFD), part B (listed in Annex VI of WFD) and other supplementary activities. For each measure in the program the planned costs were also shown.

As funds that is required to enhance the IWRM in the PMA (in the analyzed consolidated surface water bodies) approx. 200 million Euro were forecasted to cover actions of group A, while approx. 6 million Euro – for actions of group B. Moreover, approx. 40 million Euro were expected to cover costs of supplementary actions. Jointly forecasted costs of actions were almost 250 million Euro, accounting for 20 thousand

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[1] In Poland small bodies of surface water (called uniform) were combined to consolidated bodies of surface water to prepare specific action (measures) program for all of them.

Euro per 1 km^2. High costs from group A were connected first of all to the investments indicated in the National Program of Municipal Sewage Treatment [11]. Similarly, a considerable part in outlays for primary actions of group B were connected to activities resulting from the need of regulating the sewage management system, e.g. the construction of the treatment sewerage system in the non-agglomeration area. In case of auxiliary actions the greatest costs were connected to the implementation of the afforestation program.

The primary source of funding for actions aiming at improvement of water stages in the years 2007–2013 included:

- Operation Program Infrastructure and Environment 2007–2013;
- Development Program for Rural Areas 2007–2013;
- Operation Program Sustainable Development for Fishery Sector and Coastal Fishing Areas 2007–2013;
- Provincial Fund for Environmental Protection and Water Management in Poznań;
- Wielkopolska Regional Operation Program 2007–2013;
- European Territorial Community (programs of transboundary, transnational and inter-regional cooperation) 2007–2013;
- European Fishery Fund.

In successive years a major source of funding will be provided for Poland in the new EU budget for the years 2014–2020.

3.3. Significant water management problems

The review of significant water management problems for the Warta region for balance catchments within PMA indicated:

- excessive disposal of surface water resources (VII, IX, X, XIII);
- shortages of available resources of underground and surface waters (VII, IX, X, XIII);
- disadvantageous changes in the regime of surface waters (VII, X, XI, XII, XIII);
- discharge of untreated and insufficiently treated municipal and industrial sewage and cooling waste water (VII, X, XII, XIII);
- insufficient sanitation of rural and recreation areas (VII, X, XIII);
- pollutants from agricultural sources (VII, X, XIII);

- disturbed migration of salmon species (XI);
- littering in river and stream channels (VII, IX, X, XI, XII, XIII);
- discharge of pollutants from fish ponds, littering of rivers and streams (X, XI, XII, XIII);
- threat to quality of underground waters not isolated by impermeable deposits (XII);
- changes in natural hydromorphological conditions of surface waters by hydraulic engineering structures and regulation of rivers and streams (VII, X, XI, XII, XIII);
- loss of natural retention of catchments caused e.g. by compact building development of town areas, changes in land use in river valleys, e.g. from agricultural and forest to built-up areas (VII, IX, X, XI, XIII);
- mining land use (VII);
- hazard to water-dependent ecosystems (VII, X, XIII);
- flood control (VII, IX, X, XII, XIII);
- drought prevention (VII, IX, X, XI).

Moreover, PMA included particularly threatened areas, specified by the Poznań RZGW Director, as identified by the Directive 91/676/EEC of 12 December 1991 on water protection against pollution caused by agricultural nitrates [6] (the nitrate directive) (4 catchments in 14 communes).

The above mentioned 121 threatened uniform water bodies were subjected to derogation, i.e. in their area it is expected that deviations will be needed from the basic requirements of environmental objectives as a result of:

- extension of deadlines to reach good water status to 2021 or 2027 (art. 4 item. 4 Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy – WFD) – in the case of a lack of technical facilities to implement actions, disproportional action implementation costs or natural conditions preventing improvement of status in some waters;
- specification of less strict objectives (art. 4 item 5 WFD) – in the case of a lack of technical facilities to implement actions, disproportional action implementation costs;

- failure to reach objectives due to the realization of new investments (art. 4 item 7 WFD) – in the case of new changes in physical characteristics of uniform water bodies or new forms of sustainable economic activity.

3.4. Analysis of planning and strategic documents

In Polish spatial management the most important wee two rules:

1. **Spatial order**, i.e. such space management, which forms a harmonious whole and within ordered relations takes into consideration all functional, socio-economic, environmental, cultural as well as composition and aesthetic conditions and requirements (art. 2.1. *Act of 27 March 2003 on spatial planning and land development* (SPaLD Act) [20].
2. **Sustainable development**, i.e. such socio-economic development, in which a process of integration occurs between political, economic and social actions, with the maintenance of natural equilibrium and sustainability of basic natural processes, in order to guarantee the potential to meet the basic needs of individual communities or citizens of both the present and future generations (art. 3 point 50 of the *Act of 27 April 2001 on the Environmental Protection Law* (EPL Act) [19].

Unfortunately, Polish legal act did not contain a definition of IWRM or IUWM, contrary to the sustainable development principle, which was written even into the Constitution.

Spatial planning comprises three levels: local (communes), regional (provinces) and national. In contrast, planning water management in practice is executed at only two levels (Table 1.). The basic problem in the coordination of these two scales of action is connected with the boundaries of areas covered by planning. Poland is divided into 16 provinces [Polish "województwo"] (i.e. administrative regions) and 7 water regions (Regional Water Management Boards) (Fig. 1). The foundation for spatial development is the administrative division, while water management is based on the division into areas of river basins, water regions and catchments.

In planning water resources all activities are limited to the requirements of WFD. On the other hand strategic documents are associated with European Union Strategy Europe 2020 and financial perspectives for 2014–2020. The last years in Poland new management system was introduced. This implicates changes in strategic and planning document at regional level. One of crucial goals in new strategies is to provide spatial order (Strategic area: Effective and efficient state). One of the major challenges in this broad task is to ensure proper water management as part of biodiversity, but also as the basis for regional and economic development. Accordingly strategic documents sustainable water management are also important for flood protection and have close links with the spatial policy and spatial order. In documents, there are also problems of water scarcity mentioned, water degradation, and availability of drinking water. It also highlights the need to introduce in water management planning documents: water retention programs, stormwater management in urban areas, the principle of recovery of the costs of water services in accordance with the polluter-pays principle and incentives for users to make use of water resources more efficient. Implementation of a new water pricing policies to support financing of water and taking into the account all the main sectors (municipal, industry, agriculture) is planned for 2012–2015. It is also assumed to reduce water consumption in the economy, rational management of agricultural production and fishing. It is important to continue to invest in water conservation, water and sewage. Actions will be taken to manage urban environment and adopt to climate change. All activities aimed at minimizing the risk of flooding will be included in the flood risk management plans. The plans place particular emphasis on prevention, protection and proper state security, including flood forecasts and early warning systems, and take into account the characteristics of the river basin or sub-basin. They may include measures for sustainable spatial development, for effective water retention and controlled flooding of certain areas (e.g. polders, dry reservoirs) in case of a flood. Infrastructure, warning and monitoring activities (development of small and large retention, proper maintenance of rivers, restoration of river channels and wetlands, effective flood warning system) are also planned.

The introduction of modern planning system based on GIS should resolve the issue of permits for construction in floodplains. Speed up decision-making process and reduce the administrative barriers in the field of risk management requires, inter alia, effective water management in river basin system. All planned actions should be integrated with spatial development plans. Inclusion of planning documents at the all planning levels of areas at risk of flooding, according to flood hazard maps is organized for

2012–2020. In addition, it is assumed to introduce building standards for reducing losses associated with natural disasters (2012–2015).

Table. 2. A comparison of levels of planning in spatial planning and water resources management
Tabela. 2. Porównanie poziomów planowania w planowaniu przestrzennym i w planowaniu w gospodarowaniu wodami

		Spatial planning	Planning in water resources management	Strategic documents
		Name of document (individual responsible for development of a project)		
level of planning	national	Concept for national spatial development (2030) (Minister of Regional Development)	National water and environmental program, including the division into areas of river basins (President of the National Water Management Authority)	Long-term national development strategy (2030) (Minister of Administration and Digitization)
		Programs comprising national government tasks for the realization of public investments on the national scale (ministers and competent central government administrative bodies)	Water resources management plan in the area of a river basin (President of the National Water Management Authority)	Mid-term national development strategy (2020) (Minister of Regional Development)
			Flood risk management plan (President of the National Water Management Authority)	9 Integrated development strategies, e.g. and Energy security and Environment (competent ministers, e.g. Minister of Economy)
			Drought prevention plan in the area of a river basin (President of the National Water Management Authority)	
	regional	Provincial spatial development plans and Spatial development plans of the metropolitan area comprising its part (2020) (Speaker of the Provincial Parliament)	Drought prevention plan in water regions (Directors of Regional Water Management Boards)	Development strategy of the voivodship (2020) (Speaker of the Provincial Parliament)
			Water use conditions for waters of a water region (Directors of Regional Water Management Board)	
	local	Study on the conditions and directions of spatial development (borough leader, mayor or president of a city)	Water use conditions for waters of a catchment (Directors of Regional Water Management Board)	Development strategy of the commune (borough leader, mayor or president of a city)
		Local spatial development plan (borough leader, mayor or president of a city)		

Currently, the new rules of strategic management taking into account basic elements of IWRM must be implemented in planning documents at local and regional level. A change of legislation is also required.

3.5. Role of local spatial development plans in IUWM

Land function, allocation of public investments as well as types of management and conditions of land building development are specified in the local spatial development plan (local plan) (art. 4. of SPaLD Act), which is an act of local law. Moreover, local plans obligatorily specify e.g. principles of environmental protection, nature conservation and protection of cultural landscape, boundaries and types of land development or protected objects, specified on the basis of separate regulations, including e.g. those at risk of floods. The draft of the local plan has to be agreed on with the provincial governor, the provincial management board and the board of the county in the field of respective central government and local government tasks and with other competent organs, among which the legislator did not directly mention the director of the Regional Water Management Board (art. 17. of SPaLD Act).

This study analyzed 38 binding local plans, passed in the years 1995–2012, with the total area of 165 ha. They covered varied areas ranging from 0.03 ha to 31.7 ha. The smallest plans with an area of up to 1 ha predominated strongly (16 local plans), in extreme cases developed for one plot. Mean area of the analyzed plans was 4.3 ha. These numbers show that only in several percent of cases we may talk of the establishment of spatial order for a certain greater functionally coherent area. Plans being a result of adaptation to wishes of individual investor predominate.

In the analyzed local plans, the basic land use is single-family housing development, although in numerous cases also economic activity, first of all harmless services, is also admissible as a supplementary function. A detailed qualitative analysis of binding local plans was conducted just for local plans concerning single-family housing development (a total of 25 plans). Analyzed plans concerned first of all previously agriculturally utilized areas.

Among the investigated plans only 40% considered the index of minimum share of biologically active area. For housing development with admissible economic activity this index was as low as 20%. In the case of one local plan from 2001 for housing development this index was only 25%. Most frequently for housing and service development this index ranges from 30 to 60%, which indicates very high variation and a lack of generally accepted guidelines.

Based on the Skórzynka catchment, it may be stated that frequently there is no correlation of investment activity connected with housing development with the regulation of water and sewage management. As a consequence of insufficient technical infrastructure it reaches a threshold value, which limits further development and causes financial losses of inhabitants as a result of flooding. According to the threshold theory proposed by Malisz [13], exceeding these thresholds is connected with considerable financial outlays. They may be avoided in the case of consistent water resources management within a catchment, conducted across administrative divisions.

4. Conclusion

The result described in the paper demonstrate that the polish planning and strategic documents at national level take account of the main pillars of Integrated Water Resources Management. Although IWRM is not explicitly defined in these documents. Problems can arise in the implementation phase, e.g. by implementation of a new water pricing policies. More and more noticeable is the lack of law on metropolitan areas (division of responsibilities and tasks). New rules of strategic management must be implemented now in planning documents at local and regional level. Especially at the local level, it may prove a barrier to the high costs of planned activities, and a low level of understanding of the integrated approach. It is particularly important to take account of flood risk map.

Realization of water management within the boundaries of the catchment is possible only across administrative divisions. The required dialogue of communes located upstream and downstream of the watercourse is hindered by the differing interests of the central city (the core of the metropolitan area) and suburban communes (particularly rural and town and rural).

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Literatura

1. **Carter J.**: *Spatial planning, water and the Water Framework Directive: insights from theory and practise*. The Geographical Journal. 173(4), 330–342 (2007).
2. **Chen D. Ch., Maksimovic C., Voulvoulis N.:** *Institutional capacity and policy options for integrated urban water management: a Singapore case study*. Water Policy. 13(1), 63–68 (2011).
3. **De Graaf R. E., Dahm R. J., Icke J., Goetgeluk R. W., Jansen S.J.T., Van De Ven F.H.M.:** *Receptivity to transformative change in the Dutch urban water management sector*. Water Science & Technology. 60(2), 311–320 (2009).
4. Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (L 327/1 of *22.12.2000*).
5. Directive 2007/60/EC of the European Parliament and the Council of 23 October 2007 on the assessment and management of flood risks (L 288/27 of 6.11.2007).
6. Directive 91/676/EEC of the European Parliament and the Council of 12 December 1991 on water protection against pollution caused by agricultural nitrates (L 375 of 31.12.1991)
7. *Europe's environment. The fourth assessment*. European Environment Agency. Copenhagen. 2007.
8. **Gourbesville P.:** *Challenges for integrated water resources management*. Physics and Chemistry of the Earth. 33, 284–289 (2008).
9. **Hoff H.:** *Global water resources and their management*. Current opinion in Environmental Sustainability. 1, 141–147 (2009).
10. **Kowalczak P.:** *Hierarchia potrzeb obszarowych małej retencji w dorzeczu Warty. Hierarchy of regional requirements of small-scale retention in the Warta catchment.* [In Polish], IMGW. Warszawa 2001.
11. *Krajowy program oczyszczania ścieków komunalnych. The National Programme for Municipal Waste Water Treatment.* [In Polish], KZGW. Warszawa 2011.
12. **Królikowska J., Królikowski A.:** *Opłaty za odprowadzanie wód opadowych – potrzeby i możliwości. Fees for a Storm Water Discharge – Needs and Possibilities.* [In Polish], Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1143–1152 (2013).
13. **Malisz B.:** *Ekonomika kształtowania miast. Economics of city shaping.* [In Polish], Warszawa 1963.

14. **Mrozik K., Przybyła Cz.:** *An attempt to introduce cultivation and planning measures into the planning decision making process in order to improve water retaining capacity of river catchment*. Pol. J. of Environ. Stud. 22(6), 1767–1773 (2013).
15. *Program wodnośrodowiskowy kraju. National Water and Environmental Program*. [In Polish], KZGW, Warszawa 2010.
16. **Przybyła Cz., Bykowski J., Mrozik K., Napierała M.:** *Rola infrastruktury wodno-melioracyjnej w procesie suburbanizacji. The Role of Water and Drainage System Infrastructure in the Process of Suburbanization.* [In Polish], Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 769–786 (2011).
17. **Savenije H.H.G., Van der Zaag P.:** *Integrated water resources management: Concepts and issues*. Physics and Chemistry of the Earth. 33, 290–297 (2008).
18. Ustawa z dnia 18 lipca 2001 r. Prawo wodne [Dz. U. z 2012 r. poz. 145 ze zm.]. The Act of 18 July 2001 The Water Act (The Journal of Law of 2012, item 145 with later amendments) [In Polish].
19. Ustawa z dnia 27 kwietnia 2001 r. Prawo ochrony środowiska [Dz. U. z 2008 r. nr 25 poz. 150 ze zm.]. The Act of 27 April 2001 The Environmental Protection Act (The Journal of Law of 2008, no. 25, item 145 with later amendments) [In Polish].
20. Ustawa z dnia 27 marca 2003 r. o planowaniu i zagospodarowaniu przestrzennym [Dz. U. z 2012 r. poz. 647 ze zm.]. The Act of 27 March 2003 on planning and spatial development (The Journal of Law of 2012, item 647 with later amendments) [In Polish].

Problemy zintegrowanego zarządzania zasobami wodnymi na terenach zurbanizowanych na przykładzie Poznańskiego Obszaru Metropolitalnego

Streszczenie

Zintegrowane zarządzanie zasobami wodnymi na terenach zurbanizowanych (ang. IUWM – Integrated Urban Water Management) jest częścią europejskiej polityki wodnej opierającej się na zasadach zintegrowanego zarządzania zasobami wodnymi (ang. IWRM – Integrated Water Resources Management), która zakłada m. in., że zlewnia hydrograficzna stanowi podstawowy obszar wszelkich działań planistycznych i decyzyjnych. Z kolei system planowania przestrzennego w Europie opiera się na granicach administracyjnych, co utrudnia holistyczne podejście do zarządzania zasobami wodnymi w granicach zlewni. Zatem w celu realizacji IUWM niezbędna jest dobra wola polityczna, właściwe zarządzanie i spójna polityka wodna.

Niniejsza praca koncentruje się na problemach zarządzania zasobami wodnymi w Poznańskim Obszarze Metropolitalnym (POM), a jej głównym celem jest analiza dokumentów planistycznych i strategicznych pod kątem ich podejścia do problemów IUWM oraz wskazanie potencjalnych rozwiązań. Według delimitacji zaproponowanej przez Wielkopolskie Biuro Planowania Przestrzennego POM obejmuje 45 gmin wraz z Poznaniem. W jego skład wchodzi 15 miast powiatowych i 15 pozostałych miast. Powierzchnia POM stanowi ok. 21% powierzchni województwa wielkopolskiego. Szczegółowe analizy dotyczyły zlewni Skórzynki zlokalizowanej na terenie miasta Poznania oraz gmin wiejskich Tarnowo Podgórne i Dopiewo. Zlewnia Skórzynki zajmuje 21% powierzchni swojego recypienta – Potoku Junikowskiego. Potok Junikowski został określony jako silnie zmieniona część wód i jest zagrożony nieosiągnięciem celów środowiskowych. Ze względu na silne zmiany morfologiczne przewiduje się dla niego derogacje czasowe z powodu braku możliwości technicznych oraz dysproporcjonalne koszty związane z renaturyzacją cieku (obszar silnie zurbanizowany).

W pracy wykorzystano dokumenty z trzech poziomów planowania (lokalnego, regionalnego i krajowego), koncentrując się przede wszystkim na miejscowych planach zagospodarowania przestrzennego, które są aktami prawa miejscowego i decydują o przeznaczeniu i sposobie zagospodarowania przestrzeni. W pracy przeanalizowano łącznie 38 obowiązujących planów miejscowych uchwalonych w latach 1995–2012 o łącznej powierzchni 165 ha. W planach dominowało przeznaczenie na budownictwo mieszkaniowe. Często jednak dopuszczano jednocześnie jako funkcję uzupełniającą nieuciążliwe usługi. Tylko 40% z analizowanych planów uwzględniało wskaźnik powierzchni i biologicznie czynnej.

Wykonane analizy potwierdzają, że dokumenty planistyczne i strategiczne na poziomie krajowym uwzględniają zasady IWRM, pomimo braku jednoznacznej definicji tej polityki. Problemy mogą się jednak pojawić na etapie implementacji. Jednym z nich jest brak ustawy metropolitalnej, która mogłaby złagodzić konflikty pomiędzy gminami w strefie suburbanizacji a rdzeniem ośrodka metropolitalnego – głównym ośrodkiem miejskim.

Słowa kluczowe:
zintegrowane zarządzanie zasobami wodnymi na terenach zurbanizowanych, Poznański Obszar Metropolitalny, planowanie w gospodarowaniu wodami, planowanie przestrzenne

Keywords:
Integrated Urban Water Management (IUWM), Poznań Metropolitan Area, Planning in water resources management, spatial planning

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Alternative Fuel Production Based on Sewage Sludge Generated in the Municipal Wastewater Treatment

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1. Introduction

One of the most interesting types of waste which can be used in power industry in the most effective and environmentally friendly way is the sewage sludge produced in municipal wastewater treatment plants [9,10]. It is estimated that sewage sludge constitutes approximately 3% of the volume of all treated wastewater. Extension of sewerage networks and construction of new wastewater treatment plants resulted in a rapid increase in the sewage sludge volume and caused problems with its disposal [3].

The above-mentioned issues constitute a problem mainly in the EU Member States, including Poland, where sewerage networks have been considerably extended in the recent years. The EU Directives 86/278/EEC [2] and 99/31/EC [1] significantly restrict the use of sewage sludge in agriculture and impose a ban on its storage. Therefore, seeking new solutions for safe sewage sludge disposal becomes a necessity. The main problems related to sewage sludge management include: high sludge humidity, odour emission, concentration of heavy metals and other potentially hazardous substances. These factors make the utilization of sewage sludge one of the most difficult processes of environment protection [5]. Even though the use of sewage sludge as an agricultural fertilizer may have a beneficial effect on the environment, it may also negatively influence people and soil productivity [5,7,11,13].

Presently, the most common methods of sewage sludge disposal include the use for agricultural purposes and storage [4]. Sewage sludge is deposited in landfills designed exclusively for this purpose, in lagoons or together with municipal waste.

Thermal methods of sewage sludge utilization have recently been drawing more and more attention [8]. In the field of sludge management this tendency, widespread in Europe, is governed by the following hierarchy of priorities: avoidance, minimization, recycling and application of thermal methods with energy recovery.

Thermal processes enable a significant sewage sludge mass and volume reduction. The content of heavy metals in sewage sludge prevents its use in agriculture. Additionally, the fact that there are no lands suitable for agricultural use situated in the vicinity of municipal wastewater treatment plants encourages the development of thermal methods. The application of thermal methods of sewage sludge utilization depends on the sludge properties: the heat of combustion (calorific value) and sludge composition (including the humidity level). The calorific value of crude sludge equals approximately 17 MJ/kg, of activated sludge – about 15 MJ/kg and of stabilized sludge – roughly 11 MJ/kg. Thermal energy contained in sewage sludge can be recovered through the combustion process carried out in combustion plants designed for the treatment of municipal wastewater [6, 16] or through the process of co-combustion with other energy carriers carried out e.g. in power plants, thermal power stations or municipal waste combustion facilities [12, 14, 15, 17].

The aim of this study was to determine the possibilities for the utilization of sewage sludge produced in mechanical-biological wastewater treatment plant as an alternative fuel in clinker production.

2. Methods

Samples of sewage sludge produced in ”Hajdów“ Wastewater Treatment Plant were taken for testing. First, the tests on the hydration level of the mechanically dewatered sludge were carried out. Further on, the dry mass content was determined and the following values were calculated:

- energy required to heat a sample of sewage sludge from 20 to100°C,
- the total energy required to dry 1 kg of sludge,

- the calorific values of wet and dry sludge calculated with the use of the following formulas.

In the course of the experiment, the analysis of the cement kiln waste gases was carried out with the use of the oxides of nitrogen analyzer and gas chromatograph, as well as with the application of traditional methods (e.g.: SO_2 – iodometric method, NO_2 – measured spectrophotometrically). The analyses of the solid samples, e.g. the chemical composition of clinker and sludge were carried out by means of ASA and ICP methods after prior mineralization of the tested material in a CEM microwave oven.

3. Results and discussion

When it comes to the use of sewage sludge as a fuel in a cement burning kiln, the most significant – and in fact the decisive – factor is the energy balance of the mechanically dewatered sludge. There are no doubts that the attractiveness of sewage sludge as a fuel increases together with its calorific value. From the point of view of environment protection the chemical composition of sludge is of great importance, especially when it comes to the components of the kiln waste gases (Table 1.)

Mineral substances contained in sewage sludge should in the vast majority be bound up with clinker, thus undergoing the total and lasting immobilisation. The said components are: Ca, Fe, Si, K, P, A and heavy metals. During the combustion process sulphur can be released to the gas phase and emitted to the atmosphere together with the waste gases. Its content in sewage sludge (in dry mass) is rather significant and comparable to that in the low quality hard coal. Therefore, the problem of sulphur liberation in the sludge combustion process must be taken very seriously.

The dry mass content of organic substances varies within the range of 52.6–58.4%, ensuring a positive energy balance for the sludge. The value of the dried sludge combustion changes within the narrow range of 14.4–14.5 MJ/kg (Table 2). Thus, the dried sludge is a fuel comparable in thermal terms to wood whose calorific value varies within the range of 14–19 MJ/kg. It must be emphasised that the dried sludge combustion heat value is extremely stable which is definitely related to its virtually stable level of content of organic substances.

Table 1. Chemical composition of sewage sludge
Tabela 1. Skład chemiczny osadów ściekowych

Parameter	Unit	Average concentration	Range (based on 10 tests)
CaO	g/kg d.m	384	299.0–412.0
Fe_2O_3	- ” -	188	142.0–208.0
SiO_2	- ” -	139	102–156.0
S	- ” -	19.4	15.2–24.6
P_2O_5	- ” -	93	46.0–157.0
K_2O	- ” -	18.3	14.6–21.8
Al_2O_3	- ” -	22.4	16.8–28.4
H_2O	%	77.0	75.0–79.2
Residue on ignition (600°C)	%	9.7	8.63–11.4

Table 2. Energy balance of sewage sludge
Tabela 2. Bilans energetyczny osadów ściekowych

Sample no.	Dry mass content	C_s[1]	Q_{H2O}[2]	W_U^S[3]	W_U^M[4]
	g/kg	MJ/kg	kJ/kg	kJ/kg	kJ/kg
1	247.80	14.51	2023.86	3595.58	1571.72
2	250.00	14.50	2018.43	3625.00	1606.57
3	238.80	14.49	2046.18	3460.21	1414.03
4	232.00	14.48	2063.02	3359.36	1296.34
5	228.50	14.44	2017.71	3299.54	1227.83
6	216.00	14.50	2102.68	3132.00	1029.32
5	208.10	14.50	2122.24	3017.45	895.21
8	221.34	14.52	2089.53	3214.77	1125.24
9	227.63	14.43	2040.88	3285.11	1244.24
10	237.60	14.39	2055.86	3419.06	1363.20
11	243.00	14.43	2035.78	3506.49	1470.71
12	246.00	14.57	2028.34	3584.22	1555.88

[1] C_s – dried sludge combustion heat value
[2] Q_{H2O} – energy needed for drying up 1 kg of wet sludge
[3] W_U^S – calorific value of the substance contained in 1 kg of wet sludge
[4] W_U^M – total net calorific value of 1 kg of wet sludge

The analysis of the amount of energy required for sewage sludge drying, that is the energy to be used for heating water from 20 up to 100°C and for its vaporization, is proportional to the amount of water and varies within the range of 2018–2122 kJ/kg of wet sludge.

The calculated wet sludge value varies within the range of 895–1607 kJ/kg. Therefore, the dewatered sewage sludge can hardly be treated as an attractive fuel; however, the combination of its utilization with a possible application in the cement kiln burning process should be treated as economically justified.

At present, when the number of wastewater treatment plants equipped with mechanical sludge dewatering stations is growing, sewage sludge is becoming an increasingly valuable alternative fuel.

4. Utilization of sewage sludge in cement kilns

Combustion of sewage sludge was carried out in one of the cement plants in Lubelskie Voivodship region. Sewage sludge was added to the clinker slurry in the proportion of 2%. The addition of such small amount of sludge resulted in a slight change of its chemical composition and, in particular, in a slight increase of the content of volatile substances with subsequent dilution of the mineral components of the cement slurry. The phenomenon described above is presented in Table 3.

Table 3. Chemical composition of the Portland cement slurry with and without the addition of sewage sludge

Tabela 3. Skład chemiczny szlamu portlandzkiego z dodatkiem i bez osadu ściekowego

Parameter	Without the addition of sewage sludge	With 2% addition of sewage sludge
Loss on ignition	36.4%	37.5%
SiO_2	13.7%	13.4%
Al_2O_3	2.5%	2.5%
Fe_2O_3	1.2%	1.2%
CaO	45.2%	44.3%

The process of utilisation was carried out over the time of 8 hours. During the experiment, the analysis of exhaust gases and dust emissions was carried out in the rotary kiln no. 3, while the cement samples used for the cement quality analysis were taken both from kiln no. 3 and kiln no. 4.

Measurements of dust emissions and of the composition of waste gases were carried out two days before the experiment, on the day of the experiment – in the eighth hour of the tests – and on the day following the completion of the experiment.

In fact, no negative processes which would have led to increased emissions of gases and dust were observed. However, the tests revealed a reduction in the dust and sulphur emissions from kiln no. 3 fed with the clinker slurry containing sewage sludge in the proportion of 2%, while the level of nitrogen oxides emission remained unchanged. The results of the analysis were provided by the cement plant laboratory (Table 4).

Table 4. Results of the measurements of dust emission (measurements taken behind the electro-filter)
Tabela 4. Wyniki pomiarów emisji pyłowej (miejsce pomiaru za elektrofiltrem)

			Before the experiment	During the experiment	After the experiment
Chemical composition of exhaust gases	CO_2	%	12.6	13.5	12.6
	CO	%	0.1	0.1	0.1
	O_2	%	10.1	10.1	10.1
	N_2	%	61.4	60.6	61.4
	H_2O	%	15.8	15.6	15.8
Average emission of SO_2		kg/h	8.0	10.6	7.9
SO_2 emission coefficient		kg/t	0.4	0.6	0.4
Average emission of NO_2		kg/h	19.0	18.6	19.0
NO_2 emission coefficient		kg/t	0,9	0.9	1.0

Based on the results obtained it is not possible to state unequivocally whether the observed reduction in dust and SO_2 emission results directly from the fact that sewage sludge was added to the process. We need to consider further experiments enabling thorough understanding of the phenomenon to be carried out in future. The emission of organoleptically detectable odorous substances was undoubtedly the negative effect of the combustion of sewage sludge supplied to the kiln together with clinker slurry. In order to regulate the emission of such substances to the atmosphere, it is necessary to modernise the cycling of the cement kiln waste gases.

The analysis of the chemical and phase composition of the Portland cement revealed slight fluctuations (Table 5). Therefore, it needs to be emphasised that the utilization of sewage sludge had absolutely no influence on the quality of the product obtained.

Table 5. Chemical and phase composition of the Portland cement clinker (in%)
Tabela 5. Skład chemiczny i fazowy klinkieru portlandzkiego w% wag.

Compound	Before the experiment	During the experiment	After the experiment
Loss on ignition	0.3	0.3	0.34
SiO_2	22.1	21.7	22.0
Al_2O_3	5.0	5.2	5.2
Fe_2O_3	2.1	2.1	2.0
CaO	65.8	66.4	67.6
MgO	0.7	0.7	0.8
SO_3	0.4	0.4	0.4
Free CaO	1.2	1.1	1.1
C_3S	61.0	60.2	60.7
C_2S	19.9	19.6	19.4
C_3A	9.2	9.6	10.0
C_4AF	6.1	6.2	6.2

5. Conclusions

The results of the tests performed made it possible to draw the following conclusions:

- Combustion of sewage sludge in rotary cement kilns does not lead to increased dust, sulphur dioxide or nitrogen oxides' emissions to the atmosphere. However, odorous substances (detectable) are emitted which requires adequate modernization of the cycling of the cement kiln waste gases to be carried out.

- The dry sludge combustion heat value varies within a narrow range of 14.43–14.57 MJ/kg, which makes this type of waste a fuel comparable in energy terms to wood, the calorific value of which varies between 14 and 19 MJ/kg.
- The calorific value of wet sludge varies within the range of 895–1607 kJ/kg, and therefore the mechanically dewatered sludge can hardly be regarded as an attractive fuel.
- The stability of the sewage sludge combustion heat value is related to the stable content of organic substances.
- Co-combustion of sewage sludge with clinker slurry seems to be a justified method of its utilization, especially because it does not in any way affect the quality of the product obtained.

References

1. Commission of European Communities 1999 Council Directive 99/31/EC of 26 April 1999 on the Landfill of Waste.
2. Commission of European Communities 1986 Council Directive UE 86/278/EEC 4 July 1986 on the Protection of Environment and in Particular of the Soil when Sewage Sludge is used in Agriculture.
3. The National Waste Management Plan 2010, 2006 The Council of Ministers Resolution No. 233; 29.
4. **Kim, E.H, Cho, J. K., Yim, S.:** *Digested sewage sludge solidification by converter slag for landfill cover*. Chemosphere, 59(3), 387–395 (2005).
5. **Mantis, I., Vousta, D., Samara, C.**: *Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods*. Ecotoxicol Environ Saf., 62(3), 397–407 (2005).
6. **Murakami T., Suzuki Y., Nagasawa H., Yamamoto T., Koseki T.:** *Combustion characteristic of sewage sludge in an incineration plant for energy recovery, Fuel Processing Technology 90, 778-77-83. processing of sewage sludge*. Applied Thermal Engineering 26, 1420–1426 (2009).
7. **Nicholson F. A., Shmith, S. R., Alloway, B.J., Carlton-Smith C., Chambers B.J.:** *An inventory of heavy metals inputs to agricultural soils in England and Wales*. Sci. Total Environ. 311 (1–3), 205–219 (2003).
8. **Pawłowski L., Pawłowski A.:** *Method for producing fuel from sewage sludge*, Patent nr EP09174096.9 z dnia 2009.10.26.
9. **Pawłowska M., Siepak J., Pawłowski L., Pleczyński J.:** *Method for sewage sludge utilisation for intensification of biogas production in refuse collection depot*. Patent nr EP08165556.5 z dnia 2008.09.05.

10. **Piekarski J., Kogut P., Kaczmarek F., Dąbrowski T.:** *Biogazownie utylizacyjne jako propozycja utylizacji osadów ściekowych w odniesieniu do ustawodawstwa polskiego*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 14 (2012).
11. **Sahlström L., Aspan A., Bagge E., M.L. Danielsson-Tham M. L., Albihn A.**: 2004 *Bacterial pathogen incidences in sludge from Swedish sewage treatment plants*. Water Res. 38 (8), 1989–1994 (2004).
12. **Sanger M., Wether J., Ogada T.:** *NO_x and N_2O emission characteristics from fluidized bed combustion of semi-dried municipal sewage sludge*, Fuel 80, 161-177 (2001).
13. **Schowanek D., Carr R., David H., Douben P., Hall J, Kirchmann H., Patria L., Sequi P., Smith S., Webb S.:** *A risk-based methodology for deriving quality standards for organic contaminants in sewage sludge for use in agriculture—Conceptual Framework.* Ekotoxicol Environ. Saf., 40 (3), 227–251 (2004).
14. **Stasta P., Boran J., Bebar L., Stehlik P., Oral J.:** *Thermal processing of sewage sludge.* Applied Thermal Engineering, 26, 1420–1426 (2006).
15. **Stelmach S. and Wasilewski R.:** *Co-combustion of dried sewage sludge and coal in pulverized coal boiler*. Journal of Material Cycles and Waste Management, 10, 110-115 (2008).
16. **Wether J. and Ogada T.:** *Sewage sludge combustion*, Progress in Energy and Combustion Science, 25, 55–119 (1999).
17. **Wetle S. and Wilk R.:** *A review of methods for the thermal utilization of sewage sludge. The Polish perspective*, Renewable Energy 35, 1914–1919 (2010).

Wytwarzanie alternatywnego paliwa z wykorzystaniem osadów ściekowych z miejskiej oczyszczalni ścieków

Streszczenie

Problem osadów ściekowych, towarzyszy nierozłącznie procesom oczyszczania ścieków i nigdy nie był traktowany równorzędnie z ich oczyszczaniem. Jeszcze do niedawna przyjmowane były proste rozwiązania przeróbki osadów polegające na odsączaniu i suszeniu, które miały wpływ na późniejsze ich wykorzystanie. Każda z metod zagospodarowania osadów ściekowych ma swoje zalety i wady. Najbardziej radykalną metodą utylizacji osadów ściekowych jest ich spalanie. Podstawą tego procesu jest maksymalne wykorzystanie ciepła spalania i zmniejszenie objętości osadu. Przy prawidłowym doborze technologii osad może być spalony bez znacznego dodatku paliwa. W piecach cementowych przy wysokiej temperaturze i dużej stabilności gwarantowany jest całkowity rozkład substancji organicznej i uniemożliwia powstawanie wtórnych zanieczyszczeń charakteryzujących procesy spalania. W takich warunkach substancje organiczne przechodzące przez strefę wysokich temperatur w piecu do wypalania klinkieru, ulegają pirolizie i spaleniu do prostych związków nieorganicznych. Powstające popioły nie stanowią większego problemu, gdyż ulegają wbudowaniu w klinkier.

Spalanie osadów ściekowych w chwili obecnej ma największą szansę rozwoju, tym bardziej, że wraz ze wzrostem zużycia energii przez przemysł, rolnictwo i indywidualną konsumpcję ludności rośnie proporcjonalnie emisja gazów spalinowych, ścieków i odpadów stałych. Wymienione powyżej czynniki, jak i szereg innych powodują, że poszukuje się alternatywnych źródeł energii, ale również dąży się do wykorzystania materiałów odpadowych jako źródło dodatkowej energii. Powszechnie obowiązująca praktyka składowania odpadów w litosferze, nie tylko wiąże się z bezpowrotną utratą cennych terenów i energii zawartej w osadach ściekowych, lecz dodatkowo powstające w wyniku tych procesów gazy i ścieki mogą zanieczyszczać środowisko.

Przeprowadzone badania miały na celu rozeznanie możliwości wykorzystania osadów z mechaniczno-biologicznej oczyszczalni ścieków jako paliwa do wypału klinkieru.

W wyniku przeprowadzonych badań stwierdzono, że ciepło spalania wysuszonego osadu ściekowego zmienia się w wąskim zakresie 14,4–14,5 MJ/kg, a wiec jest paliwem porównywalnym energetycznie z drewnem,. co związane jest ze stałym poziomem zawartości substancji organicznych. Wartość opałowa mokrego osadu zmienia się w zakresie 895–1607 kJ/kg, zatem trudno uznać mechanicznie odwodnione osady ściekowe za atrakcyjne paliwo. Jednak połączenie utylizacji z ewentualnym wykorzystaniem osadu do opalania pieca cementowego zyskuje ekonomiczne uzasadnienie. Przeprowadzone badania w skali technicznej wykazały, że dodanie osadów ściekowych do szlamu klinkierowego w ilości 2% powoduje niewielkie zmiany ich składu chemicznego, w szczególności zwiększa nieznacznie ilość substancji lotnych. Zaobserwowane wahania składu chemicznego i fazowego cementu portlandzkiego są niewielkie i należy stwierdzić, że utylizacja osadów ściekowych nie wpływa w żaden negatywny sposób na jakość otrzymanego produktu.

Słowa kluczowe:
osady ściekowe, spalanie, paliwa alternatywne

Keywords:
sewage sludge, combustion, alternative fuels

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Investigations of Hydrological Regime Changes in an Area Adjacent to a Mine of Rock Raw Materials

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1. Introduction

Water conditions for a given area are the outcome of a number of various factors, either natural or related to the human impact on the natural environment [1,5,7,14,17]. Apart from the geological structure, these factors also include the surface morphology and the mining. The most important consequences of the open pit mining include the occupation and the transformation of land for the purpose of mining activities and the changes thus caused to the water conditions in the area adjacent to the pit in relation with its dewatering [13,15,16]. Open pit mining of calcareous aggregates requires the rock mass to be drained before other activities can commence. This involves sweeping changes in the water conditions in the area which is either directly used for exploitation, or only adjacent to it. These changes are concerned with the quality of both the surface and the groundwater, the water usage patterns and the transformation of the surface hydrographic network [3,9,10,23].

Drainage within the mine mainly shows through the formation of a depression cone and the change in the direction of the groundwater flow. This last phenomenon leads to a decreased flow in the surface watercourses. It also lowers the groundwater table and the humidity of soils, which ultimately translates to reduced yield of crop. Mine dewatering is related to the lowering of the groundwater table below the mining level and to the drainage of the precipitation water from the excavation site and its forefield [6,19,20,21]. The overall inflow of water to all the mines in Poland is estimated at 3 million m^3/day (24 hours), of which: 43% goes to the brown coal mining, 23% goes to the hard coal mining, 16% – rock raw material mining (including the Triassic limestone), 15% – zinc and lead ore mining and 3% – any others [4,11,24].

This paper analyses the impact of the rock (limestone) mining to the water conditions in the vicinity of mines. Our discussion is exemplified by the mine in Tarnów Opolski.

On the one hand the operation of this mine translates to the depression in the surrounding area and the lowering of the groundwater table. On the other, however, the dumping of mine water supplements the scarce surface water resources in the drainage basin of the river Struga. This water shortage is caused by the slotted structure of soil (Triassic limestone) and the low level of precipitation in this part of Poland. The dumping of water from the mine conditions the ecological continuity of the Struga watercourse and enables the ecosystem to develop by ensuring a certain supply of water for various purposes, e.g. agriculture or fire-fighting or other [2].

This paper is concerned with:

- a characterisation of the mine and of the river Struga,
- the measurements on the river Struga,
- an analysis of the precipitation and a hydrological calculation of inflow of the surface water from the drainage basin and from the pipelines that evacuate water from the mine,
- the hydraulic calculations of the flow capacity of the river and an initial numerical simulation of the water levels.

2. Characterisation of the Mine and of the River Struga

The limestone plant and the Tarnów Opolski mine are located to the south of Tarnów Opolski, between the villages of Kosorowice and Kamień Opolski and the town of Tarnów Opolski (Fig. 1). The surface in the area is slightly undulating, with slopes going down to the north and to the west. The elevation is in the range of 200 m ASL, with 185 m ASL in the mine and 173 m ASL in the region of Tarnów Opolski.

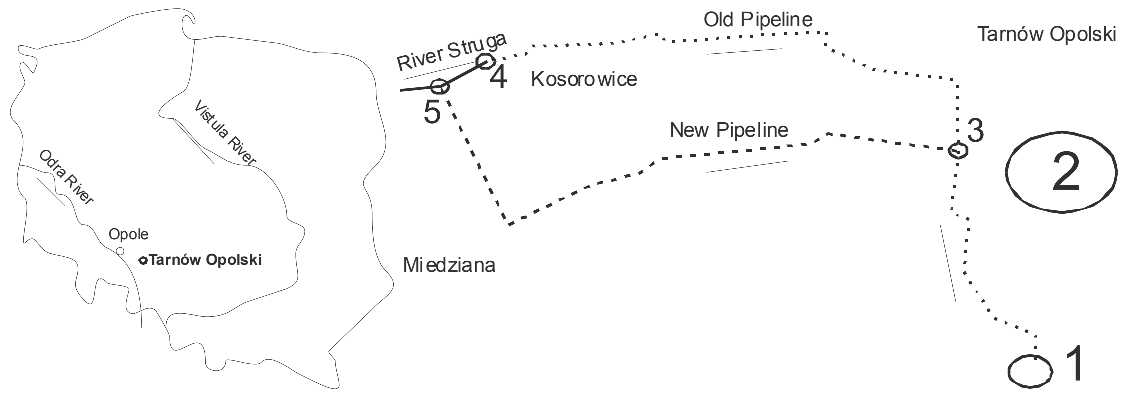


Fig. 1. Location of the research site and a schematic diagram of the system which evacuates water from the Tarnów Opolski mine to the river Struga: 1– the mine, 2–the production plant, 3–connection between the old and the new pipeline, 4–mouth of the old pipeline to the Struga river, 5–mouth of the new pipeline to the Struga river

Rys. 1. Lokalizacja obiektu badawczego i schemat systemu odprowadzającego wody kopalniane z kopalni Tarnów Opolski do rzeki Strugi: 1–kopalnia, 2–zakład produkcyjny, 3–połączenie starego i nowego rurociągu, 4–wylot starego rurociągu do rzeki Strugi, 5–wylot nowego rurociągu do rzeki Strugi

The mine is situated in the basin of the Struga which joins the Odra on its right bank. The mine and the limestone plant are located in the communes of Tarnów Opolski (the Opolski district) and Gogolin (the Krapkowicki district). Geologically, the area under study consists of the Quaternary and Triassic formations made of shell limestone. The thickness of the Quaternary layers varies from several dozen cm to about fifteen or so meters. The deposit of the Triassic limestone, which consists of the eastern and western field, is located almost entirely on the lands belonging to Kamień Śląski. Only about 3 ha belong to the commune of Tarnów Opolski. Currently, only the eastern field is used. The raw material being mined is used for the production of lime. The mining is done in two open pits at two levels: level 1 at 167–170 m ASL and level 2 at 155 m ASL. The second level is below the groundwater table and has to be continuously drained. Water from the mine is removed through pipelines to the Struga, and from there to the Odra (Fig. 1, 2, 3).

Originally, the existing old pipeline built in the 1970s had a capacity of about 8,000 m^3/day. Water from the receiving pit is transported through pumps and two steel pipelines of 500 mm in diameter and 650 m in length each. Next, both these pipelines join to form a third one, which is also made of steel, has a diameter of 800 mm and is 965 m long. There is a concrete collector in its final section having 1,000 mm in diameter with a mouth in the river channel of the Struga (Fig. 1). Currently both the mine water and the precipitation water flows through this pipeline.

The second pipeline, which is a new one, receives water from the mine and also evacuates it to the Struga. The mouth of this pipeline is about 300 m down of the mouth of the old pipeline. It is located on the left bank of the Struga (Fig. 1). The new pipeline is to receive all the water which is removed from the mine and helps to protect the inhabitants of the Kosorowice village from flooding during intensive rainfalls. This pipeline passes though the lands of the villages Tarnów and Kosorowice. According to the calculations carried out by the authors, the velocity of water "v" in the new pipeline depends on the volume of water discharged from the mine Q_z and varies from v=1.35 m/s for the current discharge Q_z=74,000 m^3/day to v=2.55 m/s for the forecast discharge Q_z=14,000 m^3/day.

3. Characterisation of the Areas Adjacent to the Mine and to the River Struga

3.1. Adjacent Areas

The Opolskie province is situated in the south-western part of the country. The area has a character of a compact basin with mountain fragments in it and is a lowland region with a poorly varied topographic profile. In the lowland band, the terrace-dune valleys, accumulation plains and old glacial denudation plains are dominant. The share of the cultivated land in the overall province surface is 62.7%, and that of the areas protected for their natural values is about 30% of the province.

Soils

The main factor which determines the spatial distribution and the quality of soils is the geological structure. The quality of soils, i.e. their production capacity is relatively high. This is proved by the existence of soils classified as very good and good (class I – III). Arable land constitutes 43.2% of the overall surface of the Opolskie province. The share of soils of medium quality (class IV) stands at 33.5%. The soils of poor quality are 22.4% of the total.

Mineral raw materials

The geological structure and the topographic profile are related to the type and availability of raw mineral materials. In the geological structure post-glacial forms prevail, which are the basis for the concrete-lime industry. The largest deposits are near Opole, Krapkowice and Strzelce Opolskie. Other raw materials include filling sands (13.9%), moulding sands (12.7%), natural aggregates (10.6%), silty raw materials (4.1%) and phyllite shales (100% of national resources). Other raw materials are of no importance for the industry.

Climate

The Opolskie province is one of the warmest regions in Poland. Most of the area belongs to the Lower Silesian Southern Climatic Region. According to the Romer's agricultural and climatic classification, the climate in the entire province is that of the submontage lowlands and valleys. One of the characteristic features of this climate is the low variation of temperature. The warmest town is Opole, with the average yearly temperature at 8.4°C and the coldest is Olesno with 7.7°C. The warmest month is July (av. temp. 18°C) and the coldest ones are January and February with the temperatures averaging about -1.5°C. The vegetation season starts early and lasts 200–225 days. The long growing season and the mild winters create favourable conditions for the agriculture in this area.

Precipitation

The multiannual average yearly precipitation for the investigated area is around 650 mm. An analysis of precipitation in the flood year 2010, during which intensive flooding took place in the village of Kosorowice among others, revealed that:

- over the period of 16–31 May the total precipitation amounted to only 76.8 mm,
- over the period of May–June–July the cumulative precipitation was 414 mm, i.e. two-thirds of the average yearly total,
- monthly precipitation totals were as follows: January 55.4 mm, February 24 mm, March 63.1 mm, April 51 mm, May 210 mm, June 70 mm, July 134 mm, August 89.3 mm, September 106.9 mm.

In the area under study, the amount of water from precipitation penetrating through infiltration to the water-bearing layers was 20% (115 mm/year) on the average.

3.2. The Struga River

The Struga joins the Odra on its right bank at km 145.35 in the region of the villages Przywory and Grotowice (Fig. 2). The total surface area of its drainage basin is 41 km^2. This basin includes several small watercourses and drainage ditches. The adjacent land consists of meadows, pastures, forests and arable land. The river starts at the mouth of the old pipeline which evacuates water from the mine. Part of the drainage basin dried due to the cone of depression formed as a result of aggregate mining. In the 1980s, some river regulation works were carried out on the Struga. Its channel was considerably widened and deepened. These works changed the conditions of water infiltration from the river to the ground. Apart from it, the flow capacity of the channel increased considerably. Measurements carried out by the authors in the drainage basin of the Struga prove that abundant rainfall has no influence on the increase of flow along the watercourse. The run-off of water at the start and at the end of the river remains the same and in some periods even decreases. This is caused by the specific geological structure of the river basin. A considerable increase in the run-off rate in the river over the last several years results from its widening and deepening and is also caused by the very good hydraulic conditions (systematic maintenance and strengthening of the river channel).

Fig. 2. The channel of the River Struga at its confluence with the Odra (left) and below the mouth of the pipeline from the Tarnów Opolski mine (right)
Rys. 2. Koryto rzeki Strugi przy ujściu do rzeki Odry (strona lewa) i poniżej wylotu rurociągu z kopalni Tarnów Opolski (strona prawa)

4. Water Conditions in the Facility – Research and Discussion

4.1. Cone of Depression within the Mine

In the Tarnów Opolski mine a constant drainage of water from the adjacent land can be observed. In natural conditions water was being received by the Struga River valley. Because of the dewatering of the mine a downflow of groundwater was forced from the main natural north-west (NW) direction to the south-east (SE) direction and to the centre of the excavation site.

The range of the mine depression cone is delimited by the isoline of the lowering of the water table with respect to the average multiannual position. The dynamics and the development of the depression cone depend on the discharge of the mine dewatering system, the geological structure, the hydrogeological conditions in the vicinity of the excavation site and the meteorological conditions (mainly the amount of precipitation) [6,14,15,19].

The range of the depression cone is now as follows:

- 4 km to the east (near Izbick),
- 2.7 km to the north and to the west (near Tarnów Opolski and Kosorowice),
- 2 km to the south (near Kamień Śląski).

The range of the depression cone visibly increases on the north-eastern side. Due to the intensive and long-lasting rainfall in the period from May to July 2010 and because of the spring melt in March and April 2010, the inflow of underground water to the mine increased markedly. As a result, the groundwater table rose in the mine and the intensity of pumping of water had to be increased too.

The monitoring of groundwater levels near the mine confirms a highly dynamic nature of the changes in the water table. In May 2010 the water table rose by 1.5 m within 15 days. A similar rise was observed in August 2010: up to 162.62 m in the area of Kosorowice and up to 170.68 m in the area of Izbick. Compared to May, this means a rise by 2.31 m and 3.29 m, respectively.

4.2. Mine Water Dumping into the Struga River

Because of the scarce surface water supply in the drainage basin of the Struga, an analysis was carried out of the management of water being dumped from the Tarnów Opolski mine to the Struga. Dumping of water to this river is fundamental for:

- its channel to be kept in an appropriate technical and natural condition. The most important role is to prevent the river from overgrowing due to the insufficient amount of water [8],
- its ecological continuity to be maintained,
- the various fire-fighting purposes,
- the groundwater table to be kept at an appropriate level in the forested areas, green lands and arable land [8],
- the irrigation and the supply of water to small reservoirs and fish ponds [22].

Calculations were carried out for the years 2010 and 2011. 2010 was the so called "flood year", during which heavy rainfall occurred in the river basin of the upper and central Odra, as well as on its tributaries. In contrast, the 2011 was a year of a very limited precipitation and even drought in the area under study. During the heavy rains in June 2010, it was necessary to increase the pumping of water to prevent the mine from being flooded. The pumping of water increased from 3,000 m^3/h to 4,200 m^3/h. Water from the mine was evacuated by the old concrete collector having 1,000 mm in diameter and passing through the village of Kosorowice to the Struga. The existing section of this collector is 2997 m long and has a diameter of 1,000 mm. In the region of Kosorowice this collector is not entirely watertight, which is due to its age and wear and to the technical problems or damage (very deep ploughing, the use of the pipeline by the inhabitants of Kosorowice for irrigation during dry years etc.). Over the last years, a new pipeline was built to transport the mine water. This pipeline is also intended to evacuate the excess amounts of water during extreme (abnormal) rainfalls.

The authors compared the mine water dumping to the Struga channel in selected research periods: in May 2010 and in November 2011. During this time, the mine water dumping volumes in m^3/day and the corresponding discharges on the river in m^3/s were at a similar level:

- May 2010: 73,400 m^3/day (0.850 m^3/s) – 74,000 m^3/day (0.856 m^3/s),
- November 2011: 65,250 m^3/day (0.755 m^3/s) – 74,400 m^3/day (0.861 m^3/s),
- The average dumped volume stood at 73,755 m^3/day (0.854 m^3/s) and 71,223 m^3/day (0.824 m^3/s) in May 2010 and November 2011, respectively.

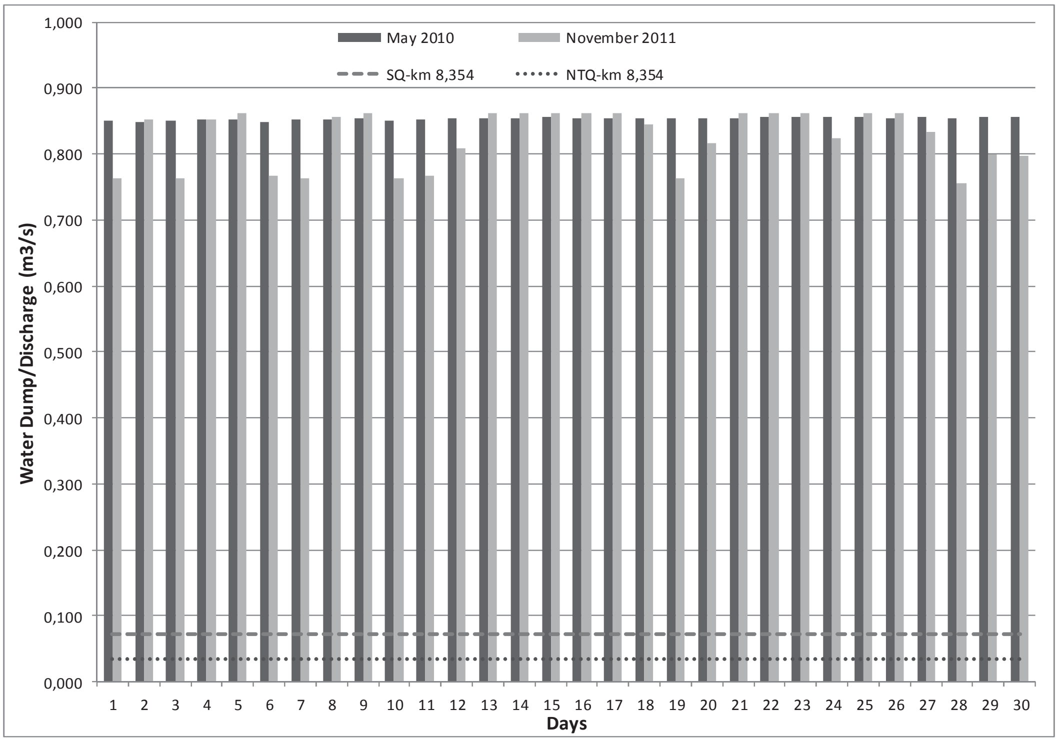
Our hydrological calculation of the so called own flows resulting from the inflow of water from the drainage basin to the Struga river showed that:

- the average multiannual discharge SQ took the following values: 0.072 m^3/s (km 8,354 of the Struga i.e. at the cross section at the mouth of the old pipeline); 0.156 m^3/s (km 6.080 of the Struga); 0.191 m^3/s (km 0.0 of the Struga, i.e. at the cross section where the river joins the Odra),
- the longest multiannual discharge (of the longest duration during the year) NTQ took the following values: 0.034 m^3/s (km 8.354 of the Struga i.e. at the cross section at the mouth of the old pipeline); 0.082 m^3/s (km 6.080 of the Struga); 0.100 m^3/s (km 0.0 of the Struga, i.e. at the cross section where the river joins the Odra).

A comparison between the discharge on the Struga which is due to the mine water dumping Q_z and the characteristic own discharges SQ and NTQ, which correspond to the water incoming from the drainage basin (Fig. 3), leads us to believe that:

- if a SQ discharge occurs on the Struga, then the dumping Q_z is 4–11 times higher than SQ (depending on the location of the measurement cross section),
- if a NTQ discharge occurs on the Struga, then the dumping Q_z is 8–24 times higher than SQ (depending on the location of the measurement cross section).

An analysis carried out by the authors reveals that the own flows on the Struga resulting from the precipitation and the surface flow cannot meet all the needs (ecology, agriculture, irrigation, fishing etc.) of the area. Mine water dumping, however, enables an efficient water management of the river and of the adjacent land. Thus it becomes a very important and positive element of the natural environment.



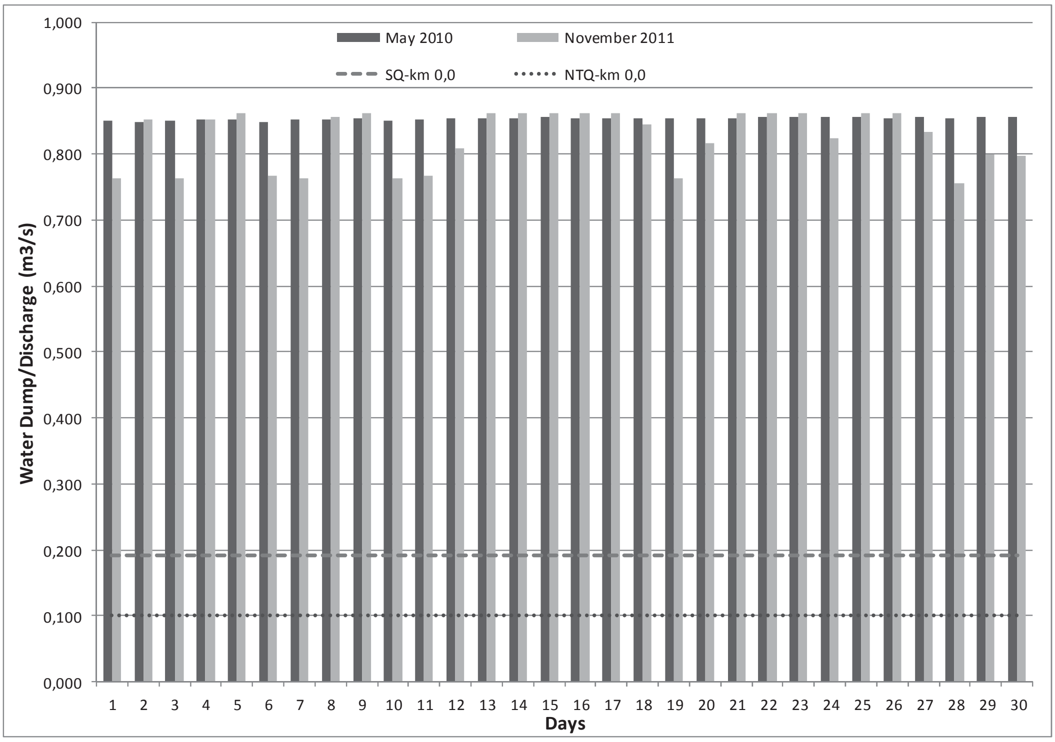


Fig. 3. Dumping from the mine and own flows on the Struga River in May 2010 and November 2011, km 8.354 (upper) and km 0.0 (lower)

Rys. 3. Zrzuty z kopalni i przepływy własne rzeki Struga w maju 2010 roku i listopadzie 2011 roku, km 8.354 (góra) i km 0.0 (dół)

4.3. Velocity and Flow Rate Measurements in the River Channel of the Struga

The measurements of the velocity and volume of the water flow through the river basin of the Struga were carried out in October and November 2011 (Fig. 4). These measurements were performed using a handheld flow meter, the FLO–MATE 2000. Such a research allows the velocities and the flow/discharge values on the Struga to be determined realistically. Hence, it can be determined which part of the flow comes from the mine and which form the drainage basin. The obtained velocities and discharge values are also a basis for the development and the calibration of a numerical model allowing a simulation of the flow capacities and the water levels in the watercourse and on the adjacent land.

The measurements show that:

- the water level in the river channel was approx. 0.40 m,
- the total discharge on the Struga (about 50 m down the mouth of the old pipeline) was about 0.70 m^3/s and coincided with the value of the mine water dumping,
- the average velocity in the cross section was 0.40 m/s,
- the pointwise velocities in the trapezoid cross section ranged from 0.21 to 0.63 m/s.

Fig. 4. Velocity and flow rate measurements on the Struga river
Rys. 4. Pomiary prędkości i przepływu wody w rzece Strudze

4.4. Hydrological Calculations of the Run-Off of Surface Water in the Drainage Basin of the River Struga

Heavy rains and melting result in a surface flow and in the consequent water erosion [18]. This erosion is particularly problematic in those areas where the slopes are of several % and more. Land adjacent to the Struga consists of dusty limestone soils which is highly susceptible to erosion. Among the many agricultural and technical actions aimed to prevent the erosion of soils and the loss of crop, the technical land improvement work is particularly noteworthy. The network of land improvement structures, both the basic ones and the very specific ones, is equally important and includes e.g. the so called absorptive ditches. These ditches collect the excess of water and prevent it from forming streams, prevent the surface flow and the washing out of soil and crop.

The authors calculated and analysed the surface flow of water coming from precipitation for the investigated area during the flood period in May 2010. During this period the dumping of water from the Tarnów Opolski mine was in the range of 73,400 – 74,000 m^3/day, similarly to November 2011, when the flow measurements on the Struga were carried out. The maximum discharge WQ through the Struga took place in May 2010 and was calculated empirically based on the precipitation formula:

$$WQ = 0.278\alpha IA = BA\ (m^3/s) \tag{1}$$

where: 0.278 – coefficient, α – coefficient of the run–off from the rainfall for the maximal flows equal to 0.65, I – intensity of rain (mm/h), A – surface area of the Struga discharge basin at a given cross section used for the measurements and calculations (km^2).

The calculation of the maximal discharge in the Struga corresponding to the rainfall in May 2010 was carried out for two periods, at three research cross sections:

- 16–18 May 2010, rainfall=59.9 mm, I=0.832 mm/h,
- 21–22 May 2010, rainfall=55.3 mm, I=1.150 mm/h.
- The cross section at km 8.354, at the mouth of the old pipeline from the mine, A=14.0 km^2,
- The cross section at km 7.820, at the mouth of the new pipeline from the mine, A=15.5 km^2,
- The cross section at km 6.080, A=33.1 km^2.

Our calculations show that:

- At the cross section at the mouth of the old pipeline (km 8.354) which evacuates water from the mine, the run-off corresponding to the rainfall on 21–22 May 2010 was at most 2.91 m^3/s. The overall discharge through the Struga, i.e. the sum of the rainfall component, the mine water dumping component (74,000 $m^3/d = 0.86\ m^3/s$) and the sewage dumping component from the sewage treatment plant in Kosorowice (102 $m^3/h = 0.028\ m^3/s$) was 3.80 m^3/s. This flow passes through the river channel of the Struga without breaking its banks.
- At the cross section at the mouth of the new pipeline (km 7.820) which also evacuates water from the mine, the run-off corresponding to the rainfall on 21–22 May 2010 was at most 3.22 m^3/s. The overall discharge through the Struga, i.e. the sum of the rainfall component, the mine water dumping component (74,000 $m^3/d = 0.86\ m^3/s$) and the sewage dumping component from the sewage treatment plant in Kosorowice (102 $m^3/h = 0.028\ m^3/s$) was 4.108 m^3/s. This flow passes through the river channel of the Struga without breaking its banks.
- At the cross section at km 6.080 (near the gravel pit on the left bank of the Struga) the run–off on 21–22 May 2010 was at most 6.88 m^3/s. The overall discharge through the Struga, i.e. the sum of the rainfall component, the Tarnów Opolski mine water dumping component (74,000 $m^3/d = 0.86\ m^3/s$) and the sewage dumping component from the sewage treatment plant in Kosorowice (102 $m^3/h = 0.028\ m^3/s$) was 7.77 m^3/s. This flow passes through the river channel of the Struga without breaking its banks.

Hydrological calculations of the maximal yearly discharges with given probabilities of occurrence of the average and low discharges were carried out at the cross sections of the Struga at km 8.354, km 6.080 and km 0.0. These hydrological calculations were performed using the formula of Lambor for the maximal discharge and that of Iszkowski for the average and low discharge (Tab. 1).

Initial numerical simulations of the flow capacity of the Struga river channel and of the water levels in the river were performed using the HEC–RAS software. This system was calibrated for the previously known hydraulic conditions in the Struga River channel [12]. Calculations were performed for four discharge values i.e. 4.60 m^3/s, 6.00 m^3/s, 10.80 m^3/s and 20.60 m^3/s. These discharges are the sum of the Struga's own discharge (corresponding to the inflow from its drainage basin, with a given probability), the dumping of water from the mine and the sewage component from the sewage treatment plant in Kosorowice. Simulation of the water levels in the Struga shows that only the catastrophic flows (which have never occurred yet) with a discharge of about 20 m^3/s could cause the water to break through the river banks. All other discharge values, i.e. 4.6 m/s, 6.0 and 10.8 m/s pass through the channel and do not cause any flooding of the adjacent land.

Table 1. The likely and characteristic maximal discharges on the Struga River
Tabela 1. Przepływy maksymalne prawdopodobne oraz charakterystyczne w rzece Strudze

Probable flows (m^3/s)			
p (%)	km 8.354	km 6.080	km 0.0
1	5.60	9.30	11.37
2	5.10	8.51	10.33
3	4.79	7.98	9.75
5	4.36	7.32	8.92
10	3.81	6.36	7.75
20	3.31	5.89	7.11
25	3.16	4.50	6.70
50	2.61	4.50	5.51
100	2.10	3.64	4.46
Characteristic flows (m^3/s)			
SQ	0.072	0.156	0.191
NQ	0.011	0.024	0.029
SNQ	0.022	0.048	0.058
NTQ	0.034	0.082	0.100

SQ – average multiannual discharge, NQ – low multiannual discharge, SNQ – average low multiannual discharge, NTQ – longest multiannual discharge (longest duration within the year).

5. Conclusions

The deep drainage of groundwater shapes the water environment not only in the vicinity of the Tarnów Opolski mine, but even at a considerable distance from it. Dewatering of the Triassic limestone deposits required to ensure a safe operation of the mine, has a significant impact on both the groundwater and the surface water environment. Drainage within the mine mainly shows through the formation of a depression cone and the change in the direction of the groundwater flow. The range of the mine depression cone varies from 2 km to the south to 4 km to the east. In 2010, after the heavy precipitation and floods on the tributaries of the Odra, groundwater levels rose in the mine surroundings by approx. 5 m.

A comparison between the mine water dumping volumes and the own flows from the drainage basin of the Struga indicates that the dumping is from several times to fifteen or so times higher than the natural flow through the river.

It should also be noted that the dumping of water evacuated from the mine during its dewatering supplements the heavy surface water shortage in the basin of the Struga. This water scarcity is caused by the slotted structure of soil (the Triassic limestone) and the low level of precipitation in this part of Poland. The dumping of water from the mine conditions the ecological continuity of the Struga watercourse and enables the ecosystem to develop by ensuring a certain supply of water for various purposes – agriculture or fire-fighting, among other things.

The water flow measurements on the Struga show that the volumes of water passing through the channel do not change or even decrease. This is due to the very specific geological structure of the terrain with numerous faults, cones and splits which often have considerable dimensions and make the surface waters to run-off and penetrate deeper into the ground.

The authors' analysis shows that the flooding of Kosorowice in 2010 was caused by the damage of the pipeline carrying the water from the mine.

Calculations of the flow capacity of the Struga channel and computer simulations of the water levels along the entire reach of this river indicate that for the maximal own flows with a 20% probability, the Tarnów Opolski mine water dumping at a rate of about 140,000 m^3/day and the dumping of sewage from the treatment plant in Kosorowice, there will be no flooding of the adjacent land. The free surface of water will remain within the channel of the Struga. Our analysis also indicates that even flows of which the probability exceeds 20% will not break through the banks of the river.

Lastly, the authors claim that the systematic maintenance works and the strengthening of the Struga River bed and banks enables flows and dumping with no adverse impact in the form of excessive rise in the groundwater level or flooding.

References

1. **Akabzaal T. M., Banoeng-Yakubo B. K., Seyire J. S.:** *Impact of mining activities on water resources in the vicinity of the Obuasi mine*. West African Journal of Applied Ecology. 11, 129–139 (2007).
2. **Bartnik W.:** *Charakterystyka hydromorfologiczna rzek i potoków górskich*. Infrastruktura i Ekologia Terenów Wiejskich. 4/1, 143–174 (2006).
3. **Baszczyńska M., Kaźmierczak U.:** *Zachowanie bioróżnorodności w ramach rekultywacji poeksploatacyjnych kopalni wapienia „Górażdże"*. Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej 132, Studia i Materiały 39, 12–22 (2011).
4. **Dulewski J., Walter A.:** *Gospodarka wodami kopalnianymi w górnictwie węgla brunatnego na tle całego przemysłu wydobywczego*. Materiały Warsztatów „Zagrożenia naturalne w górnictwie", Wyższy Urząd Górniczy, Katowice. 29–38 (2007).
5. **International Council on Mining and Metals.:** *Water management in mining: a selection of case studies*. Published by International Council on Mining and Metals, London 2012.
6. **Jończyk I., Stachowicz Z., Szczepiński J.:** *Dynamika rozwoju leja depresji BOT KWB Bełchatów SA w następstwie eksploatacji systemu odwadniania wgłębnego*. Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej, 112 (2005).
7. **Kacprzak M., Bruchal M.:** *Procesy rekultywacji terenów pogórniczych na przykładzie kopalni wapienia „Górażdże"*. Inżynieria i Ochrona Środowiska, 14/1, 49–58 (2011).
8. **Kasperek R., Wiatkowski M.:** *Ocena skuteczności działania rowów melioracyjnych na terenach rolniczych*. Zeszyty Problemowe Postępów Nauk Rolniczych, 528, 213–222 (2008).
9. **Kasperek R., Mokwa M., Wiatkowski M.:** *Modelling of pollution transport with sediment on the example of the Widawa River*. Archives of Environmental Protection, 39/2, 29–43, DOI: 10.2478/aep–2013-0017 (2013).
10. **Kasperek R., Wiatkowski M.:** *Hydropower Generation on The Nysa Klodzka River*. Ecological Chemistry and Engineering S, 21/2, 327–336, DOI: 10.2478/eces–2014–0025 (2014).
11. **Kozioł W., Czaja P.:** *Górnictwo skalne w Polsce. Stan Obecny, perspektywy i uwarunkowania rozwoju.* Górnictwo i Geologia, 5/3, 41–48 (2010).
12. **Laks I., Kałuża T., Sojka M.:** *Problems with Modelling Water Distribution in Open Channels with Hydraulic Engineering Structures*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 245–257 (2013).

13. **Martyniak K.:** *Ważniejsze uwarunkowania przyrodnicze a wydobywanie kruszyw*. Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej 132, Studia i Materiały 39, 199–206 (2011).
14. **Motyka J., Czop M., Jończyk W., Stachowicz Z., Jończyk I., Martyniak R.:** *Wpływ głębokiej eksploatacji węgla brunatnego na zmiany środowiska wodnego w rejonie kopalni Bełchatów*. Górnictwo i Geoinżynieria, 31/2, 477–487 (2007).
15. **Nash T.:** *Overview of Mine Drainage Geochemistry at Historical Mines, Humboldt River Basin and Adjacent Mining Areas, Nevada*. In Geoenvironmental Investigations of the Humboldt River Basin, Northern Nevada, *Edited by* Lisa L. Stillings, U.S. Geological Survey Bulletin 2210–E (2003).
16. **Plumlee S. G., Smith K. S., Montour W. H., Ficklin W. H., Mosier E. L.:** *Geologic controls on the composition of natural eaters and mine waters draining diverse mineral deposits types* . Environmental Geochemistry of Mineral Deposits, 373–409 (1999).
17. **Poros M., Sobczyk W.:** *Rewitalizacja terenu pogórniczego po kopalni surowców skalnych na przykładzie kamieniołomu Wietrznia w Kielcach*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 2369–2380 (2013).
18. **Radecki-Pawlik A.:** *Hydromorfologia rzek i potoków górskich. Działy wybrane*. Wydawnictwo Uniwersytetu Rolniczego w Krakowie (2011).
19. **Stachowski P., Oliskiewicz-Krzywicka A., Kozaczyk P.:** *Ocena warunków meteorologicznych na terenach pogórniczych Konińskiego Zagłębia węgla brunatnego*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 1834–1861 (2013).
20. **Szczepański A.:** *Wpływ górnictwa na środowisko wodne*. Przegląd Geologiczny, 52/10, 968–971 (2004).
21. **Szlagowski A.:** *Zmiany środowiska przyrodniczego spowodowane działalnością górniczą w monitoringu regionalnym i lokalnym*. Monitoring Środowiska Regionu Świętokrzyskiego, 1, 39–46 (1993).
22. **Wiatkowski M., Kasperek R.:** *Gospodarka wodna i eksploatacja małego zbiornika wodnego "Adymacz" na rzece Prószkowski Potok*. Zeszyty Problemowe Postępów Nauk Rolniczych, 528, 457–466 (2008).
23. **Wiatkowski M., Rosik-Dulewska Cz., Kuczewski K., Kasperek R.:** *Ocena jakości wody zbiornika Włodzienin w pierwszym roku funkcjonowania*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 2666–2682 (2013).
24. **Wyższy Urząd Górniczy.:** *Zagrożenia naturalne w odkrywkowych zakładach górniczych*. Raport, Katowice (2007).

Badania zmian reżimu hydrologicznego na obszarze przyległym do kopalni surowców skalnych

Streszczenie

Stosunki wodne określonego obszaru są wypadkową czynników pochodzenia naturalnego oraz oddziaływania człowieka na środowisko przyrodnicze [1,5,7,14,17]. Oprócz budowy geologicznej należą do nich morfologia terenu oraz działalność górnicza. Do najistotniejszych skutków eksploatacji, jakie powoduje górnictwo odkrywkowe można zaliczyć zajmowanie i przekształcanie terenów pod działalność górniczą oraz zmianę stosunków wodnych w rejonie funkcjonowania odkrywki, związaną z jej odwodnieniem [13,15,16]. Drenaż w obrębie kopalni ujawnia się głównie w postaci leja depresji i zmianie kierunku przepływu wód podziemnych. W efekcie powoduje on zmniejszanie przepływu w ciekach powierzchniowych, obniżanie poziomu wód gruntowych i zmniejszanie stanu uwilgotnienia i plonowania gleb [6,19,20,21].

Niniejsza praca jest poświęcona analizie wpływu działalności górnictwa wapieni na kształtowanie się stosunków wodnych terenów przyległych na przykładzie kopalni Tarnów Opolski. Zakres pracy dotyczy charakterystyki kopalni i rzeki Strugi, pomiarów w rzece Strudze, analizy opadów i hydrologicznych obliczeń dopływu wód powierzchniowych ze zlewni i z zrzutu wód kopalnianych, hydraulicznych obliczeń przepustowości rzeki i wstępnych numerycznych symulacji położenia zwierciadła wody.

Z jednej strony działalność tej kopalni powoduje depresję terenów wokół oraz obniżanie zwierciadła wód gruntowych. Natomiast z drugiej strony, zrzuty wód kopalnianych uzupełniają duże niedobory wód powierzchniowych w zlewni rzeki Strugi, spowodowane szczelinowatą budową podłoża (wapienie triasowe) oraz małą ilością opadów w tym regionie Polski. Dzięki zrzutom wody z kopalni możliwa jest ciągłość ekologiczna cieku Struga, rozwój ekosystemu oraz zapewnienie określonej ilości wody dla celów m.in. rolniczych, hodowlanych (stawy rybne) i przeciwpożarowych [2].

Teren kopalni znajduje się w zlewni rzeki Struga, która uchodzi do Odry na jej prawym brzegu. Kopalnia i zakłady wapiennicze położone są na terenie gminy Tarnów Opolski (powiat Opolski) i Gogolin (powiat Krapkowicki). Badany obszar pod względem geologicznym charakteryzuje się utworami czwartorzędowymi i triasem z wapienia muszlowego. Wydobywany surowiec służy do produkcji wapna. Wydobycie prowadzone jest metodą odkrywkową na dwóch poziomach wydobywczych. Wody kopalniane odprowadzane są do rzeki Strugi za pomocą rurociągów, a następnie do rzeki Odry (Fig.1, 2, 3).

W wyniku odwodnienia kopalni spływ wód podziemnych został wymuszony z głównego naturalnego kierunku północno-zachodniego NW w kierunku

południowo–wschodnim SE, do centrum wyrobisk górniczych. Zasięg leja depresji wynosi obecnie: 4 km w kierunku wschodnim, 2,7 km w kierunku północnym i zachodnim (okolice Tarnowa Opolskiego i Kosorowic), oraz 2 km w kierunku południowym (okolice Kamienia Śląskiego).

Ze względu na niewielkie zasoby wód powierzchniowych w zlewni rzeki Strugi przeanalizowano zrzuty wód kopalnianych oraz ich zagospodarowanie w zlewni rzeki Strugi. Zasilanie rzeki tymi wodami ma szczególne znaczenie m.in. dla utrzymania jej koryta w odpowiednim stanie techniczno-przyrodniczym oraz zasilania w wodę zbiorników małej retencji, stawów rybnych oraz nawadniania [22].

Na podstawie analizy porównawczej zrzutów wód kopalnianych oraz własnych przepływów rzeki Strugi (Fig. 3) autorzy stwierdzają, że:

- w przypadku wystąpienia przepływów średnich SQ, zrzuty Q_z są 4–11 razy wyższe od SQ,
- w przypadku wystąpienia przepływów najdłużej trwających NTQ, zrzuty Q_z są 8–24 razy wyższe od NTQ (w zależności od położenia przekroju pomiarowego).

Należy również zaznaczyć, że zrzuty wód kopalnianych z jej odwodnienia uzupełniają duże niedobory wód powierzchniowych w zlewni rzeki Strugi. Niedobory te są spowodowane szczelinowatą budową podłoża (wapienie triasowe) oraz niską ilością opadów w tym regionie. Dzięki zrzutom wody z kopalni możliwa jest ciągłość ekologiczna cieku Struga, rozwój ekosystemu oraz zapewnienie określonej ilości wody dla celów np. rolniczych, gospodarczych i przeciwpożarowych.

Pomiary przepływu wody w Strudze wskazują, że ilość wody wraz z jej biegiem nie zmienia się, a nawet zmniejsza się. Spowodowane jest to specyficzną budową geologiczną tego terenu (liczne uskoki, leje i rozłamy o znacznych rozmiarach, powodujące odpływ wód powierzchniowych w głąb podłoża).

Obliczenia przepustowości koryta rzeki Strugi oraz symulacje komputerowe położenia zwierciadła wody wzdłuż całego jej odcinka wskazują na to, że podczas maksymalnych przepływów własnych ze zlewni o prawdopodobieństwie 20% wraz z zrzutami z kopalni (rzędu 140,000 m^3/dobę) i z oczyszczalni Kosorowice, nie będzie podtopień terenów przyległych. Zwierciadło wody będzie się mieścić w korycie Strugi. Analiza wykazała również, że przepływy o prawdopodobieństwie wyższym od 20% będą mieścić się w korycie rzeki.

Słowa kluczowe:
zrzut wody z kopalni, rzeka, reżim hydrologiczny

Keywords:
water dumping from the mine, river, hydrological regime

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Cultivation Parameters Adjustment for Effective Algal Biomass Production

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1. Introduction

Seemingly inevitable energy crisis makes it a high priority for today's society to become independent of already exhausting fossil fuels. Most researched energy sources, regarded as possible alternatives for the currently leading one, are solar, wind, water and biofuels. The latter are produced from high calorific chemical compounds being natural metabolites of living, usually autotrophic, organisms. Although there are many plants that can be used as the biofuel feedstock, it is aquatic organisms, mainly algae, to be the most relevant, since their cultivation involves practically no land requirements and relatively small agricultural input [1,18]. Moreover, their complex biological activity may present algae farming as a beneficial contribution to nutrient cycling and waste water treatment. The considerable potential of algal-based biofuels makes them a subject of thorough investigation. The greatest challenge is to optimize the conditions of algae cultivation.

In the natural, as well as human-created media algae are exposed to a number of environmental factors. Variable chemical and physical conditions influence all the aspects of algal activity, including biomass increase rate and metabolism intensity, thus their efficiency as fuel feedstock. The most important factors are temperature, pH, light intensity, salinity, accessible biogenic elements concentrations and optical activity of the medium. Simultaneously, all of these conditions are constantly altered by the culture itself, which in turn affects the quantitative and qualitative algae growth etc. Additionally, there is a strong interdependence between particular environmental factors. Therefore the development of algal cultures must be ceaselessly monitored and their properties adjusted, which, combined with our still insufficient understanding of the occurring processes, proves to impede the introduction of algal-based fuels on the global scale [2].

The crucial question concerns the actual impact of previously mentioned environmental conditions on the growth of algae. One of the most vital factors, at the same time one most difficult to control in large-scale cultivation in open ponds, is temperature. Closely related with thermal energy, it determines the enzymatic activity, being the limiting factor for most biochemical processes in the cells. It also affects the physical and chemical properties of the medium, such as density and solubility of most substances, resulting in significant changes within the molecular structure of the algae [1,2]. Other energy-related factor is the culture illumination. It can be modified by either changing the light intensity and spectral composition or the optical activity of the medium. The luminous energy regulates photosynthesis, directly leading to carbon incorporation and biomass increase rate. The metabolic activity of the algae depends also on nutrient availability. The most essential elements that must be supplied are carbon, nitrogen and phosphorus, in the desirable proportions of approximately 100:6:1 [14]. Their accessibility can vary due to environmental factors such as acidity or salinity.

In this project microalgae were grown on pre-treated reject water. This type of wastewater is formed while drainage the digested sewage sludge. As the nutrient concentration in this type of wastewater is comparatively high, effluent cannot be directly discharged, and is normally directed back into the raw sewage for removal of nitrogen and phosphorus. This results in wrong C:N ratio in influent and has a negative influence on microbial processes and structure of biocenoses in biological reactors [9]. From the perspective of microalgae cultivation, the reject water has several advantages: (1) the ratio between inorganically and organically bound nutrients is higher in the reject water than in raw sewage, (2) the nutrient concentration in the reject water is relatively constant as compared to the changing nutrient concentrations in raw sewage, (3) compared to the turbid raw and treated sewage, the reject water is relatively clear, permitting a higher degree of light availability for algal photosynthesis; and (4) in a working environment perspective, the reject water is safer and more hygienic, since the anaerobic digestion causes sanitation of the pathogens that are inevitably present in raw as well as treated sewage water [19]. Microalgae growing on this type of medium have a dual use – firstly, they purify wastewater from high load of nutrients and heavy metals (on the way of sorption) and secondly, obtained biomass can be used as a biofuel, for example as a feedstock in fermentation chamber and in the production of biogas.

Of all the factors which are growth-limiting for algae, a few can be controlled or adjusted. In order to ascertain their impact on algal biomass increase rate and to analyse physicochemical parameters of a working algal culture, before transferring it to a larger bioreactor, a series of laboratory-scale experiments were conducted. The ultimate target was to intensify the culture growth and receive maximal biomass increase for biomass further usage as an energy source.

2. Materials and methods

2.1. Growth medium

Algae biomass was suspended in pre-treated reject water, obtained from the first stage of purification – SBR reactor (sequencing batch reactor). In this reactor a partial nitrification – anammox processes occurred. Loads of inorganic nitrogen and phosphorus were partially removed, but still high. N-NH_4 concentration in effluent from SBR reactor was on the level of 60–70 mg/l, N-NO_2 on the level of 8–10 mg/l and N-NO_3 on the level of 14–20 mg/l. Concentration of P-PO_4 in growth medium was variable but also high, reached a level of 30–70 mg/l. Medium was also characterized by pH on the level of 7.4–7.6, COD on the level of 80–180 mg/l and alkalinity on the level of 1.5–3.6 mM/l.

Reject water derives from Gliwice WWTP, from wastewater treatment processes – precisely, they were formed during treatment of sewage sludge. Sludge in first stage was thickened with polymers and then stabilized by biological method – anaerobic digestion in mesophilic conditions. After this process sludge was dewatered by mechanical methods (with usage of filter presses and centrifuges). Reject water formed in this processes were directed to the test system. Scheme of this system is illustrated at figure 1.

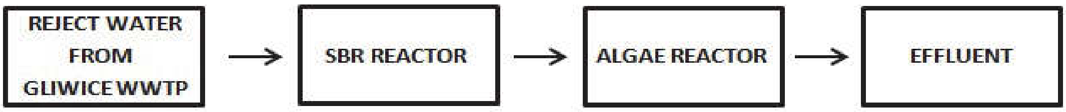

Fig. 1. Test system for treating the reject water in Gliwice WWTP
Rys. 1. Układ badawczy służący do podczyszczania wód osadowych w Centralnej Oczyszczalni Ścieków w Gliwicach

2.2. Influence of microalgae suspension dilution on biomass production

The tested property was relative biomass increase depending on the probe dilution. From a bioreactor 1.5 litres of *Chlorella* sp. culture were taken. The algae were centrifuged at 3500 rpm, after their sedimentation the supernatant was drained off and the algae were suspended in 1.5 litres of effluent from SBR reactor. 100 ml of the resultant suspension was filtered through a previously dried and weighed quality filter paper (medium pore size) and left to dry as a biomass reference. Determination of dry mass was carried out in accordance with PN-75 C-04616/01. 15 flasks were prepared, 3 of every kind:

- control samples with 100 ml of the suspension,
- samples with 80 ml suspension, 20 ml medium (80%),
- samples with 60 ml suspension, 40 ml medium (60%),
- samples with 40 ml suspension, 60 ml medium (40%),
- samples with 20 ml suspension, 80 ml medium (20%).

Flasks were stoppered with cotton wool plugs and incubated on a rotary shaker at 150 rpm for 3 days in ambient temperature (25 ± 2°C). After the incubation period the samples were filtered, dried and weighed. The results were compared with the control samples and the reference. Based on obtained data growth rate of each culture was estimated according to the equation:

$$\mu = \frac{1}{t}\ln\left(\frac{N_t}{N_o}\right) \tag{1}$$

In which:
μ – growth rate [1/day],
t – time of the experiment [day],
N_t – biomass in day ‘t’ [g],
N_0 – biomass in day ‘0’ [g].

2.3. Influence of environmental factors on algae biomass production

The next experiment tested the susceptibility of algae to different environmental factors (N:P ratio, carbonates concentration, optical density of microalgae suspension, photosynthetically active radiation) measured by biomass increase rate. A *Chlorella* sp. suspension was prepared as previously described (100 ml was filtered, dried and weighed as a reference). The algae were placed in 15 flasks with 100 ml suspension each, 3 flasks of following kinds:

- control samples containing the prepared suspension;
- samples with a different optical density of microalgae suspension, achieved through dilution of the culture (50 ml of the suspension, 50 ml of pure medium) – without change in nutrients concentration;
- samples with increased ammonium nitrogen concentration (0.0336 g $(NH_4)_2SO_4$ added to each flask) – reached a value of 160 mg/l, total nitrogen ca. 190 mg/l and phosphates ca. 30 mg/l;
- samples with increased concentration of carbonates (0.1 g Na_2CO_3 added to each flask);
- samples additionally exposed to light of a sodium lamp, surrounded with reflecting foil.

The flasks were stoppered with cotton wool plugs and incubated on a rotary shaker at 150 rpm for 5 days at ambient temperature (25 ± 2°C). After the incubation period the samples were filtered, dried and weighed. The results were compared with the control samples and the reference. Obtained data were used to calculate the growth rate as previously described.

3. Results and discussion

3.1. The first batch test experiment – optical density of microalgae suspension influence

Results of the experiment in which influence of suspension optical density on growth increase was tested are shown in table 1 and as a graph in figure 3. Figure 4 shows a value of growth rate of each culture obtained in this experiment.

Table 1. Dry biomass obtained from the filtrate – experiment with different dilutions (optical density of algae suspension)
Tabela 1. Ilość suchej masy otrzymanej po przefiltrowaniu zawiesiny – eksperyment z różnym rozcieńczeniem próbki (różną zawartością glonów w medium)

	CONTROL SAMPLE [g]	20% [g]	40% [g]	60% [g]	80% [g]
0	0.011	0.0022	0.0044	0.0066	0.0088
1	0.0211	0.0055	0.0124	0.0196	0.0213
2	0.0219	0.0058	0.0126	0.019	0.0206
3	0.0218	0.0054	0.0125	0.0199	0.0211
MEDIUM	0.0216	0.0056	0.0125	0.0195	0.021
INCREASE	0.0106	0.0034	0.0081	0.0129	0.0122
INCREASE [%]	96.36	153.03	184.09	195.45	138.64

The first test, in which the influence of dilution was checked, gave interesting results. Dilution of algae suspension on the level of 40% and 60% was related with the highest biomass increase (184.09% and 195.45%, respectively). Biomass at start day for these dilutions was 0.0044 g and 0.0066 g, after 3 days reached a value of 0.0125 g and 0.0195 g. Growth rate of algae in these cultures was on the level of 0.361 1/day·and 0.348 1/day. Dilution on the level of 80% (80 ml of control culture and 20 ml of growth medium) was too low and gave unsatisfactory results (increase – 138.64%; growth rate – 0.290 1/day). The highest tested dilution (20% – 20 ml of control culture and 80 ml of medium) gave better results of increase than 80%, but was too high for quick period of retention time tested in experiment. Obtained growth rate was on the level of 0.311 1/day. For further tests 50% dilution of algae suspension was assumed.

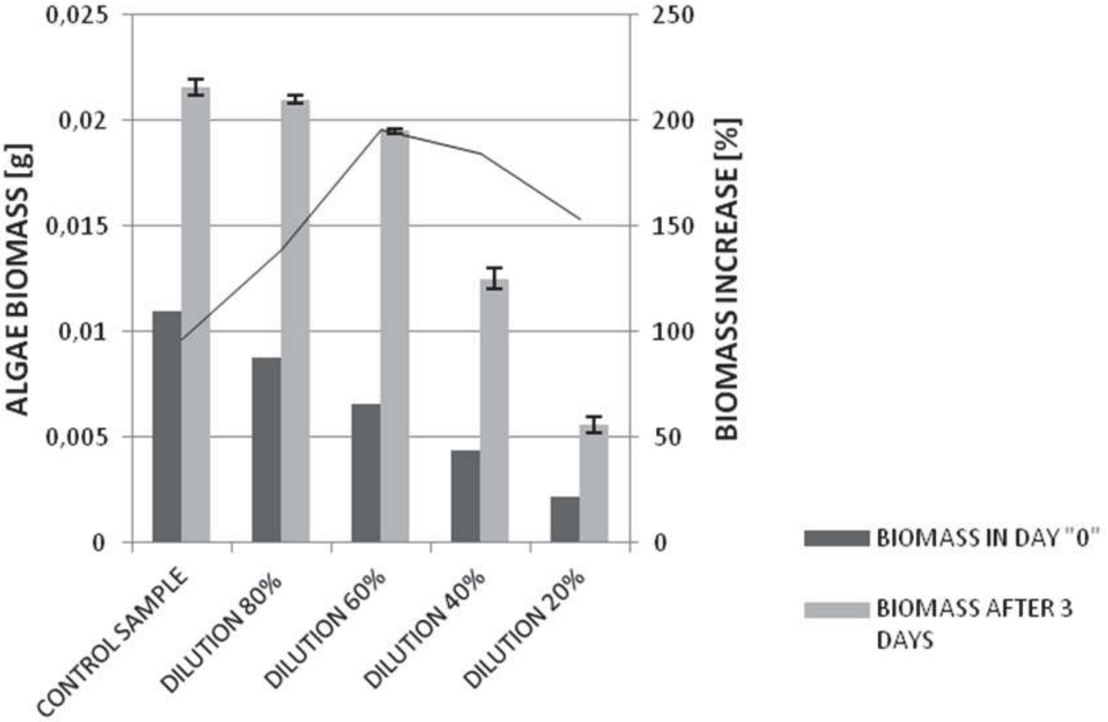

Fig. 3. Results of batch test experiment with different dilutions
Rys. 3. Wykres ilustrujący wyniki eksperymentu z różnym rozcieńczeniem

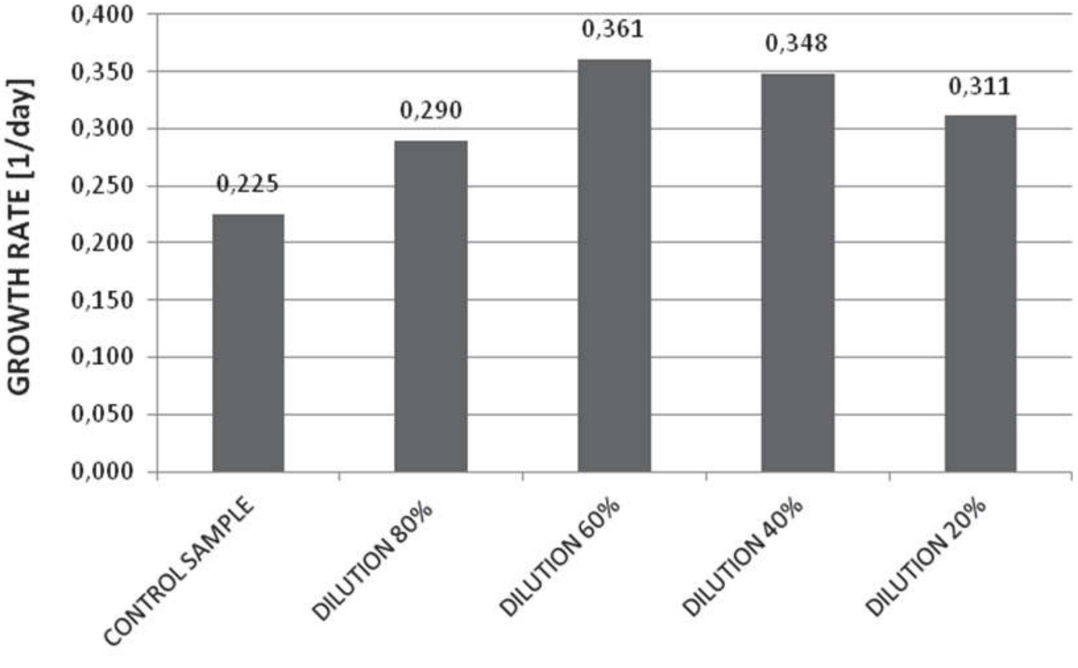

Fig. 4. Growth rate of *Chlorella* sp. depending on culture dilution
Rys. 4. Szybkość wzrostu *Chlorella* sp. w zależności od rozcieńczenia zawiesiny wyjściowej

3.2. The second batch test experiment – environmental factors influence

Results of batch-test with different environmental conditions are shown in table 2 and illustrated as a graph in figure 5. Figure 6 shows growth rate of each algal culture obtained in this test.

Table 2. Biomass obtained after drying the filtrate from flasks – batch test with influence of environmental factors
Tabela 2. Ilość suchej masy otrzymanej po przefiltrowaniu zawiesiny – eksperyment z różnymi czynnikami środowiskowymi

	CONTROL SAMPLE [g]	DILUTION [g]	$(NH_4)_2SO_4$ [g]	Na_2CO_3 [g]	PAR [g]
0	0.0314	0.0157	0.0314		
1	0.0523	0.0514	0.057	0.0678	0.0646
2	0.0545	0.0509	0.0583	0.0677	0.072
3	0.0573	0.0457	0.055	0.0649	0.0646
MEDIUM	0.0547	0.0493	0.0568	0.0668	0.0671
INCREASE	0.0233	0.0336	0.0254	0.0354	0.0357
INCREASE [%]	74.2	214.23	80.79	112.74	113.59

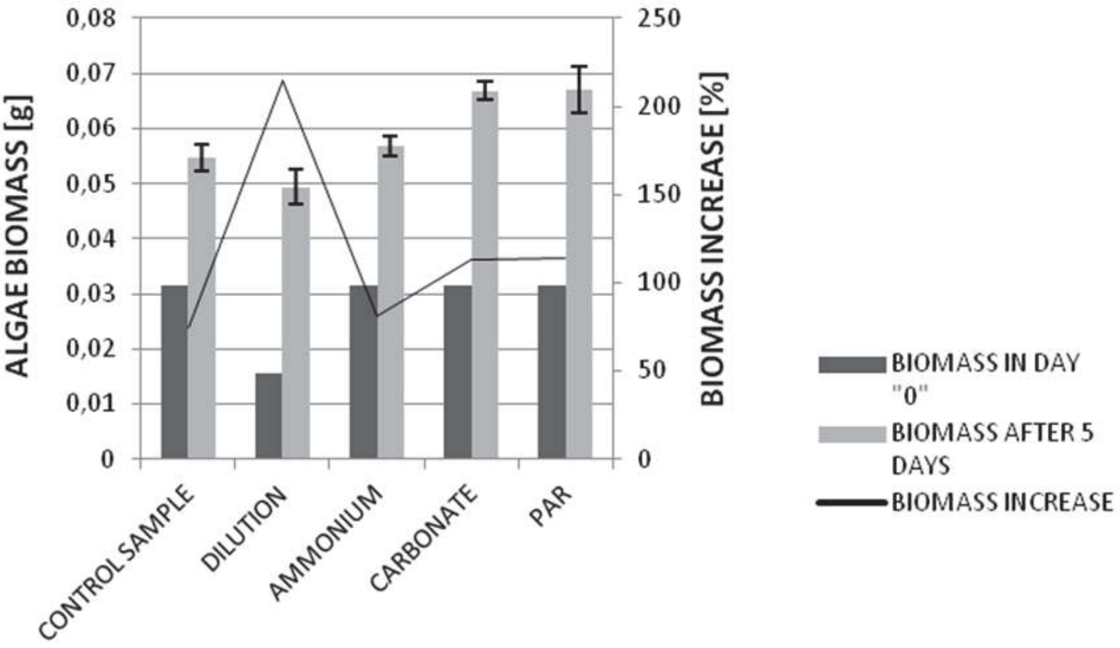

Fig. 5. Results of batch test experiment with different environmental factors
Rys. 5. Wykres ilustrujący wyniki eksperymentu z różnym czynnikami środowiskowymi

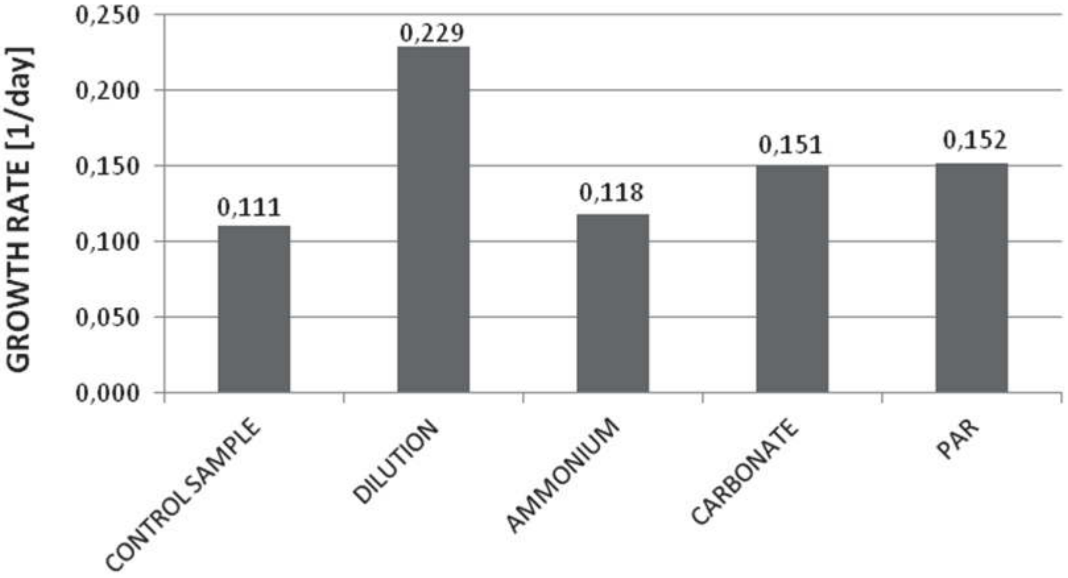

Fig. 6. Growth rate of *Chlorella* sp. depending on influence of environmental factors
Rys. 6. Szybkość wzrostu *Chlorella* sp. w zależności od badanego czynnika środowiskowego

Results of second batch-tests showed that reducing the concentration by half caused in more than a double increase (214.23%) of obtained dry biomass, in comparison with control samples. Growth rate was on the level of 0.229 1/day, and was the highest of other tested factors. Addition of sodium carbonate as a carbon dioxide source and lightening by PAR also resulted in higher biomass growth in comparison with control samples (increase on the level of 112.74% and 113.59% respectively). N/P ratio change from 3.5 to 6.5 had no significant impact on the amount of biomass, but this result must be subjected to further analysis. In this case biomass increase and growth rate was at similar level as in control cultures (80.79%; 0.118 1/day). The highest growth increase was obtained for diluted samples. It showed that the optical density of algae suspension was a major factor which limited biomass increase in the test flasks.

3.3. Discussion

As literature sources and preliminary tests showed, microalgae are undemanding in their cultivation. These aquatic organisms only need the access to basic nutrients and sunlight (or artificial photosynthetically active radiation – PAR) for growth and multiplication. Environmental conditions, like pH or temperature are also very important (too low value of these parameters can be growth limiting) but in general – microalgae cultivation is an uncomplicated and relatively cheap procedure. It is also a carbon-neutral process because for each kilogram of algal biomass produced, about 1.88 kilograms of CO_2 are sequestrated from atmosphere [10]. Among the requirements for algal growth the most expensive are nutrients – if their production involves natural resource and energy utilization. Optimization of this factor can mitigate biomass production costs and improve process economics [3]. For their cultivation different types of wastewater can be used – also reject water, which are difficult to treat [19]. Additionally – obtained biomass can be used as a bioenergy source, for the production of different biofuels, including biodiesel, bio-oil, biogas and biohydrogen [5,7,12,15]. This is the reason why they are interesting for researchers. The most important problem in applicable solutions is how to increase the growth and nutrients uptake in short period of time. In our experiment we have done a series of batch tests in laboratory conditions to check, which of the most important environmental factors can influence on the growth rate. Similar studies have been done by several research groups interested in this topic. Blair et al. [3] analysed the impact of different light wavelength on the algal growth rate and volumetric biomass productivity. Their study shown that clear and blue light wavelengths had a positive impact on the growth rates, compared to the red and green light. Shriwastav et al. [17] studied adaptability of growth and nutrient uptake potential of *Chlorella sorokiniana* with variable nutrient loading. Researchers harvested algae in mineral, diluted BG11 media with different concentrations of nitrate (as $NaNO_3$) and phosphate (as K_2HPO_4) to achieve required nutrient levels. Results shown the ability of *C. sorokiniana* to regulate its nutrient uptake in accordance with the available nutrients levels in the surrounding without any harmful effect on growth or productivity until either nutrient became rate limiting. These results indicate that the typical Redfield molar ratio of 16N:1P [16] in algae could be variable. Deviations of this ratio have been also reported by Hullat et al. [8] and Klausmeier et al. [11]. Effect of algal density on growth and nutrient removal as other important parameter was investigated by Tam et al. [20]. High algal density lead to self-shading, reduction in photosynthetic efficiency and accumulation of auto-inhibitors [4,6], so there is a great need to indicate optimal level of this factor. Value of this parameter obtained in this study was similar to growth rates of algae harvested in commercial Bristol medium (0.3664 1/day), however inoculum size was characterized as a number of cells of *Chlorella vulgaris*, not as a dry weight [13].

3. Conclusion

The experiment showed that among the studied factors (in the tested range) the most important for the algae growth intensification is the density of the culture suspension. Too high density results in poor access to sunlight and high competition. In effect low removal of nutrients from reject water is bound to occur. Too low density may create a necessity to extend the hydraulic retention time in bioreactor and cause technological problems (very low flows). The best results of biomass increase of *Chlorella* sp. in pretreated reject water correspond with the 0.045–0.067 g/l of microalgae suspended in the medium. Growth rates related with these values were on the level of 0.348 and 0.361 1/day, respectively.

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References

1. **Ankita J., Ceballos R.M., Murthy G.S.:** *Effects of Environmental Factors and Nutrient Availability on the Biochemical Composition of Algae for Biofuels Production: A Review.* Energies, 6, 4607–4638 (2013).
2. **Ariful H.M., Bangrak P., Sirisansaneeyakul S., Choorit W.:** *Factors Affecting the Biomass and Lipid production from Chlorella sp. TISTR 8990 under Mixotrophic Culture***.** Walailak Journal Sci&Tech, 9, 4, 347–359 (2012).
3. **Blair M.F., Kokabian B., Gude V.G.:** *Light and growth medium effect on Chlorella vulgaris biomass production.* Journal of Environmental Chemical Engineering, 2, 665–674 (2014).
4. **Darley W.M.:** *Algal biology: A physiological Approach*, Basic Microbiology, Blackwell Scientific Publications, Oxford 1982.

5. **Ferreira A.F., Ortigueira J., Alves L., Gouveia L., Moura P., Silva C.M.:** *Energy requirement and* CO_2 *emissions of bio*H_2 *production from microalgal biomass*. Biomass Bioenergy, 49, 249–259 (2012).
6. **Fogg G.E.:** *Algal Cultures and Phytoplankton Ecology, second edition*, The University of Wisconsin Press, Madison 1975.
7. **Gude V.G., Grant G.E., Patil P.D., Deng S.:** *Biodiesel production from low cost and renewable feedstock.* Central European Journal of Engineering, 3, 595–605 (2013).
8. **Hullat C., Lakaniemi A.M., Puhakka J., Thomas D.:** *Energy demands of nitrogen supply in mass cultivation of two commercially important microalgal species, Chlorella vulgaris and Dunaliella tertiolecta.* Bioenergy Research, 5, 3, 669–684 (2012).
9. **Janus H.M., van der Roest H.F.:** *Don't reject the idea of treating reject water.* Water Science and Technology, 35, 10, 27–34 (1997).
10. **Keffer J.H., Kleinheinz G.T.:** *Use of Chlorella vulgaris for* CO_2 *mitigation in a photobioreactor*. Journal of Industrial Microbiology and Biotechnology, 29, 275–280 (2002).
11. **Klausmeier C.A., Litchman E., Daufresne T., Levin S.A.:** *Phytoplankton stoichiometry.* Ecological Research, 23, 3, 479–485 (2008).
12. **Kokabian B., Gude V.G.:** *Photosynthetic microbial desalination cells (PMDCs) for clean energy, water and biomass production.* Environmental Science: Processes& Impacts, 15, 2178–2185 (2013).
13. **Lau P.S., Tam N.F.Y., Wong Y.S.:** *Effect of organic-N sources on algal wastewater treatment system.* Resources, Conservation and Recycling, 11, 197–208 (1994).
14. **Lavens P., Sorgeloos P.:** *Manual on the Production and Use of Live Food for Aquaculture.* FAO Fisheries Technical Paper, 361, Corporate Document Repository 2.3.1.1–6*,* Ghent, Belgium 1996.
15. **Li Y., Horsman M., Wu N., Lan C.Q., Dubois-Calero N.:** *Biofuels from microalgae.* Biotechnology Progress, 24, 815–820 (2008).
16. **Redfield A.C.:** *The biological control of chemical factors in the environment.* American Scientist, 46, 3, 205–221 (1958).
17. **Shriwastav A., Gupta S.K, Ansari F.A., Rawat I., Bux F.:** *Adaptability of growth and nutrient uptake potential of Chlorella sorokiniana with variable nutrient loading*. Bioresource Technology, 174, 60–66 (2014).
18. **Slade R., Bauen A.:** *Micro-algae cultivation for biofuels: Cost, energy balance, environmental impacts and future prospects.* Biomass and Bioenergy, 53, 29–38 (2013).

19. **Sode S., Bruhn A., Thorsten J.S. Balsby, Larsen M.M., Gotfredsen A., Rasmussen M.B.:** *Bioremediation of reject water from anaerobically digested waste water sludge with macroalgae (Ulva lactuca, Chlorophyta).* Bioresource Technology, 146, 426–435 (2013).
20. **Tam N.F.Y., Wong Y.S.:** *Effect of ammonia concentrations on growth of Chlorella vulgaris and nitrogen removal from media*, Bioresource Technology, 57, 45–50 (1996).

Określenie optymalnych warunków hodowlanych dla efektywnej produkcji biomasy glonowej

Streszczenie

Mikroglony są niewielkimi organizmami wodnymi o bardzo dużym potencjale w zakresie oczyszczania ścieków. Ma to związek z faktem, że są mało wymagające w hodowli, a do wzrostu i rozmnażania mogą z powodzeniem wykorzystywać związki biogenne zawarte w ściekach. Dodatkowo, powstająca biomasa może posłużyć jako substrat energetyczny – może zostać wykorzystana do produkcji biopaliw, takich jak biodiesel, bioetanol czy biobutanol lub jako wsad do komory fermentacji, czyli do produkcji biogazu. Ze względu na rosnące zainteresowanie pozyskiwaniem znacznych ilości biomasy glonów podjęto próbę zoptymalizowania warunków hodowlanych pozwalających na pozyskanie największej ilości surowca przetwórczego. W eksperymencie przeprowadzono w warunkach laboratoryjnych serię analiz w zawiesinie, w których jako medium wzrostowe dla mikroglonów z rodzaju *Chlorella* wykorzystano wody z odwadniania przefermentowanych osadów ściekowych, pochodzące z Centralnej Oczyszczalni Ścieków w Gliwicach. Wody osadowe charakteryzują się wysokim stężeniem azotu nieorganicznego w postaci jonów amonowych, które z powodzeniem wykorzystywane są przez mikroglony do wzrostu. Dodatkowo ścieki takie, w porównaniu z surowymi ściekami komunalnymi, są relatywnie klarowne, dzięki czemu możliwe jest przenikanie światła w głąb medium hodowlanego. W przeprowadzonym eksperymencie wody osadowe w pierwszym etapie poddane zostały podczyszczaniu w reaktorze typu SBR, a następnie skierowane jako dopływ do reaktora glonowego. Celem badań było określenie wpływu podstawowych czynników środowiskowych na tempo wzrostu glonów, a tym samym na przyrost biomasy. W pierwszym teście analizowano wpływ gęstości optycznej hodowli na szybkość przyrostu biomasy. Zawiesinę glonów jednokomórkowych rozcieńczano medium wzrostowym odpowiednio w stosunku 1:5, 2:5, 3:5 oraz 4:5 w odniesieniu do hodowli kontrolnych. Uzyskane wyniki pozwoliły określić optymalną gęstość zawiesiny mikroglonów w reaktorze (odpowiadającą największym przyrostom biomasy, a tym samym wysokiemu usunięciu związków biogennych). Początkowe stężenie zawiesiny mikroglonów na poziomie 0,045–0,067 g/l odpowiadało największym przyrostom biomasy w próbach (tempo wzrostu odpowiednio 0,348 i 0,361 1/dzień). W drugiej serii testów analizowano dodatkowo wpływ takich czynników jak: stosunek N:P, dodatek węglanów jako źródła dwutlenku węgla oraz dodatkowe oświetlanie promieniowaniem aktywnym fotosyntetycznie (falą świetlną o długości w zakresie absorpcji chlorofilu a oraz b), w odniesieniu do próby kontrolnej, a także do uzyskanej wcześniej optymalnej gęstości zawiesiny mikroglonów. W eksperymencie wykazano również, że wody osadowe, charakteryzujące się wysokim ładunkiem nieorganicznych związków azotu i fosforu, a także obecnością metali ciężkich mogą być z powodzeniem wykorzystywane jako medium wzrostowe dla glonów z rodzaju *Chlorella*.

Słowa kluczowe:
mikroglony, wody osadowe, przyrost biomasy

Keywords:
microalgae, reject water, growth rate

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Estimation of Chemical Oxygen Demand Fractions of Municipal Wastewater by Respirometric Method – Case Study

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1. Introduction

Nowadays, a detailed characterization of influent wastewater is one of the most relevant factor to efficient operation of wastewater treatment plants (WWTPs). Moreover, in recent years, the increasing utilization of plant simulation models such a ASMs (activated sludge models) developed by IWA (IAWQ Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment Processes) required accurate and precise description of raw wastewater, especially organic matter presented in the inflow [1, 2]. Traditionally, those compounds were characterized by COD (chemical oxygen demand), BOD (biological oxygen demand) and TOC (total organic carbon) parameters, but only division of COD into fractions with different microbiological properties gives more precise information on the biodegradation of the carbonaceous substrate [3, 4]. The total COD (C_T) is divided into two main fractions: biodegradable (C_S) and nonbiodegradable (inert) (C_I). The biodegradable COD is further divided into readily biodegradable substrate (S_S) and slowly biodegradable, particulate substrate (X_S) [5–7]. The readily biodegradable substrate consists of simple soluble compounds such as volatile fatty acid, alcohol etc. which can be easily absorbed by organisms and metabolized for energy and synthesis [8, 9]. The slowly biodegradable fraction is mainly composed of particulate, colloidal and complex organic molecules. In case of this fraction, many of these components could be absorbed and utilized only after the hydrolysis by extra cellular enzymes of bacteria [7, 10]. The nonbiodegradable soluble substrate is transferred in the effluent without any significant modification. The particulate inert fraction (X_I) is mostly accumulated in the activated sludge and removed from the system with primary and secondary sludge [11].

Several methods have been proposed for estimation COD fractions, but only respirometric and physical-chemical techniques have most commonly been applied. The physic-chemical methods used processes such as filtration and flocculation to separate particulate fractions. The main disadvantage of this technique is that those processes couldn't effectively divide the biodegradable substrates (S_S and X_S). On the other hand, the physic-chemical methods are relatively fast and facile [11, 12]. The respirometric measurement is based on analysis of the biological oxygen consumption rate (OUR) under well-defined experimental conditions [5, 13]. This method demands special equipment and its more time consuming. Whereas this technique allows for obtaining more accurate data for research studies as well as for preparing wastewater treatment plant simulations [11, 14–16].

Furthermore, the chemical oxygen demand fractionation was not only used in the case of activated sludge models to increase the understanding of the effect of process changes or fluctuations on the treatment process efficiency, but also for modeling of wastewater transformation and biodegradation during the transport in sewer systems. Currently, these processes are quite well recognized and mentioned as important factor influenced the operational parameters of WWTP. This is mainly due to the fact that in sewer conduits significant part of biodegradable substances could be removed from wastewater and buildup into sewer biofilm or suspended microorganism biomass [17, 18]. In that situation at the WWTP can appear problems with proper substrate equilibrium C/N/P demanded for biological treatment of wastewater from carbon and biogenic substances. On the other hand, models of sewage biodegradation can be used to predict discharge of pollutants load into the receiver – mainly river form storm water system or combined sewer system. In that situation mentioned models can be also applied for increase and optimize processes of sewage biodegradation by provide proper dissolved oxygen concentration e.g. by wastewater reaeration in conduits, appropriate time of flowing and proper condition for sediments transport etc [17–19].

The main aim of this study is to determine COD fractions both in raw wastewater and in reject water obtained from municipal wastewater treatment plant in Malaga, Spain.

2. Materials and methods

Samples of wastewater and activated sludge were taken from municipal wastewater treatment plant Guadalhorce (145 000 m^3/d) in Malaga, Spain. The wastewater was taken from four collectors, three of them (A, B, C) collected raw municipal wastewater from different district of the city. The last one (D), recycled wastewater produced during sewage sludge treatment (Fig.1). A detailed description of collectors is shown in Table 1. Moreover, it could be noted that the research was conducted during the summer with high temperatures and absence of rain.

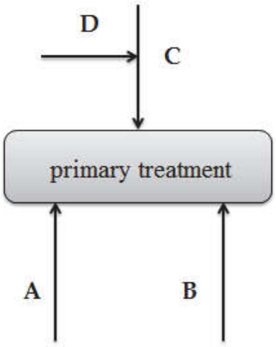

Fig. 1. Illustration of influent collectors to WWTP
Rys. 1. Kolektory wprowadzające ścieki do oczyszczalni

The experiment was carried out using a respirometer BM – T (Surcis). The equipment consisted of three main parts: batch reactor with the volume 1.0 dm^3 (BM-T analyzer), thermostatic unit and computer. The respirometer was inoculated with activated sludge from one of the biological reactors. This sample was aerated over 24 hours before the measure to reach the endogenous respiration. For all measurements the temperature was maintained at 20.0 ± 0.1°C and pH was kept in the range 7.0 and 8.0. For all batch tests, freshly collected samples (max 2 hours after collection) were used. Before the analysis (about 10 min) 10 ml solution of allylthiourea (ATU) was added to respirometer's chamber in order to eliminate oxygen consumption due to nitrification. The measurement was conducted in accordance with the procedure given by Surcis.

Table 1. The main characteristic of collectors
Tabela 1. Podstawowe cechy kolektorów

Collector	Diameter [m]	Flow [m^3/d]	Length [m]	Collector type
A	0.7	32000	3143	pressure
B	1.1	82000	5641	pressure
C	0.6	18000	10000	gravity
D	0.5	7000	100	gravity

The respirometer recorded directly two fractions: total biodegradable (C_S) and readily biodegradable (S_S) ($mg \cdot dm^{-3}$). The other fractions were defined by following calculations:

$$X_S = C_S - S_S \; [mg \cdot dm^{-3}] \tag{1}$$

$$S_I = S_T - S_S \; [mg \cdot dm^{-3}] \tag{2}$$

$$X_I = C_I - S_I \; [mg \cdot dm^{-3}] \tag{3}$$

where:
S_I soluble inert COD substrate ($mg \cdot dm^{-3}$), S_T total soluble COD ($mg \cdot dm^{-3}$), X_I particulate inert substrate ($mg \cdot dm^{-3}$), X_S slowly biodegradable organic matter ($mg \cdot dm^{-3}$), C_I total nonbiodegradable COD ($mg \cdot dm^{-3}$).

In this study the percentage values of individual fractions were presented, therefore the obtained value of particulate fraction ($mg \cdot dm^{-3}$) was compared to the total concentration of COD (C_T) ($mg \cdot dm^{-3}$). Presented results are the average of five replicates.

In order to estimate (S_T) the total soluble COD, the samples of wastewaters were filtered through 0.45 μm filter, then the chemical oxygen demand was measured. All chemical oxygen demand (S_T and C_T) analyses were performed with Hach Lange UV-VIS DR 5000 using Hach analytical methods.

3. Results and discussion

The results of presented study are shown in Figure 2. The readily biodegradable substrate (S_S) differed from 19.9 to 56.5 % of the total COD (C_T), the lowest share of this fraction was observed in collector D, which contributed wastewater from sewage sludge system. Estimations obtained for slowly biodegradable fraction of COD (X_S) varied from 4.2 to 16.6 %.

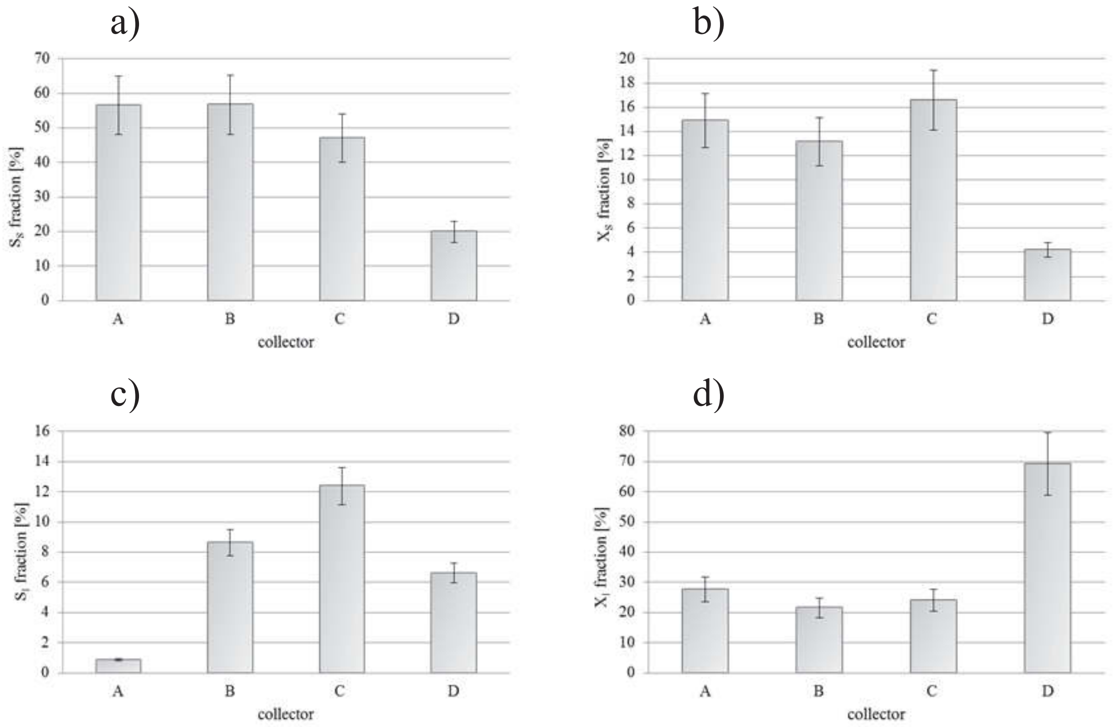

Fig. 2. Average values of a) S_S b) X_S c) S_I d) X_I fractions with standard deviation from different collectors

Rys. 2. Średnie wartości frakcji a) S_S b) X_S c) S_I d) X_I wraz z odchyleniem standardowym w poszczególnych kolektorach

As in case of readily biodegradable organic fraction, the smallest value of total COD was obtained from collector D. The wastewater from collectors A, B and C was characterized by low concentration of inert fractions, form 0.9 to 12.4% for inert soluble substrate and from 21.6 to 27.8% for inert suspended substrate. As shown in figure 2. c and d, the reject water had a significant share of non-biodegradable fractions, especially the particulate inert fraction, X_I = 69% of total COD.

Table 2. The summary of COD fractions from various countries (raw wastewater)
Tabela 2. Zestawienie frakcji ChZT z różnych krajów (ścieki surowe)

Country	S_S	X_S	S_I	X_I	References
	%				
S. Africa	20.00	62.00	5.00	13.00	[5]
	25.00	53.00	7.00	15.00	[31]
Switzerland	10–20	53–60	7–11	7–15	[6]
Spain	18.3	33.3	8.5	24.9	[32]
Netherlands	41.50	32.70	4.70	16.60	[20]
Germany	26.00	57.00	3.00	14.00	[33]
Turkey	26.00	62.00	2.00	10.00	[14]
Poland	23–29	51–56	2–3	17–19	[34]
	21–40	34–51	4–7	21–28	[35]
Denmark	35.0	35.0	5.0	10.0	[36]
Italy	12.2–0.3	27.6–66.9	1.2–14.0	8.8–33.1	[21]
Hungary	21.9	49.8	4.6	23.7	[11]

The obtained results of COD fractioning from WWTP in Malaga were substantially different from those presented in literature (Table 2), particularly in case of readily biodegradable fraction in collectors A, B and C. Frequently, the percentage of this fraction is varied from 10 to 20% of C_T. However, in the study conducted by van Veldhuizen et al. [20] and Quevauviller et al. [21] similar data was observed.

The high concentration of this fraction in municipal wastewater might have a beneficial influence on denitrification as well as the biological phosphorus removal process [22, 23]. Hydrolyzed lipids, however, could cause the growth of filamentous bacteria [23, 24]. Moreover, in the study performed for pipelines A, B and C inert fractions of total COD (S_I and X_I) were comparable to the typical value provided by researches from different countries.

The collector D was characterized by a significant share of nonbiodegradable fractions (more than 70% of C_T). This pipeline contributes the reject water, which could be defined as a high-strength wastewater, produced during sewage sludge treatment. Because of high nitrogen and phosphorus load as well as a significant amount of nonbiodegradable organic load [25], those sidestreams have a major impact on WWTP performance [26, 27]. Generally, reject water is recycled to the head of the wastewater treatment plant without any pretreatment, which could cause several problems in WWTP such a process upset, release of odors, violation of discharge limits and increased operational and maintenance costs [28, 29].

The percentage share of particular fractions depends on various factors. According to Quevauviller et al., [21] the value of readily biodegradable COD (S_S) as well as particulate inert COD (X_I) is related to the capacity of wastewater treatment plant and share of industrial wastewater in the influent. In case of large WWTPs, the lower percentage of S_S and a higher percentage of X_I might be observed. This fact is associated with the retention time of wastewater in sewage systems. Usually the larger WWTPs have more complex sewer collection system with a longer retention time of wastewater, therefore the transformation and biodegradation process occur at bigger scale in pipelines. Besides, the higher share of inert substrate in total COD is generally linked with presence of industrial wastewater. Moreover, the type of sewer systems has significant influence on the value of particulate fractions [4]. The wastewater from combined sewer has a more varied composition than in case of separate systems. Zhou et al. (2008) shown that the lower percentage of readily biodegradable fractions were caused by the dilution effect of stormwater runoff [29]. Moreover, in the study conducted by Zhou et al. proved the influence of industrial wastewater overflows on COD fractions. Additionally, the presence of accidental and infiltration water could provide a noticeable change of wastewater character.

4. Summary and conclusions

The division of COD into fractions with different microbiological properties is comprehensive tool for wastewater characterization. It could be applied to control and modeling of wastewater treatment plants and sewer systems functioning. Furthermore, it gives faster result about the presence of biodegradable substrate in raw wastewater in comparison to biological oxygen demand (BOD). The COD fractionation could give much useful information about the condition of sewer systems, particularly about contribution of infiltration water and industrial wastewater discharges.

In this study the COD fractions in municipal wastewater from various collectors and in reject water were presented. In case of raw municipal wastewater (collectors A, B and C) biodegradable fractions were dominated, from 47 to 57% for readily biodegradable fraction and from 13 to 16% for slowly biodegradable fraction. The reject water from

MWWTP (collector D) was characterized by a significant share of non-biodegradable fractions, the percentage of particulate inert fraction was 69% and the percentage of inert soluble fraction ranged 6.7%.

Acknowledgements

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References

1. **Henze M., Grady C., Gujer W., Marais G., Matsuo T.:** *Activated Sludge Model No 1, Rep. 1.* IWA 1987.
2. **Lagardea F., Tusseau-Vuillemina M., Lessardb P., He´Duita P., Dutropa F., Mouchelc J.M.:** *Variability estimation of urban wastewater biodegradable fractions by respirometry.* Water Res. 39, 4768–4778 (2005).
3. **Vollertsen J., Hvitved-Jacobsen, T.:** *Biodegradability of wastewater – a method for COD-fractionation.* Water Sci. Technol. 45(3), 25–34 (2002).
4. **Zawilski M., Brzezińska A.:** *Variability of COD and TKN Fractions of Combined Wastewater.* Polish J. of Environ. Stud. 18(3), 501–505 (2009).
5. **Ekama G.A., Dold P.L., Marais G.***: Procedures for determining influent COD fractions and the maximum specific growth rate of heterotrophs in activated sludge systems.* Water Sci. Technol. 18, 91–114 (1986).
6. **Kappeler J., Gujer W.:** *Estimation of kinetic parameters of heterotrophic biomass under aerobic conditions and characterization of wastewater for activated sludge modeling.* Water Sci. Technol. 25(6), 125–130 (1992).
7. **Henze M., Gujer W., Mino T., Van Loosdrecht M.C.M.:** *Activated sludge models ASM1, ASM2, ASM2d, and ASM3.* IWA Scientific and Technical Report No. 9 (2000).
8. **Wanner J.:** *Activated sludge bulking and foaming control.* A Technomic Publishing Company, Inc. Lancaster, Pennsylvania 1994.
9. **Montusiewicz A., Łagód G., Piotrowicz A.:** *Modelowanie systemów oczyszczania ścieków.* Monografie Komitetu Polskiej Akademii Nauk, vol. 74, Lublin 2010.
10. **Drewnowski J., Makinia J.:** *Modeling hydrolysis of slowly biodegradable organic compounds in biological nutrient removal activated sludge systems.* Water Sci. Technol. 67(9), 2067–2074 (2013).

11. **Pasztor I., Thury P., Pulai, J.:** *Chemical oxygen demand fractions of municipal wastewater for modeling of wastewater treatment.* Int. J. Environ. Sci. Te. 6(1), 51–56 (2009).
12. **Mamais D., Andreadakis A., Noutsopoulos C., Kalergis, C.:** *Causes of and Control Strategies for Microthrix parvicella Bulking and Foaming in Nutrient Removal Activated Sludge Systems.* Water Sci. Technol. 37(4/5), 9–17 (1998).
13. **Rozich A. F., Gaudy A. F.:** *Design and operation of activated sludge process using respirometry.* Lewis, Michigan 1992.
14. **Orhon D., Karahan O., Sozen S.:** *The effect of residual microbial products on the experimental assessment of the particulate inert COD in wastewaters.* Water Res. 33(14), 3191–3203 (1999).
15. **Carvalho G., Nopens I., Novais J.M., Vanrolleghem, P.A., Pinheiro H.M.:** *Modelling of activated sludge acclimisation to a non-ionic surfactant.* Water Sci. Technol. 43(7), 9–17 (2001).
16. **Dulekgurgen E., Dogruel S., Karahan O., Orhon D.:** *Size distribution of wastewater COD fractions as an index for biodegradability.* Water Res. 40, 273–282 (2006).
17. **Hvitved-Jacobsen T.:** *Sewer processes. Microbial and Chemical Process Engineering of Sewer Networks.* CRC Press, Boca Raton, London, New York, Washington 2002.
18. **Qteishat O., Myszograj S., Suchowska-Kisielewicz, M.:** *Changes of wastewater characteristic during transport in sewers.* Wseas Transactions On Environment And Development. 11(7), 349–358 (2011).
19. **Łagód G., Sobczuk H.***:* *Influence of flow parameters on aerobic biodegradation of pollutants in sewer system.* Proceedings ECOpole. 1(1–2), 181–186 (2007).
20. **Van Veldhuizen H.M., Van Loosdrecht M.C.M., Heijnen J.J.:** *Modelling biological phosphorus and nitrogen removal in a full scale activated sludge process.* Water Res. 33(16), 3459–3468 (1999).
21. **Quevauviller, P, Thomas, O., Van Der Beken, A.:** *Wastewater Quality Monitoring and Treatment.* John Wiley & Sons Ltd, England 2006.
22. **Dauknys R., Vabolienė G, Valentukevičienė M., Rimeika M.:** *Influence of substrate on biological removal of phosphorus.* EKOLOGIJA. 55, 220–225 (2009).
23. **Gavalakis E, Mamais D, Matinos C, Andreadakis, A.:** *An experimental and mathematical simulation of biological processes in a sewerage system.* Global NEST J. 8, 75–81 (2006).

24. **Mamais D, Jenkins D, Pitt P.:** *A rapid physical–chemical method for the determination of readily biodegradable soluble COD in municipal wastewater.* Water Res. 27, 195–197 (1993).
25. **Pitman A., R.:** *Management of biological nutrient removal plant sludges – Change the paradigms?* Water Res. 33(5), 1141 (1999).
26. **Marttinen S., K., Ruissalo M., Rintala J.A.:** *Removal of bis (2-thylhexyl) phthalate from reject water in a nitrogen-removing sequencing batch reactor.* J. Environ. Manage. 73, 103–109 (2004).
27. **Van Loosdrecht M.C.M., Salem S.:** *Biological treatment of sludge digester liquid.* Proc. of IWA Spec. Conf. Nutrient Management in Wastewater Treatment Process and Recycle Streams., 13–22 (2005).
28. **Janus H.M., Van Der Roest H.F.:** *Don't reject the ideas of treating reject water.* Water Sci. Technol. 35(10), 27–34 (1997).
29. **EPA**, December 1985, Sidestreams in Advanced Wastewater Treatment Plants: Problems and Remedies. 3–4 (1985).
30. **Zhou Z, Wu Z., Wang Z., Tang S., Gu G.:** *COD fractionation and parameter estimation for combined sewers by respirometric tests.* J. Chem. Technol. Biotechnol. 83, 1596–1601 (2008).
31. **Wentzel M.C., Ekama G.A.:** *Principles in the design of single sludge activated sludge systems for biological removal of carbon, nitrogen and phosphorus.* Water Environ. Res. 69(77), 1222–1231 (1997).
32. **Del La Sota A.; Larrea L.; Novak L.; Grau P.; Henze M.:** *Performance and model calibration of R-D-N processes in pilot plant.* Water Sci. Technol. 30(6), 355–364 (1994).
33. **Wichern M.; Lübken M.; Blömer R.; Rosenwinkel, K. H.:** *Efficiency of the activated sludge model No. 3 for German wastewater on six different WWTPs.* Water Sci. Technol. 47(11), 211–218 (2003).
34. **Myszograj S., Sadecka Z.:** *Frakcje ChZT w procesach mechaniczno-biologicznego oczyszczania ścieków na przykładzie oczyszczalni ścieków w Sulechowie.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 6, 233–244 (2004).
35. **Mąkinia J.:** *Performance prediction of full-scale biological nutrient removal systems using complex activated sludge models.* Veröffentlichungen des Institutes für Siedlungswasser-wirtschaft und Abfalltechnik der Universität Hannover, Heft 136 (2006).
36. **Chachaut B.; Roche N., Latifi R.:** *Long-term aeration strategies for small-size alternating activated sludge treatment plants.* Chem. Eng. Prog. 44(5), 591–604 (2005).

Wyznaczenie frakcji ChZT w ściekach komunalnych z wykorzystaniem metody respirometrycznej

Streszczenie

Jednym z ważniejszych problemów z punktu widzenia sterowania pracą oczyszczalni ścieków jest posiadanie kompletnych i dokładnych informacji na temat jakości ścieków. Do oceny parametrów jakościowych ścieków stosowane jest określanie udziałów frakcyjnych chemicznego zapotrzebowania na tlen (ChZT) pod względem właściwości fizycznych oraz podatności na biodegradację. Informacja na temat udziałów frakcyjnych ChZT może być wykorzystywana w modelowaniu pracy systemów oczyszczania ścieków jak również modelowania procesów transportu i biodegradacji zanieczyszczeń w systemach kanalizacyjnych. Opracowanie prezentuje wyniki badań udziałów frakcyjnych ścieków dopływających do miejskiej oczyszczalni ścieków w Maladze (Hiszpania). Ścieki surowe dopływały do kolektora zbiorczego z różnych dzielnic miasta kolektorami oznaczonymi jako A, B oraz C, natomiast kolektorem D doprowadzane były wody z gospodarki osadowej, zawracane na początek procesu technologicznego oczyszczalni. Do wyznaczenia udziałów frakcyjnych ChZT w analizowanych próbkach ścieków wykorzystane zostały metody respirometryczne. W przypadku ścieków surowych największy udział w całkowitym ChZT miała frakcja biodegradowalna, 47–57% przypadało na frakcje szybko ulegające biodegradacji, natomiast 13 do 16% na frakcje wolno ulegające biodegradacji. Odcieki z urządzeń gospodarki osadowej charakteryzowały się znacznym udziałem frakcji nieulegających biodegradacji, przy czym 69% przypadało na frakcje w postaci zawiesiny, natomiast 6,7% w postaci rozpuszczonej.

Słowa kluczowe:
frakcje ChZT, materia organiczna, modele symulacyjne

Keywords:
COD fractions, organic matter, wastewater plant simulation models

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Formation of CO in the Oxy-Fuel Premixed Flame

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1. Introduction

Combustion is a chemical process of great importance, as it provides man with energy that is necessary for carrying out everyday life activities, transport, heating houses, or generating electric power. The latest Energy Information Administration report says: The global consumption of energy from fossil fuels will grow by 56% in 2040 [8]. So, fossil fuels are going to remain the predominant energy source, while the strong economic growth of developing countries will be a driving force for the increase in energy demand. The increase in energy generation from fossil fuels will increase the emission of CO_2, among other gases. With the aim of reducing the emissions of greenhouse gases, which include e.g. N_2O, CH_4 and CO_2, studies are being conducted, which are concerned with oxy-combustion – changing the fuel oxidizer from air to oxygen [11, 18] or oxygen carriers, such as Fe_3O_4, NiO [14]; the addition of CO_2 to the flame [10]; the absorption of CO_2 by, e.g., concrete aggregate [15].

Flue gases from oxy-combustion contain chiefly CO_2 and H_2O. The capture of CO_2 from flue gas in oxygen combustion is easier than in air combustion. It is essential to equip oxy-combustion boilers with an integrated system for the separation and transfer of CO_2 to the place of its storage and isolation from the atmosphere. Flue gas carbon dioxide is partially reused as a coolant, as oxygen combustion considerably increases the flame temperature. Flue gas recirculation allows the protection of both the burners, as well as the devices that monitor, e.g., the combustion chamber temperature (such as thermocouples). The addition of CO_2 to oxy-combustion makes it possible to achieve a volume of substrates, which is comparable to air combustion. This enables achangeover back to air combustion (flexi-burn) to be made in case of a failure of the oxygen generation plant. An additional justification for adding CO_2 to methane (the main component of natural gas) is the fact of supplying gas turbines with a CH_4-CO_2 mixture. The CH_4-CO_2 mixture may originate from the anaerobic digestion of biomass or organic industrial wastes [7].

Experimental tests and numerical studies have found that high CO_2 concentration in oxy-combustion substrates favours incomplete combustion, that is the formation of CO [2–4, 6, 13]. Due to the slow CO combustion reaction, the concentrations of carbon monoxide in the region of the oxy-fuel burner are higher than the equilibrium values for the examined residence times [6]. Moreover, the CO increases exponentially with flame temperature and decreases with increasing pressure. Glarborg and Bentzen [6] interpreted the experimental results using a detailed mechanism of hydrocarbon oxidation. They have concluded that the high CO_2 concentration around the burner prevents the complete oxidation of fuel at temperatures higher than 1200K, in spite of the presence excess of oxygen. According to reaction $CO_2 + H \leftrightarrow CO + OH$, high CO_2 concentration in the flame uses up the hydrogen radicals, thus disturbing the course of reaction $H + O_2 \leftrightarrow O + OH$. Another effect of the above-mentioned reaction is a change in the O/H radical proportion.

Experiments and numerical computations carried out using three different combustion mechanisms have shown that the peak CO concentrations in the flame during methane combustion in air increase with increasing CO_2 addition to the air-fuel mixture [6].

The addition of oxygen to combustion air contributes to a distinct shortening and a change in the shape of the flame [4]. Controlling the flame shape may prove useful for avoiding refractory material overheating in a specific location and changing the heat flux and temperature profiles in the combustion chamber.

2. Experimental section

Experiments were carried out for the combustion of natural gas with the following composition: CH_4=98%; C_2H_6=0.6%; C_3H_8=0.3%; N_2=1%; CO_2=0.1%. Combustion was conducted with a 5% excess oxygen. The following oxy-combustion atmospheres were examined: 23%O_2/77%CO_2, 25%O_2/75%CO_2; 27%O_2/73%CO_2; 29%O_2/71%CO_2. Oxygen and carbon dioxide from cylinders were passed to a gas mixer and then to a kinetic burner of a power of approx. 1kW. The burner belongs to a group of low-swirl burners, in which the degree of stream swirl is defined with the swirl number $S<0.6$. The stream of substrates (a natural gas/O_2/CO_2 mixture) passes through the openings in the central duct and the vanes surrounding it. Such a construction of the exchangeable radial swirler creates a low vortex flow with a stable flame. The swirler with 11 vanes and a vane inclination angle of 45^{o} was situated inside the burner (0.01m away from the outlet). A movable element of the measuring position was the burner, whose distances from the flue gas sampling probe was varied in the range of 0.02 – 0.1 m with a step of 0.02 m. The inner diameter of the burner was 0.022 m, while the diameter of the flue gas sampling probe was 0.004 m. The ceramic probe was distinguished by high brittleness, therefore it remained in the same place throughout the experiment period. Flue gas sampling was done in the burner's axis. Inside the ceramic probe, a 0.0005 m-diameter PtRh10-Pt thermocouple is installed. The combustion chamber, in which measurements were taken, is illustrated in Fig. 1a. The combustion chamber is composed of a $\phi = 60$ quartz tube, a cylindrical resistance furnace and furnace lagging of 0.05 m-thick ceramic fibres. All tests were started in a location between the burner and the resistance furnace, 0.1 m away from the burner, and a constant temperature of 1443K was maintained in that location. Photograph 1b shows a flame with a length of approx. 0.13 m in the open space for the atmosphere 27%O_2/73%CO_2. Flue gas sampled from the flame was transferred to a cooler via the heating line, and then to an Horiba PG350 continuous duty analyzer. The measurement of CO in this device was done with a non- dispersion infrared absorption detector (NDIR). The uncertainty of measurement was about 1% of the magnitude of measured concentration.

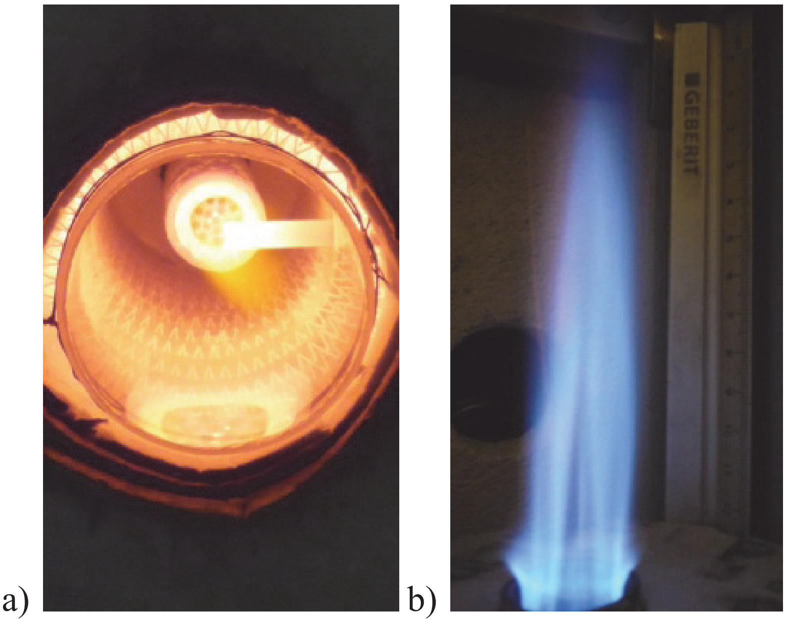

Fig. 1. A picture of the flame: a) in the combustion chamber; b) in the open space
Rys. 1. Zdjęcie płomienia: a) w komorze spalania; b) w przestrzeni otwartej

For all conditions: $\dot{V}_{fuel} = 0.08$ m^3/h; $\dot{V}_{oxygen} = 0.168$ m^3/h; $T_{oxidizer} = 300K$, $\lambda_{oxygen} = 1.05$. The tests were started from a mixture containing 29% O_2, and then CO_2 was added according to Table 1. The addition of CO_2 resulted in an increase in combustible mixture volume with a drop in oxygen content.

Table 1. Experimental conditions
Tabela 1. Warunki eksperymentalne

$\%O_2/\%CO_2$	CO_2, m^3/h	Combustible Mixture, m^3/h
23/77	0.562	0.81
25/75	0.504	0.75
27/73	0.454	0.7
29/71	0.411	0.657

The flame with the addition of 29% O_2 is less visible, as its colour becomes identical to that of the heated chamber lining. When the proportion of O_2 to CO_2 has decreased, the flame becomes clearly shining.

3. Numerical approach

The description of reactions occurring in the flame is extremely difficult and depends on numerous factors, such as temperature, pressure, burner type, fuel and oxidizing mixture compositions, etc. Depending the number of reagents and their stoichiometric coefficients, first-, second- and third-order reactions are distinguished.

For the general notation of the reaction:

$$\sum_{i=1}^{n} \nu_i{}' Z_i \overset{k}{\Rightarrow} \sum_{i=1}^{n} \nu_i{}'' Z_i \tag{1}$$

whose order can be expressed as follows:

$$m = \sum_{i=1}^{n} \nu_i{}' \tag{2}$$

the rate of production of the component Z_i of reaction (1) is

$$r_{Z_i} = \frac{dC_{Z_i}}{dt} = (\nu_i{}'' - \nu_i{}')k \prod_{i=1}^{n} \left(C_{Z_i}\right)^{\nu_i{}'} \tag{3}$$

The reaction rate constant k for reaction of any order is defined using the modified Arrhenius equation:

$$k = AT^{\beta} e^{-\frac{E_a}{RT}} \tag{4}$$

The resultant of the production rate is the sum for the reaction running to the left-hand and the right-hand direction, respectively:

$$[r_{Z_i}]_{Net} = [r_{Z_i}]_{Forward} + [r_{Z_i}]_{Reverse} \tag{5}$$

There are many detailed mechanism provided in the literature, which are intended for the analysis of the gaseous fuel combustion kinetics. The most popular include: GRI-Mech [17] and those developed by Konnov [12] and Mendiara, Glarborg [16]. Mechanisms are created by combining experimental results and theoretical models defining parameters in the modified reaction rate constant equation (4). The above-mentioned reaction mechanisms [12, 16, 17] differ in the number of reactions, chemical compounds and elements and the values of activation energy E_a and the constants A, β.

In the present study, modelling of the natural gas combustion kinetics was performed within the Chemked II software program, version 3.5.2 [9], using the combustion mechanism proposed by Mendiara, Glarborg [16]. The combustion mechanism includes 779 elementary reactions between 97 chemical compounds. The computations were conducted for a flame temperature of 1500K, at a constant pressure of p = 0.1 MPa. The ideal mixing of the combustion substrates in the burner was assumed for the computations.

The adiabatic equilibrium flame temperatures during the combustion of methane with the addition of O_2 and CO_2 were determined in the program FactSage™ [1]. Using the Equilib module operating based on the Gibbs free energy minimum principle, the state of thermodynamic equilibrium between reagents occurring in different states of aggregation was determined. As the criterion for the computations in the FactSage™ program, the equality of product and substrate enthalpies at a constant pressure was adopted. The computations were made for initial conditions consistent with the experiment, i.e. p = 0.1 MPa; T = 300K; λ = 1.05.

4. Computation and experiment results

Table 2 summarizes real and adiabatic flame temperatures, depending on the combustion atmosphere used. The real flame temperatures in the examined system are equal to the temperature of flue gas taken for the analysis of CO. The highest flame temperature of 1633K was noted at a distance of 0.06 m from the burner for the oxidizing atmosphere containing 29% O_2. The decrease in the oxygen fraction of the mix was followed by a shift in the maximum burner flame temperature closer to the burner, i.e. to a distance of 0.04 m. The change in the location of the maximum temperature in the kinetic low-swirl flame used may be indicative of a shortening of the flame length with the decrement of oxygen. The trend in flame length change is reverse to that for combustion in oxygen-enriched air [4]. From the computations made in the FactSage™ program it was found that the adiabatic flame temperature increased with increasing oxygen content of the oxidizing mixture from 1825K (for $23\%O_2/77\%CO_2$) to 2087K (for $29\%O_2/71\%CO_2$).

Table 2. Temperatures for different combustion atmospheres
Tabela 2. Temperatury dla różnych atmosfer spalania

O_2/CO_2 →	23%/77%	25%/75%	27%/73%	29%/71%
Distance, m	Temperature, K			
0.02	1275	1358	1463	1584
0.04	1512	1543	1611	1598
0.06	1486	1512	1580	1633
0.08	1463	1497	1548	1573
0.1	1443	1443	1443	1443
$T_{adiabatic}$, K	1825	1922	2009	2087

The experimentally determined variations in CO concentrations (in dry flue gas) in the flame are shown in Fig. 2. The following regularity can be observed. The increase in oxygen share in the oxy-combustion process results in a drop in CO already at a distance of 0.1 m from the burner, as marked by the broken line in Fig. 2. An opposite trend in CO concentration variations was found at a distance of 0.02 m. The farther away from the burner, the less CO in the burner region. The values of CO concentrations at particular distances from the burner oscillate within a certain concentration range. Allowing for this, two concentrations, a minimum and a maximum, are plotted at each measurement point in Figure 2. An example section of carbon monoxide variations in time, as recorded with the flue gas analyzer for the 27%O_2/73% CO_2 variant at a distance of 0.1 m from the burner outlet, is shown in Fig. 3.

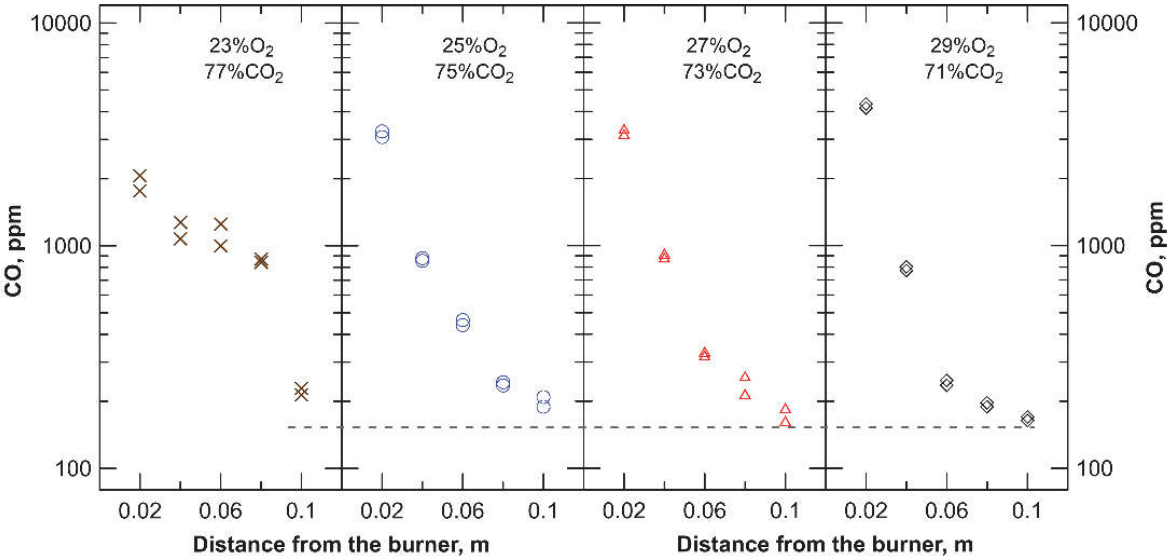

Fig. 2. CO concentration in dry flue gas for the examined variants and varying distances from the burner

Rys. 2. Stężenie CO w spalinach suchych dla rozpatrywanych wariantów i różnych odległości od palnika

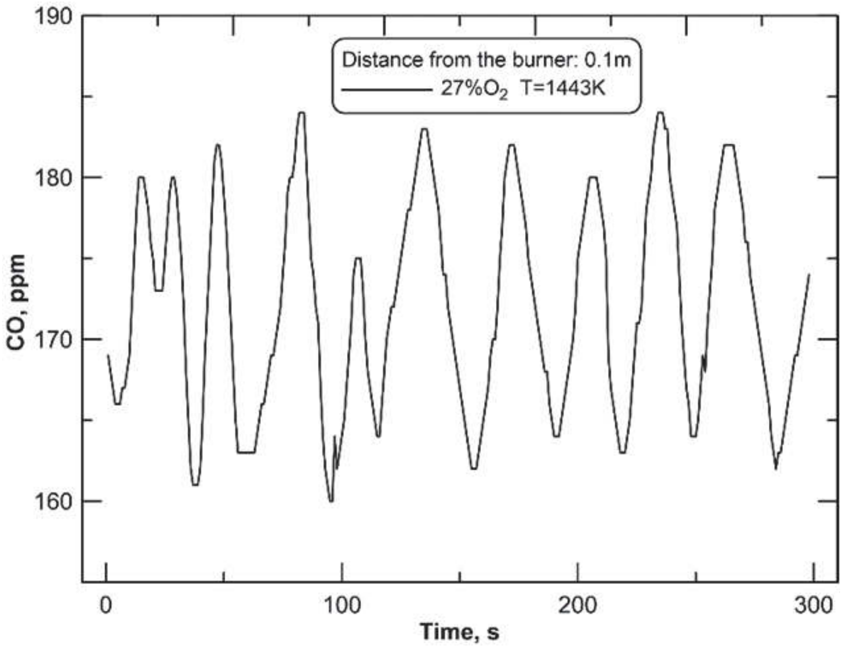

Fig. 3. Variations in CO concentration in time at a distance of 0.1 m from the burner outlet

Rys. 3. Przebieg zamian stężenia CO w czasie w odległości 0.1 m od wylotu palnika

The next figure illustrates the peak CO molar fractions (as related to dry flue gas) in the flame at a temperature of 1500K, as computed in the Chemked II program, as a function of residence time. As can be seen in Figure 4, the peak CO molar fractions form slightly faster in the conditions of a higher oxygen content of the oxidizing mixture. The maximum peak CO molar fraction value falls on the oxygen-richest atmosphere, as indicated in the magnified relevant fragment of the diagram. With the decrease in the oxygen share of the O_2/CO_2 mixture, the peak CO molar fractions decrease. The variations in CO molar fractions as a function of residence time, determined based on computations, are characterized by the same trend of changes as for the experiments. The farther away from the burner, and so the longer the residence time, the more the CO fraction grows with increasing CO_2 addition. This effect is reflected in the literature [2, 4, 5]. Carbon monoxide forms very fast in the flame in the oxy-combustion process, as indicated by its maximum concentrations in the vicinity of the burner. However, its oxidation to CO_2 is much slower, which is due to the decrease in the CO molar fractions with increasing residence time.

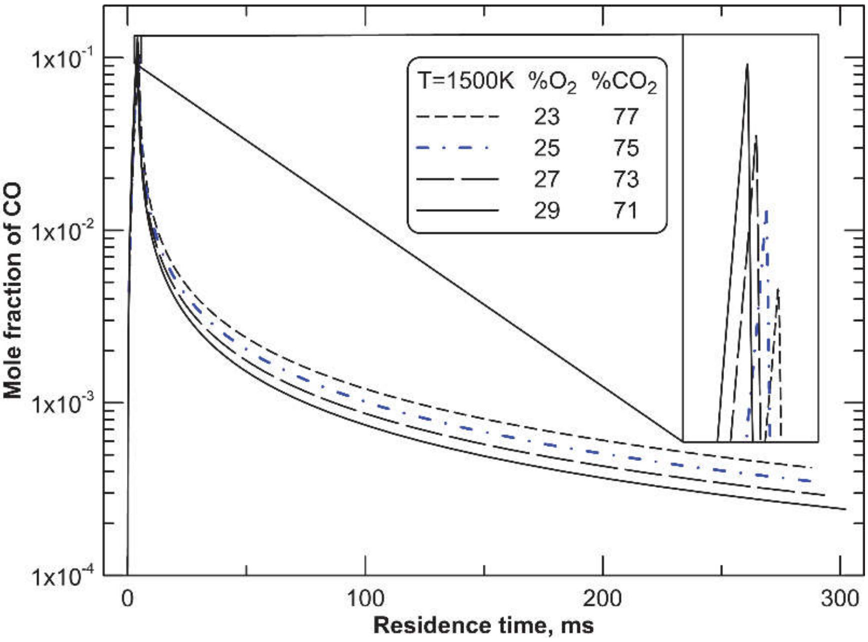

Fig. 4. The effect of residence time on the CO molar fraction for different combustion atmospheres

Rys. 4. Wpływ czasu przebywania na udział molowy CO dla różnych atmosfer spalania

The quantity of water formed in wet flue gas due to the change of combustion atmosphere is shown in Figure 5. The increase in the water molar fraction as a result of increasing the content of oxygen of the oxidizing mixture can be explained by the specificity of the conducted tests. The volume flux of combusted natural gas and oxygen is constant, so the quantity of water formed is invariable too. As a result of the addition of CO_2, the combustible mix volume is increased (according to Table 1), thus the H_2O molar fraction of the flue gas decreases.

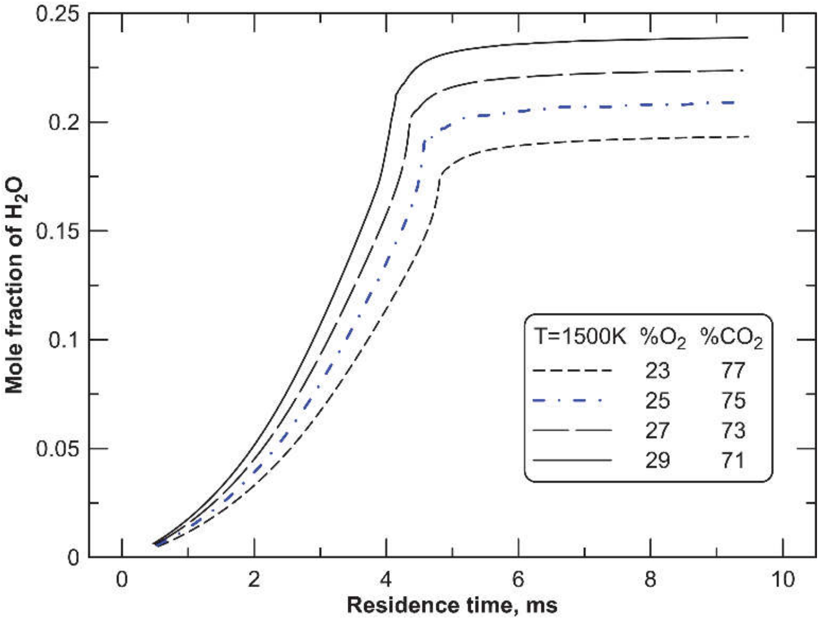

Fig. 5. The effect of residence time on the H_2O molar fraction for different combustion atmospheres

Rys. 5. Wpływ czasu przebywania na udział molowy H_2O dla różnych atmosfer spalania

Figure 6 displays the patterns of variations in CO_2 molar fractions for the examined atmospheres as a function of time. In the early phase of the diagram (0–4 ms), the CO_2 molar fraction of flame is commensurate with the content of CO_2 of the combustible mixture. This is too short time for the natural gas to be completely oxidized with the formation of water. After approx. 5 ms, the largest quantity of CO_2 (as related to dry flue gas) is for the combustible mixture 29%O_2/71%CO_2 with the smallest flux of 0.657 m^3/h. Noteworthy is the short time needed for attaining a high CO_2 molar fraction of flame at a level of 0.95. In the natural gas combustion reaction, the quantities and types of free radicals formed in the flame are not without significance.

Variations in hydrogen radicals in the flame for the examined oxy-combustion atmospheres are illustrated in Fig. 7. It follows from the figure that the greater the CO_2 fraction of the combustible mixture, the smaller the magnitude of peak H molar fractions.

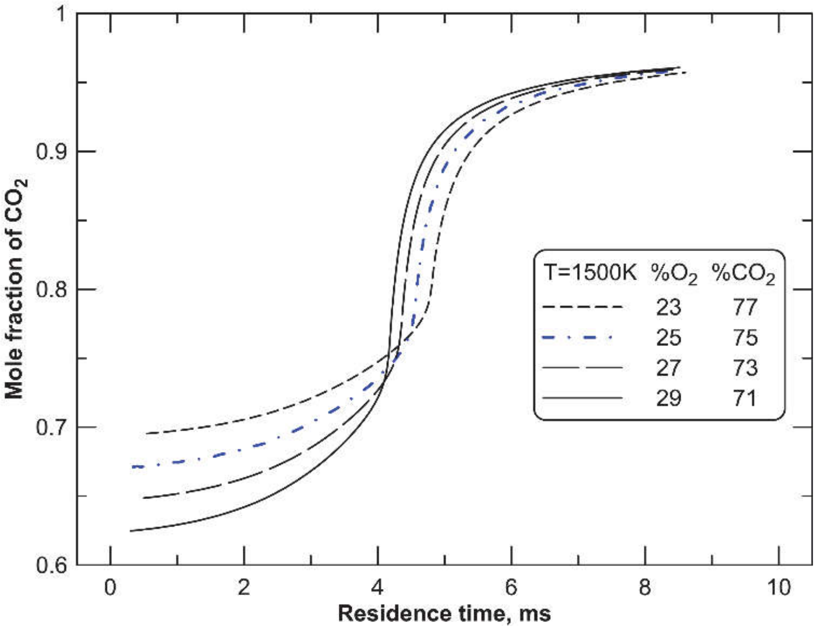

Fig. 6. The effect of residence time on the CO_2 molar fraction for different combustion atmospheres

Rys. 6. Wpływ czasu przebywania na udział molowy CO_2 dla różnych atmosfer spalania

Based on the analysis of the reaction rate in accordance with Eq. (3) at a temperature of 1500K, five predominant reactions of CO formation and consumption in the flame are listed.

$$\mathrm{OH + CO \leftrightarrow H + CO_2} \tag{6}$$

$$\mathrm{HCCO + O_2 \leftrightarrow OH + CO + CO} \tag{7}$$

$$\mathrm{HCO + H_2O \leftrightarrow H + CO + H_2O} \tag{8}$$

$$\mathrm{HCO + O_2 \leftrightarrow HO_2 + CO} \tag{9}$$

$$\mathrm{H_2 + CO + M \leftrightarrow CH_2O + M} \tag{10}$$

From among the above-mentioned reactions, reaction (6) contributes most to the formation of CO in the flame, which is confirmed in scientific studies [5, 6, 19]. The clear effect of the natural gas oxy-combustion atmosphere on the rate of reaction (6) of CO formation and consumption in the flame is demonstrated in Fig. 8. The greater oxygen fraction of the combustible mixture increases the net CO formation rate according to Eq. (5). Favourable conditions for the formation of CO in the flame following reaction (6) proceeding to the left include the H free radical fraction, which increases with increasing oxygen content of the combustible mix, as suggested by Fig. 7.

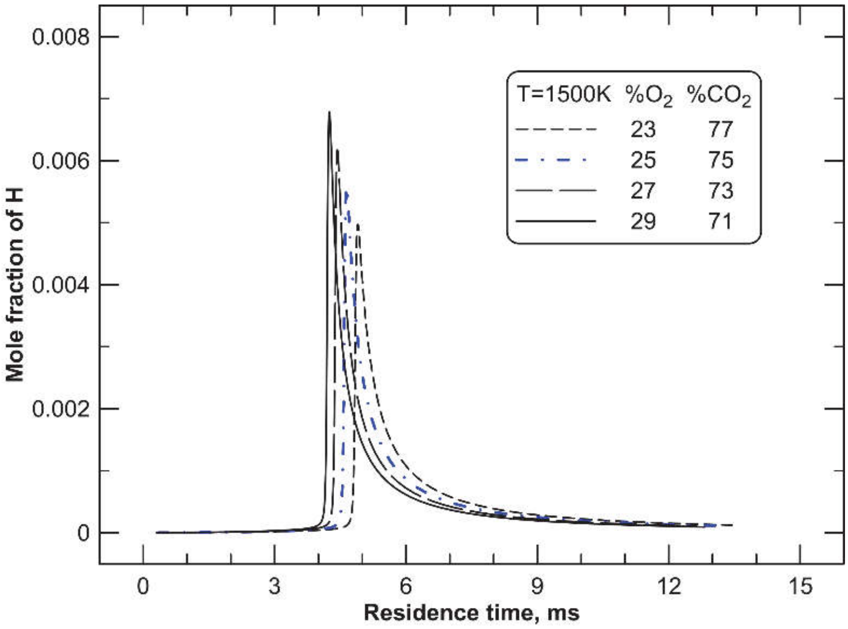

Fig. 7. The peak molar fractions of H radicals for different combustion atmospheres
Rys. 7. Szczytowe udziały molowe rodników H dla różnych atmosfer spalania

The change in the rate of reaction (6) due to the modification of the combustion atmosphere not only results in an increase in CO in the flame region, but also disturbs the proportions of free radicals in the flame. Though belonging to unstable intermediate products, H, OH or H radicals are responsible for the initiation, branching, propagation and termination of reaction chains.

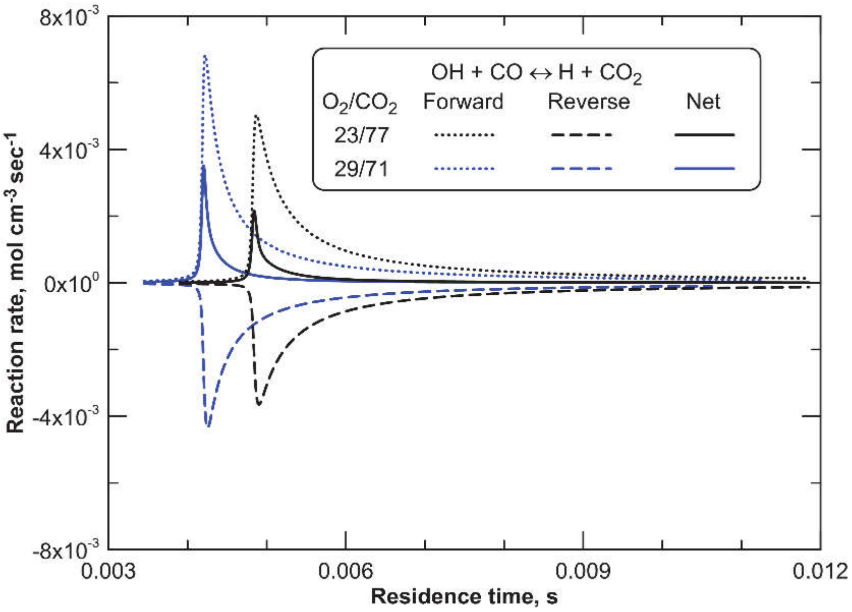

Fig. 8. The rate of reaction (6) for different combustion atmospheres
Rys. 8. Szybkość reakcji (6) dla różnych atmosfer spalania

5. Conclusions

Computations and experiments concerning the oxy-combustion of natural gas preliminarily mixed with CO_2 and 23–29 vol.% O_2 have been carried out. The richer the atmosphere,

1. the higher the magnitude of adiabatic flame temperature,
2. the higher the peak CO molar fractions at a small distance from the burner,
3. the smaller the CO molar fraction at greater distances from the burner,
4. the more H radicals are formed,
5. the lower the rate of the predominant CO formation reactions.

Many reactions are responsible for the formation of CO in the flame, with the primary being: $OH + CO \leftrightarrow H + CO_2$.

A reaction classified as second in terms of CO formation rate is: $HCCO + O_2 \leftrightarrow OH + CO + CO$.

Carbon monoxide forms very fast in the flame in the oxy-combustion process, as indicated by its maximum concentrations in the vicinity of the burner. However, the oxidation of carbon monoxide to CO_2 is much slower, which is due to the decrease in the CO molar fractions with increasing residence time. The presence of CO_2 in the combustion substrates has an inhibiting effect on the fuel oxidation process.

Acknowledgements

The author thank Mr. Piotr Mondkiewicz from the Department of Heat Engineering and Environment Protection for technical assistance in the experiments.

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List of symbols:

A – pre-exponential factor, $(\mathrm{cm^3\ mol^{-1}})^{m-1}\mathrm{s^{-1}}$
C – concentration, $\mathrm{mol\ cm^{-3}}$
E_a – activation energy of a chemical reaction, $\mathrm{J\ mol^{-1}}$
i – number of reactions,
k – reaction rate coefficient, $(\mathrm{cm^3\ mol^{-1}})^{m-1}\mathrm{s^{-1}}$
m_i – order of a reaction,-
M – third body, -
r_i – rate of reaction, $\mathrm{mol\ cm^{-3}\ s^{-1}}$
R – ideal gas constant, $\mathrm{J\ mol^{-1}\ K^{-1}}$
S – swirl number, -
T – temperature, K
Z_i – chemical symbol „i”

Greek symbols:

β – temperature exponent of the pre-exponential factor, -
λ – excess of oxygen, -
v_i' – the stoichiometric ratio of the substrate in the reaction, -
v_i'' – the stoichiometric ratio of the reaction product, -

References

1. **Bale C.W., Bélisle E., Chartrand P., Decterov S.A., Eriksson G., Hack K., Jung I.-H., Kang Y.-B., Melançon J., Pelton A.D., Robelin C., Petersen S.:** *FactSage thermochemical software and databases – recent developments.* Calphad, 2(33), 295–311 (2009).
2. **Barbas M., Costa M., Vranckx S., Fernandes R. X.:** *Experimental and chemical kinetic study of CO and NO formation in oxy-methane premixed laminar flames doped with NH_3.* Combustion and Flame, 162, 1294–1303 (2015).
3. **Baukal C. E. (ed.):** *Industrial Burners Handbook.* CRC Press LLC, Boca Raton 2003.

4. **Biett J., Deflau J.L., Pillier L., Vovelle C.:** *Influlence of CO_2 and H_2 on the Chemical Structure of a Premixed, Lean Methane-Air Flame.* Proceedings of the 3rd European Combustion Meeting. Greece 2007.
5. **Chen L., Ghoniema A. F.:** *Modeling CO_2 Chemical Effects on CO Formation in Oxy-Fuel Diffusion Flames Using Detailed, Quasi-Global, and Global Reaction Mechanisms.* Combustion Science and Technology, 186(7), 829–848 (2014).
6. **Glarborg P. and Bentzen L. B.:** *Chemical Effect of a High CO_2 Concentration in Oxy-Fuel Combustion of Methane.* Energy & Fuels, 22(1), 291–296 (2008).
7. **Gökalp I., Lebas E.:** *Alternative fuels for industrial gas turbines*. Applied Thermal Engineering, 24(11–12), 1655–1663 (2004).
8. International Energy Outlook. World Energy Outlook. 2013, July 25, www.eia.gov/forecasts/ieo/
9. **Jelezniak M., Jelezniak I.:** *Chemked-II version 3.5. Program for chemical kinetics of gas-phase reactions*. http://www.chemked.com
10. **Jerzak W.:** *Emissions of NO_x and CO from natural gas combustion with adding CO_2 at varying distances from the burner.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 16, 148–160 (2014).
11. **Kalicka Z., Jerzak W. Kawecka Cebula E.:** *The effect of combustion of natural gas with 21-29% $O_2/CO_2/N_2$ mixtures on emission of carbon monoxide.* Archives of Environmental Protection, 39(4), 93–103 (2013).
12. **Konnov A.A.:** *Remaining uncertainties in the kinetic mechanism of hydrogen combustion.* Combustion and Flame. 152(4), 507–528 (2008).
13. **Li G., Zhou H., Cen K.:** *Emission characteristics and combustion instabilities in an oxy-fuel swirl-stabilized combustor.* Journal of Zhejiang University SCIENCE A, 9(11), 1582–1589 (2008).
14. **Lyngfelt A., Leckner B., Mattisson T.:** *A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion.* Chemical Engineering Science, 56(10), 3101–3113 (2001).
15. **Mądrawski J., Ziemblińska K., Juszczak R., Zawal D., Olejnik J.:** *Tradycyjne i alternatywne metody oceny intensywności procesu sekwestracji ditlenku węgla przez kruszywo betonowe z recyklingu.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 15, 2526–2545 (2013).
16. **Mendiara T., Glarborg P.:** *Ammonia chemistry in oxy-fuel combustion of methane*. Combustion and Flame, 156(10), 1937–1949 (2009).
17. **Smith G.P., Golden D.M., Frenklach M., Moriarty N.W., Eiteneer B., Goldenberg M., Bowman C.T., Hanson R.K., Song S., Gardiner W.C., Lissianski V.V., Qin Z.:** *Gri-Mech™*, www.me.berkeley.edu/gri_mech
18. **Toftegaard M.B., Brixa J., Jensena P.A., Glarborg P., Jensen A.D.:** *Oxy-fuel combustion of solid fuels.* Progress in Energy and Combustion Science, 36(5), 581–625 (2010).

19. **Xie Y., Wang J., Zhang M., Gong J., Jin W., Huang Z.:** *Experimental and Numerical Study on Laminar Flame Characteristics of Methane Oxy-fuel Mixtures Highly Diluted with* CO_2. Energy & Fuels, 27, 6231–6237 (2013).

Powstawanie CO w kinetycznym płomieniu tlenowo-paliwowym

Streszczenie

W pracy przedstawiono wyniki badań eksperymentalnych oraz numerycznych dotyczących tworzenia tlenku węgla (II) w kinetycznym płomieniu gazu ziemnego w warunkach oksy-spalania. W doświadczeniach korzystano z palnika nisko-wirowego, w którym stopień zawirowania strugi określony za pomocą liczby wiru S < 0,6. Badano wpływ składu utleniacza zawierającego CO_2 i 23–29% obj. O_2 na zmiany stężeń CO w płomieniu. Pobór spalin do analizy realizowano w osi palnika w odległościach 0,02–0,1 m z krokiem 0,02 m. Pomiaru temperatury spalin zasysanych do analizy dokonano termoparą PtRh10-Pt.

Analizę reakcji w płomieniu o temperaturze 1500K przeprowadzono w programie Chemked II [7], po zaimplementowaniu mechanizmu spalania zaproponowanego przez Mendiara, Glarborg [14] zawierającego 779 reakcji zachodzących pomiędzy 97 związkami chemicznymi. W pakiecie FactSage™ [1] obliczono adiabatyczne równowagowe temperatury płomieni podczas spalania gazu ziemnego z dodatkiem O_2 i CO_2.

Na podstawie obliczeń w programie Chemked wytypowano dominujące reakcje odpowiedzialne za tworzenie CO w płomieniu. Największy wkład w tworzenie CO ma reakcja: $OH + CO \leftrightarrow H + CO_2$, a jej szybkość jest uzależniona od udziału CO_2 w atmosferze utleniającej. Drugą reakcją sklasyfikowaną wg szybkości tworzenia CO jest: $HCCO + O_2 \leftrightarrow OH + CO + CO$.

Ponadto określono szczytowe stężenia rodników H, biorące udział w reakcjach tworzenia CO przy współudziale CO_2 oraz ich zmiany z zawartością tlenu w mieszance palnej.

Tlenek węgla w procesie oksy-spalania powstaje w płomieniu bardzo szybko, o czym świadczą szczytowe stężenia CO występujące najbliżej palnika. Jednak jego utlenienie do CO_2 jest znacznie wolniejsze co wynika ze spadku stężenia CO z czasem rezydencji. Obecność znacznych ilości CO_2 w substratach spalania ma działanie hamujące proces utleniania gazu ziemnego.

Słowa kluczowe:
oksy-spalanie, stężenie CO w płomieniu, kinetyka spalania

Keywords:
oxy-combustion, flame CO concentration, combustion kinetics

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Inflow of Pollutants to the Bukówka Drinking Water Reservoir from the Transboundary Bóbr River Basin

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1. Introduction

Interest in water resource management issues, including water quality, in transboundary areas, is a relatively new phenomenon which has been gaining increased attention in recent years. Problems related to transboundary waters led to the introduction, under the Water Framework Directive (WFD), of a modern approach to water resource management based on the drainage basin model, in contrast to the administrative model used previously [16]. According to the WFD [6], Member States should strive to achieve the objective of at least good water status by defining and implementing the necessary measures through integrated action programs while taking into account the existing Community requirements. Moreover, within a river basin where use of water may have transboundary effects, the requirements for the achievement of the environmental objectives, and in particular all programmes of measures, should be coordinated for the whole of the river basin district. This applies, in particular, to the assessment of the condition of surface waters [16].

The situation becomes of particular relevance when a dam reservoir, which stores retention water for human consumption, is located on a transboundary river. In this case the water quality control in the drainage basin above the dam reservoir is crucial, especially in terms of inflow of pollutants into these waters, both in the transboundary river upstream, and at points further down the course of the river. One of such transboundary rivers is the Bóbr where, by the border with the Czech Republic, the Bukówka reservoir (km 271 + 540) is located. The Bukówka reservoir is a multi-purpose facility. Its basic functions include flood control, water supply in low-water periods for the Marciszów Water Treatment Plant and drinking water supply to the city of Wałbrzych. Currently, however, this function is not fulfilled and water from the reservoir is taken merely for consumption for the villagers of Bukówka and to ensure environmental flow in the riverbed of Bóbr below the reservoir. According to the literature, reconciling the functions of multi-purpose reservoirs, including drinking water reservoir, is often very difficult to achieve [10, 30, 36].

The Bukówka reservoir is exposed to a number of problems, among which the main one is the deterioration of water quality and eutrophication. This is due to the fact that, while Bukówka potentially supplies the population with drinking water and a protection zone of surface water intake is maintained on the reservoir, in the Polish part of the basin continuous monitoring of water quality does not exist.

The aim of this study was to analyse the inflow of pollutants from the transboundary Bóbr River basin to the Bukówka reservoir in view of supplying drinking water for consumption and its retention in the reservoir. The water quality of five watercourses: the rivers Bóbr, Opawa, Złotna, Bachorzyna and Paprotki supplying the reservoir has been analysed. Testing also included both the retention water and the outflow water. The causes of the variability of water quality, both spatial and in terms of time, were also identified. In addition, the study assessed the eutrophication of analysed waters, their vulnerability to nitrogen pollution from agricultural sources and the delivery of matter into the Bukówka reservoir.

2. Characteristic of study area

Bukówka reservoir (50°42'47" 15°56'46"E) was established between 1978–1989, in the Bóbr river valley at 271.540km, in place of a dry storage reservoir dam that had existed since 1907. Administratively the reservoir is located between three towns Miszkowice, Bukówka and

Paprotki (Fig. 1). Almost all reservoir basin banks are natural, except for the side dam protecting the village of Miszkowice. The reservoir includes: an earthy front dam, a bottom vent, a transfer surface, and tap water outtake for the Wałbrzych Water and Sewage Enterprise, which is not currently used, a hydroelectric power plant and the Miszkowice side dam. The administrator of the Słup reservoir is Wrocław Regional Water Management [11, 18].

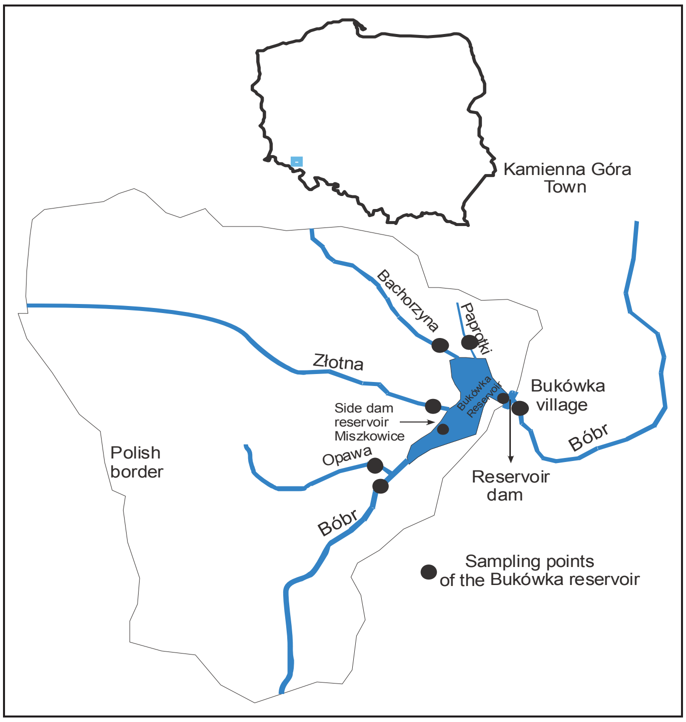

Fig. 1. Location of Bukówka reservoir on Bóbr river, including water sampling points for the physicochemical examinations

Rys. 1. Lokalizacja zbiornika Bukówka na rzece Bóbr oraz punktów poboru próbek wody do badań fizykochemicznych

From the Bóbr river basin to the Bukówka reservoir dam is approximately 58.5 km^2. The Bóbr river flows from the Lasocki Grzbiet located in the great Czech mountains. The river flows on the Czech side for about two kilometers, then for more than four kilometers on the Polish side and then flows into the Bukówka reservoir. There is also a visible basin gradient, mostly from west to east, and in the southern part of the catchment from south west to the north east. The Bukówka reservoir is a recipient of three rivers Złotna, Bachorzyna and Bóbr; it also receives water from several smaller watercourses (Including Opawa and Paprotki) and pumped water from the Miszkowice polder. The basin is dominated by agricultural lands (52%) and forests (45%). Urban areas occupy only a few percent of the area (approx. 3%).

Bukówka reservoir parameters: the operational fill level (NPP) – 534.30 m (12.917 million m^3, 167 ha), the maximum fill level (Max PP) – 536.40 meters above sea level (16.790 million m^3, 199 ha). Capacity of this reservoir at absolute maximum fill level (537.10 meters above sea level) is 18.215 million m^3, and the area of the floodplain 211 ha. The length of the reservoir is approx. 2.8 km and the largest width approx. 1.4 km. Basic hydrological data of the Bóbr river in the reservoir section are: $SNQ = 0{,}13\ m^3 \cdot s^{-1}$, $SSQ = 0{,}89\ m^3 \cdot s^{-1}$, $NNQ = 0{,}04\ m^3 \cdot s^{-1}$, the flow is $Q = 0.10\ m^3 \cdot s^{-1}$, the harmless flow (the allowed discharge) $Q = 8.0\ m^3 \cdot s^{-1}$ and the highest flow $WWQ = 74{,}50\ m^3 \cdot s^{-1}$ [18].

The Bukówka reservoir basin area is characterized by a cool climate with long winters and high precipitation. The basic data characterizing the climate: the average precipitation in the basin area is approx. 800 mm, the average annual temperature approx. 5.5°C.

3. Methods

The study performed between November 2006 and December 2007 involved water quality analysis of watercourses: Bóbr (post B_in_res), Opawa (post O_in_res), Złotna (post Z_in_res), Bachorzyna (post Ba_in_res) and Paprotki (post P_in_res). The aforementioned streams supply the Bukówka reservoir. In addition, the quality of the water impounded in the reservoir at the Miszkowice dam (W1_res post), the water impounded in the reservoir at the face dam (post W2_res) and the outflow of water from the Słup reservoir (post Out_res) were analyzed (Fig. 1). The location of each water sampling points, both in the catchment and in the Bukówka reservoir itself was selected in such a way that on the basis of it one can determine the spatial water quality in the tributaries, the reservoir and of the outflow, as well as whether the Bukówka reservoir affects the quality of the watercourses flowing through it. Samples were carried out on the following dates: 27.11.2006, 16.01.2007, 26.03.2007, 16.04.2007, 29.05.2007, 10.09.2007, 22.10.2007, 19.11.2007 and 10.12.2007.

Particular attention was paid to the important, from the point of view of the proper use of the reservoir, quality of water supplying the reservoir, primarily to the water quality of the Bóbr river, due to its dominant role in supplying the Bukówka reservoir. In order to carry out the water quality characteristics of the Bóbr river flowing into the tank, in addition to our own studies of water quality, similar data was obtained from the Provincial Inspectorate of Environmental Protection in Wrocław (RIEP) for the period 1993–2005 for the border point at km 269.6 [23] (Fig. 1) as well as the data from the Czech Republic concerning the evaluation of the quality of surface waters in the territorial scope of the Elbe's basin in 2012 [8, 9]. The evaluation was performed by analyzing the water quality indicators such as: NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, BOD_5, pH, electrolytic conductivity, water temperature, and total suspended solids. In addition, at the position W2_res (at the dam) measurements of water transparency (Secchi depth) were performed. Water pH, electrolytic conductivity and temperature were measured *in situ*, whereas other water quality analyses were made in a laboratory according to Polish standards. Water quality was rated in accordance with binding during led investigates the Decree of the Ministry of Environment on the classification of surface water bodies [29]. An assessment of the eutrophication of the waters analyzed was presented, concerning whether the waters are vulnerable to pollution by nitrogen compounds from agricultural sources based on [27]. The appropriability of the tested water was determined by comparing the studied ratios with the values which should correspond to water destined for human consumption [26], existence of fish [28] and bath [25]. The paper also presents an evaluation of the Bukówka reservoir basin's delivery of substances into the reservoir.

4. Results and Discussion

4.1. Water quality

The results of the water quality tests from the five watercourses flowing into the Bukówka drinking water reservoir from the transboundary area, the quality of the retention water in the reservoir and that of the outflow from the reservoir are shown in Table 1.

Table 1. Characteristics of the quality of water flowing into the reservoir from the reservoir's basin, reservoir's water and the water outflow from the reservoir during the period November 2006–December 2007

Tabela 1. Jakość wody dopływającej do zbiornika zze zlewni, wody w zbiorniku i wody odpływającej ze zbiornika w okresie listopad 2006–grudzień 2007

Sampling point	Value	Water quality indicators								
		Nitrates (mg NO_3^-·dm^{-3})	Nitrites (mg NO_2^-·dm^{-3})	Ammonia (mg NH_4^+·dm^{-3})	Phosphates (mg PO_4^{3-}·dm^{-3})	BOD_5 (mg O_2·dm^{-3})	Reaction pH	Electrolytic conductivity (μs/cm)	Water temperature (°C)	Total suspended solids (mg·dm^{-3})
B_in_res	Average	3.57	0.101	0.132	0.52	3.08	7.79	220	7.0	0.9
B_in_res	Max	5.30	0.320	0.380	1.10	10.00	8.40	714	21.0	80.0
B_in_res	Min	1.30	0.010	0.026	0.11	1.00	7.30	122	2.1	0.0
O_in_res	Average	7.74	0.075	0.226	0.48	3.55	7.83	210	6.8	9.8
O_in_res	Max	17.70	0.160	0.640	1.05	11.00	8.20	661	20.5	0.0
O_in_res	Min	1.30	0.010	0.050	0.04	1.00	7.35	113	2.1	9.0
Z_in_res	Average	4.22	0.025	0.064	0.32	2.01	7.9	155	7.3	1.0
Z_in_res	Max	17.70	0.100	0.260	0.85	7.00	8.5	603	19.5	20.0
Z_in_res	Min	0.88	0.003	0.020	0.02	1.00	7.3	86	2.2	0.0
Ba_in_res	Average	5.31	0.100	0.098	0.42	1.66	7.75	161	8.2	7.6
Ba_in_res	Max	17.70	0.239	0.140	1.05	4.00	9.20	639	22.5	60.0
Ba_in_res	Min	0.88	0.020	0.050	0.04	1.00	7.20	74	2.3	0.0
P_in_res	Average	4.38	0.192	0.203	0.47	1.83	7.57	126	6.6	8.0
P_in_res	Max	8.80	0.368	0.260	1.14	3.00	8.15	174	13.0	20.0
P_in_res	Min	1.30	0.100	0.150	0.20	1.00	7.00	89	2.2	0.0
W1_res	Average	2.98	0.081	0.075	0.42	3.33	7.76	159	8.4	0.3
W1_res	Max	13.30	0.446	0.130	1.28	8.00	8.60	486	21.5	0.0
W1_res	Min	0.88	0.003	0.050	0.05	1.00	7.00	96	2.0	0.0
W2_res	Average	1.70	0.112	0.137	0.22	4.03	7.93	157	8.2	2.0
W2_res	Max	4.40	0.532	0.365	0.95	7.00	8.70	490	22.0	0.0
W2_res	Min	0.88	0.010	0.026	0.02	1.00	6.78	102	1.8	0.0
Out_res	Average	2.93	0.105	0.110	0.25	2.46	7.92	155	7.6	5.1
Out_res	Max	13.30	0.558	0.280	0.88	6.00	8.60	506	18.5	40.0
Out_res	Min	0.88	0.003	0.026	0.02	1.00	7.20	97	1.9	6.0

The analysis of the flowing water data shows that the highest average values of nitrate and nitrite were observed at the Paprotki sampling post (P_in_res), ammonia at the Opawa post (O_in_res), phosphates, BZT_5 and electrolytic conductivity at the Bóbr post (B_in_res), water pH at the Złotna post (Z_in_res) and water temperature and total suspended solids at the Bachorzyna post (Ba_in_res). In the water of the reservoir (W_res) during the period of the study the highest values were recorded for the following indicators: water pH and water temperature. The analyzed data also shows that at the outflow from the Bóbr reservoir (Out_res), in comparison with the Bóbr post (B_in_res), the highest values of average concentrations of nitrite, water pH, water temperature were recorded.

Graphical comparison of the levels of nitrates, phosphates, ammonia, BZT_5, pH, conductivity, water temperature, and total suspended solids in the tested waters in Bukówka reservoir against the background of water quality classes by Decision of the Polish Minister for the Environment of 9 November 2011 [29] is shown in Fig. 2–5.

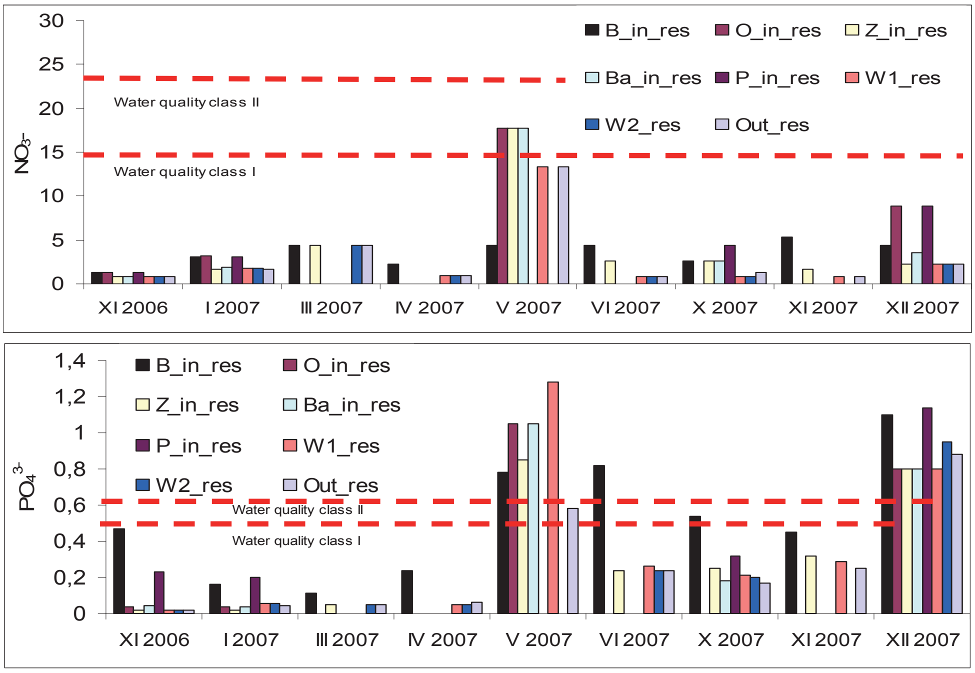

Fig. 2. Nitrates and phosphates concentration in the water from Bukówka reservoir in period 2006–2007

Rys. 2. Stężenie azotanów i fosforanów w wodzie ze zbiornika Bukówka w latach 2006–2007

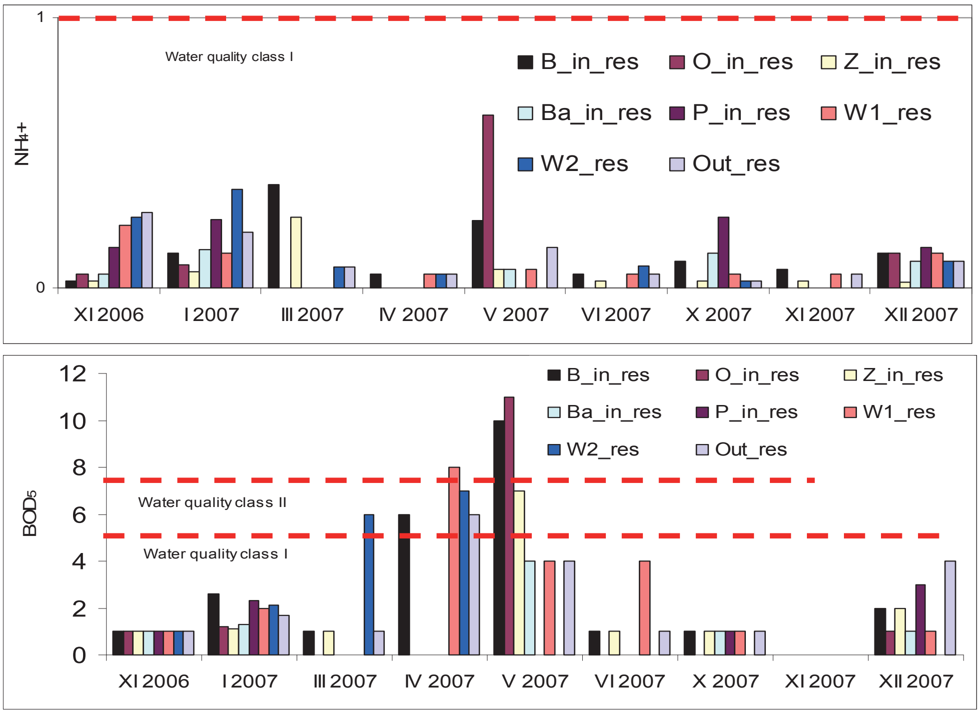

Fig. 3. Ammonia and BOD_5 concentration in the water from Bukówka reservoir in period 2006–2007
Rys. 3. Stężenie jonów amonowych i BZT_5 w wodzie ze zbiornika Bukówka w latach 2006–2007

Of the 9 tested indicators of water quality in the Bukówka reservoir, 8 (except nitrites) are taken into account for the classification of the water quality [29]. The highest nitrate concentrations at all five positions on the inflow to the reservoir were recorded in the month of May and the lowest in November (Fig. 2). Nitrate concentrations have qualified water to the class II of water quality, which concerns surface water bodies in natural watercourses such as a river [29].

Higher concentrations of phosphate in the tributaries waters were observed in the autumn and winter of 2007. The exceptions are large phosphate concentrations recorded in May 2007. This could be caused by flooding. According to [10, 20], flood water can bring a significant load of phosphorus and nitrogen in the period of raised water levels. In contrast, the smallest monthly PO_4^{3-}concentration was recorded in the spring of 2007 (Fig. 2). An analysis of the results of the study of the water quality in the reservoir showed that the phosphate quantities exceeded the limits for the II class water quality [29].

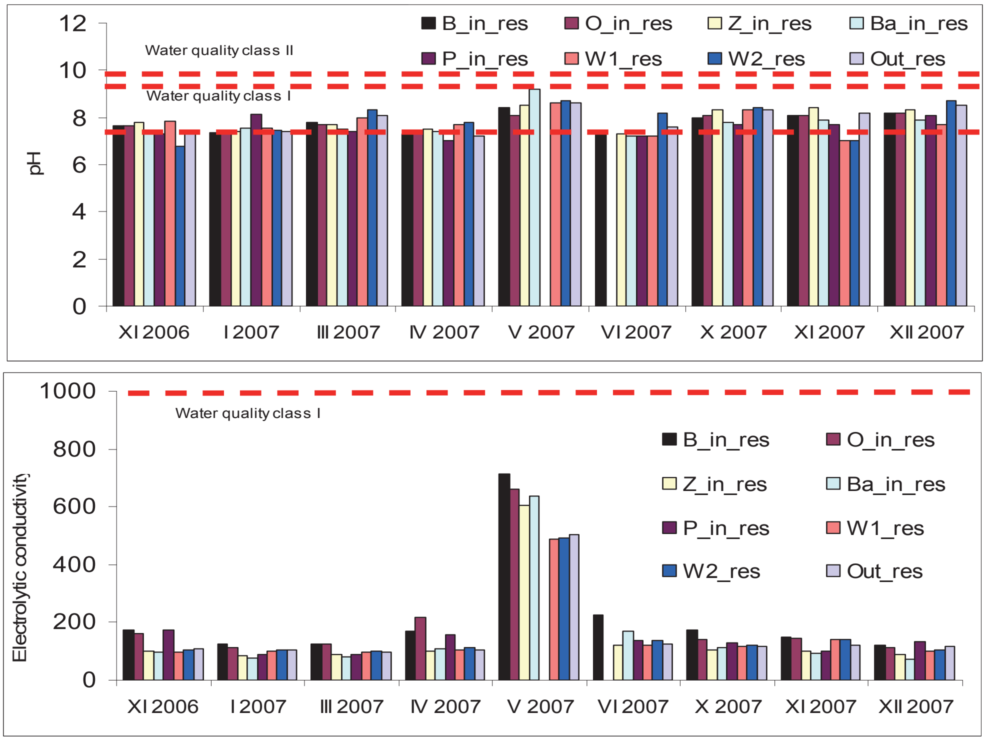

Fig. 4. pH and electrolytic conductivity in the water from Bukówka reservoir in period 2006–2007
Rys. 4. pH i przewodność wody ze zbiornika Bukówka w latach 2006–2007

An analysis of the results of the study of the water quality in the reservoir showed that the ammonia quantities did not exceed the appropriate limit for class I water quality (Fig. 3). The values of BOD_5 exceeded the limits for the class II water quality (Fig. 3). The pH value of the water at all sampling posts, except for Potok Bachorzyna (Ba_in_res) taken in May 2007 (exceeding the water quality II class), passed the test for the class II water quality (Fig. 4) [29]. Electrolytic conductivity qualified them to the class II of surface water quality at all positions (Fig. 4). The maximum values of this index were observed in May 2007.

The water in the reservoir during May 2007 heated up to a nearly same temperature of 21.5°C (Fig. 5). Water temperature values at all measuring stations in addition to water creek Bachorzyna (Ba_in_res) taken in May 2007 (exceeding the water quality I class) passed the test for class I of water quality.

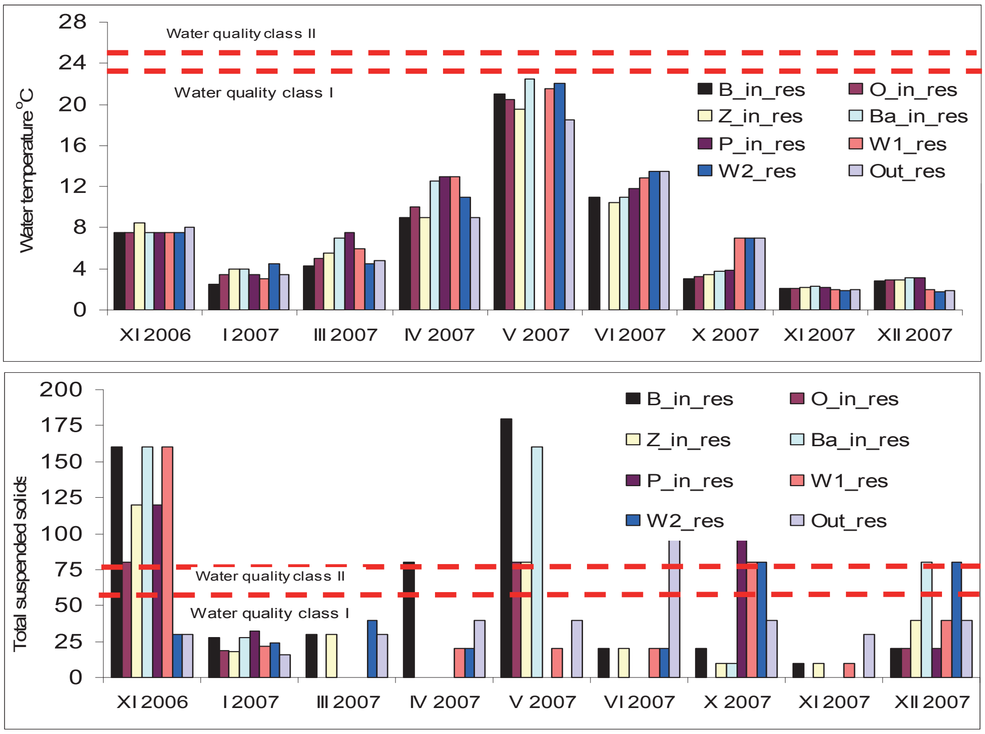

Fig. 5. Water temperature and total suspended solids in the water from Bukówka reservoir in period 2006–2007
Rys. 5. Temperatura i zawiesina ogólna w wodzie ze zbiornika Bukówka w latach 2006–2007

The highest concentration of total suspended solids – 180 mg·dm^{-3} – were recorded in the waters flowing into the tank (B_in_res) during the freshet in the Bóbr river basin in May 2007 (Fig. 5). High levels of total suspended solids were also recorded in the waters flowing out from the reservoir 140 mg·dm^{-3} (September 2007). Analysis of the results of the water quality showed that the total suspended solids exceeded the limits for the class II water quality, concerning surface water bodies in natural watercourses such as a river [29].

Transparency of the Bukówka reservoir's water, measured as Secchi depth, ranged from 150 cm (December 2007) to 320 cm. The greatest transparency in the waters of the reservoir was recorded in November 2006. Bukówka's water, because of this indicator, was considered eutrophic water. The transparency value did not exceed the border limit of this ratio (2.0 m). Similarly, the water of Opawa, Złotna and Bachorzyna (O_in_res, Z_in_res, Ba_in_res), flowing into Bukówka reservoir, were classified as eutrophic due to the excess of nitrate limits (10 mg NO$_3^-$

$\cdot dm^{-3}$), given in [27]. Moreover, according to the value of transparency given in [29] year, the Bukówka reservoir was also qualified as eutrophic, because the transparency by Schindler modulus (5.0 m^2/m^3) should be 1.7 meters. Nevertheless, it was found that the Bukówka reservoir's water is not vulnerable to pollution by nitrogen compounds from agricultural sources, as the nitrate concentration was lower than recommended (50 mg $NO_3^- \cdot dm^{-3}$) in [27].

As is indicated by the above analysis, hydrochemical conditions in the Bukówka reservoir, in terms of functions performed by the tank, are unfavorable for it. This is confirmed by tests of the Bóbr river water quality presented in [17–18, 21–22]. They showed that the main sources of pollution of the Bóbr river are industrial and domestic waste water from urban centers and rural domestic waste water from community centers. The water quality of the Bóbr river in 2005 showed a considerable variability. At the border point an unsatisfactory state of the water was recorded. Water flowing into Poland from the Czech Republic was characterized as a one of an unsatisfactory quality. The classification was decided by a large number of faecal coliform bacteria, very high phosphate and phosphorus concentrations, as well as increased color and phenolic index.

The evaluation of the consumption usefulness of the water outflow from the Bukówka reservoir showed that values of temperature, conductivity, nitrates and ammonia in any period did not exceed the limit of the A1 category domain, i.e. water requiring simple physical and chemical treatment [26]. Water pH values (May 2007) qualified the tested water to the A2 category, i.e. water requiring a typical physical and chemical treatment. However, in the remaining months this indicator did not exceed the limit values of the A1 category. Limit values of the A3 category, i.e. water requiring an efficient physical and chemical treatment were exceeded in terms of total suspended solids (September 2007), phosphate (December 2007) and BOD_5 (April 2007) [26]. In view of the fact that the reservoir is under water intake protection „Bukówka”, according to the permission OS-6210/8/97 and for the purposes of the planned water treatment plant and water transmission to Wałbrzych [18], the research should be continued. At the time the research was based only on direct sampling of water from the reservoir destined for citizens of Bukówka village, which is located below the dam.

Examination of the Bukówka reservoir's water showed that indicators such as water pH and ammonia nitrogen meet the requirements for inland waters which are the habitat of salmonids and cyprinids in their natural conditions [28]. In contrast, the water temperature meets the requirements for inland waters which are cyprinids' habitat only. The most unfavorable conditions for the existence of fish is caused by nitrites, which exceed the required [28] value of 0.01 mg $NO_2^-\cdot dm^{-3}$ for salmonids and 0.03 mg $NO_2^-\cdot dm^{-3}$ for cyprinids, by the BOD_5 value, which exceeds the required 3 mg $O_2 \cdot dm^{-3}$ for salmonids and 6 mg $O_2\cdot dm^{-3}$ for cyprinids and by the total suspended matter value, which exceeds the required on [28] average annual value by 25 $mg\cdot dm^{-3}$.

In the case of the Bukówka reservoir a positive impact on the improvement of water quality in terms of selected indicators has been found. The results obtained indicate that the Bukówka reservoir reduced levels of nitrates, ammonia, phosphate, total suspended solids and conductivity in water outflow from the reservoir in relation to the water flowing into the reservoir. However, in the water below the reservoir higher nitrites values, water pH and temperature were recorded. Another function which has been attributed to dam reservoirs is improvement of surface water quality. There is still no synonymous answer to the question whether hydrotechnical construction deteriorates or improves the quality of water. Generally, it was observed that big reservoirs receiving waters of slight or average pollution level improve their quality [35].

In order to complete the characteristics of the quality of the Bóbr river water flowing into the Bukówka reservoir, the results of the study of water quality of the Bóbr river obtained in year 2006–2007, at the position (B_in_res), were compared with the results of the state monitoring for the period from 1993 to 2005, carried out by the Provincial Inspectorate of Environmental Protection in Wrocław [23], at the border (km 269.9). Table 2 shows this comparison.

The water quality indicators of the Bóbr river show a lower value than the water quality test results obtained from PIEP Wroclaw. In the case of indicators such as BOD_5 and conductivity, the situation was reversed.

The water quality of the Bóbr river at the border showed a considerable variability. An unsatisfactory state of waters was registered. Water flowing into Poland from the Czech Republic was characterized as of an unsatisfactory quality. The classification was a result of a large number of faecal coliform bacteria, very high concentrations of phosphorus and increased color and phenolic index. Significant fluctuations in the concentrations of nutrients during every year of the examined period were observed Table 2 [23]. As it is stated by the authors of the report [23], high concentrations of biogenic compounds posed a threat of eutrophication to the Bukówka dam reservoir. Assessment of water quality of the Bóbr river, taking into account the parameters characterizing the process of eutrophication, revealed exceeding the annual average concentrations of phosphate and nitrate. Similar results, concerning the large pollution of the Bóbr river flowing from the Czech Republic, are presented in the paper Vodohospodářská bilance za rok 2011, období 2006 – 2011 a výhledu k roku 2021 Zpráva o hodnocení jakosti povrchových vod pro území ve správě Povodí Labe, státní podnik Odbor péče o vodní zdroje [8, 9]. It recommended that the Bóbr river water flowing out from the Czech Republic was classified to class II of water quality, due to the high content of total phosphorus.

Table 2. The results of the quality of river Bóbr water flowing into the reservoir at B_in_res post and the average annual values of selected water quality indicators from PIEP Wrocław for the period 1993–2005

Tabela 2. Wyniki jakości wody rzeki Bóbr wpływającej do zbiornika na posterunku B_in_res oraz średnio roczne wartości wybranych wskaźników jakości wody na podstawie WIOS Wrocław w latach 1993–2005

Indicator	WIOS investigations (1993–2005)		Self investigations (2006–2007)	
	Bóbr – border point, km 269.6		Bóbr (post B_in_res)	
	Min. (Year)	Max. (Year)	Min. (Date)	Max. (Date)
Nitrates (mg $NO_3^-\cdot dm^{-3}$)	12 (1998)	>50 (1993, 1994, 1995, 1996, 2000, 2004)	1.30 (XI 2006)	5.30 (XI 2007)
Phosphates (mg $PO_4^{3-}\cdot dm^{-3}$)	0,20 (1997)	>2.00 (1993, 1994, 2000, 2003, 2004)	0.11 (I 2007)	1.10 (XII 2007)
BOD_5 (mg $O_2\cdot dm^{-3}$)	5,0 (1997, 1999,2003)	9.0 (1995)	1.00 (XI 2006, I, IX, X 2007)	10.00 (V 2007)
Electrolytic conductivity ($\mu S\cdot cm^{-1}$)	200 (1997, 1998, 1999)	470 (1994)	122 (XII 2007)	714 (V 2007)

4.2. Bukówka reservoir's basin and the material supply to the reservoir

Water reservoirs have a great ability to capture migrating matter from the basin [14]. Water qualities in the reservoirs as well as a content of the phosphorus compounds are both largely determined by an external input [2]. The rate of eutrophication of a natural reservoir depends on its basins' physiogeographical structure, which functions as a continuous supplier of various forms of matter (including biogenic) to the reservoir, as well as morphometric parameters of the reservoir and its hydrological regime [1, 31–33]. The physiogeographical structure of a basin can promote area flows or limit them. On the other hand, the physical structure of a reservoir may be more, as well as less favorable to the maintenance of an existing reservoir's water shield. Reservoir's susceptibility to eutrophication can be assessed based on the system proposed by Bajkiewicz-Grabowska [1]. Natural features of a basin's physiogeographical environment cause that a reservoir's direct basin may accelerate or suppress the delivery of matter (including biogenic) to the reservoir.

The influence of a basin on the rate of matter supply to the reservoir is evaluated by bonitation of each of the aforementioned characteristics on a scale of 0 to 3 points, where 0 means a very weak impact on the supply of matter and the impossibility of it reaching the reservoir, and 3 means a high impact and rapid delivery of matter to the reservoir [1]. Characteristics that describe the degree of interaction basin and reservoir include Lake Ohle factor and the lake balance type. The degree of influence of the direct basin is described by: endorheicity of the area, an average decrease of the basin, a river network density, surface features and the way of the reservoir's exploitation. Table 3 presents an assessment of the Bukówka reservoir basin as a supplier of matter to the reservoir, according to the Bajkiewicz-Grabowska criteria [1].

Final assessment – the average of grades obtained from the evaluation of individual features is 1.33 and qualifies the Bukówka reservoir's basin as the second group of susceptibility: the basin is characterized by low susceptibility to launching cargo deposited in its area, and a small possibility of it reaching the reservoir. According to [34], the type of use of the basin areas of the reservoirs located in the basin of the Odra has a significant impact on the quality of water in these reservoirs. Currently, the supply of biogenic compounds from point and area sources (including agriculture), causing an anthropogenic eutrophication of water, is a major threat on the way towards a good status of waters in Poland and around the world [12, 13, 15]. Water pollution is a common problem throughout the world. Of course, there are many research methods which may determine different sources of water pollution, its scale and its impact on the environment [7]. Eutrophication is one of the most serious threats to the quality of inland waters. It is an important problem not only in Poland, but also in other countries of the European Community [3–5, 7, 19, 24, 33, 36].

Table 3. The valuation of the Bukówka reservoir's basin – from which the matter flows into the body of water of the Bukówka reservoir
Tabela 3. Ocena zlewni Bukówki – z której materia wpływa do wód zbiornika Bukówka

Characteristic of the Bukówka reservoir basin		Criterion by [1]	Amount of points
Factor lake by Ohle	35.03	10–40	1
Balance type of tank	Flow	Flow	3
Potamology parameters – density of river network – average river basin slope	 0.6 11.5	 0.5–1.0 10–20	 1 2
Geological structure of river basin	Slope and eluvium clay, Dusty clay, Peat soil	Clay, Peat	0
River basin use	woodland 45%, arable land 52%, built-up areas 3%	Forest-agricultural, grassland-agricultural	1
Mean value			1.33

5. Conclusions

1. The results of water quality testing in the period 2006–2007 show that due to the concentration of phosphates, BOD_5 and total suspended solids, the water flowing into the Bukówka reservoir from the trans-boundary drainage basin exceeds the limits of class II water quality indicators for water bodies in natural watercourses such a river. Meanwhile, the concentrations of $N\text{-}NO_3^-$ and the pH qualify this water as class II (in terms of the classification of water bodies in natural watercourses, such as a river).

2. It was found that the tested water in the Bukówka reservoir basin is not vulnerable to nitrogen pollution from agricultural sources. The Bukówka reservoir is not very susceptible to the displacement of pollutants deposited in its drainage basin; the likelihood of them getting into the reservoir is small.
3. In terms of eutrophication, the hydrochemical conditions occurring in the Bukówka reservoir catchment are unfavourable to the functions performed by the reservoir. The main reason for this is the high concentration of phosphorus from domestic waste water of localities in the studied drainage basin.
4. Evaluation of the suitability for consumption of outflow water from the Bukówka reservoir showed that the values for temperature, electrolytic conductivity, nitrates and ammonia did not exceed the A1 category limit values. The pH value qualified the tested water to the A2 category. The A3 category limit was exceeded in terms of total suspended solids and BOD_5.
5. Water from the Bukówka reservoir is not suitable as habitat for salmonids and cyprinids due to the presence of nitrites, BOD_5 and total suspended solids.
6. The Bukówka reservoir had a positive influence on the water quality of the river Bóbr and the other four tributaries: Opawa, Złotna, Bachorzyna and Paprotki. During the research, the highest values in the reservoir were observed for water pH and temperature. Compared with the water flowing into the reservoir, the outflow was characterized by higher average concentrations of nitrites and higher average water pH and temperature.
7. Due to the transboundary nature of the Bóbr River where the Bukówka reservoir is located, it is important to limit the inflow of pollutants into it and monitor the cleanliness of water in the watercourses and in the reservoir. Comprehensive hydrological and water quality monitoring in the reservoir catchment basin will help protect water in the catchment and will enable rational water management in the Polish and Czech part of the basin. The most important measures for water crossing the Polish-Czech border should relate to combating pollution and improving water quality.

References

1. **Bajkiewicz-Grabowska E.:** *Obieg materii w systemach rzeczno-jeziornych*, Warsaw University, Faculty of Geography and Regional Studies, Warszawa 2002.
2. **Bartoszek L., Koszelnik P., Tomaszek J.A.:** *Obciążenie zewnętrzne i retencja fosforu w zbiornikach zaporowych Solina–Myczkowce*. Zeszyty Nauk. Politechniki Rzeszowskiej, Bud. i Inż. Środ. 268(56), 5–15 (2009).
3. **Bartoszek L., Tomaszek J.A.:** *Analysis of the spatial distribution of phosphorus fractions in the bottom sediments of the Solina–Myczkowce Dam Reservoir complex*. Environment Protection Engineering. 37(3), 5–15 (2011).
4. **Bayram A., Önsoy H., Kömürcü M.I., Tüfekçi M.:** *Reciprocal influence of Kürtün Dam and wastewaters from the settlements on water quality in the stream Harşit, NE Turkey*. Environmental Earth Sciences. 2014, 10.1007/s12665-014-3190-0.
5. **Benndorf J., Pütz K.:** *Control of eutrophication of lakes and reservoirs by means of pre-dams – I. Mode of operation and calculation of the nutrient elimination capacity*. Wat. Res. 21, 829–838 (1987).
6. *Water Framework Directive (WFD), DIRECTIVE 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.* Official Journal of the European Communities. L 327, 1–72 (2000).
7. **Gülbahar N., Elhatip H.:** *Estimation of environmental impacts on the water quality of the Tahtalıdam watershed in İzmir, Turkey*. Environmental Geology. 47(5), 725–728 (2005).
8. **Havránek L., Kovář A., Zapletal T.:** *Zpráva o hodnocení jakosti povrchových vod pro území ve správě Povodí Labe*, státní podnik Odbor péče o vodní zdroje. Hradec Králové. 77 (2011).
9. **Havránek L., Kovář A., Skalická I., Zapletal T., Krejčí M.:** *Zpráva o hodnocení jakosti povrchových vod v územní působnosti Povodí Labe*, státní podnik za rok 2012. Vodohospodářská bilance za rok 2012. Hradec Králové. 77 (2013).
10. **Horn W., Horn H., Geiger D., Paul L.:** *Auswirkungen des Hochwassers im August 2002 auf die Wasserbeschaffenheit der Talsperre Saidenbach*. [in]: Tagungsbericht der Deutschen Gessellschaft für Limnologie, Köln. 684–689 (2003).
11. *Instrukcja gospodarowania wodą dla zbiornika wodnego Bukówka.* Integrated Engineering Sp. z o.o. na zlecenie RZGW Wrocław, Raszyn. 22 (2007).
12. **Koc J., Skwierawski A.:** *Uwarunkowania jakości wody małych zbiorników na obszarach wiejskich*. Zeszyty Problemowe Postępów Nauk Rolniczych, Polska Akademia Nauk, z. 499, Warszawa. 121–128 (2004).

13. **Koc J., Duda M., Tucholski S.:** *Znaczenie zbiornika retencyjnego dla ochrony jeziora przed spływami fosforu ze zlewni rolniczej.* Acta Sci. Pol., Formatio Circumiectus. 7(1), 13–24 (2008).
14. **Liu S. M., Zhang J., Chen H.T., Wu Y., Xiong H., Zhang Z.F.:** *Nutrients in the Changjiang and its tributaries*. Biogeochemistry. 62, 1–18 (2003).
15. **Nakashima S., Hamada Y., Tada K.:** *Characterization of the water quality of dam lakes on Shikoku Island*, Japan Limnology. 8(1), 1–22 (2007).
16. **Nałęcz T., Gidziński T., Kazimierski B., Sadurski A.:** *Transgraniczny monitoring wód podziemnych wzdłuż wschodniej granicy UE – dotychczasowe doświadczenia i plany na przyszłość*. Biuletyn PIG. 445, 437–446 (2011).
17. *Ocena stanu jakości rzek województwa dolnośląskiego w 2007 roku*. Provincial Inspectorate of Environmental Protection (PIEP) in Wrocław, 54 (2007).
18. *Operat wodnoprawny dla zbiornika wodnego Bukówka.* Integrated Engineering Sp. z o.o. na zlecenie RZGW Wrocław, Raszyn 2007.
19. **Pütz K.:** *Die Steuerung der externen Belastung der Sächsischen Talsperren als wesentliche Strategie ihrer Wassergütebewirtschaftung*. Int. Revue ges. Hydrobiol. 80, 4, 563–578 (1985).
20. **Paul L., Pütz K.:** *Suspended matter elimination in a pre-dam with discharge dependent storage level regulation*. Limnologica. 38, 388–399 (2008).
21. *Program Ochrony Środowiska dla powiatu kamiennogórskiego*, Kamienna Góra 2004.
22. *Program Ochrony Środowiska dla gminy Lubawka*, Lubawka (2008).
23. *Raport o stanie środowiska województwa dolnośląskiego w 2005 r.* Provincial Inspectorate of Environmental Protection (PIEP) in Wrocław 2005.
24. **Rast W., Thornton J. A.:** *Trends in Eutrophication research and control*. Hydrological Processes. 10, 295–313 (1996).
25. *Rozporządzenie Ministra Zdrowia z 16.10.2002r. w sprawie wymagań, jakim powinna odpowiadać woda w kąpieliskach*. Dz.U. 183, 1530 (2002).
26. *Rozporządzenie Ministra Środowiska z 27.11.2002r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia*. Dz.U. 204, 1728 (2002).
27. *Rozporządzenie Ministra Środowiska z 23.2002r. w sprawie kryteriów wyznaczania wód wrażliwych na zanieczyszczenie związkami azotu ze źródeł rolniczych*. Dz.U. 241, 2093 (2002).
28. *Rozporządzenie Ministra Środowiska z 4.10.2002r. w sprawie wymagań, jakim powinny odpowiadać wody śródlądowe będące środowiskiem życia ryb w warunkach naturalnych*. Dz.U. 176, 1455 (2002).
29. *Rozporządzenie Ministra Środowiska z 9.11.2011 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych*. Dz.U. 257, 1545 (2011).

30. **Sieber H.U.:** *Talsperren als multifunktionale Anlagen*. WWT. 12, 17–21 (2003).
31. **Sojka M., Siepak M., Gnojska E.:** *Ocena zawartości metali ciężkich w osadach dennych wstępnej części zbiornika retencyjnego Stare Miasto na rzece Powie*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1916–1928 (2013).
32. **Wegener U., Dörter K., Beuschold E.:** *Der Einfluss der landwirtschaftlichen Nutzung von Talsperreneinzugsgebieten auf den Nährstoffeintrag in Trinkwassertalsperren*. Acta hydrochim. hydrobiol. 13, 553–561 (1975).
33. **Wiatkowski M., Paul L.:** *Surface water quality assessment in the Troja river catchment in the context of Włodzienin reservoir construction*. Polish Journal of Environmental Studies. 18(5), 923–929 (2009).
34. **Wiatkowski M., Rosik-Dulewska Cz., Wiatkowska B.:** Charakterystyka stanu użytkowania małego zbiornika zaporowego Nowaki na Korzkwi. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 12, 351–364 (2010).
35. **Wiatkowski M.:** *Influence of Słup dam reservoir on flow and quality of water in the Nysa Szalona river*. Polish Journal of Environmental Studies. 20(2), 467–476 (2011).
36. **Wiatkowski M., Rosik-Dulewska Cz., Kuczewski K., Kasperek K.:** *Ocena jakości wody zbiornika Włodzienin w pierwszym roku funkcjonowania*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2666–2682 (2013).

Dopływ zanieczyszczeń do zbiornika wody pitnej Bukówka z obszaru transgranicznego zlewni rzeki Bóbr

Streszczenie

Obecnie istnieje zwiększone zainteresowanie zarządzaniem zasobami wodnymi, w tym jakością wody, na obszarach transgranicznych. Sytuacja nabiera szczególnego znaczenia, gdy na rzece transgranicznej zlokalizowany jest zbiornik zaporowy, m.in. wykorzystujący retencjonowane wody do celów zaopatrzenia w wodę. Wówczas niezmiernie ważne sa badania jakości wód w zlewni powyżej zbiornika, przede wszystkim w aspekcie wprowadzania do tych wód zanieczyszczeń, zarówno w górnym biegu rzeki transgranicznej, jak i w kolejnych punktach biegu rzeki.

Praca przedstawia analizę dopływu zanieczyszczeń z obszaru transgranicznego zlewni rzeki Bóbr do zbiornika wody Bukówka, w aspekcie jej retencjonowania w zbiorniku. Przeanalizowano jakość wody pięciu cieków zasilają-

cych zbiornik: rzeka Bóbr, Opawa, Złotna, Bachorzyna i Paprotki, jakość wody retencjonowanej w zbiorniku i odpływającej ze zbiornika oraz rozpoznano przyczyny jej przestrzennego zróżnicowania a także czasowej ich zmienności. W pracy ponadto przedstawiono ocenę eutrofizacji analizowanych wód, oceniono czy badane wody są wrażliwe na zanieczyszczenie związkami azotu ze źródeł rolniczych, do spożycia oraz wykonano ocenę zlewni zbiornika Bukówka pod kątem dostawy materii do zbiornika. Ocenę jakości wody w analizowanych ciekach i zbiorniku wykonano analizując takie wskaźniki jak: NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, BOD_5, odczyn wody, przewodność elektrolityczną, temperaturę wody i zawiesinę ogólną. Wyniki badań własnych jakości wody rzeki Bóbr uzupełniono wynikami uzyskanymi z WIOŚ Wrocław i z Czech.

Wyniki przeprowadzonych w okresie 2006–2007 badań jakości wody na terenie polskiej części zlewni zbiornika Bukówka wykazały, że wody te ze względu na stężenia fosforanów, BZT_5 i zawiesiny ogólnej przekroczyły wartości graniczne wskaźników jakości wód odnoszące się do jednolitych części wód powierzchniowych w ciekach naturalnych takich jak rzeka właściwe dla klasy II. Natomiast stężenia $N\text{-}NO_3^-$ i odczyn zakwalifikowały wody do II klasy jakości wód, odnoszących się do jednolitych części wód powierzchniowych w ciekach naturalnych, takich jak rzeka.

W pracy stwierdzono, że badane wody z terenu zlewni zbiornika Bukówka nie są wrażliwe na zanieczyszczenie związkami azotu ze źródeł rolniczych. Natomiast zlewnia zbiornika Bukówka charakteryzuje się małą podatnością na uruchomienie ładunku zdeponowanego na jej obszarze i niewielką możliwością dotarcia jej do zbiornika.

Z punktu widzenia procesu eutrofizacji uwarunkowania hydrochemiczne występujące w zlewni zbiornika Bukówka, w aspekcie realizowanych przez zbiornik funkcji, są dla niego niekorzystne. Główną przyczyną tego stanu są wysokie stężenia fosforu pochodzącego ze ścieków bytowych z miejscowości położonych w badanej zlewni.

Wody zbiornika Bukówka nie nadają się do bytowania ryb łososiowatych i karpiowatych. Natomiast ocena przydatności wody odpływającej ze zbiornika Bukówka do spożycia wykazała, że wartości: temperatury wody, przewodności elektrolitycznej, azotanów i amoniaku nie przekroczyły wartości granicznych kategorii A1. Wartości odczynu wody zakwalifikowały badane wody do kategorii A2. Wartości graniczne kategorii A3 przekroczone zostały pod względem zawiesiny ogólnej i BZT_5.

W pracy wykazano, że zbiornik Bukówka wpływał korzystnie na zmiany jakości wody rzeki Bóbr i innych czterech dopływów: Opawa, Złotna, Bachorzyna i Paprotki. Woda odpływająca ze zbiornika w porównaniu z wodą dopływającą do zbiornika charakteryzowała się większymi wartościami średnich stężeń azotynów, odczynu wody i temperatury wody.

Ze względu na transgraniczny charakter rzeki Bóbr, na której zlokalizowany jest zbiornik Bukówka, istotne jest ograniczenie dopływu zanieczyszczeń do niej oraz monitorowanie stanu czystości wody w ciekach i zbiorniku. Kompleksowy monitoring hydrologiczny i jakości wody w zlewni zbiornika będzie pomocny do podejmowania działań na rzecz ochrony wód w zlewni oraz umożliwi prowadzenie racjonalnej gospodarki wodnej na obszarze polskiej i czeskiej części zlewni. Najważniejsze działania dla wód przekraczających granicę polsko-czeską powinny dotyczyć ochrony tych wód przed zanieczyszczeniami, poprawy stanu gospodarki wodno-ściekowej w zlewni oraz poprawy jakości wody.

Słowa kluczowe:
zbiornik wodny, rzeka, zlewnia, wody transgraniczne, jakość wód

Keywords:
water reservoir, river, basin, transboundary waters, water quality

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Criteria for Sustainable Disposal of Sewage Sludge

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1. Introduction

Phosphorus and potassium compounds are considered important for plant growth. What is more, food production for a growing number of people depends on their availability. Phosphorus and potassium compounds are delivered to soil as salts obtained from mineral deposits. The problem is that mineral resources are quickly exhausted and this threatens the fundamental paradigm of sustainable development stating that providing the currently living generations with the essential livelihoods will not deprive future generations of the ability to satisfy their own needs [2,6–8,19,21,22]. This paradigm necessitates reducing the exploitation of natural reserves of phosphorus and potassium. The search for other sources of these compounds draws attention to sewage sludge produced in sewage treatment plants.

The sludge contains about 3.2% of phosphorus and 0.4% of potassium. Their reimplementation into soil, after appropriate treatment, may significantly reduce the consumption of natural reserves of phosphorus and potassium.

Sewage sludge contains multiple compounds having agriculture values, including organic matter, nitrogen, phosphorus and potassium compounds and, to a lesser extent, calcium, sulphur and magnesium compounds.

Addition of sewage sludge to land increases organic matter in the soil. The organic matter improves the physical, chemical, biological and biochemical properties of soil. Sewage sludge contains high levels of organic matter which is beneficial to the physical, chemical and biological properties of soil. Organic matter improves the physical quality of soil and the root environment by increasing the soil water retentioncapacity and improving soil aggregation and by reducing soil bulk density (see table 1).

The improved physical properties of soil and high levels of organic matter can enhance biological properties in the soil, including improvement of enzymatic, microbial and earthworm activities.

Table 1. Physical properties of soil improved by the use of sewage sludge [16]
Tabela 1. Fizyczne właściwości gleby wzbogaconej osadami ściekowymi [16]

	Experimental period (a)	Decrease in bulk density	Increase in porosity	Increase in water holding capacity
Crop land	2~3	18	12.9	4.9
Forest land	1	4.1	2.0~3.5	8~16
Turfgrass	1	5.67~35.5	9.7~10.1	29~580

On the other hand, sewage sludge also contains an array of unfavourable substances, including (1) metallic pollutants, such as zinc, copper, nickel, cadmium, lead, mercury, and chromium, (2) persistent organic pollutants, such as organochlorine pesticides and polychlorinated biphenyls (PCBs), and (3) microorganism pollutants, such as pathogens [4,5,7]. Content of those pollutants requires careful treatment and disposal of sewage sludge.

Untreated sewage sludge also contains micro-organisms that pose health risks. Therefore, sewage sludge should be treated prior to use, in order to decrease the water content and to eliminate odours and disease-causing agents. Typical sludge treatment includes thickening, dewatering, drying and stabilization (e.g. anaerobic digestion and alkaline stabilization). In general, these unit operations take place on-site (at WWPTs) and require a large amount of energy, depending on the specific process used.

After on-site treatment, sewage sludge is normally transported off-site for safe disposal or agricultural use. Currently, in majority of countries, land application and landfilling are the most often used sewage sludge disposal methods, although there are some alternatives (e.g. incineration and pyrolysis) that have been well developed [11–14]. Landfill disposal can be regarded as the least favourable, and the most unsustainable because of the following factors:

- it commonly generates undesired emissions (e.g. leachate, landfill gas and odours) to water, air and soil,
- valuable nutrient substances (e.g. compounds of N and P) contained in sludge are wasted and become pollutants, mostly presented in leachate.

For safe management of sewage sludge it is necessary to follow strict regulations.

Therefore, regulations related to the land application of sewage sludge in EU. USA, China and Poland will be characterized.
Typical composition of sewage sludge is presented in Table 2.

Table 2. Typical chemical composition and properties of primary, activated and digested sludge [10]
Tabela 2. Typowy skład chemiczny i właściwości osadów surowych, czynnych i przefermentowanych

	Primary sludge		Digested sludge		Activated sludge
	Range	Typical	Range	Typical	Range
Total dry solids (TS), %	2.0–8.0	5.0	6–12	10	0.83–1.16
Volatile solids (% of TS)	60–80	65	30–60	40	59–88
Grease and fats (% of TS)					
Ether soluble	6–30		5–20	18	
Ether extract	7–35				5–12
Protein (% of TS)	20–30	25	15–20	18	
Nitrogen (N, % of TS)	1.5–4	2.5	1.6–6	3	2.4–5

Table 2. cont.
Tabela 2. cd.

	Primary sludge		Digested sludge		Activated sludge
	Range	Typical	Range	Typical	Range
Phosphorous (P_2O_5, % of TS)	0.8–2.8	1.6	1.5–4	2.5	2.8–11
Potash (K_2O, % of TS)	0–1	0.4	0–3	1	0.5–0.7
Cellulose (% of TS)	8–15	10	8–15	10	
Iron (not as sulphide)	2–4	2.5	3–8	4	
Silica (SiO_2, % of TS)	15–20		10–20		
Alkalinity (kg/l as $CaCO_3$)	0.5–1.5	0.6	2.5–3.5		0.58–1.1
Organic acids (kg/l as Hac)	0.2–2	0.5	0–0.6	3	1.1–1.7
Energy content (MJ/kg)	23–29	25	9–14	12	19–23

2. Criteria for the European Union

As early as 1986, the Council of the European Union promulgated the Directive: "*on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC)*" [1]. The aim of the Directive is to regulate the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animals and people, while encouraging its proper use. To this end, it sets out the requirements regarding pollutant limits, operational standards, management practices, sampling and analysis methods, recordkeeping (e.g. the quantities and properties of sludge produced) and, periodical reporting. The Directive prohibits the use of untreated sludge on agricultural land unless it is injected into the soil under specific conditions.

Directive sets limit values for seven heavy metals (cadmium, copper, nickel, lead, zinc, mercury and chromium), both in soil and in sludge itself. It describes limit values for concentrations of heavy metals in soil to which sludge is applied, concentrations of heavy metals in sludge, and the maximum annual quantities of such heavy metals which may be introduced into soil (Tables 3, 4 and 5).

Table 3. Limit values for concentrations of heavy metals in soil [1]
Tabela 3. Dopuszczalne stężenia metali ciężkich w glebie [1]

Metals	mg/kg of dry matter
Cadmium	1 to 3
Copper	50 to 140
Nickel	30 to 75
Lead	50 to 300
Zinc	150 to 300
Mercury	1 to 1.5
Chromium	–

Table 4. Limit values for heavy-metal concentrations in sludge used in agriculture [1]
Tabela 4. Dopuszczalne stężenia metali ciężkich w osadach ściekowych wykorzystywanych w rolnictwie [1]

Metals	mg/kg of dry matter
Cadmium	20 to 40
Copper	1 000 to 1 750
Nickel	300 to 400
Lead	750 to 1 200
Zinc	2 500 to 4 000
Mercury	16 to 25
Chromium	–

Table 5. Limit values for amounts of heavy metals which may be added annually to agricultural land, based on a 10-year average [1]
Tabela 5. Dopuszczalne stężenia metali ciężkich, jakie można wprowadzać w ciągu roku do gleby, w oparciu o 10-letnią średnią [1]

Metals	kg/ha/yr
Cadmium	0.15
Copper	12
Nickel	3
Lead	15
Zinc	30
Mercury	0.1
Chromium	–

The current Sewage Sludge Directive addresses both pathogen reduction and the potential for accumulation of persistent pollutants in soils but sets no limits for organic contaminants. The Directive establishes limit values for seven heavy metals (cadmium, copper, nickel, lead, zinc, mercury and chromium), both in soil and in sludge itself. It specifies general land use, harvesting and grazing restrictions to provide protection against health risks from residual pathogens. The Directive requires all sludge to be treated before being applied to agricultural land, but allows the injection of untreated sludge into the soil under specific conditions. While it calls for the use of treated sludge, the Directive does not specify treatment processes.

The Member States can apply stricter restrictions than those determined in Directive 86/278/ EEC and this is observed in several cases. Specifically, 16 out of the 27 EU countries have set more rigorous national standards for heavy metals concentrations in sludge, whereas 10 out of 27 countries have set stricter limit values for the concentrations of heavy metals in soil. There is a wide variation in national limit values for heavy metals, even between similar geographical areas, such as the Nordic or Baltic countries. Nordic countries (Finland, Sweden, Denmark and Netherlands) have set the lowest limit values. On the other hand, except of France, Malta and Slovenia, Mediterranean countries have adopted the limit values proposed by the EU Directive.

Apart from heavy metals included in the EU Directive 86/278, several countries have set limit values for chromium as well as for other categories of pollutants commonly detected in sludge such as pathogens and organic micropollutants. Limit values for total chromium in sludge have been set by 19 out of the 27 countries, while different legislation on this matter is observed in different parts of Belgium. The limit values of total Cr range from 40 mg/kg dry matter (Slovenia) to 1750 mg/kg dry matter (Luxembourg).

So far, except for Hungary which has set a limit value of 1 mg/kg for Cr(VI), no limit values have been set for this chromium species by other European countries, despite the fact that it is much more toxic than total chromium [18].

3. Criteria for the USA

The US EPA introduced regulations in 1993 [9,17] that established minimum standards that must be met if sludges are to be land-applied. The regulations include concentration limits for nine metals and for pathogens, and requirements for the reduction of flies and rodents attraction. The regulations establish Class A sludges, which have been treated to total elimination of pathogens (disease-causing organisms), and Class B, in which pathogens have been reduced but are still present. Under the federal 503 rules certain site restrictions apply to Class B use, but no individual site permits are required for its use.

The federal regulations also establish standards for nine contaminants (see Table 6).

The standards include the so-called ‘exceptional quality’ (EQ) sludges, which meet certain concentration limits (no more than X parts per million of any of the nine regulated contaminants) as well as pathogen and fly and rodent reduction. With regard to metal concentrations, sludges and sludge products that fail to meet one or more of those ‘EQ’ pollutant concentrations but which fall below a higher ceiling concentration may be applied, but the applicator is directed to keep track of the total amount of each metal applied and cease application when a regulatory cumulative pollutant loading limit is reached. Sludge products that fail to meet one or more of the ‘EQ’ pollutant concentrations but which fall below the ceiling concentration may still be as long as information on the acceptable annual pollutant loading rate (APLR) is reached.

Table 6. Pollutants limits for all land applied sewage sludge [9]
Tabela 6. Limity zanieczyszczeń osadów ściekowych stosowanych na grunty[9]

Pollutant	Ceiling Concentration Limits for All Biosolids Applied to Land (milligrams per kilogram)[2]	Pollutant Concentration Limits for EQ and PC Biosolids (milligrams per kilogram)[2]	Cumulative Pollutant Loading Rate Limits for CPLR Biosolids (kilograms per hectare)	Annual Pollutant Loading Rate Limits for APLR Biosolids (kilograms per hectare per 365-day period)
Arsenic	75	41	41	2.0
Cadmium	85	39	39	1.9
Chromium	3,000	1,200	3,000	150
Copper	4,300	1,500	1,500	75
Lead	840	300	300	15
Mercury	57	17	17	0.85
Molybdenum[b]	75	–	–	–
Nickel	420	420	420	21
Selenium	100	36	100	5.0
Zinc	7,500	2,800	2,800	140
Applies to:	All biosolids that are land applied	Bulk biosolids and bagged biosolids[c]	Bulk biosolids	Bagged biosolids[c]

[a] Dry-weight basis

[b] As a result of the February 25, 1994, Amendment to the rule limits for molybdenum were deleted from the Part 503 rule pending EPA reconsideration.

[c] Bagged biosolids are sold or given away in a bag or other container.

4. Criteria for China

In China, the first regulation (Control Standards for Pollutants in Sludges from Agricultural Use) regarding land application of sewage sludge was established in l984 by the Ministry of Urban-Rural Construction and Environmental Protection (MURCEP). The regulation set limits on ten pollutants for sewage sludge used in agriculture. The maximum allowable concentrations of pollutants in sludges that are applied to land are presented in Table 6.

In addition, the regulation establishes other requirements:

- annual loading rate of sludge application should not exceed 30 ton/ha,
- if the content of any inorganic chemical contained in sewage sludges is close to the limit value shown in Table 7, the waste cannot be applied to the same site for more than 20 years,
- sewage sludges should not be used on sandy soil, land with high ground water level, or conservation area for water resources,
- before land application, sludge must be composted or digested,
- sludge should not be employed on vegetable field or grass lands used for grazing within 1 year of application,
- when sewage sludge is applied to acid soil, the soil should be treated with lime,
- sludge loading rate should be reduced if the content of more than one chemical in sludge reaches the limits,
- if crop growth is affected negatively or harmful chemical content in crop excesses any standard, sludge application should be stopped.

There have been no regulations for pathogen control for sludge land application.

Table 7. Control standards for pollutants in sludges used in agriculture [3]
Tabela 7. Standardowe stężenia zanieczyszczeń w osadach ściekowych stosowanych w rolnictwie [3]

Parameters	Limit values [$mg\cdot kg^{-1}$d.m.]	
	pH < 6.5	pH > 6.5
Cadmium	5	50
Mercury	5	15
Lead	300	1000
Chromium	600	1000
Boron	150	150
Copper	250	500
Zinc	500	1000
Nickel	100	200
Mineral oil	3000	3000
Benzo[a]pyrene	3	3

5. Criteria for Poland

Sewage sludge produced in wastewater treatment plants requires neutralization not only for practical, but also legal reasons. If possible, processed sludge should return to the natural environment mainly due to the content of valuable fertilizing components such as nitrogen or phosphorus, responsible for biomass growth. Agricultural use is recommended for small and medium treatment plants. For large treatment plants, it is impossible to use sludge in agriculture, as it contains exceeded concentrations of heavy metals.

In the Polish legal system, there is a range of regulations pertaining to sludge management. The basic regulation concerning waste management is the Act on waste of 14th December 2012 (Official Journal, Dz. U., 2013, item 21) and several regulations which determine the management of sewage sludge in a detailed way. The most important ones include: Regulation of the Polish Minister of Environment of 27th September 2001 on the Waste Catalogue (Official Journal, Dz.U., 2001, No. 112, item 1206); in the case of thermal processing of waste – Regulation of the Polish Minister of Economy of 21st March 2002 on conditions of thermal processing of waste (Official Journal, Dz.U., 2002, No. 37, item

339); and the Regulation of the Polish Minister of Economy of 8th January 2013 on the criteria and procedures of *waste* approval for *storage* at a *waste storage* facility of particular type (Official Journal, Dz.U., 2013, item 38).

One of the most important legal acts regulating sewage sludge management is the Regulation of the Polish Minister of Environment of 13th July 2010 on municipal sewage sludge (Official Journal, Dz.U., 2010, No. 137, item 924). This act contains transposed legal regulations of the European Union. It specifies the conditions which are to be met while employing municipal sewage sludge in agriculture as well as land reclamation, including agricultural lands, lands for cultivation of plants used in compost production, feed production, and plants not intended for human consumption. Similarly, as in other countries, regulations found in this act set the limit values for concentrations of seven heavy metals found in sewage sludge (see Table 8).

Table 8. Limit values for concentrations of heavy metals in municipal sewage sludge [15]
Tabela 8. Wartości graniczne stężeń metali ciężkich w komunalnych osadach ściekowych [15]

Metals	Heavy metal content [$mg \cdot kg^{-1}$d.m]	
	in agriculture and the reclamation of lands for agricultural purposes	in the reclamation of lands for non-agricultural purposes
Cadmium	20	25
Copper	1000	1200
Nickel	300	400
Lead	750	1000
Zinc	2500	3500
Mercury	16	20
Chromium	500	1000

8. Conclusions

Sewage sludge is a sustainable source of phosphorus and potassium compounds for the growth of biomass. Their application on cultivated land could be beneficial on condition that the level of pollution does not exceed the acceptable level, in particular with regard to heavy metals.

Taking into account their possible negative impact on the environment, strict regulations on the content of pollutants in sewage sludge, especially heavy metals, have been established in all the discussed regions.

Bearing in mind both the advantages of the use of sewage sludge to fertilize crops and the possible risks arising from contaminants, a number of countries introduced strict regulations governing the use of sewage sludge to fertilize soil.

Taking into consideration the example of the European Union, the U.S., Poland and China, it can be concluded on the basis of analysis of legal regulations in this regard that the use of sewage sludge to fertilize crops is controlled in an appropriate way in both the developed as well as the developing countries.

References

1. Commission of European Communities. Council Directive 86/278/EEC of 4th July 1986 on the protection of the environmental, and in particular of the soil, when sewage sludge is used in agriculture.
2. **Ecimovic T., Haw R, Kondrashin I., Weiler R, Gutierrez F., Vivanco et al.:** *Philosophy of the Sustainable Development and the Sustainable Future of Humankind the Survival of Humanity*. Problemy Ekorozwoju – Problems of Sustainable Development, 9(2), 7–25 (2014).
3. GB4284-84, Control standards for pollutants standards for pollutants in sewage sludge from agricultural use, 1984.
4. **Kelessidis A., Stasinakis A.S.:** *Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries*. Waste Management, 12, 1, 201–216, 2012.
5. **Kelessidis A., Stasinakis A.S.:** *Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries*. Waste Management, 32, 6, 1186–1195, 2012.
6. **Konstańczak S.:** *Theory of Sustainable Development and Social Practice*. Problemy Ekorozwoju – Problems of Sustainable Development. 9, 1, 37–46, 2014.

7. **Konarski W.:** *Mineral Energy Sources and Political Activities: Introduction to Mutual Dependencies and Their Selected Exemplification*.Problemy Ekorozwoju – Problems of Sustianable Development, 9, 1, 63–70, 2014.
8. **Krajewski P.:** *Food Safety and Sustainable Development*. Problemy Ekorozwoju – Problems of Sustianable Development. 9, 2, 79–86, 2014.
9. Land Aplication of sewage Sludge, EPA/831-B-93-002b, December 1994.
10. Metcalf and Eddy, I. Wastewater Engineering: Treatment and Reuse. Fourth Edition, McGraw-Hill Higher Education, New York 2003.
11. **Pawłowska M., Pawłowski L.:** *Method for elimination of mobile fraction of heavy metal ions in sewage sludge*. Patent nr EP08165555.7 z dnia 2008.09.05.
12. **Pawłowski L., Pawłowski A.:** *Method for producing fuel from sewage sludge*. Patent nr EP09174096.9 z dnia 2009.10.26.
13. **Pawłowska M., Siepak J., Pawłowski L., Pleczyński J.:** *Method for sewage sludge utilisation for intensification of biogas production in refuse collection depot*. Patent nr EP08165556.5 z dnia 2008.09.05.
14. **Piekarski J., Kogut P., Kaczmarek F., Dąbrowski T.:** *Biogazownie utylizacyjne jako propozycja utylizacji osadów ściekowych w odniesieniu do ustawodawstwa polskiego*. Rocznik Ochrony Środowiska, Tom 14 (2012).
15. Regulation of the Polish Minister of Environment of 13th July 2010 on municipal sewage sludge (Official Journal, Dz. U., 2010, No. 137, item 924).
16. **Singh R.P., Agrawal M.:** *Potential benefits and risks of land application of sewage sludge*. Waste Management 28, 347–358 (2008).
17. Standards for the use or disposal of sewage sludge, 40 CFR Part 503.
18. **Stasinakis A.S., Thomaidis N.S.:** *Fate and biotransformation of metal and metalloid species in biological wastewater treatment processes*. Critical Reviews in Environmental Science and Technology. 40, 4, 307–364 (2010).
19. **Wall G.:** *Exergy, Life and Sustainable Development*, *Egzergia, życie i rozwój zrównoważony*. Problemy Ekorozwoju – Problems of Sustianable Development. 8, 1, 27–41 (2013).
20. **Wang X., Chen T., Ge Y., Jia Y.:** *Studies on land application of sewage sludge and its limiting factors*. J Hazard Mater. 160, 554–558 (2008).
21. **Zhang Y., Sheng Li**: *The Impact of Environmental Preferences on Public Supporting for the River Ecosystem Restoration Program in China,* Problemy Ekorozwoju – Problems of Sustianable Development. 9, 2, 55–64 (2014).
22. **Zhine W., Meijun F., Ikerd J.:** *Beyond the Dilemma Facing China's Agriculture – Toward a Chinese Constructive Postmodern Agriculture*. Problemy Ekorozwoju. Problems of Sustainable Development. 8 1, 43–56 (2013).

Kryteria zrównoważonego usuwania osadów ściekowych

Streszczenie

Osady ściekowe są stanowią trwałe źródło związków fosforu i potasu niezbędnych do wzrostu biomasy. Od ich dostępności dla roślin zależy produkcja żywności dla stale wzrastającej liczby ludności. Do gleby dostarczane są związki fosforu i potasu w postaci soli pozyskiwanych jako kopaliny. Problem jednak stanowią szybko wyczerpujące się zasoby minerałów, z których pozyskiwane są wyżej wymienione pierwiastki do produkcji nawozów rolniczych. W przyszłości ich brak może pogorszyć jakość gleb, co zmniejszy skalę produkcji rolnej. Oznacza to, że podstawowy paradygmat zrównoważonego rozwoju mówiący o konieczności postępowania takiego, aby zapewnić niezbędne środki do życia obecnym pokoleniom, nie pozbawi przyszłych pokoleń możliwości zabezpieczenia ich potrzeb. Paradygmat ten nakazuje podjęcie wszelkich działań zdążających do ograniczania eksploatacji naturalnych ich zasobów. Poszukując innych źródeł zwrócono uwagę na osady ściekowe pochodzące z biologicznych oczyszczalni ścieków. Osady te zawierają związki fosforu i potasu, które po odpowiedniej obróbce mogą przyczynić się do spowolnienia zużycia naturalnych rezerw fosforu i potasu. Zastosowanie osadów ściekowych na uprawianej ziemi, może być korzystne pod warunkiem, że poziom zanieczyszczeń m.in. metalami ciężkimi nie przekracza dopuszczalnego poziomu. Biorąc pod uwagę ich możliwy negatywny wpływ na środowisko naturalne oraz surowe przepisy dotyczące zawartości zanieczyszczeń w osadach, metale ciężkie zostały uwzględnione w prawodawstwie omawianych regionów.

Biorąc pod uwagę zalety wnikające z wykorzystania osadów ściekowych do nawożenia upraw i możliwych zagrożeń wynikających z obecności w osadach ściekowych niepożądanych zanieczyszczeń, wiele krajów wprowadziło surowe przepisy regulujące wykorzystanie osadów do nawożenia gleby. Biorąc pod uwagę przykład Europejskiej, USA, Polski i Chin można stwierdzić na podstawie analizy regulacji prawnych w tym zakresie, że stosowanie osadów ściekowych do nawożenia gleb jest w pełni kontrolowane zarówno w krajach rozwiniętych jak również w krajach rozwijających się.

Słowa kluczowe:
zrównoważony rozwój, fosfor, potas, osady ściekowe, uwarunkowania prawne

Keywords:
sustainable development, phosphorus, potassium, sewage sludge,
legal conditions

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Influence of Ultrasonic Pretreatment on Anaerobic Digestion of Excess Sludge from the Food Industry

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1. Introduction

Sewage sludge is a natural product obtained after sewage treatment. The amount of sludge generated is about 1 to 3% of the volume of the supplied wastewater, but the outlays on processing the sludge amount to ca. 50% of the costs incurred on sewage and sludge treatment in the plant.

Sewage sludge treatment consists in subjecting it to a variety of processing methods based on the processes of biological, physical and chemical nature which help obtain a product which is safe for environment and human health [12, 13, 18, 19].

Current facilities in treatment plants, with high-performance biological methods of sewage sludge treatment and removal of biogenic compounds supported with chemical methods, generate huge amounts of sewage sludge. Sewage sludge is a product that causes substantial environmental nuisance due to unpleasant odour as a result of putrification and it represent a serious sanitary threat. The sludge which is generated should be processed and treated or be used in industry or agriculture. Due to sludge harmfulness to the environment, all the safety recommendations for sludge management should be respected. The main aim of anaerobic process of sludge stabilization is to reduce the sludge mass. Reduction of the amount of sludge minimizes its harmful effect on the environment. Methane fermentation is very popular since it transforms strongly hydrated and hydrophilic sewage sludge with unpleasant odour and high viscosity which is dangerous in bacteriological terms. The generated low-viscosity sludge is easily dewatered and it resembles soil [11]. Sewage sludge treatment using methane fermentation is advantageous in energetic terms since it does not necessitate the supply of high energy while a product of reactions that occur in the process is high-energy biogas. One drawback of this process is low rate of degradation of organic compounds contained in the sludge [3, 23].

In the aspect of improving the effectiveness of anaerobic stabilization, ultrasonic field disintegration represents a very good method. However, it necessitates choosing optimum value of wave frequency. Using ultrasound energy to decompose biomass involves application of low ranges of field frequencies. The choice of frequency depends on the medium exposed to the effect of ultrasound [5, 6, 8, 20].

Depending on the frequency and physical conditions of the medium, high-intensity ultrasound might cause coagulation i.e. connecting small particles into bigger aggregates or dispersion, that is, fragmentation of bigger particles into smaller ones. Ultrasonic coagulation processes occur usually in suspensions of solid particles, liquid drops, gas bubbles in gaseous or liquid medium and they consist in creation of forces in the acoustic field that take them closer to each other and connect into bigger particles that fall down due to gravity forces [17].

It is generally accepted that the disintegrating effect is mainly caused by ultrasonic cavitation. Resonance vibrations of gas bubbles that represent cavitation nuclei and rapid formation and collapsing of vacuum bubbles is observed in the area of cavitation, accompanied by local increases of temperature and pressure. The latter phenomenon is a source of impact waves that cause e.g. dispersion and homogenization of solids in the liquid [17]. Vibrations of media and particles accelerate deformation of a double diffusion layer of colloidal particles, which is manifested with changes in the potential of sonicated sludge particles and offers opportunities for improving the effect of coagulation/flocculation of the sludge [10].

Ultrasound wave is produced as a result of rhythmic vibrations of the particles in the medium it travels through. The wave is characterized by acoustic wave intensity. Intensity is given by the following formula [9]:

$$I = \frac{P}{A}, W \ \cdot cm^{-2} \tag{1}$$

where:

P – power transferred through ultrasonic waves, W;

A – surface of wave propagation, cm^2.

Basic parameters used in description of ultrasonic waves that are formed is wavelength and frequency. Wavelength depends on a medium the ultrasounds propagate in. The basic relationship that occurs between frequency and wavelength is [21]:

$$\lambda = \frac{v}{f}, m \tag{2}$$

where:

v – velocity of wave propagation in a particular medium, m/s;

f – ultrasonic wave vibration frequency, Hz.

There are five options of using ultrasonic disintegration in a technological line of a wastewater treatment plant [20].

- disintegration of activated sludge in order to improve sedimentation properties during de-clearing in order to remove a fermentation scum,
- disintegration of a partial stream of the thickened excess sludge in order to intensify methane fermentation,
- disintegration of partial stream of the suspension in order to improve thickening of excess sludge,
- disintegration of the recirculated sludge in order to utilize the potential of residue gas,
- disintegration of partial stream after initial mechanical dewatering of the sludge in order to improve dehydration.

Using ultrasonic field is a fast and convenient technology that does not generate contamination of the solid phase [4]. Ultrasonic disintegration is based on the use of ultrasonic field with the frequency of 10–50 kHz and ultrasonic field intensity of over 1 W/cm^2 [2, 7, 24].

After propagation through liquid and gaseous media, ultrasonic field creates both primary and secondary phenomena. The primary phenomena include cavitation and radiation pressure while secondary phenomena are those with physicochemical nature, such as ultrasonic coagulation, dispersion, electrokinetic phenomena, oxidation or reduction [1, 24].

The aim of this study was to evaluate the effect of excess sludge disintegration with ultrasonic field on hydrolysis that occurs during methane fermentation of the sludge from the food industry. The rate of generation and value of volatile fatty acids, as well as the degree of sludge fermentation was determinate.

2. Experimental Part

2.1. Substrate

The substrate for the experiments was excess sludge from the mechanical-chemical-biological wastewater treatment plant. This wastewater treatment plant purify wastewater from carbonated drinks factory "Jurajska” in Myszków, Poland, as well as from the mentioned city. The test excess sludge is produced by purification ca. 90% of technological wastewater and ca. 10% of domestic wastewater. Excess sludge was inoculated with fermented sludge with 10:1 ratio. The excess sludge was characterized by the following contents: dry mass 13.31–18.08 g/dm^3, dry organic matter 9.86–13.3 g/dm^3 and dry mineral mass 3.45–4.78 g/dm^3.

2.2. Methodology

During the first stage of the research, in order to determine the best conditions of disintegration possible, the authors used ultrasonic disintegrator VCX-750. The disintegrator's operation consists in active effect of ultrasonic field on the sludge. The energy is produced by power converter which converts the electrical energy supplied into mechanical vibration energy. The mechanical vibration of the converter is transferred as a longitudinal wave to a working tip. The working tip was immersed into a vessel with the excess sludge studied at the depth of 3 cm from the vessel's bottom. The volume of the conditioned sample was 0.5 dm^3 and the ultrasonic conditioning occurred in a no-flow system, with a single filling of the vessel.

During sonication by means of disintegrator VC-750, the authors used vibration amplitudes of ultrasonic field of 15, 21, 31, 37 and 46 µm and sonication time of t_s = 30–360 s.

In the case of second stage of research the aim was to analyze the influence of ultrasonic disintegration of excess sludge on the anaerobic stabilization efficiency. The tests were carried out under mesophilic laboratory conditions in ten glass flasks that represented the models of fermentation chambers. Methane fermentation processes were carried out 10 days. Every day of the process the sludge was collected for analysis from one of the flasks. The flasks were secured from air access with a rubber plug with liquid-column gauge. The plug prevented from the outflow of the biogas generated inside the flasks. The flasks with active volume of 0.5 dm^3 were incubated in a laboratory thermostat at the temperature of 37°C. In order to mix the whole volume of the sludge and prevent from formation of the areas overloaded with contaminants and to prevent from formation of the scum, the content of the flasks was mixed manually several times a day. The mixture procedure ensured mixing of the whole bacterial population in the fermented sludge used as an inoculum with the excess sludge.

Anaerobic stabilization was carried out for the following mixtures:

- Mixture 1 – excess sludge, non-conditioned + fermented sludge;
- Mixture 2 – excess sludge conditioned with ultrasonic field amplitude (A= 21 μm and sonication time of 360 s, acoustic wave intensity 1.02 W/cm^2) + fermented sludge;
- Mixture 3 – excess sludge conditioned with ultrasonic field (A= 46 μm and sonication time of 360 s, acoustic wave intensity 2.09 W/cm^2) + fermented sludge.

The following physicochemical parameters were evaluated:

- volatile fatty acids (VFAs) according to the standard PN-75/C-04616/04 [14],
- dry matter, dry organic matter, dry mineral matter by means of a direct weighing method according to the standard PN-EN-12879 [15],
- chemical oxygen demand by means of a dichromate method based on HACH 2100N IS tests according to (ISO 7027) [16].

3. Results and discussion

An increase in concentration of organic substances contained in supernatant liquor conditioned with ultrasonic field (expressed in COD) was found after exposure of excess sludge to ultrasonic field disintegration. Based on changes in the content of COD and VFAs vs. time, the authors chose the most beneficial parameters of conditioning, pointing to the amplitude of ultrasonic field vibration of A= 46μm and sonication time of 360 s (acoustic wave intensity 2.09 W/cm^2). Furthermore, the effect of disintegration with vibration amplitude of UD A=21 μm (acoustic wave intensity 1.02 W/cm^2) on methane fermentation was also measured for the most favourable sonication time of 360 s. A 3-time and 5-time increases in COD and 2-time and 3-time increases in VFAs were observed respectively for the above indices compared to the initial values.

Fig. 1–5 present changes in COD and VFAs, the indices determined in supernatant liquor depending on sonication time for individual amplitudes of ultrasonic field vibration.

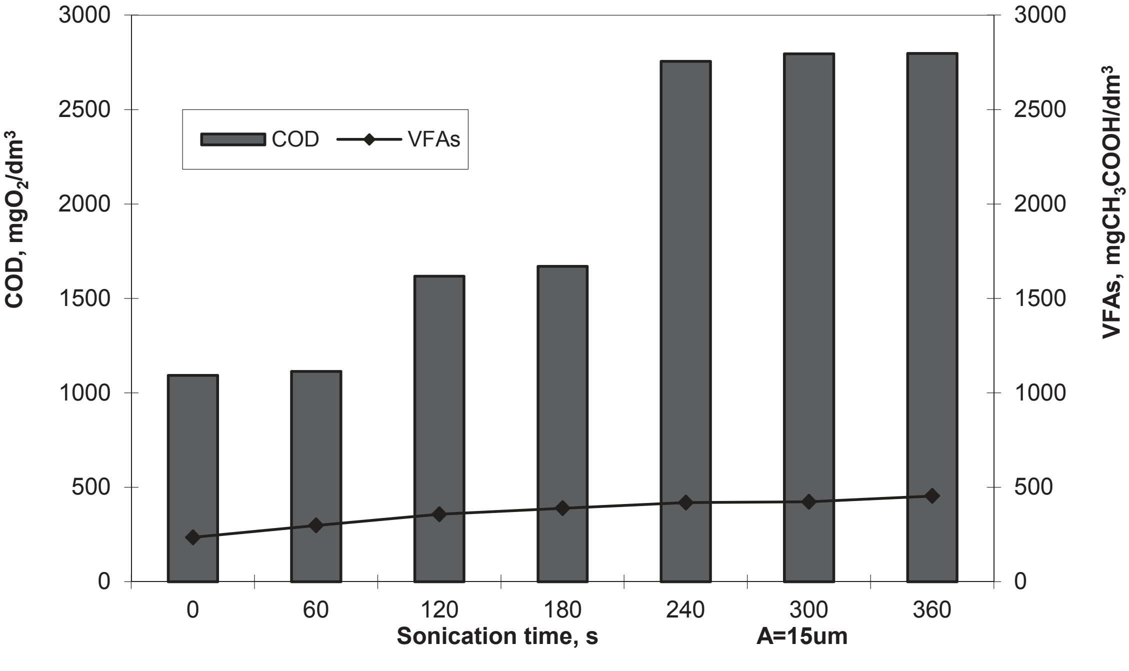

Fig. 1. Changes in COD and VFAs in supernatant liquor vs. sonication time for ultrasonic field vibration amplitude of A=15μm

Rys. 1. Zmiany wartości ChZT oraz LKT w cieczy nadosadowej, w zależności od czasu sonifikacji dla amplitudy drgań pola UD A=15μm

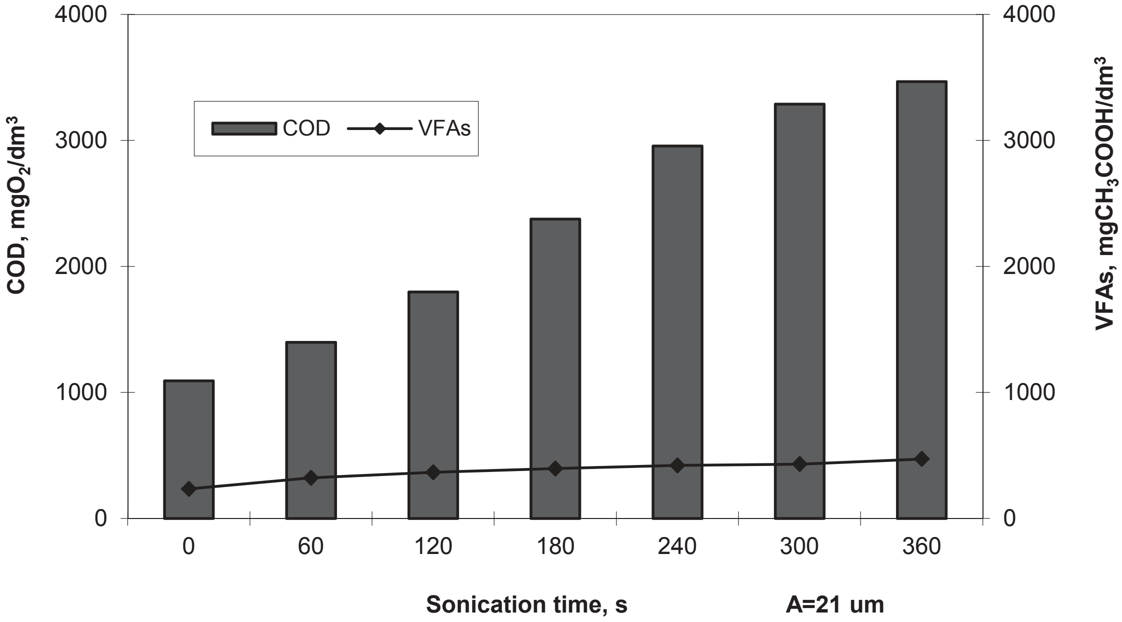

Fig. 2. Changes in COD and VFAs in supernatant liquor vs. sonication time for ultrasonic field vibration amplitude of A=21µm

Rys. 2. Zmiany wartości ChZT oraz LKT w cieczy nadosadowej, w zależności od czasu sonifikacji dla amplitudy drgań pola UD A=21µm

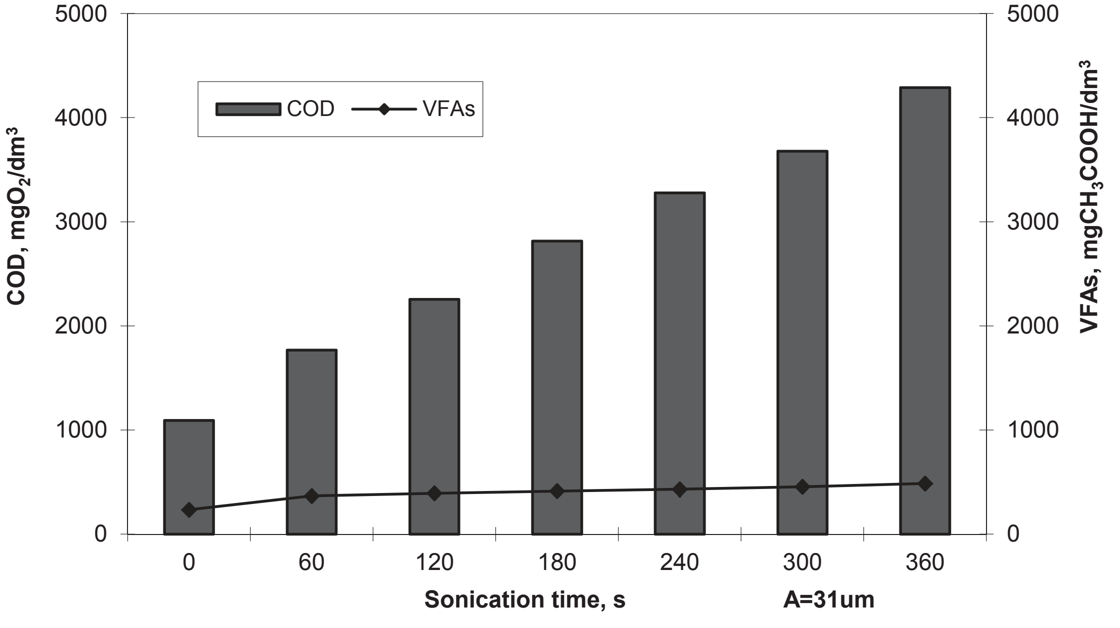

Fig. 3. Changes in COD and VFAs in supernatant liquor vs. sonication time for ultrasonic field vibration amplitude of A=31µm

Rys. 3. Zmiany wartości ChZT oraz LKT w cieczy nadosadowej, w zależności od czasu sonifikacji dla amplitudy drgań pola UD A=31µm

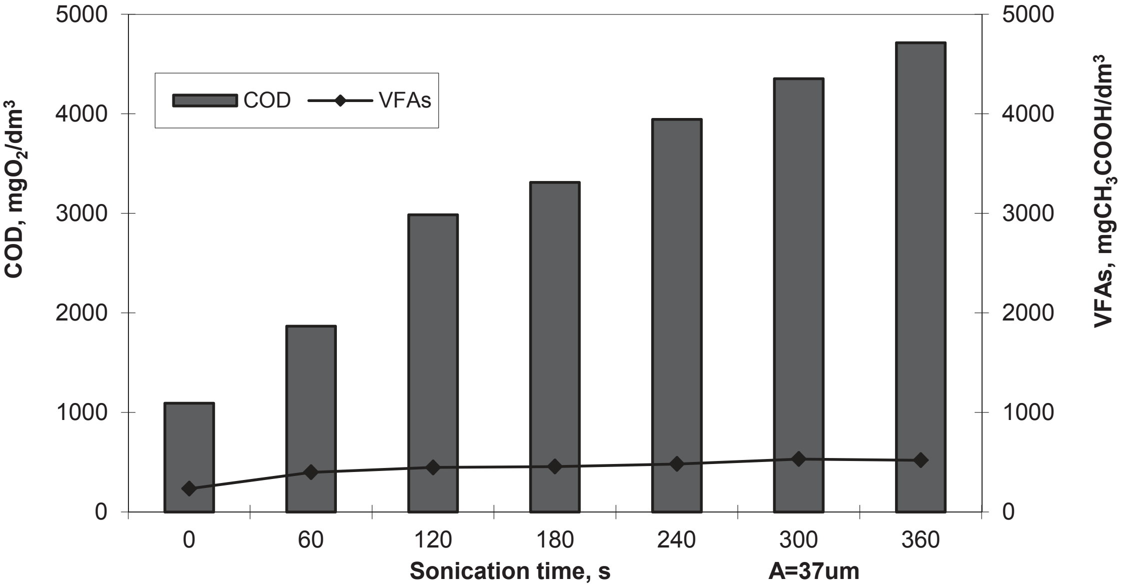

Fig. 4. Changes in COD and VFAs in supernatant liquor vs. sonication time for ultrasonic field vibration amplitude of A=37μm

Rys. 4. Zmiany wartości ChZT oraz LKT w cieczy nadosadowej, w zależności od czasu sonifikacji dla amplitudy drgań pola UD A=37μm

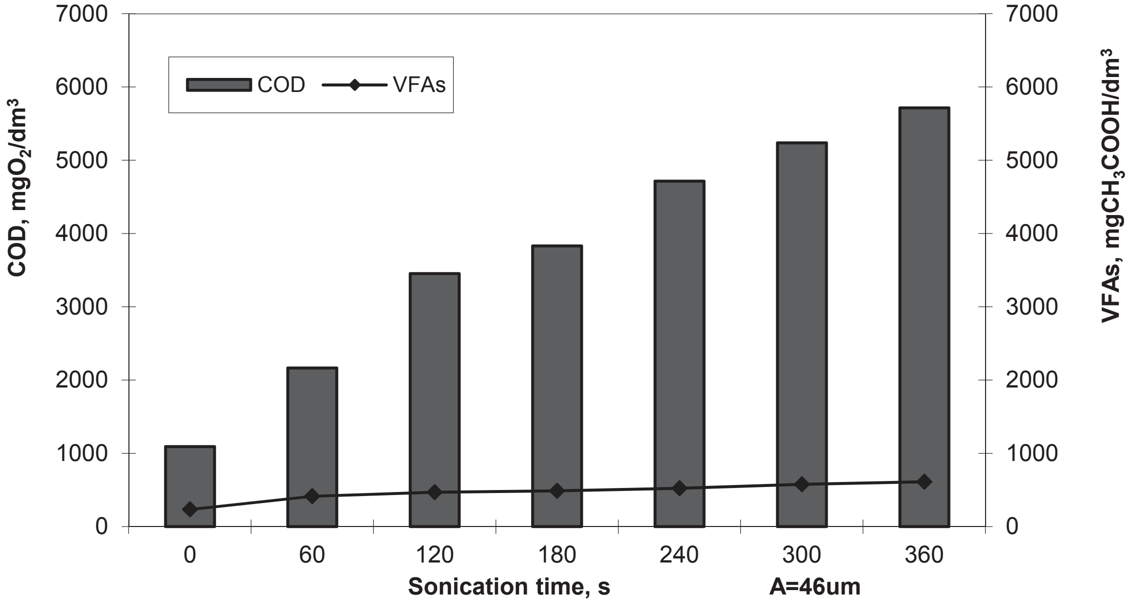

Fig. 5. Changes in COD and VFAs in supernatant liquor vs. sonication time for ultrasonic field vibration amplitude of A=46μm

Rys. 5. Zmiany wartości ChZT oraz LKT w cieczy nadosadowej, w zależności od czasu sonifikacji dla amplitudy drgań pola UD A=46μm

At the next stage of the experiments, the anaerobic stabilization was carried out for a mixture of non-conditioned sewage sludge and fermented sludge used as an inoculum. At this stage of the study, the anaerobic stabilization was carried out for Mixture 1.

Excess sewage sludge is difficult to be biochemically decomposed under anaerobic conditions. This is supported by the degree of sludge fermentation obtained on the tenth day of the stabilization process. Therefore, the results obtained in the study suggested that the effectiveness of the process might be improved through subjecting the process of initial conditioning to the exposure to ultrasonic field.

The degree of sludge fermentation during the process of methane fermentation of Mixture 1 carried out in fermentation flasks was ca. 17%. The initial value of VFA content in Mixture 1 (non-conditioned sludge) was 360 mg CH_3COOH/dm^3. The highest VFA content (805 mg CH_3COOH/dm^3) was found during anaerobic stabilization of Mixture 1, was found on the sixth day of the process. After this day, VFA was constantly decreasing until the 10th day of the process. VFAs content recorded on the last day was 102 mg CH_3COOH/dm^3.

Changes in VFAs content on individual days of methane fermentation of the non-conditioned sewage sludge is presented in Fig. 6.

The process of methane fermentation was also carried out for the excess sludge disintegrated initially with ultrasonic field (Mixtures 2 and 3) with amplitude of ultrasonic field vibration of 21 μm and 46 μm, respectively, for sonication time of 360 s.

The initial value of VFAs content for Mixture 2 was 411 mg CH_3COOH/dm^3. The highest VFAs content (737 mg CH_3COOH/dm^3) was found on the second day of the process. After this day, the value of VFAs generated showed a downward tendency until it reached the value of 257 mgCH_3COOH/dm^3 on the 10th day of the process. Changes in VFAs recorded during methane fermentation for Mixture 2 are presented in Fig. 7.

With regard to Mixture 3, VFAs content on the day of initiation of of anaerobic stabilization was 943 mg CH_3COOH/dm^3. The highest VFAs content (1714 mg CH_3COOH/dm^3) was found on the second day of the process. Final VFAs content on the 10th day of the process was 658 mg CH_3COOH/dm^3. Changes in VFAs observed during methane fermentation of the sludge disintegrated with ultrasonic field are presented in Fig. 8.

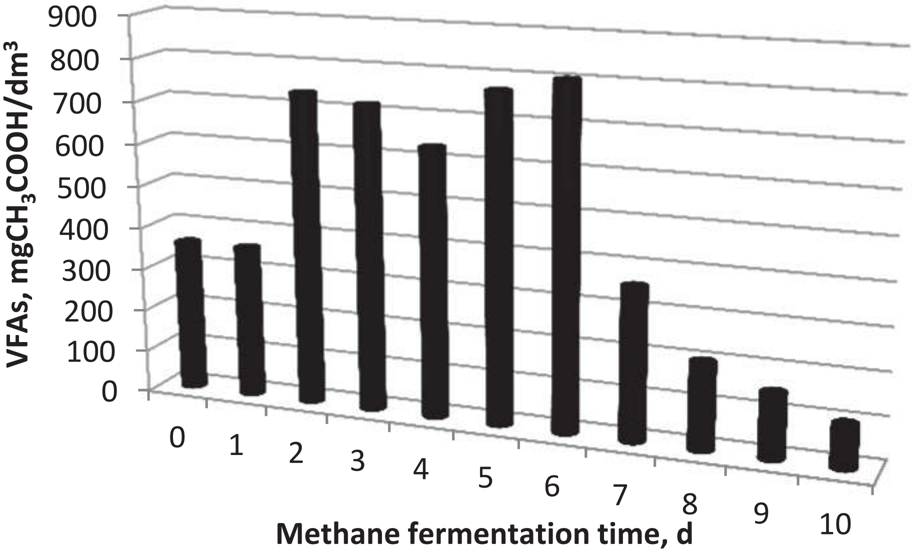

Fig. 6. Changes in VFAs recorded during methane fermentation of unconditioned excess sludge (Mixture 1)
Rys. 6. Zmiany wartości lotnych kwasów tłuszczowych odnotowane podczas procesu fermentacji metanowej niekondycjonowanych osadów nadmiernych (Mieszanina 1)

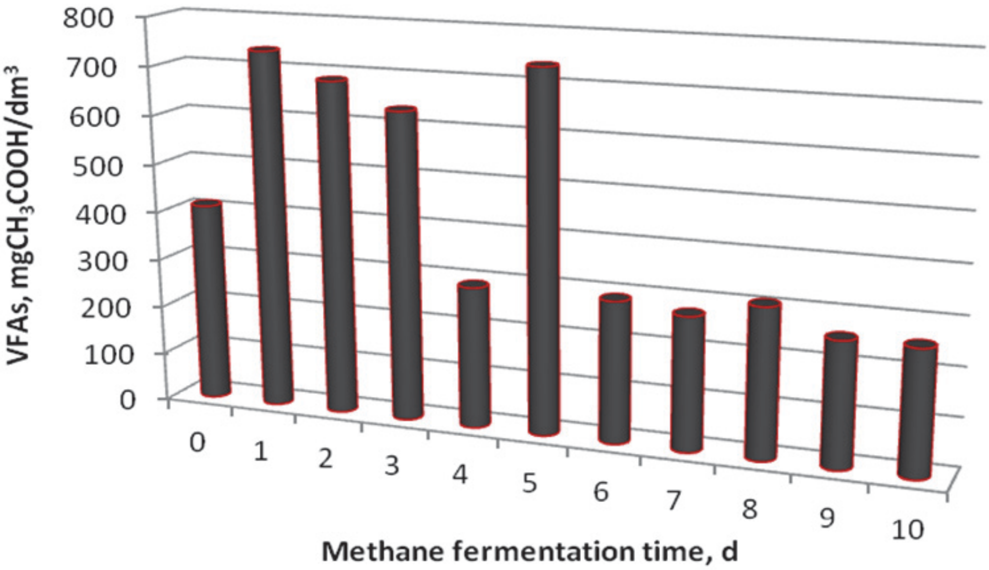

Fig. 7. Changes in VFAs observed during methane fermentation for excess sludge conditioned with ultrasonic field (Mixture 2)
Rys. 7. Zmiany wartości lotnych kwasów tłuszczowych zaobserwowane podczas procesu fermentacji metanowej osadów nadmiernych kondycjonowanych polem ultradźwiękowym (Mieszanina 2)

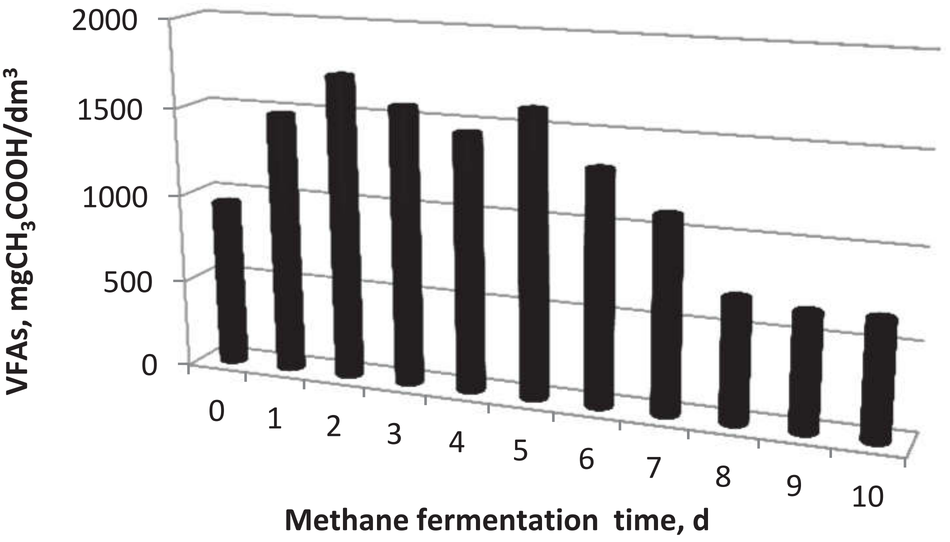

Fig. 8. Changes in VFAs observed during methane fermentation of the excess sludge conditioned with ultrasonic field (Mixture 3)
Rys. 8. Zmiany wartości lotnych kwasów tłuszczowych zaobserwowane podczas procesu fermentacji metanowej osadów nadmiernych kondycjonowanych polem ultradźwiękowym (Mieszanina 3)

It was found based on the present study that disintegration of excess sludge with ultrasonic field before anaerobic stabilization improves the degree of sludge particles disintegration, thus causing an increase in VFAs content recorded on the following days of fermentation. Maximum generation of VFAs during anaerobic stabilization of unconditioned sludge (Mixture 1) was obtained on the 6th day of the process. The use of ultrasonic field conditioning of sludge caused that the highest intensity of VFAs generation in Mixtures 2 and 3 was found on the second day of methane fermentation.

Evaluation of the effect of excess sludge disintegration with ultrasound on anaerobic stabilization included analysis of changes in the content of dry organic matter that occurred during the process. In Mixture 1, the degree of sludge fermentation after 10 days was ca. 17%. Furthermore, initial modification of sludge with ultrasonic field caused an increase in the degree of sludge fermentation during acid fermentation. In Mixture 2, the degree of fermentation was ca. 23% whereas this value for the Mixture 3 was 29%.

Fig. 9 presents changes in the content of dry organic matter of non-disintegrated sludge and the sludge disintegrated with ultrasound.

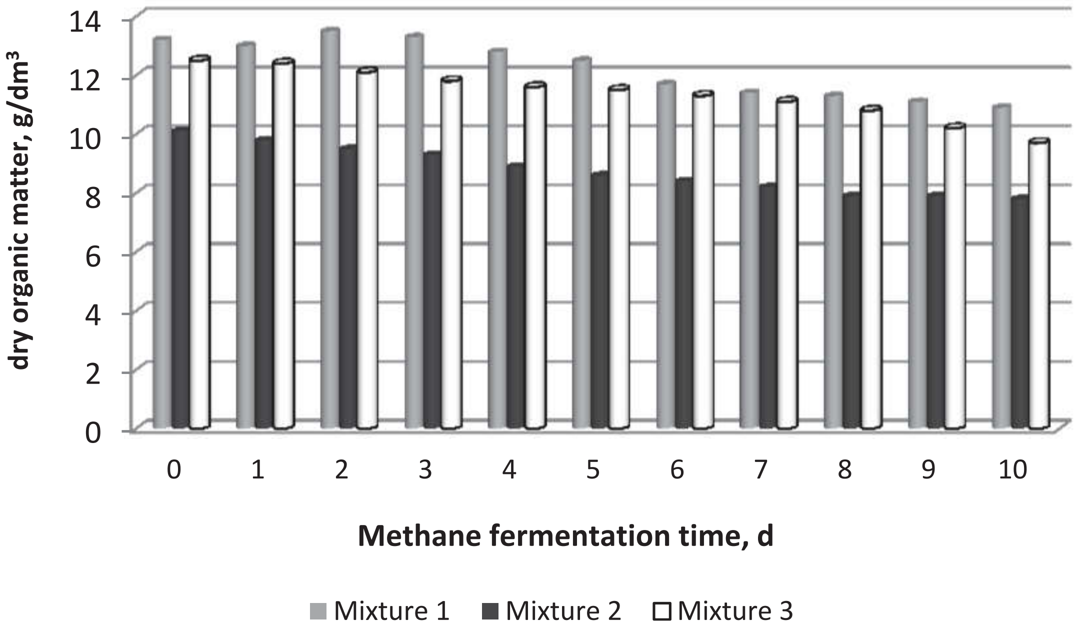

Fig. 9. Changes in the content of dry organic matter recorded during 10-day anaerobic stabilization of non-disintegrated excess sludge (Mixture 1) and the sludge disintegrated with ultrasonic field (Mixtures 2 and 3)
Rys. 9. Zmiany zawartości suchej masy organicznej odnotowane w czasie 10-dobowej stabilizacji beztlenowej osadów nadmiernych niedezintegrowanych (Mieszanina 1) oraz dezintegrowanych polem ultradźwiękowym (Mieszanina 2, 3)

4. Summary and conclusions

Excess sludge treatment using popular methods based on selected processes supported with additional disintegrating effect represents promising (in terms of the obtained degree of mineralization and economics of the process) practical solution. However, it should be stressed that the use of a disintegration method and the choice of the most favourable parameters depends on the character of the sludge that reaches treatment plant, sludge load and technical and economic aspects that condition modernization of the technological line. Obtaining the most effective solution possible in terms of optimum anaerobic stabilization necessitates compilation of current disintegration methods in consideration of the sludge modification using physical, chemical and biological processes. The analysis of the results of the present study leads to the following conclusions:

1. Sonication improved fragmentation of organic substances solved in the sludge liquor, which translated into an increase in COD and VFAs values. The greatest effectiveness of sludge disintegration with ultrasonic field was found for exposure time of 360 s and field vibration amplitude of 46 μm (acoustic wave intensity 2.09 W/cm^2). 5-time and 3-time increases in COD and VFAs with respect to initial value of the indices were observed for the above conditions of disintegration.
2. Increased susceptibility to biodegradation of the conditioned sewage sludge caused a faster increase in VFAs content recorded on the following days of the process. With regard to anaerobic stabilization of the non-conditioned sludge (Mixture 1), the highest value of VFAs was observed on the sixth day of the process. The highest content in Mixture 2 (ultrasonic field vibration amplitude: 21μm, sonication time: 360 s) and Mixture 3 (ultrasonic field vibration amplitude: 46 μm, sonication time: 360 s) was found on the second day of the process.
3. Submission of sludge ultrasonic disintegration contributed to the intensification of hydrolysis phase and the increase of efficiency of the next steps in the process of anaerobic digestion, especially methanogenic phase. This creates a 12% increase in the degree of fermentation was observed in the Mixture 3 (sludge disintegrated with ultrasonic field) compared to the value obtained for anaerobic stabilization of Mixture 1 (unconditioned sludge) after exposure of the sludge to ultrasonic field.

Acknowledgements

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References

1. **Bień J., Stępniak L., Wolny.:** *Ultradźwięki w dezynfekcji i preparowaniu osadów ściekowych przed ich odwadnianiem.* Seria Monografie, 37, Wydawnictwo Politechniki Częstochowskiej, Częstochowa 1995.
2. **Bień J.:** *Osady ściekowe – problem aktualny.* XII Konferencja Naukowo-Techniczna, Wydawnictwo Politechniki Częstochowskiej, 149–154, Częstochowa 2001.

3. **Bień J.B., Zawieja I.:** *Wpływ alkalicznego kondycjonowania osadów nadmiernych na intensyfikację produkcji biogazu w procesie stabilizacji beztlenowej*. Inżynieria i ochrona środowiska. 8(2), 201–209 (2005).
4. **Bień J.B.:** *Ultradźwięki w gospodarce osadowej.* Konferencja Naukowo-Techniczna nt. Nowe spojrzenie na osady ściekowe – odnawialne źródła energii część 1, Wydawnictwo Politechniki Częstochowskiej, Częstochowa. 19–32 (2003).
5. **Bień J., Kamizela T., Kowalczyk M., Mrowiec M.:** *Possibilities of gravitational and mechanical separation of sonicated activated sludge suspensions.* Environment Protection Engineering. 35, 67–72 (2009).
6. **Bourgrier C.H., Carrére H., Delgenés J.P.:** *Solubilisation of waste-activated sludge by ultrasonic treatment*. Chem. Eng. J. 106, 163–169 (2005).
7. **Christi Y.:** *Sonobioreactors: using ultrasound for enhanced microbial productivity.* Trends in Biotechnology. 21(2), 89–93 (2003).
8. **Chu C.P., Bea-Ven C., Liao G.S., Jean D.S., Lee D.J.:** *Observations on changes in ultrasonically treated waste activated sludge*. Water Res. 35, 1038–1046 (2001).
9. **Kamizela T.:** *Wykorzystanie sonifikacji do rozdziału faz w zagęszczaniu zawiesin osadu czynnego.* seria Monografie, nr 243, Wydawnictwo Politechniki Częstochowskiej, Częstochowa 2012.
10. **Kowalska E., Bień J., Zielewicz-Madej E.:** *Ultrasound in the suspension separation methods*. Drying Technology. 6(3), 447–471 (1988).
11. **Magrel L.:** *Metodyka oceny efektywności procesu fermentacji metanowej wybranych osadów ściekowych*. Wydawnictwo Politechniki Białostockiej, Białystok 2002.
12. **Piecuch T., Piekarski J., Malatyńska G.:** *The equation describing the filtration process with compressible sediment accumulation on a filter mesh*. Archives of Environmental Protection. 39(1), 93–104 (2013).
13. **Piecuch T.:** *Równanie Darcy jako podstawa analizy teoretycznej szczególnych przypadków procesu filtracji*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 11, 299–319 (2009).
14. Norma PN-75/C-04616/04 Woda i ścieki. Badania specjalne osadów. Oznaczanie kwasów tłuszczowych lotnych w osadach ściekowych i wodach nadosadowych metodą destylacji z parą wodną.
15. Norma PN-EN 12879 Woda i ścieki. Badania specjalne osadów Oznaczanie zawartości wody, suchej masy, substancji organicznych i substancji mineralnych w osadach ściekowych.
16. International Measurements Standards ISO 7027.
17. **Sliwiński A.:** *Ultradźwięki i ich zastosowania.* WNT, Warszawa 1993.

18. **Stańczyk-Mazanek E., Stępniak L., Kępa U.:** *Degradation of polycyclic aromatic hydrocarbons in soil with sewage sludge*. Desalination and Water Treatment. 10, 158–164 (2009).
19. **Stańczyk-Mazanek E., Piątek M., Kępa U.:** *Wpływ następczy osadów ściekowych stosowanych na glebach piaszczystych na właściwości kompleksu sorpcyjnego.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2437–2451 (2013).
20. **Wolny L., Kamizela T.:** *Technika dezintegracji ultradźwiękowej w technologii ścieków i osadów ściekowych*. Ekologia i Technika. XI(1), 3–7 (2003).
21. **Wolny L.:** *Ultradźwiękowe wspomaganie procesu przygotowania osadów ściekowych do odwadniania.* seria Monografia nr 104, Wydawnictwo Politechniki Częstochowskiej, Częstochowa 2002.
22. **Wolski P., Wolny L.:** *Wpływ dezintegracji i fermentacji na podatność osadów ściekowych do odwadniania*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 1697–1706 (2011).
23. **Wolski P., Zawieja I.:** *Effect of Ultrasound Field on Dewatering of Sewage Sludge*. Archives of Environmental Protection. 38(2), 25–31 (2012).
24. **Zhang G., Zhang P., Yang J., Liu H.:** *Energy-efficient sludge sonification: Power and sludge characteristics*. Bioresource Technol. 99, 9029–9031 (2008).

Wpływ dezintegracji ultradźwiękowej na proces stabilizacji beztlenowej osadów nadmiernych pochodzących z przemysłu spożywczego

Abstract

Przeróbka i unieszkodliwianie osadów ściekowych stanowi niezwykle aktualny problem technologiczny, co wiąże się z powstawaniem w ostatnich latach nowych obiektów oczyszczalni, modernizacją już istniejących, jak również z rozwojem wysokoefektywnych metod oczyszczania ścieków. Przez lata wiodącym trendem w zagospodarowaniu osadów ściekowych w Polsce było ich składowanie, jednak obowiązujące w Unii Europejskiej uwarunkowania prawne uniemożliwiają zastosowanie takiego rozwiązania w przyszłości. Modernizacja ciągu technologicznego oczyszczalni ścieków poprzez poprzedzenie wybranych procesów oczyszczania ścieków oraz utylizacji osadów procesem dezintegracji o odpowiednio dobranych parametrach wiąże się ze wzrostem efektywności działania obiektu, nie tylko pod względem technologicznym ale również ekonomicznym.

Dezintegracja osadów nadmiernych przed procesem stabilizacji beztlenowej wpływa na zwiększenie podatności osadów na biochemiczny rozkład w warunkach beztlenowych, czego efektem jest przyspieszenie fazy hydrolitycznej procesu, warunkującej powstawanie w kolejnych etapach procesu lotnych kwasów tłuszczowych. Wartość oraz tempo generowania LKT znajduje bezpośrednie odbicie w efektywności produkcji biogazu oraz uzyskanym stopniu mineralizacji osadów. Celem prowadzonych badań była ocena wpływu dezintegracji ultradźwiękowej osadów nadmiernych pochodzących z przemysłu spożywczego na proces hydrolizy będący pierwszym etapem fermentacji metanowej. W badaniach użyto dezintegrator ultradźwiękowy typu VC-750. Osady poddano modyfikacji polem ultradźwiękowym (UD) o amplitudzie drgań pola UD 15, 21, 31, 37, 46μm i czasie sonifikacji t_s = 60–360 s. Następnie przeprowadzono procesy 10-dobowej fermentacji metanowej osadów, poprzedzone modyfikacją osadów nadmiernych polem UD o wybranych, najkorzystniejszych parametrach dezintegracji. Największą skuteczność nadźwiękawiania osadów odnotowano dla czasu ekspozycji równego 360 s oraz amplitudy drgań pola UD 46μm, uzyskując ok. 5-kotny wzrost wartości ChZT oraz ok. 3-krotny LKT w odniesieniu do wartości początkowych wskaźników.

Słowa kluczowe:
dezintegracja, pole ultradźwiękowe (UD), lotne kwasy tłuszczowe (LKT), chemiczne zapotrzebowanie na tlen (ChZT), fermentacja metanowa, stopień przefermentowania osadów

Keywords:
disintegration, ultrasonic field, volatile fatty acids (VFAs), chemical oxygen demand (COD), methane fermentation, degree of sludge fermentation

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Research Into the Metal/Metalloid Movements in Soil and Groundwater in the Areas Surrounding the Coal Waste Dump Hałda Ruda (Upper Silesia, Poland)

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1. Introduction

Upper Silesia is highly degraded due to the anthropogenic activity. On the one hand, the industrialization facilitated the economic development of the Upper Silesian cities. On the other hand, it caused serious environmental pollution [3, 21]. Many highly urbanized and industrialized cities in Upper Silesia do not possess data on the degradation level of the surface ground or dynamics of negative phenomena. Moreover, there is no assessment of the ground transformation under severe anthropopressure conditions. Determining the influence of changes in the environment resulting from its exploitation is still an important matter [6, 7, 10, 16], particularly in degraded areas, such as those in Upper Silesia.

Heavy metals are the main soil pollutants. They pass into groundwater and pollute the surrounding areas. Increased contents of heavy metals can adversely affect biological properties of soils. They may also contaminate ground and underground water and toxically influence the plants. Natural contents of heavy metals in soils do not usually pose a threat for plants, animals or humans. Unfortunately, the area of soils with the natural heavy metal contents gradually decreases due to the impact of human civilization and industrialization, which is confirmed by many studies [36]. What is more, gaps in the knowledge of the natural heavy metal contents in soils usually result in oversimplifications in the assessments and interpretations of heavy metal pollution causes. Rock waste from hard coal mines is the main type of waste generated in Poland and stored in the dumps every year. Coal mine dumps ought to be perceived as serious and long-term sources of groundwater pollutants. The pollution potential of low-buffered capacity and acidification of waste increases with time because of FeS_2 decomposition [32].

Modern analytical methods, such as the EDXRF spectrometry and ICP-MS, enable simultaneous determinations of numerous analytes. They offer low limits of detection and high selectivity, which extends the research area. On the other hand, the amount of the obtained multidimensional data is massive. The information requires long-term analysis. Consequently, a number of problems related to the visualization and correct interpretation of the results arise. Chemometrics concerns the extraction of relevant information from measurements and chemical experiments through the effective organization of the analytical processes [5, 31]. Its tasks include experiment optimization, correct calibration, quality control and final data analysis. Chemometrics requires a proper definition of the problem, a detailed experiment plan and its realization carried out in accordance with the principles of the chemical metrology. Under such circumstances, chemometric analysis of the obtained results offer correct assessments and valid conclusions. The X-ray fluorescence (XRF) is one of the most popular methods used to examine elemental compositions of soils. The XRF meets the requirements for modern laboratory techniques [23]. It enables quick determinations of qualitative compositions. On the other hand, establishing precise quantitative compositions involves procedures of matrix effect correction, which entails a large number of standards [39]. At present, the Energy Dispersive X-Ray Fluorescence (EDXRF) is one of the best techniques for qualitative and quantitative analysis of heavy metals. It enables reasearchers to investigate concentrations of main and trace elements present in soils [4, 12, 20, 38], bottom sediments [2, 8, 18], ashes [9] or minerals [11, 22]. The EDXRF is a relatively simple and inexpensive method in comparison with other techniques for quantitative and qualitative analysis of metals.

At present, the inductively coupled plasma – mass spectrometry (ICP-MS) is the best method supporting researchers in quantitative analysis of metals and metalloids at the ppt/ppb concentration levels. It is an appropriate tool for analyzing elements in a broad range of concentrations. Importantly, it is commonly used for the environmental analysis [14, 30].

The researched site lies in the north of the Silesian Upland, namely in the north-west part of the Bytom-Katowice Plateau. The morphological diversification of the area around the coal waste Hałda Ruda is not high. Its ordinates range between +251 m and +280 m AMSL. The coal waste dump is the local uplift dominating the surroundings (+270 m – 275 m AMSL). It lies in the catchment area of the Bytomka River, which is a tributary of the Kłodnica River, placed in the basin of the Oder. The Hałda Ruda is placed on the south bank of the Bytomka River, west of Ruda Śląska. The coal waste dump covers approx. 396,137 m^2. Its cubic capacity is 5,100,000 m^3. It was opened in 1957 as a dump site of the *Zabrze-Bielszowice* coal mine, which is closed at present. The Hałda Ruda was planted with trees on its eastern side in the years 1963–1975. The northern slope was planted with trees from the Bytomka River side in the 1990s. The western part was partially reclaimed. Grass and bushes were planted with fly ashes and humus. Unfortunately, the unfinished reclamation resulted in the formation of extremely steep slopes. They are exposed to severe water and wind erosion which is increased due to the lack of the plant cover. The discussed part of the coal waste dump has been active thermally, which poses a threat to plants, animals, local inhabitants and people located at the dump. The rails from Katowice to Gliwice run south of the Hałda Ruda. Low residential buildings and allotments are situated along the neighboring Szczęść Boże Street. The area in which the coal waste dump is located is occupied by fields, fallow lands, meadows, parks and gardens. The southern and eastern parts are partially covered with trees. The climatic conditions of Zabrze are influenced by the local climate of the western part of the Upper Silesian Industrial Region. They are also modified by the city impact itself. The thickest cloud cover is observed in January. The annual cloudiness percentage varies between 0.6% and 2.9%. The average annual air temperature is +6.9°C. The average temperature values for January and July are -3.9°C and +17.5°C, respectively. The maximum precipitation is observed in July (87 mm), while the minimum is found for February (40 mm). The vegetation season lasts approx. 205 days. Zabrze is under the dominant influence of the southwest winds.

The aim of the following study was optimization and validation quantitative analysis metal(loid)s using EDXRF and ICP-MS technique to identify the pollutants occurring around the coal waste dump Hałda Ruda, which served as a storage site for waste from hard coal exploitation and processing. Its other purpose was to determine the way in which metals and metalloids moved in the surroundings of the dump site. The research was conducted to understand how the waste, stored over the years, influenced the changes in salinity and metal/metalloid concentrations in the soil and groundwater depending on the distance from the coal waste dump. It was also performed to recognize the impact of the waste on the characteristics of the soil and water environment. In the research process, total contents of metals and metalloids were determined in the soil samples with an EDXRF spectrometer. Groundwater samples were analyzed with an ICP-MS spectrometer. Additionally, the obtained results were analyzed chemometrically. The aim was to determine the correlations between the contents of particular elements, physicochemical conditions and the sampling site and genetic soil horizon of a given sample.

2. Materials and methods

2.1. Sampling

2.1.1. Soil samples

The soil was sampled at transects located at the sites shown in Figure 1. The groundwater runoff direction was taken into account during the sampling. The sampling points were situated at different distances from the coal waste dump to determine the range of the waste impact on the variations in metal concentrations in the soil samples. Specific transects were given the Roman numerals, whereas the sampling points were marked with the Arabic ones. The boreholes with the mounted piezometers were marked with the P8–P12 symbols. The soil pits were prepared at each sampling site. One was located on the groundwater runoff. The other one was placed on the groundwater inflow.

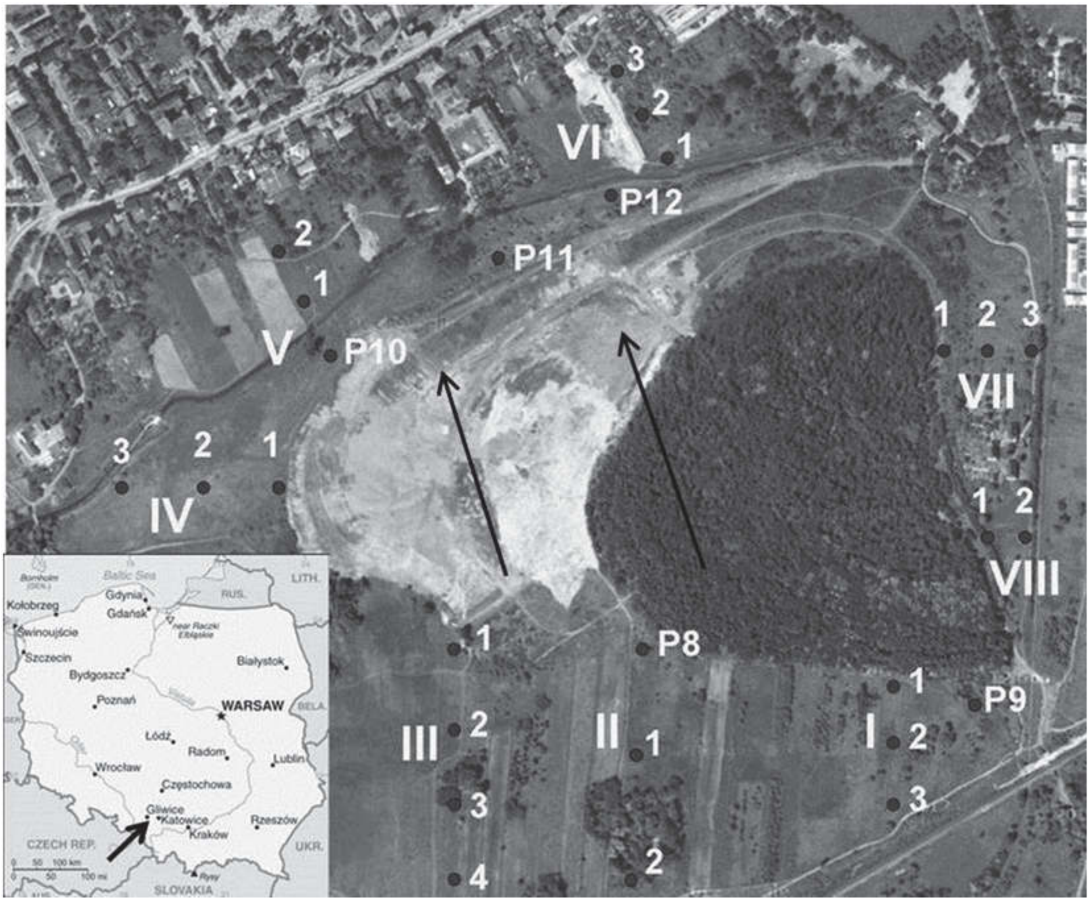

Fig. 1. Sampling sites at the Hałda Ruda: transects (I–VIII); sampling points (1–4); piezometers (P8–P12); arrows (groundwater runoff direction)
Rys. 1. Rozmieszczenie punktów poboru Hałda Ruda, I–VII transekty, 1–4 punkty poboru, P8–P12 piezometry, strzałki – kierunek spływu wód gruntowych

The soil sampling was performed with the borehole technique. The boreholes were made with manual tools equipped with Edelman drills (Eijkelkamp). They were drilled until the bedrock or aquifers were reached. The drilling was also stopped at the depth of 4 m (depth possible to reach with the drill set). Agricultural maps and several soil pits were used to determine the soil type and structural group. The soil was sampled at the sites where the owners had consented. The terrain could not be changed by agriculture and its morphology had to allow the drilling. Table 1 presents the distances of the sampling points from the coal waste dump and the borehole depth. The collected soil samples were averaged within the frame of a given genetic horizon in the field. The sample of a few kilograms was transported into the laboratory.

Table 1. Hałda Ruda sampling point locations and borehole depth
Tabela 1. Hałda Ruda odległości punktów poboru i głębokość odwiertu

Transect number	Sampling point number	Distance from the coal waste dump [m]	Borehole depth [cm]
I	1	10	80
	2	91	110
	3	180	235
II	P8	3	720
	1	89	250
	2	255	300
III	1	9	300
	2	114	190
	3	207	105
	4	310	300
IV	1	4	315
	2	117	300
	3	260	210
V	P10	18	1050
	1	71	300
	2	105	210
VI	1	27	100
	2	63	290
	3	97	200
VII	1	6	200
	2	53	160
	3	112	200
VIII	1	11	210
	2	59	245

2.1.2. Groundwater samples

Groundwater was sampled between 2010 and 2012. To do that, the piezometer network, created specifically for the project, was used. The piezometers were installed on the groundwater inflow and runoff in the examined area (Figure 1). The groundwater was sampled from the piezometers every month with the whistle, used to determine the water table level, and the Gigant water pump (max head: 20 m). The groundwater samples were always collected after the piezometers were emptied. After the piezometer was filled again, the water was collected into a 1-liter plastic container without the air access (the container was completely filled).

2.2. Sample preparation

The samples were dried in an electric dryer at 105°C for 90 minutes. Afterwards, they were sieved through a 2 mm sieve to remove any big objects (leaves, sticks, stones, etc.) from the samples. The obtained material was highly homogenous. It was dried again in the electric drier to obtain constant mass. The samples were ground in a vibratory grinder with the grinding vessel made of tungsten carbide (Testchem, Poland) for 2 minutes. For the analyses, carefully weighed amounts of standards or real samples (7.2 g) were mixed with the binder (0.8 g), i.e. synthetic wax (STW wax batch 64, PANalytical). Finally, the mixture was pressed with a manual hydraulic press (under the approx. 20 Mg pressure) for 2 minutes.

The groundwater samples were acidified with the ultrapure concentrated HNO_3 (Merck, Germany) and filtered through a 0.2 µm PES syringe filter immediately after they were transported into the laboratory. Afterwards, they were stored in a fridge at 2°C–5°C. Each sample was measured three times with the ICP-MS spectrometer.

2.3. Apparatus

Contents of the elements (Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Zr, Mo, Cd, Sb, Cs, Ba, Pb, Y, Nb, Sn, I, Bi) were determined in the soil using EDXRF spectrometer. A PANalytical Epsilon 5 was used for the measurement. The Epsilon 5 was equipped with a water-cooled X-ray tube with a side window (gadolinium anode; working range: 25 kV–100 kV; 150 µm beryllium window), a system of 9 secondary targets (Al, Ti, Fe, Ge, Zr, Mo, Ag, Ce_2O_3, Al_2O_3) and a Ge(Li) detector (resolution: 140 eV; energy range: 0.7 keV–100 keV; working surface: 30 mm^2; 8 µm beryllium window). Due to the application of the 3-D optical path in the Epsilon 5, the dispersed radiation from the X-ray tube did not reach the detector and did not disturb and/or falsify the results. Instead, it disappeared because of the polarization. It demonstrated itself through the very low background in the spectrum. Coupling the apparatus with advanced software helped to determine the intensity of peaks, even very low ones. Consequently, it was possible to determine element concentrations in the investigated sample at extremely low levels.Certified reference materials for soils were used to calibrate the spectrometer. 40 certified reference materials were used to create the calibration lines and two others were later used to verify the calibration and to establish factors such as repeatability, intermediate precision or recovery. The groundwater analyses were performed with an ICP-MS Elan DRC-e 6100 spectrometer (Perkin-Elmer). It was equipped with a standard ICP quartz torch, cross nebulizer and nickel cones. Samples and standards were fed with a peristaltic pump. The spectrometer was optimized to provide maximal intensity for ^{24}Mg, ^{115}In, ^{238}U, and minimal values for CeO/Ce (below 3%) and Ba$^{2+/}$Ba (below 3%).A special application was prepared. It helped to measure the following isotopes: ^{51}V, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{107}Ag, ^{114}Cd, ^{138}Ba, ^{205}Tl, ^{208}Pb, ^{238}U. A correction equation (Pb208=Pb208+Pb206+Pb207) was used to determine Pb quantitatively. The analyses were carried out with the method of the internal standard (10 µg/L solution of ^{103}Rh) introduced on-line with the peristaltic pump. All standards and solutions were prepared with the ultrapure deionized Milli-Q-Gradient water (Merck Millipore, Germany). A certified multi-element solution was used for calibration. It was prepared through diluting 10 mg/L of the calibration solution no. VI (Merck, Germany) and 1 g/L single element standards of Cd, Pb and Zn (Merck, Germany). A certified multi-element solution no. XXI (Merck, Germany) was applied to verify the calibration. All standards were prepared daily with the weight-to-weight dilution.

pH and electric conductivity were measured immediately after the samples were transported into the laboratory. The measurements were made with the multifunction meter CX-401 (Elmetron, Poland) in accordance with the standard [24, 25]. A soil suspension was prepared according to the Standard [26, 27] to determine soil pH and electric conductivity.

3. Results and discussion

3.1. Quality control

The aim of the analytical method validation was to decide whether the analysis process was conducted in a reliable way and the obtained results were trustworthy. The following analysis stages were validated: examination of the method accuracy and precision, determination of the detection and quantification limits, determination of the analyte recovery.

The standard definition for the detection limit in the XRF technique is that the net peak intensity should be three times higher than the standard deviation of the noise. In the research procedure, the number of background counts was obtained through averaging background counts of 31 measurements of the control real sample. The quantification limits were determined as the product of a triple detection limit value (Table 2). The results from the background measurements obtained during the determination of the detection limits were used to establish the EDXRF method repeatability. Long-term measurements of the real material sample were performed to determine the intermediate precision (reproducibility) of the method. The measurements were made between December 2011 and January 2013.

Table 2. Validation parameters for the EDXRF methodology
Tabela 2. Parametry walidacyjne dla metody EDXRF

Analyte	Limit of detection [mg/kg]	Limit of quantification [mg/kg]	NIST 2709	Obtained average results [n=31]	Recovery [%]	Relative standard deviation of repeatability [%]	Relative standard deviation of reproducibility [%]
Al_2O_3	94.78	284.34	14.17%	14.01%	98.86	37.4	12.8
SiO_2	214.48	643.45	63.4%	56.1%	88.51	2.1	4.1
K_2O	8.63	25.89	2.45%	2.13%	87.15	2.4	12.4
CaO	13.19	39.56	2.64%	2.11%	79.97	3.5	5
TiO_2	10.25	30.75	0.57%	0.52%	92.09	1.1	4.5
V	6.01	18.02	112 mg/kg	99.4 mg/kg	88.74	3.4	15.6
Cr	0.41	1.22	130 mg/kg	114 mg/kg	87.69	2.7	27.2
Mn	5.31	15.94	538 mg/kg	534 mg/kg	99.26	2	4.6
Fe_2O_3	4.63	13.9	5.00%	4.65%	93.01	0.5	8.6
Ni	2.53	7.58	88 mg/kg	86 mg/kg	98.48	3.5	12.9
Cu	0.71	2.14	34.6 mg/kg	32.5 mg/kg	93.88	7.6	10.6
Zn	0.97	2.92	106 mg/kg	109 mg/kg	103.53	0.5	6.1
As	1.02	3.06	17.7 mg/kg	18.5 mg/kg	104.29	5.8	33.5
Rb	0.34	1.01		89.8 mg/kg		0.7	4.5
Sr	0.73	2.18	231 mg/kg	214 mg/kg	92.65	1	4.6
Zr	0.67	2		141 mg/kg		0.4	6.1
Mo	0.55	1.64		1.92 mg/kg		13.8	20.2
Cd	0.8	2.4		0.66 mg/kg		17.5	25.1
Sb	0.76	2.29		7.03 mg/kg		17.5	29
Cs	0.79	2.36		4.87 mg/kg		8	12.4
Ba	0.96	2.87		916 mg/kg		0.3	3.5
Pb	0.6	1.8	18.9 mg/kg	13.6 mg/kg	71.77	1.9	6.4
Y	1.05	3.14		16.9 mg/kg		1.5	4.7
Nb	0.89	2.68		10.3 mg/kg		2.5	4
Sn	1.02	3.07		1.48 mg/kg		4.3	9.9

For the ICP-MS, the detection limit was the product of a triple standard deviation for the blank sample (n=31). The blank was an acidified water sample used afterwards to prepare calibration and dilutions of all solutions and real samples (Table 3). The quantification limits were also determined as the product of a triple detection limit value. Multiple measurements (n=31) of the standard solution no. XXI (Merck, Germany) were performed to determine the repeatability of the ICP-MS method. Long-term measurements of this solution were made to determine the intermediate precision (reproducibility) of the method. The measurements were made between March 2011 and December 2012.

Table 3. Validation parameters for the ICP-MS methodology
Tabela 3. Parametry walidacyjne dla metody ICP-MS

Analyte	Limit of detection [μg/L]	Limit of quantification [μg/L]	NIST 1643-e [μg/L]	Obtained average results [μg/L] n=31	Recovery [%]	Relative standard deviation of repeatability [%]	Relative standard deviation of reproducibility [%]
Co	0.002	0.006	27	30	110	2.6	4.6
Ni	0.024	0.072	62	67	107	3.9	4.6
Cu	0.064	0.192	23	22	96	3.5	5.8
Zn	0.181	0.543	79	63	80	7.6	11.4
Cd	0.04	0.12	6.6	6.4	97	5.3	11.8
Pb	0.036	0.108	20	21	106	7.3	13.9
As	0.096	0.288	60	53	88	3.8	5
Cr	0.013	0.039	20	24	116	3.9	5.5
Mn	0.033	0.099	39	42	108	6.3	10.4
Ba	0.01	0.03	544	562	103	6.5	8.2
Rb	0.003	0.009	14	15	105	1.9	3.1
Sr	0.008	0.024	323	347	107	3.9	5.1
Ag	0.002	0.006	1.1	1.0	95	3.2	6.9
Tl	0.002	0.006	7.4	8.0	107	3.9	7.1
V	0.09	0.27	38	42	111	3.2	3.8

3.2. Metals and metalloids movements in groundwater

Metal pollution is a problem present in many contaminated areas. Pb, Cr, As, Zn, Cd, Cu and Hg are the most popular metals in the postindustrial areas. The presence of metals in soils and groundwater can pose a considerable threat for human health and ecological systems. Surface and underground water can be polluted with metals coming from wastewater or discharges or through the direct contact with the polluted soil, slime, mine waste or debris [14]. The environmental impact of coal-mining wastes is determined by the characteristics of the extracted rock material, which can vary significantly, both horizontally and vertically through the coal-bearing Carboniferous strata. Table 4 presents results of quantitative analysis of the rock material of Hałda Ruda dump using EDXRF techniques. Table 5 presents standard deviations as well as minimum, maximum and mean values of the analyte concentrations in groundwater sampled from the piezometer network built up around the Hałda Ruda. Table 5 shows also some of the guidelines concerning the content of metals and metalloids in the waters [28, 34, 35].

Table 4. Results of quantitative analysis of the rock material of Hałda Ruda dump using EDXRF techniques
Tabela 4. Wyniki ilościowej analizy materiału skalnego zwału Hałda Ruda z wykorzystaniem techniki EDXRF

Analyte	Value	Unit
V	136	mg/kg
Cr	311	mg/kg
Mn	720	mg/kg
Fe_2O_3	4.6	%
Co	25	mg/kg
Ni	85	mg/kg
Cu	86	mg/kg
Zn	750	mg/kg
As	8.1	mg/kg
Mo	3.2	mg/kg
Cd	14	mg/kg
Sb	7.3	mg/kg
Ba	647	mg/kg
Pb	172	mg/kg

Compared with the metals and metalloid guidelines in waters exceeding the highest content of toxic elements were found in water samples taken at runoff of the groundwater. Particularly elevated concentrations were observed in the case of lead, arsenic, chromium and zinc.

Table 5. International guidelines, standard deviations, minimum, maximum and mean contents of pH, conductivity the analyzed metals in water samples collected from piezometers no. P8–P9 (groundwater inflow) and P12 (groundwater runoff) between 2010 and 2012. Water samples measured using ICP-MS technique.
LOD – Limit of Detection

Tabela 5. Międzynarodowe wytyczne, minimalne, maksymalne, średnie i odchylenie standardowe zawartości badanych metali/metaloidów w próbkach wód pobranych z piezometrów P8 i P9 (kierunek napływu wód gruntowych) oraz P12 (kierunek spływu wód gruntowych); próbki wód mierzono wykorzystując technikę ICP-MS.
LOD – granica wykrywalności

Analyte	Piezometer P8 – Inflow				Piezometer P9 – Inflow				Piezometer P12 – Runoff				International guidelines		
	min.	*max.*	*mean*	*SD*	*min.*	*max.*	*mean*	*SD*	*min.*	*max.*	*mean*	*SD*	*US EPA Drinking water*	*EU Drinking water*	*PL Ground water I class*
V [µg/L]	0.25	5.0	1.1	1.5	0.01	0.9	0.37	0.31	4.1	13	8.1	3.5			4
Mn [µg/L]	7.2	479	221	182	198	662	363	152	1094	2337	1407	404	50	40	50
Co [µg/L]	0.30	6.3	3.4	2.1	0.5	7.6	2.7	2.1	4.6	9.2	6.2	1.4		20	20
Ni [µg/L]	3.9	10	5.5	2.0	4.3	13	10	2.5	14	22	17	2		20	5
Cu [µg/L]	0.8	17	4.3	5.4	0.44	5.4	1.2	1.5	2.4	36	7.1	12	1300	2000	10
Zn [µg/L]	6.9	30	18	7.8	3.7	46	15	12	14	236	50	76	5000		50
As [µg/L]	0.39	3.5	1.6	1.0	0.6	3.0	1.6	1.0	7	15	10	2.6	6	5	10
Rb [µg/L]	0.9	8.0	4.2	2.3	0.7	2.1	1.3	0.5	1.6	7.5	2.9	2.1			
Sr [µg/L]	116	573	182	147	148	221	188	26	1245	2144	1684	313			
Ag [µg/L]	0.02	0.8	0.25	0.26	0.01	0.09	0.05	0.03	0.01	1.5	0.42	0.5	100	50	1
Cd [µg/L]	0.01	0.41	0.15	0.15	0.02	0.09	0.05	0.03	0.06	3.0	0.5	1.0	5	5	1

Table 5. cont.

Tabela 5. cd.

Analyte	Piezometer P8 – Inflow				Piezometer P9 – Inflow				Piezometer P12 – Runoff				International guidelines		
	min.	*max.*	*mean*	*SD*	*min.*	*max.*	*mean*	*SD*	*min.*	*max.*	*mean*	*SD*	*US EPA Drinking water*	*EU Drinking water*	*PL Ground water I class*
Te [µg/L]	0.32	1.1	0.6	0.26	0.46	0.8	0.6	0.12	0.36	1.1	0.7	0.26			
Ba [µg/L]	26	84	47	19	40	73	53	11	35	79	53	15	2000		300
Tl [µg/L]	0.01	0.04	0.02	0.01	0.01	0.03	0.02	0.01	0.03	0.13	0.08	0.05	2		1
Pb [µg/L]	0.01	11	1.7	3.7	0.03	2.3	0.5	0.7	<LOD	132	17	47	15	10	10
Fe [µg/L]	480	4970	2514	167	277	3126	1373	1033	1147	11559	5282	4311	300	200	200
Cr [µg/L]	0.27	3.7	1.8	1.3	0.28	3.5	1.7	1.4	17	45	28	10	100	50	10
Bi [µg/L]	0.01	5.7	1.0	1.9	0.00	0.9	0.25	0.32	0.01	0.7	0.22	0.25			
Ga [µg/L]	1.5	3.2	2.2	0.5	1.2	3	3	0.7	1	3	2	0.7			
Mo[µg/L]	0.04	0.5	0.32	0.14	0.03	0.30	0.18	0.09	0.24	0.7	0.5	0.15			3
U [µg/L]	0.14	3.1	0.9	0.9	0.21	0.9	0.5	0.24	2.6	4.6	3.5	0.6	30		9
pH	6.45	6.99	6.87	0.19	6.45	7.08	6.56	0.22	6.88	7.02	6.92	0.06			
cond. [µs/cm]	325	458	414	56	482	565	519	35	5949	6218	6043	113			

Long-term storage of coal mine waste involves the risk that the pollutants may penetrate groundwater. When taking into consideration the groundwater inflow direction, it is visible that metal/metalloid concentrations were higher in the samples collected from the piezometers located on the groundwater runoff (P10, P11, P12).

Piezometers P10 and P11 during research were often dry. Therefore, in our considerations were taken into account the groundwater results obtained from P12 piezometer.

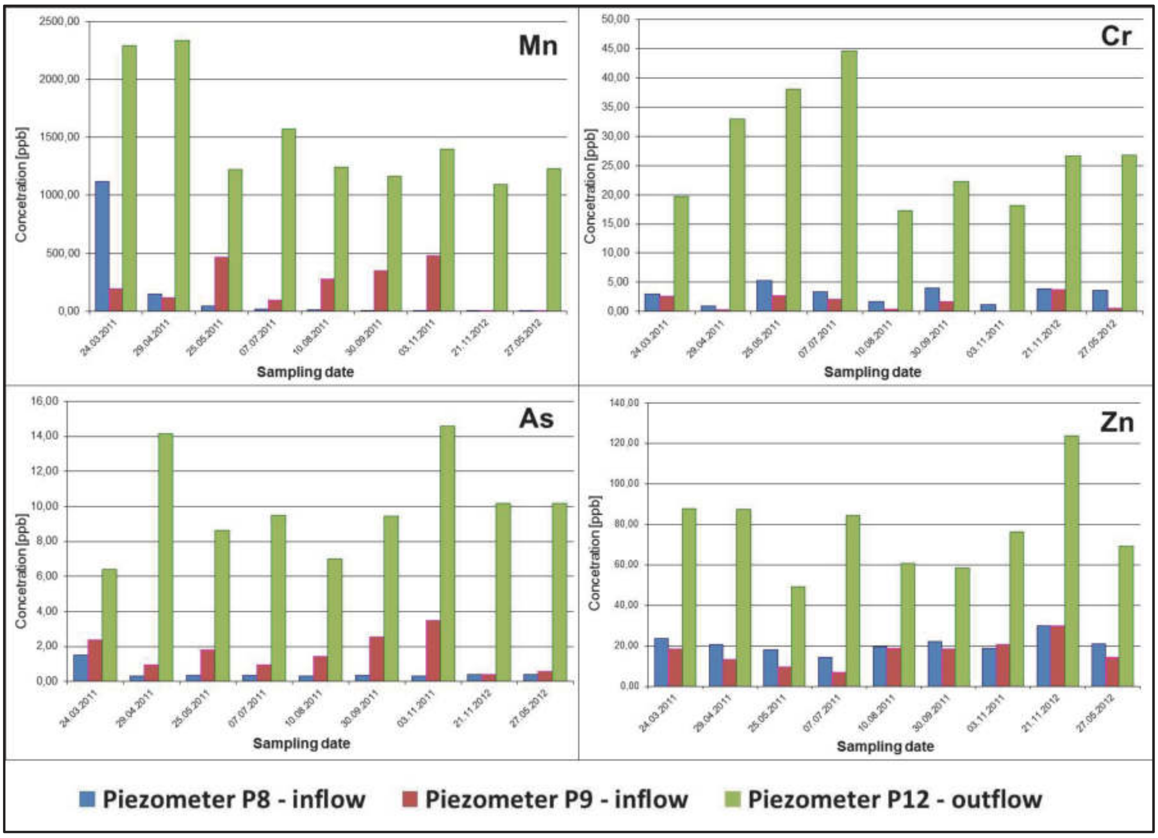

Fig. 2. Changes in concentrations of Mn, Cr, As and Zn in groundwater samples collected from the piezometers on the groundwater inflow (P8, P9) and runoff (P12)
Rys. 2. Zmiany w stężeniu Mn, Cr, As oraz Zn w próbkach wód gruntowych pobranych z piezometrów na napływie (P8 i P9) i spływie (P12)

Figure 2 shows the changes in the concentrations of Mn, Cr, As and Zn in groundwater samples collected from the piezometers on the water inflow and runoff. The parameters, together with the pH and electric conductivity values, show that the coal mine waste was the source of pollutants penetrating the surrounding environment. Moreover, the Bytomka

River flows in the groundwater runoff direction along the Hałda Ruda. The Bytomka River water and bottom sediments were polluted with the groundwater. The pollution was transferred into the Kłodnica River and from there into the Oder [17].

The electric conductivity of the groundwater samples collected on the water runoff (P12) was very high (approx. 6000 µS/cm). The data clearly shows that increased contents of chloride salts and sulfates were responsible for this situation (P8 on the groundwater inflow, $[Cl^-]$ = 20 mg/L and $[SO_4^{2-}]$ = 286 mg/L; P9 on the groundwater inflow, $[Cl^-]$ = 39 mg/L and $[SO_4^{2-}]$ = 72 mg/L; P12 on the groundwater runoff, $[Cl^-]$ = 1,167 mg/L and $[SO_4^{2-}]$ = 703 mg/L). The salts were leached from the coal waste dump.

3.3. Metals and metalloids movements in the ground environment

Chemical and physical properties of a matrix (such as coal mine waste) polluted with metals influence the metal mobility is soils and groundwater. Pollutants in the soil matrix occur in three forms, i.e. pollutants solved in the soil moisture, pollutants adsorbed on the soil surface, and permanent soil pollutants. Chemical and physical soil properties influence the metal pollution form, its mobility and the selection of the area reclamation technology [17]. Table 8 presents international guidelines, maximum, minimum and mean metal/metalloid concentrations in the soil samples collected on the groundwater inflow and runoff. Around the Hałda Ruda, 24 boreholes were prepared in the network of 8 transects (Figure 1). The soil sampling points (boreholes) moved farther and farther away from the coal waste dump at each transect. The results were analyzed in numerous ways. The changes in the concentrations of selected metals and metalloids were investigated within each transect and genetic horizon. Research on metals and metalloids concentration in soils from surrounding the pile area compared with the soil quality guidelines (Table 6) clearly indicate that the areas situated at the confluence of ground water are more polluted with metals and their number many times exceed those limits. Concentration of lead in the soil even exceeded 2000 mg/kg. In the case of copper, manganese, chromium or zinc huge exceeded permissible levels were also observed.

Additionally, chemometric analysis with the concept of dis(similarity) [40] and principal component analysis (PCA) [1, 19, 37, 41] were carried out.

Table 6. International guidelines, maximum, minimum and average contents and standard deviation of the measured elements in the soil samples in transects located on the groundwater inflow and runoff. Soil samples measured using EDXRF technique

Tabela 6. Międzynarodowe wytyczne, maksymalne, minimalne, średnie i odchylenie standardowe mierzonych pierwiastków w próbkach gleb pobranych w transektach rozmieszczonych po stronie napływu i spływu wód gruntowych. Próbki gleb mierzono przy użyciu techniki EDXRF

Analyte	Unit	Inflow – Transects 1. 2. 3. 7. 8 (n=58)				Runoff – Transects 4. 5. 6 (n=58)				International guidelines		
		min.	*max.*	*mean*	*SD*	*min.*	*max.*	*mean*	*SD*	*EPA*	*EU*	*PL A Class*
V	mg/kg	21	115	54	22	20	292	66	51	90	50	
Cr	mg/kg	23	287	102	61	5.1	1.207.60	170	219	70	40	50
Mn	mg/kg	130	671	283	112	1.0	2.675.90	330	447			
Fe_2O_3	%	1.1	4.3	2.5	0.8	0.33	13	3.2	2.3			
Co	mg/kg	<LOD	24	6.3	5.6	<LOD	46	10	9.2	20	20	20
Ni	mg/kg	7.5	79	24	16	0.71	159	29	30	40	40	35
Cu	mg/kg	<LOD	85	19	20	<LOD	2.048.50	177	381	60	40	30
Zn	mg/kg	15	695	159	162	1	9.675.30	788	1.862.20	300	150	100
As	mg/kg	1.0	7.9	4.0	1.5	0.61	42	7.4	10	10	10	20
Mo	mg/kg	0.04	3	1.0	0.6	<LOD	10	1.8	1.9			10
Cd	mg/kg	0.37	13	1.4	2.1	0.24	59	4.9	11	1	1	1
Sb	mg/kg	0.31	6	1.0	0.9	0.31	698	91	174	1	1	
Ba	mg/kg	107	584	295	110	5.8	1.057.40	305	215	200	300	200
Pb	mg/kg	5.6	164	38	43	1.4	2.185.00	161	382	45	40	50
Sn	mg/kg	1.4	6.6	3.0	1.0	1.6	292	34	62	5	1	
pH	-	5.43	8.71	6.75	0.86	6.31	8.94	7.31	1.11			
cond.	[µs/cm]	11	526	96	109	40	526	177	105			

To perform the soil type imagining, agricultural maps were used and several reconnaissance soil pits were prepared. The soils of the corresponding type, structural group and thickness were compared. The obtained data enabled specific comparisons within the entire transect. Table 1 presents the distances of particular sampling points from the coal waste dump. Transects I, II, III were placed on the groundwater inflow whereas transects IV, V, VI were located on the groundwater runoff (Figure 1). Transects VII and VIII were selected due to their close location to the houses in Trębacka Street. Transect I was placed on the groundwater inflow. The metal/metalloid mobility along the transect depended on the metal/metalloid. The Cd concentration, similarly to Pb, was high in the upper soil layers. It could be the result of the winds blowing in this area (S-W). The concentrations of the above-mentioned metals were lower in the deeper genetic horizons. Within a profile, the concentrations decreased with the growing distance from the coal waste dump. The Cr concentration, dwindling with the growing distance from the coal waste dump, was the most visible example of the metal mobility.

The Zn and Co concentrations decreased at the 100 m distance from the coal waste dump and then increased. Importantly, the large Zn content was found in the upper soil layer (0–30 cm). The increase in the Zn concentration could have been caused by the location of the rails close to Point 3 in Transect I.

Transect II, lying close to Transect I, was also placed on the groundwater inflow. The concentrations of Cd, Zn, Cu and Pb decreased dramatically in the upper layer (0–30 cm) with the growing distance from the coal waste dump. The differences at deeper genetic horizons were slight. Such a situation seems to have been influenced by the deposition of the dust from the coal waste dump. Moreover, the water running off from the dump slope polluted the areas lying close to the coal waste dump to a larger extent. Similarly to Transect I, the Cr concentration was strongly correlated with the sampling point distance from the coal waste dump. It was independent of the genetic horizon from which the sample had been collected. Interestingly, the Sb results indicate that its concentration rose at a larger distance from the coal waste dump. It could be related to the material deposition in the form of dust from which the dump had been built. Moreover, the western part of the coal waste dump was not tree-covered and constituted a significant source of such pollutants. For Ni, the decrease in its concentration was observed in the deeper soil layers and with the growing distance from the waste dump. The upper soil layer became enriched with Ni when the distance rose. It could be related to the dusting from the coal waste dump and transporting the metals on the smallest particles.

The Zn concentration decreased in Transect III when the distance from the coal waste dump rose. Its increased concentration was observed in the upper soil layer. The results indicate the profound influence of the waste from the dump on the Zn concentration in the soil surrounding the dump. The Ni, As, Cr and Cd concentrations decreased dramatically in the upper soil layers with the growing distance from the coal waste dump. When comparing metal concentrations in the soil samples collected at Transect IV, typical correlations between their decrease and the growing distance from the coal waste dump were observed. Transect V was located on the groundwater runoff in the north-west part of the Hałda Ruda, close to the Bytomka River. The Cd, Pb and As concentrations fell when the distance from the coal waste dump rose. There were large differences in concentrations between various genetic horizons. The Cr and Ni concentrations decreased with the growing distance from the coal waste dump. Nevertheless, the differences observed between various genetic horizons were much slighter. Interestingly, V, Mn, Fe, Co and Ba constituted an element group of similar mobility. The concentration charts of these elements indicate similar concentrations at Points 1 and 3. They were higher at Point 2. It was probably related to the additional impact of the municipal pollution from Biskupice, one of Zabrze's districts. For Transect VI, concentrations of most elements decreased with the growing distance from the coal waste dump. The variations in the Cr, As, Ni, Pb, Cu and Zn concentrations revealed similarities. The Hałda Ruda is partially planted with trees and partially uncovered. When taking into account the direction of the dominant winds (S-W), the increase in metal concentrations in the upper soil layer of Transect VI (northern slope) was observed. Most winds blew in this direction. They transported the waste material deposited at the coal waste dump in the form of dust (Figure 3). The process had a strong impact on the movement of pollutants.

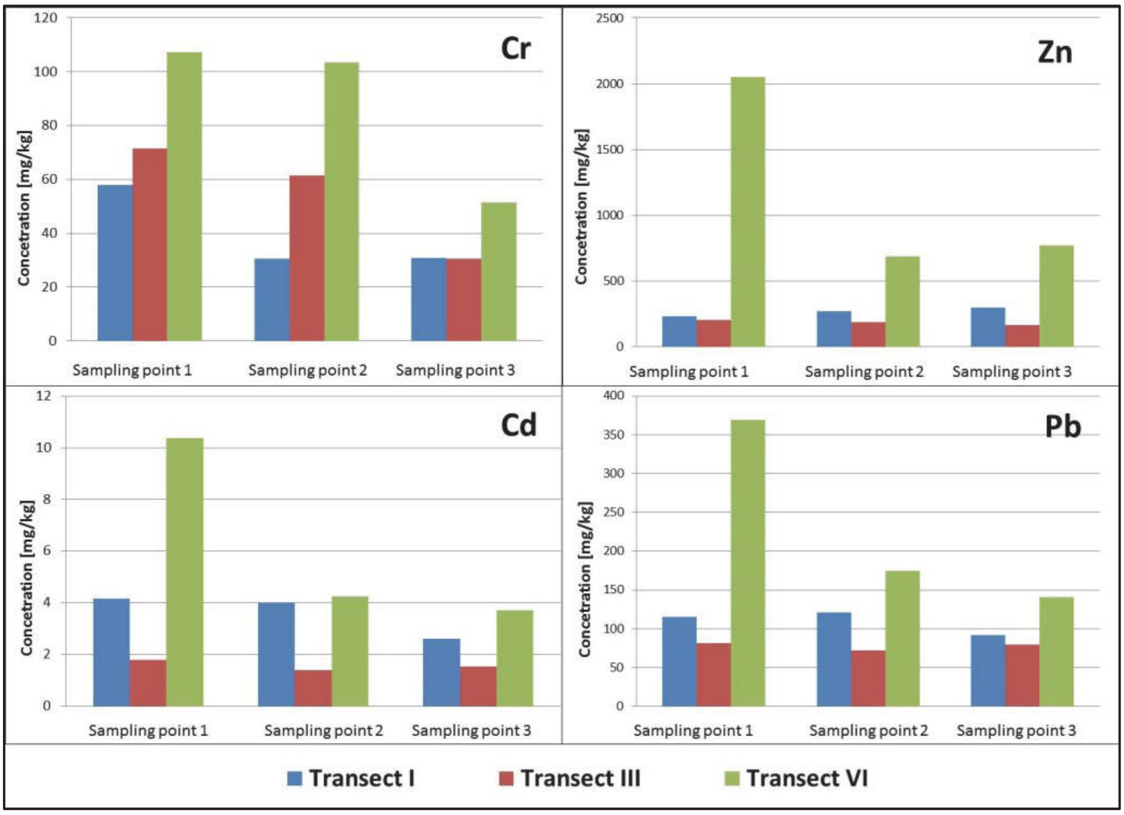

Fig. 3. Impact of the dominant winds on the increase in the Cr, Zn, Cd and Pb concentrations in the upper soil layers of the areas surrounding the Hałda Ruda
Rys. 3. Wpływ dominujących wiatrów na wzrost stężenia Cr, Zn, Cd oraz Pb w wierzchnich warstwach gleby terenu otaczającego zwał Hałda Ruda

Figure 4 shows total concentrations of Mn, Zn, Pb and Cu in 2 profiles of the polluted soil collected from the sampling points located at Transects II and VI. Significant differences in the Pb, Cu, Zn and Mn concentrations depended on the depth. It was particularly visible in the highest concentration of these metals observed in the upper soil layer collected at Point 1 of Transect VI (Figure 4A). These findings prove that the secondary deposition and runoff water were the main sources of the soil pollution. On the other hand, the differences in the concentrations of Pb, Zn, Mn and Cu in the soil profile were much lower at Point 1 of Transect II. They resulted from the location of Transect II on the groundwater inflow. The dominant winds influenced the secondary deposition of the waste material (Figure 4B) to a lesser extent.

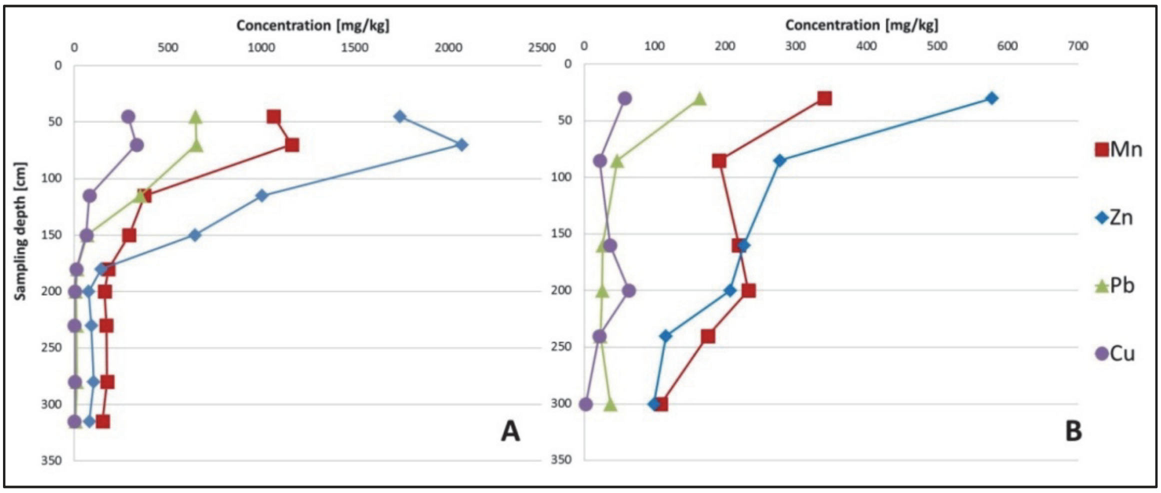

Fig. 4. Changes in total concentrations of Mn, Zn, Pb and Cu in the soil profiles collected at **A)** Point 1, Transect VI (groundwater runoff) **B)** Point 1, Transect II (groundwater inflow)

Rys. 4. Zmiany stężenia całkowitego Mn, Zn, Pb oraz Cu w profilach glebowych pobranych A) w Punkcie 1 Transekt VI (kierunek spływu wód gruntowych) B) w Punkcie 1 Transekt II (kierunek napływu wód gruntowych)

Trębacka Street, where the houses are located, lies close to the Hałda Ruda. For that reason, soil samples from Transects VII and VIII were collected at this side of the coal waste dump. The soil in this area mainly contains loam and clay. This might have been one of the reasons for building houses there despite the close location of the coal waste dump. Metal concentrations in the upper soil layer collected at these transects were much higher than those observed at lower horizons. This was probably caused by the process of the upper layer enrichment with metals originating from the runoff water. Metal concentrations decreased when the distance from the waste dump rose. As the eastern part of the Hałda Ruda was planted with trees, no influence of the dust transportation was observed. The tree cover constituted an important barrier that isolated the houses in Trębacka Street from the Hałda Ruda.

3.3. Chemometric analysis

3.3.1. Preprocessing and dissimilarity analysis

The measurement data concerning pH, electrical conductivity and contents of selected chemical substances in the soil samples collected at 8 transects were organized in the matrix **X** of 114 objects (samples) and

17 parameters. The data preprocessing embraced it centering and standardization in accordance with the dependence:

$$x_{ij,a} = \frac{\left(x_{ij} - \overline{x}_j\right)}{s_j} \tag{1}$$

where:

$\overline{x}_j$ – arithmetic mean of the *j*-th column;

s_j – standard deviation of the *j*-th parameter;

x_{ij} and $x_{ij,a}$ – *i*-th value of the *j* parameter before and after autoscaling, respectively.

After the preprocessing, the data underwent visualization through calculating the dissimilarity matrix **D** (dimensions: 114 x 114) with the Euclidean distance as the measure of dissimilarity [40]. The calculations were made according to the formula of Al-Kashi (Persian mathematician from the 15th century), whose matrix form was [41]:

$$\mathbf{D}^2 = \left(\mathrm{diag}\left(\mathbf{XX}^{\mathbf{T}}\right)\cdot \mathbf{1}^{\mathbf{T}} + \mathbf{1}\cdot \mathrm{diag}\left(\mathbf{XX}^{\mathbf{T}}\right)^{\mathbf{T}}\right) - 2\cdot\left(\mathbf{XX}^{\mathbf{T}}\right) \tag{2}$$

where:

$\mathbf{1}^{T}$ – row vector of 114 elements equal to 1;

$\mathbf{1}$·diag – an operator extracting only the diagonal elements
from the matrix represented as a column vector.

To obtain matrix **D,** the root of the matrix $\mathbf{D}^2$ value, calculated according to the formula (2), had to be calculated.

The determined dissimilarity matrix (Figure 5) helped to examine the data structure and observe the highest diversification of the objects in Transects IV and VI. The observation was corroborated when the average distance of a given object from other ones was determined (Figure 6).

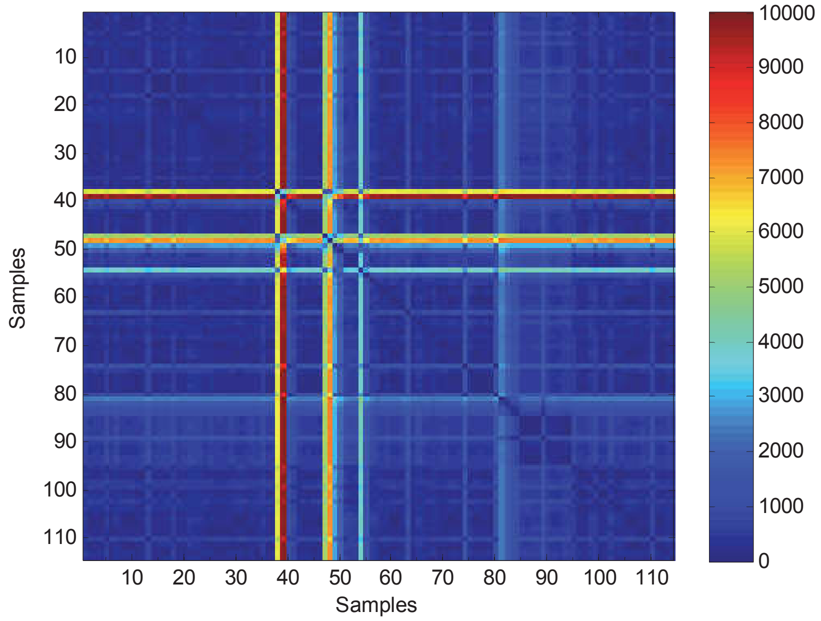

Fig. 5. Dissimilarity matrix **D** calculated with the Euclidean distance
Rys. 5. Macierz podobieństwa **D** obliczona z wykorzystaniem odległości Euklidesa

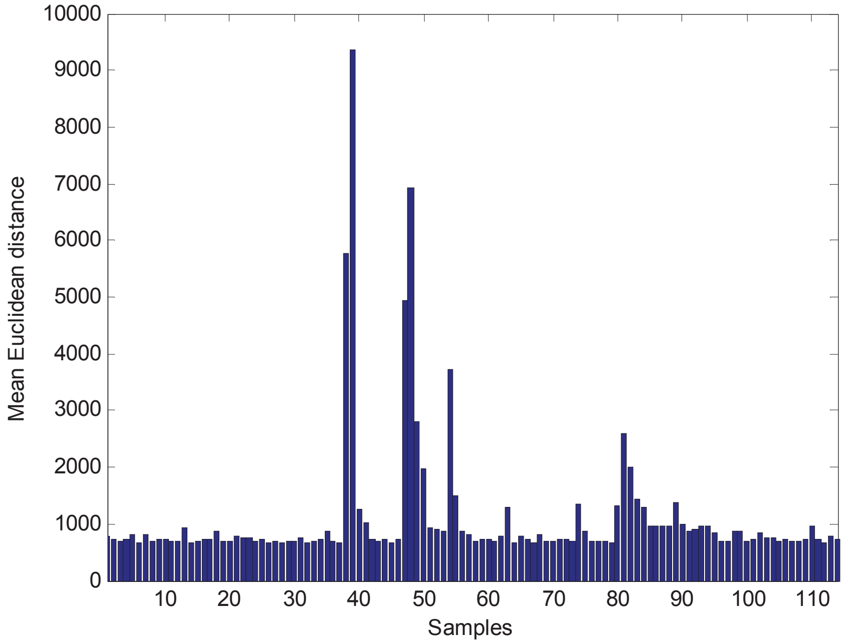

Fig. 6. Detection of distant objects with dissimilarity matrix **D**
Rys. 6. Detekcja obiektów odległych z wykorzystaniem macierzy podobieństwa **D**

The most distinctive objects were: object 39 (Point 1, Transect IV, thickness: 45–70 cm), object 48 (Point 2, Transect IV, thickness: 45–50 cm), object 38 (Point 1, Transect IV, thickness: 0–45 cm), object 47 (Point 2, Transect IV, thickness: 0–45 cm) and object 54 (Point 3, Transect IV, thickness: 0–40 cm). It is probably related to the fact that the sampling points of Transect IV were placed in the inundation area of the Bytomka River. The river overflows the banks every year during the spring thaw and covers the upper soil layer with sediments and alluvia. Soil layers characteristic for such areas (silt, peat) were found at the depth of up to 4 m, which meant that the Bytomka River had been overflowing the banks at this area for many years.

3.3.2. Principal component analysis

Principal Component Analysis (PCA) [1, 19, 37, 41] allows investigating the correlations between the measured parameters (contents of selected chemical substances and physicochemical parameters) and specific objects (samples). The algorithm of the Singular Value Decomposition (SVD) was used in the PCA. Firstly, the percentage of variance described by each principal component (PC) was calculated. The PC1, PC2 and PC3 accounted for 37.36%, 26.21% and 8.38% of variance, respectively. Further data analysis was performed for the first three components, which explained over 70% of the data variance. The correlations between 114 objects are visualized in Figure 7, which presents the projection of the objects onto the planes of PC1, PC2 and PC1, PC3.

The analysis of the PC1, PC2 (Figure 3a) and PC1, PC3 (Figure 3b) projections demonstrate that objects belonging to Transects IV and VI largely contributed to the PC1 and PC2, which proves the conclusions drawn from the dissimilarity matrix analysis. The greatest contributions to the creation of the third principal component (PC3) are the objects belonging to Transect VI. The soil samples from Transects IV and VI were the source of the greatest variance in the analyzed data set. The location in the inundation area of the Bytomka River was the main reason for the variety in Transect IV. On the other hand, the dominant direction of the blowing winds and municipal pollution were the sources of the largest variance in Transect VI. The correlations between the analyzed parameters are shown in the charts of loadings (Figure 8).

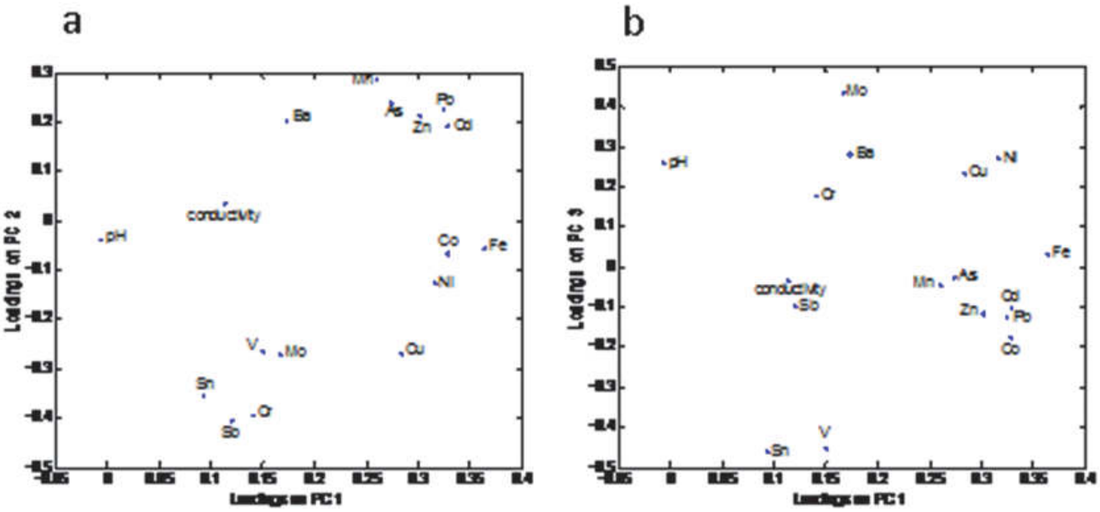

Fig. 7. Projection of objects onto the plane: a) PC1, PC2; b) PC1, PC3
Rys. 7. Projekcja obiektów na płaszczyznę: a) PC1, PC2; b) PC1, PC3

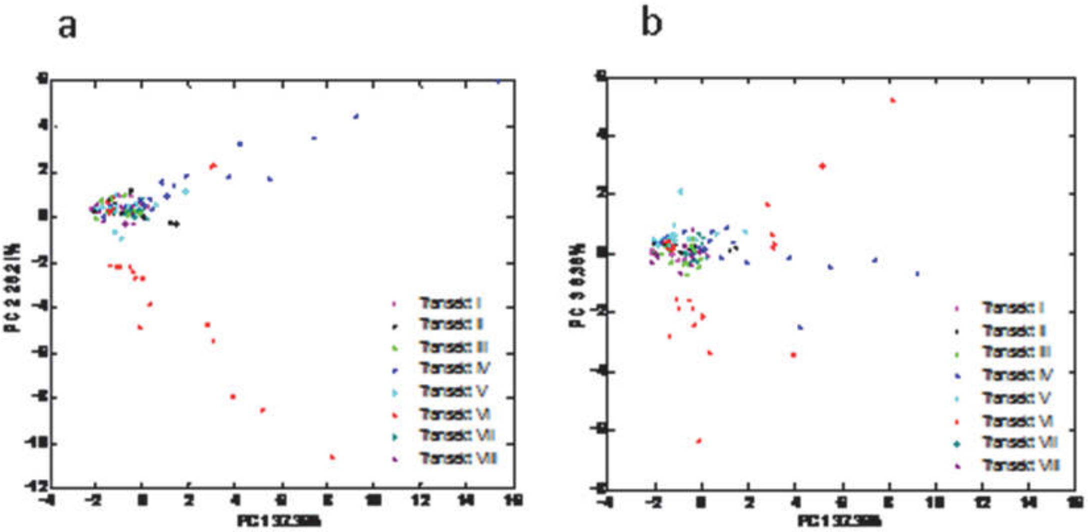

Fig. 8. Projection of charges onto the plane: a) PC1, PC2; b) PC1, PC3
Rys. 8. Projekcja ładunków na płaszczyznę: a) PC1, PC2; b) PC1, PC3

The projection of loadings onto the PC1, PC2 plane indicated a strong positive correlation between the contents of elements and chemical compounds within 3 groups. The first group was made by Ba, Mn, As, Pb, Zn and Cd. Co, Ni and Fe_2O_3 belonged to the second group. The third one contained Sn, Sb, Cr, Mo and V. Chart 4a also points to the lack of correlations between the elements from the first and third groups. The projection of loadings onto the PC1, PC3 plane confirms most conclusions from the Figure 4a analysis. An in-depth analysis of Figure 4 provides information on the parameters differentiating soil samples that belong to Transects IV and VI from other samples. The parameters included the contents of Fe_2O_3, Sb, Sn, Cr, V and Mo.

4. Conclusions

The research conducted at the Hałda Ruda clearly demonstrates that even old and no longer used coal waste dumps still pose a threat to the environment. They influence increases in the contents of heavy metals accumulating in the surrounding water and soil environment. The Hałda Ruda is relatively old in comparison with other coal waste dumps in the Upper Silesia urban area. Nonetheless, large amounts of chlorides and sulfates are leached from it with runoff and groundwater. Consequently, the Hałda Ruda is still the source of metals and metalloids leached from the waste dump. The pollution of the soil environment with metals/metalloids leaching from the deposited waste is higher on the groundwater runoff and in the area influenced by the dominant winds.

The chemometric analysis allowed to find transects with the largest degree of object diversification (Transects IV and VI). The findings were confirmed with the field research. The PCA corroborated the exitstence of a ceratin element group (Mn, As, Zn, Pb, Cd). The elements were characterized by the strong correlation between their contents in the soil samples. They were leached from the waste deposited at the coal waste dump (together with chlorides and sulfates) with groundwater.

Using the coupled EDXRF and ICP-MS spectrometers turned out to be the best solution allowing for the measurements of water and soil samples at different concentration levels.

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Abbreviations used in text:
EDXRF – Energy Dispersive X–Ray Fluorescence,
ICP–MS – Inductively Coupled Plasma Mass Spectrometry,
PCA – Principal Component Analysis,
CA – Cluster Analysis,
XRF – X-Ray Fluorescence,
AMSL – Above Mean Sea Level,

cond. – Conductivity,
LOD – Limit of Detection.

References

1. **Abdi H., Williams L. J.:** *Principal component analysis. WIREs Computational Statistics*, 2, 433–447 (2010).
2. **Akyuz S., Akyuz T., Algan A. O., Mukhamedshina N. M., Mirsagatova A. A.:** *Energy dispersive X-ray fluorescence and neutron activation analysis of surficial sediments of the Sea of Marmara and the Black Sea around Istanbul.* Journal of Radioanalytical and Nuclear Chemistry, 254, 569–575 (2002).
3. **Aleksander-Kwaterczak U., Ciszewski D.:** *Groundwater hydrochemistry and soil pollution in a catchment affected by an abandoned lead–zinc mine: functioning of a diffuse pollution source.* Environmental Earth Sciences, 65, 1179–1189 (2012).
4. **Aleksander-Kwaterczak U., Helios-Rybicka E.:** *Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of South Poland.* Journal of Soils and Sediments, 9, 13–22 (2009).
5. **Astel A., Głosińska G., Sobczyński T., Boszke L., Simeonov V., Siepak J.:** *Chemometrics in the assessment of the sustainable development rule implementation.* Central European Journal of Chemistry, 4, 543–564 (2006).
6. **Benvenuti M., Mascaro I., Corsini F., Lattanzi P., Parrini P., Tanelli G.:** *Mine waste dumps and heavy metal pollution in abandoned mining district of Boccheggiano (Southern Tuscany, Italy).* Environmental Geology, 30, 238–243 (1997).
7. **Bi X., Feng X., Yang Y., Qiu G., Li G., Li F.:** *Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China.* Environment International, 32, 7, 883–890 (2006).
8. **Boyle J. F.:** *Rapid elemental analysis of sediment samples by isotope source XRF.* Journal of Paleolimnology, 23, 213–218 (2000).
9. **Cakir C., Budak G., Karabulut A., Sahin Y.:** *Analysis of trace elements in different three region coals in Erzurum (Turkey): a study using EDXRF*. Journal of Quantitative Spectroscopy & Radiative Transfer, 76, 101–106 (2003).
10. **Dang Z., Liu C., Haigh M. J.:** *Mobility of heavy metals associated with the natural weathering of coal mine spoils*. Environmental Pollution, 118, 419–426 (2002).
11. **Dinelli E., Tateo F.:** *Factors controlling heavy-metal dispersion in mining areas: the case of Vigonzano (northern Italy), Fe-Cu sulfide deposit associated with ophiolitic rocks.* Environmental Geology, 40, 1138–1150 (2001).

12. **Dos Anjos M. J., Lopes R. T., Assis J. T., Cesareo R., Barradas C. A. A.:** *Quantitative analysis of metals in soil using X-ray fluorescence.* Spectrochimica Acta Part B: Atomic Spectroscopy, 55, 1189–1194 (2000).
13. EU report from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. The implementation of the Soil Thematic Strategy and ongoing activities
14. **Evanco C. R., Dzombak D. A.:** *Remediation of Metals Contaminated Soils and Groundwater*, Pittsburgh, USA, TE-97-01 Technology Evaluation Report, 1997.
15. **Frankowski M., Zioła-Frankowska·A., Kurzyca I., Novotný K., Vaculovic T., Kanický:** *Determination of aluminium in groundwater samples by GFAAS, ICPAES, ICPMS and modelling of inorganic aluminium complexes*. Environmental Monitoring and Assessment, 182, 71–84 (2011).
16. **Henriques F. S.:** *Heavy Metal Content of Spoil Heaps from an Abandoned Iron- and Copper-Mine and Metal Accumulation in Armeria linkiana Nieto Feliner.* Bulletin of Environmental Contamination and Toxicology, 68, 555–560 (2002).
17. **Jabłońska-Czapla M., Szopa S., Rosik-Dulewska Cz.:** *Impact of mining dump on the accumulation and mobility of metals in the Bytomka River sediments.* Archives of Environmental Protection, 40, 2, 3–19 (2014).
18. **Jha S. K, Chavan S. B., Pandit G. G., Negi B. S., Sadasivan S.:** *Fluxes of Trace and Toxic Elements in Creek Sediment Near Mumbai, India.* Environmental Monitoring and Assessment, 76, 249–262 (2002).
19. **Jollife I.T.:** Principal Component Analysis, New York, Springer-Verlag
20. **Jorgensen N., Laursen J., Viksna A., Pind N., Holm P. E.:** (2005). *Multi-elemental EDXRF mapping of polluted soil from former horticultural land.* Environment International, 31, 43–52 (2002).
21. **Lewinska-Preis L., Jabłonska M., Fabianska M. J., Kita A.:** *Bioelements and mineral matter in human livers from the highly industrialized region of the Upper Silesia Coal Basin (Poland).* Environmental Geochemistry and Health, 33, 595–611 (2011).
22. **Mahmoud H. M., Abbady A. G. E., Khairy M. A., Abdehalim A. S., El-Taher A.:** *Multi-element determination in sandstone rock by instrumental neutron activation analysis.* Journal of Radioanalytical and Nuclear Chemistry, 264, 715–718 (2005).
23. **Marguí E., Padilla R., Hidalgo M. Queralt, I. Van Grieken R.:** *High-energy polarized-beam EDXRF for trace metal analysis of vegetation samples in environmental studies.* X-Ray Spectrometry, 35, 169–175 (2006).
24. PN-90-C-04540/01: 1990 – Water and wastewater – pH, acidity and alkalinity tests – Determination of pH of water and wastewater with a conductivity of 10 μS/cm and above.

25. PN-EN 27888:1999 – Water quality – Determination of electrical conductivity.
26. PN-ISO 10390:1997 – Soil quality – Determination of pH.
27. PN-ISO 11265:1997 – Soil quality – Determination of electrical conductivity.
28. Regulation of the Minister of Health on 23 July 2008, about ground water quality, No. 143 pos. 896th.
29. Regulation of the Minister of Environment on 9 September 2002. Standards on soil quality, No. 165 pos. 1359.
30. **Skorek R., Jabłońska M., Polowniak M., Kita A., Janoska P., Buhl F.:** *Application of ICP-MS and various computational methods for drinking water quality assessment from the Silesian District (Southern Poland).* Central European Journal of Chemistry, 10(1), 71–84 (2012).
31. **Sojka M., Siepak M., Zioła A., Frankowski M., Murat-Błażejewska S., Siepak J.:** *Application of multivariate statistical techniques for evaluation water quality of the Mała Wełna river catchment, (WEST POLAND).* Environmental Monitoring and Assessment, 147, 159–170 (2008).
32. **Szczepanska J., Twardowska I.:** *Distribution and environmental impact of coal-mining wastes in Upper Silesia, Poland.* Environmental Geology, 38, 249–258 (1999).
33. US EPA Ecological Soil Screening Level (Eco-SSL) Guidance and Documents http://www.epa.gov/oerrpage/superfund/programs/risk/ecorisk/ecossl.htm.
34. US EPA The Safe Drinking Water Act (SDWA), Pub. L. 93-523, 88 Stat. 1660 (1974).
35. EU Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.
36. **Walna B., Siepak K., Drzymała S.:** *Soil degradation in the Wielkopolski National Park (Poland) as an effect of acid rain simulation*. Water, Air, and Soil Pollution, 130, 1727–1732 (2001).
37. **Wold S., Esbensen K., Geladi P.:** *Principal Component Analysis.* Chemometrics and Intelligent Laboratory Systems, 2, 37–52 (1987).
38. **Yu K. N., Yeung Z., Lee L., Stokes M. J., Kwok R.:** *Determination of multi-element profiles of soil using energy dispersive X-ray fluorescence (EDXRF).* Applied Radiation and Isotopes, 57, 279–286 (2002).
39. **Zhan X.:** *Application of polarized EDXRF in geochemical sample analysis and comparison with WDXRF*. X-Ray Spectrometry, 34, 207–211 (2005).
40. **Zerzucha P., Walczak B.:** *Concept of (dis)similarity in data analysis.* Trends in Analytical Chemistry, 38, 116–128 (2012).
41. **Zerzucha P., Boguszewska D., Zagdańska B., Walczak B.:** *Non-parametric multivariate analysis of variance in proteomic response of potato to the drought stress.* Analytica Chimica Acta, 719, 1–7 (2012).

Badania nad przemieszczaniem się metali i metaloidów w glebie i wodzie gruntowej terenów otaczających zwał odpadów pogórniczych Hałda Ruda, Górny Śląsk, Polska

Streszczenie

Górny Śląsk to najbardziej przekształcone w wyniku działalności człowieka terytorium Polski. Celem pracy była optymalizacja i walidacja ilościowego oznaczania metali i metaloidów przy użyciu techniki EDXRF i ICP-MS do identyfikacji zanieczyszczeń na obszarach wokół składowiska odpadów pogórniczych, Hałda Ruda (Zabrze, Polska Południowa) oraz określenie sposobu, w jaki metale i niemetale przenoszą się w glebach i wodach gruntowych na omawianym obszarze. Stężenia 27 metali i metaloidów oznaczano w próbkach gleb za pomocą techniki EDXRF. Próbki wód gruntowych pobierano comiesięcznie między 2010 i 2012 i analizowano techniką ICP-MS. Uzyskane wyniki badań poddano analizie chemometrycznej, co pozwoliło na znalezienie transektów z największym stopniem dywersyfikacji obiektu. Analiza PCA potwierdziła istnienie pewnej grupy pierwiastków charakteryzujących się silną korelację pomiędzy ich zawartością w próbkach gleb. Hałda Ruda nadal jest źródłem zanieczyszczeń w środowisku wodnogruntowym, szczególnie na terenach leżących w kierunku spływu wód gruntowych oraz w obszarze pod wpływem dominujących wiatrów południowo-zachodnich. W próbkach wód pobieranych na spływie wód gruntowych stwierdzono najwyższe stężenia toksycznych metali przekraczające dopuszczalne normy. Szczególnie podwyższone stężenie obserwowano w przypadku ołowiu, arsenu, chromu i cynku. Badania stężenia metali i metaloidów w glebach z obszarów otaczających teren zwału, w porównaniu z wytycznymi jakości gleb, jasno wskazują, że tereny usytuowane na spływie wód gruntowych są znacznie bardziej zanieczyszczone, a ich wartości wielokrotnie przekraczają dopuszczalne normy. Stężenie ołowiu w glebie przekraczało nawet 2000 mg/kg. Zaobserwowano również ogromne przekroczenia poziomu dopuszczalnego stężenia miedzi, manganu, chromu lub cynku. Maksymalne stężenia Cu, Zn, Pb lub Cr w wierzchnich warstwach gleby przekraczały kilka tysięcy mg/kg.

Słowa kluczowe:
ICP-MS, EDXRF, gleba, wody gruntowe, metale ciężkie,
analiza chemometryczna, PCA

Keywords:
ICP-MS, EDXRF, soil, groundwater, heavy metals,
chemometric analysis, PCA

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Assessment of Agricultural Use of the Bottom Sediments from Eutrophic Rzeszów Reservoir

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1. Introduction

Natural lakes and artificial reservoirs seem to be ecosystems with very similar structure and similar mechanisms governing their physical, chemical and biochemical changes. However, this is only apparent similarity [21]. Artificial reservoirs in comparison to natural lakes are characterized by a much more frequent water exchange, large fluctuations in water level resulting from the variation of inflow and outflow, which is evident especially in mountainous catchment areas. Reservoirs created in the river valleys by the construction of a dam have also considerably larger catchment area than the lakes. This difference is disadvantageous to the anthropogenic water bodies. A large catchment area delivers to the reservoir greater quantities of pollution produced within its territory causing adverse effects in the ecosystem. A gradual development of undesirable organisms characteristic of stagnant water is observed in the reservoirs, which utilize nutrients causing deterioration in water quality after a few years of exploitation [13].

Degradation of the reservoirs is often irreversible, therefore, the problem of their reclamation and restoration of appropriate parameters is very important [2, 13]. Deposition and settlement of mineral and organic matter proceeds much easier in artificial reservoirs than in natural lakes, also an artificial aging of the reservoirs is faster than lakes by about 10,000 times [8]. Reclamation methods for the reservoirs vary depending on the severity of the degradation. For the eutrophic water bodies following methods were used: aeration or removal of hypolimnion as well as chemical inactivation of phosphates using Fe, Al, Ca or La salts [2]. If, however, the ecosystem has accumulated debris of various origins in amounts significantly reducing its volume, it is only possible to remove the backlog of bottom sediments through dredging.

The purpose of this paper is the analysis of possible agricultural use of the bottom sediments that were dredged from a planned for reclamation eutrophic reservoir in Rzeszów, SE Poland. The reservoir's degradation strongly limits its agricultural and economic role.

2. Study area

A water reservoir in Rzeszów was built in 1974 by damming the Wislok river in 63+760 km of its course. The reservoir is supplied by two main tributaries: Wislok and Strug. Its main purpose was to allow for the proper operation of the water supply for the city of Rzeszów. Because of its the location on the outskirts of a large city it fulfills a vital role as a sports and recreation lagoon. Morphometric parameters of the reservoir at the time of flooding in 1974 and in 2014 were shown in Table 1. The total volume of the reservoir decreased by 0.7 million m^3 of its capacity during last 40 years. Consequently, the reservoir has mostly silted up and gradually transformed into land especially in its upper zone. The attempts to rehabilitate the usability of the reservoir conducted in the years 1986–87 and 1995–1997 consisted of deepening the reservoir next to the dam, and narrowing it by partial backfill on the right part of the bank just by the dam. In both cases, about 250 000–300 000 m^3 of sediment was dredged. The objective of both operations was the increase in the flow rate, thereby reducing sedimentation. Unfortunately, restoration has not brought the expected results. Just after seven (7) years, the amount of sedimentation exceeded the amount formerly removed.

The Rzeszów reservoir watershed covers an area of 2,025 km^2. Its range encompasses a significant acreage of the Subcarpathian Province (Podkarpacie). The difference in water level between the main supply of the Wislok at the source and the mouth of the reservoir is 616 m. The Wislok flows through the foothill areas that are largely agricultural, though, the upper parts are forested, while the middle part is lined with industrial centers (glassworks, tanneries, refineries). The catchment of a smaller tributary, the Strug, is vastly agricultural in nature which traditionally is comprised of fragmented farmland representing high population density. The reservoir is under strong anthropopressure associated with local agriculture that causes a severe erosion of the land, as a result of depositing the rubble and diffuse pollution [15].

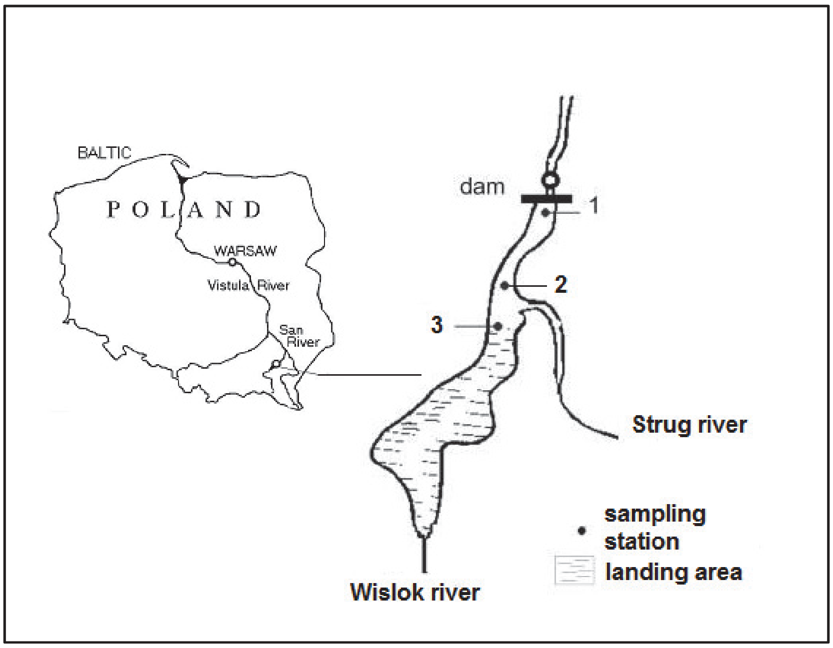

Fig. 1. Location of sampling stations
Rys. 1. Lokalizacja stanowisk badawczych

Table 1. Morphometric parameters of the Rzeszów reservoir
Tabela 1. Parametry morfometryczne zbiornika Rzeszów

Parameter	1974	2014
Surface area; km^2	0.68	0.68
Total volume; 10^6 m^3	1.79	1.10
Depth: max. (mean); m	6.2 (1.5)	4.9 (0.6)
Length; km	6.7	6.7
Hydraulic retention time; day	2	0.8

3. Methods

Sediment samples were taken from the studied reservoir fifteen times (15) in the years 2009–2013, from three points located along the axis of the reservoir (Fig 1). A gravity sediment corer (KC Kajak of Denmark) was used in all cases. Sediment subsamples were dried and further measured for Loss-on-Ignition (LOI) at 550°C for four hours (4h), construed as organic matter content (OM). Another subsample was analyzed for determining total content of organic carbon (TOC) (after the removal of inorganic carbon with 1M HCl) and total nitrogen (TN) using a CN analyzer (CN Flash EA 1112, ThermoQuest). Total phosphorus (TP) was examined spectrophotometrically after microwave mineralization in HNO_3. Some of the heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) were determined with ICP technique (ICP-OES, Quantima GBC) after microwave mineralization. All parameters examined were expressed as % or mg/kg of sediment dry matter. Moreover stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopic compositions were analyzed using IRMS DELTAPlus Finnigan coupled with CN analyzer. The stable isotopic compositions were expressed as "per mil":

$$\delta R\ (‰) = [R_a/R_b(\text{sample})/\ R_a/R_b(\text{standard}) - 1] \times 1000,$$

where R_a/R_b are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios relative to the isotopic PDB and AIR standards, respectively.

Additionally, for a better interpretation, the paper quotes data from the report of the Regional Water Management Board in Kraków where concentrations of PAHs: benzo[a]anthracene (BaA), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), dibenzo[ah]antracene (DahA), indo[1,2,3-cd]pyrene (IcdP), along with chosen congeners (28, 52, 101, 118, 138, 153 and 180) of PCBs [19] are given.

Obtained concentrations of the heavy metals were compared with most common sediment quality standards: geochemical background [7], threshold effect concentration (TEC) [17] and probable effect concentration (PEC) [17]. The last two data respectively represent the concentrations below which adverse effects are expected to occur rarely (TEC) and the concentration above which adverse effects are expected to occur frequently (PEC). For the organic compounds TEC and PEC values were also used.

4. Results and discussion

4.1. Case specifications and boundary conditions

Table 2 summarizes the content of TN, TP, OM, TOC, and the pH (KCl) in the tested samples. The noted values did not attest to statistically significant differences between stations, therefore all the data were averaged. The analysis of the physical properties of the bottom sediments described in paper [19] indicate that approximately 60% of their dry matter composition constitute of particulate matter fractions (0.002–0.05), 30% of sandy fractions (0.05–2.0) and only 10% of clay fractions (0.001–0.002). The main component is silica deposits 54–70% [19]. Analyzed LOI(OM) ranges from 6.5% to 11.6% and the highest value was noted in the area by the dam. The pH value (KCl) varies within the range of 7.04–7.42 indicating a slightly alkaline environment. The percentage of biogenic elements in bottom sediments of the reservoir is small and ranges between 0.12–0.37% of TN and 0.003–0.067% of TP. The $\delta^{15}N$ values in the sediments fall within the range -0.53 to 3.16‰, while the $\delta^{13}C$ values fall between -29.20 and -22.62‰.

The values of TOC to TN ratio (TOC:TN) and of the isotopic composition of the organic carbon and total nitrogen are the main indicators used in an effort of identifying the organic matter origin in the bottom sediments of researched aquatic ecosystems. It is assumed that TOC:TN values in excess of 12:1 are of terrestrial matter in origin. The autochthonous matter is in turn characterized by TOC:TN values below 8 [3,12,18]. The depletion of the ^{12}C isotope from the organic carbon and higher values of the $\delta^{15}N$ are also characteristic for the autochthonous matter [3,18]. The top layer (0–5 cm) of the studied bottom sediments was characterized by TOC:TN values in the range of 6.6 – 16.1. The average values for this indicator were of about 11–12. Such results indicate that the organic matter deposited in the studied sediments is of mixed origin. The reference values obtained from the literature for planktonic and terrigenous matter indicator, were of 6.8 and 17.1 respectively [14]. The obtained values for the $\delta^{15}N$ differ, but did not display any clear trends nor did not allow for drawing any definite conclusions. The $\delta^{13}C$ values suggest that the top surface layer of the sediment was poorer in the ^{12}C, this in turn indicates a greater role of autochthonic organic matter. This conclusion is consistent with the findings for TOC:TN values.

In turn, a higher values of the $\delta^{13}C$ observed in sediments suggest agreater participation of autochthonous organic matter. This is in line with the research results obtained by Tomaszek et al. [22], for the bottom sediments in Poland's largest dam reservoir. The top- and the lower parts of the sediments profiles were depleted of the ^{12}C isotope in the summer, indicating the influence of phytoplankthonic organic matter [11,18]. A high proportion of an autochthonous OM in sediments can be surprising after comparing it with low content of TOC, TP and TN. However, the reservoir is loaded with significant amount of TP and TN, and the retention of these elements are 7% and 22% of load respectively [16]. This effect is reduced by a significant denitrification and mineralization of the OM sediment regarding emissions of CO_2 and CH_4 into the atmosphere [9, 10]. Moreover, low concentrations of biogenic compounds may result from leaching during high water season (mostly in spring), when the hydraulic retention time in the reservoir is only few hours.

Table 2. Characteristic values of the parameters studied in the sediment. Abbreviations as in the text

Tabela 2. Wartości charakterystyczne stężeń badanych wskaźników. Skróty jak w tekście

Parameter	LOI(OM)	TN	TOC	TP	pH(KCl)	$\delta^{13}C$	$\delta^{15}N$
	% of dry matter				–	‰	
Mean	8.6	0.21	2.31	0.031	–	-26.56	1.75
Maximum	11.6	0.37	4.39	0.067	7.42	-22.62	3.16
Minimum	6.5	0.12	1.61	0.003	7.04	-29.20	-0.53
Std. dev.	1.2	0.06	0.67	0.002	0.12	1.72	1.07

4.2. Heavy metals in the sediment

An important indicator of reservoirs pollution is concentration of heavy metals in bottom sediments [24]. In water, compounds of those elements remain in a dissolved form for a very short time and quickly precipitate into the sediments. The accumulation of the metals in the deposits is a permanent phenomenon, especially in the case of clay fractions with a high sorption capacity [23]. Table 3 lists the concentrations of metals. On the basis of calculated values of arithmetic means of observed metals concentrations, it can be concluded that the Rzeszów reservoir sediments were contaminated with zinc (Zn) (103.9 mg/kg), copper (Cu) (32.7 mg/kg), lead (Pb) (53.5 mg/kg), nickel (Ni) (35.6 mg/kg), chromium (Cr) (56.3 mg/kg) and cadmium (Cd) (2.5 mg/kg).

Table 3. Concentrations of selected heavy metals in studied sediments. Abbreviations as in the text

Tabela 3. Stężenia wybranych metali ciężkich w badanych osadach. Skróty jak w tekście

Concentrations, mg/kg of dry matter	Cd	Cr	Cu	Ni	Pb	Zn
Mean	2.5	56.3	32.7	35.6	53.5	103.9
Maximum	3.1	67.7	38.6	42.9	63.9	133.6
Minimum	2.1	46.9	24.4	28.5	37.8	79.6
Std. dev.	0.2	5.9	4.1	4.2	7.2	15.4
Geochemical background	0.5	6.0	7.0	5.0	15.0	73.0
TEC	0.6	37.3	35.7	18.0	35.0	123
PEC	5.0	111.0	149.0	48.6	128	459

It should be acknowledged that the studied sediments are moderately polluted with the heavy metals. Average concentrations of all metals exceeded the geochemical baseline and the TEC level, moreover only Cu and Zn minimum values were detected below the TEC. The PEC value has not been exceeded in none of the samples analyzed. Despite noted levels of the analyzed metals, there is a risk tied to leaching of the heavy metals into uncontaminated sediments which in turn may pose a threat to the agricultural soils [1].

4.3. Organic compounds

Analysis of the obtained results, in terms of selected compounds content from the PAHs and PCBs group, showed that within PAHs benzo[k]fluoranthene was dominant-reaching an average of 0.1 mg/kg. This value is more than 10-fold higher compared to the dibenzo[a,h] anthracene for which the lowest concentration was observed in studied sediment (Table 4). However, the greatest impact on the quality of the bottom sediments is connected with the presence of benzo[a]pyrene, mainly due to its high toxicity. In addition, an identifying of BaP in any one element of the environment proves its participation in the overall ecosystem.

Table 4. Characteristic values of the organic compounds studied in the sediment. Data from [19]. Abbreviations as in the text
Tabela 4. Charakterystyczne wartości stężeń zanieczyszczeń organicznych w badanych osadach. Dane opracowane na podstawie [19]. Skróty jak w tekście

Concentrations mg/kg of dry matter	Mean	Max.	Min.	Std. dev.	TEC	PEC
BaP	0.0894	0.1436	0.0605	0.0256	0.1500	1.5200
BaA	0.0801	0.1382	0.0558	0.0277	–	–
BbF	0.0906	0.1540	0.0573	0.0191	–	–
BkF	0.1000	0.1639	0.0675	0.0275	–	–
BghiP	0.0543	0.0908	0.0348	0.0120	–	–
DahA	0.0097	0.0150	0.0060	0.0022	–	–
IcdP	0.0676	0.1101	0.0424	0.0164	–	–
PCBs	0.0012	0.0028	0.0005	0.0005	0.0590	0.6760

In obtained samples concentrations of BaP were within 0.0605–0.1436 mg/kg and did not exceed the threshold values of PEC (1.52 mg/kg). However, at all studied sites higher amounts of TEC were found with respect to the bottom level of contaminants (0.15 mg/kg). In the same year, an average concentration of the BaP noted for 150 Polish lakes was 3.5-fold higher (0,315 mg/kg) in comparison with sediment cored from the Rzeszów reservoir [6]. A similar range of values was characterized by benzo[b]fluoranthene (0.0573÷0.1540 mg/kg) and benzo[a]anthracene (0.0584÷0.1328 mg/kg). In turn, a slightly lower concentrations were reported for benzo[ghi]perylene at the levels of 0.0348 to 0.0908 mg/kg and indo[1,2,3-c,d]pyrene in the range 0.0424–0.1101 mg/kg.

An important part of the growing problem of the sediments enrichment with organic compounds is an observation of changes within the time context. In 2004 content of BaP in sediments of the Warta river was of ca. 0.02 mg/kg, and in 2005 it already increased to almost 0.4 mg/kg [5]. In the bottom sediment of the Besko reservoir, located in the top section of the Wislok river about 40 km above the Rzeszów reservoir, 0.549 mg/kg of BaP was detected in 2012, which accounted for almost 400 % of the maximum value in the Rzeszów reservoir in 2009 [6]. There is a risk that during high water or flood those deposits will be washed away and transported down the river [4,6]. In addition, conducted correlation analysis has shown that the increase in the concentration of BaP is accompanied by an increase in concentration of other studied PAHs, which confirms the relationship between BaP and other PAHs noted in sediments. The highest correlation coefficient was observed for benzo[a]anthracene ($r = 0.992$), the lowest for benzo[b]fluoranthene ($r = 0.814$, Fig. 2). As reported in the literature, there is a correlation between all 4–6 ring group of PAHs (except for perylene – dominates in the uncontaminated sediments located far from developed areas), which points to a common source of origin, which are combustion processes [5,6]. The degree of contamination of the Rzeszów reservoir bottom sediments with PAHs was relatively low, it does not exceed the values specified by the regulations. The largest was for BaP and accounted for 14% of the allowed amount, whereas all compounds except for dibenzo[a,h]anthracene were characterized by a high variability of concentrations (Table 4).

The studied sediments of the Rzeszów reservoir were also uncontaminated with the PCBs. Their concentration was in the range from 0.0005 mg/kg to 0.0028 mg/kg, which did not exceed the values of TEC (0.059 mg/kg). Despite that, the literature suggests that the content of polychlorinated biphenyls in organisms living in the aquatic ecosystem is much higher than its concentration in sediments [20].

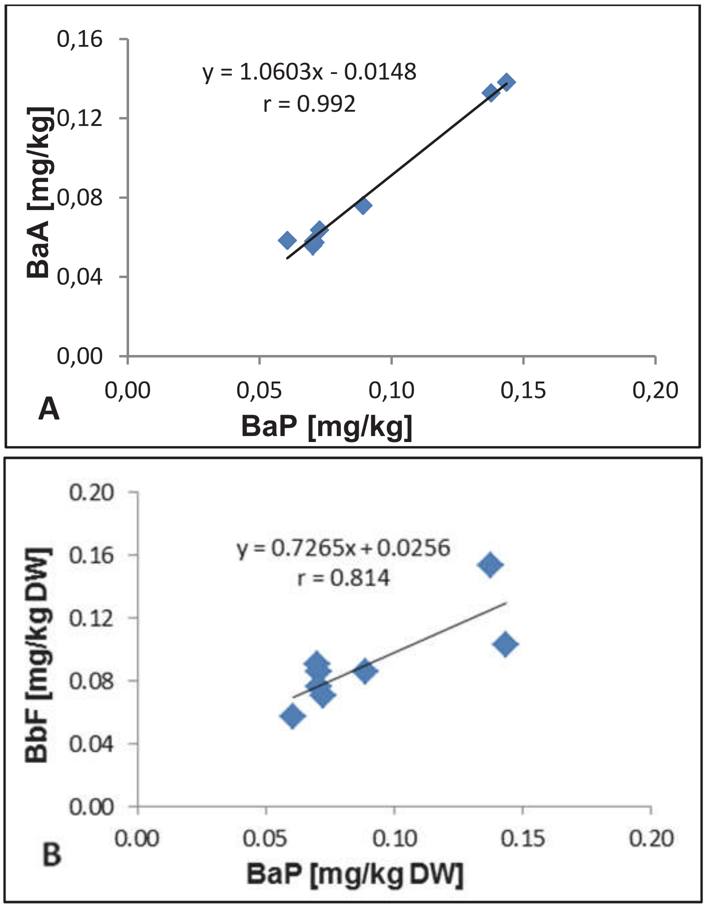

Fig. 2. Relationships between concentrations of benzo[a]pyrene and benzo[a]anthracene (A) and benzo[b]fluoranthene (B)
Rys. 2. Zależność pomiędzy stężeniem benzo[a]pirenu i benzo[a]antracenu (A) oraz benzo[b]fluorantenu (B)

5. Conclusions

The origin of the Rzeszów reservoir bottom sediments is mixed. The unexpectedly high proportion of the autochthonous material is the result of an eutrophic processes. Despite this fact the sediments are relatively poor in nutrients and characterized by slightly elevated concentrations of the heavy metals. Hazardous organic compounds of anthropogenic origin remain in the studied sediments at low concentrations. The characteristics of researched sediments indicate that they are not suitable for agricultural use due to contamination and lack of fertility. However, they can be used for non-agricultural land reclamation. Remediation of the dredged material could possibly result in the removal of these metals, but due to the significant amounts of dredged materials the process may prove to be an unprofitable operation.

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References

1. **Baran A., Tarnawski M.:** *Content of heavy metals in water extracts prepared from bottom sediment collected from Rzeszów reservoir*. Proceedings ECOpole. DOI: 10.2429/proc.2012.6(2)090, (2012).
2. **Bartoszek L., Koszelnik P.:** *Lakes and reservoirs restoration – Short description of the chosen methods*. In: Tomaszek J.A., Koszelnik P., (editors): *Progress in the Environmental Engineering. Water, Wastewater Treatment and Environmental Protection Issues.* CRC Press/Balkema, Taylor & Francis Group, London, 51–58 (2015).
3. **Bernasconi S.M., Barbieri A., Simona M.:** *Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano*. Limnology and Oceanography, 42, 1755–1765 (1997).
4. **Bielak S.:** *Zanieczyszczenia antropogeniczne w osadach dennych rzek Biebrzańskiego Parku Narodowego*. Ekoprofit, 1, 73–81 (2006).
5. **Bojakowska I., Sokołowska G.:** *Polycyclic aromatic hydrocarbons in materials of burned peatlands.* Polsh Journal of Environmental Studies. 12(4), 401–408 (2003).
6. **Bojakowska I., Sztuczyńska A., Grabiec-Raczak E.:** *Badania monitoringowe osadów jeziornych w Polsce: wielopierścieniowe węglowodory aromatyczne*. Biuletyn Państwowego Instytutu Geologicznego. 450, 17–26 (2012).
7. **Bojakowska I.:** *Kryteria oceny zanieczyszczenia osadów wodnych*. Przegląd Ekologiczny. 49(3), 213–218 (2001).
8. **Gough J.D., Ward J.C.:** *Environmental decision-making and lake management*. Journal of Environmental Management. 48, 393–407 (1996).
9. **Gruca-Rokosz R., Tomaszek J.A., Koszelnik P., Czerwieniec E.:** *Methane and carbon dioxide fluxes at the sediment-water interface in reservoirs*. Polish Journal of Environmental Studies. 20, 81–86 (2001).

10. **Gruca-Rokosz R., Tomaszek J.A., Koszelnik P.:** *Denitrification in the sediment of a eutrophic reservoir measured with the isotope pairing technique*. Oceanological and Hydrobiological Studies. 38(1), 75–81 (2009).
11. **Gu B., Schelske C.L., Brenner M.:** *Relationship between sediment and plankton isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) and primary productivity in Florida lakes*. Canadian Journal of Fisheries and Aquatic Sciences. 53, 875–883 (1999).
12. **Gulia L., Guidi M., Bonadonna F., Macera P.:** *A preliminary geochemical study of two cores from Massaciuccoli eutrophic lake, Northern Tuscany, and paleoclimatic implications*. Atti Della Società Toscana Di Scienze Naturali Residente In Pisa. Memorie. Serie A. 109, 97–102 (2004).
13. **Kostecki M., Suschka J.:** *The successful results of Pławniowice reservoir (Upper Silesia Region – South of Poland) restoration by hypolimnetic withdrawal*. Archives of Environmental Protection. 39(1), 17–25 (2013).
14. **Koszelnik P., Gruca-Rokosz R., Bartoszek L.:** *Identifying sources of organic matter in the reservoir's sediment using stable isotope model*. Proceedings of the IWA World Water Congress & Exhibition. 2014 Sep 21–26, Lisbon (Portugal), International Water Association, (2014).
15. **Koszelnik P., Tomaszek J.A.:** *Loading of the Rzeszów reservoir with biogenic elements – mass balance*. Environment Protection Engineering. 28(1), 99–106 (2002).
16. **Koszelnik P., Tomaszek J.A.:** *Relationship between dynamics of phosphorus compounds and nitrogen retention in some dam reservoirs from Podkarpacie (SE Poland)*. Environment Protection Engineering. 30(4), 73–80 (2004).
17. **MacDonald D., Ingersoll C., Berger T.:** *Development and Evaluation of consensus-based Sediment Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems*. Archives of Environmental Contamination and Toxicology. 39, 20–31 (2009).
18. **Machiwa J.F.:** *Stable carbon and nitrogen isotopic signatures of organic matter sources in near-shore areas of Lake Victoria, East Africa*. Journal of Great Lakes Research. 36, 1–8 (2010).
19. **Regional Water Management Board in Kraków**. *Report no. 233/09/Wn50/NE-GW-TX/D (1601/U/ZK/2009)*. (2009). Unpublished data.
20. **Rosińska A.:** *Badania zawartości polichlorowanych bifenyli w wodzie i osadach dennych Warty na wysokości Częstochowy*. Ochrona Środowiska. 1(32), 15–20 (2010).
21. **Straškraba M.:** *Limnological differences between deep valley reservoirs and deep lakes*. International Review of Hydrobiology. 83, 1–12 (1998).

22. **Tomaszek J.A., Koszelnik P., Gruca-Rokosz R.:** *The distribution and isotopic composition of carbon and nitrogen as indicators of organic-matter fluxes in the Solina Reservoir (south-east Poland)*. Marine and Freshwater Research. 60, 647–652 (2009).
23. **Wiater J.:** *Impact of organic and mineral-organic wastes on heavy metals mobility in soil*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection) 11, 183–192 (2009).
24. **Wojtkowska M.:** *Content of selected heavy metals in water and riverbed sediments of the Utrata river*. Environment Protection Engineering. 37(3), 55–62 (2011).

Ocena możliwości rolniczego wykorzystania osadów dennych z eutroficznego zbiornika zaporowego Rzeszów

Streszczenie

Zbiornik zaporowy Rzeszów na rzece Wisłok w południowo-wschodniej Polsce, został zbudowany w 1973 roku. W trakcie jego eksploatacji, niektóre strefy zbiornika zostały zamulone i zalądowione, przez co jego powierzchnia i głębokość istotnie się zmniejszyły. Pomimo kilkukrotnych rekultywacji, zbiornik jest nadal silnie zamulony i jego funkcje użytkowe są mocno ograniczone.

Celem pracy jest analiza zanieczyszczeń i możliwość wykorzystania rolniczego urobku wydobytego ze zbiornika. W pracy dokonano analizy ilościowej zarówno substancji potencjalnie toksycznych jak i biogennych w próbkach osadów pobranych w ciągu ostatnich pięciu lat ze stanowisk zlokalizowanych wzdłuż osi zbiornika. Ponadto, zostało oszacowane pochodzenie materii organicznej zawartej w tych osadach. W tym celu wykorzystano analizy zawartości stabilnych izotopów N i C jak również stosunków elementarnych tych pierwiastków.

Krzemionka była dominującym składnikiem osadu (około 67% suchej masy osadu), zaś materia organiczna (OM) stanowiła około 10% s.m.o. Stężenia związków biogennych: OWO, azotu ogólnego i fosforu ogólnego wynosiły średnio odpowiednio 2,31%, 0,21% i 0,031% s.m.o. Pochodzenie osadów dennych zbiornika Rzeszów jest mieszane. Niespodziewanie wysoki udział materii autochtonicznej może być wynikiem intensywnej eutrofizacji wód zbiornika. Zawartości WWA były stosunkowo niskie. Najwyższe zauważone stężenie wynosiło 0,164 ppm w przypadku benzo(k)fluorantenu. Zawartość benzo(a)pirenu była niższa od 0,14 ppm. Poziomy stężeń wybranych kongenerów PCB mieściły się w przedziale od 0,0006 do 0,003 ppm i były poniżej wartości normatywnych. Badane osady były umiarkowanie zanieczyszczone metalami ciężkimi (Cu, Cd, Cr, Zn, Ni, Pb). Średnie stężenia wszystkich metali przekraczały sporadycznie tło geochemiczne i poziom TEC, ale wartość PEC nie została przekroczona w żadnej z analizowanych próbek.

Charakter badanych osadów wskazuje, że nie są one odpowiednie do stosowania w rolnictwie ze względu na zanieczyszczenie i brak żyzności. Jednak mogą one być wykorzystywane do rekultywacji gruntów nierolniczych. Istnieją metody umożliwiające usunięcie z wydobytego materiału z tych zanieczyszczeń, głównie metali ciężkich, ale z uwagi na znaczne ilości urobku proces może okazać się nieopłacalny.

Słowa kluczowe:
zbiornik zaporowy, osady denne, stabilne izotopy

Keywords:
reservoirs, bottom sediment, stable isotope

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Selected Heavy Metals in Settled Dust from Apartments Located in Lublin, Poland

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1. Introduction

Nowadays people spend almost 90% of their time indoors, where the air creates a unique microclimate, with a composition different from the outdoor air and increased level of pollutants [15,21]. Indoor air pollutants may be found in the form of gas molecules, aerosols and suspended particles. Particulate matter is one of major interests of researchers and analysts, however, so far measurements were conducted mainly on the basis of particle size. Less attention was paid to the chemical composition of particles. Only information about SVOC sorbed on particles or alkali metals in ambient aerosols have been published [5,10,20,25,26,28].

Human activities increase concentrations of different elements and compounds in the atmosphere [9,23], for example heavy metals (Ba, Cu, Pb, Cr, Cd, Zn, Fe, Sn) [27], so as a result of atmospheric deposition one gram of dust may contain 700 million particles of different components including heavy metals. Heavy metals can impair important biochemical processes posing a threat to plant growth and animal life [13,17,22,29]. The exposure of these elements may have various health consequences depending on the exposure time.

However research on the heavy metals levels in the environment was focused on soil, sludge, food or roadside dust [7,19,24]. There is a limited number of data about heavy metals concentration in indoor dust and lack of information about heavy metals levels in relation to particle size distribution.

House dust is a highly heterogeneous mixture of aerosol particles settled on the surfaces. It consists of mineral and biological material, therefore it may contains organic and inorganic carbon, alkaline elements, heavy metals and complicated substances, including persistent organic pollutants.

Its precise composition in any particular building, or even room, will depend on a large number of factors including the location and construction of the building, the use of the room, types of decorating and furnishing materials used, heating and ventilation systems, how well and often the area is cleaned and even the time of year [8,10].

Health hazards of dust, which stem purely from its physical nature, especially from the presence of very small particle sizes, have been well recognized and documented for many years. However, the significance of dusts as accumulation of chemicals in a house, a potential source of chemical exposure, require further examination. Regular disposal of house dusts collected in vacuum cleaners undoubtedly act also as a potential source of more pervasive contamination, as in the case of outdoor dusts flow (especially roadside dusts) to sewers and storm-drains, which can lead to substantial secondary inputs to rivers [11].

The objective of this study is to assess the level of Sn, Pb, Cr, Zn, Cd (tin, lead, chromium, zinc, cadmium) in house dusts. Those heavy metals have high toxicity, which during life accumulate in the human body. Over the past decades, there has been increasing concern about exposure of people, especially of vulnerable groups such as children [17]. The reason is their behavior increasing indirect ingestion by way of hand-to-mouth activities, touching and mouthing of various dust-contaminated objects. Moreover, lower body-weight of children would result ingestion of greater amounts of dust compared to adults [6]. Moreover, children are less tolerant to most of the contaminates [1].

2. Material and Methods

The settled dust collected during the heating season in 5 apartments in Lublin (Fig. 1), Poland, was the object of the research. These apartments are located in the city center, along major thoroughfares as well as near to industrial area. The apartments are different in terms of the age of construction and indoor equipment (Table 1).

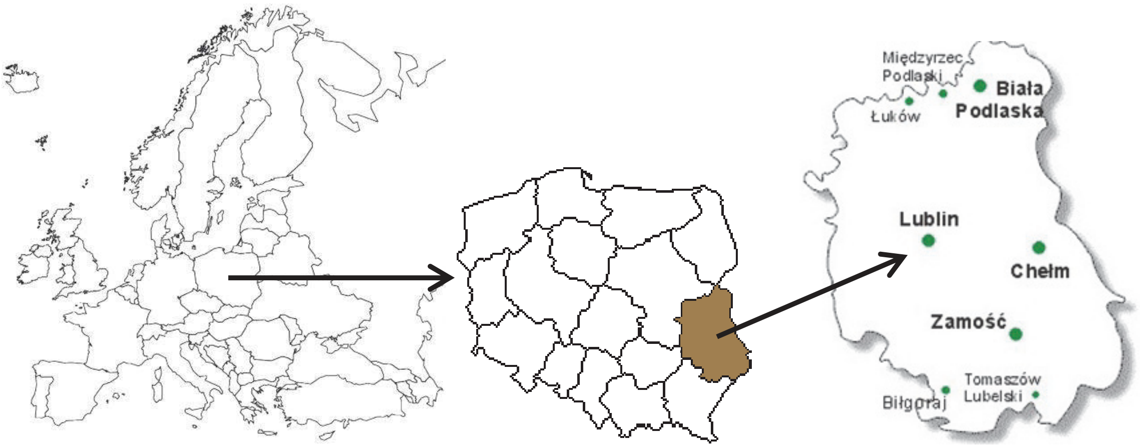

Fig. 1. Map showing the location of Lublin
Rys. 1. Mapa obrazująca lokalizację Lublina

Table 1. Description of the apartments
Tabela 1. Opis mieszkań

Code	Description of the apartment	Area $[m^2]$	Ventilation	Number of persons	Animals
A1	three-room apartment on the 4th floor; block of flat built of concrete slabs in the city center built in 80's; furnished with a leather sofa	60	natural	4	no animals
A2	two-room apartment on the 2nd floor, block of flat built in 70's	50	natural	2	cat
A3	apartment on the 2nd floor of a pre-war building	59	natural	3	no animals
A4	two-storey detached house built in 70's, near the industrial site (new windows)	150	natural	4 (one smoking person)	cat
A5	one-room apartment located on the 1st floor in block built in 80's	25	natural	2	no animals

In the research, the presence of heavy metals like tin, lead, chromium, zinc and cadmium was analyzed. The dust samples used in the study were taken from vacuum bags used in those particular apartments. Vacuum cleaners were with HEPA filters. In each apartment were carpets. The owners were asked to vacuuming at least once a week. The resulting material was sieved into different ranges of particle size (< 20, 20–25, 25–50, 50–100, 100–125 microns) using vibratory (GmbH &

Co.KG. Han) and pneumatic (HOKOSAWA ALPINE AG 200 LS) sieve shakers. The first process that dust samples were subjected to is the process of mineralization. This process was performed with the use of microwave digestion system Multiwave 3000 Microwave Anton Paar Company. In each range of particle size approximately 0.3 g of dust were measured and then introduced to a reaction flask. Then, 6 cm^3 of 65% HNO_3, 1 cm^3 of 30% HCl, 0.5 cm^3 49% HF and 1 cm^3 of 30% H_2O_2 were added to the dust samples. The process was conducted at the temperature of 160°C and a pressure of about $2x10^6$ Pa. After 55 minutes, 3 cm^3 of H_3BO_3 were added to the samples and mineralization process was continued in microwave mineralizer for 50 minutes. After mineralization, the samples were analyzed with the use of chemical technique ICP-OES 3000 conducted on sequential spectrometer ISA JobinYvon– JY 238 ULTRACE.

3. Results and discussion

The average concentrations of Sn, Pb, Cr, Zn, Cd in the indoor dust samples are summarized in Table 1. For all investigated metals the smallest range of particle size (<20 μm) achieved the highest average concentration. The concentrations of heavy metals in indoor dust from homes ranged from 3.5 to 27.26 mg/kg dust for Sn, from 17.21 to 113.40 mg/kg dust for Pb, from 30.76 to 172.82 mg/kg dust for Cr, from 198.30 to 1782.93 mg/kg dust for Zn, from 0.52 to 13.41 mg/kg dust for Cd. Sn, Pb, Cd obtained maximum concentration value for range of particle size lower than 20 μm, while Cr and Zn for 125–100 μm. When it comes to the minimum value, Sn, Cr, Zn, Cd reached it for range of 125–100 μm and Pb for 50–25 μm.

Figure 2 shows the measured concentration of Sn in different ranges of particle size. The highest concentration was achieved in apartment A4, while the lowest in A5.

When it comes to Pb, in the past it was a universal pollutant in an urban environment due to automobile emission [4]. Despite the gradual shift from leaded to unleaded petrol used as fuel for automobile, it still remains a major pollutant in some urban areas. Currently, additional research should be conducted to establish the source of this metal. The highest concentration of Pb were observed in apartments A1 and A4

(Fig. 3). In the case of the apartments A1 and A2, there was an upward trend with decreasing particle size distribution of the settled dust.

It is believed that car components, tires abrasion, lubricants, corrosion of cars, engine wear, thrust bearing, brushing, bearing metals and brake dust constitute the source of Cr in dust [2–4]. The highest concentration of Cr (Fig. 4) was noted in the apartment A1, which is located in the central part of the city. This component may have got into the apartment probably through an opened window or gravity ventilation system. Additional research should be conducted to establish the source of this element. The apartments A2, A3 and A5 reached the maximum concentration value for range lower than 20 µm.

In the case of Sn and Pb, the apartments with the highest number of residents (A1 and A4) obtained higher concentrations of those heavy metals. While recognizing the fact that the movement of occupant's in and out from building also contributed the heavy metals concentration in the building, its contribution was less obvious from the contribution from ambient sources [15]. Further studies are planned to analyze the sources of these metals.

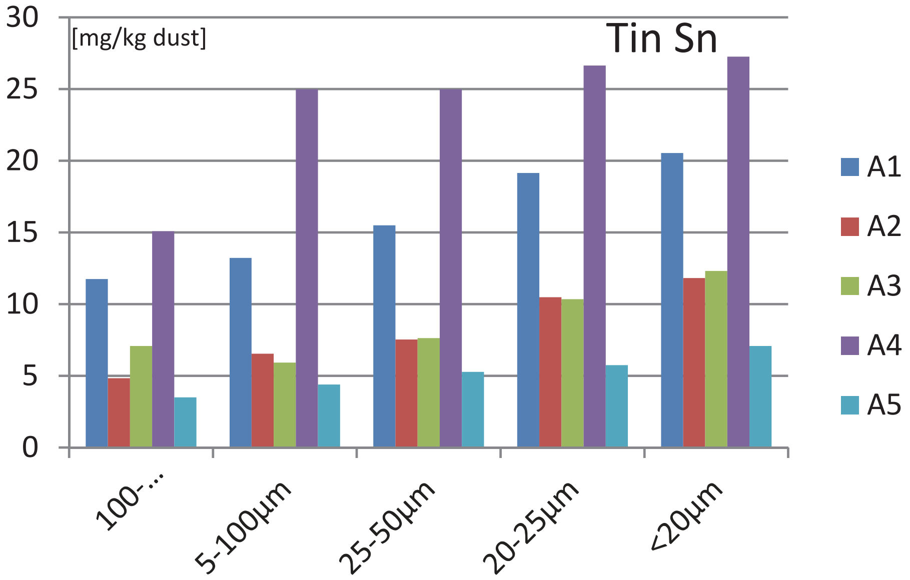

Fig. 2. Concentration of tin with respect to particle size range
Rys. 2. Stężenie cyny w zależności od zakresu wielkości cząstek

Table 2. Descriptive statistics of indoor dust heavy metal concentration
Tabela 2. Zestawienie stężenia metali ciężkich w kurzu domowym

		125–100 μm	100–50 μm	50–25 μm	25–20 μm	<20 μm
Sn	Min. [mg/kg dust]	3.50	4.39	5.27	5.74	7.08
	Max. [mg/kg dust]	15.08	24.99	24.98	26.64	27.26
	Average [mg/kg dust]	8.45	11.01	12.18	14.47	15.80
	Median	7.07	6.54	7.63	10.48	12.31
	Standard deviation	4.34	7.62	7.28	7.47	7.18
Pb	Min. [mg/kg dust]	18.50	20.51	17.21	21.35	29.97
	Max. [mg/kg dust]	80.51	100.79	96.28	93.69	113.40
	Average [mg/kg dust]	40.14	43.43	47.55	56.93	68.43
	Median	39.55	29.22	36.21	50.74	65.38
	Standard deviation	21.95	30.11	29.65	30.54	33.19
Cr	Min. [mg/kg dust]	30.76	32.27	42.44	47.40	57.27
	Max. [mg/kg dust]	172.82	114.17	92.93	80.21	133.40
	Average [mg/kg dust]	65.08	67.67	61.49	69.08	84.40
	Median	34.79	59.42	57.12	70.27	74.33
	Standard deviation	54.38	27.00	17.72	11.62	27.53
Zn	Min. [mg/kg dust]	198.30	296.72	434.68	425.09	502.41
	Max. [mg/kg dust]	1782.93	1518.13	1137.00	1239.09	1380.40
	Average [mg/kg dust]	721.71	676.30	621.22	694.12	819.12
	Median	588.88	522.41	482.87	574.80	689.64
	Standard deviation	555.04	430.63	264.62	289.96	300.17
Cd	Min. [mg/kg dust]	0.52	0.59	0.53	0.73	0.88
	Max. [mg/kg dust]	7.38	9.05	9.67	12.30	13.41
	Average [mg/kg dust]	2.59	2.81	3.29	4.23	5.10
	Median	1.25	1.40	2.03	3.14	4.17
	Standard deviation	2.59	3.15	3.32	4.17	4.47

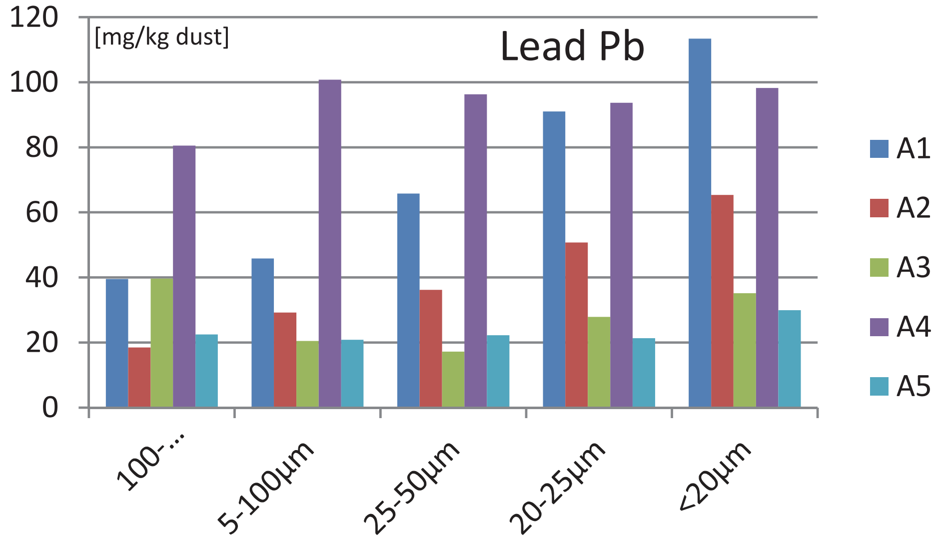

Fig. 3. Concentration of lead with respect to particle size range
Rys. 3. Stężenie ołowiu w zależności od zakresu wielkości cząstek

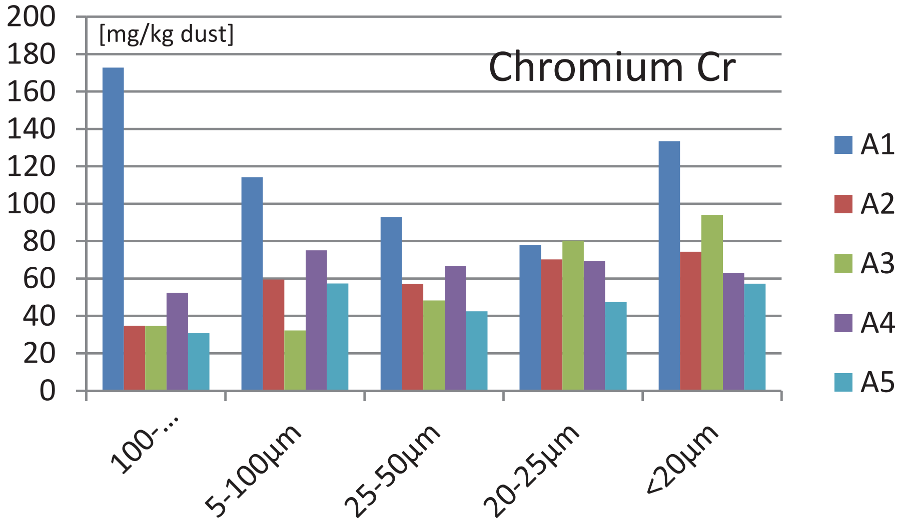

Fig. 4. Concentration of chromium with respect to particle size range
Rys. 4. Stężenie chromu w zależności od zakresu wielkości cząstek

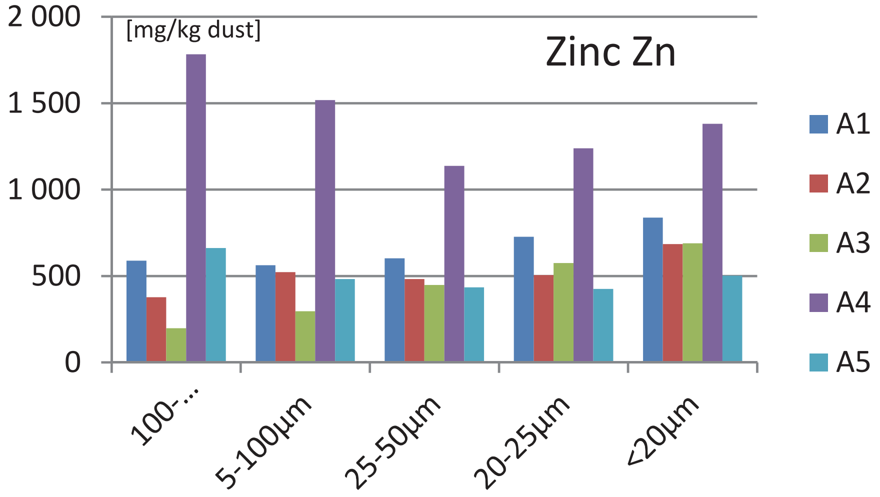

Fig. 5. Concentration of zinc with respect to particle size range
Rys. 5. Stężenie cynku w zależności od zakresu wielkości cząstek

Zinc is the fourth most common metal in use, as zinc oxide is widely used as a white pigment in paints. Zinc chloride is often added to lumber as a fire retardant and can be used as a wood preservative. Also zinc could be used as a vulcanization agent in tires. Moreover rubber carpets were identified as a significant source of zinc [13]. Figure 5 shows the concentration of Zn in different ranges of particle size. The highest concentration was achieved in apartment A4, while the lowest in A3. Probably the results were caused by the location of the apartments and varieties of furniture.

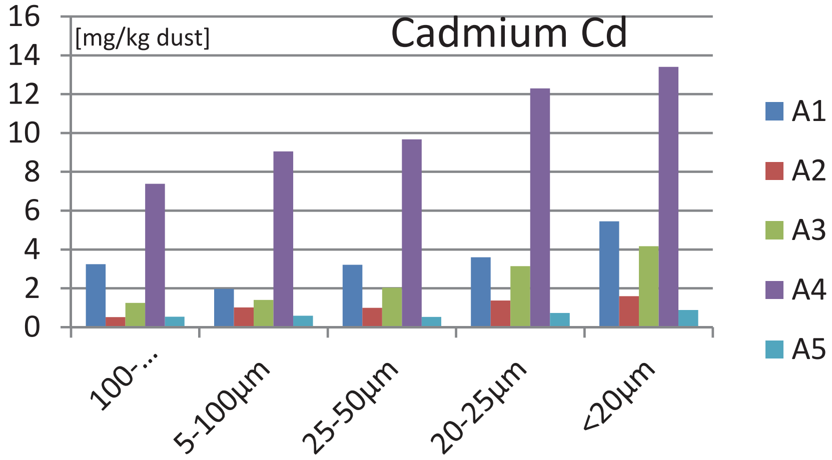

Fig. 6. Concentration of cadmium in different ranges of particle size
Rys. 6. Stężenie kadmu dla różnych zakresów wielkości cząstek

In the case of Cd ambient is not only likely source of cadmium in indoor air. Indoor sources, such a smoking and the agents used to color carpets and furniture, could result in increased cadmium in house dust. Figure 6 shows the concentration of Cd in different ranges of particle size. The highest concentration was achieved in apartment A4, while the lowest in A5. Similar like in the case of Zn results could be caused by the location of the apartments and varieties of furniture. Further studies are planned to analyze the sources of these metals.

4. Summary

Distribution of Sn average concentration in samples was characterized by an upward trend with decreasing particle size distribution of the settled dust.

The concentration of chromium in the tested material is higher in smaller ranges of particle size (except for the apartment A1).

Results reveal that the average concentration of all investigated metals in the dust samples was found in order Zn > Cr > Pb > Sn > Cd.

Monitoring plan is necessary to evaluate the evolution of metal concentration in dust in order to develop the proper measures for reducing the risk of inhalation.

Further studies are planned to analyze a larger number of apartments and sources of heavy metals in indoor dust.

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References

1. **Acosta J.A., Cano A.F., Arocena J.M., Debela F., Martinez-Martinez S.:** *Distribution of metals in soil particie size fractions and its implication to risk assessment of playground in Murcia City, Spain*. Geoderma 149, 101–109 (2009).
2. **Al-Khashman O. A.:** *The investigation of metal concentrations in street dust samples in Aqaba city, Jordan*. Environmental Geochemistry and Health, 29, 197–207 (2007).
3. **Al-Khashman, O.A.:** *Heavy metal distribution in dust, street dust and soils from the work place in Karak Industrial Estate, Jordan*. Atmospheric Environment, 38, 6803–6812 (2004).
4. **Al-Rahji, M.A., Seaward M.R.D.:** *Metal level in indoor and outdoor dust in Riyadh, Saudi Arabia*. Environmental International, 22 (3), 315–324 (1996).
5. **Amato F., Pandolfi M., Viana M., Querol X., Alastuey A., Moreno T.L.:** *Spatial and chemical patterns of PM10 in road dust deposited in urban environment*. Atmospheric Environment 43, 1650–1659 (2009).
6. **Beamer P., Key M.E., Ferguson A.C., Canales R.A., Auyeung W., Leckie J.O.:** *Quantified activity pattern data from 6 to 27 month-old farmworker children for use in exposure assessment*. Environmental Research 108, 239–246 (2008).
7. **Boruszko D.:** *Fractionation of Heavy Metals in Sewage Sludge Processed by Low-input Methods*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 1778–1803 (2013).
8. **Butte, W., Heinzow, B.:** *Pollutants in house dust as indicators of indoor contamination*. Reviews in Environmental Contamination and Toxicology 175, 1–46 (2002).
9. **Cholewa T., Pawłowski A.:** *Zrównoważone użytkowanie energii w sektorze komunalnym*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 11, 1165–1177 (2009).

10. **D'Hollander W., Roosens L., Covaci A., Cornelis C., Reynders H., van -Campenhout K., de Voogt P., Bervoets L.:** *Brominated flame retardants and perfluorinated compounds in indoor dust from homes and offices in Flanders, Belgium*. Chemosphere 81, 478–487 (2010).
11. **Edwards, R.D., Yurkow, E.J., Lioy, P.J.:** *Seasonal deposition of housedusts onto household surfaces*. The Science of the Total Environment 224, 69–80 (1998).
12. **Irvine, K.N., Loganathan, G.G.:** *Localized enrichment of PCB levels in street dust due to redistribution by wind*. Water Air and Soil Pollution 105(3–4), 605–615 (1998).
13. **Jarup L.:** *Hazards of metal contamination*. Brazilian Med. Bull. 68, 425–462 (2003).
14. **Kim N., Fergusson J.:** *Concentrations and sources of cadmium, copper, lead and zinc in house dust in Christchurch, New Zealand*. Science of The Total Environment 138, 1–21 (1993).
15. **Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., and Engelmann W.H.:** *The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants*. J. Exposure Analysis and Environmental Epidemiology, 11, 231–252 (2001).
16. **Komarnicki, G.J.K.:** *Lead and cadmium in indoor air and the urban environment*. Environmental Pollution, 136, 47–61 (2005).
17. **Mashi S.A., Yaro S.A., Eyong P.N.:** *A survey of Trends Related to the Contamination of street dust by heavy metals in Gwagwalada, Nigeria*. Int. J. Environ. Qual., 16(1), 71–76 (2005).
18. **Mitchell C.S., Ahang J.J., Sigsgaard T., Jantunen M., Lioy P.J., Samson R., et al.:** *Current state of the science: health effects and indoor environmental quality*. Environmental Health Perspective 115, 958–964 (2007).
19. **Ociepa E.**, **Ociepa-Kubicka A., Okoniewska E., Lach J.:** *The immobilization of Zinc and Cadmium in the Soil as a Result of the Use of Waste Substrates*. Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 15, 1772–1786 (2013).
20. **Parker J. L., Larson R. R., Eskelson E.,Wood E. M., Veranth J. M.:** *Particle size distribution and composition in a mechanically ventilated school building during air pollution episodes*. Indoor Air 18, 386–393 (2008).
21. **Sharpe, M.:** *Safe as houses? Indoor air pollution and health*. J. Environmental Monitoring, 6, 46–49 (2004).

22. **Silva A.L.O., Barrocas PRG, Jacob S.C., Moreira J.C.:** *Dietary intake and health effects of selected toxic elements*. Braz. J. Plant Physiol. 17, 79–93 (2005).
23. **Siuta-Olcha A., Cholewa T.:** *Energy saving and storage in residential buildings*. Nova Science Publisher. 978-1-62100-167-6, 2012.
24. **Sojka M., Siepak M., Gnojska E.:** *Assesment of Heavy Metal Concentration in Bottom Sediments of Stare Miasto Pre-dam Reservoir on the Powa River*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 1916–1928 (2013).
25. **Staszowska A., Połednik B., Dudzińska M.R., Czerwiński J.:** *Commercial Penta-BDE Mixtures in Dust Samples from Indoor Environments in Lublin – A Case Study*, Archives Environ. Prot., 34 (3), 239–247 (2008).
26. **Toms L.M.L., Bartkow M., Symons R., Paepke O., Mueller J.F.:** *Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia*. Chemosphere 76, 173–178 (2009).
27. **Tong, S.T.Y., Lam, K.C.:** *Home sweet home? A case study of household dust contamination in Hong Kong*. The Science of the Total Environment 256, 115–123 (2000).
28. **Wang J., Ma Y.M., Chen S.J., Tian M., Luo X.J., Mai B.X.:** *Brominated flame retardants in house dust from e-waste recycling and urban areas in South China: Implications on human exposure*. Environment International 36, 535–54 (2010).
29. **Ward I.N., Brooks R.R., Roberts E., Boswell C.:** *Heavy Metal Pollution from Automotive Emission and its Effect on Roadside Soils and Pastures in New Zealand*. Environmental Science Technology 1, 917–20 (1977).

Wybrane metale ciężkie w wysedymentowanym kurzu domowym z mieszkań zlokalizowanych w Lublinie, Polska

Streszczenie

Kurz domowy nie jest jednorodną substancją pod względem fizycznym czy chemicznym, ale stanowi bardzo niejednorodną mieszaninę cząstek organicznych, nieorganicznych i substancji chemicznych. Jego skład w budynku, czy nawet w pokoju będzie zależeć od wielu czynników, między innymi od lokalizacji obiektu, jego konstrukcji, rodzaju wykorzystania, umeblowania, materiałów użytych do wykończenia lub dekoracji, systemu ogrzewania i wentylacji, jak również od częstotliwości sprzątania czy pory roku.

Celem tych badań jest określenie stężenia Sn, Pb, Cr, Zn, Cd (cyny, ołowiu, chromu, cynku, kadmu) w kurzu domowym. Wybrane do badań metale ciężkie mają wysokość toksyczność. Długotrwała ekspozycja powoduje ich kumulację w organizmie. W ciągu ostatnich dziesięcioleci wzrosło zainteresowanie związane z narażeniem ludzi na substancje zawarte w kurzu domowym, zwłaszcza wśród grup szczególnie narażonych takich jak dzieci. Powodem jest ich zachowanie i odruchy związane z poznawaniem otoczenia (dotykanie przedmiotów, branie ich do ust). Dlatego w stosunku do swojej niskiej wagi ciała dzieci spożywają większe ilości pyłów niż osoby dorosłe. Ponadto gorzej tolerują większość zanieczyszczeń.

Przedmiotem badań był wysedymentowany kurz domowy zbierany w sezonie grzewczym z 5 mieszkań zlokalizowanych w Lublinie. Próbki pobierano z worków odkurzaczy. Uzyskany materiał przesiewano do różnych zakresów wielkości cząstek (< 20, 20–25, 25–50, 50–100, 100–125 mikrometrów) za pomocą przesiewacza wibracyjnego i pneumatycznego.

W przypadku wszystkich badanych metali najmniejszy zakres wielkości cząstek (< 20 mikrometrów) osiągnął największe średnie stężenia. Stężenie metali ciężkich w kurzu domowym wahało się od 3,5 do 27,26 mg/kg kurzu dla Sn, od 17,21 do 113,40 mg/kg kurzu dla Pb, od 30,76 do 172,82 mg/kg kurzu na Cr, od 198,30 do 1782,93 mg/kg kurzu dla Zn, od 0,52 do 13,41 mg/kg kurzu dla Cd. Sn, Pb, Cd uzyskało maksymalną wartość stężenia dla zakresu wielkości cząstek poniżej 20 mikrometrów, a Cr i Zn dla 125-100 mikrometrów. Jeśli chodzi o wartości minimalne Sn, Cr, Zn, Cd osiągnęły ją dla zakresu 125–100 mikrometrów a Pb dla 50–25 mikrometrów. Wyniki pokazują, że średnie stężenie wszystkich badanych metali w kurzu wystąpiło w kolejności Zn > Cr > Pb > Sn > Cd.

Koniecznym staje się opracowanie sposobu monitorowania i oceny zmian stężenia metali w kurzu w celu opracowania odpowiednich środków zmniejszających ryzyko narażenia.

Słowa kluczowe:
stężenie metali ciężkich, cyna, ołów, chrom, cynk, kadm, kurz domowy

Keywords:
heavy metal contamination, tin, lead, chromium, zinc, cadmium, house dust

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Possibilities of Coffee Spent Ground Use as a Slow Action Organo-mineral Fertilizer

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1. Introduction

The purpose of soil fertilization is the provision of nutrients essential to plants in order for them to develop normally, fruit optimally and improve biological and chemical as well as physical characteristics of the soil in a range that is desirable for plants. A shortage of nutrients in soil might lead to the loss of crops. Over-fertilization might also lead to a reduction of crops, a decrease in their value, a rise in production costs and pollution of the environment. In Poland nearly 2,000,000 Mg of mineral fertilizers are used every year, though the most essential for soil fertility is natural fertilization [21].

Due to the fact that natural fertilizers gradually release nutrients to soil solution, they become a valuable source of organic matter and elements important for cultivation. They also improve the structure of the soil. Among the organic fertilizers most commonly used are: manure, slurry, green manure, post-fermentation waste and compost. Biodegradable wastes might be disposed through various methods, though they might be rarely used in an unprocessed form [13]. In case of natural fertilizers/recycled materials exploitation the only threat to cultivation is the possibility of bringing large quantities of heavy metals and organic compounds to the soil, which then might be absorbed by plants [10, 22]. A significant simplification of fertilizers usage in private gardens and potted cultivation is possible through the application of fertilizers in the form of tablets. However, to make fertilization complete, one should also provide easily absorbed elements through the application of organic-mineral fertilizer. "A fertilizer" in which mineral material (A) has been mixed with organic coffee spent grounds (CSG) might make a crucial contribution to a sustainable fertilization, which might be performed even by unqualified individuals. Ashes formed during burning of biomass might be used as a source of mineral elements. Such ashes form not only in biomass power plants, but also in numerous private households. Biomass is becoming more and more popular source of energy, which is connected with the formation of large quantities of ashes. Polish energy policy for the subsequent years assumes a constant rise in renewable energy, which is going to simultaneously cause a rise in the forming of ash, including ash formed as a result of straw burning. The Polish agricultural sector produces approximately 200–300 million Mg of biomass, including 25 million Mg of straw [6, 16]. Around 740 thousand Mg of ash, ready to be used in fertilizer production, might be formed after its incineration. The properties of the ash, if well examined, allow to use it in industry or agriculture.

Similar attempts were made towards furnace ashes [1, 24, 25]. Usage of ash fertilizers has been known for many years, though nowadays ash from the incineration of plants fertilized with sewage sludge should be subject to detailed supervision [4]. The essence of a balanced organic-mineral fertilization is the possibility of usage of multi-component, long-acting fertilizer, which could be applied in the moment of sowing, planting or replanting. Research on the impact of natural waste fertilizers (sewage sludge, food industry wastes) on soil and crops quality has been carried out for years, also in the case of granulated fertilizers, but we wish to emphasize that tests of our unique fertilizer were taken in Poland for the first time [3, 17, 23, 24].

2. The legal basis

Polish law defines fertilizers in the Act of 10 July 2007 about fertilizers and fertilization (Reg. 2007 no. 147 item 1033) as mineral, natural, organic, mineral and organic-mineral fertilizers meant to provide nutrients to plants or increase the fertility of soils and fish ponds. Basic parameters (including content of heavy metals) setting the quality of fertilizers are included in the decree of the Minister of Agriculture and Rural Development of 21 December 2009 about the execution of some regulations of the act regarding fertilizers and fertilization (Reg. 2009 no. 224 item 1804). In case of tablet fertilizers, which are the subject of this paper, containment norms of elements and pollutions for organic fertilizers are to be applied. The definition of a biomass is included in the decree of the Minister of Environment of 20 December 2005 about emission standards (Reg. 2005 no 260 item 2181). According to the decree a biomass is a product entirely or partially consisting of plants, coming from agriculture or forestry, which are burned in order to recover energy within them. The term 'biomass' refers also to agricultural, forestry or food industry plant waste. According to this definition coffee spent grounds (CSG) are considered as a biomass.

3. Materials and methods

The research was carried out using coffee spent grounds, formed after the preparation of coffee (under pressure of 15 atmospheres), dried in the sun and then dried to a constant mass at a temperature of 105°C. Gelatin, available in the retail trade, was used as a binder. The binding gelatin solution was prepared through the soaking of a weighed amount of gelatin in cold deionized water. Thus the obtained gel was then put into boiling deionized water. The final volume of the binding solution was 180 cm^3, which means that it was 2.8 times more concentrated than a typical food gelatin solution. The mineral supplement was made of ash formed during the incineration of oak's biomass, while magnesium sulfate in a line of an anti-needle-browning fertilizer. The oak wood in the form of woodchips was incinerated with bark. In order to obtain ash the biomass was incinerated at a temperature of 600°C for 3 hours in the muffle furnace and then finished at the same temperature for 1 hour [27]. The ash (A), which had been formed that way, was sieved through a 2 mm sieve and then dried to a constant mass. Capsules were made from cellulose sheets and collagen stick, available in the retail trade in the form of orange-yellow pearls.

3.1. Types of fertilizer tablets

After initial experiments concerning the optimal composition of specific types of fertilizers, the proper mass proportions were set and 3 series of fertilizer tablets were made (Table 1), including: acid organic fertilizer (K0), neutral mineral-organic fertilizer (K10) and acid organic anti-needle-browning fertilizer (K12).

Table 1. Mass proportion of components in fertilizer tablets
Tabela 1. Proporcje masowe składników w tabletkach nawozowych

	Coffee spent grounds (CSG)	Biomass ash (A)	Magnesium sulphate (MS)	Gelatine
K0	10	0	0	1
K10	9	1	0	1
K12	9	0.1	0.9	1

3.2. Method of making fertilizer tablets

CSG dried to a constant mass were mixed with ash A and magnesium sulfate MS. Later hot gelatin solution was added and all ingredients were mixed together. Then the obtained hot substance was put into the plastic matrix. The matrix was cooled and kept at a temperature of 10°C for 6 hours and then dried for 24 hours at a temperature of 105°C. Consequently the obtained tablets were then removed from the matrix and covered with a double sheet of cellulose, dampened and dried at a temperature of 105°C for 2 hours. The tablets were then covered with a hot collagen stick solution and dried at room temperature for 24 hours.

The tablets' density, the content of organic substance by weight method and the content of organic carbon by non-dispersive infrared (NDIR) method, after sample mineralization at a temperature of 1200°C, were determined. The content of phosphorus and Kjeldahl nitrogen was determined after mineralization by sulfuric acid. The content of sodium, potassium and calcium was determined with mineral solutions by FES method with BWB XP apparatus. The content of magnesium and heavy metals like zinc, copper, lead, nickel, chromium and cadmium were determined by atomic absorption spectroscopy (AAS) method with iCE

Thermo 3500 apparatus after microwave mineralization with aqua regia in Mars-X apparatus.

In order to determine the initial release of nutrients, a water extraction was performed, according to the PN-Z-15009 norm. In the extracts pH, EC, content of organic carbon and nitrogen were determined by NDIR method, after sample mineralization at a temperature of 850°C. The content of phosphate and nitrate ions was determined by titration, while phosphate and calcium ions content were determined in mineral solutions by FES method with BWB XP apparatus.

The pot research was carried out during a period of 2 months on the area exposed to the sun, but protected from the wind. The pot's capacity was 2.75 dm^3. They were filled with ready-made garden substrate available in the retail trade. Two fertilizer tablets were put in to each pot, 7.6-8.2 g each. Doses of fertilizer ($N/P_2O_5/K_2O/CaO$) per hectare were: 139/34/24/5, 169/47/62/76 and 168/33/55/28 kg respectively for K0, K10 and K12. In the control group no fertilization was applied. The experiment was repeated three times for every fertilizer serie. The plant chosen for testing was cucumber. Four seeds were planted in every pot. During the experiment an even humidity was ensured through watering with rain water, if needed. After 60 days the above ground parts of the plants were harvested and dried to a constant mass.

4. Results and discussion

All the tablets, before being covered with cellulose and collagen, were characterized by a dark brown-black color and despite the identical way of production and same size of matrices, different types of tablets differed in both size and mass (Table 2).

Tablets K10 were the smallest, which was caused by the highest share of ash in their content, which, due to its binding properties, enabled the highest density of CSG. The highest mass was a characteristic for K12 line of tablets due to magnesium sulfate, the lowest – K0, which was a line without any additives. This also caused the highest share of implemented material in reference to the overall mass of a tablet, which was 76.6 and 68.7 respectively for K12 and K0.

Table 2. Basic characteristics of investigated fertilizer tablets and comparison with data obtained for composts and law requirements for organic fertilizers
Tabela 2. Charakterystyka badanych OPK, tabletek nawozowych K0, K10 I K12 oraz porównanie do danych uzyskanych dla kompostów i wymagań prawnych dla nawozów organicznych

	CSG	K0	K10	K12	Composts made of sewage sludge [5]	Composts [7]	Reg. 2009 no.224 item 1804
Dimensions (xyz) [mm]	–	25x25x19	20x20x15	23x23x18	–	–	
Mass of fertilizer [g]	–	5.33(0.13)	5.76(0.15)	6.28(0.54)	–	–	
Mass of tablet [g]	–	7.76(0.12)	7.67(0.25)	8.19(0.17)	–	–	
Organic substances [%]	98.4	98.5	92.3	95.6	–	7.5–67.0	30
TOC [%]	34.1	33.6	32.2	32.5	43.2–72.4[1]	3.1–25.8	
$N_{Kiejd.}$ [%]	0.72	1.75	2.16	2.01	1.16–2.74[1]	0.52–2.90	0.3
C/N	47.4	19.2	14.9	16.2	19.6–42.7		
CaO [g/kg dw]	0.57(0.12)	0.61(0.03)	9.69(0.18)	2.58(0.32)	10.6–58.7	16–92	
MgO [g/kg dw]	4.85(0.59)	5.07(0.43)	6.57(0.02)	156(21.4)	1.8–11.5	–	
Na_2O [g/kg dw]	1.30(0.16)	1.32(0.26)	1.76(0.09)	1.56(0.03)	–	–	
K_2O [g/kg dw]	3.05(0.18)	3.00(0.21)	7.97(0.01)	3.29(0.10)	–	3.2–7.8	2.0
P_2O_5 [g/kg dw]	4.54(0.81)	4.35(1.0)	6.03(0.70)	3.97(1.13)	24.1–55.8	7.6–16.0	2.0

[1] *– data concerns TC and TN parameters.*
SD value in brackets

The content of organic matter in the examined tablets was high (above 90%), which is particularly crucial in the case of fertilizing sand soils, and have a limited time of holding water. The content of fat in the implemented fertilizer might strengthen water retention in the soil, which was confirmed during the field research using sewage from olive oil mill [3]. Poor substrates used in gardening do not only allow us to lower costs, but also limit the consumption of nonrenewable peat resources. Gelatin, used in the process of tablets creation, plays a crucial role not only as a binder for CSG and A, but also as a source of organic matter and nitrogen in a form that is possible for plants to absorb. It is important that the tablets' covers consist mainly of collagen, which is rich in organic carbon (37.1%) and, while swelling, slowly melts into the soil. The organic substance, being slowly mineralized, simultaneously releases elements into the soil, thus preventing over-fertilization and significantly prolonging the fertilizer's uptime. Due to this fact the assumed fertilizer's uptime exceeds 6 months. Another asset of the examined tablets is also the fact that in a case of drought the collagen covering hardens and consequently does not release the elements from the tablets filling. An important asset is also high (above 30%) content of organic carbon – a value comparable with the one in manure and higher than noted in composts [20].

The content of Kjeldahl nitrogen is similar in all 3 lines of tablets (lowest in K0) and is comparable with good quality compost. Examination of the nitrogen content in the tablets' filling indicated the highest amount of this element in K10 line (1.45% of the filling), with lower amounts in K12 and K0 (respectively 0.84% and 0.74% of the filling). The nitrogen content is high and it fulfills the demands of the Decree of the Minister of Agriculture and Rural Development about the execution of some regulations of the act regarding fertilizers and fertilization (Reg. 2009 no. 224 item 1804). An occurrence of this element in organic form ensures a balanced and slow release of it into the soil, which not only has a positive effect on long-range fertilization by preventing leaf chlorosis, but also prevents the leaching of the element into the groundwater.

The content of calcium (Table 2) is, as planned, highest in the line K10 and lowest in the line K0, intended for acidophilic plants, in case of which an excess of this element could have a negative effect by rising the pH of the substrate. The main calcium source in the fertilizer is the biomass ash, which mixed with CSG and bound with gelatin is relatively resistant to quick leaching, having a positive effect on the pH of the soil and contributing to the reduction of the availability of heavy metals for the plants, as well as the interchangeable aluminum activity [8, 12]. In the K10 line, designed as a neutral fertilizer proper for most plants, the content of calcium is relatively high; lower though than in composts and organic fertilizers (manure). Stabilization of pH is an important element of farming due to the fact of its' limited ability to absorb heavy metals.

The source of magnesium in the analyzed samples is magnesium sulfate (K12 line), as well as both the biomass ash and collagen covering. Content of MgO exceeding over 15% is favorable here, due to the fact of the crucial role of these elements in building chlorophyl, as well as its vulnerability to leaching. In both K0 and K10 lines the magnesium content is much lower and does not exceed 1%. Yet even in the case of fertilizer K12 the complex structure of the tablets ensures its slow release into the soil, which prevents losses caused by leaching.

The content of potassium is high in all types of tablets. Although the highest amount of this element (nearly 8 g K_2O/kg) was found in K10 line, no differences were noted between series K0 and K12. It shows a high share of organic potassium, which is favorable due to its slow release during mineralization of the tablets' organic matter. In all the series the content of potassium fulfills the regulations for organic fertilizers.

The content of phosphorus is interesting. The carried out tests of the tablets filling, as well as the finished product in covering, show that the main source of this element in all three lines is the filling material. Regardless of the line, the content of phosphorus in the finished product is 60.3% (0.45) in relation to the content of this element in the filling. The content of phosphorus is similar in K0 and K12 lines and about 40% higher in K10, which indicates the presence of mineral phosphorus. Phosphorus from the biomass ash is characterized by a limited solubility, which limits its absorption, though the presence of an organic phosphorus shall, to a large extent reduce shortages of this element [9]. The content of phosphorus in the tablets fulfills the regulations of the Decree Reg. 2009 no. 224 item 1804.

The heavy metals content in the examined types of fertilizers is presented in the Table 3. An addition of a biomass ash stabilizes the pH of a given fertilizer and also serves as a source of elements crucial to plants' metabolism [15]. The results show that the ash is a donor of those elements, though designated numbers are low and thus even in the line with the highest share of the biomass ash there is no risk of soil and plant pollution with toxic metals (Pb, Ni, Cr, Cd). It is possible then to use tablets in the farming of vegetables for direct use.

Table 3. Heavy metals content in biomass ash, investigated fertilizer tablets, composts and maximum levels for organic fertilizers [mg/kg dw]
Tabela 3. Zawartość metali ciężkich w popiele z biomasy, badanych tabletkach nawozowych, kompostach oraz dopuszczalne poziomy dla nawozów organicznych [mg/kg sm]

	A	K0	K10	K12	Composts [7]	Reg. 2009 no. 224 item 1804
Zn	609(117)*	25.3(1.79)	53.0(2.86)	25.9(2.65)	277-1756	–
Cu	121(9.6)	7.84(1.05)	14.6(0.71)	7.08(0.03)	36.3-283	–
Ni	19.0(4.4)	0.31(0.11)	1.06(0.07)	0.45(0.24)	11.3-217	60
Pb	23.0(2.3)	<0.03	1.63(0.23)	<0.03	24.6-545	140
Cd	1.72(0.48)	0.07(0.04)	0.15(0.04)	0.04(0.02)	<0.5-4.28	5
Cr	20.5(4.7)	<0.03	<0.03	<0.03	22.4-79.8	100
Mn	2481(403)	11.7(0.31)	281(31.2)	39.4(1.31)	–	
Fe	1217(328)	30.3(0.02)	130(7.3)	40.4(1.02)	–	

** SD value in brackets*

Regulations of the Decree of the Minister of Agriculture and Rural Development regarding the execution of some regulations of the act regarding fertilizers and fertilization (Reg. 2009 no. 224 item 1804) set a maximum content of nickel, cadmium, chromium, lead and mercury in organic fertilizers. The noted concentrations are 33–85 times lower than the norms in the Decree. Organic fertilizers (e.g. manure) might contain higher amounts of those elements, which is potentially dangerous for cultivated plants [26]. It confirms the validity of the usage of fertilizer tablets analyzed herein, which are based on materials nearly entirely free of metal pollutions. It is assumed that a number of bio-available metals in the examined fertilizers will not exceed 40–50% of their overall content, which in future should be confirmed or negated through specialist research [22, 24]. From the perspective of plants metabolism content of iron is particularly important. Its shortage (besides lack of magnesium and nitrogen) is the main reason for chlorosis.

The results of the leaching test provide only initial information about the number of elements released to the aqueous solution during the first 24 hours (Table 4). The shaking caused a partial disintegration of K0 line tablets and, to a smaller extent, K12 line of tablets. It depicts a strong binding of K10 tablets' filling, including ash with CaO. It was indicated that although the supplementation of the biomass ash provides water-soluble elements, they are released gradually into the soil due to the slow decomposition of the fertilizer tablet observed during the experiment. The final content of elements released into the soil (in the moment of making an extraction) will depend also on the precision of the covering creation, as well as on the time required for the mineralization of organic compounds in the examined tablets; in the case of gardening fertilizer tablets, both mineral and organic.

Table 4. Characteristic of water extract of investigated fertilizer tablets
Tabela 4. Charakterystyka wyciągu wodnego z badanych tabletek nawozowych

	K0	K10	K12
Reaction (pH)	5.39	6.91	5.65
EC [mS/cm]	1.21	1.20	3.29
N_{Kiejd} [mg/dm^3]	874.0	615.2	617.7
NO_3^- [mg/dm^3]	24.9	8.55	22.9
PO_4^{-3} [mg/dm^3]	54.3	20.7	36.0
K^+ [mg/dm^3]	230	378	252
Ca^{2+} [mg/dm^3]	44.1	63.2	113.5
Na^+ [mg/dm^3]	192	116	132
TOC [g/dm^3]	4.408	2.970	2.985

Crucial parameters (applied also to rare and valuable plants) are: pH and electrolytic conductivity. The series of initial experiments enabled to optimize an amount of biomass ash, which opened the possibility of producing tablets of adequately low pH (proper for acidophilic plants) in case of K0 line, as well as of neutral pH in case of K10 line (a universal fertilizer for most plants). K12 line has acidic pH and the supplement of magnesium sulfate fills in the lack of magnesium ions, thus preventing needle chlorosis (Table 1). According to Arvidsson, Lundkvist [2], Park et all [19] a tree ash alkalizes a soil, enlarges cation-exchange capacity and maximum level of alkaline cations, although a significant rise of pH might cause iron to move to its +3 form, which might cause a lack of this element [2, 19].

Soil salinity caused by an overdose of mineral fertilizers results in deteriorated growth and even in the death of plants [18]. The essence of the proposed "fertilizer" is then a slow release of minerals within it, in order to limit leaching of elements and enable plants to absorb them. Electrolytic conductivity of K0 and K10 fertilizer lines is similar, although probably it is a result of a lack of decomposition of the tablets. It is supposed that after decomposition of K10 tablets, the amount of ions released to the solution should rise. The test confirmed the stability of the examined tablets. In case of K12 line, as an effect of magnesium sulfate supplement, the electrolytic conductivity is too high, i.e. 3,29 mS/cm, which, in the case of an overdose, might cause harmful soil salinity. It is especially important in the case of plants of limited demand for fertilizers and it also happens while applying commercial, long-lasting fertilizers [11]. A strong rise of conductivity was noted also after modifying ash-sewage sludge granules (coal ash + municipal sewage sediments) with potassium salts (KCl and K_2SO_4). The noted conductivity was 44 mS/cm [23]. the small amount of nitrate ions released into the solution is particularly important in the analyzed fertilizers. NO_3^- ion is not subject to exchangeable sorption in the soil and thus it is vulnerable to leaching [28]. Nitrogen in the analyzed fertilizer tablets is almost entirely organic, which limits its losses and positively influences its slow release, replacing the partition of a basic dose of a traditional fertilizer (manure, slurry) on a few portions, which always makes additional courses of a spreader necessary. Such courses are not always possible due to environmental conditions, e.g. ground humidity or a rise of production costs [14]. An additional asset is the possibility to apply the fertilizer in the moment of planting, because of the delayed release of compounds, which enables the regeneration of the root system.

The high content of calcium in the solution of K12 line tablets is interesting. Despite the lower content of this element in the tablets concentration of Ca^{2+} ions, in the solution was nearly two times higher. This can be explained by the higher stability of K10 tablets and, in consequence, lower release of calcium during shaking. The content of calcium might also have an influence on the relatively high crops in the pot experiment.

The initial pot research showed the stability of the fertilizer tablets during the period of two months. While analyzing roots, many healthy, small roots were noted to overgrow the fertilizer tablets. The applied fertilization on the level of the maximum allowed dose of nitrogen (170 kg N/ha) did not show an ecotoxic influence [28]. The obtained biomass of cucumber shoots was higher than in the control group: 1.6, 2.6 i 2.4x respectively for the lines K0, K10 and K12. Although in the case of K10 line crop mass was the highest (an average 5.4 g dw/shoot), the more balanced results were attained due to the slightly lower mass of the K12 line. Standard deviation value was 0.61 for K12 and 1.74 for K10. It shows a cucumber's invulnerability to low pH and salinity higher than in K0 and K10, characteristic for K12 fertilizer.

5. Conclusion

1. Fertilizer tablets, very popular in both professional and amateur gardening, are usually products of a big gardening company, characterized by a relatively high price. An important alternative for them would be the possibility of producing them on one's own or in small, family companies operating in a local market.
2. In the process of tablet production the main component of the fertilizer might be cumbersome and easily rotting coffee spent ground. Production of fertilizer tablets from CSG, biomass ash and magnesium sulfate not only allows it to lower the mass of produced wastes, but might also contribute to improving the productivity of soils.
3. These fertilizers, rich in nitrogen, potassium, calcium and organic substance, decompose slowly, which is essential from the point of view of nutrients' availability (usually in the organic form).
4. Slow decomposition of tablets prolongs the time of the fertilizer's influence, which gradually releases elements, according to the rules of constant and balanced development.
5. The low content of heavy metals proves the high quality of the analyzed fertilizers, which enables them to be used in the cultivation of edible plants. These fertilizers used in professional or amateur gardening, might significantly lower cultivation costs, due to the possibility

of fertilization only once a season - in the moment of planting or sowing. It is particularly important in the case of plants cultivated in containers, in which fertilization is time-consuming and the possibility of using a poor mineral substrate might contribute to lowering production costs and minimizing the environmental pressure through limitation of peat exploitation - the material which is now commonly used in the production of gardening subtracts.

References

1. **Antonkiewicz J.:** *Wykorzystanie popiołów paleniskowych do wiązania metali ciężkich występujących w glebie*. Ochrona Środowiska i Zasobów Naturalnych, 41, 398–405 (2009).
2. **Arvidsson H., Lundkvist H.:** *Effects of crushed wood ash on soil chemistry in young Norway spruce stands.* For. Ecol. Manage., 176, 121–132, (2003).
3. **Barbera A.C., Maucieria C., Cavallarob V., Ioppoloa A., Spagna G.:** *Effects of spreading olive mill wastewater on soil properties and crops, a review.* Agricultural Water Management, 119 43–53, (2013) http://dx.doi.org/10.1016/j.agwat.2012.12.009.
4. **Bielicka A., Bojanowska I., Krupa A., Schuetz P., Leszczyński J.:** Biomasa – produkt II stopnia oczyszczania ścieków jako źródło energii odnawialnej. Ochrona Środowiska i Zasobów Naturalnych, 31, 296-301, (2007).
5. **Boruszko D.:** *Badania i ocena wartości nawozowej kompostów i wermikompostów*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 13, 1417–1428 (2011).
6. **Bzdawka-Piątkowska K.:** *Stan obecny i perspektywy rozwoju energetyki odnawialnej w Polsce.* Ochrona Środowiska i Zasobów Naturalnych, 33, 20–26, (2007).
7. **Ciesielczuk T., Rosik-Dulewska Cz., Karwaczyńska U.:** *Komposty z odpadów jako potencjalne źródło substancji organicznej i biogenów w produkcji roślinnej.* (w) Kompostowanie i mechaniczno-biologiczne przetwarzanie odpadów (red.) G. Siemiątkowski, 108–116, Opole (2011).
8. **Ciba J., Skwira M., Zołotajkin M.:** *Wpływ wybranych substancji chemicznych na zawartość glinu wymiennego i pH gleb leśnych – przegląd literaturowy*. Ochrona Środowiska i Zasobów Naturalnych, 31, 63–67, (2007).
9. **Demeyer A., Voundi Nkana J.C., Verloo M.G.:** *Characteristics of wood ash and influence on soil properties and nutrient uptake: on overview*. Bioresource Technol., 77, 287–295 (2001).

10. **Fekri M., Kaveh S.:** *Heavy metal accumulation in soil after application of organic wastes*. Arab J Geosci 6, 463–467, 2013DOI 10.1007/s12517-011-0328-1
11. **Golcz A., Komosa A.:** *Uwalnianie się azotu, fosforu i potasu z nawozu wolnodziałającego osmocote plus w uprawie papryki (Capsicum annuum L.)* Acta Agrophysica, 7(3), 567–576 (2006).
12. **Hermann J., Harasimowicz-Hermann G.:** *Przydatność popiołów ze spalania biomasy do stosowania w rolnictwie i rekultywacji gruntów*. Inżynieria Ekologiczna, 12, 195–196 (2005).
13. **Kazimierowicz J.:** *Organic waste used in agricultural biogas plants***.** Journal of Ecological Engineering Volume 15, No. 2, April 2014, pp. 88–92. DOI: 10.12911/22998993.1094983
14. **Krawczyk W., Walczak J., Paraponiak P., Dąbrowska-Wieczorek M., Herbut E.:** *Determining the burden of organic fertilizers on the soil and water environment*. Rocz. Nauk. Zoot., 40, 2 209–226 (2013).
15. **Kucharski J., Jastrzębska E.:** *Liczebność drobnoustrojów i właściwości fizyko-chemiczne gleby zanieczyszczonej popiołem drzewnym*. J. Elementol., 10(3), 513–525 (2005).
16. **Kwaśniewski D.:** *Ocena produkcji i potencjalnych możliwości wykorzystania słomy do celów grzewczych na przykładzie powiatu żywieckiego*. Inżynieria Rolnicza, 6, 113–119 (2008).
17. **Ociepa-Kubicka A., Pachura P.:** *Wykorzystanie osadów ściekowych i kompostu w nawożeniu roślin energetycznych na przykładzie miskanta i ślazowca.* Rocznik Ochrona Środowiska, 15, 2267–2278 (2013).
18. **Mazur Z., Radziemska M., Tomaszewska Z., Świątkowski Ł.:** *Effect of sodium chloride salinization on the seed germination of selected vegetable plants*. Scientific Review – Engineering and Environmental Sciences, 62, 444–453 (2013).
19. **Park B.B., Ruth D.Y., James M.S, Don K.L., Lawrence P.A.:** *Wood ash effects on plant and soil in a willow bioenergy plantation*. Biomass Bioenerg., 28(4), 355–365 (2005).
20. **Poulsen P.H.B., Magid J., Luxhøi J., de Neergaard A.:** *Effects of fertilization with urban and agricultural organic wastes in a field trial - Waste imprint on soil microbial activity*. Soil Biology & biochemistry 57 794e802 doi:10.1016/j.soilbio.2012.02.031.
21. Rocznik Statystyczny Rolnictwa 2011. Główny Urząd Statystyczny, 165, Warszawa 2012.

22. **Rosik-Dulewska Cz., Karwaczyńska U., Głowala K., Robak J.:** *Elution of heavy metals from granulates produced from municipal sevage deposits and fly-ash of hard and brown in the aspect of recycling for fertilization purposes*. Archives of Environment Protection, 34(2), 63–71 (2008).
23. **Rosik-Dulewska Cz., Karwaczyńska U., Ciesielczuk T., Głowala K.:** *Possibilities of non industrial re-usage of waste according to rules in of environment protection*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 11, 863–874 (2009).
24. **Rosik-Dulewska Cz., Karwaczyńska U., Ciesielczuk T.:** *Metale ciężkie w granulatach popiołowo-osadowych wykorzystywanych do celów nawozowych*. Przemysł Chemiczny 92/8 :1520–1524 (2013).
25. **Roszyk J., Nowosielski O., Komosa A.:** *Przydatność ekstraktów z popiołu węgla brunatnego do nawożenia dolistnego kalafiora.* Roczniki Akademii Rolniczej w Poznaniu – CCCLVI, 189–197 (2004).
26. **Tella M., Doelsch E., Letourmy P., Chataing S., Cuoq F., Bravin M.N., Saint Macary H.:** *Investigation of potentially toxic heavy metals in different organic wastes used to fertilize market garden crops*. Waste Management, 33, 184–192, (2013) http://dx.doi.org/10.1016/j.wasman.2012.07.021
27. **Xiao R., Chen X., Wang F., Yu G.:** *The physicochemical properties of different biomass ashes at different ashing temperature*. Renewable Energy, 36, 244–249 (2011).
28. **Wójcik P., Dyśko J., Kaniszewski S., Kowalczyk W., Nowak J.:** *Zrównoważone nawożenie roślin ogrodniczych*. Skierniewice (2014).

Możliwości zastosowania odpadów poekstrakcyjnych kawy jako wolno działającego nawozu organiczno-mineralnego

Streszczenie

Biodegradowalna frakcja odpadów po wydzieleniu jej ze strumienia odpadów komunalnych może stanowić ważne źródło materii organicznej, która zawracana do użytkowania mogłaby stanowić cenny nawóz rolniczy. W szczególności materia organiczna zawarta w odpadach przemysłu spożywczego oraz powstająca w gospodarstwach domowych może służyć do wytwarzania nawozu. W niniejszej pracy przedstawiono wyniki badań zastosowania nawozu wykonanego z odpadów poekstrakcyjnych kawy (CSG) modyfikowanych dodatkiem popiołu z termicznego przekształcania biomasy (A) lub siarczanem magnezu (MS), jako wolnodziałającego nawozu organicznego (organiczno-mineralnego) konfekcjonowanego w postaci tabletek. Nawóz taki może być zastosowany w momencie sadzenia roślin, ponieważ uwalnianie składników w nim zawartych następuje dopiero po pełnym uwilgotnieniu tabletki nawozowej. Dzięki otoczce kolagenowej, uwalnianie składników pokarmowych do gleby następuje powoli, co zmniejsza ryzyko przenawożenia lub utraty składników w drodze wymywania ich w głąb profilu gleby. Tabletkowane nawozy wykonane z mieszaniny CSG oraz A wpisują się w realizację zasad dobrej praktyki rolniczej oraz zrównoważonego rozwoju, a tematyka tak unikalnie skonstruowanego nawozu jest podejmowana po raz pierwszy.

Słowa kluczowe:
nawóz, odpady poekstrakcyjne kawy, popiół z biomasy

Keywords:
fertilizer, coffee spent ground, biomass ash

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Experimental Evaluation of Circular Frequency Supply of Radiant Floor Heating System

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1. Introduction

Nowadays, a lot of attention is paid to the rationalization of energy consumption [1, 3, 10, 11, 13], which is caused, among others, by the deficit of non-renewable raw materials and particularly energy carriers [19, 20].

Therefore the development of new energy sources (especially renewable ones) creates new technical, economic and ecological challenges [2, 7, 12, 16, 17, 22]. Modern heat sources, such as condensing boiler or heat pumps are used more and more often, because of their high energy efficiency. Such a heat source mostly used low temperature radiant floor as heat emitter in the heated room, which is supplied by low-temperature (t_z<55°C) heating medium. Taking this into account, it may be stated that a lot of research is made to optimize such system [5, 8, 9, 14, 15, 18, 23] during the dimensioning and exploitation phase.

However, there is very few research [4, 6, 21] focusing on the regulation of radiant floor heating system, and the possibilities of achieving energy savings. Moreover, there is still a lack of experimental and numerical research presenting the evaluation of circular frequency supply of massive radiant floor heating system.

Hence, this paper presents experimental research on circular frequency supply of massive radiant floor heating system.

2. Materials and methods

Experimental research on radiant floor heating system in the function of the circular frequency supply was made in the laboratory room (on a semi-technical scale) at the Faculty of Environmental Engineering of the Lublin University of Technology.

The analyzed radiant floor with the area equal to 2.43 m^2 (1.56 m x 1.56 m) consisted of the following layers (layers counted from below):

- styrofoam (thickness equal s = 0.06 m, and conductivities $\lambda = 0.045$ $Wm^{-1}K^{-1}$),
- pipes (PE-RT/Al/PE-RT) with 16 x 2.0 diameter, and high heat conduction coefficient $\lambda = 0.40$ $Wm^{-1}K^{-1}$, pipes were arranged with the spacing amounting to 0.15 m,
- concrete with the plasticizer (s = 0.065 m, $\lambda = 1.2$ $Wm^{-1}K^{-1}$),
- ceramic tiles (s = 0.01 m, $\lambda = 1.05$ $Wm^{-1}K^{-1}$).

For the purpose of isolating the radiant floor from the environment, it was placed in the climatic chamber (1.56 x 1.56 x 2.21 m) the walls of which were insulated with the 10 cm thick styrofoam. From the inside, the walls of the chamber were painted black and characterized with the constant and well-known emissiveness equal to $\varepsilon = 0.95$. The climatic chamber was situated in the laboratory room in which the indoor temperature was maintained at the constant of 20°C.

In order to evaluate the characteristic thermal parameters of analyzed radiant heating system by circular frequency supply, the following values were measured:

- the temperature of heating medium on supply (t_z) and on return (t_p),
- the flow of heating medium in the system (V),
- the indoor air temperature in the climatic chamber at 110 cm ($t_{a1.1}$),
- temperatures of black globe in the climatic chamber at 110 cm ($t_{g1.1}$),
- the temperature of the surface of radiant floor (t_{s1}-t_{s9}), which was measured by the use of nine sensors situated in the representative area for this radiant floor (Fig. 1),
- heat flux densities (Wm^{-2}), which is emitted from radiant surface.

All temperature sensors were characterized with accuracy to 0.1K.

The system works with a special computer program for monitoring, archiving and data visualization. All parameters are being recorded every 5 minutes.

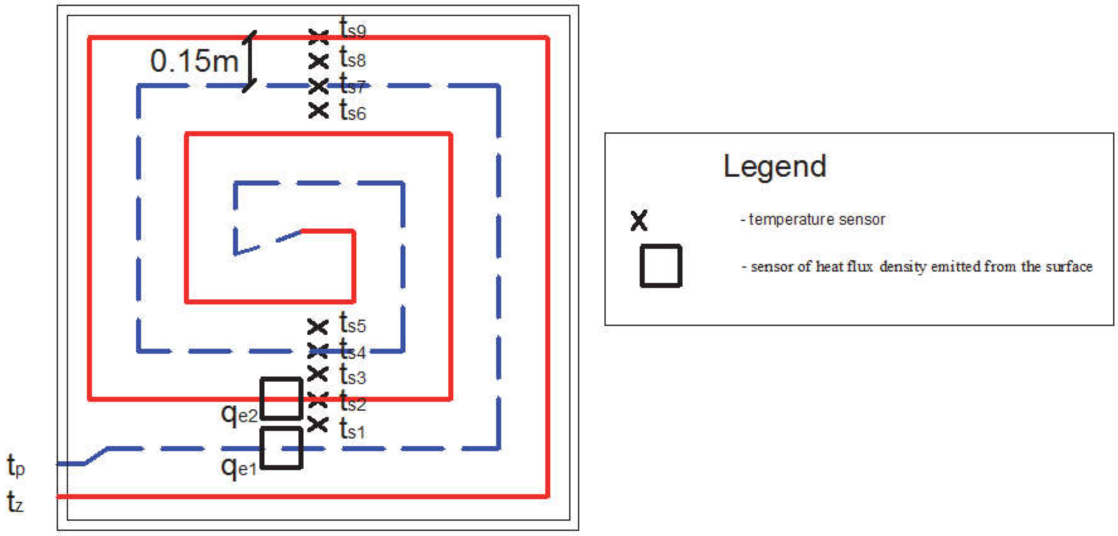

Fig. 1. Schema of location of sensors on radiant floor surface
Rys. 1. Schemat usytuowania czujników na powierzchni grzejnika podłogowego

Research methodology consisted in circular frequency supplying of the analyzed radiant floor with heating medium, the temperature of which on supply was equal to 45°C and the flow of the heating medium was amounted to of 2.2 dm^3 per minute.

Experimental research was made for seven cases of the circular frequency supply, which differed in the relation of the period of supply to the period of pause and the length of the given period (Table 1).

Table 1. The characteristic of the analyzed cycles in the circular frequency supply
Tabela 1. Charakterystyka analizowanych cykli ogrzewania pulsacyjnego

ON/OFF	Time		
	15 min	30 min	60 min
1/1	15/15	30/30	60/60
1/2	15/30	30/60	–
1/3	15/60	30/90	–

On the basis of archived measurement, the operative temperature in the exploratory chamber was calculated at 1.1 m using Equation 1.

$$t_o = \frac{t_{a1.1} + t_{mr1.1}}{2} \; (^{o}\mathrm{C}) \tag{1}$$

where:
$t_{a1.1}$ – indoor air temperature at 1.1 m,
$t_{mr1.1}$ – the average radiation temperature at 1.1 m, which was calculated by use of Equation 2.

$$t_{mr1.1} = \left(t_g + 273\right)^4 + 0.4 \cdot 10^8 \left|t_g - t_{a1.1}\right|^{0.25} \cdot \left(t_g - t_{a1.1}\right)^{0.25} - 273 \; (^{o}\mathrm{C}) \tag{2}$$

where:
t_g – black globe temperature at 1.1 m.

In order to evaluate the energy efficiency of each kind of the regulation, the heat flux densities were specified: the one supplied to heating system (Equation 3) and the one emitted from the radiant surface (q_e), which is the average value from two sensors of heat flux density (q_{e1}, q_{e2} see Figure 1).

$$\dot{q}_s = \frac{\dot{m} \cdot c_w \cdot \Delta t}{F} \; (\mathrm{W\ m^{-2}}) \tag{3}$$

where:
$\dot{m}$ – mass flow of heating medium (kg s^{-1}),
c_w – specific heat of heating medium in the given temperature (J$kg^{-1}K^{-1}$),
Δt – the average difference of the temperature of heating medium on supply and return from the radiant floor (K),
F – the radiant floor area, F = 2.43 m^2.

3. Results and discussion

On the basis of experimental research, a considerable decrease of operative temperature was observed for the ON/OFF cycle of 30/90 min, 15/60 min and 60/60 min, while in cycle 30/60 min, 15/30 min, 30/30 min and 15/15 min, the operative temperature fluctuated only to a limited degree, which can be observed in Figure 2 and Figure 3.

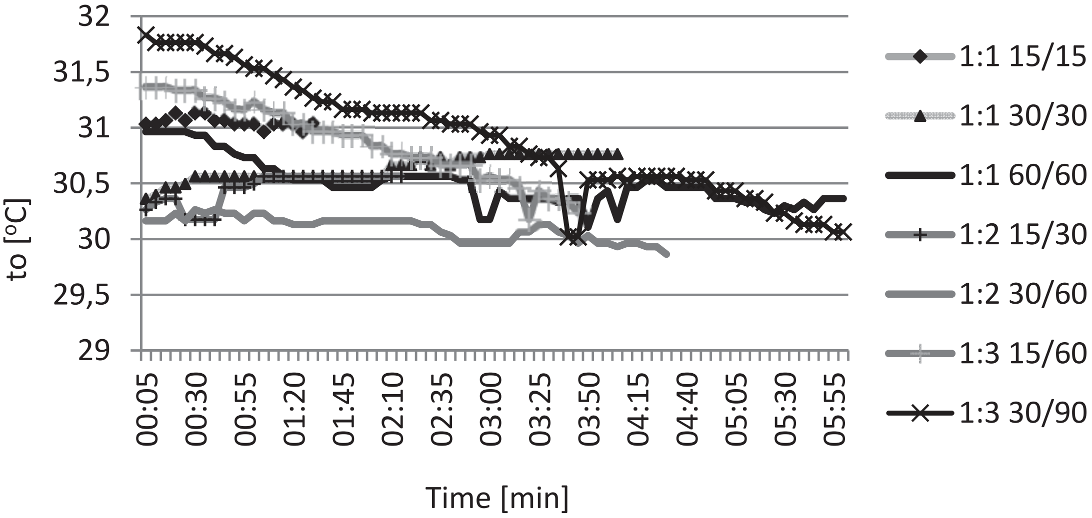

Fig. 2. Operative temperature in the climatic chamber for the analyzed circular frequency supply

Rys. 2. Temperatura operatywna w komorze klimatycznej dla analizowanych opcji zasilania pulsacyjnego

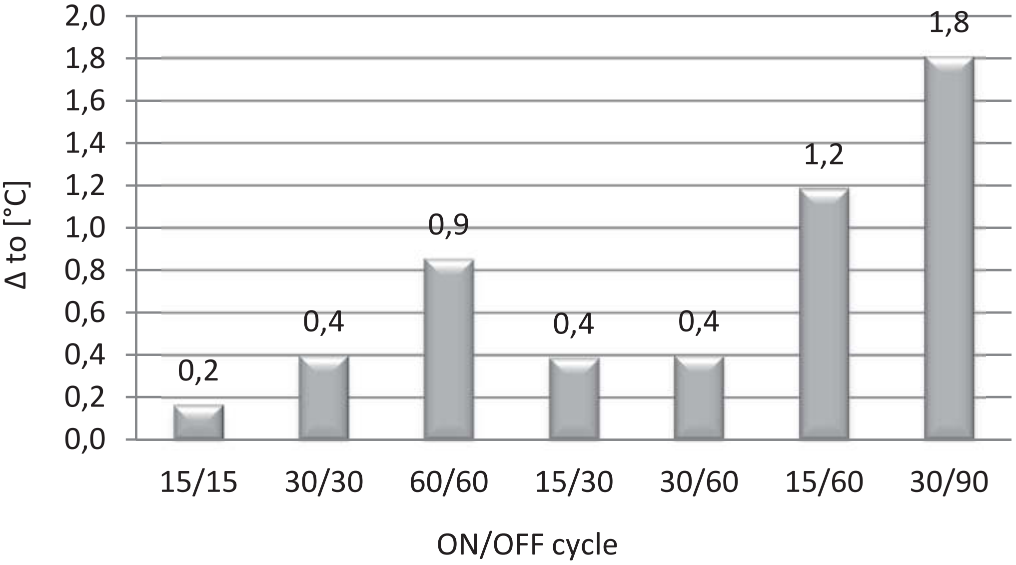

Fig. 3. Fluctuations of operative temperature depending on the cycle of circular frequency supply

Rys. 3. Wahania temperatury operatywnej w zależności od zastosowanego cyklu zasilania pulsacyjnego

Drawing on the data presented in Figure 3 it can be stated that greatest oscillations of operative temperature (1.8°C) were observed in the cycle in which heating was turned off for the longest time (30/90 min). The operative temperature drops considerably due to the long period of pause and when the heating installation is switched back on, it does not return to its previous state. However, for short operation and pause times, such as 15/15 min, the operative temperature is practically on the constant level (0.2°C fluctuations).

While analyzing the heat flux density delivered to the system, it was noticed that the first phase of heating was followed by a significant increase of this value, which then decreased in time (Figure 4). This is connected with greater energy input, which is required to return to the previous state.

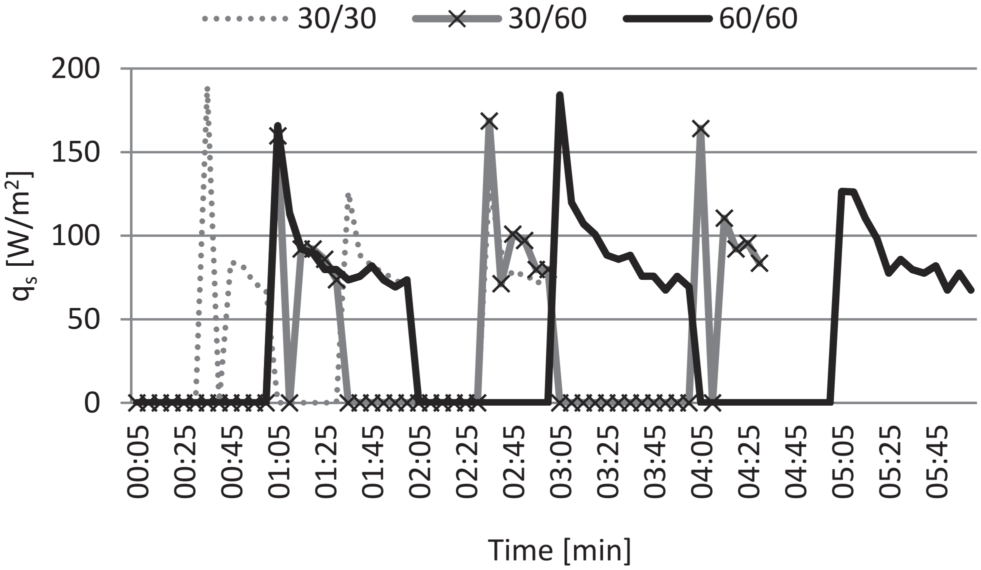

Fig. 4. Densities of heat flux delivered to heating system (q_s)
Rys. 4. Gęstości strumienia ciepła dostarczanego do układu (q_s)

In the case of heat flux emitted from the radiant floor, it decreases temporarily after the pause period, due to the lengthened reaction time of system. Then, it gradually increases (Figure 5). Nevertheless, the heat emitted from the surface in cycles with short period of warming compared to pauses, maintains the general downward trend, because the system cools itself too much during the long period of pause, while the installation works too short to return to its previous state.

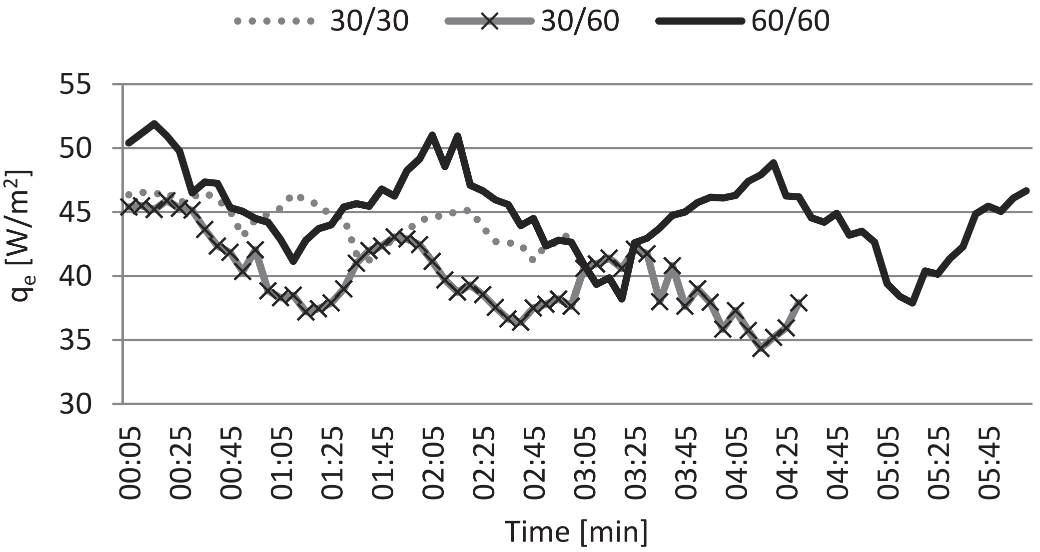

Fig. 5. Densities of heat flux emitted from the radiant floor surface (q_e)
Rys. 5. Gęstości strumienia ciepła przejmowanego z powierzchni grzejnika (q_e)

Therefore, the greatest consumption of the delivered heat was noticed in the cycles which were characterized by the equal durations of heating and pause phases. The greater the disproportion between the working and pause period, the less heat was emitted from the radiant surface to the room (Figure 6).

Moreover, for each circular frequency supply cycle, the amount of delivered and emitted energy for 6 hours of work (Figure 7) was calculated based on received data from three measuring-series. Depending on the ON/OFF cycle, the energy delivered to the system ranges from 0.2 to 0.6 kWh, while the energy emitted from the radiant floor equals between 0.6 and 0.8 kWh.

Hence, in every ON/OFF cycle, the quantity of the energy emitted from the radiant surface exceeds the value of the energy delivered to the heating system.

Therefore, the relation of the emitted energy to the delivered one equals over 100% in every investigated case (Figure 8), which enables energy savings while maintaining the thermal comfort in heated rooms.

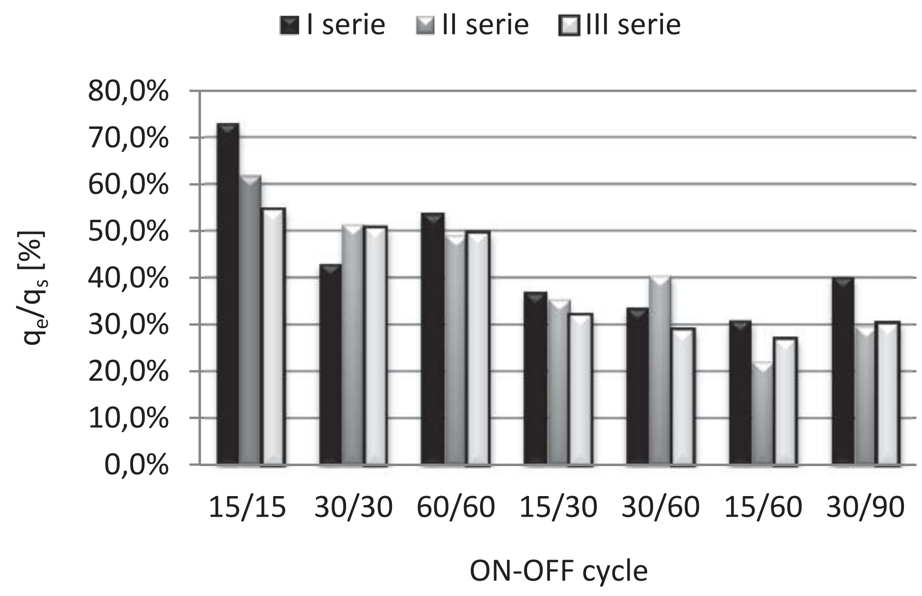

Fig. 6. The relation between the density of heat flux emitted to the room (q_e) to the delivered one (q_s) for analysed ON/OFF cycles
Rys. 6. Stosunek gęstości strumienia ciepła przejmowanego (q_e) do dostarczanego (q_s) dla analizowanych cykli włącz/wyłącz

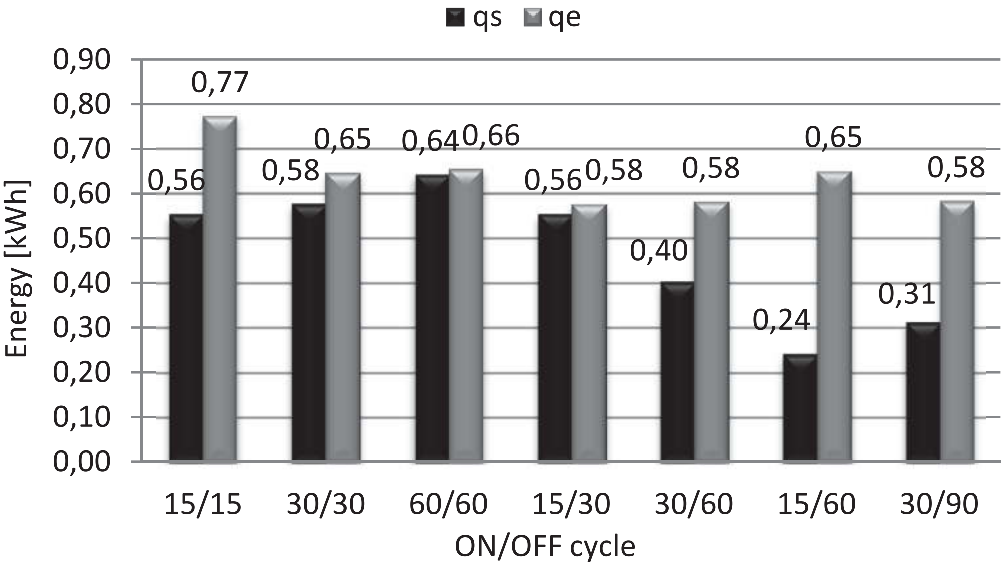

Fig. 7. The energy delivered to the system and emitted from the surface during 6 hours of radiant heating work for the analyzed ON/OFF cycles
Rys. 7. Energia dostarczana i przejmowana w czasie 6 h pracy instalacji ogrzewania podłogowego dla analizowanych cykli ON/OFF

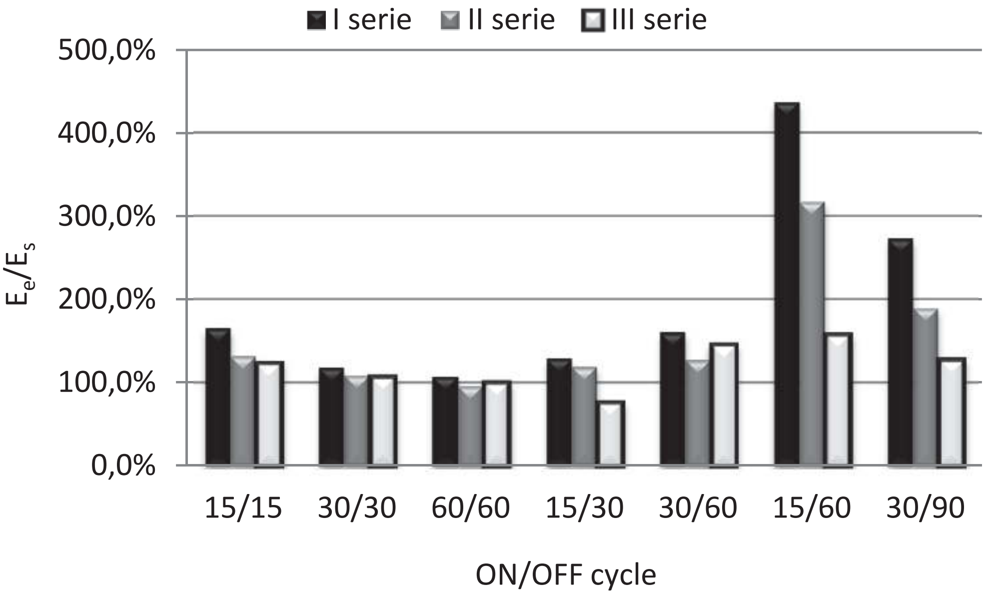

Fig. 8. The relation of the emitted energy (E_e) to delivered energy (E_s) in three measuring series for the analyzed ON/OFF cycles
Rys. 8. Stosunek energii przejmowanej (E_e) do dostarczanej (E_s) w trzech seriach pomiarowych dla analizowanych cykli włącz/wyłącz

4. Conclusions

Experimental research done on the laboratory stand allowed for the evaluation of circular frequency supply of radiant floor heating system in the aspect of the energy saving and maintenance of the thermal comfort.

It was noticed that the greatest fluctuations of operative temperature appeared in the cycle with the longest pause phase. The operative temperature considerably drops due to the long period of pause.

However, in the case of short work and pause periods, such as 15/15 min, the operative temperature is practically on the constant level (oscillations within 0.2°C).

Additionally, it was noticed that in every ON/OFF cycle, the quantity of the energy emitted from the radiant floor is higher that the value of the energy delivered to the system, which enables energy saving. However, changes of thermal comfort parameters in heated rooms which can appear at longer periods of pause should be taken into account.

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References

1. **Cao B., Zhu Y., Li M., Ouyang Q.:** *Individual and district heating: A comparison of residential heating modes with an analysis of adaptive thermal comfort*. Energy and Buildings, 78, 17–24 (2014).
2. **Cao Y., Shan S.:** *Energy Recovery from Sewage Sludge*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 14, 81–95 (2012).
3. **Chengmin C., Yufeng Z., Lijun M.:** *Assessment for central heating systems with different heat sources: A case study*. Energy and Buildings, 48, 168–174 (2012).
4. **Cho S.-H., Zaheer-uddin M.:** *An experimental study of multiple parameter switching control for radiant floor heating systems.* Energy, 24, 433–444 (1999)
5. **Cholewa T., Rosiński M., Spik Z., Dudzińska M.R., Siuta-Olcha A.:** *On the heat transfer coefficients between heated/cooled radiant floor and room*. Energy and Buildings, 66, 599–606 (2013).
6. **Cholewa T., Rosinski M., Spik Z., Siuta-Olcha A., Dudzinska M.R**.: *Heat capacity control of floor heating system*. IN Proceedings of 43 International Congress & Exhibition on Heating, Refrigerating and Air-Conditioning, Edited by Branislav Todorovic. Belgrad, Serbia, 5–7 December 2012.
7. **Dąbrowski J., Piecuch T.:** *Mathematical Description of Combustion Process of Selected Groups of Waste*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 13, 253–268 (2011).
8. **Dudkiewicz E., Jadwiszczak P., Jeżowiecki J.:** *Examination of operational dynamics of radiant ceiling panel*. Central European Journal of Engineering. 1 (2), 159–167 (2011).
9. **Dudkiewicz E., Fidorów N., Jeżowiecki J.:** *Analiza zużycia energii dla grzewczych systemów promieniujących.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 2293–2308, (2013).
10. **Dumała S.M., Dudzińska M.R.:** *Microbiological Indoor Air Quality in Polish Schools***.** Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 231–244 (2013).

11. **Dumała S.M., Skwarczyński M.A.:** *Rozwiązania konstrukcyjno-instalacyjne budynku a zapotrzebowanie na energię cieplną***.** Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 11, 1795–1808 (2011).
12. **Duran J., Golusin M., Ivanovic O.M., Jovanovic L., Andrejevic A.:** *Renewable Energy and Socio-economic Development in the European Union*. Problems of Sustainable Development, 8 (1), 105–114, 2013.
13. **Dyczkowska M., Szkarowski A.:** *Metoda energooszczędnego sterowania pracą instalacji grzewczych w budynkach o podwyższonej izolacyjności cieplnej – porównanie modelu matematycznego z wynikami badań.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 11, 583–594 (2009).
14. **Fontana L.:** *Thermal performance of radiant heating floors in furnished enclosed spaces*. Applied Thermal Engineering 31, 1547–1555 (2011).
15. **Hajabdollahi F., Hajabdollahi Z., Hajabdollahi H.**: Thermo-economic modeling and optimization of underfloor heating using evolutionary algorithms. Energy and Buildings 47, 91–97 (2012).
16. **Jarzyna W., Pawłowski A., Viktarovich N.:** *Technological development of wind energy and compliance with the requirements for sustainable development*. Problems of Sustainable Development, 9 (1), 167–177 (2014).
17. **Mroczek B., Kurpas D., Klera M.:** *Sustainable Development and Wind Farms*. Problems of Sustainable Development, 8 (2), 113–122 (2013).
18. **Odyjas A., Górka A.:** *Simulations of floor cooling system capacity*. Applied Thermal Engineering 51, 84–90 (2013).
19. **Pawłowski A.:** *Sustainable Development and Globalization*. Problems of Sustainable Development, 8 (2), 5–16 (2013).
20. **Pawłowski A., Pawłowski L.:** *Sustainable development in contemporary civilisation. Part 1: The environment and sustainable development*. Problems of Sustainable Development, 3 (1), 53–65 (2008).
21. **Rekstad J., Meir M., Kristoffersen A.R.:** *Control and energy metering in low temperature heating systems.* Energy and Buildings 35, 281–291 (2003).
22. **Wall G.:** *Exergy, Life and Sustainable Development*. Problems of Sustainable Development, 8(1), 27–41 (2013).
23. **Zhang L., Liu X.H., Jiang Y.:** *Simplified calculation for cooling/heating capacity, surface temperature distribution of radiant floor*. Energy and Buildings 55, 397–404 (2012).

Ocena zasilania pulsacyjnego systemu ogrzewania podłogowego na podstawie badań eksperymentalnych

Streszczenie

Badania eksperymentalne ogrzewania podłogowego w funkcji zasilania pulsacyjnego przeprowadzono w warunkach laboratoryjnych w skali półtechnicznej. Analizowany grzejnik podłogowy miał powierzchnię równą 2,43 m^2 i wymiary 1,56 m x 1,56 m. W celu odizolowania grzejnika od otoczenia, umieszczono go w komorze badawczej o wymiarach 1,56 x1,56 x 2,21 m, której ściany były zaizolowane styropianem o grubości 10 cm. Ponadto ściany komory od wewnątrz były pomalowane na kolor czarny i charakteryzowały się stałą i znaną emisyjnością równą $\varepsilon = 0,95$. Komora badawcza była umieszczona w pomieszczeniu laboratorium, w którym temperatura powietrza wewnętrznego była utrzymywana na stałym poziomie równym 20°C.

Badania polegały na zasilaniu analizowanego układu czynnikiem grzewczym o temperaturze równej 45°C i przepływie objętościowym na poziomie 2,2 dm^3/min. Badania eksperymentalne wykonano dla siedmiu przypadków zasilania pulsacyjnego, które różniły się między sobą stosunkiem okresu zasilania układu do okresu przerwy w zasilaniu, jak i długością danego okresu. Na podstawie archiwizowanych pomiarów wyznaczono charakterystyczne parametry pracy układu, co pozwoliło na ocenę zużycia energii przez układ oraz parametrów komfortu cieplnego w pomieszczeniach ogrzewanych.

Zauważono, że dla krótkich czasów pracy i postoju, takich jak 15/15 min, temperatura operatywna jest praktycznie na stałym poziomie (wahania w granicach 0,2°C).

Poza tym największe wykorzystanie ciepła dostarczanego zauważono przy cyklach, które charakteryzowały się takim samym czasem trwania fazy grzania, jak i postoju.

Słowa kluczowe:
ogrzewanie podłogowe, regulacja, efektywność energetyczna

Keywords:
radiant floor heating, regulation, energy efficiency

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Ultrasonic Processors and Drainage of Sewage Sludge

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1. Introduction

Implementation of new technologies in sewage treatment involves generation of even greater volumes of sewage sludge which, in the raw form, is considered as a dangerous substance. According to the standards used in Poland, sewage sludge should be subjected to treatment and then properly managed [1, 5, 11].

The volume of sludge is reduced using the process of thickening and dewatering [9, 10]. In order to intensify this process, sludge is subjected to different methods of conditioning (physical, chemical) [2, 4, 7]. One of the methods which have been researched extensively in different technological processes of environmental engineering is exposure to the ultrasonic field [6, 8, 13, 15]. Sonication causes dispersion of the particles in the sludge flocs, which affects their properties during thickening and dewatering. Effectiveness of using the ultrasonic field depends on the amplitude used, time of exposure and volume of the samples subjected to modification [3, 14,16].

Disintegration of sewage sludge is carried out using ultrasonic processes. Previous studies have demonstrated the improvement in the effects of dewatering, thus reducing the costs of final sludge management. The ultrasonic field does not case a secondary pollution to the environment [12, 17].

The paper presents the results obtained for thickening and dewatering of sewage sludge expressed by capillary suction time (CST), subjected to the effect of ultrasonic processors with varied power, amplitudes and volume of the samples sonicated.

2. Experimental methodology

The study examined excess sewage sludge collected from a mechanical and biological wastewater treatment plant. Non-conditioned sewage sludge and the sludge conditioned with the ultrasonic field was analysed. In order to determine the effect of power of ultrasonic processors on thickening and dewatering, the study used three ultrasound disintegrators: VCX 1500 (power 1500 W, frequency 20 kHz, amplitude 100%, corresponding to the wavelength of 39.42 μm), VC 750 (power 750 W, frequency 20 kHz, amplitude 100% corresponding to the wavelength of 61 μm) and UD 20 (power 180 W, frequency 22 ± 1,65 kHz, amplitude 100%, corresponding to the wavelength of 16 μm). Sewage sludge used in the study was conditioned with the amplitudes of 0%, 60%, 80% during sonication for 0, 2, 4, 6, 8, 10 minutes with volumes of sonicated samples of 0.25 L, 0.5 L, 1 L. The effect of the parameters of sonication adopted on changes in thickening and dewatering was presented by means of the values obtained after 120 minutes of thickening in Imhoff cones and values of capillary suction time determined by means of the set for CST measurements.

3. Results and discussion

3.1. Thickening

Sewage sludge exposed to the ultrasonic field showed improved effectiveness of thickening. This relationship was found for the sludge subjected to the three ultrasonic processors with different powers. Effectiveness of sedimentation was higher for longer times of exposure. The improvement in thickening was reported after 30 minutes of sedimentation. The sludge was thickened the most noticeably at the amplitude of 60% and sonication time of 10 minutes where, after 120 minutes, the volume of sludge was 620 ml (processor 1500 W) (Table 1). Similar relationships were observed in other disintegrators used in the study. In the processors with power 750 W and 180 W, the sludge after 10 minutes of sonication and amplitude of 60% were thickened more effectively for each of the samples studied. Improved thickening of sludge with time was observed in all the cases.

Table 1. Thickening of sewage sludge subjected to the effect of different amplitudes and times of exposure to the ultrasonic field
Tabela 1. Zagęszczanie osadów ściekowych poddanych działaniu różnym amplitudom i czasom działania pola ultradźwiękowego

Thickening of the sewage sludge, ml												
Thickening time, min		0	5	10	15	20	25	30	45	60	90	120
Non-conditioning sludge		1000	990	990	990	990	980	980	970	960	950	940
Ultrasonic disintegrator 1500W	Amplitude 60%,5 min	1000	1000	1000	1000	1000	1000	1000	990	990	990	990
	Amplitude 80%,5 min	1000	1000	1000	1000	1000	1000	1000	990	990	990	980
	Amplitude 60%,10 min	1000	990	980	980	960	960	970	750	700	670	620
	Amplitude 80%,10 min	1000	990	980	970	960	950	940	810	790	770	720
Ultrasonic disintegrator 750W	Amplitude 60%,5 min	1000	1000	1000	990	990	990	990	990	990	990	990
	Amplitude 80%,5 min	1000	1000	1000	990	990	990	990	990	990	990	990
	Amplitude 60%,10 min	1000	980	960	940	920	900	880	820	800	700	650
	Amplitude 80%,10 min	1000	980	970	960	950	930	910	860	800	680	630
Ultrasonic disintegrator 180W	Amplitude 60%,5 min	1000	990	980	970	970	970	960	950	930	890	850
	Amplitude 80%,5 min	1000	990	990	990	990	980	980	970	960	940	910
	Amplitude 60%,10 min	1000	980	980	980	980	970	970	950	940	920	880
	Amplitude 80%,10 min	1000	980	980	980	980	980	970	960	960	950	920

Analysis of the results of examination of the effect of the ultrasonic field at different volumes of samples showed that the best effects of thickening were recorded for the sample with volume of 500 ml. This relationship was observed for processors with power of 1500 and 750 W

(Table 2). Sewage sludge subjected to 10 minutes of exposure to the ultrasonic field and then thickened by 120 minutes had the volume of 620 ml (for the processor of 1500 W) and 650 ml (for the processor of 750 W). An insignificant reduction in the volume of the sample subjected to disintegration was observed in the case of the processor with power of 180 W (volume of the sludge of 250 ml, time of sedimentation 120 minutes, volume of the sludge 990 ml). The best thickening was found for the sludge with volume of 1000 ml, which, after 120 minutes of sedimentation, reached the value of 790 ml.

Table 2. Thickening of sewage sludge subjected to the effect of ultrasonic field with different power and for different volumes of the samples
Tabela 2. Zagęszczanie osadów ściekowych poddanych działaniu procesorom ultradźwiękowym o różnej mocy przy różnych objętościach próbek

Thickening of the sewage sludge, Amplitude of vibration 60%, Time 10 min												
Thickening time, min		0	5	10	15	20	25	30	45	60	90	120
Non-conditioning sludge		1000	990	990	990	990	980	980	970	960	950	940
Ultrasonic disintegrator 1500 W,	250 ml	1000	990	980	980	970	970	970	980	980	980	980
	500 ml	1000	990	980	980	960	960	970	750	700	670	620
	1000 ml	1000	990	980	980	970	970	970	970	970	970	970
Ultrasonic disintegrator 750 W	250 ml	1000	1000	1000	1000	1000	1000	1000	1000	1000	990	990
	500 ml	1000	980	960	940	920	900	880	820	800	700	650
	1000 ml	1000	1000	1000	1000	1000	1000	1000	1000	1000	995	995
Ultrasonic disintegrator 180 W	250 ml	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
	500 ml	1000	980	980	980	980	970	970	950	940	920	880
	1000 ml	1000	980	980	980	960	960	950	930	900	790	790

3.2. Capillary suction time

The exposure to the ultrasonic field caused an increase in capillary suction time with respect to the non-conditioned sludge (Fig. 1, 2).

For the time of exposure to the ultrasonic field of 5 minutes, CST levels increased with higher ultrasound wavelengths. Capillary suction times for the processor 750 W were 500.4 s (amplitude 60%) and 1702.2 s (amplitude 80%), respectively, whereas for the processor 180 W, these values were 686.3 s (amplitude 60%) and 894.4 s (amplitude 80%), respectively. The highest CST times were found for the sludge conditioned with the processor with the highest power (1500 W; 3463 s; amplitude 60%) and 2774 s (amplitude 80%).

After extension of the time of exposure to the ultrasonic field to 10 minutes, higher values of CST were also recorded with respect to the non-conditioned sludge. However, longer time of exposure yielded shorter CST times in the sludge compared to the levels obtained for 5 minutes.

In all the disintegrators used, an increase in capillary suction time was recorded in the sludge for higher times of exposure to the ultrasounds (Fig. 3). After 8th minute of exposure, a decline in the value of the parameter discussed was observed. Lower values were found in all the ultrasonic processors used.

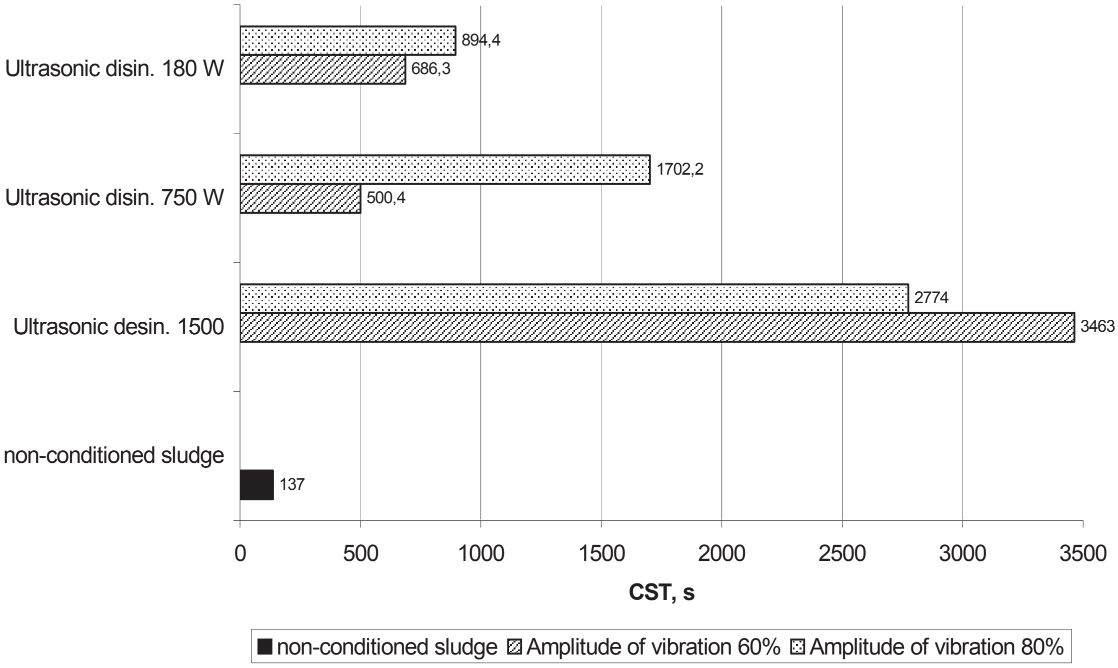

Fig. 1. Capillary suction time in sewage sludge exposed to the ultrasonic field with different power (5 minutes)
Rys. 1. Czas ssania kapilarnego osadów ściekowych poddanych działaniu procesorom ultradźwiękowym o różnej mocy (UD 5 min)

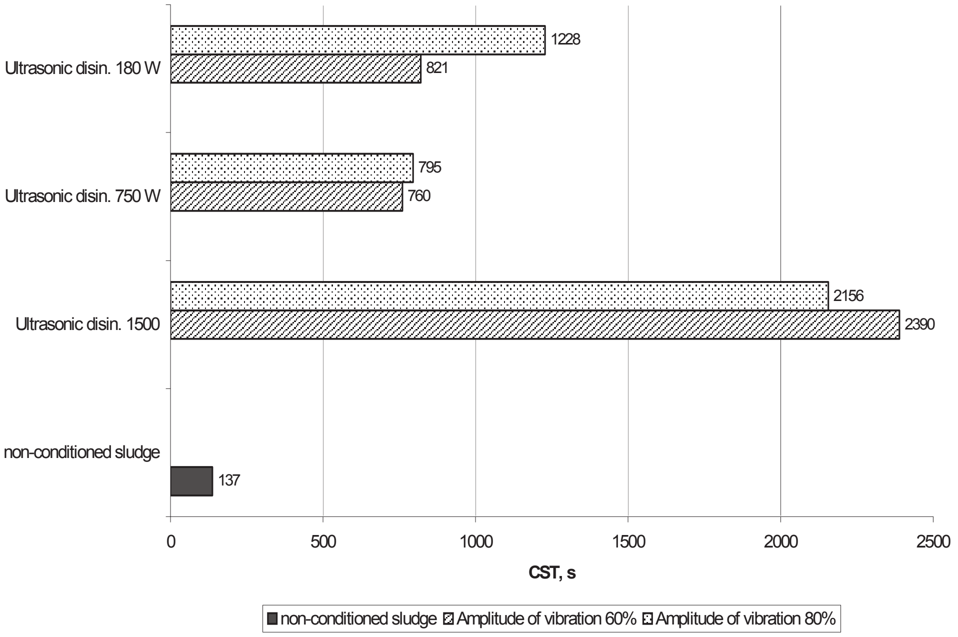

Fig. 2. Capillary suction time in sewage sludge exposed to the ultrasonic field with different power (10 minutes)
Rys. 2. Czas ssania kapilarnego osadów ściekowych poddanych działaniu procesorom ultradźwiękowym o różnej mocy (UD 10 min)

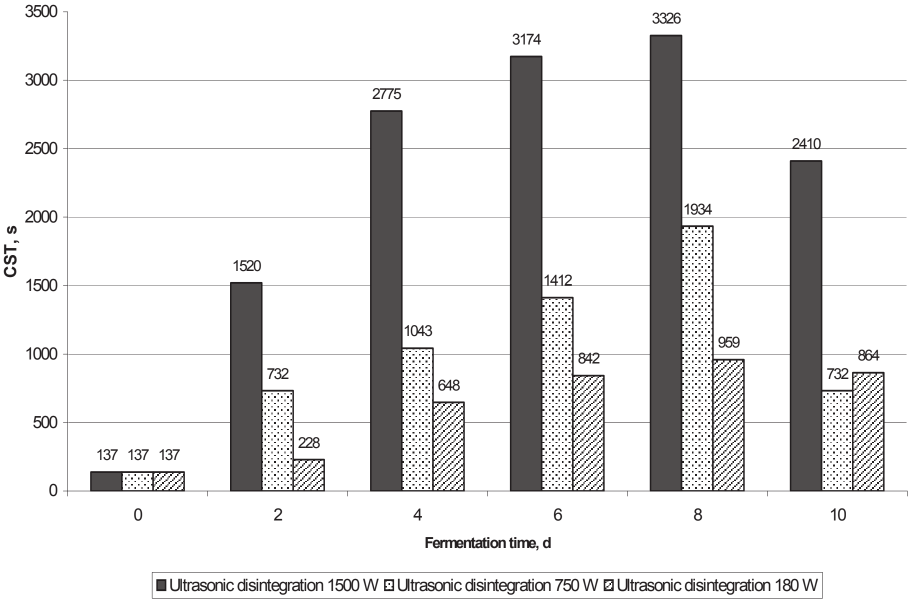

Fig. 3. Capillary suction time in sewage sludge subjected to different times of exposure to the ultrasonic field
Rys. 3. Czas ssania kapilarnego osadów ściekowych poddanych różnym czasom działania pola ultradźwiękowego

Changes in the capillary suction times were also observed for exposure of the sludge with different volumes. Sewage sludge conditioned at the lower volume of the sample (250 ml) had the highest values of CST. For the time of exposure of 5 minutes with the processor 1500 W, the highest values of CST were found for the volume of 500 ml (3463 sec), whereas the lowest level (1785 sec) was observed for the volume of 1000 ml (Fig. 4). In two processors (750W and 180W), the highest CST value was recorded for the volume of 250 ml, which was respectively 2105 s and 1094 s. High CST was found in all the processors used for the exposure time of 10 minutes and volume of the sample of 250 ml. The highest value 2962 s was found for the processor 1500 W with the volume of the sample of 1000 ml (Fig. 5). In the case of two other processors, the value of CST for this volume of the sample was much lower (below 1000 s). The lowest value of CST was observed for the sludge sonicated with processor 180 W at the volume of 1000 ml.

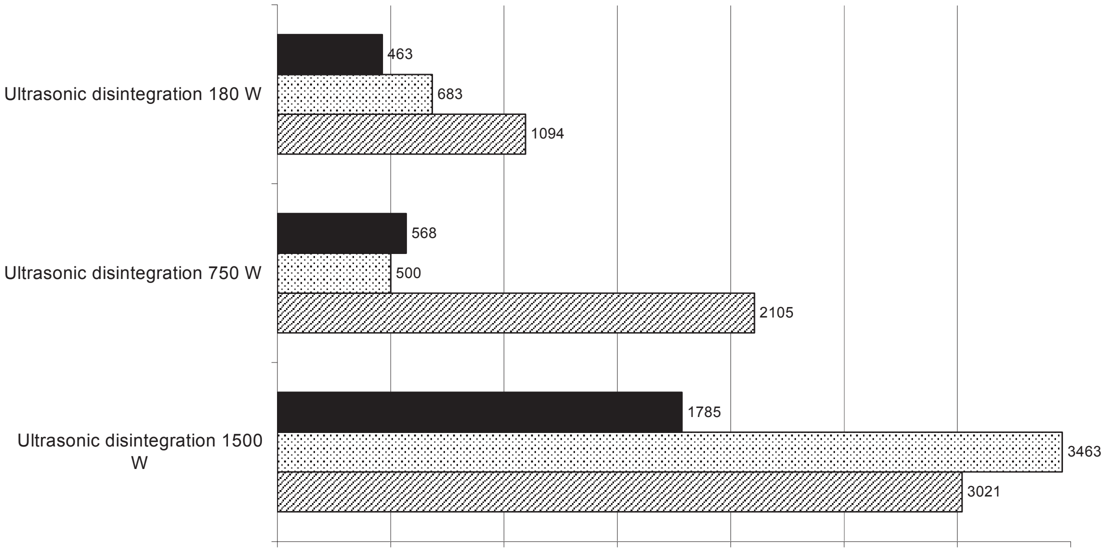

Fig. 4. Capillary suction time for sewage sludge subjected to 5-minute exposure to the ultrasonic field for different volumes of the samples

Rys. 4. Czas ssania kapilarnego osadów ściekowych poddanych 5 minutowemu działaniu polem ultradźwiękowym przy różnych objętościach prób

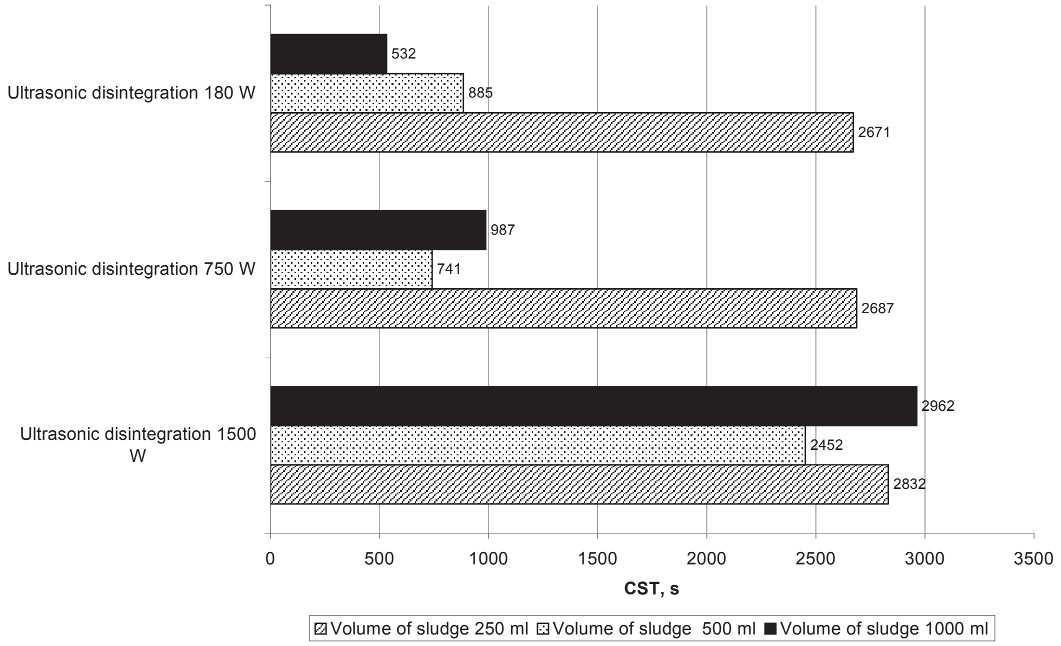

Fig. 5. Capillary suction time for sewage sludge subjected to 10-minute exposure to the ultrasonic field for different volumes of the samples
Rys. 5. Czas ssania kapilarnego osadów ściekowych poddanych 10 minutowemu działaniu polem ultradźwiękowym przy różnych objętościach prób

4. Summary and conclusions

The parameters of the ultrasonic field had a positive effect on thickening of the sewage sludge samples studied. The dispersive influence of the exposure to the ultrasonic field caused an increase in sedimentation capability in the sewage sludge studied. The ultrasonic field caused fragmentation of the structure of the sludge, thus causing better compression of the particles and improved release of the free water. The noticeable effect of the factor discussed on sedimentation capability was observed after 10 minutes of sonication. The best results of sedimentation were recorded for the volume of 500 ml.

The use of three ultrasonic processors showed higher CST times in the sewage sludge studied proportionally to the increase in wavelength and processor power. The process of disintegration caused dispersion of sewage flocs by clogging the pores in the filtration paper. This also resulted in prolonged capillary suction times and, consequently, reduction of the dewatering capability. CST increased until the 8th minute of sludge sonication, and then, for each of the processor used, a decline in the value of the parameter studied was observed. The highest values of capillary suction time were found for the VCX 1500 processor, whereas the lowest values were observed for the processor with the lowest power (UD 20).

The analysis of the results obtained in this study leads to the following conclusions:

- With longer times of exposure to the ultrasonic field, sewage sludge was thickened more effectively, which was caused by the dispersion of flocs in the sewage sludge studied. Lower amplitude and shorter duration of exposure to the ultrasonic field had more beneficial effect on sedimentation in the sewage sludge studied;
- For the parameters of the sonication process assumed, capillary suction time was extended in proportion to the increase in sonication time, ultrasound processor wavelength and processor power;
- Reduction in the volume of the samples conditioned caused an increase in capillary suction time in the sludge. Dispersion of particles caused clogging of the pores in the filtration paper, and, consequently, longer CST values.

Acknowledgements

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References

1. **Bień J.:** *Sewage sludge – theory and practice.* Czestochowa University of Technology Publishing House 2007.
2. **Bień J., Kamizela T., Kowalczyk M., Mrowiec M.:** *Possibilities of gravitational and mechanical separation of sonicated activated sludge suspensions.* Environment Protection Engineering. 35(2), 67–71 (2009).
3. **Bień J., Kowalczyk T., Kamizela M., Stępniak L.:** *The analysis of sedimentation and thickening of sewage sludges after ultrasonic disintegration.* Environment Protection Engineering. 30(4), 23–28 (2004).
4. **Dieudé-Fauvel E., Dentel S.K.:** *Sludge conditioning: Impact of Polymers on Floc structure.* Journal of Residuals Science and Technology. 8(3), 101–108 (2011).
5. **Grosser A., Worwąg M., Neczaj E., Grobelak A.:** *Semi-continuous Anaerobic Co-digestion of Mixed Sewage Sludge and Waste Fats of Vegetable Origin.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2108–2125 (2013).

6. **Li H., Jin Y.., Rasool B. M., Wang Z., Nie Y.:** *Effects of ultrasonic disintegration on sludge microbial activity and dewaterability.* Journal of Hazardous Materials. 161, 1421–1426 (2009).
7. **Mikkelsen L.H., Keiding K.:** *Physico-chemical characteristics of full scale sewage sludges with implications to dewatering.* Water Research. 36, 2451–2462 (2002).
8. **Na S., Kim Y., Khim J.:** *Physiochemical properties of digested sewage sludge with ultrasonic treatment.* Ultrasonics Sonochemistry. 14, 281–285 (2007).
9. **Piecuch T., Piekarski J., Malatyńska G.:** *Filtration of mixtures forming compressible sediments.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1, 39–58 (2013).
10. **Piecuch T., Piekarski J., Malatyńska G.:** *The equation describing the filtration process with compressible sediment accumulation on a filter mesh.* Archives of Environmental Protection. 39(1), 93–104 (2013).
11. **Podedworna J., Umiejewska K.:** *Technology of sewage sludge.* Warsaw University of Technology Publishing House, Warsaw 2008.
12. **Stańczyk-Mazanek E., Piątek M., Kępa U.:** *Effect of sewage sludge applied to sandy soils on the sorption complex properties.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15 (3), 2437–2451 (2013).
13. **Wolny L., Stępniak L., Stańczyk-Mazanek E.:** *Changes of Sludge Characteristic after Ultrasonic Field Action.* Polish Journal of Environmental Studies. 16(2A), III, 573–576 (2007).
14. **Wolski P., Wolny L.:** *Effect of disintegration and fermentation on the susceptibility of sewage sludge to dewatering.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 1697–1706 (2011).
15. **Zawieja I., Wolny L.:** *Effect of sonicator power on the biodegradability of sewage sludge.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 1719–1730 (2011).
16. **Zawieja I. Wolny L.:** *Ultrasonic disintegration of sewage sludge to increase biogas generation.* Chem. Biochem. Eng., 27(4), 491–497 (2013).
17. **Zhang G., Zhang P., Yang J., Liu H.:** *Energy-efficient sludge sonification: Power and sludge characteristics.* Bioresource Technology. 99, 9029–9031 (2008).

Procesory ultradźwiękowe a odwadnianie osadów ściekowych

Abstract

W Polsce najczęstszym sposobem końcowego zagospodarowania osadów ściekowych jest ich składowanie. Ze względu na skład i właściwości osadów często są one traktowane jako odpad, a nie surowiec. Osady ściekowe poddawane unieszkodliwianiu poddawane są różnym procesom technologicznym, gdzie jednym z nich jest zmniejszenie objętości. Odwadnianie to podstawowy proces zmniejszania objętości osadów. W celu zwiększenia zdolności osadów do oddawania wody stosuję się różne procesy wspomagające. Jedną z metod jest wykorzystanie działania pola ultradźwiękowego. Sonifikacja osadów ściekowych zmienia strukturę oraz właściwości osadów, powodując zakłócenia równowagi układu oraz wywołuję dyspersję cząstek, co sprzyja zwiększeniu zdolności do zagęszczania i odwadniania.

W artykule przedstawiono wyniki badań dotyczące zastosowania dezintegratorów ultradźwiękowych o różnej mocy (1500W, 750W, 180W) na zmianę stopnia zagęszczania i odwadniania osadów ściekowych. W badaniach wykorzystano różne długości fal dezintegratorów UD (60, 80%), czasy ekspozycji z przedziału od 2 do 10 sekund oraz różne objętości prób poddane działaniu pola ultradźwiękowego.

Przy założonych parametrach prowadzenia badań dezintegrujące działanie pola UD spowodowało znaczną poprawę zagęszczania osadów ściekowych w odniesieniu do osadów niekondycjonowanych. Duża moc procesorów ultradźwiękowych powodowała rozdrobnienie kłaczków osadowych zatykając przegrodę filtracyjną, co odnotowano w wartościach czasu ssania kapilarnego (CSK) oraz oporu właściwego osadów.

Słowa kluczowe:
osady ściekowe, dezintegracja ultradźwiękowa, zagęszczanie, odwadnianie

Keywords:
sewage sludge, ultrasonic disintegration, thickening, dewatering

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Wybrane aspekty prawno-techniczne i ekologiczne stosowania sprężarkowych pomp ciepła

Tadeusz Bohdal, Henryk Charun, Małgorzata Sikora
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1. Wstęp

Gwarancją odtwarzalności populacji ludzkiej jest zagwarantowanie odpowiedniej ilości pożywienia, czystego środowiska oraz energii. Od zarania dziejów energię czerpano ze źródeł naturalnych, tzw. energię pierwotną, którą uzyskiwano przez konwersję energii chemicznej, zawartej w paliwach kopalnych na drodze spalania. Podstawy współczesnej energetyki konwencjonalnej oparte są na spalaniu paliw stałych (węgla kamiennego i brunatnego), paliw ciekłych (głównie ropy naftowej) i paliw gazowych (gaz ziemny i jego pochodne). Kurczące się zasoby energii pierwotnej i degradacja środowiska naturalnego w skali lokalnej, a przede wszystkim globalnej, spowodowały i wymusiły oddziaływania społeczeństw w skali międzynarodowej.

Raport Klubu Rzymskiego stał się podstawą Deklaracji Konferencji Narodów Zjednoczonych w sprawie ochrony środowiska człowieka przyjętej w Sztokholmie 16 czerwca 1972 roku [1]. To tam właśnie sformułowano po raz pierwszy założenia, opisujące zrównoważony rozwój społeczeństw w kontekście politycznym, ekologicznym, ekonomicznym i społecznym. Ideę zrównoważonego rozwoju ujęto nazwą „samopodtrzymującego się rozwoju populacji ludzkiej w skali globalnej". W krótkim streszczeniu można tę ideę określić słowami: „*żyj racjonalnie, daj żyć innym w tym i w następnych pokoleniach*". Jak prorocze były te zapisy świadczą fakty, związane z potwierdzeniem istnienia dziury ozonowej oraz destrukcyjnym efektem cieplarnianym.

W 1985 r. podpisano Konwencję Wiedeńską o Ochronie Warstwy Ozonowej (Polska ratyfikowała postanowienia tej konwencji w roku 1992 [2]). Na Światowym Szczycie Ekologicznym „Ziemia 2000” w Rio de Janeiro w 1992 r. kraje - sygnatariusze podpisały zobowiązanie do redukcji w perspektywie do 2050 roku emisji dwutlenku węgla o połowę, w odniesieniu do stanu z 1987 roku [3]. Prekursorskie zmiany w prawodawstwie międzynarodowym wywołały lawinę porozumień lokalnych i światowych w zakresie szeroko rozumianej ochrony środowiska. Po wejściu Polski do Unii Europejskiej prawodawstwo krajowe musiało implementować dyrektywy, normy i inne obowiązujące przepisy określone przez kraje członkowskie. Szczególnie ważny był tzw. pakiet klimatyczny 3 x 20, zobowiązujący kraje UE do zmniejszenia do 2020 roku emisji CO_2 o 20%, zwiększenia o 20% produkcji energii elektrycznej oraz zwiększenie o 20% udziału energii ze źródeł odnawialnych (OZE) w bilansie energetycznym kraju.

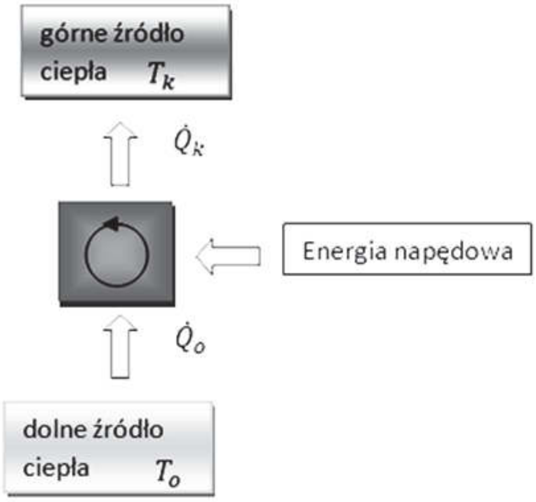
Wobec takich radykalnych wyzwań konieczne było i jest poszukiwanie metod pozyskiwania energii w ramach proekologicznej energetyki niekonwencjonalnej. Pod tą nazwą należy rozumieć pozyskiwanie energii ze źródeł przyjaznych otaczającemu środowisku. Zgodnie z harmonogramem wzrostu udziału energii ze źródeł odnawialnych (OZE), przyjętym w krajach Unii Europejskiej, tempo tego wzrostu nie jest jednak zadowalające. Szczególnie widać to na przykładzie Polski, gdzie dopiero w marcu 2015 r. doszło do uchwalenia przez Sejm RP Ustawy o Odnawialnych Źródłach Energii (w innych krajach Unii Europejskiej zrobiono to znacznie wcześniej). Poza tym obecnie przepisy polskie nie kwalifikują np. pompy ciepła (w tym Ustawa Prawo Energetyczne [4]) do odnawialnych źródeł. Według Ustawy [4]: *„odnawialnym źródłem energii jest źródło wykorzystujące w procesie przetwarzania energię wiatru, promieniowania słonecznego, aerotermalną, hydrotermalną, geotermalną, fal prądów i pływów morskich, spadku rzek oraz energię pozyskiwaną z biomasy, biogazu”.*

Brak właściwego usankcjonowania prawnego przysługującego pompie ciepła, w której wykorzystuje się rzeczywiście energię z niskopotencjalnych źródeł środowiska (powietrze, woda, grunt itp.) utrudnia w znaczący sposób rozpowszechnienie tej formy pozyskiwania energii oraz ogranicza lub uniemożliwia pomoc finansową dla użytkowników, którzy podejmują takie przedsięwzięcia (w wielu krajach Unii Europejskiej wspomaganie takich inwestycji jest normą).

W opracowaniu przedstawiono wybrane problemy techniczno-prawne i ekologiczne związane z wprowadzeniem inwestycji energetycznych pod nazwą „*pompa ciepła*" do obszaru energetyki niekonwencjonalnej.

2. Transformacja przepływu energii w pompie ciepła

Samorzutny przepływ ciepła może następować tylko ze źródła o temperaturze wyższej do źródła o temperaturze niższej. Jeżeli chcemy zrealizować przepływ w kierunku odwrotnym, wówczas zgodnie z II zasadą termodynamiki, należy doprowadzić do układu energię napędową z otoczenia (rys. 1).



Rys. 1. Zasada transportu energii w pompie ciepła
Fig.1. Energy transport rule in the heat pump

Z rys. 1 wynika, że transport strumienia ciepła w ilości $\dot{Q}_O$ ze źródła dolnego o temperaturze T_o do górnego o temperaturze $T_k > T_o$ możliwy jest, jeżeli z otoczenia doprowadzi się strumień energii napędowej $\dot{E}_N$. Wtedy, zgodnie z równaniem bilansu energetycznego (I zasada termodynamiki) do źródła górnego dostarczony zostanie strumień energii w ilości $\dot{Q}_k$:

$$\dot{Q}_k = \dot{Q}_o + \dot{E}_N. \tag{1}$$

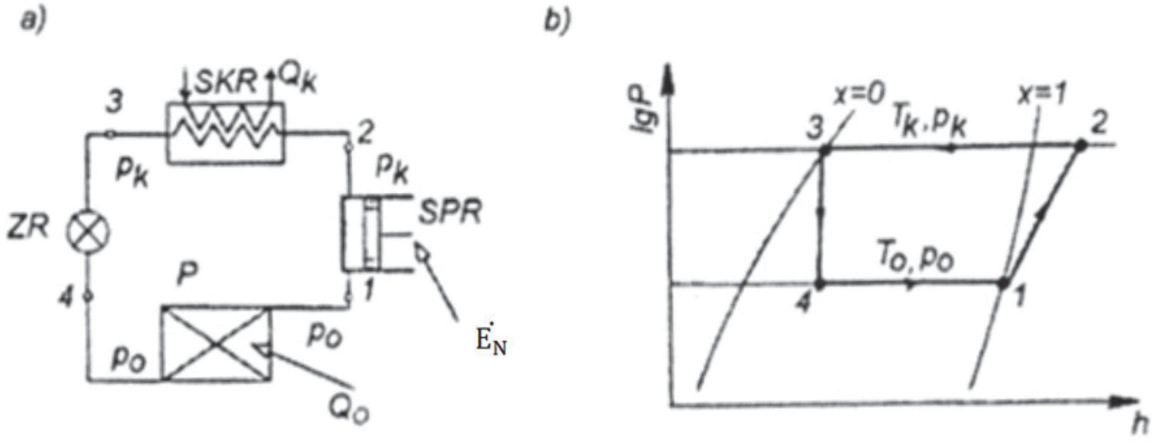
Jeżeli chcemy uzyskać efekt użyteczny w sposób ciągły, wówczas stosuje się obieg lewobieżny. W przypadku, gdy efektem użytecznym uzyskiwanym z obiegu lewobieżnego jest strumień ciepła $\dot{Q}_k$odprowadzany do źródła górnego o temperaturze T_k strumienia, wtedy mamy do czynienia z pompą ciepła. Gdy efektem tym jest strumień ciepła $\dot{Q}_o$ „podnoszony" ze źródła dolnego o temperaturze T_o – jest to urządzenie chłodnicze. W sensie zasady działania nie ma więc różnicy między urządzeniem chłodniczym i pompą ciepła. W przypadku jednoczesnego wykorzystania dwóch efektów cieplnych, tzn. $\dot{Q}_o$ i $\dot{Q}_k$ urządzenie nazywane jest chłodniczo-grzejnym.

Strumień energii napędowej $\dot{E}_N$ może być doprowadzany różnymi sposobami i stąd uzyskuje się różne nazwy pomp ciepła. W przypadku, gdy $\dot{E}_N$ doprowadza się w postaci strumienia pracy mechanicznej $\dot{E}_N = \dot{W} = P$ (P – moc) mamy sprężarkową pompę ciepła; gdy $\dot{E}_N = \dot{Q}_N$ jest to sorpcyjna pompa ciepła ($\dot{Q}_N$ - strumień ciepła napędowego); gdy $\dot{E}_N = \dot{E}_k$ - strumieniowa pompa ciepła ($\dot{E}_k$ – strumień energii kinetycznej).

Ograniczając zakres opracowania do pomp ciepła sprężarkowych trzeba wskazać, że w zależności od rodzaju czynnika roboczego wyróżnia się pompy ciepła sprężarkowe: gazowe – jeżeli czynnik w obiegu (np. powietrze nie podlega przemianom fazowym) lub parowe – gdy czynnikiem jest płyn, który podlega w obiegu przemianom. Sprężarkowe parowe pompy ciepła są najbardziej rozpowszechnione w różnych obszarach zastosowań i służą przede wszystkim, jako urządzenia grzejne w instalacjach centralnego ogrzewania, ciepłej wody użytkowej, klimatyzacji itp.

3. Zasada działania sprężarkowej pompy ciepła

Przy zastosowaniu czynnika chłodniczego jednoskładnikowego stosuje się zwykle obieg zbliżony do obiegu *Lindego* (rys. 2) z zaworem rozprężnym, natomiast w przypadku czynnika dwuskładnikowego obiegiem wzorcowym jest obieg *Lorenza*.



Rys. 2. Schemat ideowy układu chłodniczego sprężarkowego (a) oraz interpretacja przemian termodynamicznych (b) w obiegu *Lindego* suchym, bez dochłodzenia – w układzie współrzędnych *lgp – h* [5]*; P* – parownik, *SPR* – sprężarka, *SKR* – skraplacz, *ZR* – zawór rozprężny
Fig. 2. Schematic diagram of compressor refrigeration system (a) and interpretation of thermodynamic transformation (b) in dry Linde circuit, without sub cooling, in a coordinate system of lgp-h [5], P – evaporator, SPR – compressor, SKR – condenser, ZR – expansion valve

Rys. 2 przedstawia schemat ideowy oraz interpretację przemian w obiegu lewobieżnym parowej sprężarkowej pompy ciepła z czynnikiem jednoskładnikowym w układzie współrzędnych *lgp-h* (*p* – ciśnienie, *h* – entalpia właściwa) [1]. W przedstawionym na rys. 2b) układzie współrzędnych *lgp-h* mamy do czynienia z obiegiem *Lindego* suchym, bez dochłodzenia. Jest to obieg lewobieżny, w którym znajduje się 1 kg czynnika chłodniczego. Ten typ obiegu porównawczego składa się z kolejno następujących po sobie przemian termodynamicznych: *1→ 2* – izentropowe sprężanie (*s = const*; *s* – entropia właściwa), *2→ 3* izobaryczny proces skraplania (na części przemiany *2”→ 3* jest przemianą izobaryczno-izotermiczną), *3→ 4* izentalpowa przemiana ($h_3=h_4$) dławienia izentalpowego w zaworze rozprężnym *ZR*, *4→ 1* jest izobaryczno-izotermiczną przemianą wrzenia czynnika chłodniczego w parowniku *P*.

W odniesieniu do 1 kg czynnika wyróżnia się charakterystyczne wielkości obiegu *Lindego* (rys. 2):

- jednostkowa masowa wydajność chłodnicza:

$$q_o = h \quad - h_4, \tag{2}$$

- jednostkowa wydajność cieplna skraplania:

$$q_k = h_2 - h_3, \tag{3}$$

- jednostkowa praca napędowa (praca techniczna) doprowadzania do 1 kg czynnika sprężanego w sprężarce *SPR*:

$$w_t = h_2 - h_1. \tag{4}$$

Jeżeli uwzględni się, że masowe natężenie czynnika chłodniczego w obiegu wynosi $\dot{m}[\frac{kg}{s}]$ i pomnoży się wielkości jednostkowe podane wzorami (2)–(4), wtedy otrzymamy:

$$\dot{Q}_o = \dot{m} \cdot q_o, \qquad \dot{Q}_k = \dot{m} \cdot q_k, \qquad P = \dot{m} \cdot w_t, \tag{5}$$

gdzie:

$\dot{Q}_o$ – strumień ciepła „podnoszony” z dolnego źródła obiegu (tzw. wydajność chłodnicza parownika),

$\dot{Q}_k$ – strumień ciepła odprowadzany do źródła górnego o temperaturze T_k, (wydajność cieplna skraplacza – efekt użyteczny pompy ciepła),

T_k – temperatura skraplania,

P – teoretyczna moc napędowa ($\dot{E}_d = P$, moc doprowadzana do napędu sprężarki *SPR*).

W rzeczywistych sprężarkowych, parowych pompach ciepła realizowane są obiegi przegrzane. W pompach o małej i średniej wydajności montowane są, jako zawory rozprężne *ZR* (rys. 2), termostatyczne zawory rozprężne (oznaczone symbolem TZR), które powodują że stan *1* pary zasysanej przez sprężarkę *SPR* leży w obszarze pary przegrzanej. Oprócz tego, ciecz czynnika opuszczająca skraplacz jest dochłodzona przed zaworem rozprężnym. Dla celów porównawczych będzie w dalszej części artykułu wykorzystany obieg z rysunku 2.

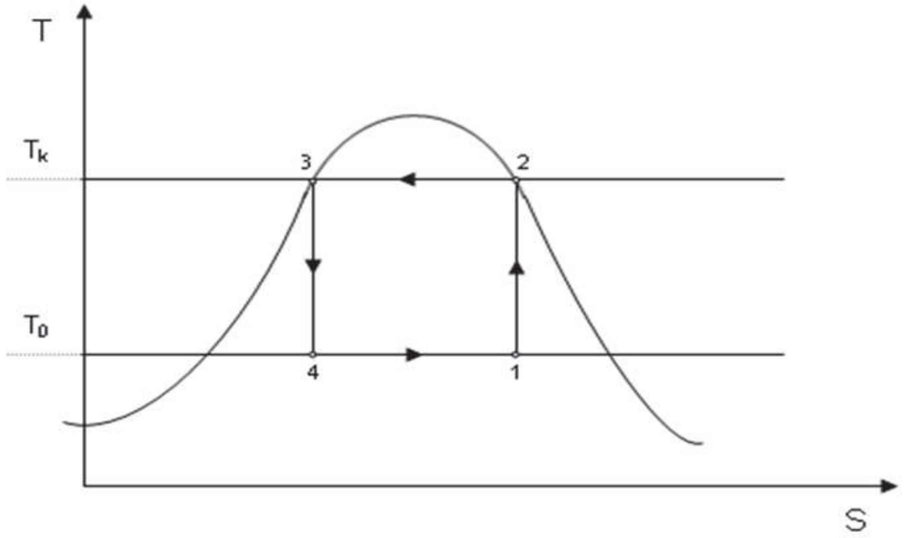
4. Aspekty techniczno-prawne oceny efektywności obiegów sprężarkowych, parowych pomp ciepła

Miarą efektywności obiegu pompy ciepła jest stosunek efektu użytecznego $\dot{Q}_k$ do nakładu – mocy napędowej *P*, zwany współczynnikiem wydajności cieplnej obiegu pompy i oznaczany symbolem ε_{pc} [5] lub *COP* (ang. *coefficient of performance*) [6]:

$$\varepsilon_{pc} = COP = \frac{\dot{Q}_k}{P} = \frac{q_k}{w_t}, \tag{6}$$

gdzie w_t jest jednostkową pracą techniczną sprężania w przemianie $1 \rightarrow 2$.

Efektywność pompy ciepła pracującej wg obiegu *Lindego* (lub obiegu przegrzanego) może być porównywana z efektami, które uzyskałoby się, gdyby pompa ciepła pracowała według odwracalnego, lewobieżnego obiegu *Carnota* (rys. 3).



Rys. 3. Lewobieżny odwracalny obieg *Carnota*
Fig. 3. Reversible *Carnot* left – racing circle

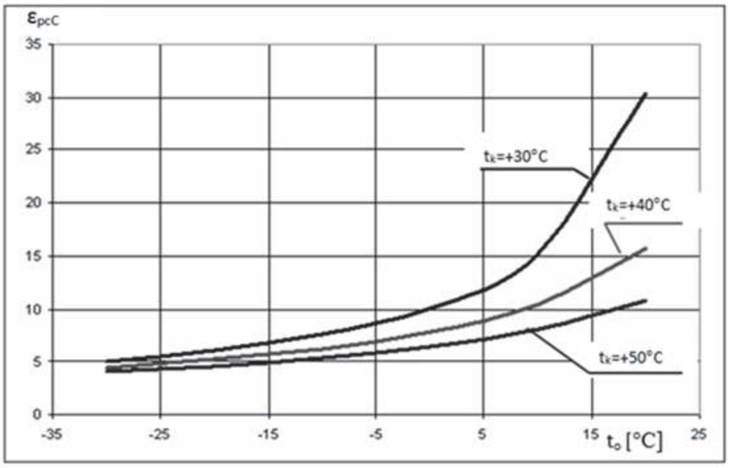
Współczynnik wydajności cieplnej obiegu porównawczego *Carnota* jest opisany zależnością:

$$\varepsilon_{pc_C} = COP_C = \frac{T_k}{T_k - T_o}, \tag{7}$$

gdzie:
T_o – temperatura parowania [K],
T_k – temperatura skraplania czynnika chłodniczego [K].

W przypadku obiegu *Carnota* wartość współczynnika COP_C nie zależy od rodzaju czynnika chłodniczego, ale od wartości temperatury bezwzględnej źródeł ciepła górnego T_k i dolnego T_o.

Na rysunku 4 przedstawiono zależność współczynnika wydajności cieplnej ε_{pc_C} obiegu *Carnota,* w zależności od temperatury parowania t_o dla stałego poziomu temperatury skraplania t_k [^{o}C].



Rys. 4. Wykres zależności współczynnika $\varepsilon_{pc_C} = f(t_o)$ obiegu *Carnota* dla stałego poziomu temperatury skraplania t_k
Fig. 4. Coefficient $\varepsilon_{pc_C} = f(t_o)$ dependence of Carnot circuit for constant level of condensation temperature t_k

Ocenę jakości energetycznej obiegu realizowanego w sprężarkowej parowej pompie ciepła dokonuje się stosując pojęcie stopnia doskonałości (odwracalności) obiegu [6], zwanego też sprawnością egzergetyczną η_b pompy ciepła [1, 7]:

$$\eta_b = \frac{\varepsilon_{pc}}{\varepsilon_{pc_C}} = \frac{COP}{COP_C}. \tag{8}$$

Dla rzeczywistych, sprężarkowych pomp ciepła o małej wydajności i wyposażonych w chłodnicze agregaty hermetyczne można obliczyć współczynnik wydajności cieplnej $\varepsilon_{pc_{rz}}$ ze wzoru [6]:

$$\varepsilon_{pc_{rz}} = COP_{rz} = \left[1 + \eta_i \cdot \left(\varepsilon_{pc} - 1\right)\right] \cdot \eta_m \cdot \eta_s, \tag{9}$$

gdzie:

ε_{pc} – współczynnik wydajności pompy ciepła pracującej obiegu teoretycznym (np. *Lindego* lub przegrzanego),
η_i – sprawność wewnętrzna sprężarki,
η_m – sprawność mechaniczna sprężarki,
$\eta_ś$ – sprawność silnika elektrycznego.

Dyrektywą 2009/28/WE [7] wprowadzono do oceny pomp ciepła pojęcie sezonowego współczynnika efektywności energetycznej pompy ciepła sprężarkowej *SPF* (ang. *Seasonal Performance Factor*) opisanego wzorem:

$$SPF = \frac{Q}{E_{el}}, \tag{10}$$

gdzie:
Q – ilość ciepła uzyskanego w sezonie grzewczym za pomocą pompy ciepła [kWh],
E_{el} – ilość energii elektrycznej zużytej do napędu pompy [kWh].

Wg [8] współczynnik *SPF* określa stosunek ilości ciepła przekazanego przez pompę ciepła do instalacji grzewczej, do ilości dostarczonej do niej energii elektrycznej. Jako okres porównawczy przyjmuje się jeden rok. Można zdefiniować kilka rodzajów współczynnika *SPF*, tzn.: źródła, systemu, instalacji itp. W dyrektywie unijnej podano metodykę obliczenia *SPF* z zależności [9]:

$$SPF =,1{,}15 \cdot \frac{1}{\eta}, \tag{11}$$

gdzie η – średnia w Unii Europejskiej sprawność energetycznej konwersji energii pierwotnej na energię elektryczną określona jako stosunek między całkowitą produkcją energii elektrycznej brutto i pierwotnym zużyciem energii dla celów produkcji energii elektrycznej. Proponuje się [9] stosować jako standardowe, minimalne wartości *SPF*:

- pompy powietrze – powietrze – 3,0,
- pompy solanka – woda – 3,7,
- pompy woda – woda – 4,0.

W pracy [10] podano, że decyzją Komisji Europejskiej z 1.03.2013 r. nr 2013/114/UE (C(2013), 1083) przedstawiono wytyczne dla państw Unii Europejskiej dotyczące szacowania ilości energii odnawialnej pochodzącej z różnych typów pomp ciepła. Okazuje się, że minimalna wartość *SPF* dla sprężarkowych pomp ciepła zasilanych energią elektryczną powinna wynosić co najmniej 2,5 ($\eta = 0{,}455$ do wzoru (11)). Jeżeli współczynnik SPF ≥ 2,5, wówczas energia może być uznana, jako odnawialna w rozumieniu Dyrektywy 2009/28/WE. Można się spodziewać, że pompy ciepła dostępne na polskim rynku (w tym z dolnym źródłem – powietrzem) będą mogły być traktowane jako *OZE*. Dla pomp ciepła absorpcyjnych *SPF* ≥ 1,15. Autor pracy [10] podaje szczegółowe wyjaśnienia na temat metodyki szacowania współczynnika *SPF*.

Przedstawione powyżej aspekty można uznać jako techniczno-prawne i wynikające z dostosowania prawodawstwa polskiego do unijnego, co w przypadku sprężarkowych pomp ciepła jest szczególnie widoczne i ważne, bowiem przekładają się one na rozliczenia finansowania inwestycji energetycznych.

5. Wybrane aspekty techniczno-ekologiczne oceny sprężarkowych pomp ciepła

Pompy ciepła wymieniane są przez Komisję Europejską ECCP w grupie produktów posiadających duży potencjał wpływu na efekt cieplarniany, przy czym oprócz pomp ciepła wyróżnia się: urządzenia gospodarstwa domowego, systemy o napędzie elektrycznym i systemy *HVAC* (ogrzewanie, wentylacja i klimatyzacja) [11, 12]. Rozporządzenie Ministra Gospodarki i Pracy z 20 maja 2005 r. [13] określa, że w odniesieniu do pomp ciepła trzeba brać pod uwagę następujące kryteria:

1. wskaźnik efektywności obiegu *COP*,
2. wskaźnik efektywności energetycznej *SPF* (*EER*),
3. rodzaj czynnika chłodniczego,

4. rodzaj czynnika pośredniczącego,
5. hałas,
6. rodzaj substancji negatywnie oddziałującej na środowisko,
7. kompletna dokumentacja instalacji i uprawniony jej eksploatator.

Omówienie wszystkich uwarunkowań, które mają wpływ na efektywność sprężarkowej pompy ciepła (opisaną współczynnikami *COP* i *SPF*) przekracza ramy niniejszego opracowania. Dlatego rozważania ograniczono do wybranego aspektu techniczno-ekologicznego, dotyczącego wpływu rodzaju czynnika chłodniczego na efektywność energetyczną obiegu sprężarkowej pompy ciepła.

5.1. Wpływ rodzaju czynnika chłodniczego

Przenoszenie strumienia energii (ciepła) $\dot{Q}_o$ z poziomu dolnego źródła ciepła na poziom źródła górnego jest możliwe w sprężarkowych, parowych pompach ciepła, bowiem wykorzystuje się czynnik chłodniczy pośredniczący w wymianie ciepła między źródłami. W pracy [5] podano kryteria idealnego czynnika chłodniczego charakteryzującego się takimi właściwościami, jak: odpowiednio niska normalna temperatura wrzenia, mała wartość objętości właściwej i lepkości, mała masa cząsteczkowa, nietoksyczność, niepalność, ekologiczność itp. Oczywiście bierze się pod uwagę czynniki, które posiadają najlepsze właściwości termodynamiczne i ekologiczne oraz mają niewielki stopień odchylenia od czynnika modelowego.

Z punktu widzenia właściwości termodynamicznych najlepszymi czynnikami w zastosowaniu do urządzeń chłodniczych i pomp ciepła sprężarkowych były czynniki chlorowcopochodne, jednorodne z grupy HFC (*chlorofluorowęglowodory*), zwane freonami, w tym freon R12 oraz z grupy HCFC (*wodorochlorofluorowęglowodory*), w tym freon R22 [14]. O ile właściwości termodynamiczne tych czynników spełniały w większości kryteria czynnika idealnego, to jednak ze względu na destrukcyjny wpływ na środowisko zostały one, na mocy postanowień Konwencji Wiedeńskiej i Protokołu Montrealskiego (w pierwszej kolejności freon R12) wycofane z zastosowań.

Do oceny destrukcyjnego wpływu na warstwę ozonową oraz efektu cieplarnianego wprowadzono kilka wskaźników ekologicznych, wśród których najważniejsze to:

- *GWP* (*Global Warming Potential*) – globalny potencjał efektu cieplarnianego; czynnikiem odniesienia jest CO_2, dla którego *GWP* = 1,
- *ODP* (*Ozone Depletion Potential*) – potencjał niszczenia ozonu; czynnikiem odniesienia jest freon R11, dla którego *ODP* = 1,
- *HGWP* (*Halocarbon Global Warming*) – potencjał zdolności to tworzenia efektu cieplarnianego; czynnikiem odniesienia jest freon R11, dla którego *HGWP* = 1.

Oprócz tego stosuje się też inne wskaźniki oceny ekologicznej, w tym *TEWI* (*Total Equivalent Warming Impact*) – całkowity wskaźnik efektu cieplarnianego. Wskaźnik *TEWI* ujmuje nie tylko bezpośredni wpływ danej substancji na tworzenie efektu cieplarnianego, ale również wpływ pośredni, przez określenie zużycia energii niezbędnej do napędu urządzenia chłodniczego w okresie jego eksploatacji.

Wyeliminowanie w pierwszej kolejności z zastosowania w chłodnictwie czynnika – freonu R12, a z dniem 1.01.2010 r. także czynnika R22, spowodowało konieczność znalezienia ich substytutów. W zasadzie problem ten trwa do dnia dzisiejszego, bowiem nie wskazano dotychczas jednoznacznie ich proekologicznych zamienników. Zastąpienie freonu R12 czynnikiem chłodniczym R134a z grupy HFC (*hydrofluorowęglowodory*), pozwoliło na funkcjonowanie tego czynnika przez wiele lat w urządzeniach chłodniczych i pompach ciepła o małej i średniej wydajności. Zakłóceniem tego stanu rzeczy była Dyrektywa Parlamentu Europejskiego i Rady nr 2006/40/EC z 17 maja 2006 r. [15]. Na mocy tej dyrektywy muszą być wyeliminowane z samochodowych instalacji klimatyzacyjnych czynniki, dla których wskaźnik *GWP* > 150. Aktualnie stosowany czynnik chłodniczy R134a cechuje wartość *GWP* = 1300 [14], co spowoduje jego wycofanie z tych instalacji od dnia 1 stycznia 2017 r. (uprzednio termin ten był ustalony na 1.01.2013 r.). Problem ograniczenia wartości *GWP* czynników chłodniczych znalazł też odzwierciedlenie w polskiej normie PN-EN 378-1÷3 [16]. Do poszukiwania substytutów wycofanych freonów dołączył zatem następny problem, dotyczący wskazania zamienników czynnika R134a (HFC134a).

W zakresie stosowania dopuszczonych do eksploatacji czynników chłodniczych w sprężarkowych, parowych urządzeniach chłodniczych i pompach ciepła można w obecnym stanie wymienić następujące: R407C, R404A, R410A, R1234yf, R1234ze(E) oraz R717(NH_3), R744(CO_2), a także R290 (propan) i R600 (butan). W tabeli 1 przedstawiono wartości wskaźników destrukcji ekologicznej *ODP* i *GWP* niektórych wybranych czynników chłodniczych.

Zauważa się, że stosowane obecnie w instalacjach chłodniczych i pompach ciepła czynniki, będące mieszaninami zeotropowymi (R404A, R407C, R410A), wyróżniają się wskaźnikiem *GWP* przewyższającym nie tylko *GWP* = 150, ale także wartość *GWP* = 1300, jak dla czynnika R134a. Można się spodziewać, w jakim kierunku pójdą przyszłe oddziaływania proekologiczne instytucji międzynarodowych. Pole zastosowania czynników R290 (propan) i R600a (izobutan), z uwagi na ich właściwości wybuchowe, jest mocno ograniczone. Podobnie jest z czynnikiem R744 (CO_2), który cechuje bardzo wysoka wartość ciśnienia w instalacji.

Tabela 1. Wartości wskaźników destrukcji ekologicznej wybranych czynników chłodniczych do zastosowań w sprężarkowych pompach ciepła

Table 1. Values of indicators ecological destruction of the selected refrigerants to the use in compressor heat pumps [14, 17]

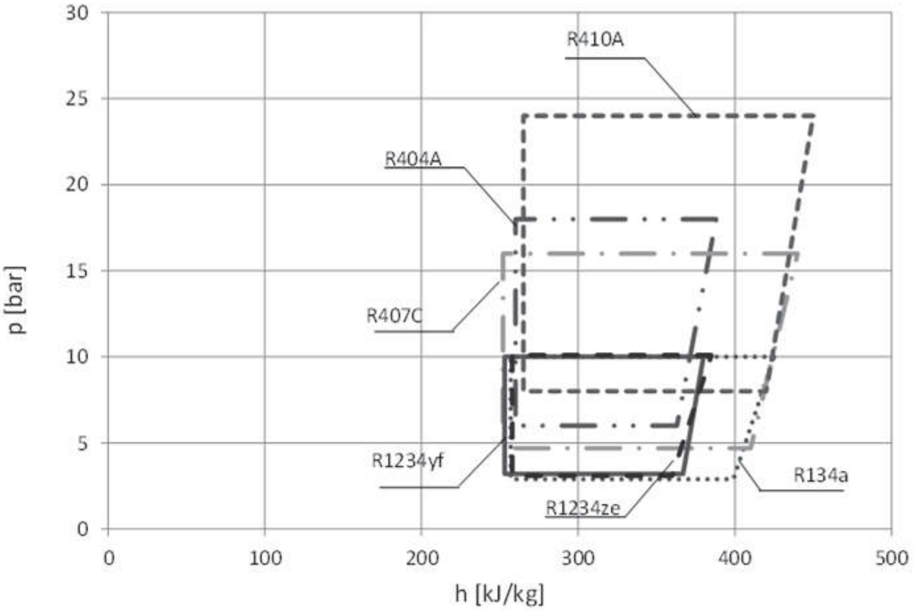
Czynnik chłodniczy	Wskaźnik	
	ODP	*GWP*
R12	1	10600
R22	0,055	1810
R134a	0	1300
R404A	0	3260
R407C	0	1530
R410A	0	1730
R1234yf	0	4
R1234ze(E)	0	4
R290 (propan)	0	0
R600a (izobutan)	0	3
R717 (NH_3)	0	<1
R744 (CO_2)	0	1

Nowymi interesującymi czynnikami chłodniczymi, lansowanymi przez ich producentów (w tym *Honeywell*, *Du Point*, *Solway*) są: R1234yf (HFO – 1234yf) oraz R1234ze(E) (HFO–1234ze(E)), gdzie R1234yf będzie prawdopodobnie zamiennikiem czynnika R134a w samochodowych instalacjach klimatyzacyjnych od 2017 roku. W odniesieniu do wymienionych czynników stosowane są różne, symboliczne ich oznaczenia. Na przykład czynnik R1234yf oznacza się, jako HFO-1234yf (gdzie: HFO hydro-fluoro-olefin, 1234 – oznacza kolejno: *1* – jedno wiązanie podwójne w strukturze cząstki, *2* – dwa atomy węgla, *3* – trzy atomy wodoru, *4* – cztery atomy fluoru, *yf* – określa, że jest to izomer). W tablicy 2 porównano charakterystyczne właściwości nowych czynników R1234yf ($C_3H_2F_4$) i R1234ze(E), z już stosowanym czynnikiem R134a (CH_2FCF_3).

Na podstawie różnych źródeł literatury [14, 17, 19, 20] wykonano porównawcze zestawienie wykresu obiegu suchego *Lindego* we współrzędnych *lp – h* dla czynników chłodniczych: R134a, R404A, R407C, R410A, R1234yf. Zauważa się, że dla poszczególnych czynników krzywe graniczne (lewa - dla $x = 0$ i prawa - dla $x = 1$) mają różną rozpiętość.

Tabela 2. Porównanie charakterystycznych właściwości czynników R1234yf i R1234ze(E) i czynników już stosowanych w pompach ciepła [14, 18, 19]
Table 2. Comparison of the characteristic properties for R1234yf and R1234ze(E) refrigerant used heat pumps [14, 18, 19]

Wyszczególnienie	R134a	R404A	R407C	R1234yf	R1234ze(E)
Względna masa cząsteczkowa M, [kg/kmol]	102,02	97,6	86,2	114,04	114,04
Normalna temperatura wrzenia przy ciśnieniu 1,013 bar, [^oC]	-26	-46,2	-43,6	-29	-19
Temperatura krytyczna t_{kr}, [^oC]	101	72	86,7	94,7	109,4
Ciśnienie w punkcie krytycznym p_{kr}, [bar]	40,6	37,3	46,0	33,82	36,32



Rys. 5. Porównanie obiegu suchego *Lindego* w układzie współrzędnych *lgp – h* dla analizowanych czynników chłodniczych
Fig.5. Comparison of dry *Linde* circuit in coordinate system *lgp-h* for analyzed refrigerants

Tabela 3. Wartość jednostkowego ciepła skraplania *r* w temperaturze nasycenia $t_k = 40^{o}$C (temperatura skraplania) dla analizowanych czynników chłodniczych
Table 3. The unit value of the condensation heat *r* in a saturation temperature $t_k = 40^{o}C$ (condensation temperature) for analyzed refrigerants

Czynnik	R134a	R404A	R407C	R410A	R1234yf
r, [kJ/kg]	162,9	123,3	168,3	164,4	130

Dla czynnika R134a rozchylenie krzywych granicznych jest większe, niż dla R1234yf. Ma to oczywiście wpływ na wartość jednostkowego ciepła skraplania *r* [kJ/kg] – tabela 3.

W ostatnich latach następuje wzrost zainteresowania nowymi czynnikami z grupy HFO-1234, co potwierdza znaczna liczba prac opublikowanych w czasopismach o zasięgu światowym i referatów na konferencjach międzynarodowych [21–24]. Mimo tego istnieją duże trudności uzyskania dobrze sprawdzonych i udokumentowanych danych, dotyczących właściwości termodynamicznych i cieplno-fizycznych czynników z grupy HFO-1234.

5.1. Analiza przydatności nowych czynników chłodniczych do zastosowań w sprężarkowych pompach ciepła

Z tabeli 1 wynika, że nowe czynniki chłodnicze z grupy HFO-1234: R1234ye(E), R1234yf, R1234ze(E),R1234ze(Z) [22], a w szczególności R1234yf, odznaczają się wyjątkowo małą wartością wskaźnika *GWP* = 3–4, co predysponuje do ich proekologicznej eksploatacji. Dotychczas, niektórzy autorzy wykonywali analizy, mające na celu określenie przydatności nowego czynnika R1234yf do zastosowania w instalacjach chłodniczych, obsługujących samochodowe układy klimatyzacyjne. Z ich punktu widzenia brano pod uwagę, przede wszystkim, wpływ na wydajność chłodniczą parownika tej instalacji.

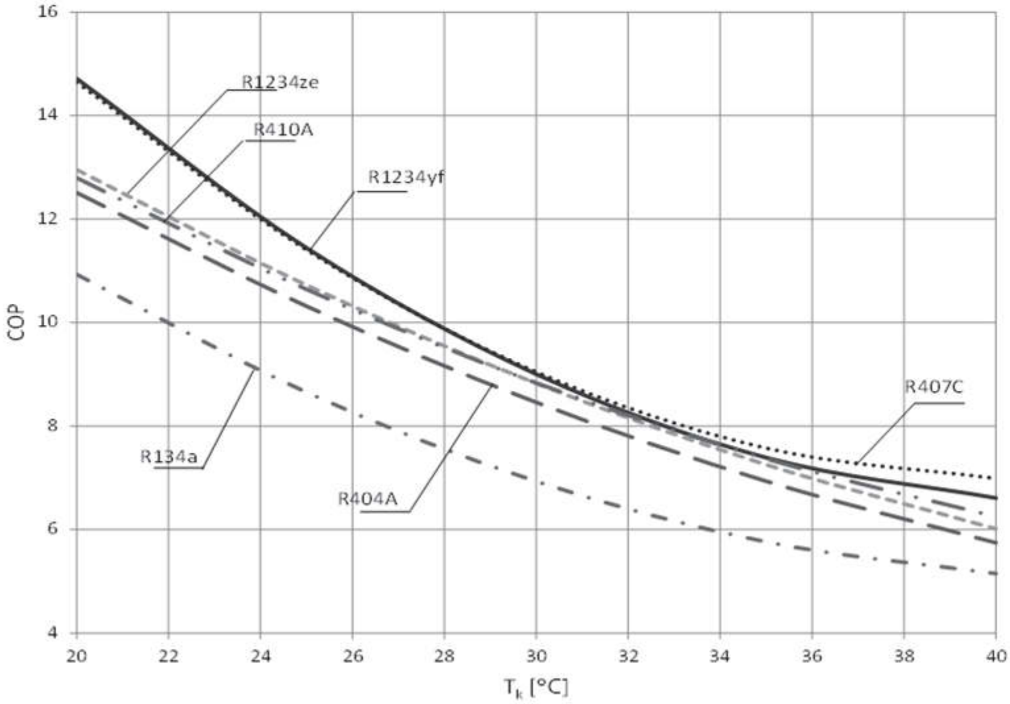
W niniejszym opracowaniu podjęto próbę oceny przydatności czynnika R1234yf w sprężarkowych, parowych pompach ciepła. Autorzy wykonali analizę porównawczą oceny efektywności obiegu *Lindego* suchego (rys. 2) z zastosowaniem czynników chłodniczych: R134a, R407C, R407C i R1234yf. Obieg *Lindego* suchy różni się od obiegu *Carnota* tym, że przemianę rozprężania izentropowego czynnika w obiegu *Carnota* zastąpiono nieodwracalną przemianą dławienia izentalpowego w zaworze rozprężnym. Ocena dotyczy więc, w pierwszym przybliżeniu, określenia wpływu stopnia nieodwracalności dławienia w zaworze na efektywność tego obiegu (pracującego zamiennie z różnymi czynnikami). W budowie porównawczego obiegu suchego *Lindego* (rys. 2) założono:

- stały poziom temperatury parowania t_o = 0°C,
- temperaturę skraplania t_k, w zakresie (t_k = 20–40°C) umożliwiającym realizację obiegu w sprężarkowej pompie ciepła.

Rysunek 6 prezentuje porównawcze zestawienie wyników obliczeń współczynnika wydajności cieplnej *COP* pompy ciepła pracującej w obiegu suchym *Lindego* z różnymi czynnikami chłodniczymi. Z rysunku 6 wynika, że dla wszystkich czynników chłodniczych wartość współczynnika *COP* obiegu pompy ciepła zmniejsza się ze wzrostem temperatury t_k (górnego źródła ciepła obiegu). Wartości współczynnika *COP* dla pompy ciepła pracującej z czynnikiem R1234yf są w podanym zakresie wartości t_k, wyraźnie większe, niż dla czynnika R134a. Może to świadczyć, że czynnik R1234yf może być, z punktu widzenia termodynamicznego, brany pod uwagę jako substytut czynnika R134a.

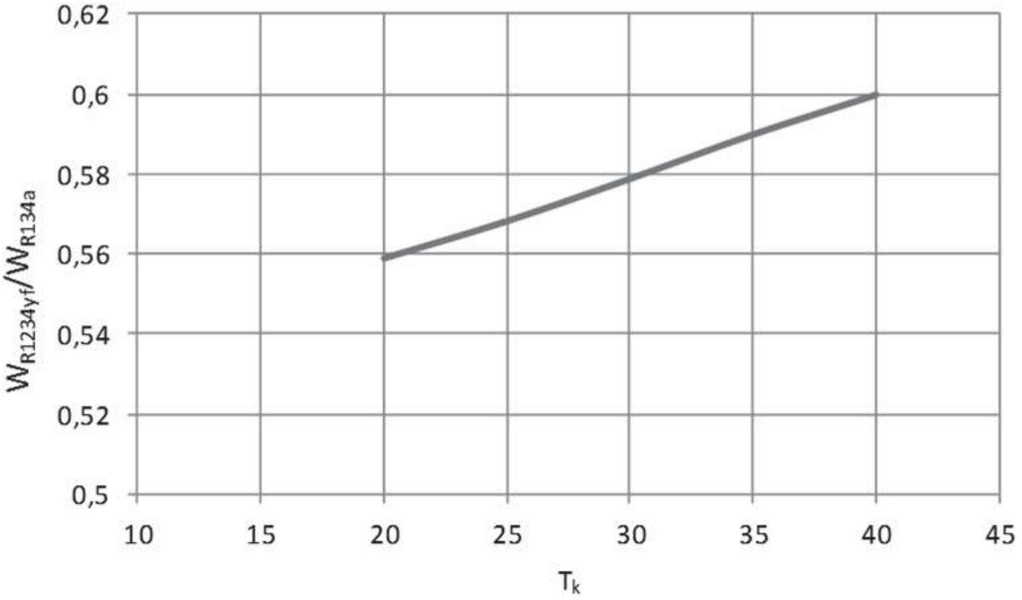
Teoretyczne, obliczeniowe wartości współczynnika wydajności *COP* pompy ciepła podane na rysunku 6 są relatywnie wysokie, co jest wystarczające dla celów porównawczych, jednak w warunkach rzeczywistych pracy pompy należy mieć na uwadze duży spadek tych wartości.

Wartość współczynnika *COP* nie ma rozstrzygającego wpływu na dobór czynnika chłodniczego do instalacji pompy ciepła, chociaż stanowi bardzo istotną informację dotyczącą wpływu właściwości na charakterystyki energetyczne pompy ciepła.



Rys. 6. Porównawcze zestawienie wyników obliczeń współczynnika wydajności *COP* pompy ciepła pracującej według suchego obiegu *Lindego* w zależności od temperatury skraplania t_k (przy t_o = 0°C) z czynnikami chłodniczymi: R134a, R1234yf, R1234ze, R404A, R407C i R410A
Fig. 6. Comparison of heat pump coefficient COP calculation results with is working as a dry left – racing Linde circle in dependence on condensation temperature t_k (when t_o = 0°C) with refrigerants: R134a, R1234yf, R1234ze, R404A, R407C i R410A

Wykonując obliczenia do wykresów z rysunku 6 zwrócono uwagę na elementy składowe wielkości współczynnika *COP*, tzn. na wartości jednostkowej pracy napędowej (praca techniczna w_t odniesiona do 1 kg czynnika) oraz jednostkowej ilości ciepła q_k odprowadzanego przez 1 kg czynnika ze skraplacza. Wobec powyższego pokazano na rysunku 7 zależność stosunku jednostkowych prac napędowych obiegu z czynnikami R1234yf i 134a, $w_{t,R1234yf} / w_{t,R134a} = f(t_k)$ dla obu porównywanych czynników. Na na rys. 8 podano zależność stosunku jednostkowego ciepła skraplania $q_{k,R1234yf} / q_{k,R134a}$, od temperatury skraplania t_k.

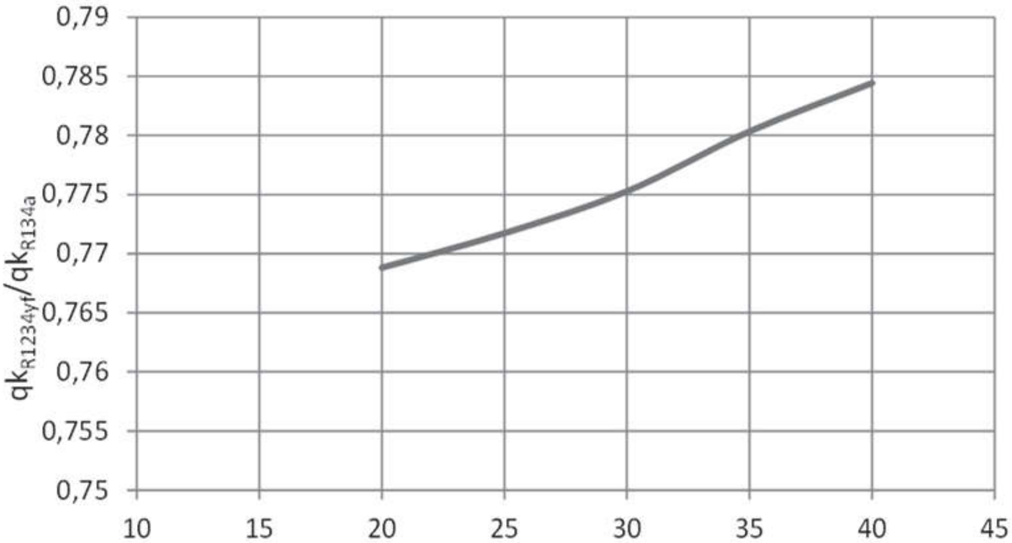


Rys. 7. Porównanie zależności $w_{t,R1234yf} / w_{t,R134a} = f(t_k)$ czynników chłodniczych R134a i R1234yf

Fig. 7. Dependence of $w_{t,R1234yf} / w_{t,R134a} = f(t_k)$ for R134a and R1234yf refrigerants

Wykonując obliczenia do wykresów z rys. 6 zwrócono uwagę na elementy składowe wielkości współczynnika *COP*, tzn. na wartości jednostkowej pracy napędowej (praca techniczna w_t odniesiona do 1 kg czynnika) oraz jednostkowej ilości ciepła q_k odprowadzanego przez 1 kg czynnika ze skraplacza. Wobec powyższego pokazano na rysumku 7 zależność stosunku jednostkowych prac napędowych obiegu z czynnikami R1234yf i 134a, $w_{t,R1234yf} / w_{t,R134a} = f(t_k)$ dla obu porównywanych czynników. Na rysunku 8 podano zależność stosunku jednostkowego ciepła skraplania $q_{k,R1234yf} / q_{k,R134a}$, od temperatury skraplania t_k.

W zakresie temperatury skraplania t_k = 20–40°C można z przebiegów obu wykresów (rys. 7 i 8) określić następujące wnioski: pompa ciepła pracująca z nowym czynnikiem chłodniczym R1234yf wymaga zmniejszonej mocy napędowej, w odniesieniu do czynnika R134a, przy czym ilość ciepła odprowadzana do górnego źródła stanowi 77–78% tej ilości, którą odprowadzałaby pompa z czynnikiem R134a. Wprawdzie współczynnik *COP* pompy ciepła wskazuje na lepszą efektywność energetyczną pompy z nowym czynnikiem, jednak ilościowo ciepło skraplania jest bezpośrednim efektem użytecznym jej pracy. Problem ten wymaga dokładniejszych badań w oparciu o wyniki eksperymentalne, co wskazałoby możliwość oceny egzergetycznej w odniesieniu do warunków rzeczywistych. Dla urządzenia chłodniczego pracującego zamiennie z czynnikami R134a i R1234yf przedstawiono rozszerzoną wersję analizy egzergetycznej obiegu lewobieżnego przegrzanego z dochłodzeniem w pracy autorów [18].



Rys. 8. Porównanie zależności $q_{k,R1234yf} / q_{k,R134a} = f(t_k)$ czynników chłodniczych R134a i R1234yf

Fig. 8. Dependence of $q_{k,R1234yf} / q_{k,R134a} = f(t_k)$ R124a and R1234yf for refrigerants

W pracy [24] wykazano, że stosując czynnik R1234yf w układach klimatyzacji samochodowej trzeba mieć na uwadze mniejszą o 8–10% wydajność chłodniczą parownika w stosunku do czynnika R134a oraz wzrost mocy napędowej silnika spalinowego pojazdu samochodowego o około 5,4%. Potwierdzają to również badania przedstawione w pracy [25].

Wzrastająca liczba publikacji poświęconych wynikom badań czynników chłodniczych alternatywnych dla R134a dotyczy również wyników badań wymiany ciepła podczas przemian fazowych wrzenia i skraplania. W pracy [26] podano, że wartość współczynnika przejmowania ciepła podczas skraplania czynnika R1234yf jest mniejsza o około 15–30% w porównaniu z R134a. Ma to oczywiście wpływ na wielkość powierzchni wymiany ciepła skraplacza, co jest istotnym problemem w pompie ciepła, ponieważ ciepło wyprowadzone ze skraplacza stanowi efekt użyteczny pracy tej pompy. Dla przemiany fazowej realizowanej w parowniku zauważono [25], że wartość współczynnika przejmowania ciepła w procesie wrzenia jest największa dla R290 i CO_2, natomiast dla R1234yf i R134a wartości są porównywalne, przy czym w przypadku czynnika R1234yf opory przepływu są mniejsze.

Przedstawiona wstępna analiza możliwości zastosowania czynnika chłodniczego R1234yf, jako alternatywnego w sprężarkowych pompach ciepła o małej wydajności wykazała, że pod względem termodynamicznym użycie tego zamiennika wobec czynnika R134a jest na razie problematyczne. Poza tym właściwości fizyczne i ekologiczne nowego czynnika chłodniczego budzą wątpliwości i czynnik jest obecnie nazywany *kontrowersyjnym* [24]. Fluorowany węglowodór R1234yf ($C_3H_2F_4$) wykazuje bowiem właściwości palne (temperatura zapłonu 405°C). W procesie palenia tego czynnika wydziela się kwas trójfluorowy oraz fluorek wodoru, szczególnie trujące i szkodliwe dla ludzi i zwierząt, a w przypadku fluorku wodoru uaktywniają się oddziaływania korozyjne. Poza tym, według doniesień [24] w produkcji czynnika R1234yf wykorzystuje się związki HCFC, które jako destrukcyjne ekologicznie zostały już wycofane z zastosowań. Dlatego czynnik R1234yf wzbudza wiele emocji i kontrowersji, zwłaszcza przez niektóre koncerny samochodowe, gdyż od 2017 roku jest proponowanym substytutem czynnika R134a.

Nie budzą więc zdziwienia poszukiwania innych, niż R1234yf, zamienników czynnika R134a. Pomimo bardzo wysokich wartości ciśnienia w instalacjach z czynnikiem CO_2 (R744) oraz konieczności stosowania obiegów nadkrytycznych (wobec niskiego położenia punktu krytycznego przy +31,05^{o}C) dwutlenek węgla jest proponowany przez wielu autorów, jako bardzo dobry, ekologiczny czynnik, alternatywny wobec R134a. Podobne argumenty są przedstawiane dla naturalnych czynników chłodniczych R290 (propan) i R600a (izobutan). Duża liczba publikacji dotyczy szerszego zastosowania propanu R290 w pompach ciepła.

Pompy ciepła są szczególnym typem urządzenia energetycznego, którego efektem jest doprowadzanie ciepła grzewczego, przy czym wprowadzenie do ich eksploatacji wymaga zainwestowania znacznych środków finansowych. Również z tego powodu niepewność, jaką wykazuje nowy czynnik R1234yf (obecnie kilkanaście razy droższy od R134a) ogranicza zastosowanie go w pompach ciepła. Jeżeli czynnik ten zostanie zaakceptowany przez producentów sprężarkowych pomp ciepła można przypuszczać, że będzie brany pod uwagę dla małych wydajności cieplnych.

6. Podsumowanie

W zakończeniu rozważań na temat wybranych aspektów prawno-technicznych i ekologicznych stosowania sprężarkowych pomp ciepła, zwłaszcza w warunkach możliwości wycofywania z eksploatacji czynnika chłodniczego R134a można sformułować następujące wnioski:

1. Pompy ciepła zalicza się do grupy niekonwencjonalnych urządzeń energetycznych, których funkcjonowanie jest aktywnie związane z odnawialnymi źródłami energii (*OZE*).
2. Pompy ciepła nie są w polskim prawodawstwie w sposób bezpośredni zaliczane do *OZE*. Procedury stosowane w Unii Europejskiej i kolejne decyzje Parlamentu Europejskiego i Rady Europy zmierzają do zrealizowania postulatu włączenia tych urządzeń do tej grupy. Oczekiwane są ustawowe orzeczenia w tej sprawie.
3. Pompy ciepła odznaczają się relatywnie niskimi kosztami eksploatacji, jednak wymagają uruchomienia dużych, początkowych nakładów inwestycyjnych.
4. Istotnym problemem w pracy sprężarkowych pomp ciepła jest właściwy dobór czynnika chłodniczego. Konieczność wycofania od 2017 roku z przyczyn ekologicznych, czynnika R134a stosowanego aktualnie w pompach ciepła o średniej i małej wydajności, stwarza potrzebę wprowadzenia jego proekologicznego substytutu.

5. Wśród czynników chłodniczych jednorodnych i jednoskładnikowych proponowanych jako substytuty R134a wymienia się: NH_3 (R718), CO_2 (R744), propan (R290) i izobutan (R600a). Obecnie w pompach ciepła o średniej i dużej wydajności są stosowane mieszaniny azeotropowe: R404A, R407C i R410A.
6. W opracowaniu rozważono możliwość zastosowania czynnika chłodniczego R1234yf (z grupy tzw. fluorowanych węglowodorów) proponowanego, jako substytut czynnika R134a w klimatyzacji samochodowej od 2017 roku, w obiegach sprężarkowych pomp ciepła o małej wydajności.
7. Zastosowanie zamienników czynnika R134a w pompach ciepła w postaci czynnika R1234yf jest możliwe, jednak należy się liczyć z mniejszą wydajnością górnego źródła ciepła i koniecznością zwiększenia pola powierzchni skraplacza. Każdą decyzję o wprowadzeniu tego substytutu należy przeanalizować pod kątem szkodliwych właściwości palnych i trujących.
8. Aktualnie brak jest jednoznacznych decyzji proponowanego substytutu R134a; oprócz R1234yf wymienia się: R744, R290 i R600a. Bezwzględną koniecznością jest wykonanie wielu badań eksperymentalnych pozwalających na określenie rzeczywistych wartości współczynnika COP i przeprowadzenie analizy egzegetycznej dla warunków rzeczywistych pracy pompy.

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Literatura

1. **Charun H.:** *Podstawy gospodarki energetycznej w zarysie, tom 1*. Wydawnictwo Uczelniane Politechniki Koszalińskiej, Koszalin 2014.
2. Oświadczenie rządowe z dnia 26 maja 1992 r. w sprawie przystąpienia Rzeczpospolitej Polskiej do Protokołu montrealskiego w sprawie substancji zubożających warstwę ozonową, sporządzonego w Montrealu dnia 16 września 1987 (Dz.U. z 1992 r., nr 98, poz. 488, 491 i 490).
3. **Skonieczna J., Ciesielczyk W.:** *Analiza pracy pomp ciepła z czynnikiem roboczym R407C*. Chemia, 106, z4(4), 127–139 (2009).
4. Ustawa Prawo Energetyczne z dnia 10.04.1997 r. z późniejszymi zmianami (tekst jednolity w Dz.U. z 2006, nr 89, poz. 625 – stan tekstu ustawy dostępny w Biurze Prasowym URE w dniu 5.09.2014 r.).

5. **Bohdal T., Charun H., Czapp M.:** *Urządzenia chłodnicze sprężarkowe parowe*. WNT, Warszawa 2003.
6. **Rubik M.:** *Sprężarkowe pompy ciepła w Polsce*. Chłodnictwo & Klimatyzacja, 12, 68–78 (2007).
7. Dyrektywa 2009/28/WE Parlamentu Europejskiego i Rady o promowaniu energii ze źródeł odnawialnych.
8. **Lachman P.:** *Spór o minimalną wartość SPF w dyrektywie OZE*. Polski Instalator, nr specjalny PI3, 78–83 (2010).
9. **Kubski P.:** *Unijna sprawność*. Magazyn Instalatora, 1, 42 (2010).
10. **Lachman P.:** Kiedy *pompy ciepła korzystają z OZE?* Czysta Energia, 12, (2013).
11. **Bohdal L, Kukielka L.:** *Application of variational and FEM methods to the modelling and numerical analysis of guillotining process for geometrical and physical nonlinearity*. Mechanika, 20(2), 197–204 (2014).
12. **Langman E.:** *Pompy ciepła – projekt europejskich kryteriów ekologicznych*. Chłodnictwo & Klimatyzacja, 4, 82–85 (2007).
13. Rozporządzenie Ministra Gospodarki i Pracy z 20.05.2005 r. w sprawie wymagań dotyczących dokumentacji technicznej, stosowania etykiet i charakterystyk technicznych (Dz.U. nr 78 z 2005 r., poz. 825).
14. **Bonca Z., Butrymowicz D., Dambek D., Depta A., Targański W.:** *Czynniki chłodnicze i nośniki ciepła. Własności cieplne, chemiczne i eksploatacyjne*. Wyd. JPPU MASTA, Gdańsk 1997.
15. Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to emissions from air-conditioning system In motor vehicles and amending Council Directive 70/156/EC.
16. PN-EN378:2002 Instalacje ziębnicze i pompy ciepłą. Wymagania dotyczące bezpieczeństwa i ochrony środowiska.
17. **Higashi Y., Iwaki J.C.:** *Thermophysical properties of HFO-1234yf and HFO-1234ze(E)*. International Symposium on Next Generation Air Conditioning and Refrigeration Technology, Tokyo 2010.
18. **Ansari N.A., Yadan B., Kumar J.:** *Theoretical Exergy analysis of HFO-1234yf and HFO-1234ze as an alternative replacement refrigeration system*. International Journal of Scientific&Engineering Research, 4(8), 137–144 (2013).
19. Materiały firmy Solway.
20. Materiały firmy Honeywell.
21. **Akasara R., Tanaka K., Higashiy:** *Thermodynamic property modelling for 2,3,3,3 – tetrafluoropropene (HFO-1234yf)*. International Journal of Refrigeration, 33, 52–60 (2010).

22. **Brown J.S., Zilio C., Cavallini A.:** *Thermodynamic properties of eight fluorinated defines.* International Journal of Refrigeration, 33, 235–241 (2010).
23. **Minor B., Spatz M.:** *HFO-1234yf low GWP refrigerant update*. International Refrigeration and Air Conditioning Conference, 2008, Purdue University.
24. **Wesołowski A.:** *Kontrowersje związane z r1234yf jako czynnikiem chłodniczym.* Chłodnictwo & Klimatyzacja, 10, 16–19 (2010).
25. **Andrzejczyk R., Muszyński T.:** *Alternatywne do R134a czynniki proponowane jako płyny robocze w klimatyzacji samochodowej i innych instalacjach chłodniczych o małej wydajności.* Chłodnictwo, 5 – Część 1, 2012, 6–7 – Część 2, 2013, 10 – Część 3.
26. **Del Col D., Torresie D., Cavallini A.:** *Heat transfer and pressure drop during condensation of the low GWP refrigerant R1234yf.* International Journal of Refrigeration, 33, 1307–1318 (2010).
27. **Baj P., Butrymowicz D.:** *Optymalne ciśnienie robocze dla obiegu dwutlenku węgla w obszarze nadkrytycznym*. Chłodnictwo & Klimatyzacja, 10, 30–34 (2010).

Selected Aspects of Legal, Technical and Ecological Use of Compression Heat Pumps

Abstract

Destructive impact of chlorofluorocarbons refrigerants (CFCs), especially R12 and R22, on the environment (creation of the ozone hole and the greenhouse effect) led to their withdrawal from use in refrigeration and heat pumps. Due to the high global warming potential (GWP=1300) also widely used R134a refrigerant will be withdrawn from use from 2017. Ongoing search for environmentally friendly alternatives refrigerants among which are listed the refrigerants from the R1234 group – especially R1234yf. In previous publications of various authors, was analyzed the use of this refrigerant in refrigeration. The authors have made an attempt on the possibility of the application of this refrigerant in the compressor, steam heat pumps. Made comparative calculations indicate that implementation of this substitute is possible in a limited scope resulting from the reduction of the heating capacity outputted to the upper source.

Słowa klucze:
pompy ciepła, czynniki chłodnicze, R1234yf, R1234ze, COP, GWP, ODP

Keywords:
heat pumps, refrigerants, R1234yf, R1234ze, COP, GWP, ODP

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Studium nad łączeniem mikro kanalikowych wymienników ciepła w wymiennik integralny

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1. Wstęp

W pracy przyjęto nową koncepcję realizacji wymienników ciepła przy pomocy sieci wymienników elementarnych, tworzących zespolony wymiennik, zamiast projektowania typoszeregu wymienników. Pozwala to na większą swobodę w doborze sieci wymienników, w konsekwencji czego, zbędne staje się projektowanie konkretnego pojedynczego wymiennika. Zespolony wymiennik ciepła to wymiennik składający się z elementarnych wymienników ciepła o jednakowej konstrukcji i wielkości. Łączenie wymienników w sieci może być równoległe lub szeregowe. Im mniejsze elementy w sieci i większa ich liczba, to tym większa złożoność struktury sieci, jak również większa możliwość uzyskania integralnego wymiennika ekwiwalentnego, indywidualnie zaprojektowanego. Konfiguracja sieci może być optymalizowana, np. przy pomocy zasady „drzewa" Bejan'a.

Projektowanie sieci wymienników to nowy kierunek rozwoju architektury wymienników ciepła, dzięki któremu można osiągnąć jednocześnie dwa cele: (i) minimalny opór hydrauliczny (lub moc pompowania) oraz (ii) minimalny opór cieplny przepon rekuperatora. Optymalizacja przepływu w sieci wymienników przy pomocy zasady strukturalnej „drzewa" [1, 10] reprezentuje nowy trend w optymalizacji i miniaturyzacji urządzenia do przenoszenia ciepła [1, 5–7, 9, 10]. Optymalne „drzewa" obiecują lepsze wykorzystanie dostępnej przestrzeni: wyższe gęstości strumieni ciepła.

Poprawa ogólnych parametrów termodynamicznych systemu oznacza spadek nieodwracalności (lub generacji entropii, niszczenia egzergii), która charakteryzuje wszystkie składniki procesów w układzie termodynamicznym. Entropia generowana przez każdy element układu jest proporcjonalna do oporu przepływu czynnika i wymienianego ciepła. Innymi słowy, cały proces optymalizacji termodynamicznej sieci wymienników opiera się na zminimalizowaniu wszystkich oporów strumienia ciepła i oporów przepływowych.

To prawo opiera się na wspólnej (uniwersalnej) zasadzie zaobserwowanej przez Bejan'a, która mówi, że jeśli system przepływowy (np. dorzecze rzeki, naczynie krwionośne) obdarzony jest wystarczającą swobodą zmiany jego konfiguracji, to ów system tworzy konfigurację, która daje coraz to lepszy dostęp do tras przepływu prądów oraz najmniejsze opory przepływu. Jest to zgodne z Drugą Zasadą Termodynamiki. Strzałka czasu wiąże się tu z sekwencją konfiguracji przepływu układu. Powyższa zasada była sformułowana po raz pierwszy w formie książkowej przez Bejan'a (1997). Stanowi ona nowe rozszerzenie fizyki: termodynamiki przepływu systemów z konfiguracjami (Bejan i Lorente 2004, 2005). Aby zadać sobie pytanie, dlaczego zasada wyżej sformułowana jest prawem fizyki, należałoby zapytać, dlaczego ta zasada jest inna niż (tj., w odróżnieniu od, lub uzupełnieniem) pozostałe zasady termodynamiki. Myśląc termodynamicznie, rozważmy układ, który początkowo jest w stanie wewnętrznej nierównowagi (np. istnieją regiony wyższego i niższego ciśnienia lub temperatury, oddzielone przegrodami, które nagle zostają przerwane), zgodnie z pierwszą i drugą zasadą opisującą tendencję układu do osiągnięcia równowagi w dostatecznie długim czasie. Jeśli wystarczy czasu, układ przechodzi do stanu równowagi (nie ma wówczas wewnętrznych przepływów, osiąga maksimum entropii przy zachowaniu stałej energii, itp.). Pierwsza i druga zasada termodynamiki mówią o „czarnej skrzynce". Nic nie mówią o konfiguracjach przepływu, jakie przechodzi układ. Zasada strukturalna Bejan'a opiera się na zasadach fenomenologicznych obserwacji (uniwersalnych). Jeśli system jest obdarzony swobodą zmiany jego konfiguracji, to system tworzy konfiguracje, które stanowią coraz lepszy dostęp do tras przepływu dla prądów i strumieni. Obserwacji tego rodzaju są miliardy, i one oznaczają jedno: strzałka czasu wiąże się z sekwencją konfiguracji strumieni. Istniejące konfiguracje są zastępowane przez łatwiejsze przepływowo konfiguracje.

Zasada ta będzie wykorzystywana do projektowania optymalnych sieci wymienników tworzących zintegrowany wymiennik ciepła w układzie termodynamicznym.

2. Sformułowanie problemu i zasady tworzenia sieci wymienników

Głównym problemem jest odpowiedź na pytanie, ile trzeba połączyć wymienników elementarnych w sieć, aby uzyskać zintegrowany wymiennik ciepła o założonych charakterystykach cieplno-przepływowych.

Łączenie elementarnych wymienników wymieniających ciepło między czynnikiem gorącym i zimnym może być szeregowe lub równoległe z uwagi na każdy z czynników.

Załóżmy, że każdy elementarny wymiennik ciepła jest identyczny pod względem konstrukcyjnym i znane są jego charakterystyki geometryczne i cieplno-przepływowe.

Przyjmując dodatkowo, że własności termodynamiczne nie zależą od temperatury i ciśnienia, mamy:

1. Przy połączeniu szeregowym strumieni poszczególnych czynników natężenie przepływu czynnika jest stałe, a zmiany temperatury, zgodnie z bilansem energii, są sumą spadków temperatury na poszczególnych wymiennikach elementarnych. Całkowity spadek ciśnienia na strumieniu czynnika jest sumą spadków ciśnienia na poszczególnych wymiennikach elementarnych. Można to zapisać jako:

$$\dot{m} = \mathrm{const} \tag{1}$$

$$\Delta t_{total} = \sum \Delta t_i \tag{2}$$

$$\Delta p_{total} = \sum \Delta p_i \tag{3}$$

2. Przy łączeniu równoległym poszczególnych strumieni czynników natężenie przepływu czynnika jest sumą natężeń przepływu w wymiennikach elementarnych, a zmiany temperatury, zgodnie z bilansem energii, są stałe na poszczególnych wymiennikach elementarnych. Całkowity spadek ciśnienia jest równy spadkowi ciśnienia na poszczególnych wymiennikach elementarnych. Można to zapisać jako:

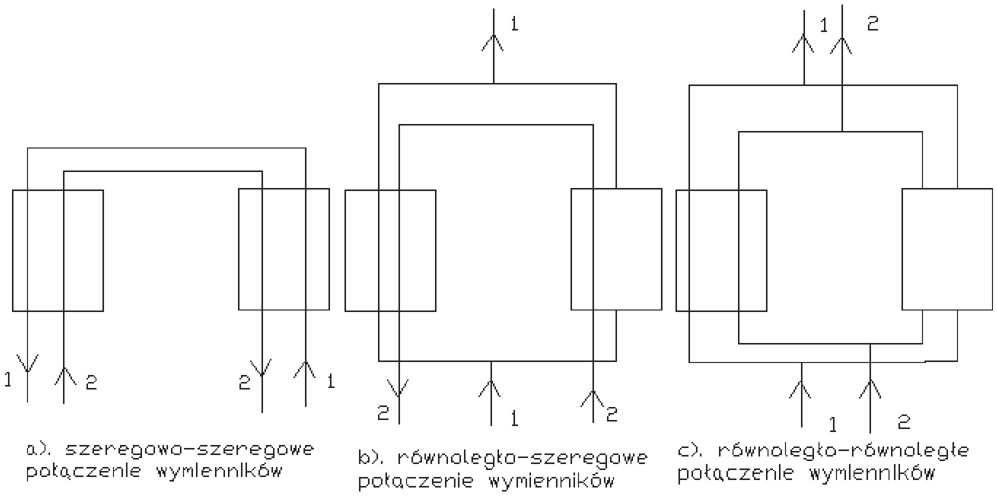
$$\Delta t_i = \mathrm{const} \tag{4}$$

$$\dot{m}_{total} = \sum \dot{m}_i \tag{5}$$

$$\Delta p_{\mathrm{total}} = \Delta p_{\mathrm{i}} \tag{6}$$

zakładając, że straty ciśnienia nie są istotne przy przepływie czynnika roboczego przez sieć wymienników.

Jak wynika z powyższych rozważań, istnieją dwie sieci połączeń strumieni. Sieć strumienia gorącego i sieć strumienia ogrzewanego – zimnego. Wobec tego dwa elementarne wymienniki ciepła o znanej konstrukcji i charakterystykach cieplno-przepływowych można połączyć na trzy sposoby: szeregowo-szeregowy, równoległo-szeregowy i równoległo-równoległy (rysunek 1) Każdy z elementarnych wymienników może pracować jako współprądowy albo przeciwprądowy wymiennik.

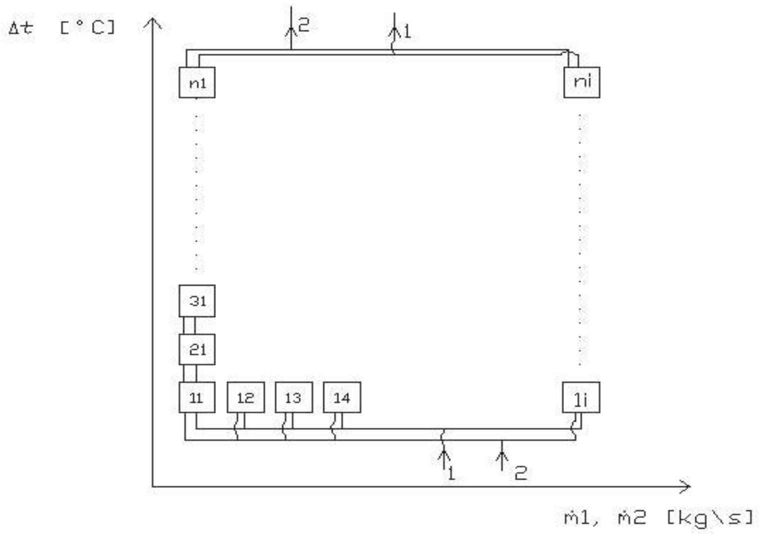


Rys. 1. Połączenia dwóch elementarnych wymienników ciepła: a) szeregowo-szeregowe, b) równoległo-szeregowe, c) równoległo-równoległe
Fig. 1. Outline of two primary micro channel heat exhangers connection: a) serial-serial, b) paralel-serial, c) paralel-parallel

W przypadku a) mamy do czynienia z klasycznym wymiennikiem podzielonym na sekcje i jego sposób obliczeń nie odbiega od konwencjonalnego. W przypadkach b) i c), wymienniki elementarne, składające się na sieć, są obliczane zgodnie z opisanymi w niniejszej pracy zasadami. Do tak połączonych wymienników można dołączyć kolejny wymiennik, który będzie z zespołem dwóch wymienników połączony na sposób a, b lub c. Zespoły elementarnych wymienników tworzą wówczas jednostkowy wymiennik ciepła.

Zastąpienie wymiennika siecią wymienników może być realizowane przez sieć jednostkowych wymienników ciepła odpowiadających schematowi a, b lub c. Jednostkowe wymienniki ciepła zbudowane z elementarnych wymienników pozwalają na realizację określonego, wynikającego z bilansu ciepła, stosunku natężeń przepływu czynnika gorącego do zimnego oraz odpowiedniego stosunku zmian temperatury czynników.

Aby uzyskać wymianę ciepła przy całkowitych natężeniach przepływu czynników oraz pożądaną różnicę temperatur pomiędzy wyjściem a wejściem czynników z zespolonego wymiennika ciepła, należy połączyć równolegle i kolumn jednostkowych wymienników posiadających n jednostkowych wymienników w kolumnie, rysunek 2.



Rys. 2. Schemat zespolonego wymiennika ciepła zbudowanego z jednostkowych wymienników ciepła
Fig. 2. Scheme of the integral micro channel heat exchanger made of unitary micro channel heat exchangers

Ostatecznie, otrzymamy jako zintegrowany wymiennik, wymiennik o $i \times n$ wymiennikach jednostkowych, w którym każdy jednostkowy wymiennik posiada $k + 1$ wymienników elementarnych, gdzie k jest stosunkiem natężeń przepływu czynnika gorącego do zimnego. Opracowana metoda projektowania wymienników ma charakter hierarchiczny, o trzech poziomach : wymienniki elementarne, wymienniki jednostkowe, wymiennik integralny.

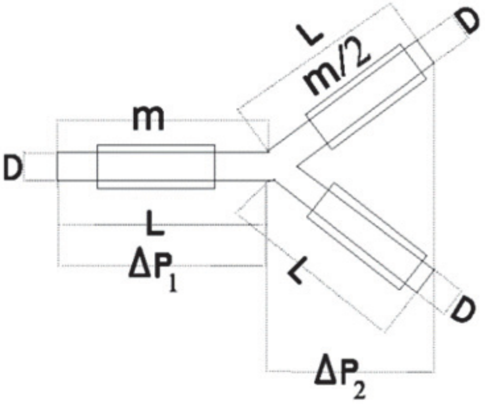
W przedstawionym powyżej schemacie połączeń jednostkowych wymienników ciepła kolumny wymienników są niezależne, gdyż pracują równolegle. Można sobie wyobrazić bardziej złożoną sieć, w której czynniki przepływające przez elementarne wymienniki ciepła tworzą dwa „drzewa". Wówczas, taką sieć należałoby zoptymalizować zgodnie z zasadą Bejan'a.

Przyjmując, że przepływ czynników w elementarnych wymiennikach jest laminarny, to każde rozdzielenie przepływu na przepływy równoległe powoduje redukcję tarciowego spadku ciśnienia o połowę, przy zachowaniu w każdym z wymienników składowych tego samego współczynnika przejmowania ciepła, co jest charakterystyczne dla ruchu laminarnego. Ilustruje to rysunek 3. Rozwinięty przepływ laminarny daje tym wyższe współczynniki przejmowania ciepła im mniejsza jest średnica hydrauliczna kanału. Stąd też jako elementarne wymienniki ciepła mogą być zastosowane mikro-wymienniki opracowane w IMP PAN [5,6]. Podczas rozgałęziania się przepływu na dwa identyczne strumienie, otrzymuje się dwa razy mniejsze spadki ciśnienia. To stwierdzenie jest słuszne dla przepływu laminarnego. Mając na względzie (7) oraz równanie ciągłości, otrzymano ostatecznie (8) (rysunek 3).

$$\Delta p = \xi \frac{\varrho w^2}{2} \frac{L}{D_h} \tag{7}$$

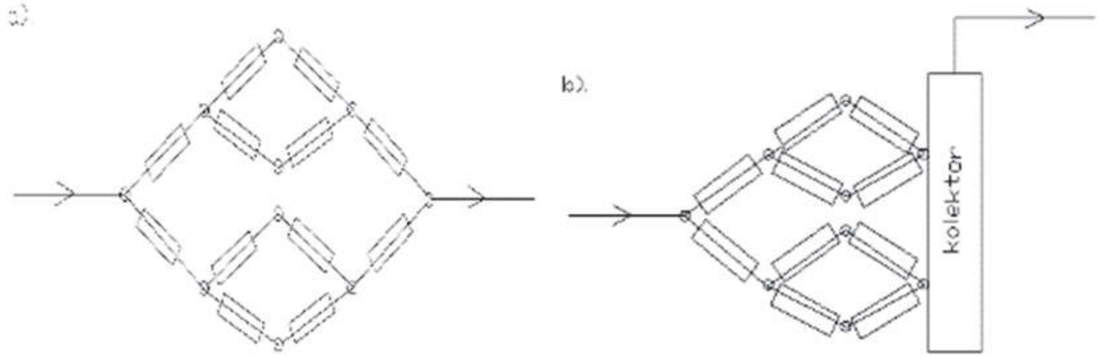
gdzie $\xi = \frac{64}{Re}$ – dla przepływu laminarnego.

$$\Delta p_2 = \frac{\Delta p_1}{2} \tag{8}$$



Rys. 3. Rozpływ laminarny czynnika na dwa równoległe kanały
Fig. 3. Laminar spread of the refrigerant flow onto two parallel channels

W celu redukcji tarciowego spadku ciśnienia w integralnym wymienniku, można zastosować sieci w postaci drzew, jak na rysunku 4.



Rys. 4. Fragment sieci wymienników realizujących rozpływ przepływu laminarnego; a). bez kolektora, b). z kolektorem
Fig. 4. Fragment of the micro channel heat exchangers grid realizing spread of the laminar flow ; a) without a collector, b) with the collector

W celu dalszej intensyfikacji wymiany ciepła można zastosować sieć wymienników elementarnych, w których wykorzystywany jest laminarny rozbieg termiczny. W tym przypadku kanały wymiennika ciepła powinny być krótsze od długości rozbiegu termicznego, określonego zależnością [3]:

$$\frac{L_{rt}}{D} \le 0.16\frac{w\,D}{\nu}, Pr > 1 \tag{9}$$

gdzie:
L_{rt} – długość rozbiegu termicznego
w – prędkość płynu
ν – lepkość
D – śrdenica

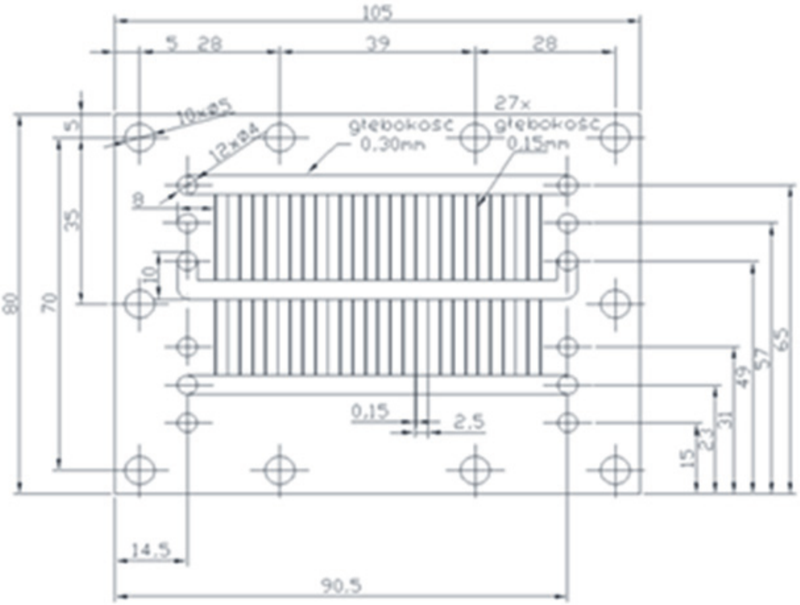
Efektywność rozwiązania sieciowego w porównaniu z projektowaniem bezpośrednim wymiennika ciepła można określić jako stosunek powierzchni zintegrowanego wymiennika do powierzchni wymiennika specjalnie do tego celu zaprojektowanego:

$$\varepsilon = \frac{A_{int}}{A_{proj}} \tag{10}$$

3. Przykład obliczeniowy

W niniejszej pracy, dotyczącej łączenia mikrowymienników, jako najbardziej podstawowy komponent, wybrano pojedynczą parę płyt z mikrokanalikami. Na rysunku 5 przedstawiono schemat takiej płyty. Wykonana jest ona z blachy o grubości 0.3 [mm], na której znajdują się dwa rzędy po 67 kanalików o długości 17 [mm] i przekroju poprzecznym (0.3x0.1) [mm]. Te dwa rzędy kanalików połączone są szeregowo, co powoduje spadek ciśnienia dwa razy większy niż dla pojedynczego kanalika (zaniedbano niewielkie opory przepływu w kolektorach zbiorczych). Podstawowym elementem jest w tym przypadku para płyt. Przez jedną z nich przepływa czynnik grzewczy (w tym przypadku woda grzejąca), a przez drugą płytę czynnik roboczy (w tym przypadku R134a). Obliczono wymaganą liczbę takich par płyt, pogrupowanych w tzw. wymienniki elementarne, z których jeden, wg założeń, ma przenosić moc cieplną 10 kW. Z kolei, para takich wymienników elementarnych składa się na wymiennik jednostkowy, co opisano w podpunktach 3.2 i 3.3.

Czynnik roboczy wybrano na podstawie analizy pracy [2], w której to przedstawiono porównanie kilku proekologicznych płynów roboczych. Zgodnie z tym, co podaje autor, R134a charakteryzuje się najwyższymi wartościami współczynnika przejmowania ciepła.

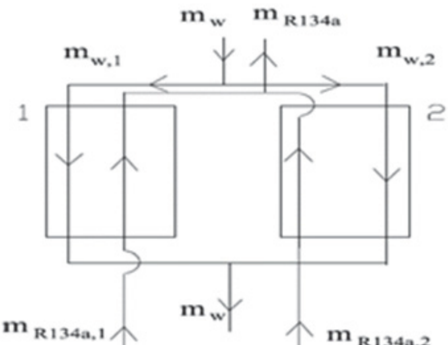


Rys. 5. Schemat pojedynczej płytki
Fig. 5. Scheme of the single plate with micro channels

3.1. Model odniesienia – połączenie równoległo (woda) – równoległe (R134a)

Łączenie mikrowymienników jest złożonym i nietrywialnym zagadnieniem, które dotychczas było rozważane w literaturze w sposób ogólny, a nie tak, jak to poczyniono w niniejszej pracy. Przeanalizowano zatem model odniesienia, zilustrowany na rysunku 6. Poniżej przedstawiono dane wejściowe, które posłużyły do obliczeń:

1. Zestaw mikrowymienników ma posłużyć do tego, aby podgrzać czynnik R134a od temperatury $t_{R134a} = 32.8$ [°C] do $t_{R134a} = 85$ [°C] przy użyciu medium grzewczego w postaci wody o temperaturze wlotowej i wylotowej równej odpowiednio $t_w = 90$ [°C] i $t_w = 60$ [°C].
2. Dysponowana całkowita moc cieplna niesiona przez strumień gorącej wody wynosi $\dot{Q}_{cał} = 83.2\ [MW_t]$.
3. Przyjęto, iż wymiennik elementarny ma realizować wymianę ciepła między czynnikiem grzejącym i ogrzewanym na poziomie $\dot{Q}_e = 10\ [kW]$, przy założonych temperaturach podanych w punkcie 1.
4. Zadano ciśnienie wody w kanalikach o wartości $p_w = 1.1\ [bar]$ oraz ciśnienie czynnika R134a wynoszące $p_{R134a} = 42\ [bar]$.
5. Mikrokanaliki wymiennika, o prostokątnym przekroju poprzecznym, mają długość $L = 17 \cdot 10^{-3} [m]$, przy czym powierzchnia przekroju poprzecznego ma wymiar:
$F = a \cdot b = 3 \cdot 10^{-8} [m^2]$. Wymiennik elementarny składa się z płytek o 134 kanalikach.



Rys. 6. Schemat połączenia równoległo-równoległego dwóch płytek z mikro kanałami
Fig. 6. Scheme of the parallel-parallel connection of two plates with micro channels

Mając dane powyższe, dokonano następujących obliczeń:

1. Określono wartość wydatku masowego wody oraz czynnika R134a w pojedynczym wymienniku elementarnym.

   Z bilansu energii wynika, że:

$$\dot{Q}_{w,e} = \dot{m}_{w,e} \Delta h_{w,e} \tag{11}$$

$$\dot{m}_{w,e} = 0.08 \left[\frac{kg}{s}\right]$$

   oraz, że masowe natężenie czynnika roboczego R134a wynosi:

$$\dot{m}_{R134a,e} = 0.12 \left[\frac{kg}{s}\right]$$

2. Z uwagi na fakt, iż opór cieplny ścianek jest zaniedbywalnie mały, wzór na współczynnik przenikania ciepła sprowadza się do postaci: $\frac{1}{k} = \frac{1}{\alpha_{R134a}} + \frac{1}{\alpha_w}$. Wartości współczynników przejmowania ciepła dla obu mediów wyliczono korzystając z poniższego wzoru:

$$\alpha = \frac{Nu\,\lambda}{d_h} \tag{12}$$

Wartość Liczby Nusselt'a dla stosunku $\frac{a}{b} = \frac{0.3}{0.1} = 3$ wynosi $Nu = 4.79$ [7], przy w pełni rozwiniętym przepływie laminarnym. Z kolei średnica hydrauliczna, dana wzorem:

$$d_h = \frac{2ab}{a+b} \tag{13}$$

ma wartość $d_h = 0.15 \cdot 10^{-3}\ [m^2]$. Dodatkowo, przy użyciu programu EES, wyliczono wartości współczynników przewodzenia ciepła dla obu płynów, dla średniej temperatury każdego z nich, tj.

$\lambda_{R134a} = 0.07 \left[\frac{W}{mK}\right]$ oraz $\lambda_w = 0.65 \left[\frac{W}{mK}\right]$.

Zgodnie z powyższym, otrzymano:

$\alpha_w = 20856 \left[\frac{W}{m^2K}\right]$, $\alpha_{R134a} = 2229 \left[\frac{W}{m^2K}\right]$,

natomiast $k = 2013.47 \left[\frac{W}{m^2K}\right]$.

3. Mając dane cztery temperatury, tj. temperatury wody i czynnika R134a na wlocie i wylocie z wymiennika jednostkowego, obliczono $\Delta t_{log} = 13.11$ [°C].

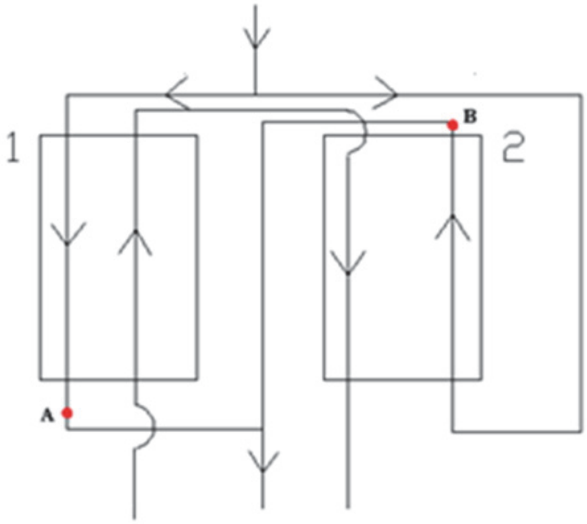
4. Korzystając ze wzoru Peclet'a, wyznaczono całkowitą powierzchnię wymiany ciepła w wymienniku elementarnym:
$$A_e = \frac{\dot{Q}_e}{k\ \Delta t_{log}} [m^2] \tag{14}$$
$A_e = 0.38\ [m^2]$
5. Powierzchnia pojedynczego kanalika wynosi:
$$A_{kanalik} = 2(a+b)L \tag{15}$$
$A_{kanalik} = 13.6 \cdot 10^{-6} [m^2]$
6. Liczba kanalików w jednym wymienniku elementarnym, przez które przepływa woda i czynnik R134a, odpowiednio: $n_{w,e} = \frac{A_e}{A_{kanalik}} \approx 27868$ oraz $n_{R134a,e} = \frac{A_e}{A_{kanalik}} \approx 27868$
7. Liczba płytek w wymienniku elementarnym po stronie czynnika R134a i wody, pamiętając, że $N_e = N_{w,e} + N_{R134a,e}$, gdzie: $N_{R134a,e} = \frac{n_{R134a,e}}{ilość\ kanalików\ w\ płytce} \approx 208$, $N_{R134a,e} = \frac{n_{R134a,e}}{ilość\ kanalików\ w\ płytce} \approx 208$, $N_e = 416$ – jest to ilość płytek mikro kanałowego wymiennika realizująca wymianę ciepła na poziomie $\dot{Q}_e = 10\ [kW]$. Natomiast, chcąc wykorzystać $\dot{Q}_{cał} = 83.2\ [MW_t]$ należy użyć $N_{wymienników} = \frac{\dot{Q}_{cał}}{\dot{Q}_e} = 8320$ wymienników elementarnych, tj. całkowita liczba płytek $N_{cał} = N_{wymienników} \cdot N_e = 3.5 \cdot 10^6$.

3.2. Przykład połączenia równoległo (woda) – szeregowego (R134a)

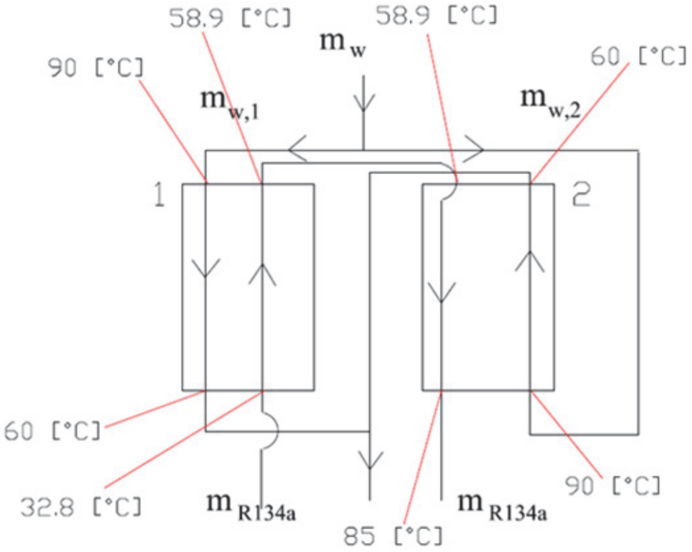
Rysunek 7 przedstawia schemat ogólny połączenia szeregowo-równoległego dwóch mikrowymienników składających się na wymiennik jednostkowy.

Na rysunku 8 przedstawiono schemat ilustrujący połączenie równoległo (woda grzejąca) – szeregowe (R134a), którego analizę opisano poniżej. Celem zilustrowania omawianego zagadnienia łączenia mikro kanałowych wymienników w sieci, przedstawiono stosowne przykłady, mające na celu wskazanie praktycznych zastosowań owej teorii. Pisząc ogólnie, problem sprowadza się do zagospodarowania ciepła, którego nośnikiem jest woda o temperaturze wlotowej i wylotowej równej odpowiednio $t_{w,wlot} = 90$ [°C], $t_{w,wylot} = 60$ [°C], oraz mocy cieplnej

$\dot{Q}_{wody} = 83{,}2\ [MW]$. Ogrzewanym medium, o całkowitym masowym natężeniu przepływu $\dot{m}_{R134a,cał} = 410{,}5\left[\frac{kg}{s}\right]$, jest czynnik roboczy R134a. Temperatura końcowa tego czynnika wynosi $t_{R134a,wylot} = 85[°C]$.



Rys. 7. Schemat ogólny połączenia szeregowo-równoległego dwóch mikrowymienników
Fig. 7. General scheme of the serial-parallel combination of two plates with micro channels



Rys. 8. Równoległo (woda) – szeregowe (R134a) połączenie dwóch wymienników elementarnych, składających się na wymiennik jednostkowy
Fig. 8. Parallel (heating water) – serial (R134a) connection of two primary micro channel heat exchangers, which make up the unitary heat exchanger

W tym miejscu należy sprecyzować poczynione założenia, dla analizowanego układu, przedstawionego na rysunku 8, które są następujące:

i) Oba wymienniki elementarne 1 i 2 połączone są ze sobą w taki sposób, że woda przepływa przez nie równolegle, a czynnik R134a szeregowo.

ii) Rozpływ wody na dwa równoległe strumienie ma charakter nierównomierny

iii) Wiadomym jest, iż przy przepływie szeregowym, przez wymienniki elementarne, czynnika R134a, jego wydatek będzie taki sam, wobec czego: $\dot{m}_{R134a,1} = \dot{m}_{R134a,2}$.

iv) Całkowita moc cieplna wymiennika jednostkowego, $\dot{Q}_{jedn}$ jest sumą mocy cieplnych wymienników elementarnych, tj.: $\dot{Q}_1 + \dot{Q}_2 = \dot{Q}_{jedn}$.

v) W rozpatrywanym przypadku nie uwzględnia się strat ciepła do otoczenia, wobec czego można zapisać, że dysponowany strumień ciepła niesiony przez czynnik ogrzewający zostanie w pełni przekazany czynnikowi ogrzewanemu. Tak więc, w przypadku obu wymienników elementarnych 1 i 2, bilans ciepła przedstawia się następująco:

$$\dot{Q}_1 = \dot{m}_{w,1} \cdot c_{p,w} \cdot \Delta t_{w,1} \tag{16}$$

$$\dot{Q}_1 = \dot{m}_{R134a,1} \cdot c_{p,R134a} \cdot \Delta t_{R134a,1} \tag{17}$$

$$\dot{Q}_2 = \dot{m}_{w,2} \cdot c_{p,w} \cdot \Delta t_{w,2} \tag{18}$$

$$\dot{Q}_2 = \dot{m}_{R134a,2} \cdot c_{p,R134a} \cdot \Delta t_{R134a,2} \tag{19}$$

Z powyższych równań wynika następująca zależność:

$$\frac{\dot{m}_{w,1}}{\dot{m}_{w,2}} = \frac{\Delta h_{R134a,1}}{\Delta h_{R134a,2}} = \frac{\dot{Q}_1}{\dot{Q}_2}$$

vi) Ponadto przyjęto, iż w kanalikach wymiennika występuje przepływ laminarny płynu, a co za tym idzie, liczba Nusselt'a ma następującą stałą wartość: $Nu = \frac{\alpha \cdot d}{\lambda} = 4{,}79$, gdzie:

$\alpha \left[\frac{W}{m^2K}\right]$ – współczynnik przejmowania ciepła

$d\ [m]$ – grubość ścianki kanalika

$\lambda \left[\frac{W}{mK}\right]$ – współczynnik przewodzenia ciepła ścianki kanalika

Mając na względzie powyższe, otrzymano wyrażenie na α :

$\alpha = \frac{Nu \cdot \lambda}{d}$.Oczywiście, $\alpha = const, d = const, \lambda = const,$ więc współczynnik przenikania ciepła $k = \frac{1}{\alpha_1} + \frac{1}{\frac{\delta}{\lambda}} + \frac{1}{\alpha_2} = const$ dla wymienników elementarnych. Zatem, z równania Peclet'a, można wyznaczyć wartość następującą zależność :

$$\dot{Q}_1 = k \cdot A_1 \cdot \Delta\, t_{log,1} \tag{20}$$

$$k = \frac{\dot{Q}_1}{\Delta\, t_{log,1} A_1} \tag{21}$$

$$\dot{Q}_2 = k \cdot A_2 \cdot \Delta\, t_{log,2} \ = \frac{\dot{Q}_1}{\Delta\, t_{log,1} A_1} \cdot \Delta\, t_{log,2}$$

Wobec tego, stosunek strumieni ciepła przekazanych czynnikowi roboczemu, odpowiednio w drugim i pierwszym wymienniku, odpowiada ilorazowi:

$$\frac{\dot{Q}_2}{\dot{Q}_1} = \frac{A_2 \cdot \Delta\, t_{log,2}}{A_1 \cdot \Delta\, t_{log,1}} \tag{22}$$

Zgodnie z powyższym, możliwym staje się wyliczenie strumienia ciepła, jaki przekazany zostanie czynnikowi ogrzewanemu w wymienniku elementarnym numer 2.

vii) Przyjęto moc wymiennika elementarnego numer 1 na poziomie $\dot{Q}_1 = 10[kw]$.

viii) Założono, iż w celu określenia optymalnego rozwiązania należy przyjąć, iż przyrost temperatury czynnika po przepłynięciu przez oba wymienniki elementarne jest taki sam.

3.2.1. Zestawienie obliczeń oraz wyników dla obu wymienników elementarnych składających się na wymiennik jednostkowy

Wiadomo, iż:

$$\dot{Q}_1 = \dot{Q}_e = 10[kw]$$

$$\dot{Q}_1 = \dot{m}_{w,1} \Delta h_{w,1}$$

$$\dot{m}_{w,1} = \frac{\dot{Q}_1}{\Delta h_{w,1}}$$

Ponadto, różnica entalpii wody wyliczona została dla danych temperatur, $t_{w,wlot} = 90\ [°C]$, $t_{w,wylot} = 60\ [°C]$ oraz ciśnienia $p = 1{,}1\ [bar]$.

$$\dot{m}_{w,1} = 0.08 \left[\frac{kg}{s}\right]$$

Z danych wejściowych wiadomo, jaki jest spadek temperatury wody w wymienniku elementarnym:

$$\Delta t_w = t_{w,wlot} - t_{w,wylot} = 30[℃].$$

Nieznana temperatura R134a na wylocie z wymiennika 1 i wlocie do wymiennika 2 obliczona została zgodnie z poniższą formułą, przy czym, przyjęto $\Delta t_{R134a,1} = \Delta t_{R134a,2}$, wobec czego można obliczyć nieznaną wartość temperatury, t_x, czynnika na wyjściu z wymiennika 1 i wejściu do wymiennika 2 :

$$t_x - t_{R134a,1,wlot} = t_{R134a,2,wylot} - t_x$$

$$t_x = \frac{t_{R134a,2,wylot} + t_{R134a,1,wlot}}{2}$$

$$t_x = 58.9\ [℃]$$

Wobec powyższego, przyrost temperatury czynnika w wymienniku elementarnym wynosi:

$$\Delta t_{R134a,1} = \Delta t_{R134a,2} = 26.1[℃].$$

Masowe natężenie czynnika R134a wyliczone zostało następująco:

$$\dot{m}_{R134a} = \frac{\dot{Q}_1}{\Delta h_{1,R}}$$

$$\dot{m}_{R134a} = 0.26\ \left[\frac{kg}{s}\right]$$

Moc cieplna drugiego wymiennika elementarnego wynosi:

$$\dot{Q}_2 = \dot{m}_{R134a} \cdot \Delta h_{R134a,2}$$

$$\dot{Q}_2 = 11442{,}14\ [W]$$

$$\Delta t_{log1} = 29{,}11$$

$$\Delta t_{log2} = 2{,}58$$

z kolei jego powierzchnia ma wartość:

$$A_2 = \frac{\dot{Q}_2}{k\ \Delta t_{log2}} = 2.21[m^2]$$

Natomiast wydatek wody w drugim wymienniku elementarnym jest równy:

$$\dot{m}_{w,2} = \frac{\dot{Q}_2}{\Delta h_{2,w}}$$

$$\dot{m}_{w,2} = 0{,}091 \left[\frac{kg}{s}\right]$$, co jest równoważne:

$$\frac{\dot{m}_{w,1}}{\dot{m}_{w,2}} = \frac{\Delta h_{R134a,1}}{\Delta h_{R134a,2}} = \frac{\dot{Q}_1}{\dot{Q}_2}$$

$$\dot{m}_{w,2} = \frac{\dot{Q}_2 \dot{m}_{w,1}}{\dot{Q}_1} = 0.091 \left[\frac{kg}{s}\right].$$

Z powyższej analizy wynika, iż połączenie obu wymienników elementarnych 1 i 2 w taki sposób, że woda przepływa przez nie równolegle, a czynnik R134a szeregowo nie jest najlepszym, ponieważ, z uwagi na niską różnicę logarytmiczną temperatur w wymienniku 2 musiałby on mieć powierzchnię:

$$A_2 = \frac{\dot{Q}_2}{k\ \Delta t_{log2}} = 2.21[m^2]$$

Warto wspomnieć, iż wymiennik elementarny numer 1 miałby znacznie mniejszą powierzchnię, wobec czego, należy poszukiwać lepszych rozwiązań. Dla porównania, przedstawiono wyliczoną powierzchnię wymiennika numer 1:

$$A_1 = \frac{\dot{Q}_1}{k\ \Delta t_{log1}} = 0.17[m^2]$$

Dla porządku dodać należy, iż stosunek powierzchni obu wymienników przedstawia się następująco:

$$\frac{A_1}{A_2} = 0.08$$

Przy takim połączeniu oba wymienniki elementarne realizują wymianę energii na sposób ciepła na poziomie :

$$\dot{Q}_{jedn} = \dot{Q}_1 + \dot{Q}_2 = 21\ 442{,}14\ [W]$$

Całkowity strumień masowy czynnika R134a wyliczono zgodnie z poniższym równaniem, mając dany całkowity strumień ciepła oraz różnicę entalpii czynnika na wylocie/wlocie z sieci ków:$\dot{m}_{R134a,cał} = \frac{\dot{Q}_{cał}}{\Delta h_{R134a}} = 1006.98 \left[\frac{kg}{s}\right]$

Ilość wymienników jednostkowych *n* potrzebnych do zagospodarowania $\dot{Q}_{cał} = 83.2[MW_t]$.

$$n = \frac{\dot{m}_{R134a,cał}}{\dot{m}_{R134a,jedn}} \approx 3881$$

Obliczono zastępczą powierzchnię wymiennika jednostkowego zgodnie z poniższą formułą:

$$A_{jedn,zast.} = \frac{\dot{Q}_1+\dot{Q}_2}{k\,\Delta t_{log}}[m^2] = 0.81[m^2],$$

gdzie Δt_{log} jest logarytmiczną różnicą temperatur całego wymiennika jednostkowego, który realizuje podgrzew R134a z temperatury $32{,}8[°C]$ do temperatury $85[°C]$ i ochłodzenie wody z $90[°C]$ do $60[°C]$.

$$\Delta t_{log} = 13.11\ [°C]$$

Zatem, całkowita zastępcza powierzchnia zestawu mikrowymienników wyniesie:

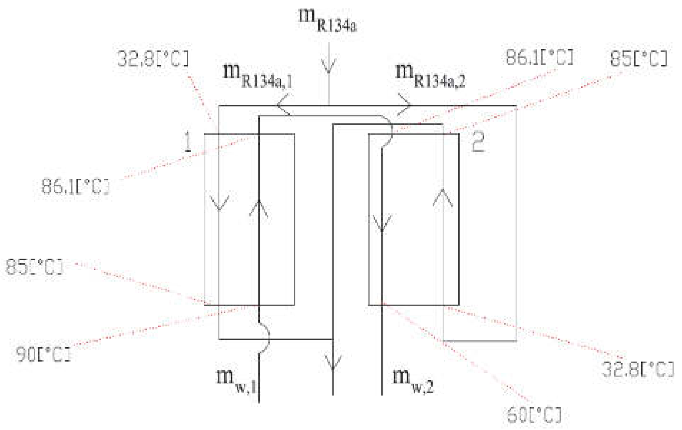
$$\frac{\dot{Q}_{cał}}{\dot{Q}_{jedn}} = \frac{A_{cał,zast}}{A_{jedn,zast}}$$

$$A_{cał,zast} = \frac{\dot{Q}_{cał}}{\dot{Q}_{jedn}} A_{jedn,zast} = 3152.67$$

3.3. Przykład połączenia równoległo (R134a) – szeregowego (woda)

W tym przypadku, gdy woda przepływa szeregowo, nie można wyliczyć jej temperatury na wyjściu z pierwszego wymiennika elementarnego w taki sposób, w jaki obliczono, w poprzednim przykładzie temperaturę czynnika R134a z uwagi na fakt, iż tak obliczona wartość temperatury byłaby o $10[°C]$ niższa niż temperatura czynnika na wlocie do drugiego wymiennika elementarnego, co wyraźnie widać na rysunku 9.

Chcąc jednak zachować pewne warunki, umożliwiające porównanie obu mieszanych typów połączenia wymienników elementarnych w jednostkowy, utrzymano tę samą różnicę temperatury między wodą a czynnikiem, na wlocie do drugiego wymiennika elementarnego, której wartość wynosi 1.1 [°C].



Rys. 9. Schemat połączenia równoległo (R134a) – szeregowego (woda)
Fig. 9. Scheme of the parallel (R134a)-serial (water) connection of two plates with micro channnels

W pierwszej kolejności wyliczono różnice logarytmiczne temperatur.

$$\Delta t_{log1} = 20.41\ [°C]$$
$$\Delta t_{log2} = 8.14\ [°C]$$

Tak, jak w poprzednim przypadku, tak i w tym, założono, iż $\dot{Q}_1 = 10\ [kW]$. Ponadto, z równań bilansu, zapisanych dla wymienników połączonych szeregowo (woda) – równolegle (czynnik), otrzymano kolejną zależność:

$$\dot{Q}_1 = \dot{m}_{R1} \cdot \Delta h_R = \dot{m}_w \cdot \Delta h_{w1}$$
$$\dot{Q}_2 = \dot{m}_{R2} \cdot \Delta h_R = \dot{m}_w \cdot \Delta h_{w2}$$

Po podzieleniu stronami :

$$\frac{\dot{Q}_1}{\dot{Q}_2} = \frac{\dot{m}_{R1}}{\dot{m}_{R2}} = \frac{\Delta h_{w1}}{\Delta h_{w2}}$$

Z powyższego wynika, iż moc wymiennika elementarnego numer 2 winna wynosić:

$$\frac{\dot{Q}_1}{\dot{Q}_2} = \frac{\Delta h_{w1}}{\Delta h_{w2}}$$
$$\dot{Q}_2 = \frac{\dot{Q}_1 \Delta h_{w2}}{\Delta h_{w1}}$$
$$\dot{Q}_2 = 66723.82[W]$$

Z kolei wydatki czynnika, przepływającego przez wymienniki elementarne, wyliczone zostały w następujący sposób:

$$\dot{m}_{R1,e} = \frac{\dot{Q}_1}{\Delta h_R} = 0.12 \left[\frac{kg}{s}\right]$$

$$\dot{m}_{R2,e} = \frac{\dot{m}_{R1}\dot{Q}_2}{\dot{Q}_1} = 0.81 \left[\frac{kg}{s}\right]$$

Natomiast, masowe natężenie wody przepływającej szeregowo przez wymienniki elementarne określa równość:

$$\dot{m}_{w,e} = \frac{\dot{m}_{R1} \cdot \Delta h_R}{\Delta h_{w1}} = 0.61 \left[\frac{kg}{s}\right]$$

Powierzchnie obu wymienników elementarnych zostały wyliczone według danych formuł:

$$A_1 = \frac{\dot{Q}_1}{k \cdot \Delta t_{log1}} = 0.24\ [m^2]$$

$$A_2 = \frac{\dot{Q}_2}{k \cdot \Delta t_{log2}} = 4.14\ [m^2]$$

$$\frac{A_1}{A_2} = 0.058$$

Z przeprowadzonej analizy wynika, iż przy niniejszym połączeniu wymienników, ich całkowita moc będzie wynosiła: $\dot{Q}_{jednostkowe} = \dot{Q}_1 + \dot{Q}_2 = 76723.82\ [W]$

$\dot{Q}_{całkowite} = 83.2[MW]$, więc $\frac{\dot{Q}_{całkowite}}{\dot{Q}_{jednostkowe}} = 1085.$

Zatem całkowita powierzchnia wymienników będzie miała wartość:

$$A_{jedn,zast.} = \frac{\dot{Q}_1 + \dot{Q}_2}{k\ \Delta t_{log}}[m^2] = 2.91[m^2]$$

$$A_{cał,zast} = A_{jedn,zast} \cdot \frac{\dot{Q}_{całkowite}}{\dot{Q}_{jednostkowe}} = 3152.7[m^2]$$

Obliczono wartość liczby Reynolds'a, aby udowodnić, że przepływ czynnika w mikro kanałowym wymienniku ma charakter laminarny.

$$G = \frac{4 \cdot L \cdot k \cdot \Delta t_{log,1}}{d_h \cdot \Delta h_{R134a}}\left[\frac{kg}{s \cdot m^2}\right] = 225.48 \left[\frac{kg}{s \cdot m^2}\right]$$

$$Re = \frac{G \cdot d_h}{\mu_{R134a}} = 247.96$$

$$\Delta p_e = \frac{Po \cdot 2 \cdot G^2 \cdot L}{Re \cdot \rho_{R134a} \cdot d_h} [Pa] = 728.67\ [Pa]$$

gdzie:

Po – współczynnik Poiseuille'a, który, dla stosunku $\frac{a}{b} = \frac{0.3}{0.1}$ =3, wynosi *17.09* [7]

$G \left[\frac{kg}{s \cdot m^2}\right]$ – gęstość strumienia masy

Przez wymiennik jednostkowy, składający się z dwóch wymienników elementarnych, połączonych ze sobą szeregowo (woda) – równolegle (R134a), przepływa czynnik roboczy o wydatku masowym $\dot{m}_{Rjedn}$:

$\dot{m}_{R134a,jedn} = \dot{m}_{R1} + \dot{m}_{R2} = 0.93 \left[\frac{kg}{s}\right]$.

Dla porządku obliczono strumień masowy wody zasilającej wymiennik. Dodać należy, iż różnica entalpi została obliczona dla temperatur 32,8 [°C] i 85 [°C] dla czynnika R134a oraz 60 [°C] i 90 [°C] dla wody.

$$\dot{m}_{w,cał} = \dot{m}_{R134a,cał} \cdot \frac{\Delta h_{R134a}}{\Delta h_w} = 661.70 \left[\frac{kg}{s}\right]$$

Całkowite natężenie przepływu czynnika R134a wynosi 1006,98 $\left[\frac{kg}{s}\right]$. Wobec tego, chcąc wykorzystać cały masowy strumień czynnika należy równolegle połączyć ze sobą wymienniki jednostkowe, których ilość wyniesie: $\frac{\dot{m}_{R134a,cał}}{\dot{m}_{R134a,jedn}} \approx 1085$.

4. Podsumowanie

Przeprowadzone obliczenia miały na celu wykazanie tego, jakie jest optymalne połączenie dwóch mikrowymienników elementarnych w taki sposób, ażeby powstały w ten sposób mikro kanałowy wymiennik jednostkowy jak najlepiej realizował podgrzew czynnika roboczego R134a. Przeanalizowano trzy różne typy połączeń mikrowymienników elementarnych, tj. równoległo – równoległe, równoległo (woda) – szeregowe (R134a) oraz równoległo (R134a) – szeregowe (woda). Należy podkreślić, iż najbardziej podstawowym komponentem była para płytek, której rysunek poglądowy przedstawia rys. 5. Z owych płytek tworzono wymienniki elementarne, a z nich z kolei wymienniki jednostkowe. Dodatkowym założeniem było, iż jeden z elementarnych wymienników ma realizować wymianę ciepła na poziomie 10 [kW].Biorąc pod uwagę dwa ostatnie opisane modele, można by pokusić się o stwierdzenie, iż projekt połączenia dwóch wymienników elementarnych w sposób szeregowo (woda)- równoległy (R134a), wydaje się być lepszy pod względem mocy cieplnej. Aczkolwiek, należy zwrócić uwagę na wyliczone wartości powierzchni zastępczych, gdyż są one stosunkowo niewielkie. Dlatego właśnie najbardziej korzystne połączenie dwóch mikrowymienników elementarnych będzie realizował model równoległo (woda grzejąca)-równoległy(R134a).

Koniecznie dodać należy, że w mikrowymienniku elementarnym przepływ czynnika roboczego ma charakter laminarny, o czym świadczy wyliczona niska wartość liczby Reynolds'a, $Re = 247.96$. Zatem, w przypadku połączenia równoległo-równoległego, chcąc wykorzystać $\dot{Q}_{cał} = 83.2\ [MW_t]$ należy użyć $N_{wymienników} = \frac{\dot{Q}_{cał}}{\dot{Q}_e} = 8320$ wymienników elementarnych, tj. całkowita liczba płytek $N_{cał} = N_{wymienników} \cdot N_e = 416\ \cdot 8320 = 3.5 \cdot 10^6$.

Literatura

1. **Arun Prasad Raja V., Basak T., Kumar Das S.:** *Thermal performance of a multi-block heat exchanger designed on the basis of Bejan's constructal theory.* International Journal of Heat and Mass Transfer, vol. 51, 3582–3594 (2008).
2. **Bohdal T.:** *Investigations of Environmentally Friendly Refrigerants' Phase Changes in Minichannels.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 15, 1, 107–126 (2013).
3. **Madejski J.:** *Teoria wymiany ciepła.* Politechnika Szczecińska, Szczecin 1998.
4. **Mikielewicz J., Mikielewicz D.:** *The Dynamics of heat exchangers and instabilities in ORC circulation.* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 13, 425–440 (2011).
5. **Mikielewicz D., Wajs J., Muszyński T.:** *Badania wpływu liczby płyt na charakterystyki cieplno-przepływowe prototypowego mikrokanalikowego wymiennika ciepła.* Opracowanie wewnętrzne IMP PAN, nr arch. 205/2012
6. **Mikielewicz D., Wajs J., Muszyński T.:** *Mikrokanalikowy wymiennik ciepła – konstrukcja i charakterystyki cieplno-przepływowe prototypu w układzie woda-woda*, Opracowanie wewnętrzne IMP PAN, nr arch. 66/2012

7. **Myzychka Y. S.:** *Constructal design of forceed convection cooled microchannel heat sinks and heat exchangers.* International Journal of Heat and Mass Transfer, 48, 3119–3127 (2005).
8. **Rybiński W., Mikielewicz J.:** *Analytical solutions for laminar flow exchanging heat in rectangular channels.* Renewable Sources of Energy, ZUT, 229–238 (2012).
9. **Wolf A.:** *Synteza i analiza optymalnych sieci odzysku ciepła.* Politechnika Krakowska, Kraków 1987.
10. **Zimparov V. D., Da Silva A. K., Bejan A.:** *Thermodynamic optimization of three-shaped flow geometries with constant channel wall temperature.* International Journal of Heat and Mass Transfer, 49, 4839–4849 (2006).

Studies on the Micro Heat Exchangers Coupling into Integral Heat Exchanger

Abstract

As it is commonly known, heat exchangers are widely used in power generators equipment. The biggest disadvantage of conventional heat exchangers is that, in case of the energy load variation, it must be replaced by the one of different size.

The aim of this work is to specify a method of combining micro channel heat exchangers into a grid, realising different powers. It was ment to specify the most accurate micro channel heat exchangers connection, in order to increase the intensity of the heat exchange process. Studied problem was about heating the ORC working medium (R134a) using waste heat (hot water).

In this paper, there has been studied the fenomenon of the heat exchange process in the micro channel heat exchanger grid, which will be further called the integral heat exchanger. There have been studied three cases of micro channel heat exchangers connections, such as: parallel-parallel, parallel (heating water)-serial (R134a) and parallel (R134a) – serial (heating water). On the basis of the results of the analytical analysis it has been stated, that the serial (heating water)-parallel (R134a 7) micro channel heat exchangers combination is the most suitable for the most intensive heat exchange.

Słowa kluczowe:
mikro kanalikowy wymiennik ciepła, sieć wymienników, ORC

Keywords:
micro channel heat exchanger, heat exchangers grid, ORC

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Piaski odpadowe jako wartościowe kruszywo do wytwarzania fibrokompozytów

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1. Wstęp

Stawiane obecnie wymagania dotyczące spełnienia stanu granicznego nośności i użytkowalności nowoczesnych konstrukcji z betonu spowodowały konieczność poszukiwania rozwiązań dotyczących polepszenia właściwości mechaniczno-fizycznych betonu zwykłego. Jednym ze sposobów jest stosowanie dodatku w postaci włókien. Kompozyty mineralne z włóknami rozproszonymi, ogólnie nazywane fibrokompozytami, stają się coraz popularniejsze zarówno w kraju, jak i na świecie. Włókna stalowe pełnią rolę wzmocnienia i w znaczący sposób poprawiają niektóre właściwości kompozytu [1,12,18]. Fibrokompozyty stanowią więc pewną alternatywę dla betonu zwykłego, gdyż cechuje je, między innymi, większa wytrzymałość na rozciąganie i ścinanie, wytrzymałość zmęczeniowa i udarność oraz większa odporność na ścieranie. Włókna zapobiegają propagacji rys i sprawiają, że materiał staje się bardziej jednorodny [3,4,19]. Zanika kruchy charakter betonu zwykłego, co bezpośrednio wpływa na bezpieczeństwo użytkowania konstrukcji [24]. Dzięki tym właściwościom fibrokompozyty znajdują zastosowanie w wytwarzaniu różnych elementów konstrukcyjnych, takich jak: płyty stropowe, belki, powłoki, posadzki przemysłowe, a nawet nawierzchnie mostów, tuneli, czy też elementy do wzmocnień wyrobisk kopalnianych [5,6,21].

Prowadzone w Katedrze Konstrukcji Betonowych i Technologii Betonu badania [8,9,12–17] związane z drobnokruszywowym kompozytem, wykonanym na bazie piasków odpadowych, z dodatkiem włókien stalowych dowodzą, że istnieje możliwość częściowego zastąpienia betonu zwykłego i wykonywania niektórych elementów konstrukcyjnych z fibrokompozytu. Kompozyt drobnokruszywowy, charakteryzujący się lepszymi właściwości niż beton zwykły (np. większą wytrzymałością na rozciąganie, ściskanie, ścinanie, większą odpornością na ścieranie i obciążenia dynamiczne), jest doskonałym rozwiązaniem dla regionów, w których brakuje naturalnych złóż kruszywa grubego, niezbędnego do produkcji betonu zwykłego.

Takim regionem bez wątpienia jest Pomorze. Szacuje się, że około 90% złóż kruszyw grubych znajduje się w regionie południowym Polski, 6% w regionie środkowymi tylko 4% w regionie północnym [20]. W związku z powyższym region Pomorza bogaty jest w piaski odpadowe, które są wynikiem hydroklasyfikacji, technologii pozyskiwania kruszywa grubego opartej na jego wypłukiwaniu ze złóż.

Rys. 1. Widok hałd piasków odpadowych na Pomorzu (gm. Białogard)
Fig. 1. Waste sand heaps in Pomerania (Białograd)

Powstałe w ten sposób wyrobiska (rysunek 1) powinny być poddane kosztownej rekultywacji. Alternatywnym rozwiązaniem tego problemu może być możliwość wykorzystania piasku odpadowego, jako pełnowartościowego surowca budowlanego [16, 25]. Częściowe zastąpienie betonu zwykłego kompozytem drobnoziarnistym ze zbrojeniem rozproszonym może przyczynić się do znacznego ograniczenia dalszej degradacji środowiska. Pozwoli to na zrównoważone wykorzystanie regionalnych surowców. Działania te przyczynią się również do stopniowego zmniejszania hałd piasku.

2. Cel i znaczenie badań doświadczalnych

Celem przeprowadzonych badań doświadczalnych było określenie wpływu dodatku włókien stalowych na wybrane właściwości mechaniczno–fizyczne kompozytu wykonanego na bazie lokalnego kruszywa odpadowego. Kolejnym zadaniem było wskazanie takiej zawartości włókien stalowych, przy której kompozyt drobnokruszywowy wykazuje najlepsze właściwości użytkowe.

Opracowanie fibrokompozytu drobnokruszywowego, którego właściwości spełniają wymagania stawiane materiałom konstrukcyjnym oraz który byłby w wybranych zastosowaniach alternatywą dla betonu zwykłego, daje możliwość zagospodarowania zalegających w rejonie Pomorza hałd. Możliwość wykorzystania piasku odpadowego jest korzystnym, przede wszystkim pod względem ekonomicznym oraz ekologicznym, rozwiązaniem problemu rekultywacji wyrobisk.

3. Wykonanie i pielęgnacja elementów próbnych

Do badań użyto mieszankę kompozytu wykonaną na bazie piasku odpadowego z Kopalni Kruszyw Naturalnych w Lepinie, cementu portlandzkiego CEM II/AV 42,5R, wody z wodociągu miejskiego, plastyfikatora BETONCRETE 406 FM, pyłów krzemionkowych oraz włókien stalowych EKOMET 50x0,8 mm, o kształcie haczykowatym i smukłości równej $\lambda = 62{,}5$.

Matrycę kompozytu zaprojektowano metodą doświadczalno-analityczną. Zastosowanie domieszki uplastyczniającej oraz dodatku pyłu krzemionkowego pozwoliło na uzyskanie stosunku w/c=0,38.

Jako zmienną składową fibrokompozytu przyjęto zawartość włókien stalowych, które dozowano co 0,5%, do 2,5% w stosunku do objętości kompozytu. Włókna w mieszance rozmieszczone były w sposób przypadkowy.

Tabela 1. Charakterystyka techniczna włókien stalowych użytych w badaniach [7]
Table 1. Technical characteristics of steel fibre and fibre-composite [7]

Cecha	Wartość
Grupa konstrukcyjna [-]	I
Wytrzymałość na rozciąganie [MPa]	1200
Kształt włókien: odkształcone haczykowate	–
Konsystencja (Ve-Be) przy zawartości włókien 12-14 kg/m^3 [s]	4
Wpływ na wytrzymałość betonu (12-14 kg/m^3) przy CMOD*= 0,5 mm [MPa]	1,5
Wpływ na wytrzymałość betonu (12-14 kg/m^3) przy CMOD*= 3,5 mm [MPa]	1,0
*- rozwarcie naciętej szczeliny wg metody przedstawionej w PN-EN 14651	

W badaniach wytrzymałości na ściskanie, wytrzymałości na rozciąganie przy rozłupywaniu, mrozoodporności, gęstości oraz dynamicznego modułu sprężystości wykorzystano próbki sześcienne o boku 150 mm. Próbki cylindryczne o wymiarach 150x300 mm użyto przy określaniu statycznego modułu sprężystości. Badanie odporności na ścieranie wykonano na próbkach sześciennych o boku 71 mm, a badanie resztkowej (rezydualnej) wytrzymałości na zginanie na belkach o wymiarach 150x150x700 mm, których połówki, uzyskane po badaniu wytrzymałości, wykorzystano do określenia wytrzymałości na ścinanie. Skurcz określono na próbkach o wymiarach 40x40x500 mm. Wszystkie elementy próbne wykonano zgodnie z zaleceniami normy PN-EN 12390-2. Każdorazowo, przed rozpoczęciem formowania próbek, określano gęstość oraz konsystencję mieszanki betonowej metodą Ve-be.

Po zaformowaniu, próbki przez 24 godziny przechowywano w formach w warunkach laboratoryjnych przy średniej dobowej temperaturze (20±2)°C i wilgotności względnej powietrza (50±5)%. Po upływie doby rozformowane próbki przez kolejne 27 dni poddawano pielęgnacji w temperaturze (20±2)°C i wilgotności względnej ok. 100%. Następnie elementy próbne pozostawiono przez 2 dni w pomieszczeniu o średniej dobowej temperaturze (20±2)°C i wilgotności względnej (50±5)%. Badania wykonywano po 30 dniach od momentu zaformowania próbek.

Niezbędną liczbę próbek do określenia średniej wartości statystycznej badanej cechy wyznaczono na podstawie analizy statystycznej wyników badań wstępnych za pomocą rozkładu t-Studenta, przy tolerancji υ=10% i poziomie istotności α=0,05. Liczba próbek zawierała się w przedziale od 6 przy określaniu ścieralności do 16 przy badaniu gęstości i dynamicznego modulu sprężystości, dla każdego rodzaju kompozytu. Dla fibrokompozytu o wybranej, z uwagi na najlepsze właściwości mechaniczno-fizyczne i konsystencję, zawartości włókien stalowych przeprowadzono badania każdej z cech na 20 próbkach.

4. Metodyka badań

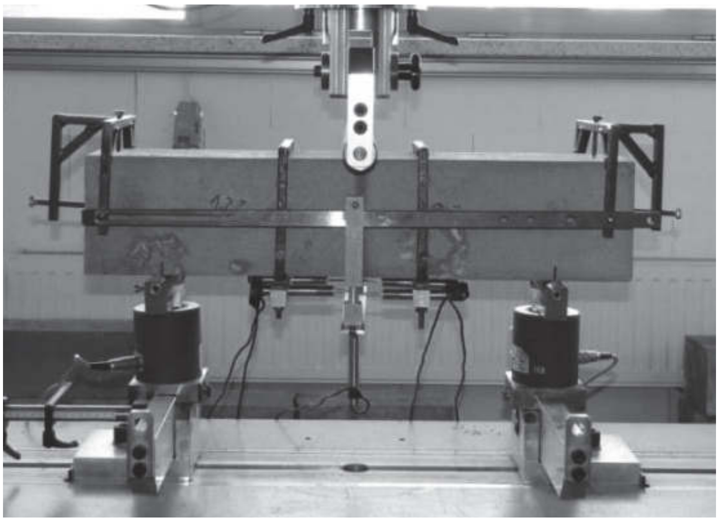
Badanie gęstości nasypowej oraz jamistości kruszywa odpadowego przeprowadzono zgodnie z normą PN-EN 1097-3. Skład ziarnowy określono według PN-EN 933-1. Badania cementu przeprowadzono po 2, 14 i 28 dniach dojrzewania zgodnie z PN-EN 196-1.

Z uwagi na brak szczegółowych wytycznych dotyczących badań kompozytów ze zbrojeniem rozproszonym, metodyka większości badań oparta została o normy dotyczące badań betonu zwykłego. Wytrzymałość na ściskanie (f_c) określono według PN-EN 12390-3, natomiast na rozciąganie przy rozłupywaniu (f_{ct}) przy wykorzystaniu metodyki przedstawionej w PN-EN 12390-6. Statyczny moduł sprężystości (E_c) wyznaczono (rysunek 2) zgodnie z PN-EN 12390-13 oraz instrukcją ITB 194/98, według której wykonano również pomiar skurczu fibrokompozytu.

Rys. 2. Ogólny widok stanowiska do badania modułu sprężystości
Fig. 2. Overall view of the position to study the elasticity module

Gęstość pozorną (ρ) oznaczono według zaleceń PN-EN 12390-7, a dynamiczny moduł sprężystości (E_d) zdefiniowany został na podstawie analizy prędkości przebiegu fali ultradźwiękowej [23]. Badanie resztkowej wytrzymałości na zginanie (f_{Rj}) wykonano w badaniu trzy punktowego zginania wg PN-EN 14651 (rysunek 3).

Po określeniu resztkowej wytrzymałości na zginanie połówki belek wykorzystano do określenia wytrzymałości na ścinanie (τ) według normy JCI Standards for Test Methods of Fiber Reinforced Concrete.



Rys. 3. Ogólny widok stanowiska do badania wytrzymałości resztkowej
Fig. 3. Overall view of the position of the residual strength test

Mrozoodporność fibrokompozytu oznaczono zgodnie z PN-88/06250, przyjmując w badaniu 50 cykli zamrażania-odmrażania. Badanie przeprowadzono wg zasad metody zwykłej, która stwarza możliwość określenia jednocześnie wewnętrznego zniszczenia materiału, charakteryzowanego poprzez wytrzymałość na ściskanie, jak i zewnętrznego, określonego wizualnie oraz ubytkiem masy. Do określenia odporności na ścieranie (A) fibrokompozytu wykorzystano zasady przedstawione w PN-EN 13892-3.

5. Wyniki badań i ich analiza

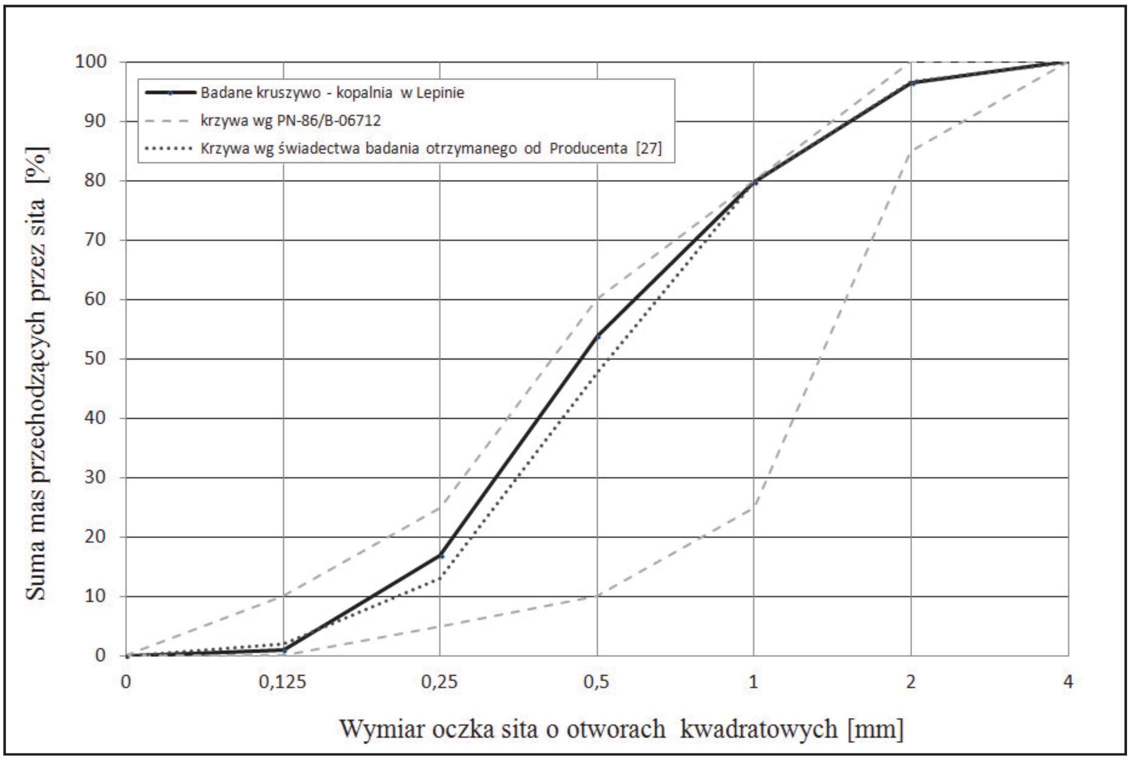
W celu sprawdzenia czy wyniki poszczególnych serii próbek należą do jednej populacji wykorzystano rozkład t-Studenta. Do odrzucenia wyników obarczonych systematycznym błędem grubym posłużono się testem Dixona [26]. Przeprowadzona analiza statystyczna wykazała, że przyjęta liczba próbek, użytych w badaniach, była wystarczająca. Wartości wskaźników zmienności badanych właściwości, zawierające się w przedziale od 3% w przypadku badania wytrzymałości na ściskanie do 8% dla wytrzymałości na rozciąganie, wskazują na bardzo dobrą jakość zaprojektowanego kompozytu drobnokruszywowego na bazie piasków odpadowych. Użyte kruszywo odpadowe, jak wykazała analiza wyników badań, spełnia wymagania stawiane kruszywom mineralnym do betonu zwykłego (tabela 2).

Tabela 2. Podstawowe właściwości kruszywa użytego do badań
Table 2. The basic properties of aggregates used for the test

Właściwość	Wartości uzyskane z badań	Wartości zalecane
Gęstość nasypowa w stanie luźnym, [kg/m^3]	1634	–
Gęstość nasypowa w stanie zagęszczonym, [kg/m^3]	1802	≤ 1850
Gęstość ziarn, [kg/m^3]	2632	1800–3000
Zawartość pyłów mineralnych, [%]	1,3	–
Jamistość w stanie luźnym, [%]	38	–
Jamistość w stanie zagęszczonym, [%]	32	20–28
Ziarno mediana, [mm]	0,46	0,4–0,7
Wskaźnik uziarnienia wg Kuczyńskiego	5,55	–
Zawartość ciał obcych, [%]	brak	0,5

Krzywa uziarnienia kruszywa odpadowego zawiera się w przedziale krzywych dla piasku uszlachetnionego wg PN-86/B-06712 (rysunek 4).

Użyty w badaniach cement portlandzki popiołowy o wysokiej wczesnej wytrzymałości CEM II/A-V 42,5R spełnia wymagania normy PN-EN 197-1. Uzyskane wytrzymałości na ściskanie cementu charakteryzowały się małym wskaźnikiem zmienności oraz dużym współczynnikiem jednorodności, co wskazuje na wysoką jakość użytego materiału.



Rys. 4. Krzywa uziarnienia kruszywa użytego w badaniach
Fig. 4. Aggregate grading curve used in the study

Przeprowadzone badania fibrokompozytu wykazały korzystny wpływ dodatku włókien stalowych na jego właściwości mechaniczno-fizyczne (tabela 3).

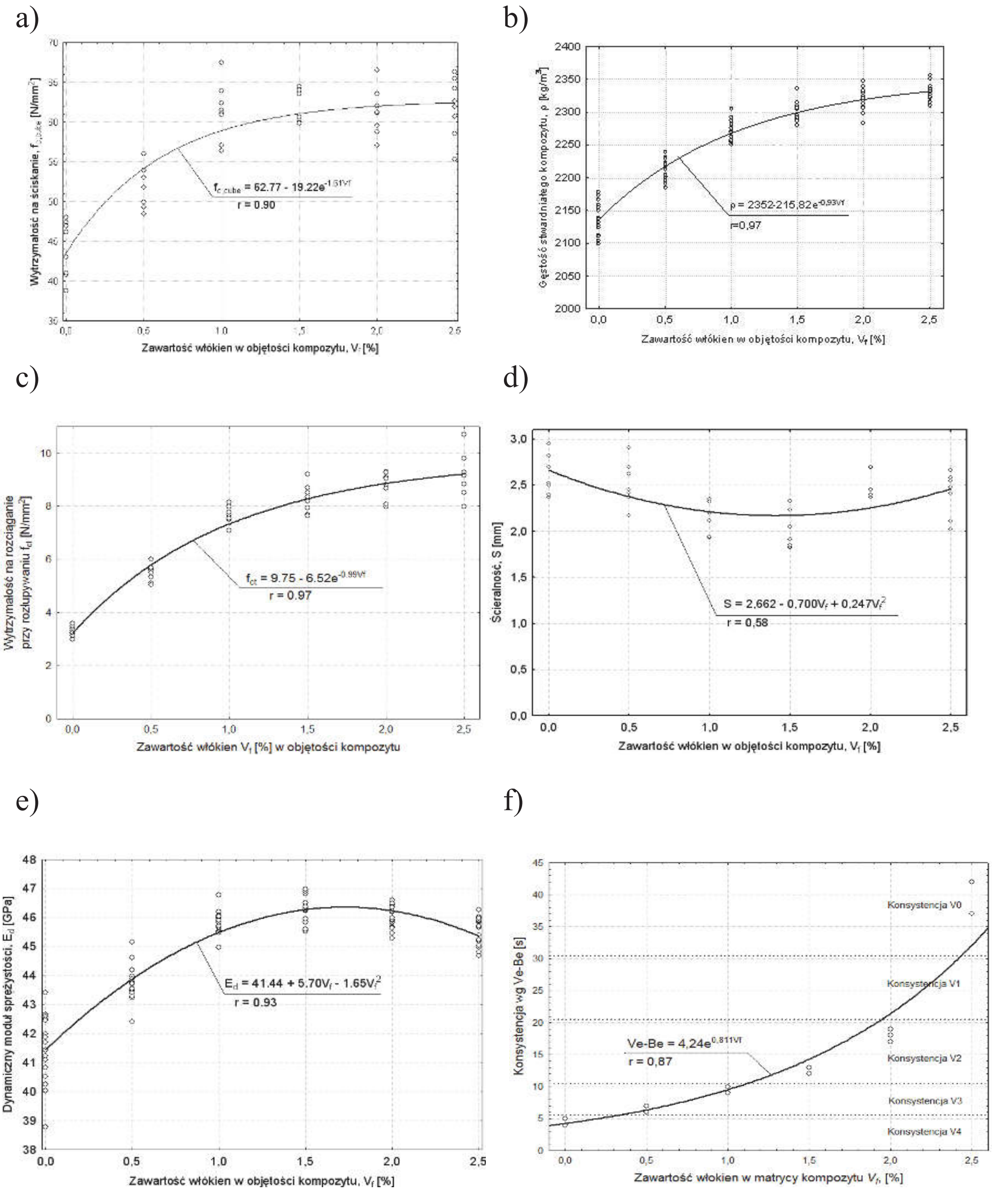
Na rysunku 5 przedstawiono wybrane wyniki badań.

Tabela 3. Właściwości fibrokompozytu przy różnej zawartości włókien stalowych
Table 3. The properties of fine aggregate composite with a different content of the steel fibers

Właściwość / postać funkcji, współczynnik korelacji	Zawartość włókien w kompozycie [%]					
	0	0,5	1,0	1,5	2,0	2,5
Gęstość pozorna [g/cm^3] $\rho = 2352 - 215{,}8e^{-0{,}93V_f}$, $r = 0{,}97$	2,1	2,2	2,3	2,3	2,3	2,3
Wytrzymałość na ściskanie [MPa] $f_c = 63 - 19e^{-1{,}61V_f}$ $r = 0{,}90$	44	51,8	61,4	61,6	61,3	61,9

Tabela 3. cd.
Table 3. cont.

Właściwość / postać funkcji, współczynnik korelacji	Zawartość włókien w kompozycie [%]					
	0	0,5	1,0	1,5	2,0	2,5
Wytrzymałość na rozciąganie przy rozłupywaniu [MPa] $f_{ct} = 9{,}75 - 6{,}5e^{-0{,}99V_f}$, $r = 0{,}97$	3,3	5,5	7,7	8,3	8,8	9,2
Ścieralność [mm] $S = 2{,}6 - 0{,}7V_f + 0{,}25V_f^2$, $r = 0{,}58$	2,6	2,5	2,1	2,0	2,5	2,4
Dynamiczny moduł sprężystości [GPa] $E_d = 41{,}5 + 5{,}7V_f - 1{,}65V_f^2$, $r = 0{,}93$	41,5	43,7	45,8	46,3	46	45,5
Statyczny moduł sprężystości [GPa] $E_s = 32{,}7 + 2{,}35V_f - 0{,}76V_f^2$, $r = 0{,}88$	32,9	33,3	34,5	34,7	34,0	33,9
Skurcz [mm/m] $\varepsilon_s = 0{,}89\left(1 - e^{-0{,}2t^{0{,}6}}\right) - 0{,}048V_f$, $r = 0{,}93$	0,9	0,87	0,85	0,83	0,8	0,78
Konsystencja Ve-Be [s] $K = 4{,}24e^{0{,}8V_f}$ $r = 0{,}87$	4,2	6,4	9,5	14,3	21,5	32,2



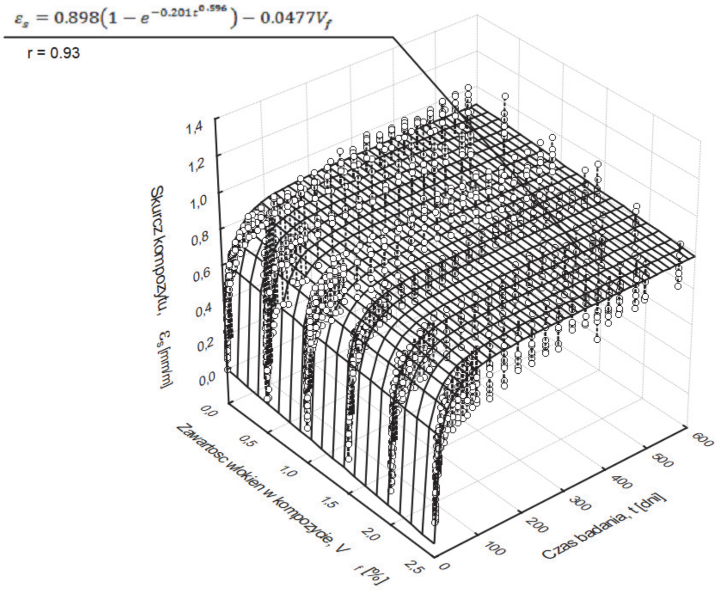
Rys. 5. Zależności wybranych cech kompozytu drobnokruszywowego od zawartości włókien stalowych

Fig. 5. Depending on the specific characteristics of fine aggregate composite of content of steel fibres

Przeprowadzona analiza uzyskanych wyników badań wykazała, że wraz ze wzrostem ilości włókien w kompozycie następuje ciągły przyrost wartości wytrzymałości na ściskanie (rysunek 5a) i rozciąganie (rysunek 5c). Wzrost ten nie jest jednak proporcjonalny do objętości użytego zbrojenia rozproszonego. Analiza wyników badań wykazała, że zawartość włókien w kompozycie powyżej 1,5% dla ściskania i 2% dla rozciągania przy rozłupywaniu nie powoduje już znaczącego przyrostu wartości tych wytrzymałości. Ponadto wraz ze wzrostem ilości włókien w kompozycie znacznie pogarsza się urabialność mieszanki. Zbyt duża ilość włókien stalowych powoduje także pogorszenie jego odporności na ścieranie (rysunek 5d). Badania dowodzą, że fibrokompozyt na bazie piasków odpadowych wykazuje najmniejszą ścieralność przy zawartości włókien stalowych w przedziale od 1% do 1,5%, przy czym maksimum osiąga przy zawartości włókien równej 1,3%. Pogorszenie tej właściwości ma związek ze zwiększającą się wraz ze wzrostem zawartości włókien porowatością matrycy, wynikającą ze zdolności włókien do jej napowietrzania [2]. Wpływa to również na gęstość pozorną fibrokompozytu (rysunek 5b). Wzrasta ona wraz z dodatkiem włókien stalowych, jednak po przekroczeniu objętości włókien w mieszance kompozytu równej 1,5%, obserwuje się bardzo powolny wzrost jego gęstości.

Z analizy krzywej regresji dynamicznego modułu sprężystości (rysunek 5e) wynika, że korzystny wpływ dodatku włókien stalowych ma miejsce przy ich zawartości w kompozycie drobnokruszywowym do 1,7%. Po przekroczeniu tej wartości następuje znaczne napowietrzenie mieszanki spowodowane zawartością włókien i wartość dynamicznego modułu sprężystości ulega pogorszeniu.

Ponadto stwierdzono, że skurcz kompozytu drobnokruszywowego o zawartości włókien od 0,5% do 2,5% (rysunek 6) określony w warunkach stałej wilgotności względnej powietrza (50±5)% i temperaturze (20±2)°C jest prawie dwukrotnie większy niż skurcz betonu zwykłego [23]. Stabilizacja odkształceń skurczowych fibrokompozytu nastąpiła po 600 dniach od chwili rozpoczęcia badań. Większy w porównaniu do betonu zwykłego skurcz fibrokompozytu wynika z zastosowania, jako wypełniacza, kruszywa drobnego [10,23].



Rys. 6. Zależność skurczu kompozytu drobnokruszywowego od zawartości włókien stalowych
Fig. 6. Shrinkage dependence of fine aggregate composite of content of steel fibres

Przeprowadzone badania dowodzą, że zwiększenie ilości zbrojenia rozproszonego w kompozycie ponad wartość 1,5% może mieć negatywny wpływ na niektóre jego właściwości (dynamiczny moduł sprężystości, ścieralność, konsystencja). Właściwym jest więc określenie takiej zawartości włókien stalowych w kompozycie, która pozwoli na uzyskanie materiału o właściwościach mechaniczno-fizycznych odpowiadających właściwościom betonu zwykłego, przy jednoczesnym zachowaniu odpowiedniej konsystencji mieszanki (por. rysunek 5f).

Analizując krzywe regresji (por. tabela 3) wyznaczono taką zawartość włókien stalowych w kompozycie drobnokruszywowym, przy której spełnione są wymagania stawiane betonowi zwykłemu.

W związku z tym, iż wartości wytrzymałości na ściskanie oraz rozciąganie przy rozłupywaniu utrzymują ciągłą tendencję wzrostową w zakresie przyjętych procentowych zawartości włókien stalowych, do wyznaczenia poszukiwanej wielkości posłużono się funkcjami regresji cech, które ulegały pogorszeniu wraz ze wzrostem ilości włókien. Takimi cechami są: ścieralność, dynamiczny moduł sprężystości i konsystencja. Wyznaczono więc maksymalną zawartość dodatku włókien stalowych (ekstrema funkcji regresji przedstawionych w tabeli 3), po przekroczeniu których następował spadek wartości rozważanych cech. Ustalono, że pod względem najkorzystniejszych właściwości oraz ekonomicznym, maksymalna zawartość włókien stalowych w drobnokruszywowym kompozycie na bazie piasków odpadowych wynosi 1,2%. Dla fibrokompozytu o zawartości włókien 1,2% wykonano serię kolejnych badań (tabela 4).

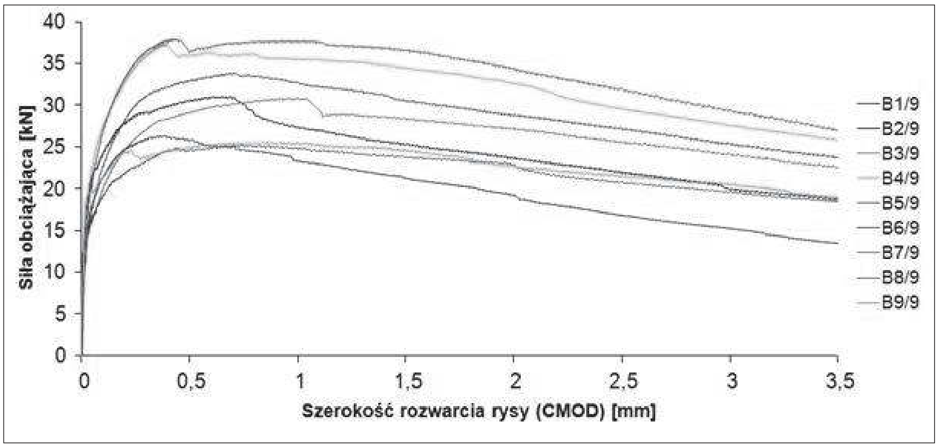
Tabela 4. Właściwości kompozytu drobnokruszywowego przy zawartości włókien stalowych 1,2%.
Table 4. Features of fine aggregate composite with a 1,2% content of the steel fibers

Parametry analizy statystycznej	Badana cecha					
	f_c [MPa]	f_{ct} [MPa]	E_c [GPa]	$f_c^{50cykli}$ [MPa]	τ [MPa]	A [cm^3/50 cm^2]
Wartość średnia	67 (20÷58)	7,3 (1,6÷4,1)	36,7 (27÷37)	65,9	12,9	9,0 (≤12,2)
Wartość minimalna	63,1	5,9	32,7	56,1	10,9	7,1
Odchylenie standardowe	2,2	0,6	2,8	4,5	1,1	0,6
Wskaźnik zmienności [%]	3	8	8	7	8	7
Współczynnik jednorodności [-]	0,94	0,81	0,90	0,85	0,85	0,84
Przedział ufności	65,9 68,0	7,0 7,6	35,3 38,1	63,9 67,8	12,3 13,5	8,7 9,3
W nawiasach podano właściwości betonu zwykłego wg: PN-EN 1992-1-1:2008 oraz PN-83/B06256. Oznaczenia cech wyjaśniono w tekście (por. pkt. 4).						

Przeprowadzone badania (tabela 4), wykazały wzrost wytrzymałości na ściskanie fibrokompozytu o zawartości włókien 1,2% o ok. 50% oraz wytrzymałość na rozciąganie przy rozłupywaniu o ok. 120% w stosunku do kompozytu bez włókien.

Wyniki badania odporności na działanie mrozu pozwalają określić stopień mrozoodporności kompozytu drobnokruszywowego na poziomie F50. Próbki nie wykazywały pęknięć, a średni ubytek masy próbek wyniósł 0,22%. Nie nastąpił również spadek wytrzymałości na ściskanie w stosunku do próbek niezamrażanych. Analizy dowodzą, że przy zawartości włókien w ilości 1,2% badany fibrokompozyt wykazuje również większą, w porównaniu do betonu zwykłego, odporność na ścieralnie, spełniając wymagania normy PN-83/B-06256 „Beton odporny na ścieranie”.

Wyniki badań resztkowej wytrzymałości na zginanie wyraźnie wskazują na ciągliwy charakter materiału. Ponieważ włókna w dużym stopniu hamują powstawanie i rozwój zarysowań w betonie ich dodatek pozwala uzyskać duży wzrost wytrzymałości na rozciąganie. Zastosowanie zbrojenia rozproszonego powoduje, że kompozyt nie ulega nagłemu zniszczeniu, jak ma to miejsce w przypadku betonu zwykłego. Wykresy zależności siły obciążającej od szerokości rozwarcia rysy CMOD przedstawiono na rysunku 7, na którym B1/9 do B9/9 oznaczają numery badanych belek. Analizując kształt wykresu pokazanego na rysunku 7 można stwierdzić, że belki o zawartości włókien 1,2% wykazują cechę *pcs* [22], tj. powolny spadek siły niszczącej wraz ze wzrostem wartości *CMOD* po pojawieniu się rysy.



Rys. 7. Zależność siły obciążającej od szerokości rozwarcia rysy
Fig. 7. Depending of the loading force of CMOD

Po pojawieniu się pierwszej rysy obserwowano spadek siły niszczącej, a następnie jej wzrost. Można zauważyć, że po osiągnięciu maksymalnej siły rozciągającej i powstaniu rys badana próbka zachowuje zdolność przenoszenia obciążenia rozciągającego. Zdolność ta zmniejsza się wraz ze wzrostem szerokości rozwarcia rys. Średnie wartości resztkowej wytrzymałości przy zginaniu i towarzyszące im szerokości rozwarcia rysy przedstawiono w tabeli 5.

Tabela 5. Średnie wartości wytrzymałości resztkowej w zależności od szerokości rozwarcia rysy
Table 5. Average values of residual strength depending on the width of the opening cracks

Szerokość rozwarcia rysy CMOD [mm]	0,5	1,5	2,5	3,5	f_{R3k} / f_{R1k}	Klasyfikacja według Model Code 2010 [22]
Wytrzymałość na zginanie [MPa]	f_{R1k}	f_{R2k}	f_{R3k}	f_{R4k}	0,8	**8b**
	8,38	8,18	7,36	6,37		

Wytrzymałości resztkowe $f_{R,1}$, $f_{R,2}$, $f_{R,3}$ i $f_{R,4}$ oznaczają wartości naprężeń rozciągających w przekroju dla danych szerokości rozwarcia rysy CMOD, równych odpowiednio: 0,5, 1,5, 2,5, 3,5 mm.

Klasyfikacja 8b wg [22] definiuje badany materiał, jako fibrokompozyt o bardzo wysokiej wartości f_{R1} (zakres od 1–8), litera „b” oznacza, że badany fibrokompozyt wykonany na bazie piasków odpadowych charakteryzuje cechą *pcs* , którą wyznaczono z zależności f_{R3}/f_{R1} (wg [22] „a” i „b” – *pcs*, „d” i „e” – *psh*). Wartości wytrzymałości podane w tabeli mogą posłużyć do projektowania elementów konstrukcyjnych na zginanie oraz ścinanie, wykonanych z fibrokompozytu na bazie piasków odpadowych.

Dodatek włókien stalowych nieznacznie, co potwierdza literatura [11], wpływa jedynie na przyrost statycznego modułu sprężystości, jego wartość wzrasta o ok. 2 MPa w stosunku do kompozytu bez włókien. Brak znaczącego wpływu dodatku włókien na tę cechę może być spowodowany dobrą wytrzymałością na ściskanie betonu, przypadkowym ułożeniem włókien stalowych oraz stosunkowo małą powierzchnią włókien w porównaniu z przekrojem betonowym.

W celu dalszej identyfikacji właściwości fibrokompozytu wykonanego na bazie piasków odpadowych, jako materiału konstrukcyjnego, prowadzone są badania właściwości reologicznych: pełzanie. Zaplanowano także wykonanie badań pełnowymiarowych elementów konstrukcyjnych, płyty i belki (w trakcie badań).

6. Podsumowanie

Wyniki przeprowadzonych badań dowodzą, że właściwości mechaniczno-fizyczne drobnokruszywowego kompozytu wykonanego na bazie piasków odpadowych ze zbrojeniem rozproszonym w ilości 1,2% odpowiadają wymaganiom stawianym materiałom konstrukcyjnym. Proponowany fibrokompozyt dzięki swoim właściwościom może, w niektórych przypadkach, stanowić alternatywę dla betonu zwykłego. Przeprowadzone studia literaturowe i otrzymane wyniki badań pozwalają stwierdzić, że istnieje możliwość użycia tego materiału do wykonywania elementów konstrukcyjnych takich, jak: płyty stropowe, belki, posadzki przemysłowe czy powłoki, a tym samym stwarza perspektywę na wykorzystanie kruszywa odpadowego.

Możliwość wykorzystania piasków odpadowych jako pełnowartościowego kruszywa do wytwarzania materiału konstrukcyjnego w skali przemysłowej rozwiązałaby, w dużej mierze, problem zagospodarowania hałd zalegających w rejonie Pomorza Zachodniego.

Duże zasoby kruszyw drobnych, występujące w postaci odpadów poprodukcyjnych, mogłyby stać się bogactwem dla tego Regionu, a tym samym podstawowym składnikiem materiałów przeznaczonych do wytwarzania elementów konstrukcyjnych.

Literatura

1. **Altun F., Haktanir T., Ari K.:** *Effects of steel fiber addition on mechanical properties of concrete and RC beams.* Construction and Building Materials, 21, 654–661 (2007).
2. **Aruntas H.Y. et al.:** *Effect of super plasticizer and curing conditions on properties of concrete with and without fiber*. Materials Letters, 62, 3441–344 (2008).
3. **Błaszczyński T., Przybylska-Fałek M.:** *Fibrobeton jako materiał konstrukcyjny*, Izolacje, 11–12, 44–50 (2012).
4. **Błaszczyński T., Przybylska-Fałek M.:** *Durability of SFRC material,* 10th International Conference on Durability of Composite Systems, DURACOSYS 2012, Brussels, 17–20 September 2012.
5. **Bonaszewska-Wyszomirska T.:** *Beton (nie)zwykły.* Inżynier Budownictwa, 10, 79–82 (2007).
6. **Brandt A.M.:** *Cement based composites: materials, mechanical properties and performance*, Taylor&Francis, 2009.

7. **Deklaracja własności użytkowych** nr 2/2013/E
8. **Domski J.:** *Long-term Study on Fibre Reinforced Fine Aggregate Concrete Beams Based on Waste Sand.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection) 17, 2015 – w druku.
9. **Domski J.:** *Ugięcie belek fibropiaskobetonowych wykonanych na bazie piasku odpadowego.* Przegląd Budowlany, 3, 32–37 (2012).
10. **Dondelewski H., Marcinkowski S.:** *Badanie sprężystości, skurczu i pełzania betonów drobnokruszywowych.* Archiwum Inżynierii Lądowej, PWN, Warszawa 1980.
11. **Glinicki M. A.:** *Beton ze zbrojeniem strukturalnym.* XXV Ogólnopolskie warsztaty pracy projektanta konstrukcji, Szczyrk 2010.
12. **Głodkowska W., Kobaka J.:** *Zastosowanie piasków odpadowych do wykonania posadzek przemysłowych.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection) 11, 193–206 (2009).
13. **Głodkowska W., Kobaka J.:** *Statystyczny model opisu rozkładu włókien w drobnokruszywowym kompozycie mineralnym.* Materiały Budowlane, 9, 6–8 (2011).
14. **Głodkowska W., Kobaka J.:** *The Model of Brittle Matrix Composites for Distribution of Steel Fibers.* Journal of Civil Engineering and Management. 145–150 (2012).
15. **Głodkowska W., Kobaka J.:** *Nieniszcząca ocena wybranych cech drobnokruszywowego betonu zbrojonego włóknami stalowymi. VI Konferencja Naukowo-Techniczna „Zagadnienia materiałowe w inżynierii lądowej”.* MATDUB. Wyd. Politechniki Krakowskiej, 108–116 (2011).
16. **Głodkowska W., Kobaka J., Laskowska-Bury J.:** *Wpływ włókien stalowych na kształtowanie właściwości kompozytu drobnokruszywowego.* Materiały Budowlane, 10, 28–30 (2013).
17. **Głodkowska W., Kobaka J.:** *Modelling of properties and distribution of steel fibres with in a fine aggregate concrete.* Construction and Building Materials. 44, 646–653 (2013).
18. **Jamroży Z.:** *Drutobeton.* Politechnika Krakowska, Kraków 1985
19. **Jasiczak J., Mikołajczak P.:** *Technologia betonu modyfikowanego domieszkami i dodatkami.* Wydawnictwo Politechniki Poznańskiej, Poznań 1997.
20. **Kondratowicz W.:** *Jednorodność udziału piasku w krajowych kruszywach naturalnych przeznaczonych do betonu. Stan i znaczenie.* Prace Naukowe Instytutu Budownictwa Politechniki Wrocławskiej. Wrocław 1978.
21. **Mehmet Özcan D., Bayraktar A., Sahin A., Haktanir T., Türker T.:** *Experimental and finite element analysis on the steel fiber-reinforced concrete (SFRC) beams ultimate behavior.* Construction and Building Materials, 23, 1064–1077 (2009).

22. **Model Code 2010**, first complete draft, bulletin 55, 1.
23. **Neville A.:** *Właściwości betonu*. Polski Cement, Kraków 2000.
24. **Parra–Montesinos G.:** *Shear Streinght of Beams with Deformed Steel Fibres*. Concrete International, 11, 57–67 (2006).
25. **Praca zbiorowa (red. Brandt A.M.):** *Własności mechaniczne i struktura kompozytów betonowych. Zakład Narodowy Imienia Ossolińskich*. Wydawnictwo Polskiej Akademii Nauk, Wrocław-Warszawa-Kraków-Gdańsk 1974.
26. **Strzałkowski A., Śliżyński A.:** *Matematyczne metody opracowania wyników pomiarów*. Wyd. 3, PWN, Warszawa 1978.
27. **Świadectwo badania kruszywa** F-08-P-14/25. Laboratorium Budowlane BETOTEST POLSKA sp. z o.o.

Waste Sands as a Valuable Aggregates to Produce Fibre-composites

Abstract

In the paper an issue of waste sand utilization was raised. The *heaps* of waste sand located in Polish region Pomerania are *by-product* obtained during the process called hydroclassification of all-in-aggregate for concrete production. One of examples how to resolve the waste sand utilization problem could be its application for the production of steel fiber reinforced mineral composites. The authors introduced their tests results physical-mechanical properties of fibrous composites made on the basis of waste sands with different amounts of steel fibers. Steel fiber content is from 0 to 2.5% relative to the volume of the composite. The fibers in the mixture were arranged at random. Based on these results proposed composite of the best properties, which meets the requirements for construction materials. It was specified the exact composition of the material of this composite. For the selected composite steel fibre content of 1.2% of tests taken basic properties: compressive strength, tensile strength, residual strength, modulus of elasticity, shear strength, resistance to frost, resistance to abrasion. Tests were performed on samples having a side of 150 cubic mm and cylindrical with the dimensions 150x300 mm.

Carried out research, literature studies and analysis of the obtained results allow to conclude that this material can be used for the performance of structural elements and thus creates a perspective on the use of waste aggregates.

In view of the above, the large resources of small aggregates present in the form of waste could become a wealth for the region of Pomerania. Sands waste could become a basic component of materials intended for the manufacture of certain structural elements.

The use of waste to produce aggregate composites constructional on a wider scale, and partial replacement of concrete simple-it such material can significantly reduce further degradation of the environment.

Słowa kluczowe:
ekologia, piaski odpadowe, fibrokompozyt, włókna stalowe, właściwości

Keywords:
ecology, waste sands, fiber composite, steel fibers, properties

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Analiza specjacyjna w badaniach środowiska

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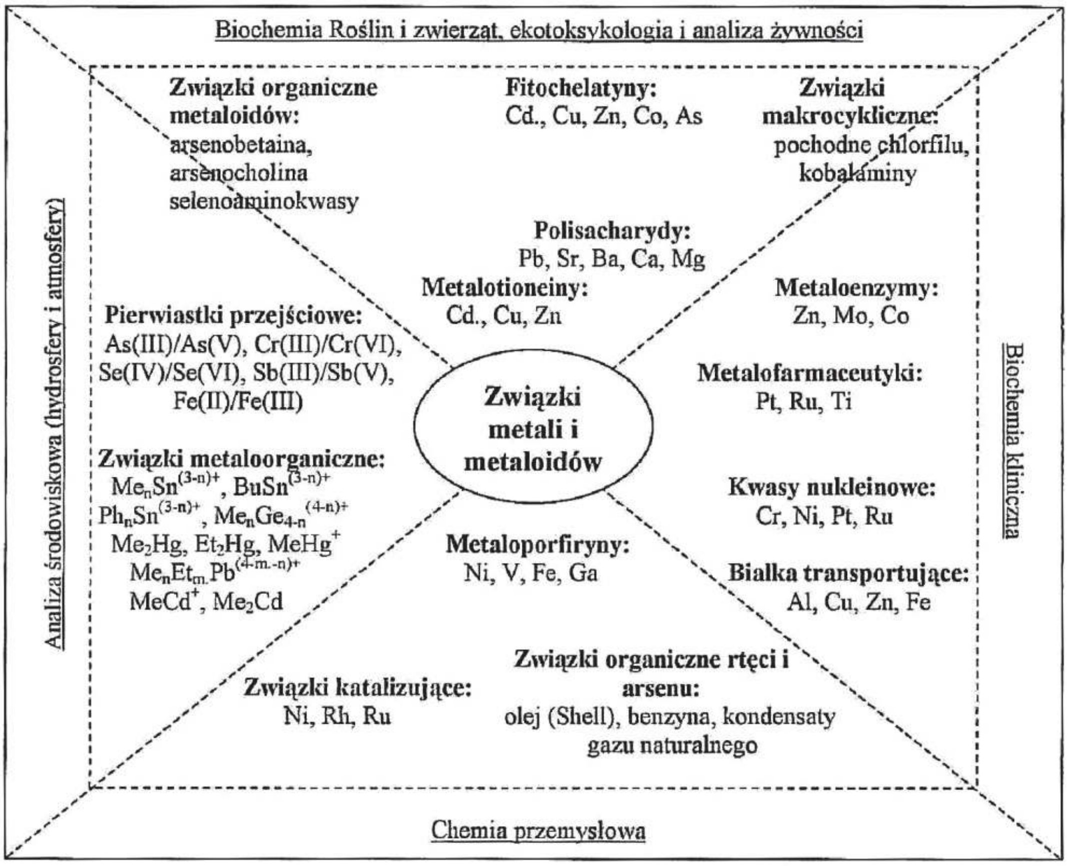
Wstęp

Ekoanalityka jako interdyscyplinarna nauka wskazuje na ścisłe powiązanie osiągnięć nauk podstawowych z praktycznymi zastosowaniami. Współczesna analityka próbek środowiskowych dostarcza ważnych wyników na bardzo niskim poziomie stężeń przy jednocześnie niewielkiej masie próbki, szczególnie w ostatnich dwudziestu latach. Specjalistyczna aparatura została rozbudowana o wiele nowych instrumentalnych rozwiązań przy wsparciu coraz lepszych programów komputerowych. Badając stan środowiska i określając poziom analitów dostarczamy istotnie ważnych o praktycznym znaczeniu danych, niezbędnych w wielu rozwijających się dziedzinach oraz w globalnym monitoringu środowiska. Perspektywy rozwoju inżynierii ochrony środowiska są uzależnione od dobrej ekoanalityki w laboratoriach wyposażonych w najnowszą aparaturę laboratoryjną. Śledzenie procesów technologicznych uzdatniania wody, oczyszczania ścieków, remediacji gruntów, rekultywacji jezior, recyklingu i utylizacji odpadów to główne problemy wsparte i rozwijane poprzez nowoczesną analitykę, a obecnie o techniki łączone [1]. Współczesne technologie wymagają często oznaczeń składników śladowych. Granicą, od której można mówić o analizie śladów jest stężenie 100 ppm. Zaproponowana obecnie przez IUPAC granica za kilka lat ponownie ulegnie przesunięciu. Nauka i technika wymusza na bieżąco rozwój metod i technik analitycznych przeznaczonych do oznaczania małych i bardzo małych zawartości analitu. Najczystszy materiał technologiczny otrzymany przez człowieka określa się zapisem 11N, 10^{-9}%

czyli ppt. Podobna czystość jest niezbędna w biotechnologii, inżynierii genetycznej, inżynierii środowiska i w ochronie środowiska.

Specjacja

Zjawisko występowania różnych fizycznych i chemicznych form tego samego pierwiastka zostało opisane terminem specjacja. Słowo to zostało zapożyczone z nauk biologicznych z łacińskiego słowa species – gatunek, ewolucja gatunku. Specjacja określa występowanie pierwiastka w różnych, wyraźnie zdefiniowanych formach chemicznych i ma wyraźny sens jakościowy. Ewaluacja terminu specjacja została przedstawiona w artykule przeglądowym w Ekologii i Inżynierii Ekologicznej [2]. Specjacja chemiczna – termin, który pojawił się w literaturze w 1993 roku i był wpierw określany jako „przemieszczanie i przekształcanie się form pierwiastka w środowisku" [3]. W tym samym roku pojawił się termin „szeroki zakres związków lub form chemicznych lub pierwiastków, układów, w jakich występować, lub różnych grup atomów obecnych w różnym środowisku" [3]. Dojlido [3] określił termin specjacji „występowaniem substancji w różnych postaciach jako uwodnione wolne jony, jako kompleksy i pary jonowe, jako związki organiczne i inne", a w 1997 [3] jako „występowanie substancji w różnych postaciach (formach)". Również Hulanicki w 1998 [3] specjację określił „występowaniem zróżnicowanych chemicznych, a także fizycznych form danego pierwiastka", lub „wszystkie fizyczne i chemiczne formy występowania pierwiastka w danej matrycy środowiska" [3]. Termin ten był również określany następująco „ wyszczególnienie rodzaju wiązań w danym związku chemicznym oraz określenie stopnia utlenienia jonów metali" [3]. Namieśnik, Łukasiak i Jamrógiewicz [4] wprowadzili pojęcie „proces identyfikacji różnych form chemicznych i fizycznych w jakich dany pierwiastek występuje w badanej próbce". Międzynarodowa Unia Chemii Czystej i Stosowanej IUPAC [5] definiuje specjację jako proces mający dostarczyć dowodów na fakt istnienia postaci atomowych i molekularnych analitów. W odniesieniu do środowisku Caroli zdefiniował specjację jako identyfikacje i weryfikację różnorodnych form analitu pod względem ryzyka dotyczącego zdrowia ludzi i kondycji środowiska [17, 19]. Główne obszary badań analizie specjacyjnej przedstawiono na rys. 1.



Rys. 1. Obszary badań w analizie specjacyjnej
Fig. 1. Research areas in speciation analysis

Analiza specjacyjna

Wiedza o całkowitym stężeniu analitu w badanej próbce stała się obecnie niewystarczająca. Powstały realne analityczno-instrumentalne przy wsparciu komputerowym możliwości oznaczania form (fizycznych i chemicznych) tego samego pierwiastka (lub związku chemicznego) w tej samej próbce w warunkach ustalonej – naturalnej równowagi. Analiza specjacyjna ma sens ilościowy. Każda z form oznaczonego analitu ma inne właściwości bio(geo)chemiczne, a tym samym toksykologiczne. Badania biochemiczne, toksykologiczne, farmaceutyczne, kliniczne, hydrobiologiczne, hydrogeologiczne, hydrochemiczne i w inżynierii ochrony środowiska rozwinęły intensywnie analizę specjacyjną tak próbek środowiskowych, jak i technologicznych i biologicznych. Szereg procesów badawczych jak: kumulacja, migracja, biodostępność, biomagnifikacja, toksyczność, rozpuszczalność i sorpcja może być opisana analizą korelacyjna, wykorzystując oznaczone formy analitów.

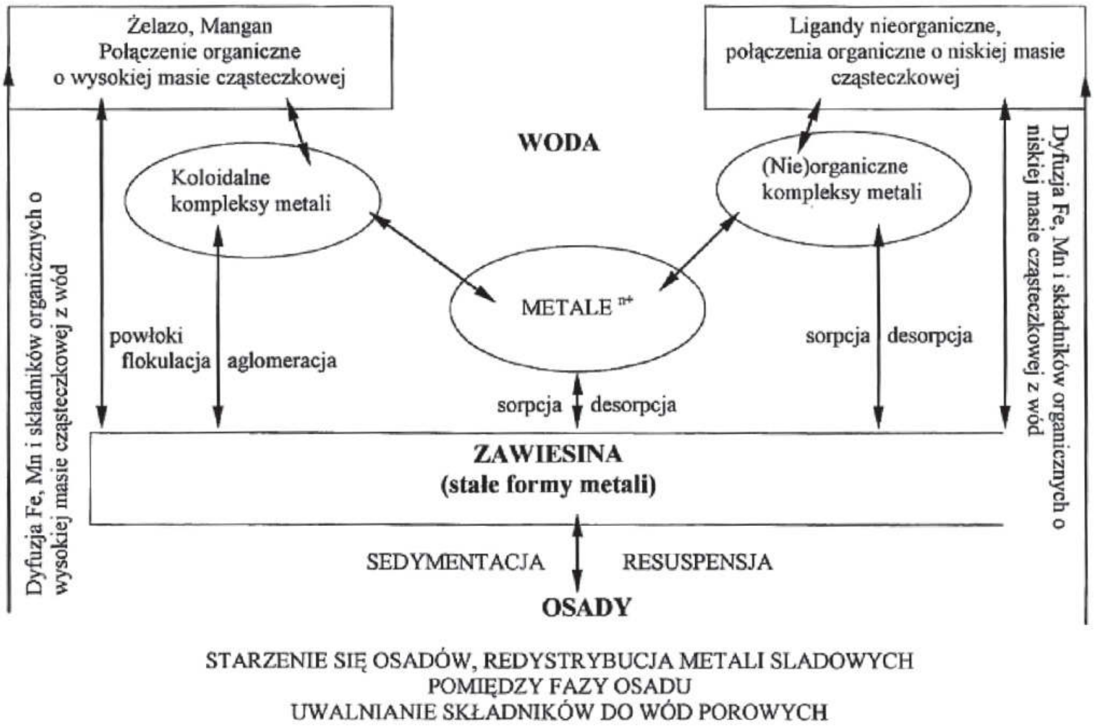
Analiza specjacyjna to analiza konkretnych form chemicznych, a rozwinięte w literaturze pojęcie „to proces identyfikacji i oznaczania róznych form chemicznych i fizycznych, w jakich dany pierwiastek występuje w badanej próbce" [1–5].

Namieśnik określa kilka typów analizy specjacyjnej – fizycznej i chemicznej. Specjacja fizyczna uwzględnia występowanie wolnego analitu i analit w postaci związanej. Frakcją związaną z zawiesiną od frakcji rozpuszczonej oddzielono na sączku 0,45 μm. W ten sposób można wykazać, że na zawiesinie sorbuje się około 80% oznaczanego analitu, a tylko 20% rozpuszcza się i przechodzi do wody jako rozpuszczalnika naturalnego, względem którego można określić wymywanie zanieczyszczeń z próbek środowiskowych. W ten sposób określono poziom zagrożenia związkami organicznymi: wielopierścieniowymi węglowodorami aromatycznymi (WWA), polichlorowanymi bifenylami (PCB) i dioksynami (PCDD i PCDF).

Specjacja fizyczna analizy wody rzecznej wskazuje, że wodę jako medium należy rozpatrywać jako rozpuszczalnik i zawiesinę rzeczną. Jest to układ dwufazowy, na co nie zwraca uwagi Rozporządzenie Ministra Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa w sprawie klasyfikacji wód oraz warunków, jakim powinny odpowiadać ścieki wprowadzane do wód lub do ziemi z dnia 5. listopada 1991 roku Dz. U. Nr 116 z 16. grudnia 1991 roku.

W myśl polskich przepisów należy pobrać wodę z rzeki i wykonać analizę wody. W przypadku zawiesiny w wodzie odsączyć na sączku bibułowym i odrzucić. W myśl przepisów niemieckich należy wodę z rzeki przesączyć przez sączek 0,45 μm i wykonać analizę np. metali w wodzie i osobno w zawiesinie. Przepisy niemieckie LAWA 1998 [6] określają dopuszczalne stężenia metali w wodzie (faza podstawowa) i osobno w zawiesinie. Dlatego trudno jest porównywać powyższe wyniki.

Rozwinięcie analizy specjacyjnej tylko na typ fizyczny powoduje, że w polskich przepisach prawnych konieczna jest nowelizacja na wzór Unii Europejskiej. Wodę rzeczną należy traktować jako układ trójfazowy: woda – zawiesina – osad denny z odrębnymi przepisami kwalifikacyjnymi stanu czystości tych trzech odrębnych faz (rys. 2). Natomiast specjacja chemiczna [4] wyróżnia cztery typy analizy: specjacja przesiewowa, specjacja grupowa, specjacja dystrybucyjna i specjacja indywidualna. Typ specjacji przesiewowej określa tylko jeden analit najbardziej niebezpieczny w badanej matrycy. Takim przykładem jest oznaczanie tri bu tyl o-cyny w wodzie morskiej lub w tkankach lub oznaczanie metylortęci w tkankach.



Rys. 2. Główne procesy i mechanizmy reakcji wzajemnego oddziaływania między rozpuszczonymi i stałymi formami metali w wodach
Fig. 2. Main processes and reaction mechanisms concerning interaction between melted and liquid forms of metals in water

Typ specjacji dystrybucyjnej wiąże się z próbkami biologicznymi w płynach fizjologicznych i w surowicy krwi. Ostatni typ specjacji to specjacja indywidualna. Jest to najtrudniejsza analiza specjacyjna, bowiem polega na identyfikacji i oznaczeniu w próbce wszystkich indywiduów chemicznych, które zawierają w swoim składzie dany pierwiastek [1]. W tym przypadku obecnie obserwowany jest szeroki zakres zastosowań nie tylko w określaniu stanu środowiska, lecz również w szerokich badaniach jakości żywności, ekotoksykologii i inżynierii ochrony środowiska.

Wraz z rozwojem tych dziedzin naukowych mamy coraz więcej informacji odnośnie występowania i roli arsenu, antymonu i selenu w ekosystemach. Zainteresowanie oznaczeniami tych pierwiastków wynika z kilku przyczyn. Pierwiastki te rzadko osiągają w (nawet zanieczyszczonym) środowisku stężenia toksyczne, jednakże niewielka rozpiętość dawki przyjmowanej przez organizmy (często koniecznej dla ich prawidłowego funkcjonowania) i dawki toksycznej przy powszechności ich występowania wymaga kontroli. Zawartość związków arsenu, antymonu i selenu w środowisku może stanowić element monitoringu rozprzestrzeniania się zanieczyszczeń, informować o nasileniu procesów antropopresyjnych. Wreszcie istotnym staje się określanie poziomu naturalnego – tła hydrogeochemicznego, bądź przy niemożności wykluczenia zmian antropopresyjnych, poziomu odniesienia dla czasu wykonania analizy. Istotności nabiera tu rozróżnienie form występowania pierwiastków w środowisku – analiza specjacyjna gdyż przykładowo związki nieorganiczne selenu są kilkaset razy bardziej toksyczne od form metylowanych, podobnie dla arsenu, związki zawierające antymon (III) są bardziej toksyczne od zawierających antymon (V). Oznaczenia takie rozszerzając wiedzę o środowisku naturalnym stanowią często punkt odniesienia przy określaniu tendencji zachodzących w ekosystemach i ich dynamiki, co za tym idzie stanowiąc podstawę do dalszych działań w zakresie czy ochrony środowiska czy inżynierii ekologicznej.

Ogólny schemat analizy specjacyjnej As, Sb i Se w wodach przedstawiono w odrębnej monografii Niedzielskiego [7].

Ekstrakcja sekwencyjna

W pracach nad specjacją metali ciężkich w osadach dennych badacze często posługują się podziałem zaproponowanym przez Tessiera i współpracowników, którzy wyróżnili i zdefiniowali pięć frakcji [8].

Frakcja I. Metale wymienialne.

Są to metale zaadsorbowane na powierzchni ciał stałych, które w wyniku zmian składu jonowego wody, w wyniku przesunięcia równowagi w układzie sorpcja-desorpcja mogą przejść do toni wodnej.

Frakcja II. Metale związane z węglanami.

Frakcja ta obejmuje metale występujące w formie węglanów, lub współstrącone z węglanami. W wyniku spadku wartości pH wody w strefie przydennej może nastąpić zachwianie równowagi węglanowej i w konsekwencji ponowne przejście metali do toni wodnej.

Frakcja III. Metale związane z uwodnionymi tlenkami żelaza i manganu.

Są to metale zaadsorbowane na rozwiniętej powierzchni wytrącających się uwodnionych tlenków żelaza i manganu. W warunkach beztlenowych (redukujących), w wyniku redukcji żelaza i manganu, może nastąpić rozpuszczenie osadu i zawrócenie metali do toni.

Frakcja ta obejmuje metale występujące w formie węglanów, lub współstrącone z węglanami. W wyniku spadku wartości pH wody w strefie przydennej może nastąpić zachwianie równowagi węglanowej i w konsekwencji ponowne przejście metali do toni wodnej.

Frakcja IV. Metale związane z materią organiczną.

Są to metale zaadsorbowane na powierzchni materii organicznej lub metale związane z tą materią (wbudowane). Są one chwilowo unieruchomione, jednak w wyniku naturalnie postępującej mineralizacji osadów czasem muszą one przejść do jednej z pozostałych frakcji lub zawrócić do toni wodnej.

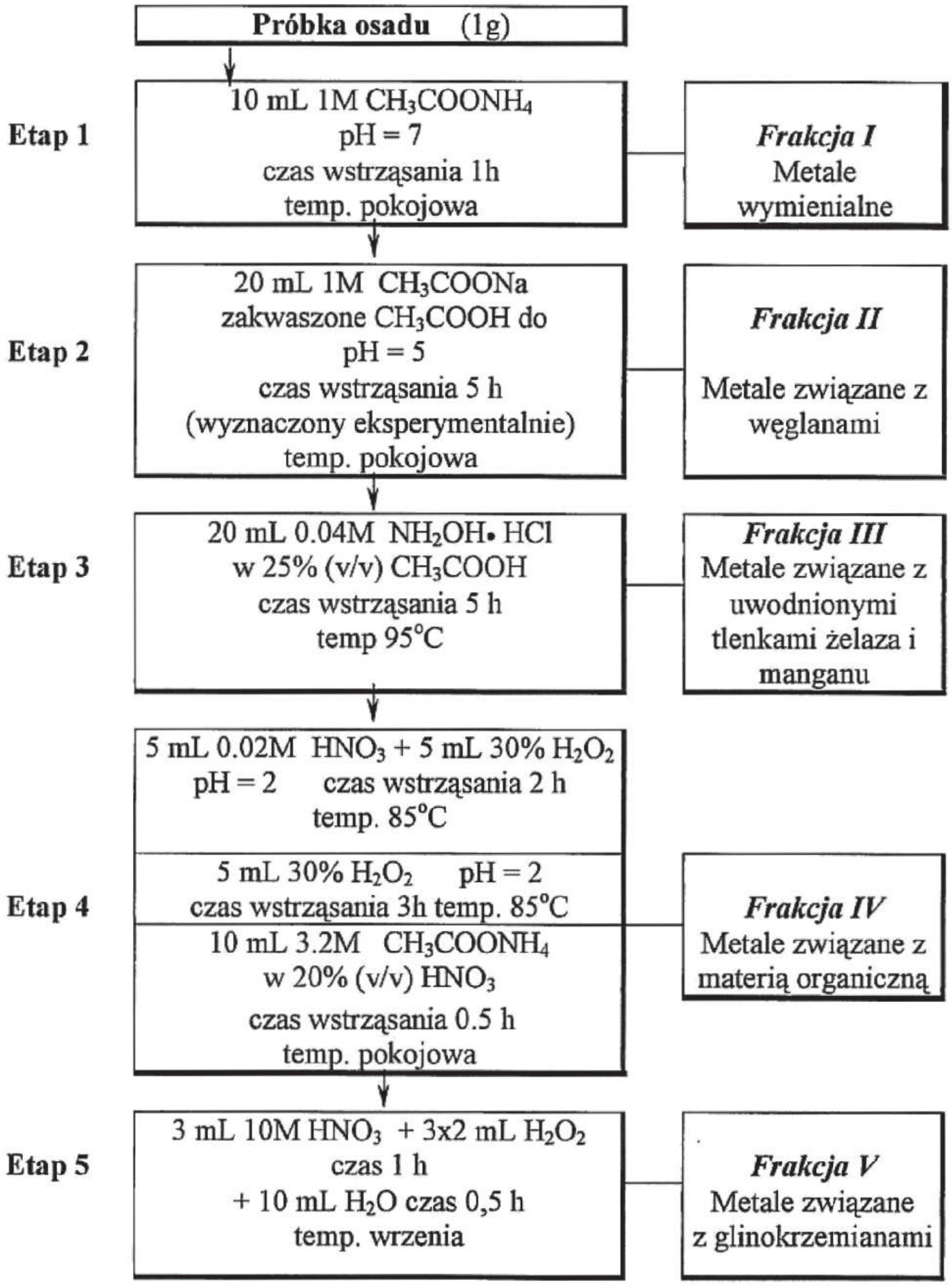
Frakcja V. Metale pozostałe, trwale związane z minerałami.

Frakcja ta obejmuje metale wbudowane w sieć krystaliczną minerałów, zarówno wtórnych jak i pierwotnych. Są trwale unieruchomione i w warunkach naturalnych, w przewidywalnym czasie nie przejdą do toni wodnej, nie stanowią więc realnego zagrożenia dla ekosystemu.

Pierwszym problemem, jaki napotyka badacz zajmujący się analizą specjacyjną osadów dennych na zawartość metali ciężkich, jest wypracowanie techniki pobierania próbek i ich wstępnej obróbki [9]. W tym pierwszym etapie należy uwzględnić lokalizację miejsc pobierania reprezentatywnych próbek, samą technikę pobierania, sposób oddzielenia interesującej nas warstwy osadu, przechowywanie próbek, suszenie, rozdrabnianie i przesiewanie. Poszczególne czynności muszą być tak wykonywane, by z jednej strony nie dopuścić do zanieczyszczenia próbek oznaczanymi metalami, z drugiej zaś maksymalnie zabezpieczyć je przed wszelkimi niepożądanymi procesami mogącymi spowodować zmianę form występowania pierwiastków. Zanieczyszczenie próbek metalami może nastąpić w czasie ich pobierania, rozdrabniania i przesiewania. Czynności te należy więc wykonywać przy użyciu sprzętu nie zawierającego części metalowych. Przy zachowaniu dużej ostrożności kontaminacje próbek można ograniczyć praktycznie do zera. Znacznie trudniejszym zadaniem jest przechowywanie i suszenie próbek w ten sposób, aby nie dopuścić do zmiany formy występowania metali. Należy dążyć do jak najkrótszego przechowywania próbek w stanie wilgotnym. W czasie tym powinny być one silnie wychłodzone lub zamrożone, co znacznie hamuje zachodzące w nich procesy biologiczne. Odwodnienie próbki następuje przez odwirowanie, suszenie w suszarce bądź pod lampami promiennikowymi lub, co wydaje się być najbardziej korzystne dla poprawności analizy specjacyjnej, poprzez liofilizację. Pomimo stosowania skomplikowanych często zabiegów, jak np. realizowanie wszystkich wyliczonych czynności w atmosferze gazu obojętnego, nigdy nie mamy całkowitej pewności, czy skład próbki w pełni odpowiada rzeczywistemu składowi osadu, zalegającego w warunkach naturalnych dno zbiornika.

Następnym etapem jest rozróżnienie i ilościowe wyodrębnienie form występowania metali w badanym osadzie. Jedną z podstawowych technik rozdzielania poszczególnych, wymienionych wcześniej frakcji, jest metoda ekstrakcji sekwencyjnej [10]. Polega ona na wielokrotnym ekstrahowaniu wcześniej przygotowanej próbki osadu coraz to innymi, specyficznymi dla danej frakcji ekstrahentami. W celu uzyskania porównywalnych, nadających się do interpretacji wyników, należy w badaniach stosować ujednoliconą procedurę. Dla celów monitoringowych koniecznym staje się więc opracowanie metod standardowych. Umożliwiło by to również przygotowanie materiałów referencyjnych, tak istotnych przy ocenie poprawności wykonywania tej skomplikowanej, wieloetapowej analizy [16].

Ostatnim etapem jest ilościowe oznaczenie w otrzymanych ekstraktach zawartości metali. Wykorzystuje się do tego celu różne, powszechnie dostępne techniki instrumentalne [11]. Tak więc stosuje się spektrofotometry absorpcji atomowej, zarówno z atomizacją w płomieniu jak i elektrotermiczną, ICP, metody polarograficzne, wolt amperometryczne i potencjometryczne. Przy doborze odpowiedniej techniki analitycznej należy brać pod uwagę zarówno wpływ substancji przeszkadzających, ekstrahowanych z osadu, jak i oznaczalność metody. Jest to szczególnie istotne przy analizie próbek osadów dennych z obszarów niezanieczyszczonych, w których metale występują w bardzo małych, często śladowych ilościach [12].



Rys. 3. Schemat frakcjonowania metali z osadów dennych według Tessiera
Fig. 3. Fractionation scheme for metals from sediments according to Tessier

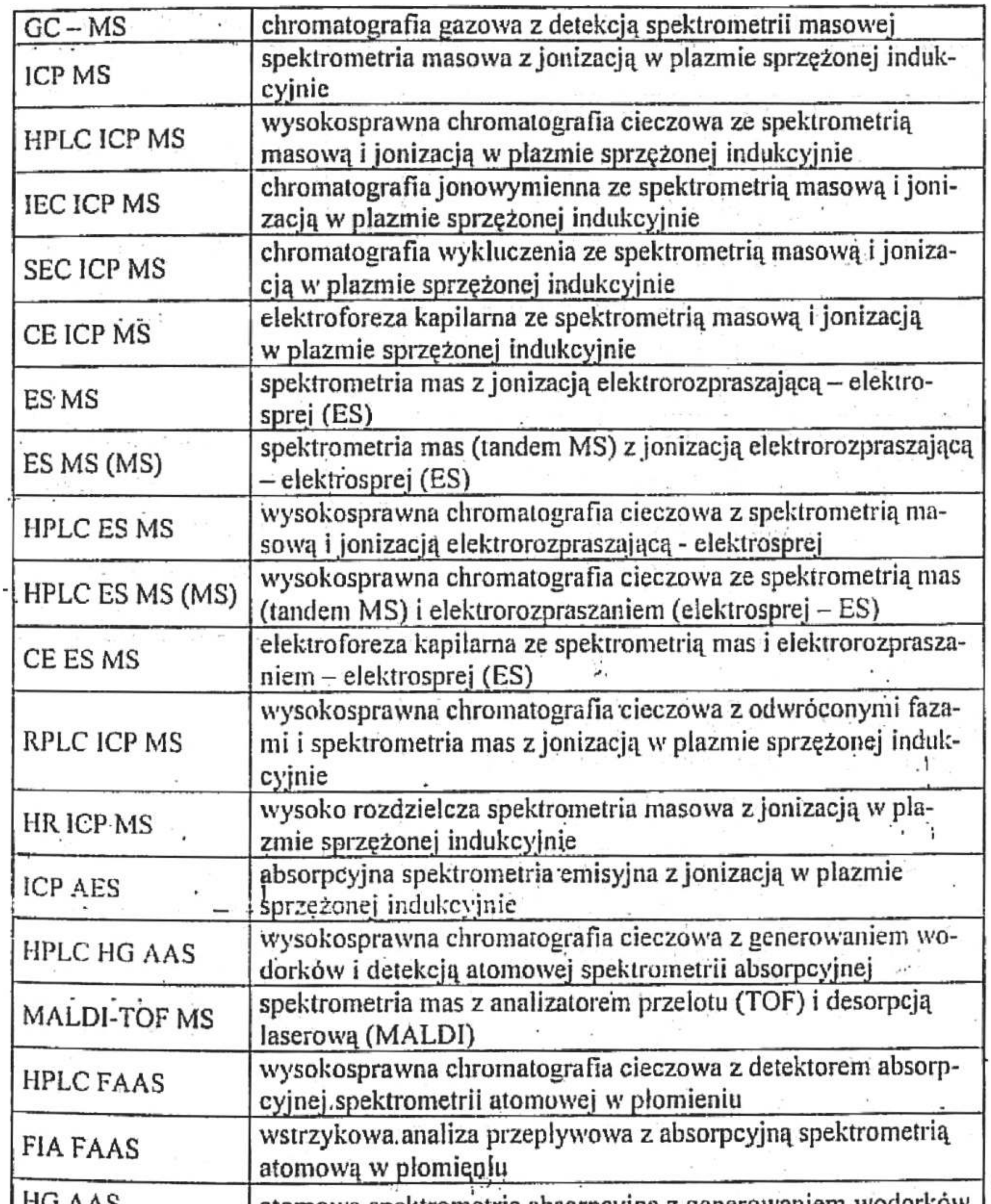
Materiały referencyjne

Istnieje wiele materiałów referencyjnych do oznaczania całkowitej zawartości pierwiastków w wodach naturalnych. Jednakże tylko kilka jest przydatnych do analizy specjacyjnej. Wymienić tu można wodę rzeczną o certyfikowanej zawartości różnych nieorganicznych i organicznych związków arsenu i liofilizowany roztwór wodny do oznaczania Cr(III) i Cr(VI). Szereg materiałów jest na etapie badań, które nie tylko wymagają perfekcyjnej techniki analitycznej, ale są też pracochłonne i wymagają zaangażowania wielu laborantów analitycznych. W stadium opracowania są materiały do badań specjacji selenu i oznaczania trimetylooołowiu w wodach. Trudności występują też z doborem warunków przechowywania, gdyż np. trwałość certyfikowanych materiałów do oznaczania selenu, przechowywanych w naczyniach polietylenowych jest zadawalająca w odróżnieniu od naczyń polipropylenowych. Aby zapewnić trwałość obu stopni utlenienie chromu w liofilizowanym roztworze, powinien być on przechowywany pod ochronną atmosferą azotu w ciemności.

Certyfikowane materiały odniesienia do analizy specjacyjnej osadów morskich z oznaczaniem konkretnych indywiduów zostały opracowane do oznaczania związków alkilocyny i metylortęci. Ponieważ celem oznaczania jest zdefiniowany związek, takie materiały mogą być stosowane również do kontroli jakości nowo opracowanych metod analitycznych. Natomiast materiały służące do badania specjacji operacyjnej muszą być zaopatrzone w bardzo ściśle zdefiniowaną procedurę analityczną, a wykorzystanie ich do kontroli innych procedur, wobec umowności celu, na ogół nie ma sensu. Takimi materiałami są: gleba wapienna (CRM 600), gleby ze szlamem ściekowym (CRM 483 i CRM 484) w których certyfikowane są zawartości kadmu, chromu, miedzi, niklu ołowiu i cynku [3, 13–14].

Techniki łączone

Selektywne oznaczenia specjacyjnych form pierwiastków możliwe są do przeprowadzenia na przykład poprzez wstępna separację form specjacyjnych, a następnie ich oznaczenia ilościowe z wykorzystaniem metod stosowanych w oznaczeniach całkowitej zawartości oznaczanego pierwiastka. Separacja form specjacyjnych może być prowadzona z wykorzystaniem odpowiednich, zwykle czasochłonnych i trudnych do zastosowań rutynowych technik czy procedur, które zwykle prowadzą jednak do uzyskiwania przybliżonych wyników oznaczeń. Ponadto manualne procedury separacyjne stwarzają duże możliwości wystąpienia błędów już na tym etapie analizy. Stąd zainteresowanie technikami łączącymi procedury separacji form specjacyjnych i następnie ilościowego oznaczania określanymi jako techniki łączone [18]. W swej zasadniczej formie idea tych technik oparta jest na zastosowaniu do rozdziału form specjacyjnych jednej z metod chromatograficznych: chromatografii gazowej (GC) czy wysokosprawnej chromatografii cieczowej (HPLC), lub też innych technik separacyjnych jak na przykład elektroforeza kapilarna (CE), jako detektory stosowane są natomiast głównie metody spektrometryczne znane jako samodzielne metody oznaczania całkowitej zawartości pierwiastków: absorpcyjna spektrometria atomowa (AAS), atomowa spektrometria fluorescencyjna (AFS), mikrofalowo wzbudzana plazma z detekcja emisyjną (MIP-AES), indukcyjnie wzbudzona plazma z detekcją emisyjną (ICP-AES) czy też detekcją masową (ICP-MS). Techniki łączone stanowią więc rozwinięcie znanych metod chromatograficznych, w których „klasyczne" detektory chromatografii gazowej: wychwytu elektronów (ECD), termo przewodnictwa (TCD), płomieniowo jonizacyjny (FID), fotojonizacyjny (PID), spektrometria mas (MS), czy chromatografii cieczowej: spektrofotometryczne (UV-Vis, IR, UV) czy fluorymetryczny (RF), (te ostatnie będące również samodzielnymi metodami analitycznymi) nieselektywne w stosunku do związków różnych metali i metaloidów, a zwykle charakteryzujące się niewystarczającymi granicami wykrywalności, zastąpione zostały metodami selektywnego oznaczania pierwiastków oferującymi odpowiednio niskie granice wykrywalności. Ponadto metody plazmowe (MIP-AES, ICP-AES, ICP-MS) umożliwiają oznaczenia wielu pierwiastków jednocześnie. Dlatego techniki łączone stają się najlepszymi narzędziami analizy specjacyjnej które mimo wysokich kosztów zakupu i eksploatacji urządzeń, stają się coraz częściej spotykanymi w laboratoriach analitycznych, a w niektórych konfiguracjach (np. GC-MIP-AES, HPLC-ICP-MS) dostępnymi komercyjnie [7, 15]. Najczęściej spotykany układ technik łączonych zawarto na rys. 4.



GC – MS	chromatografia gazowa z detekcją spektrometrii masowej
ICP MS	spektrometria masowa z jonizacją w plazmie sprzężonej indukcyjnie
HPLC ICP MS	wysokosprawna chromatografia cieczowa ze spektrometrią masową i jonizacją w plazmie sprzężonej indukcyjnie
IEC ICP MS	chromatografia jonowymienna ze spektrometrią masową i jonizacją w plazmie sprzężonej indukcyjnie
SEC ICP MS	chromatografia wykluczenia ze spektrometrią masową i jonizacją w plazmie sprzężonej indukcyjnie
CE ICP MS	elektroforeza kapilarna ze spektrometrią masową i jonizacją w plazmie sprzężonej indukcyjnie
ES MS	spektrometria mas z jonizacją elektrorozpraszającą – elektrosprej (ES)
ES MS (MS)	spektrometria mas (tandem MS) z jonizacją elektrorozpraszającą – elektrosprej (ES)
HPLC ES MS	wysokosprawna chromatografia cieczowa z spektrometrią masową i jonizacją elektrorozpraszającą - elektrosprej
HPLC ES MS (MS)	wysokosprawna chromatografia cieczowa ze spektrometrią mas (tandem MS) i elektrorozpraszaniem (elektrosprej – ES)
CE ES MS	elektroforeza kapilarna ze spektrometrią mas i elektrorozpraszaniem – elektrosprej (ES)
RPLC ICP MS	wysokosprawna chromatografia cieczowa z odwróconymi fazami i spektrometria mas z jonizacją w plazmie sprzężonej indukcyjnie
HR ICP MS	wysoko rozdzielcza spektrometria masowa z jonizacją w plazmie sprzężonej indukcyjnie
ICP AES	absorpcyjna spektrometria emisyjna z jonizacją w plazmie sprzężonej indukcyjnie
HPLC HG AAS	wysokosprawna chromatografia cieczowa z generowaniem wodorków i detekcją atomowej spektrometrii absorpcyjnej
MALDI-TOF MS	spektrometria mas z analizatorem przelotu (TOF) i desorpcją laserową (MALDI)
HPLC FAAS	wysokosprawna chromatografia cieczowa z detektorem absorpcyjnej spektrometrii atomowej w płomieniu
FIA FAAS	wstrzykowa analiza przepływowa z absorpcyjną spektrometrią atomową w płomieniu
HG AAS	atomowa spektrometria absorpcyjna z generowaniem wodorków

Rys. 4. Najczęściej stosowane techniki łączone
Fig. 4. The most frequently used combined methods

Praca powyższa będzie prezentowana w odrębnym multimedialnym wydaniu.

Literatura

1. **Hulanicki A.:** *Analiza specjacyjną próbek biologicznych*. Wiadomości chemiczne. 51(3–4), 189–203 (1997).
2. **Głosińska G., Boszke L., Siepak J.:** *Ewaluacja pojęć specjacja i analiza specjacyjna w literaturze Polskiej.* Chemia i inżynieria ekologiczna. 8(11), 1110–1119 (2001).
3. **Siepak J. (red):** *Analiza specjacyjną metali w próbkach wód i osadów dennych*. Wyd. UAM, Poznań 1998.
4. **Namieśnik J., Łukasiak J., Jamrógiewicz Z.:** *Pobieranie próbek środowiskowych do analizy.* Wydawnictwo Naukowe PWN, Warszawa 1995.
5. http://iupac.org (stan z dnia 19.03.2015)
6. LAWA – Landesarbewitsgemeinschaft Wasser: Beurteilung der Wasserbeschaffen-heitm von Fliesgewassern In der Bundesrepublik Deutschland – chemische Gewasserguteklassifikation, Zielvorgaben zum Schutz oberirdischer binnengewasser – Band 2, Berlin 1998.
7. **Niedzielski P., Siepak M., Przybyłek J., Siepak J.:** *Arsen, antymon i selen w wodach miasta Poznania mikrozanieczyszczenia czy mikroskładniki.* Wyd. UAM, Poznań 2002.
8. **Kowalski A., Frankowski M., Siepak J.:** *Specjacja rtęci w glebach i osadach dennych przy zastosowaniu układu technik łączonych HPLC-UV-CV-AFS.* Fundacja Rozwoju Uniwersytetu Gdańskiego. 305–312 (2010).
9. **Frankowski M., Zioła-Frankowska A., Siepak J., Kurzyca I., Novotny K., Vaculoivic T., Kanicky V.:** *Determination of aluminium In groundwater Samales by GFAAS, ICPAES, ICPMS and model ling on inorganic aluminium complexes.* Environ. Monit. Asses. 182, 71–84 (2011).
10. **Frankowski M., Zioła-Frankowska A., Kowalski A., Siepak J.:** *Frakcjonowanie metali ciężkich we frakcjach granulometrycznych.* Laboratorium. 11, 18 (2011).
11. **Zacharyasz P., Siepak J.:** *Petroleum contaminated soil and water in the city Międzychód.* Reclamation and revitalization of demoted areas. 251–273 (2012).
12. **Frankowski M., Zioła-Frankowska A., Siepak J.:** *From soil to leaves – aluminium fractination by single step extraction procedures in polluted and protected area.* Journal of Environmental Management. 127, 1–9 (2013).
13. **Siepak J. (red):** *Problemy analityczne badań osadów dennych.* Sympozjum Naukowe Komitetu Chemii Analitycznej PAN, Radom 2001.
14. **Siepak J. (red):** *Problemy analityczne oznaczania rtęci i jej form specjacyjnych próbkach środowiskowych.* Konferencja Naukowa Komitetu Chemii Analitycznej PAN, Słubice 2003.

15. Jander/Blasius, *Chemia nieorganiczna, Tom I. Wprowadzenie i analiza ilościowa.* Redakcja wydania I polskiego Franciszek Buhl, Jerzy Siepak, wyd. MedPharm Polska, 2013.
16. **Szyczewski P.:** *Badania i analityka wybranych substancji o wysokiej lepkości.* Praca doktorska, UAM Poznań 2015.
17. **Ociepa A.:** *Trofia jezior powiatu poznańskiego w świetle rozporządzeń Ministerstwa Ochrony Środowiska.* Praca doktorska, UAM Poznań 2015.
18. **Zacharyasz P.:** *Badania form specjacyjnych ropopochodnych w rejonie jezior Międzychodu.* Praca doktorska, UAM Poznań 2015.
19. **Majewska M.:** *Trofia jezior gnieźnieńskich na przestrzeni wielolecia.* Praca doktorska, UAM Poznań 2015.

Speciation Analysis in the Study of the Environment

Abstract

The review article contains basic definitions of speciation and speciation analysis in various aspects of human activity. It also features new approaches in fractionation analysis, problems related to reference materials and the most frequently used methods.

Słowa kluczowe:
analiza specjacyjna, fractionation analysis, materiały referencyjne,
techniki łączone

Keywords:
speciation analysis, fractionation analysis, reference materials,
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Interdyscyplinarny charakter chemii sanitarnej

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1. Wstęp

Chemia sanitarna jest częścią szeroko pojętej chemii środowiska. Zakres tematyki chemii sanitarnej obejmuje analizy jakościowe wody i ścieków [5, 7, 11, 16, 18].

W ramach analiz wód badaniami obejmowane są wody podziemne i powierzchniowe, będące źródłem zaopatrzenia w wodę gospodarki narodowej czyli ludności, przemysłu i rolnictwa. Wody podziemne i powierzchniowe charakteryzują się zmiennymi właściwościami jakościowymi. Skład wód podziemnych jest odmienny od składu wód powierzchniowych. Chemia sanitarna mająca podstawy w chemii ogólnej i analitycznej pozwala na dostarczenie informacji o jakości tych wód [22, 27, 34, 36]. Ma to decydujące znaczenie w projektowaniu i prowadzeniu procesów uzdatniania wody. Uwzględniając zróżnicowane wymagania odnośnie składu jakościowego wody przeznaczonej do wykorzystania, zakres wykonywanych analiz jest niejednolity. Wynika to także z wymagań określonych odpowiednimi aktami prawnymi dotyczącymi wody do spożycia, wody przeznaczonej do celów przemysłowych, w tym do celów energetycznych, chłodniczych, przemysłu spożywczego, farmaceutycznego i innych [22, 40, 41]. W odniesieniu do wód powierzchniowych i podziemnych należy wspomnieć także o zakresie ich monitoringu oraz o substancjach priorytetowych dla środowiska wodnego [33, 39]. Zakres analiz dla tych wód jest ciągle poszerzany i realizowany w ramach Programów Monitoringu Środowiska. Aktualny program został opracowany na lata 2013–2015 i obecnie jest w trakcie realizacji [55]. Należy dodać, że lista substancji priorytetowych dla środowiska wodnego jest ciągle uaktualniana, także w przepisach Unii Europejskiej. W 2013 roku przyjęto do realizacji Dyrektywę polegającą na wprowadzeniu obowiązku analizy nowych jedenastu związków głównych z uwzględnieniem niektórych ich izomerów. Dla kolejnych jedenastu wyznaczono mniejsze dopuszczalne stężenia. Zmienione środowiskowe normy jakości dla obecnych substancji priorytetowych powinny zostać po raz pierwszy uwzględnione w planach gospodarowania wodami w dorzeczach na lata 2015–2021. Nowo zidentyfikowane substancje priorytetowe oraz ich środowiskowe normy jakości powinny zostać uwzględnione przy tworzeniu dodatkowych programów monitorowania, które mają zostać przedstawione do końca 2018 r. W celu poprawy stanu chemicznego wód powierzchniowych, zmienione środowiskowe normy jakości dla obecnych substancji priorytetowych powinny zostać osiągnięte do końca 2021 r., natomiast środowiskowe normy jakości dla nowo zidentyfikowanych substancji powinny zostać osiągnięte do końca 2027 r. [9].

W ramach badań dotyczących ścieków, zakres analiz dostosowany jest do ich rodzaju. Wynika to z odmiennej charakterystyki jakościowej ścieków bytowo-gospodarczych, opadowych i przemysłowych, a także ich mieszanin o zróżnicowanych udziałach, które często wprowadzane są do miejskich oczyszczalni jako komunalne [35, 38]. Podobnie jak w przypadku wód uzdatnianych do konkretnych celów, także w przypadku ścieków skład jakościowy decyduje o wyborze metody i urządzeń do ich oczyszczania. Analizy chemiczne są wykonywane na każdym etapie oczyszczania, natomiast najistotniejsze z punktu widzenia ochrony środowiska są badania ścieków oczyszczonych. Zakres tych analiz jest odpowiedni do wymagań jakie wynikają z przepisów prawnych dotyczących warunków wprowadzania ścieków do odbiorników powierzchniowych, ziemi czy kanalizacji. W aktualnie obowiązującym rozporządzeniu dotyczącym ścieków oczyszczonych wymienia się pięć podstawowych wskaźników dla ścieków bytowych - gospodarczych, szesnaście – dla ścieków przemysłowych szczególnie szkodliwych dla środowiska wodnego oraz 59 – dla pozostałych zanieczyszczeń. Dla 75 wskaźników podano metodyki referencyjne do ich oznaczania z odniesieniem do zbioru Polskich Norm [38].

Również odnośnie wprowadzania ścieków do kanalizacji opracowane są i obowiązują odpowiednie przepisy prawne określające warunki jakim powinny odpowiadać ścieki wprowadzane do sieci [31, 46]. Warunki te obejmują dopuszczalne stężenia trzynastu substancji uznanych za szczególnie szkodliwe dla środowiska wodnego oraz 49 innych związków (m.in. rtęć, kadm, związki organiczne oznaczane jako AOX, BTX, VOX, WWA czy surfaktanty). Analizy chemiczne wykonywane są także w odniesieniu do wód opadowych. Badania jakościowe wód opadowych pozwalają na ocenę przydatności tych wód do celów przemysłowych oraz gospodarczych. Badania te są wykonywane najczęściej w zakładach przemysłowych w celu oceny możliwości wykorzystania ich do celów chłodniczych lub innych przemysłowych. Obowiązek wykonywania analiz chemicznych ścieków wynika także z konieczności zachowania warunków odprowadzania ścieków do środowiska, określonych w pozwoleniach wodnoprawnych, które wymagane są przy szczególnym korzystaniu ze środowiska i wprowadzaniu do kanalizacji substancji pochodzenia przemysłowego [37, 47].

Analizy chemiczne są niezbędne także w przypadku osadów ściekowych przeznaczonych do przyrodniczego wykorzystania (rolniczego i poza rolniczego). W tym przypadku wymagania prawne dotyczą siedmiu metali ciężkich oraz organizmów patogennych [35]. W przypadku jednak wykorzystania rolniczego osadów do nawożenia przepisy polskie są niewystarczające wobec faktu, że w osadach ściekowych zidentyfikowano mikrozanieczyszczenia organiczne. Są to grupy związków halogenoorganicznych, do których należą: polichlorowane dibenzodioksyny/dibenzofurany (PCDD/, PCDF), polichlorowane bifenyle (PCB), wielopierścieniowe węglowodory aromatyczne (WWA), adsorbowalne na węglu aktywnym halogenki organiczne (AOX) oraz etyloheksyloftalany (DEHP), nonylofenole i ich etoksylaty (NPE) czy też środki powierzchniowo czynne (liniowe alkilowe benzosulfoniany-LAS). Identyfikacja tych związków w osadach jest ważna, gdyż wymienia się je w propozycji zmian Dyrektywy osadowej Unii Europejskiej z podaniem dopuszczalnych stężeń w osadach ściekowych przeznaczonych do rolniczego wykorzystania [14].

Na obecnym etapie rozwoju technik analitycznych, w chemii sanitarnej wykorzystywane są nie tylko metody badawcze, które są znane od dawna lecz także inne, oparte na nowoczesnych technikach analitycznych (instrumentalnych). Metody znane od wielu lat są ciągle udoskonalane, a nowe wykorzystują najnowsze osiągnięcia nauki. Powszechnie stosowane są metody badawcze zaliczane do optycznych, elektroanalitycznych, chromatograficznych oraz spektroskopowe, spektrometryczne i termometryczne. Do metod optycznych zalicza się spektrofotometrię absorpcyjną w zakresie nadfioletu i światła widzialnego, spektrofotometrię w podczerwieni, spektroskopię ramanowską, metody fluorescencyjne, spektralną analizę emisyjną oraz absorpcyjną spektrometrię atomową. Wśród metod elektroanalitycznych wymienia się potencjometrię i kulometrię (wraz z miareczkowaniem), polarografię, konduktometrię oraz amperometrię i woltamperometrię. Natomiast metody chromatograficzne to: chromatografia gazowa, wysokociśnieniowa cieczowa i cienkowarstwowa. Ponadto w analizach chemicznych wykorzystywane są także takie metody, jak spektroskopia rezonansu jądrowego i elektronowa, spektrometria mas czy promieniowania rentgenowskiego. W wielu procedurach badawczych wykorzystywane są techniki sprzężone, pozwalające na uzyskanie wiarygodnych wyników w przypadku złożonych matryc środowiskowych. Przykładem jest połączenie chromatografii gazowej ze spektrometrem mas GC-MS oraz kwadrupolowym GC-MS/MS, chromatografu cieczowego z detektorem fluorescencyjnym HPLC-Flu i inne [17, 23, 26, 43].

Wybór metodyki oznaczania powinien głównie uwzględniać kryteria zapewniające dokładność wyników, istniejące możliwości aparaturowe oraz ekonomiczne. W przypadku analiz wód oraz ścieków metodyki referencyjne są określone w odpowiednich przepisach prawnych oraz w zbiorze Polskich Norm [38]. Nie zawsze jednak procedury obowiązujące i określone w tych dokumentach są wystarczające do oznaczania szerokiej gamy związków chemicznych, występujących w wodach lub ściekach.

Przegląd przepisów prawnych dotyczących warunków jakie powinna spełniać: woda kierowana do uzdatniania z przeznaczeniem do spożycia, woda wprowadzana do sieci wodociągowej, woda do celów przemysłowych oraz ścieki bytowe, przemysłowe odprowadzane do odbiorników, pozwala uzasadnić stwierdzenie, że zakres wymaganych analiz chemicznych jest szeroki. Obejmuje bowiem związki nieorganiczne i organiczne oraz grupy związków określane wskaźnikami ogólnymi, a tendencja zmian w przepisach prawnych polega m.in. na poszerzaniu list analizowanych substancji. Należy jednak zaznaczyć, że w praktyce inżynierskiej nie wszystkie związki i substancje analizowane są z jednakową częstotliwością. Wynika to z zakresu obowiązujących analiz w odniesieniu do różnych mediów, a także z dostępności aparatury badawczej.

Możliwości analityczne w chemii sanitarnej zapewniają oznaczanie ilościowe różnych związków, także występujących w ilościach śladowych. A doskonalenie procedur i nowoczesne instrumentarium umożliwia oznaczanie coraz szerszej grupy związków z większą dokładnością i precyzją. Wiarygodność wyników analiz chemicznych ma także wymiar ekonomiczny, gdyż jest istotna z punktu widzenia obciążenia przedsiębiorstw karami za przekroczenie warunków wprowadzania ścieków do wód lub do ziemi [29, 30].

2. Powiązania chemii sanitarnej z innymi dyscyplinami naukowymi

W wykazie obszarów wiedzy, dziedzin nauki i dyscyplin, jaki znajduje się w Rozporządzeniu Ministra Nauki i Szkolnictwa Wyższego, chemia sanitarna nie jest wymieniana jako oddzielna dyscyplina. W obszarze nauk ścisłych wyszczególnia się dziedzinę nauk chemicznych i dyscyplinę pod ogólną nazwą „chemia". Ze względu na tematykę, opisaną w pkt. 2.1 dotyczącą analiz wód i ścieków, chemia sanitarna jest ściśle związana z ochroną środowiska pozostającą w tej samej dziedzinie i obszarze wiedzy. Dyscyplina pod nazwa „ochrona środowiska" znajduje się także w dziedzinie nauk biologicznych w obszarze nauk przyrodniczych. Natomiast dyscyplina „ochrona i kształtowanie środowiska" znajduje się w dziedzinie nauk rolniczych w obszarze nauk rolniczych, leśnych i weterynaryjnych. Ze względu na aplikacyjny charakter chemii sanitarnej można stwierdzić, że jest ona także ściśle związana z dyscypliną pod nazwą „inżynieria środowiska", którą umieszczono w wykazie w dziedzinie i obszarze wiedzy wśród nauk technicznych [32].

Metodyka badań analitycznych stosowana jest w laboratoriach Inspektoratów Ochrony Środowiska w placówkach badawczych i naukowych oraz uczelniach wyższych i zakładach przemysłowych. Część z tych laboratoriów, po spełnieniu odpowiednich wymagań akredytacyjnych, posiada certyfikaty na wykonywanie konkretnych oznaczeń w wodzie i w ściekach (laboratoria akredytowane). W przypadku badań analitycznych, jakie są wykonywane dla wody i ścieków, niezwykle ważna jest obróbka statystyczna wyników oraz walidacja procedur analitycznych. Obróbka statystyczna wyników wymaga znajomości testów statystycznych, warunków ich stosowania oraz umiejętności ich interpretacji i weryfikacji. Walidacja procedur analitycznych jest niezbędna nie tylko w przypadku opracowywania nowej metody lecz jest dokonywana także przy rozszerzeniu zakresu stosowania opracowanej wcześniej metody, wykorzystywaniu innej aparatury lub w przypadku, gdy stosowana metoda nie zapewnia otrzymania wiarygodnych wyników [20]. Laboratoria w Inspektoratach Ochrony Środowiska są stosunkowo dobrze wyposażone w aparaturę analityczną, często posiadają odpowiednie certyfikaty, co gwarantuje otrzymywanie wiarygodnych wyników. W laboratoriach tych wykonywane są analizy kontrolne dla zakładów przemysłowych emitujących ścieki oraz badania monitoringowe. Laboratoria zakładowe natomiast wykonują oznaczenia ściśle związane z profilem produkcji, najczęściej zawężając zakres analiz do wskaźników wyznaczonych w pozwoleniach wodnoprawnych. Zatem wykorzystanie niektórych metodyk badawczych chemii sanitarnej dotyczy także zakładów przemysłowych .

W praktyce inżynierskiej instrumenty i wyniki analiz prowadzone w ramach chemii sanitarnej wykorzystywane są przy projektowaniu sieci wodociągowych oraz kanalizacyjnych. Dotyczy to zwłaszcza instalacji transportujących ścieki przemysłowe lub inne, zawierających szczególnie toksyczne czy też agresywne zanieczyszczenia. Tym samym istotny jest dobór rodzaju materiałów z których wykonywane są sieci i instalacje.

Wyniki analiz jakościowych wody i ścieków wykorzystywane są odpowiednio w projektowaniu procesów jednostkowych uzdatniania wody oraz oczyszczania ścieków. Potwierdza to ścisły związek chemii sanitarnej z inżynierią środowiska. Analizy chemiczne są wykonywane nie tylko na etapie projektowania lecz także podczas eksploatacji stacji uzdatniania wody i oczyszczalni ścieków. Badania chemiczne pozwalają określić efektywność poszczególnych procesów jednostkowych w usuwaniu zanieczyszczeń wody oraz ścieków [8, 54]. Wyniki analiz chemicznych umożliwiają także bieżące sterowanie procesami technologicznymi w celu uzyskania możliwie najlepszych efektów w usuwaniu zanieczyszczeń w istniejących układach technologicznych. Obróbka statystyczna wyników analiz chemicznych jakości wody ujmowanej lub/i oczyszczanej oraz ścieków wskazuje kierunki modernizacji i wymiany urządzeń lub zmiany technologii. Analizy chemiczne wykonywane są także w zakładach przeróbki osadów ściekowych, kompostowniach, biogazowniach i spalarniach odpadów. Dlatego w aspekcie przyrodniczego i przemysłowego wykorzystania ustabilizowanych biologicznie materiałów występują istotne powiązania chemii sanitarnej z rolnictwem i energetyką.

Jak wykazano, badania będące w obszarze chemii sanitarnej pozwalają na ocenę stanu środowiska, zatem można stwierdzić, że tematyka ta związana jest z ochroną zdrowia człowieka. W literaturze naukowej wykazano, że wiele zanieczyszczeń występujących w środowisku wodnym posiada działanie toksyczne na organizmy. Związki te lub substancje występują w niewielkich ilościach, zatem ich wykrycie jest analitycznie trudne ale niezwykle istotne. Z punktu widzenia zdrowia człowieka należy jeszcze wspomnieć, że mimo niskich stężeń związki te ulegają kumulacji w organizmie, przemianom metabolicznym, a w konsekwencji mogą inicjować zmiany o charakterze rakotwórczym, mutagennym i teratogennym. Przykładem są niektóre z połączeń organicznych zaliczanych do PCDD, PCDF, PCB, WWA, substancje aktywne stosowane jako składniki pestycydów czy insektycydów oraz inne halogenowe pochodne organiczne [6, 13, 15,19, 21, 50, 44].

Chemia sanitarna dostarczając informacji o stanie środowiska ma podstawowe znaczenie także w opracowaniu przepisów prawnych dotyczących zagadnień gospodarki wodno-ściekowej, a także przepisów związanych z ochroną zdrowia. Do tego celu badania kontrolne składników środowiska prowadzone są w warunkach laboratoryjnych i terenowych. Uważa się jednak, że z punktu widzenia ochrony zdrowia szczególnie ważne są badania prowadzone w warunkach terenowych [16, 28, 48].

3. Aktualny stan rozwoju chemii sanitarnej w Polsce

3.1. Syntetyczny przegląd problemowy osiągnięć naukowych w latach 1990–2012

Na podstawie informacji uzyskanych z uczelni krajowych można stwierdzić, że w latach 1990–2012 prowadzone badania skupiały się wokół następujących problemów i zagadnień:

- oznaczanie składników wód i ocena stanu jakości wód powierzchniowych i podziemnych oraz identyfikacja źródeł zanieczyszczeń,
- badania migracji zanieczyszczeń w środowisku wodnym i gruntowo-wodnym,
- badania przemian zanieczyszczeń organicznych i nieorganicznych w procesach technologicznych,
- uzdatnianie wody i oczyszczanie ścieków, a także przeróbka odpadów, w tym także osadów ściekowych.

Nawiązując do danych, które znajdują się w załączniku do niniejszej monografii, w Politechnice Białostockiej głównie oceniano jakość wód podziemnych i powierzchniowych z uwzględnieniem zbiorników retencyjnych. Ponadto w obszarze badań było usuwanie związków powierzchniowo czynnych z wody i ze ścieków. Szeroko zakrojone badania, m.in. w Politechnice Koszalińskiej, dotyczyły też transformacji zanieczyszczeń organicznych i nieorganicznych w środowisku, jak i podczas procesów technologicznych stosowanych do oczyszczania ścieków i przeróbki odpadów. Spośród składników nieorganicznych analizowano metale ciężkie w odciekach składowiskowych, osadach ściekowych i kompostach. Procesy technologiczne będące w obszarze badań to procesy fizyczne takie jak adsoprcja metali ciężkich z odcieków składowiskowych, podciśnieniowe odwadnianie i spalanie oraz biochemiczne takie jak fermentacja metanowa czy kompostowanie. Ponadto prowadzono badania biologicznego przetwarzania odpadów organicznych z uwzględnieniem odzysku energii. W odniesieniu do zanieczyszczeń organicznych określano migrację fenolu i chlorofenoli w strefie saturacji. Badania prowadzone w Politechnice Krakowskiej skupiały się wokół oznaczania substancji priorytetowych dla środowiska wodnego oraz procesu koagulacji stosowanego w uzdatnianiu wód. W Politechnice Poznańskiej badania z zakresu chemii sanitarnej dotyczyły głownie chemicznych i biologicznych podstaw inżynierii środowiska. Zakres badań prowadzony w Politechnice Śląskiej był także stosunkowo szeroki. W obszarze badań była ocena stanu jakości wód powierzchniowych z uwzględnieniem metali ciężkich oraz identyfikacja obszarowych źródeł zanieczyszczeń. Badania technologiczne polegały na separacji mikrozanieczyszczeń w procesach membranowych, w tym także na membranach enzymatycznych. Ponadto prowadzono badania usuwania prekursorów ubocznych produktów dezynfekcji z wody. W Politechnice Świętokrzyskiej natomiast prowadzono badania migracji substancji ropopochodnych oraz metali ciężkich w wodzie i w osadach ściekowych. W Uniwersytecie Zielonogórskim badaniami objęto zbiorniki acidotroficzne z określeniem ich pochodzenia i rozwoju. Chemizm wód podziemnych oraz wpływ procesów geogenicznych i czynników antropogennych na ich jakość badano w Uniwersytecie Rolniczym w Krakowie. W obszarze badań były także wody powierzchniowe, gdzie określano zależność jakości od warunków hydrogeologicznych i budowy geologicznej oraz warunki retencji zbiornikowej. W Uniwersytecie Techniczno-Przyrodniczym w Bydgoszczy głównym tematem badań były analizy spektrometryczne wody do spożycia, wód powierzchniowych, podziemnych i chłodzących. W Zachodniopomorskim Uniwersytecie Technologicznym natomiast tematyka badań związana była z oczyszczaniem ścieków przemysłowych oraz przeróbką osadów ściekowych wydzielonych ze ścieków przemysłowych.

3.2. Wpływ chemii sanitarnej na rozwój i postęp naukowo-techniczny w wodociągach i kanalizacji

Stan rozwoju chemii sanitarnej determinuje rozwój innych obszarów wiedzy, o których pisano wyżej. Doskonalenie technik analitycznych pozwala na poszerzanie i uszczegółowienie informacji dotyczących jakości wód i ścieków. Jak wiadomo sieci wodociągowe i kanalizacyjne znajdują się na drodze obiegu wody od miejsca poboru (wody powierzchniowe, wody podziemne), poprzez instalacje oczyszczania i jej wykorzystanie, a następnie oczyszczanie i odprowadzanie ścieków do odbiornika. Obieg ten zamyka się, gdyż najczęściej odbiornikiem ścieków oczyszczonych są wody powierzchniowe.

4. Światowe tendencje rozwoju metod analitycznych

Chemia sanitarna wprawdzie nie jest oddzielną dyscypliną naukową w świetle prawa, aczkolwiek odgrywa bardzo ważną rolę interdyscyplinarną, gdyż pozwala na pozyskiwanie informacji niezbędnych dla rozwoju innych dyscyplin naukowych i innych obszarów wiedzy. Podstawowym kierunkiem rozwoju chemii sanitarnej są działania zmierzające do uzyskania wyczerpujących i wiarygodnych informacji analitycznych. Te działania prowadzone są w obszarach [20]:

- doskonalenia technik analitycznych,
- opracowania nowych metod oznaczania pierwiastków i związków chemicznych w próbkach środowiskowych, w tym także dotychczas nie analizowanych,
- szerszej identyfikacji związków nowo powstających „*emerging organic contaminants*”,
- opracowania procedur przygotowania i oznaczania analitów w próbkach środowiskowych, pozwalających na oznaczanie substancji, w tym także takich, które występują w ilościach śladowych (<0,01%), mikrośladowych ($<10^{-4}$ %), ultraśladowych ($<10^{-6}$ %) oraz submikrośladowych ($<10^{-8}$ %),

- minimalizacji strat analitów, aparatury oraz czasochłonności analiz,
- obróbki statystycznej wyników analiz

Doskonalenie technik analitycznych polega na automatyzacji i łączeniu różnych metod pozwalających na równoczesne oznaczanie kilku analitów. Wśród nich wymienia się połączenia technik chromatograficznych z ekstrakcją płynem w stanie nadkrytycznym, ekstrakcję z desorpcją termiczną czy ekstrakcję membranową, w tym także z wykorzystaniem membran ciekłych [10, 26, 49]. Wykorzystanie zautomatyzowanych urządzeń pomiarowo-kontrolnych jest szczególnie ważne w badaniach *in situ*, gdyż pozwala na uzyskanie informacji o stanie środowiska, migracjach zanieczyszczeń oraz umożliwia bieżącą kontrolę zmian jakościowych. Nowe metody natomiast polegają na wykorzystywaniu bieżących osiągnięć fizyki, biochemii i inżynierii genetycznej, a także ekotoksykologii i biooanalityki.

Pozwala to na oznaczanie coraz większej ilości składników nawet w bardzo małych stężeniach oraz identyfikację nowych. Należy zaznaczyć, że w środowisku wodnym w sposób ciągły zachodzą przemiany biotyczne oraz abiotyczne. W wyniku przemian biochemicznych powstają metabolity oraz inne związki, których identyfikacja nierzadko jest powierzchowna. Ponadto w środowisku wodnym oraz w ściekach coraz częściej identyfikuje się pozostałości substancji chemicznych, które określane są „*emerging contaminats*”. Do tej grupy zanieczyszczeń zalicza się pozostałości farmaceutyków, środków kosmetycznych (*personal care products*), surfaktantów, konserwantów i związków zabezpieczających przed zapłonem (*flame retardants*) oraz innych chloro- i bromoorganicznych. Ponadto szeroką i dotychczas słabo przebadaną grupę związków stanowią związki chemiczne zaburzające działanie układu endokrynologicznego EDC *(Endorcine Disrupting Compounds*). Do tej grupy zalicza się dioksyny PCDD, furany PCDF, polichlorowane bifenyle PCB, DDT, ftalany DEHP i alkilofenole. Oprócz wymienionych oznacza się także hormony pochodzenia naturalnego i syntetyczne, które są m.in. składnikami farmaceutyków. Grupy te wzajemnie się przenikają, a działanie poszczególnych związków, jak i ich mieszanin, na organizmy w większości przypadków jest toksyczne. Głównym źródłem tych związków są ścieki oraz spływy powierzchniowe. Spośród ścieków szczególnie obciążone są ścieki przemysłowe z produkcji tworzyw sztucznych, kosmetyków, farmaceutyków, przeróbki paliw i innych, a też szpitalne i z gospodarstw hodowlanych. Równocześnie wysokie stężenia ww. zanieczyszczeń obserwuje się w ściekach bytowo-gospodarczych. Uwzględniając fakt, że ścieki wprowadzane do kanalizacji i oczyszczalni ścieków miejskich są mieszaniną o różnym składzie oraz, że w klasycznych procesach oczyszczania, zanieczyszczenia nie są usuwane w wystarczającym stopniu, można stwierdzić, że ścieki komunalne są głównym nośnikiem tych związków, obecnych w środowisku wodnym [1–4, 45].

W opracowywaniu nowych procedur oznaczania znanych związków chemicznych działania te prowadzone są dwutorowo: w kierunku oznaczania analitów występujących w ilościach submikrośladowych oraz w kierunku rozdzielania i izolowania poszczególnych analitów. Do związków występujących w małych stężeniach w wodach, których identyfikacja wymaga wyodrębniania poszczególnych związków zalicza się: WWA, dioksyny, furany, lub/i inne węglowodory, a też chlorowcopochodne organiczne. W tych przypadkach ważnym etapem analizy jest przygotowanie próbek przy zachowaniu warunków ograniczających straty analitów. Elementem potwierdzającym prawidłowość analizy jest wyznaczenie stopnia odzysku, stosowanie materiałów certyfikowanych lub wzorców znakowanych izotopowo [12, 24, 51–53]. Ważnym obecnie zagadnieniem jest obecnie identyfikacja poszczególnych związków organicznych, które zwykle oznaczane są poprzez wskaźniki ogólne, np. ChZT, OWO, BZT_5, AOX. Mimo tego, że w zbiorze procedur analitycznych znajduje się 3500 metodyk oznaczania 4000 analitów w środowisku wodnym (wody powierzchniowe, wody do spożycia, ścieki) to można stwierdzić, że lista ta nie wyczerpuje składników, które w tym środowisku występują.

W 1998r opracowano i opublikowano koncepcję rozwoju współczesnej chemii w nawiązaniu do zasad zrównoważonego rozwoju. Autorami tej koncepcji po nazwą „Zielona chemia” są naukowcy z Amerykańskiego Towarzystwa Chemików. Główne zasady tej koncepcji polegają na minimalizacji:

- zużycia odczynników, w tym także rezygnacji z odczynników toksycznych,
- ilości usuwanych odpadów powstających w czasie analiz chemicznych,
- zużycia energii, nakładu pracy i czasu trwania analiz.

Ograniczanie zużycia odczynników w analizach chemicznych polega na wykorzystaniu tzw. technik bezpośrednich czyli z pominięciem wstępnego przygotowania próbki. Szersze zastosowanie dotyczy tu metod elektrochemicznych (jonoselektywne elektrody), spektroskopii absorpcji atomowej z termicznym wzbudzeniem w płomieniu grafitowym (GFAAS) lub ze wzbudzeniem w indukowanej plaźmie (AES-ICP) oraz techniki analizy powierzchni takie, jak SEM, SIMS, ISS, XPS/ESCA, a także fluorescencja promieniowania rentgenowskiego. W kierunku minimalizacji ilości lub całkowitej eliminacji odczynników rozwijają się techniki bezrozpuszczalnikowe. Przykładem tych rozwiązań jest np. ekstrakcja płynem w stanie nadkrytycznym SFE, ekstrakcja membranowa czy ekstrakcja SPE z desorpcją termiczną. Duże znaczenie w kontekście ochrony środowiska ma minimalizacja ilości produktów odpadowych. Można to osiągnąć poprzez zmniejszenie ilości odczynników lub/i poprzez zmniejszenie wielkości próbek przeznaczanych do analizy. Wiąże się to z zastosowaniem detektorów o większej wykrywalności. Ponadto duże znaczenie ma analiza *in situ* oraz tzw. suche techniki. Rozwój tych technik polega na zastosowaniu mikrosystemów całkowitej analizy chemicznej (μ-TCAS, μ-TAS), wykorzystaniu technologii chipów i mikrochipów, immunoanaliza (immunoassays IMA, radioimmunoanaliza RIA, immunoanaliza enzymatyczna EIA). Z kolei minimalizację zużycia energii i czasu analizy zapewnia automatyzacja i techniki sprzężone, polegające na łączeniu etapu wstępnego z aparatem pomiarowym. Przykładem mogą być ekstraktory kompatybilne z układami chromatograficznymi i odpowiednimi detektorami [25].

Ważnym zagadnieniem współczesnej analityki chemicznej jest zastosowanie specjacji w analizach środowiska oraz w badaniach monitoringowych. Dotychczas badania te skupiały się głównie na specjacji metali ciężkich, natomiast obecnie analizą obejmuje się także inne pierwiastki i związki chemiczne. Wykazano bowiem, że ogólna zawartość różnych związków nie daje wyczerpujących informacji o stanie zanieczyszczenia środowiska, gdyż niezwykle istotna jest forma w jakiej występują te składniki. Wyodrębnienie form biodostępnych, związanych z materią organiczną trwale i form mobilnych, a także związków występujących w formie zaadsorbowanej, rozpuszczonej czy gazowej, pozwala na dokładniejsza ocenę i kontrolę stanu środowiska wodnego. Wśród kierunków rozwoju chemii sanitarnej należy wspomnieć także o wprowadzeniu metod biologicznych do analiz środowiskowych. W bioanalityce wykorzystuje się materiał biologiczny do analiz chemicznych. Zastosowanie mają tutaj immunosorbenty, biokatalizatory oraz biokolumny. Ponadto wprowadzane są biotesty i bioczujniki (enzymatyczne, bakteryjne, tkankowe). Przykładem może być zastosowanie małży, jako bioindykatora, w stacjach uzdatniania wody, co pozwala na wczesną informację dotyczącą zmiany składu jakościowego wody. Korzystając z różnorodnych metod obróbki statystycznej wyników analiz chemicznych, można prognozować zmiany jakości wody ujmowanej ze źródeł naturalnych, monitorować kinetykę przemian biochemicznych poszczególnych wskaźników zanieczyszczeń w trakcie procesu oczyszczania wód i ścieków oraz modyfikować istniejące układy technologiczne.

5. Perspektywa rozwoju naukowego chemii sanitarnej w Polsce

W zakresie rozwoju wymienionych wyżej dyscyplin naukowych, poziom rozwoju chemii sanitarnej ma kluczowe znaczenie. Dla rozwoju badań naukowych konieczne jest stałe podnoszenie jakości pracy i precyzji badań w laboratoriach analitycznych, w tym także działań zmierzających do uzyskiwania akredytacji i certyfikacji. Na podstawie dostępnych informacji poniżej wymieniono priorytetowe zagadnienia w tym zakresie [1, 5, 12, 13, 43]:

- dalsze doskonalenie procedur badawczych z uwzględnieniem walidacji (precyzja, dokładność, granica wykrywalności, granica oznaczalności, niepewność pomiarów),
- projektowanie i budowa nowych urządzeń pomiarowo-kontrolnych,
- automatyzacja aparatury badawczej oraz układów sprzężonych,
- oznaczanie składników na poziomie śladowym, oznaczanie mikrozanieczyszczeń, produktów przemian metabolicznych, produktów pośrednich powstających w procesach uzdatniania wody oraz podczas oczyszczania ścieków,
- oznaczanie składników nowopowstających „*emerging contaminants*”,
- minimalizacja zużycia reagentów chemicznych i technik bezrozpuszczalnikowych,
- minimalizacja kosztów i energii oraz usuwanych materiałów odpadowych,

- rozszerzenie zakresu analiz specjacyjnych i zastosowanie ich w analizach środowiska wodnego oraz monitoringu,
- rozwój metod biologicznych w analityce: bioanalityka, bioczujniki i biotesty,
- analizy ciągłe w monitoringu środowiska,
- podniesienie jakości wyników analiz chemicznych,
- obróbka statystyczna wyników analiz chemicznych pozwalająca na prognozowanie zmian jakości środowiska wodnego,
- wprowadzenie obowiązku kontroli składników toksycznych w wodach i ściekach oraz osadach ściekowych.

Najważniejsze zadanie jakie stawia się przed chemią sanitarną to uzyskanie wiarygodnych informacji odnośnie stanu jakościowego wód i ścieków oraz określenie tendencji zmian zachodzących w środowisku. Informacje te są wykorzystywane w planowaniu przedsięwzięć w zakresie gospodarki wodno-ściekowej w regionach. Przedsięwzięcia te, to nie tylko infrastruktura wodociągowo-kanalizacyjna lecz także lokalizacja przedsiębiorstw przemysłowych i ocena ich oddziaływania na środowisko. Właściwe i oparte na wiarygodnych analizach projektowanie przedsięwzięć z zakresu gospodarki wodno-ściekowej pozwala na zachowanie zasad zrównoważonego rozwoju. W zakresie analiz środowiskowych ważne jest rozszerzenie metodyk oznaczanych składników, wprowadzenie nowych przepisów prawnych i obowiązku kontroli tych składników w środowisku. Konieczność rozszerzenia zakresu badań monitoringowych wynika także ze zobowiązań międzynarodowych w zakresie sieci europejskich. Zatem doskonalenie technik analitycznych i ich wdrażanie do systemu kontroli środowiska jest obecnie niezbędne i ważne w rozwoju gospodarczym kraju.

6. Podsumowanie

Chemia sanitarna jest elementem chemii środowiska opartym na podstawach chemii ogólnej, organicznej i instrumentalnej. Mimo, że nie stanowi oddzielnej dyscypliny nauki, jest nieoceniona w dostarczaniu informacji do rozwoju innych dziedzin i obszarów wiedzy, takich jak inżynieria, ochrona i kształtowanie środowiska, będących w obszarach nauk technicznych, przyrodniczych i rolniczych. Badania realizowane w ramach chemii sanitarnej prowadzone są w dwóch kierunkach. Pierwszym jest ocena jakościowa wód powierzchniowych i podziemnych, będących źródłem zaopatrzenia w wodę ludności, przemysłu i rolnictwa, monitorowanie środowiska wody oraz procesów jej uzdatniania. Drugi kierunek to charakterystyka ścieków wprowadzanych do kanalizacji, oczyszczalni ścieków oraz ścieków oczyszczonych wprowadzanych do odbiorników. Rozwój chemii sanitarnej polega na rozwoju technik analitycznych i procedur pozwalających na identyfikację nowych związków oraz oznaczanie jakościowo-ilościowe coraz większej ilości zanieczyszczeń występujących w środowisku wodnym, w tym mikrozanieczyszczeń występujących w ilościach submikrośladowych. Dotyczy to głównie mikrozanieczyszczeń organicznych, które wykazują działanie rakotwórcze, mutagenne i teratogenne na organizmy. Umożliwia to odpowiednie projektowanie procesów jednostkowych w oczyszczaniu wody i ścieków. Dlatego rozwój chemii sanitarnej w kierunku zapewnienia wiarygodnych wyników jest jednym z czynników rozwoju inżynierii środowiska. Ponadto jest wskazaniem i podstawą do opracowania nowych przepisów prawnych uwzględniających coraz to nowe identyfikowane związki chemiczne. Tendencje rozwoju chemii sanitarnej na świecie wskazują na ciągłe doskonalenie technik analitycznych oraz urządzeń pomiarowo-kontrolnych, opracowanie nowych procedur analitycznych oraz rozwijanie już istniejących.

Literatura

1. **Barcelo D.:** *Emerging pollutants in water analysis – Editorial.* Trends in Analytical Chemistry. 22(10) (2003).
2. **Bhandari A., Surampalli R.Y., Adams C.D., Champagne P., Ong S.K., Tyagi R.D., Zhang T.C.:** *Contaminants of Emerging Environmental Concern*, American Society of Civil Engineering, Reston, Virginia 2009.
3. **Bodzek M., Konieczny K.:** *Wykorzystanie technik membranowych w uzdatnianiu wody do picia, Cz. II. Usuwanie związków organicznych*, Technologia Wody. 2, 15–31 (2010).
4. **Bolong N., Ismail A.F., Salim M.R., Matsuura T.:** *A review of the effects of emerging contaminants in wastewater and options for their removal,* Desalination. 239(1–3), 229–246 (2009).
5. **Buszewski B., Kosobudzki P.:** *Fizykochemiczne metody analizy w chemii środowiska*, Wydawnictwo Uniwersytetu M. Kopernika, Toruń 2008.

6. **Czarnomski K., Izak E.:** *Trwałe zanieczyszczenia organiczne w środowisku, Rozporządzenie Wspólnoty Europejskiej Nr 850/2004.* Materiały informacyjne, Ministerstwo Środowiska, Wydawca Instytut Ochrony Środowiska, Warszawa 2008.
7. **Dojlido J., Dożańska W., Hermanowicz W., Koziorowski B., Zerbe J.:** *Fizyczno-chemiczne badanie wody ścieków.* Wydawnictwo Arkady, Warszawa 2010.
8. **Dymaczewski Z. (red):** *Poradnik eksploatatora oczyszczalni ścieków.* Wyd. PZiTS O/Poznań, Poznań 2011.
9. Dyrektywa Parlamentu Europejskiego i Rady 2013/39/UE z dnia 12 sierpnia 2013 r. zmieniająca dyrektywy 2000/60/WE i 2008/105/WE w zakresie substancji priorytetowych w dziedzinie polityki wodnej (Dz. Urz. UE, 24.8.2013, L226/1)
10. **Dżygiel P., Wieczorek P.P.:** *Supported liquid membranes and their modifications: definition, classification, theory, stability, application and perspectives.* Chapter 3, 73–140 (in) Liquid Membranes. Principles and Applications in Chemical Separations and Wastewater Teatment, Eds. V. Kislik, Elsevier 2010.
11. **Evangelou V.P.:** *Environmental soil and water chemistry, Principles and Applications.* J.Willey & Sons, Inc, New York 1998.
12. **Gdaniec-Pietryka M., Wolska L., Namieśnik J.:** *Physical speciation of polychlorinated biphenyls in the aquatic environment.* Trends in Analytical Chemistry. 22(10), 1005–1012 (2007).
13. **Grochowalski A.:** *Badania nad oznaczaniem polichlorowanych dibenzodioksyn, dibenzofuranów i bifenyli.* Wydawnictwo Politechniki Krakowskiej, Monografia 272, Kraków 2000.
14. **Gromiec M.J.:** *Kierunki planowanych zmian dyrektywy osadowej w Unii Europejskiej.* Inżynieria i Ochrona Środowiska. 4(2), 149–160 (2001).
15. **Grung M., Holth T.F., Jacobsen M.R.:** *Polycyclic Aromatic Hydrocarbon (PAH) metabolites in Atlantic cod exposed via water or diet to a synthetic produced water.* Journal of Toxicology and Environmental Health, A, 72(3–4), 254–265 (2009).
16. **Hermanowicz W.:** *Chemia sanitarna.* Wydawnictwo Arkady, Warszawa 1984.
17. **Hulanicki A.:** *Współczesna chemia analityczna.* Wydawnictwo Naukowe PWN, Warszawa 2001.
18. **Kiedryńska L., Papciak D., Granops M.:** *Chemia sanitarna.* Wydawnictwo Szkoły Głównej Gospodarstwa Wiejskiego, Warszawa 2006.

19. **Kobayashi S., Kitadai M., Sameshima K., Ishii Y., Tanaka A.:** *A theoretical investigation of the conformation changing of dioxins in the binding site of dioxin receptor model; role of absolute hardness-electronegativity activity diagrams for biological activity.* Journal of Molecular Structure. 475(2–3), 203–217 (1999).
20. **Konieczka P., Namieśnik J., red.:** *Ocena i kontrola jakości wyników pomiarów analitycznych.* Wydawnictwo Naukowo-Techniczne WNT Warszawa 2007.
21. **Kookana R.S., Correll R.L., Miller R.B.:** *Pesticide impact Rating Index – A pesticide risk indicator for water quality.* Water, Air and Soil Pollution. 5(1–2), 45–65 (2005).
22. **Kowal A.L., Świderska-Bróż M.:** *Oczyszczanie wody.* Wydawnictwo Naukowe PWN, Warszawa 2009.
23. **Kupryszewski G.:** *Wstęp do chemii organicznej.* Wydawnictwo Naukowe PWN, Warszawa 1998.
24. **Mechlińska A., Wolska L., Namieśnik J.:** *Isotope-labeled substances in analysis of persistent organic pollutants in environmental samples.* Trends in Analytical Chemistry. 29(8), 820–831 (2010).
25. **Namieśnik J.:** *Trendy w analityce i monitoringu środowiska*, dostępne na stronie www.pg.gda.pl
26. **Namieśnik J., Jamrógiewicz Z., Pilarczyk M., Torres L.:** *Przygotowanie próbek środowiskowych do analizy.* Wydawnictwo Naukowo-Techniczne, Warszawa 2000.
27. **Nawrocki J. red.:** *Uzdatnianie wody. Procesy fizyczne, chemiczne i biologiczne.* PWN, Warszawa 2010.
28. Obwieszczenie Ministra Środowiska w sprawie ogłoszenia aktualizacji Krajowego Programu Oczyszczania Ścieków Komunalnych (MP Nr 62 poz. 589, 2011).
29. Obwieszczenie Ministra Środowiska w sprawie wysokości stawek kar za przekroczenie warunków wprowadzania ścieków do wód lub do ziemi oraz za przekroczenie dopuszczalnego poziomu hałasu, na rok 2012 (MP Nr 94, poz. 957, 2011)
30. Obwieszczenie Ministra Środowiska w sprawie wysokości stawek kar za przekroczenie warunków wprowadzania ścieków do wód lub do ziemi oraz za przekroczenie dopuszczalnego poziomu hałasu na r. 2014 (MP poz. 821, 2013).
31. Rozporządzenie Ministra Budownictwa w sprawie sposobu realizacji obowiązku dostawców ścieków przemysłowych oraz warunków wprowadzania ścieków do urządzeń kanalizacyjnych (DZ.U. Nr 136 poz. 964, 2006).
32. Rozporządzenie Ministra Nauki i Szkolnictwa Wyższego w sprawie obszarów wiedzy, dziedzin nauki i sztuki oraz dyscyplin naukowych i artystycznych (Dz. U Nr 179, poz. 1065, 2011).

33. Rozporządzenie Ministra Środowiska w sprawie form i sposobu prowadzenia monitoringu jednolitych części wód powierzchniowych i podziemnych (Dz. U Nr 258, poz. 1550, 2011).
34. Rozporządzenie Ministra Środowiska w sprawie klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych (Dz. U Nr 162, poz. 1008, 2008, Dz. U. Nr 257, poz. 1545, 2011).
35. Rozporządzenie Ministra Środowiska w sprawie komunalnych osadów ściekowych (Dz. U. Nr 137, poz. 924, 2010).
36. Rozporządzenie Ministra Środowiska w sprawie kryteriów i sposobu oceny stanu wód podziemnych (Dz. U. Nr 143, poz. 896, 2008).
37. Rozporządzenie Ministra Środowiska w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, których wprowadzenie w ściekach przemysłowych do urządzeń kanalizacyjnych wymaga uzyskania pozwolenia wodno prawnego (Dz. U. Nr 233 poz. 1988, 2005; Dz. U Nr 229 poz. 1538, 2009).
38. Rozporządzenie Ministra Środowiska w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego (Dz.U. Nr 137, poz. 984, 2006 oraz Dz.U. Nr 27, poz. 169, 2009).
39. Rozporządzenie Ministra Środowiska w sprawie wykazu substancji priorytetowych w dziedzinie polityki wodnej (Dz.U. 254, poz. 1528, 2011)
40. Rozporządzenie Ministra Środowiska w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wody przeznaczone do spożycia (Dz.U. Nr 204, poz. 1728, 2002).
41. Rozporządzenie Ministra Zdrowia w sprawie jakości wody przeznaczonej do spożycia przez ludzi (Dz.U. Nr 61, poz. 417, 2007; Dz.U. Nr 72, poz. 466, 2010).
42. **Schecter A., Birnbaum L., Ryan J.J., Constable J.D.:** *Dioxins: An overview.* Environmental Research. 101(3), 419–428 (2006).
43. **Szczepaniak W.:** *Metody instrumentalne w analizie chemicznej.* Wydawnictwo Naukowe PWN, Warszawa 2005.
44. **Szymański K., Siebielska I.:** *Analityczne aspekty oceny jakości zanieczyszczonych wód podziemnych.* Ochrona Środowiska. 76(1), 15–18 (2000).
45. **Tadeo J.L., Sanchez-Brunete C., Albero B., Garcia-Valcarcel A.I., Perez R.A.:** *Analysis of emerging organic contaminants in environmental solid samples.* Central European Journal of Chemistry. 10(3), 480–520 (2012).
46. Ustawa o zbiorowym zaopatrzeniu w wodę i zbiorowym odprowadzaniu ścieków (Dz. U. Nr 72 poz. 747, 2001).
47. Ustawa. Prawo wodne (Dz. U. Nr 115 poz. 1229, 2001).

48. **VanLoon G.W., Duffy S.J.:** *Chemia środowiska.* Wydawnictwo Naukowe PWN, Warszawa 2007.
49. **Wieczorek P.P.:** *Membrany ciekłe jako efektywna metoda wydzielania, rozdziału i oczyszczania mieszanin.* Przemysł Chemiczny. 86(10), 996–1000 (2007).
50. **Włodarczyk-Makuła M.:** *Wybrane mikrozanieczyszczenia w środowisku wodnym i glebowym.* Monografie Komitetu Inżynierii Środowiska PAN, Vol. 104 (2013).
51. **Wolska L.:** *Miniaturised analytical procedure of determining polycyclic aromatic hydrocarbons and polychlorinated biphenyls in bottom sediments.* Journal of Chromatography A., 959(1–2), 173–180 (2002).
52. **Wolska L., Gdaniec-Pietryka M., Konieczka P., Namieśnik J.:** *Problems of PAH quantification by GC-MS method using isotope-labelled standards.* Talanta. 78(3), 730–735 (2009).
53. **Wolska L., Rawa-Adkonis M., Namieśnik J.:** *Determining PAHs and PCBs in aqueous samples: finding and evaluating sources of error.* Analytical and Bioanalytical Chemistry. 382, 1389–1397 (2005).
54. **Wowk J.:** *Naturalna technologia wody.* Wydawnictwo Naukowo-Techniczne WNT, Warszawa 2012.
55. www.gios.gov.pl

Interdisciplinary Character of Sanitary Chemistry

Abstract

Sanitary chemistry is a component of environmental chemistry, based on the issues of general, organic and instrumental chemistry. The level of chemistry development is important for the development of other scientific disciplines such as: environmental engineering or planning, design and protection of the environment. These disciplines are mentioned in the areas of technical, natural and agricultural sciences. As part of the sanitary chemistry research in two directions: the study of water and wastewater quality are conducted. The studies include an assessment of water quality of surface- and groundwater, which are the source of water supply for: population, industry and agriculture, water treatment processes and water monitoring. The wastewater research are concerning the wastewater introduced into the sewage system, wastewater treatment plants and to the receivers. The development of sanitary chemistry involves the development of analytical techniques and procedures in order to determine a greater number of pollutants in water and wastewater and enhancing the accuracy of compounds which has been already designated. Therefore, in framework of sanitary chemistry development following actions are performed:

- improvement of research procedures including the validation,
- design and construction of new measuring and control devices,
- automation of test equipment, including the coupled systems,
- determination of trace-level components: micro-pollutants, metabolic products, intermediate products, water and wastewater treatment,
- determination of "emerging contaminants",
- development of solvent-free techniques,
- minimization of cost, energy and the waste materials emission,
- the extension the scope of speciation analysis and their applications,
- development of biological methods in chemical analysis,
- introduction the continuous analysis into monitoring,
- improvement of the quality of chemical analysis results, statistical processing of chemical analysis, which allows on forecasting changes in water quality.

Trends in the sanitary chemistry development in the world indicate a continuous improvement of analytical techniques and measurement and control appliances, the elaboration of new analytical procedures and develop existing ones.

Słowa kluczowe:
chemia sanitarna, techniki analityczne, układy sprzężone, walidacja procedur badawczych, monitoring środowiska, mikrozanieczyszczenia, emerging contaminants, woda, ścieki, osady ściekowe, odpady

Keywords:
sanitary chemistry, analytical techniques, coupled systems, validation of research procedure, environmental monitoring, micropollutants, emerging contaminants, water, wastewater, sewage sludge, waste

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Pokrywa śnieżna jako ośrodek depozycji zanieczyszczeń

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1. Wstęp

Skład chemiczny wody pochodzącej z roztopionego śniegu jest cennym źródłem informacji o zanieczyszczeniu atmosfery oraz o ilości i jakości zanieczyszczeń wprowadzanych do wód i gleby w wyniku topnienia śniegu. W czasie długiego zalegania pokrywy śnieżnej może nastąpić kumulacja zanieczyszczeń wnoszonych przez kolejne opady atmosferyczne. Do głównych wskaźników zanieczyszczenia ścieków opadowych pochodzących z terenów zurbanizowanych należą: pH, zawiesiny ogólne, chemiczne zapotrzebowanie na tlen, chlorki, substancje ropopochodne, substancje ekstrahujące się eterem naftowym. Natomiast normatywnymi wskaźnikami zanieczyszczeń tych ścieków zgodnie z obowiązującymi przepisami są jedynie zawiesiny ogólne i węglowodory ropopochodne [22]. Bardzo ważnym wskaźnikiem są zawiesiny ogólne, ponieważ na ich powierzchni adsorbują się inne zanieczyszczenia będące poważnym źródłem zagrożeń środowiska wodnego i glebowego [17]. W zawiesinie kumuluje się większość zanieczyszczeń o czym świadczą wysokie wartości ich wskaźników: ChZT – 83–92%, BZT5 – 90–95%. Badania wskazują, że 97–99% ołowiu, 65–80%, azotu ogólnego i 82–99%, węglowodorów jest związana z zawiesiną [3].

Niebezpiecznym dla środowiska, a najmniej rozpoznanym wskaźnikiem są metale ciężkie ponieważ przedostanie się ich do wód czy gleb jest szczególnie groźne ze względu na ich trwałość oraz zdolność do kumulowania w organizmach żywych, nawet gdy są wprowadzane w niewielkich ilościach i okresowo. W literaturze krajowej i zagranicznej publikowane są wyniki badań składu fizyczno-chemicznego opadów oraz spływów wód opadowych i roztopowych [7,9,23,27]. Należy zwrócić uwagę na fakt, że tylko w nielicznych krajowych publikacjach można znaleźć zakresy zawartości metali ciężkich w ściekach roztopowych, a podawane wartości dotyczą przede wszystkim badań zagranicznych [11,24].

W niniejszej pracy przedstawiono wyniki badań zanieczyszczenia śniegu pobranego z poboczy dróg, parkingów na tle obszarów poza oddziaływaniem transportu. Porównano stopień zanieczyszczenia ścieków z roztopionego śniegu ze ściekami deszczowymi spływającymi z analogicznych powierzchni. Należy podkreślić, że konieczność badań wpływu wód opadowych i roztopowych spływających z dróg na jakość wód powierzchniowych i podziemnych wynika między innymi z Rozporządzenia Rady Ministrów z 9.11.2004 r. w sprawie określenia rodzajów przedsięwzięć mogących znacząco oddziaływać na środowisko oraz szczegółowych uwarunkowań związanych z kwalifikowaniem przedsięwzięcia do sporządzenia raportu oddziaływania na środowisko (Dz.U. nr 257, poz. 2573).

2. Źródła zanieczyszczeń występujących w śniegu

Zanieczyszczenia zawarte w śniegu pochodzą zarówno ze źródeł antropogenicznych, jak również naturalnych. Rozwój przemysłu, komunikacji i rolnictwa przyczynia się do zanieczyszczenia wszystkich elementów środowiska, w tym także atmosfery. Opady atmosferyczne sorbują z atmosfery zawarte w niej cząstki stałe, ciekłe i gazowe, takie jak pyły, dymy, substancje chemiczne [3,20,13].

Opady ulegają zanieczyszczeniu już w czasie trwania opadu w wyniku kontaktu z mniej lub bardziej zanieczyszczonym powietrzem atmosferycznym. Szczególnie emisje szkodliwych substancji z różnych gałęzi przemysłu oraz transportu przyczyniają się do zanieczyszczenia atmosfery a tym samym pokrywy śniegowej. Badania wskazują, że największe ilości substancji zanieczyszczających atmosferę powstaje w wyniku spalania paliw kopalnych skutkiem czego jest emisja do powietrza olbrzymich ilości gazów spalinowych (CO, CO_2, SO_2, SO_3, NO_x i inne) oraz pyłów, popiołów, sadz. Źródłem tych zanieczyszczeń jest przede wszystkim przemysł, komunikacja, gospodarstwa domowe.

Wskutek spalania paliw w silnikach pojazdów do powietrza trafiają: tlenki azotu, tlenek węgla, węglowodory, w tym wielopierścieniowe węglowodory aromatyczne oraz cząstki stałe i metale ciężkie. Według danych Głównego Urzędu Statystycznego [14] w naszym kraju transport drogowy odpowiedzialny jest za ponad 33% całkowitej emisji tlenków azotu, przeszło 23% emisji tlenku węgla oraz powyżej 20% zanieczyszczeń pyłowych. Emisja substancji szkodliwych zawartych w spalinach jest poważnym zagrożeniem dla środowiska, trudnym często do jednoznacznej oceny pod względem ekologicznym i ekonomicznym [5]. W miastach, szczególnie o scentralizowanym systemie ciepłownictwa, udział transportu drogowego w całkowitej emisji tych zanieczyszczeń jest znacznie większy, dochodząc w dzielnicach centralnych nawet do 90%. Bezpośrednim źródłem zanieczyszczeń pochodzących z transportu drogowego są m.in.:

- gazy spalinowe zawierające Pb, Zn, Fe, Cu, Cd, Ni, tlenki węgla, tlenki azotu, dwutlenek siarki, węglowodory itp.,
- materiały pędne, oleje, smary, pyły, sadza, materiały sypkie,
- produkty zużywających się nawierzchni drogowych, opon zawierające min. Cr, Cu, Ni, Pb, Zn, Fe, Cd,
- środki używane do zimowego utrzymania dróg.

Wody roztopowe spływające z dróg obciążone są znacznymi stężeniami zawiesin ogólnych, ChZT, ekstraktu eterowego, metali ciężkich, substancji ropopochodnych, a w okresie roztopów – chlorków.

Do uwolnienia zanieczyszczeń z pokrywy śnieżnej i ich wprowadzania do gleby, wód powierzchniowych i podziemnych dochodzi dopiero w czasie odwilży. W naszych warunkach klimatycznych na ogół, w krótkim czasie (kilku dni), duży ładunek zanieczyszczeń nagromadzony w wodach roztopowych trafia do wód i gleb. Szczególnie podczas wiosennych roztopów, zachodzi najbardziej wydajne odprowadzanie zanieczyszczeń, co może prowadzić do niekorzystnych zmian ekosystemów lądowych i wodnych. Nasilenie i szkodliwość tego zjawiska zależy przede wszystkim od następujących czynników: ilości cyklów topnienia i zamarzania oraz szybkości topnienia [1] zmienności stężenia jonów w profilu pokrywy śnieżnej [6]. Dlatego też znajomość składu chemicznego śniegu może być podstawą do uzyskania cennych informacji na temat poziomu zanieczyszczeń atmosfery, oraz stanowić podstawę do oceny zagrożeń zanieczyszczenia gleb i wód.

3. Materiał i metodyka badań

3.1. Materiał badań

Przedmiotem badań były próbki śniegu pobierane w latach 2009, 2010 i 2011 z parkingów, pasów dróg, obszaru zieleni dzielnicy mieszkaniowej i ogródków działkowych Częstochowy. Pobór próbek śniegu odbywał się w okresie 8 do 16 lutego 2009, od 18 do 24 lutego 2010 i od 16 do 26 lutego 2011. Temperatura w okresie pobierania próbek wynosiła od -1 do -10°C. Grubość warstwy śniegu w czasie poboru próbek w roku 2009 wynosiła od 7 do 13 cm, w 2010 od 24 do 36 cm, a w 2011 od 5 do 12 cm. Do pobrania próbek użyto metalowej rury w ten sposób, że w środku zostawał profil śniegu z całej grubości warstwy. W celu uzyskania reprezentatywnej próbki śniegu z każdego punktu pobierano trzy próbki i przesypywano do jednej butelki. Próbki z obszarów sąsiadujących bezpośrednio z drogami pobierano w odległości od 2 do 5 m od krawędzi jezdni z nienaruszonego przez ruch pojazdów czy urządzenia odśnieżające profilu w celu wykluczenia pobierania błota pośniegowego. Ogółem w latach 2009–2011 pobrano 120 próbek. Następnie próbki przewieziono do laboratorium i przechowywano w temperaturze 4 st. do czasu wykonania analiz.

Tabela 1. Charakterystyka miejsc poboru próbek
Table 1. Characteristics of sample collection places

Nr stanowiska poboru próbek śniegu	Ilość próbek			Opis miejsca
	2009	2010	2011	
1	8	7	4	parking osiedlowy (dzielnica Raków Zachód)
2	6	6	5	parking marketu Auchan
3	7	6	5	pobocze drogi osiedlowej (ul. Orkana)
4	5	6	5	pobocze ulicy w centrum miasta (ul. Brzeźnicka)
5	6	6	4	pobocze drogi szybkiego ruchu (trasa A1)
6	7	5	5	osiedle mieszk. – obszar zieleni (Raków Zachód)
7	6	5	6	teren ogródków działkowych

3.2. Metody badań

Zawiesiny ogólne oznaczano metodą wagową PN-EN 872:2007.

Oznaczenie pH ścieków wykonano metodą potencjometryczną PN-EN ISO 1-0523:2012.

Metale ciężkie oznaczono metodą ICP-AES w spektrometrze plazmowym Thermo Scientific IRIS Interpid II XSP.

Do oznaczenia ChZT zastosowano metodę dwuchromianową z wykorzystaniem spektrofotometru HACH DR/4000V, PN-ISO 15705:2005.

4. Wyniki badań i ich dyskusja

4.1. Zawiesiny ogólne i ChZT

W tabeli 2 przedstawiono średnie zawartości zawiesin i ChZT próbek ścieków pochodzących z roztopionego śniegu w latach 2009–2011.

Tabela 2. Parametry wód z roztopionego śniegu – wartości średnie
Table 2. Parameters of meltwaters – medium values

Nr stanowiska	ChZT mg O_2/dm^3			Zawiesiny ogólne mg/dm^3		
	2009	2010	2011	2009	2010	2011
1	97	82	112	181	210	200
2	320	305	359	995	865	780
3	95	105	100	237	167	230
4	110	187	155	490	665	500
5	430	405	355	650	720	690
6	73	86	80	126	98	110
7	69	80	85	98	100	90

Należy podkreślić, że dane przedstawione w tabeli 2 są wartościami średnimi dla danego punktu pomiarowego w określonym roku. Najwyższe ilości zawiesin stwierdzono w próbkach ścieków z roztopionego śniegu pochodzącego z terenu parkingu marketu Auchan. Zawartość zawiesin w tych próbkach mieściła się w szerokim zakresie od 502 do 1325 mg/dm^3 przy średnich dla poszczególnych lat przedstawionych w tabeli 2. Wyniki badań autorów niniejszego artykułu wskazują na niższe zawartości zawiesin w ściekach deszczowych spływających z ulic Częstochowy w porównaniu do ich ilości w próbkach ścieków z topniejącego śniegu. Wcześniejsze badania jednej z autorek artykułu wskazują, ze w pierwszej najbardziej zanieczyszczonej fazie deszczu spływającej z ulic o dużym natężeniu ruchu zawartość zawiesin ogólnych wynosiła do 860 mg/dm^3, a z parkingu marketu Auchan ok. 420 mg/dm^3 [15]. Potwierdzają tą prawidłowość badania ze zlewni Kielc, w których średnia zawartość zawiesin ogólnych w ściekach deszczowych mieściła się w przedziale od 106 g/m^3 do 630 g/m^3, a w ściekach roztopowych od 1224 g/m^3 do 5514 g/dm^3[2].

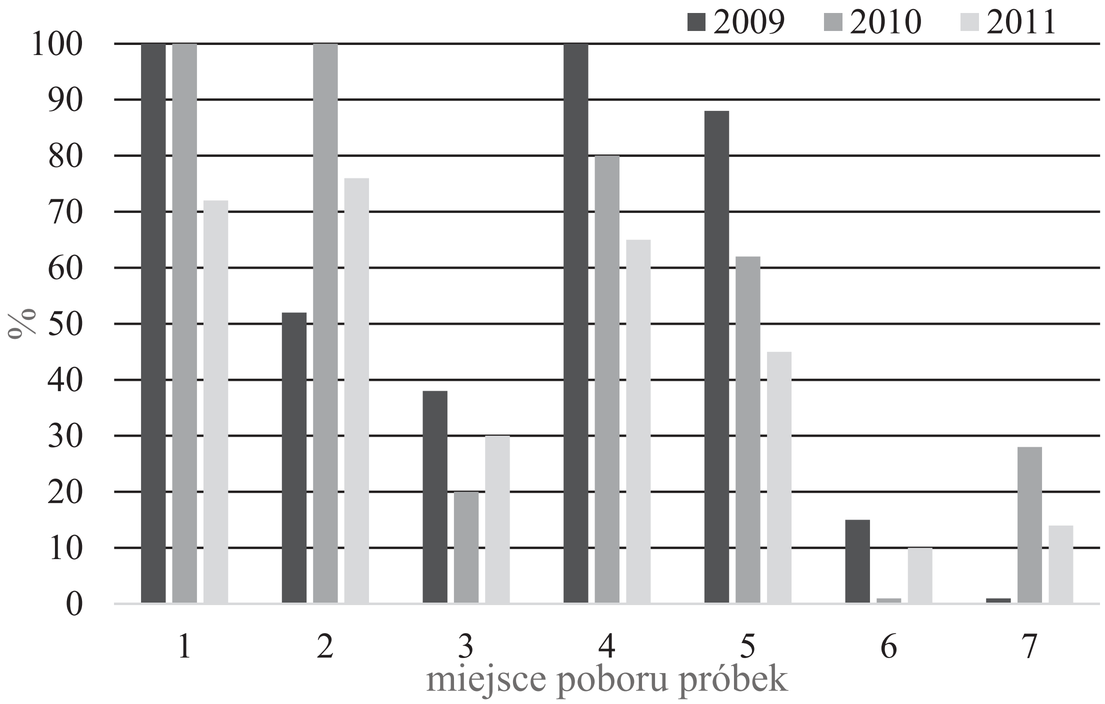
Wartości ChZT wahały się również w szerokim zakresie od 46,0–120,0 mg O_2/dm^3 (osiedle mieszk. – obszar zieleni) do 89–825,0 mg O_2/dm^3 (pobocze drogi szybkiego ruchu), średnie wartości przedstawiono w tabeli 2. Dla ścieków deszczowych spływających z poboczy ruchliwych dróg wskaźnik ChZT wynosił max. ok. 200 mg O_2/dm^3 [15].

Analiza wyników przedstawionych w tabeli 2 wskazuje na wysokie zróżnicowanie zanieczyszczenia próbek śniegowych związane z miejscem ich poboru. Duże wahania zanieczyszczeń w zależności od punktu poboru stwierdzili także inni autorzy [2]. Wyższe zanieczyszczenie wody z topniejącego śniegu w porównaniu z wodami deszczowymi spływającymi z tych samych zlewni wiąże się przede wszystkim z długim okresem zalegania śniegu i stopniowej kumulacji kolejnych partii zanieczyszczeń oraz stosowanymi środkami zabezpieczenia dróg przed gołoledzią (piasek, sól).

4.2. Odczyn

W warunkach naturalnych pH opadu atmosferycznego wynosi 5,65. Lekko kwasowy odczyn spowodowany jest obecnością w powietrzu CO_2. Istotnym jest fakt by nie były to zbyt niskie wartości pH. Opad, którego wartość pH jest niższa od 5,6 przyjęto określać mianem kwaśnego opadu atmosferycznego. Zmierzone pH próbek ścieków z roztopionego śniegu w latach 2009–2011 kształtowało się na poziomie 4,75–6,50. Natomiast pH badanych próbek ścieków deszczowych z różnych zlewni miasta Częstochowy było nieco wyższe i kształtowało się na poziomie 5,60– 6,90 [15].

W latach 2009–2010 aż dla ok.55%, a w roku 2011 dla 44% próbek śniegu stwierdzono wartość pH < 5,6 co świadczy o ich kwaśnym charakterze (rys.1). Należy podkreślić, że w roku 2009 dla ok. 20%, w roku 2010 dla 14%, a w roku 2011 dla ok. 18% próbek śniegu stwierdzono wartość pH < 5,0. Silnie kwaśnego charakteru próbek śniegu (pH < 4,0) nie zaobserwowano.



Rys. 1. Procentowy udział próbek śniegu o pH < 5,6
Fig. 1. Percentage share of snow samples with pH < 5,6

Analiza powyższych wyników pozwala stwierdzić, że zdecydowana większość próbek charakteryzowała się naturalnym lub lekkim zakwaszeniem. Wartość pH była związana z miejscem oraz czasem poboru próbki. Kwaśny odczyn wyraźnie dominował w próbkach z obszaru parkingów i dróg o dużym natężeniu ruchu. Spowodowane było to najprawdopodobniej wzrostem zawartości kwaśnych tlenków pochodzących z procesów transportu i spalania. Różnice pH dla badanych zlewni i lat można uznać za średnie `(max. 1,75 jednostki). Przeprowadzone w latach 2003–2004 badania pH śniegu z terenu Gdańska i Sopotu wskazywały na szerszy zakres pH – od silnie kwaśnego do obojętnego (od ok. 4,0 do powyżej 7,0, przy średnim w granicach 5,6–6,2). Autorzy to wyjaśniali z jednej strony nasiloną emisją kwaśnych tlenków z drugiej zaś zróżnicowaną cyrkulacją powietrza i zmienną zawartością substancji zobojętniających kwaśne tlenki [19]. Podobnie badania pokrywy śnieżnej wyspy Wolin prowadzone w 2010 roku wskazywały na duży zakres zmienności pH wynoszący od 2,44 do 6,95. Średnie pH śniegu było niskie i wynosiło 3,67 pH [25].

Również badania pokrywy śnieżnej obszaru Sudetów Zachodnich – stacje pomiarowe Orle, Kamiennik, Szrenica prowadzone w latach 2008–2012 wskazują na szeroką rozpiętość wartości pH od 3,56 do 7,2 i kilkunastoprocentowy udział próbek o pH<5,0. Silnie kwaśne opady o pH<4,0 stwierdzono tylko na stacji Orle i stanowiły one 1,45% badanych próbek śniegowych [4]. Tak więc wyniki badań różnych autorów dotyczące odczynu opadów atmosferycznych są nadal zróżnicowane, co wskazuje na konieczność dalszych działań zmierzających do ograniczenia kwaśnych emisji do atmosfery. Należy jednak podkreślić, że część autorów na podstawie badań pH prób śniegowych, deszczowych czy glebowych w bezpośrednim sąsiedztwie dróg stwierdza alkalizację środowiska w wyniku stosowania środków do zimowego utrzymania dróg (chlorki sodu i wapnia) [26].

4.3. Metale ciężkie

Woda z roztopionego śniegu może zawierać toksycznie oddziałujące na środowisko metale jak ołów, kadm, cynk, miedź czy nikiel, pochodzące z produktów spalania, zużycia pojazdów, katalizatorów, materiałów ściernych w okładzinach hamulcowych oraz niespalonych dodatków do paliwa. Metale ciężkie z tych źródeł ulegają przemieszczaniu w środowisku i z zanieczyszczonymi wodami roztopowymi czy deszczowymi migrują do wód powierzchniowych, podziemnych, gleby i bezpośrednio lub poprzez rośliny dostają się do organizmów zwierząt i człowieka. Charakterystyczną cechą metali ciężkich jest, w przeciwieństwie do substancji organicznych, brak możliwości rozkładu [12,16,17].

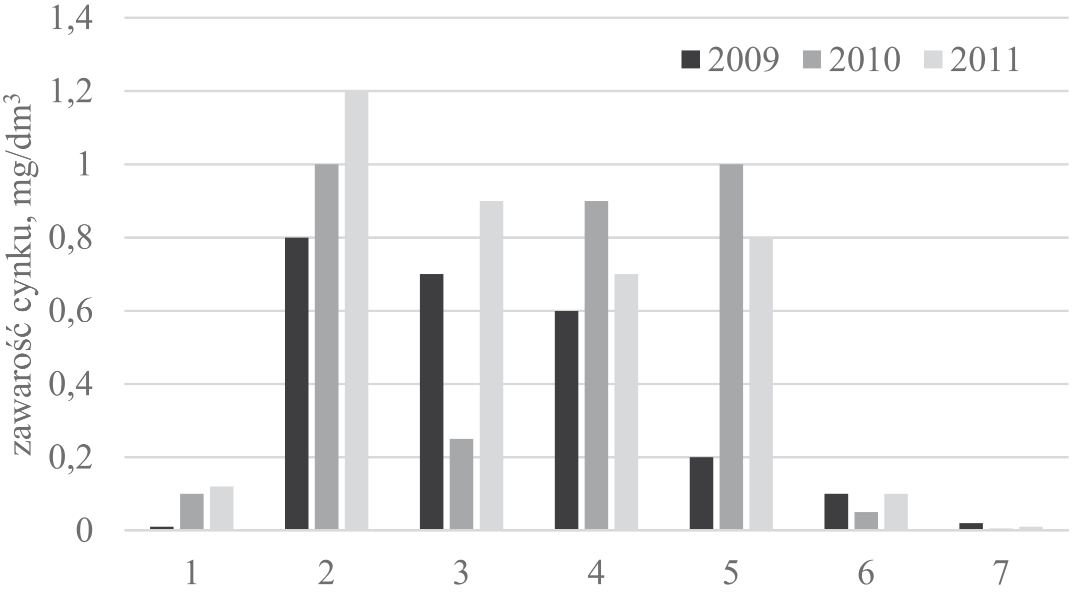
Metale ciężkie w badanych próbkach śniegu występowały w niewielkich stężeniach. Stwierdzone minimalne i maksymalne zawartości Cd, Pb, Zn, Cu i Ni dla poszczególnych miejsc poboru w latach 2009–2011 przedstawiono w tabeli 3, a średnie zawartości na rysunkach 2–5.

Tabela 3. Zawartości minimalne i maksymalne metali ciężkich w ściekach z roztopionego śniegu w latach 2009–2011, mg/dm^3
Table 3. Minimum and maximum heavy metal concentrations in meltwater in years 2009–2011, mg/dm^3

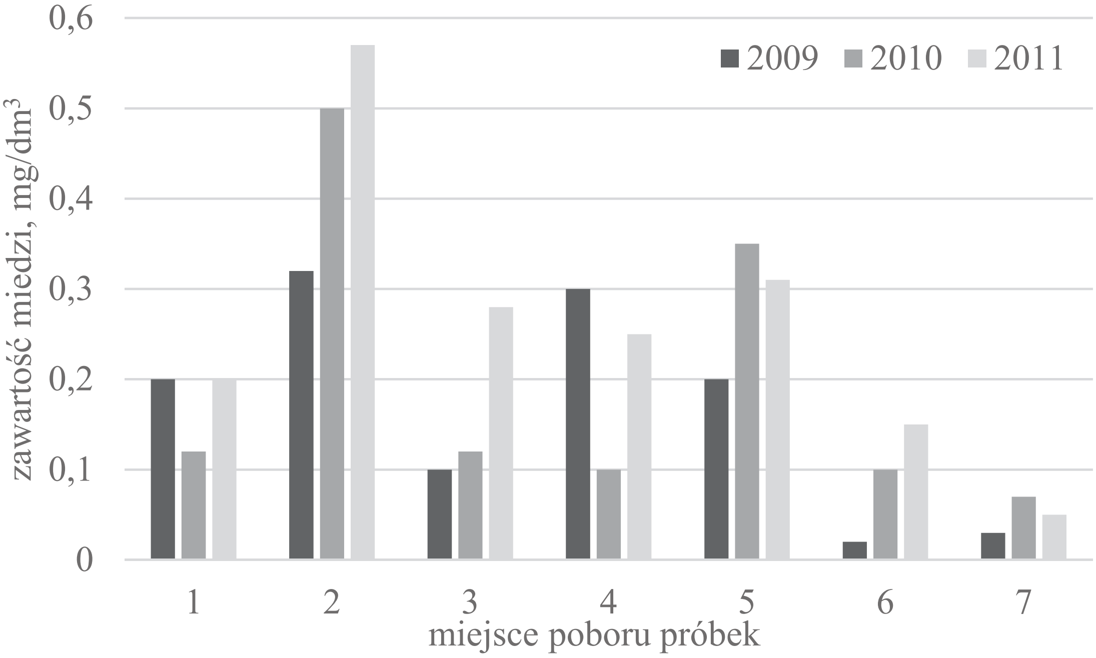
Nr stanowiska	kadm	ołów	cynk	miedź	nikiel
1	0,00–0,08	0,02–0,09	0,08–0,20	0,10–0,23	0,06–0,12
2	0,03–0,10	0,09–0,38	0,10–1,90	0,40–0,67	0,10–0,35
3	0,01–0,06	0,02–0,07	0,06–1,30	0,12–0,32	0,20–0,30
4	0,03–0,08	0,06–0,20	0,30–0,90	0,15–0,35	0,04–0,26
5	0,02–0,09	0,04–0,09	0,20–1,40	0,11–0,40	0,12–0,34
6	0,00–0,01	0,01–0,06	0,00–0,03	0,08–0,12	0,07–0,14
7	0,00–0,03	0,00–0,04	0,00–0,02	0,02–0,07	0,00–0,03

Niskie stężenie metali ciężkich w próbkach ścieków z roztopionego śniegu może wynikać z faktu, iż pierwiastki te zasorbowane są przede wszystkim na powierzchni cząstek stałych, a zawartość metali określano po odsączeniu zawiesiny. Usunięcie ich, zatem przyczyniło się do spadku stężenia metali w próbkach ścieków. Należy jednak podkreślić, że śnieg z obszarów narażonych na bezpośrednie oddziaływanie transportu zawierał na ogół kilka a nawet kilkanaście razy więcej badanych metali w porównaniu z obszarami oddalonymi od ruchliwych dróg czy parkingów. Na tej podstawie można stwierdzić, że głównym źródłem metali ciężkich w analizowanej zlewni był ruch komunikacyjny, natomiast w mniejszym stopniu zanieczyszczenie atmosfery pochodzące z innych źródeł. Według Reinosdotter i Viklander zawartość metali ciężkich w wodach roztopowych jest zależna przede wszystkim od natężenia ruchu i zastosowanych środków do zimowego utrzymania dróg. W przypadku dróg o dużym natężeniu zawartość ołowiu mieściła się w zakresie 0,08–0,12 mg/dm^3, a dla dróg o małym natężeniu ruchu do 0,03 mg/dm^3. Ponadto autorzy stwierdzają wysoką ujemną korelację między ilością zawiesin, a stężeniem rozpuszczonych metali ciężkich w przypadku używania NaCl jako substancji rozmrażającej. Badania wskazują, że podwyższony poziom stężeń metali rozciąga się na odległość do około 50–100 m od dróg o dużym natężeniu ruchu (autostrad)

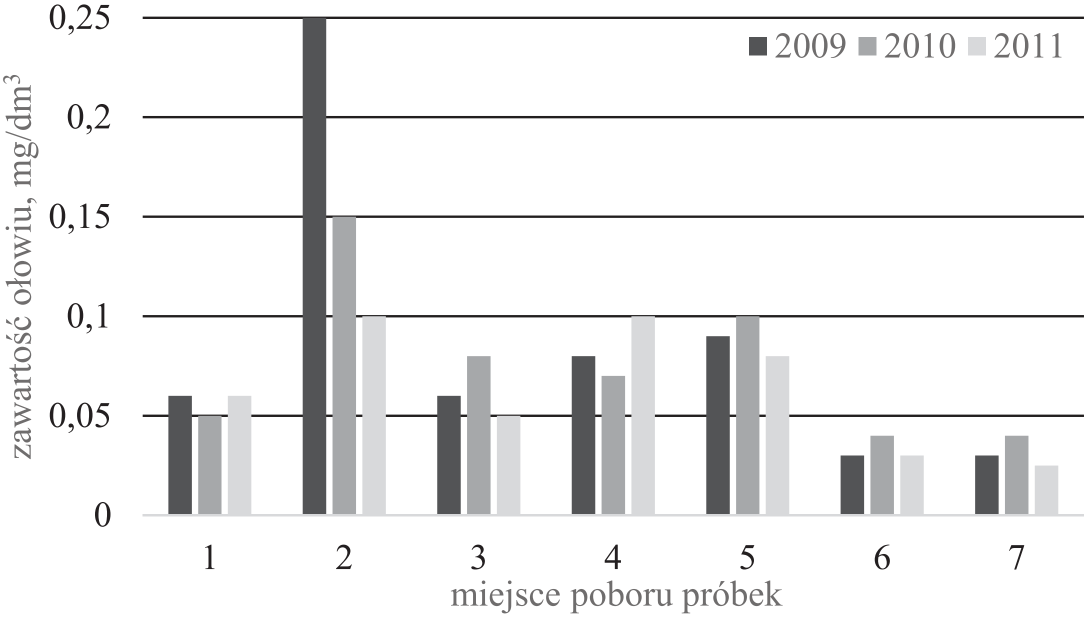
[21]. Podwyższone stężenia są stwierdzane w powietrzu, ściekach deszczowych i roztopowych, a także w glebie i roślinach znajdujących się w tej strefie. Badania Bąka i in. wskazują na zdecydowanie wyższe zawartości ołowiu w ściekach roztopowych (do 1,405 mg/dm^3) w porównaniu ze ściekami deszczowymi, natomiast wyższe zawartości kadmu (do 0,09 mg/dm^3) w ściekach deszczowych [2]. Autorzy niniejszego artykułu stwierdzili niższe zawartości badanych metali w ściekach deszczowych spływających z ulic Częstochowy w porównaniu do ilości w ściekach z topniejącego śniegu. Przegląd wyników badań wskazuje na bardzo wysokie zróżnicowanie zawartości Cd, Zn, Pb, Ni i Cu w ściekach opadowych w zależności od czasu trwania deszczu i miejsca poboru próbki. Najbardziej zanieczyszczonymi są na ogół ścieki spływające z ulic, parkingów i dachów budynków [8,9,15]. Również zawartości metali ciężkich w ściekach roztopowych wskazywały na dużą zmienność w zależności od roku i miejsca poboru próbek. Świadczą o tym graniczne zawartości metali ciężkich przedstawione w tabeli 3 oraz średnie zawartości Zn, Cu, Pb i Cd przedstawione na rysunkach 2–5. Jest to związane przede wszystkim ze stanem zanieczyszczenia atmosfery oraz czasem zalegania pokrywy śnieżnej [18].



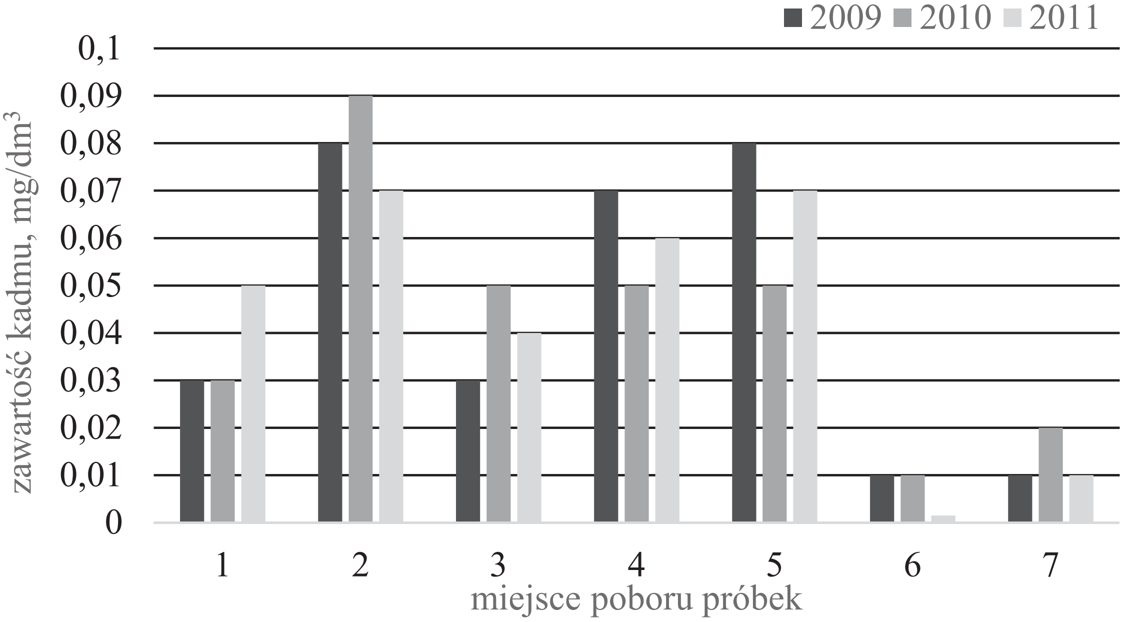
Rys. 2. Średnia zawartość cynku w ściekach z roztopionego śniegu
Fig. 2. Average concentration of Zinc in meltwater



Rys. 3. Średnia zawartość miedzi w ściekach z roztopionego śniegu
Fig. 3. Average concentration of Copper in meltwater



Rys. 4. Średnia zawartość ołowiu w ściekach z roztopionego śniegu
Fig. 4. Average concentration of Lead in meltwater



Rys. 5. Średnia zawartość kadmu w ściekach z roztopionego śniegu
Fig. 5. Average concentration of Cadmium in meltwater

5. Wnioski

Na podstawie przeprowadzonych badań oraz analizy danych literaturowych stwierdza się wysokie zróżnicowanie stężenia zanieczyszczeń w pokrywie śnieżnej związane przede wszystkim z miejscem poboru próbki, długością zalegania pokrywy śnieżnej, temperaturą zewnętrzną, z okresem wykonywanych badań, kierunkiem wiatrów, natomiast w przypadku dróg z panującym natężeniem ruchu oraz z rodzajem substancji rozmrażających, a także ze sposobem pobierania próbek, który nie jest ujednolicony. Stężenia zanieczyszczeń w pokrywie śniegowej obszarów bezpośrednio przylegających do dróg i parkingów z uwagi na wysokie stężenia i dużą zmienność powinny być monitorowane. Na podstawie przeprowadzonych badań sformułowano następujące wnioski szczegółowe:

1. Zawartość zawiesin w próbkach śniegu z poboczy tras komunikacyjnych i parkingów była wysoka i mieściła w szerokim zakresie od 165 do 1325 mg/dm^3, wartości ChZT wynosiły od 55,0 do 825,0 mg O_2/dm^3.
2. Wartość pH śniegu kształtowała się na poziomie 4,75–6,50. W latach 2009–2010 aż dla ok. 55%, a w roku 2011 dla 44% próbek śniegu

stwierdzono wartość pH < 5,6 co świadczy o ich kwaśnym charakterze. Kwaśny odczyn wyraźnie dominował w próbkach z obszaru parkingów i dróg o dużym natężeniu ruchu.

3. Średnia zawartość metali ciężkich w próbkach ścieków roztopowych była na ogół niska, co mogło wynikać z faktu, że badania stężenia metali wykonywano w ściekach roztopowych po odsączeniu zawiesiny. Należy jednak podkreślić, że próbki śniegu z obszarów narażonych na bezpośrednie oddziaływanie transportu zawierały kilka, a nawet kilkanaście razy więcej metali w porównaniu z obszarami oddalonymi od ruchliwych dróg czy parkingów.
4. W oparciu o wyniki badań można stwierdzić, że głównym źródłem zanieczyszczeń pokrywy śnieżnej analizowanych zlewni był ruch pojazdów, w znacznie mniejszym stopniu zanieczyszczenie atmosfery pochodzące z innych źródeł emisji. Śnieg z terenu ogródków działkowych i obszaru zieleni osiedla mieszkaniowego zawierał znacznie mniejszą ilość zanieczyszczeń w porównaniu z poboczami tras komunikacyjnych i parkingami.
5. Należy zwrócić uwagę na konieczność ujednolicenia procedury poboru próbek śniegu. Metody poboru próbek śniegowych przedstawiane w publikacjach są zróżnicowane co wpływa na wyniki badań i często uniemożliwia ich porównanie.

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Literatura

1. **Bales R.C., Davis R.E., Willliams M.W.:** *Tracer release in melting snow: Diurnal and seasonal patterns*. Hydrol. Proc. 7, 389–401 (1993).
2. **Bąk Ł., Górski J., Górska K., Szeląg B.:** *Zawartość zawiesin i metali ciężkich w wybranych falach ścieków deszczowych w zlewni miejskiej.* Ochrona Środowiska. 34(2), 49–52 (2012).
3. **Błaszczyk P.:** *Zasady odprowadzania wód opadowych z terenów miejskich.* Mat. IV Konf. Naukowo-Technicznej, Łódź , 25–34 (2002).
4. **Cichała-Kamrowska K.:** *Pokrywa śnieżna jako źródło informacji o zanieczyszczeniu środowiska.* Rozprawa doktorska, Politechnika Gdańska, Wydz. Chemiczny, Katedra Chemii Analitycznej, 2012.
5. **Deluga W.:** *Współczesne trendy w motoryzacji ograniczające zagrożenie środowiska.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 1, 205–2013 (1999).

6. **Domine F., Thibert E.:** *Relationship between atmospheric composition and snow composition for HCl and HNO_3.* In: Tonnessen, K. A., Williams, M. W., M. (Eds.) Biogeochemistry of Seasonally Snow Covered Catchments. Tranter, IAHS Publ. 228, 3–10 (1995).
7. **Gnecco I., Berretta T.C., Lanza L.G., Barbera P.La.:** *Storm water pollution in the urban environment of Genoa, Italy*. Atmospheric Research. 77, 60–73 (2005).
8. **Göbel P., Dierkes C., Coldewey W.G.:** *Storm water runoff concentration matrix for urban areas.* Journal of Contaminant Hydrology. 91, 26–42 (2007).
9. **Grabarczyk K., Gwoździej-Mazur J.:** *Analiza zanieczyszczeń ścieków opadowych ze zlewni zurbanizowanych.* Monografie Komitetu Inżynierii Środowiska PAN. Vol. 32, 2005.
10. **Hofman M., Wachowski L.:** *Badania zawartości platyny i ołowiu w glebie wzdłuż dróg wylotowych z Poznania.* Ochrona Środowiska. 32(3), 43–47 (2010).
11. **Królikowski A., Garbarczyk K., Gwoździej-Mazur J.:** *Metale ciężkie w osadach z wpustów ulicznych.* Monografie Komitetu Inżynierii Środowiska PAN. Vol. 32, 2005.
12. **Lach J., Okoniewska E., Stępniak L.:** *The influence of modification of activated carbon on adsorption of Ni(II) and Cd(II).* Desalination and Water Treatment. 52, 19–21 (2014).
13. **Mangani G., Berloni A., Bellucci F., Tatano F., Maione M.:** *Evalution of the pollutant content in road runoff first flush waters.* Water, Air Soil Pollut. 160, 213–228 (2005).
14. Materiały GUS, Ochrona Środowiska, 2013.
15. **Ociepa E.:** *Ocena zanieczyszczenia ścieków deszczowych trafiających do systemów kanalizacyjnych*. Inżynieria i Ochrona Środowiska. 14(4), 357–364 (2011).
16. **Ociepa E., Ociepa-Kubicka A. Okoniewska E.:** *The Immobilization of Zinc and Cadmium in the Soil as a Result of the Use of Waste Substrates,* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1772–1786 (2013).
17. **Ociepa, A., Pruszek K., Lach J.:** *Evaluation of the usage of organic fertilizers and sewage residues as regards polluting soils by heavy metals*. Proceedings of ECOpole. 1, 195–199 (2007).
18. **Ociepa E.:** *Zanieczyszczenia wód opadowych i roztopowych spływających ze zlewni miejskiej.* Mat. IX Konf. „Wody opadowe – aspekty prawne, ekonomiczne i techniczne”, Iława, Wyd. Abrys Poznań 2014.

19. **Polkowska Ż., Demkowska I, Cichała-Kamrowska K, Namieśnik J.:** *Zanieczyszczenia obecne w próbkach śniegu pobranego z warstw jako źródło informacji o stanie środowiska w dużej aglomeracji miejskiej.* Ecological Chemistry and Engineering S. 17(2), 203–230 (2010).
20. **Polkowska Ż., Namieśnik J.:** *Road and roof runoff waters as a source of pollution in a big urban agglomeration.* Ecological Chemistry and Engineering S. 15(3), 375 – 385 (2008).
21. **Reinosdotter K., Viklander M.:** *A comparison of snow quality in two Swedish municipalities Luleå and Sundsvall.* Water, Air and Soil Pollution. 167, 3–16 (2005).
22. Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz.U. 2006.
23. **Sawicka-Siarkiewicz H.:** *Ograniczanie zanieczyszczeń w odpływach opadowych.* Mat Sem. „Kierunki rozwoju systemów odprowadzania i oczyszczania wód opadowych na terenach m. st. Warszawy”. Warszawa 2005.
24. **Thomson N.R., McBean E.A., Snodgrass W., Monstrenko I.B.:** *Highway stormwater runoff quality: Development of surrogate parameter relationships.* Water, Air and Soil Pollution. 94(3–4), 307–347 (1997).
25. **Tylkowski J., Samołyk M.:** *Monitoring fizykochemicznych właściwości pokrywy śnieżnej wyspy Wolin.* Monitoring środowiska przyrodniczego, Kieleckie Towarzystwo Naukowe, Kielce. 11, 73–80 (2010).
26. **Wiśniowska-Kielian B., Niemiec M., Arasimowicz M.:** *Przydrożne zbiorniki ścieków opadowych jako element ochrony jakości wód.* Inżynieria Ekologiczna. 34, 62–75 (2013).
27. **Zobrist J., Müller S.R., Ammann A., Mottier V., Ochs M., Schoenenberger R., Eugster J.:** *Quality of roof runoff for groundwater infiltration.* Wat. Res. 34(5), 1455–1462 (2000).

Snow Cover as a Medium for Deposition of Pollution

Abstract

The paper presents the results of snow contamination collected from roadsides and parks of Czestochowa in these areas which are out of the impact of a transport. The study was conducted within 2009–2011, in which 120 samples were tested in general. In snowmelt and rain waters that are brought to the sewer or land there are the following pollutants such as: suspended solids, hydrocarbons, heavy metals, biogenic compounds, and even bacteriological con-

tamination. The scope of the research included: pH, total suspended solids, COD and heavy metals in waste water coming into the sewer.

On the basis of the survey and analysis of the literature data it is possible to admit the high variation in pollutant concentrations in snow cover, mainly related to the place of sampling. It should also be noted that the other factors, such as: the length of snow cover, the outside temperature, the duration of test runs, the direction of the winds, in the case of the particular type of a substance thawing roads, have affected the results of measurements substantially as evidenced by their differentiation to the point for further measurements.

The samples of snow from the sides of roads and parking areas have been characterized by a high content of suspended solids falling within the broad range from 165 to 1325 mg/dm^3, COD values ranged from 89.0 to 825.0 mg O_2/dm^3. The pH of the snow stood at the level of 4.75–6.50. The analysis of the results has shown that the vast majority of the samples has been characterized by a natural or light acidity. The pH value was associated with a place and time of sampling. Most of the snow samples, collected from roadsides with heavy traffic and parking spaces, pointed to their acidic or slightly acidic character. The average content of heavy metals: Cd, Pb, Zn, Cu and Ni within the snow was generally low, which could be due to the fact that the tests were performed within metals concentration in water after the filtration of a suspension. It should be pointed out, however, that the snow from these areas that are exposed to the direct impact of transport, contained more metals for several times, compared with the periphery of busy roads or parking lots. On this basis it can be concluded that the main source of pollution of snow cover was, as analyzed, the catchment traffic, much less air pollution from the other sources. Therefore, the concentration of pollutants in snow cover areas directly adjacent to roads and parking spaces, due to the high concentration of pollutions, ought to be monitored. It should be paid attention to the need to standardize the procedures within sampling the snow.

Słowa kluczowe:
źródła zanieczyszczeń śniegu, zanieczyszczenie ścieków deszczowych, metale ciężkie, zawiesiny ogólne

Keywords:
snow contamination sources, runoff contamination, heavy metals, total suspended solids

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Badania doświadczalne a dokładność opracowanego modelu

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1. Wstęp

Dość często z powodu obszernego zakresu badań eksperymentalnych, bez pogorszenia wiarygodności zakładanych przez nas założeń badawczych poszukuje się drogi, która skróciłaby nasz czas pracy i zmniejszyła liczbę pomiarów. Znanym sposobem na to jest metoda planowania eksperymentów. Drugim takim rozwiązaniem okazuje się opracowanie teoretycznego modelu fizyko-matematycznego. Taką też drogę wykorzystuje w swojej pracy badawczej zespół autorów.

W ramach prowadzonych prac doświadczalnych zespół autorów zajmował się w głównej mierze modernizacją kotłów przemysłowych i grzewczych w celu poprawy wskaźników ich pracy pod względem sprawności, jak i ekologiczności. Realizując kolejny etap takich badań opracowane zostały zasady polioptymalizacji procesu spalania paliwa według energo-ekologicznego kryterium [4].

W tym celu zaprojektowany został i wykonany mikroprocesorowy system automatycznego sterowania jakością spalania paliwa [3]. Na bazie tego systemu zbudowano stanowisko eksperymentalne do badań jakości spalania paliwa zgodnie z założeniami powyższego kryterium. Badania wykonywano na rzeczywistych obiektach firmy URAN SPB oraz TERA, wyposażonych w kotły parowe o wydajnościach od 6 do 25 t/h. W celu skrócenia drogi poszukiwania wieloczynnikowego optimum jakości spalania paliwa oraz definitywnego zmniejszenia liczby eksperymentów zaproponowany został nowy model fizyko-matematyczny [5].

2. Cele badań

Celem opracowania modelu fizyko-matematycznego było uzyskanie sposobu określenia przedziału, w którym oczekuje się optymalnych wartości następujących wskaźników sprawności i ekologiczności spalania paliwa:

- temperatury spalin wzdłuż traktu spalinowego $\boldsymbol{t_{sp}}$;
- sprawności kotła (lub agregatu kotłowego) netto $\boldsymbol{\eta_n}$;
- stężenia tlenku węgla CO i tlenków azotu NO_x w spalinach;
- mocy zużywanej przez silnik wentylatora nadmuchowego, w postaci natężenia prądu $\boldsymbol{I_w}$ oraz współczynnika mocy $\cos\varphi_w$;
- mocy zużywanej przez silnik wentylatora wyciągowego ($\boldsymbol{I_{wy}}$, $\cos\varphi_{wy}$).

Model powinien zapewnić wykonywanie swych zadań w zakresie możliwych zmian następujących czynników wpływu [5]:

- zużycia paliwa $\boldsymbol{B_g}$;
- współczynnika nadmiaru powietrza w palenisku $\boldsymbol{\alpha_p}$;
- zmiany współczynnika nadmiaru powietrza na skutek nieszczelności $\boldsymbol{\Delta\alpha_i}$;
- temperatury powietrza $\boldsymbol{t_p}$ i paliwa $\boldsymbol{t_g}$;
- wartości opałowej paliwa $\boldsymbol{Q_d}$;
- stopnia zanieczyszczenia ekranowych powierzchni kotła;
- sprawności cieplnej konwekcyjnych powierzchni kotła.

Największy problem w trakcie opracowywania modelu stanowiło określenie zmian stężenia CO i NO_2 w zależności od czynników wpływu. Analiza literatury naukowo-technicznej w tym zakresie [1, 7–9] świadczy o skrajnie skomplikowanym charakterze zagadnienia opracowania uniwersalnego modelu fizyko-matematycznego zmiany stężenia CO i NO_2 z uwzględnieniem kinetyki pośrednich i końcowych produktów reakcji spalania. Większość uzyskanych w ten sposób metod posiada ograniczoną dokładność, w związku z czym nie może być stosowana do rozwiązania zdefiniowanego zagadnienia.

Opracowanie modelu matematycznego polegało na analizie zmian czynników wpływu na wartości wskaźników określających jakość spalania paliwa oraz wskaźników pracy palników; aproksymacji danych doświadczalnych i ustaleniu stopnia adekwatności uzyskanych modeli.

Za pomocą opracowanego modelu fizyko-matematycznego zostały następnie wykonane obszerne badania w zakresie sprawności i ekologiczności spalania paliwa w wybranym rodzaju techniki cieplnej: ustalenie wpływu typu palników i ich usytuowania na froncie kotła, mocy kotła, jego stanu technicznego oraz trybu spalania paliwa. Za pomocą stworzonego modelu dokonywano oceny optymalności spalania z punktu widzenia zarówno sprawności jak i ekologiczności dokonywanej na podstawie opracowanego przez autorów kryterium energo-ekologicznego. Podstawowymi czynnikami określającymi wartość kryterium był zredukowany wskaźnik toksyczności oraz bilansowa sprawność zespołu kotłowego.

Wykorzystanie modelu pozwoliło znacznie zmniejszyć liczbę wymaganych zmian trybu pracy kotłów i prowadzonych pomiarów na rzeczywistych obiektach przemysłowo-grzewczych.

3. Wyniki badań

Podczas prac doświadczalnych zbadano wpływ ilościowych i jakościowych wskaźników dostarczania powietrza do strefy spalania, a także mocy kotła na emisję CO i NO_x [2]. Ważne znaczenie miał także rodzaj palników. Dlatego badania prowadzone były na jednakowych kotłach parowych typu DKVR-20-13 wyposażonych w różne palniki nadmuchowe: GMGB-5,6, GMGm-5 oraz GMG-7.

Uzyskane wyniki badań doświadczalnych na bieżąco zestawiano z opracowanym wcześniej modelem matematycznym w celu określenia stopnia adekwatności uzyskanych wyników.

Według [6] wiarygodność modelu matematycznego sprawdza się na podstawie kryteriów zgodności. Jako takie kryterium autorzy wybrali kryterium korelacji Pearsona, a właściwie jego kwadrat – $\boldsymbol{r}^2$ (tzw. współczynnik determinacji). Za wiarygodną zależność aproksymującą, która opisywała dane doświadczalne, przyjmowano funkcję posiadającą $\boldsymbol{r}^2$ powyżej 0,95. Ogólny widok funkcji aproksymujących dane pomiarów stężenia CO i NO_2 w zależności od α_p i $\boldsymbol{B_g}$, dla palników typu GMGm-5, GMGB-5,6, GMG-7, podano we wzorach (1) i (2), natomiast odpowiednie współczynniki aproksymacji podano w tabeli 1 i 2.

$$\mathrm{CO} = \frac{\boldsymbol{a} + \boldsymbol{b} \cdot \alpha_p + \boldsymbol{c} \cdot \boldsymbol{B}_g}{1 + \boldsymbol{d} \cdot \alpha_p + \boldsymbol{e} \cdot \boldsymbol{B}_g + \boldsymbol{f} \cdot \boldsymbol{B}_g^2} \tag{1}$$

$$NO_2 = \frac{\boldsymbol{a} + \boldsymbol{b} \cdot \alpha_p + \boldsymbol{c} \cdot \boldsymbol{B}_g}{1 + \boldsymbol{d} \cdot \alpha_p + \boldsymbol{e} \cdot \alpha_p^2 + \boldsymbol{f} \cdot \boldsymbol{B}_g} \tag{2}$$

Tabela 1. Współczynniki aproksymacji zależności CO = **f**(α_p, B_g)
Table 1. Approximation coefficients in dependence of CO = $f(\alpha_p, B_g)$

Współczynniki do określania CO	3×GMGB-5,6	3×GMGm-5	2×GMG-7
a	–161,49	–285,39	–273,77
b	144,44	228,71	207,88
c	0,007700	0,023335	0,026841
d	–1	–0,9571	–0,81543
e	$-8{,}3\cdot10^{-6}$	$1{,}018\cdot10^{-5}$	–0,00019
f	$3{,}89\cdot10^{-9}$	$-1{,}049\cdot10^{-8}$	$5\cdot10^{-8}$
Współczynnik determinacji	0,998	0,991	0,988

Tabela 2. Współczynniki aproksymacji zależności NO_2 = **f**(α_p, B_g)
Table 2. Approximation coefficients in dependence of $NO_2 = f(\alpha_p, B_g)$

Współczynniki do określania NO_2	3×GMGB-5,6	3×GMGm-5	2×GMG-7
a	19,274	–26,6	–19,31
b	–17,725	24,5	16,66
c	0,00712	0,00183	0,00406
d	1,61	–1,75	–1,69
e	0,659	0,8	0,741
f	$5{,}522\cdot10^{-6}$	$-1{,}233\cdot10^{-5}$	$-3{,}760\cdot10^{-7}$
Współczynnik determinacji	0,989	0,987	0,968

Zależności zmiany I_w, I_{wy}, $\cos\varphi_w$, $\cos\varphi_{wy}$, aproksymujące doświadczalne dane dla wentylatora nadmuchowego BDN-11,2 i wentylatora wyciągowego DN-13,5, przedstawiono w postaci funkcji wielomianowej trzeciego rzędu we wzorach (3)–(6), natomiast odpowiednie wielkości współczynników wielomianu podano w tabeli 3.

$$\boldsymbol{I}_w = \boldsymbol{a} + \boldsymbol{b} \cdot \boldsymbol{V}_p + \boldsymbol{c} \cdot \boldsymbol{V}_p^2 + \boldsymbol{d} \cdot \boldsymbol{V}_p^3 \tag{3}$$

$$\cos\varphi_w = \boldsymbol{a} + \boldsymbol{b} \cdot \boldsymbol{V}_p + \boldsymbol{c} \cdot \boldsymbol{V}_p^2 + \boldsymbol{d} \cdot \boldsymbol{V}_p^3 \tag{4}$$

$$\boldsymbol{I}_{wy} = \boldsymbol{a} + \boldsymbol{b} \cdot \boldsymbol{V}_g + \boldsymbol{c} \cdot \boldsymbol{V}_g^2 + \boldsymbol{d} \cdot \boldsymbol{V}_g^3 \tag{5}$$

$$\cos\varphi_{wy} = \boldsymbol{a} + \boldsymbol{b} \cdot V_g + \boldsymbol{c} \cdot V_g^2 + \boldsymbol{d} \cdot V_g^3 \qquad (6)$$

gdzie:

I_w, I_{wy} – prąd zużywany na napęd wentylatora nadmuchowego i wyciągowego [A];

$\cos\varphi_w, \cos\varphi_{wy}$ – współczynnik mocy wentylatora nadmuchowego i wyciągowego [j. u.];

α_p – współczynnik nadmiaru powietrza w palenisku [j. u.];

B_g – zużycie gazu [m^3/h];

V_p – zużycie powietrza, [m^3];

V_g – strumień objętości gazów spalinowych [m^3/m^3];

a, ***b***, ***c***, ***d***, ***e***, ***f*** – współczynniki modelu matematycznego [j. u.].

Tabela 3. Współczynniki wielomianów przy określaniu I_w, I_{wy}, $\cos\varphi_w$, $\cos\varphi_{wy}$
Tabela 3. Polynomial coefficients in defining I_w, I_{wy}, $\cos\varphi_w$, $\cos\varphi_{wy}$

Współczynniki	I_w	I_{wy}	$\cos\varphi_w$	$\cos\varphi_{wy}$
a	–12,2	9,2	0,056	0,083
b	0,0116	0,074	0,00017	$1{,}32 \cdot 10^{-4}$
c	10^{-6}	$-6{,}332 \cdot 10^{-7}$	$-1{,}484 \cdot 10^{-8}$	$1{,}249 \cdot 10^{-8}$
d	$2{,}9 \cdot 10^{-11}$	$1{,}887 \cdot 10^{-11}$	$4{,}29 \cdot 10^{-13}$	$3{,}962 \cdot 10^{-13}$
Współczynnik determinacji	0,987	0,991	0,963	0,949

Aproksymując zależności do określania I_w, I_{wy}, $\cos\varphi_w$, $\cos\varphi_{wy}$ pokazano, że wraz ze wzrostem mocy i zwiększeniem objętości gazów spalinowych zwiększa się ich temperatura, a zatem temperatura t_g pośrednio uwzględniana jest przy określaniu strat energii na nadmuch i wyciąg spalin. Uwzględniając, że palniki i krótkie odcinki przewodów można ujmować jako opory miejscowe, ogólne zależności przepływu gazu B_g i powietrza V_p przez kontrolne odcinki od spadku ciśnień powietrza $\Delta P_p = P_p - P_{pal}^p$ i gazu $\Delta P_g = P_g - P_{pal}^g$ między kontrolnym punktem a paleniskiem będą miały postać:

$$V_p = A_p \cdot \Delta P_p^{\,0,5} \qquad (7)$$

$$B_g = A_p \cdot \Delta P_g^{0,5} \qquad (8)$$

gdzie:

$\boldsymbol{P_p}$ – ciśnienie powietrza w punkcie kontrolnym [Pa];

$\boldsymbol{P_g}$ – ciśnienie gazu w punkcie kontrolnym [Pa];

$\boldsymbol{P^p_{pal}}, \boldsymbol{P^g_{pal}}$ – ciśnienie odpowiednio powietrza i gazu w palenisku [Pa];

$\Delta \boldsymbol{P_p}, \Delta \boldsymbol{P_g}$ – spadek ciśnienia odpowiednio powietrza i gazu [Pa];

A_p – współczynnik przepływu palnika [j. u.].

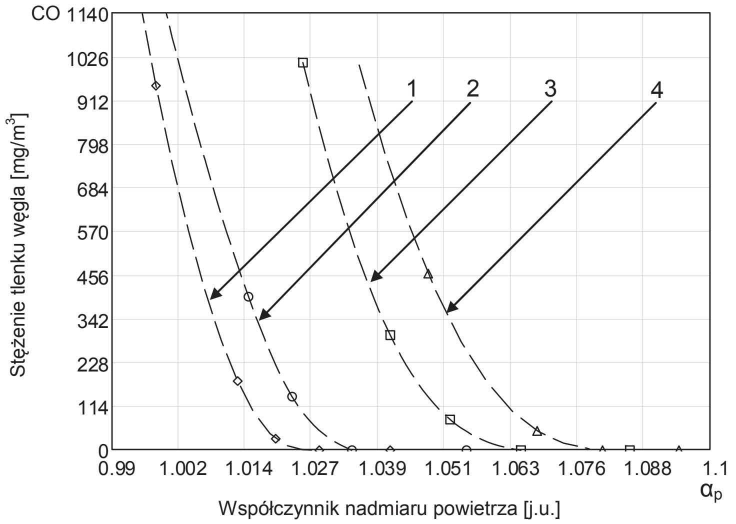
Dla badanych rodzajów palników typu GMG i GMGm aproksymacja doświadczalnych danych według wzoru (7) nie dała pozytywnych wyników, co spowodowane było dwupotokowym schematem ruchu powietrza w palniku. Dlatego też pomiar ciśnienia powietrza wykonywano za wentylatorem. Otrzymane współczynniki aproksymacji dla wariantów wyposażenia kotłów w palniki 2×GMG-7, 3×GMGm-5, 3×GMGB-5,6 podano w tabeli 4.

Tabela 4. Wartość współczynnika $\boldsymbol{A_p}$ w zależnościach (7) i (8)
Table 4. Value of coefficient $\boldsymbol{A_p}$ in *equations* (7) and (8)

Wartość współczynnika	3×GMGB-5,6	3×GMGm-5	2×GMG-7
A_p we wzorze (8)	88,365	119,14	121,08
Współczynnik determinacji	0,987	0,991	0,988
A_p we wzorze (7)	2213,02	2007,31	1991,65
Współczynnik determinacji	0,975	0,991	0,937

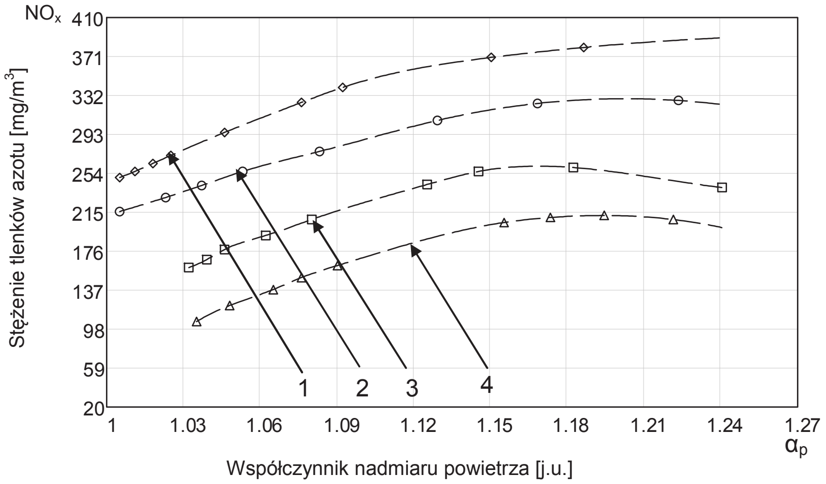
4. Wykorzystanie wyników

Uzyskane wyniki badań dla palników typu GMGB-5,6 oraz GMGm-5 dla dwóch różnych obciążeń kotła wraz z wykorzystaniem opracowanego modelu przedstawiono na poniższych wykresach. Punkty na poszczególnych wykresach obrazują wyniki uzyskane w trakcie badań doświadczalnych, natomiast linie przerywane to krzywe uzyskane poprzez aproksymację danych doświadczalnych za pomocą opracowanego modelu matematycznego.



Rys. 1. Zależność stężenia CO w spalinach od rodzaju palnika, współczynnika nadmiaru powietrza i obciążenia kotła: 1 i 2 – palnik GMGB-5,6: 1 – obciążenie 100%; 2 – 87%; 3 i 4 – palnik GMGm-5: 3 – 110%; 4 – 100%

Fig. 1. CO emission in exhaust fumes in dependence of burner type, surplus air coefficient and boiler's load: 1 and 2 – burner GMGB-5,6: 1 – load 100%; 2 – 87%; 3 and 4 – burner GMGm-5: 3 – 110%; 4 – 100%



Rys. 2. Zależność stężenia NO$_x$ w spalinach od rodzaju palnika, współczynnika nadmiaru powietrza i obciążenia kotła: 1 i 2 – palnik GMGB-5,6: 1 – obciążenie 100%; 2 – 87%; 3 i 4 – palnik GMGm-5: 3 – 110%; 4 – 100%

Fig. 2. NO$_x$ emission in exhaust fumes in dependence of burner type, surplus air coefficient and boiler's load: 1 and 2 – burner GMGB-5,6: 1 – load 100%; 2 – 87%; 3 and 4 – burner GMGm-5: 3 – 110%; 4 – 100%

5. Wnioski

Celem badań doświadczalnych wykonywanych za pomocą modelu matematycznego było ustalenie charakteru wpływu nieregulowanych czynników na optymalne wartości ciśnienia powietrza przed palnikiem, stężenia tlenu oraz tlenku węgla. Aproksymację doświadczalnych danych CO i NO_x w funkcji $\boldsymbol{f}(\boldsymbol{\alpha}_p, \boldsymbol{B}_g)$ w postaci zależności algebraicznych dokonano za pomocą pakietu programów stosowanych „Table Curie-3D”. Zależności aproksymujące wyprowadzono dla warunków odpowiadających warunkom eksperymentów. W celu uwzględnienia wpływu zewnętrznych czynników na otrzymane wartości wprowadzono poprawki na następujące wartości:

- zmianę współczynnika nadmiaru powietrza na skutek zasysania przez nieszczelności do paleniska;
- zmianę przepływu powietrza lub gazu w przypadku zmiany ich temperatury.

Literatura

1. **Акимченко Е. М., Каган Р. Г.**: *Опыт эксплуатации горелок ГМГ на котлах типа ДКВР*, Газовая промышленность. 10(1), 31–33 (1970).
2. **Kalicka Z., Jerzak W., Kawecka Cebula E.**: *The Effect of combustion of natural gas with 21–29% $O_2/CO_2/N_2$ mixtures on emission of carbon monoxide.* Archives of Environmental Protection. 39(4), 93–103 (2013).
3. **Szkarowski A., Janta-Lipińska S.**: *Automatyczne sterowanie jakością spalania paliwa stałego w kotłach przemysłowo-grzewczych*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 11, 241–257 (2009).
4. **Szkarowski A., Janta-Lipińska S.**: *Optymalizacja pracy kotłów metodą sterowanego poziomu niezupełności spalania*. Polityka energetyczna. 12(1), 129–137 (2009).
5. **Szkarowski A., Janta-Lipińska S.**: *Modelowanie optymalnego spalania w kotłach przemysłowo-grzewczych*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 13, 511–525 (2011).
6. **Розенфельд Э.И.**: *Сжигание газа и мазута с минимальным выбросом продуктов неполного сгорания.* ВИНИТИ. Сер. "Топлив. баланс" 1980.
7. **Романов А. К.**: *Микропроцессорная техника – основа автоматизации народного хозяйства*, Микропроцессорные средства и системы. 1(1), 3–5 (1984).
8. **Росляков П. В., Егорова Л. Е.**: *Влияние основных характеристик зоны активного горения на выход оксидов азота*, Теплоэнергетика. 9(1), 22–26 (1996).

9. **Ротач В.Я.**: *Теория автоматического управления теплоэнергетическими процессами*, М.: Энергоатомиздат 1985.

Experimental Research Vs. Accuracy of the Elaborated Model

Abstract

For an extensive range of experimental studies one is constantly looking for the way which would shorten our worktime as well as decrease the amount of measurements and at the same time not worsen the credibility of set research assumptions. One way is the method of planning experiments or elaborating a theoretical physico-mathematical model. The authors' team decided to elaborate a new physico-mathematical model, as a work line, which determined the range of optimal values for efficiency and ecology ratio of fuel combustion.

While conducting the experimental research the authors' team dealt mainly with the modernization of industrial boilers and heaters to improve their operation ratio in respect of efficiency and ecology. Thanks to the created model the assessment of combustion optimality was performed from the viewpoint of both efficiency and ecology made on the basis of energo-ecological criteria elaborated by the authors.

The use of model allowed the authors to considerably decrease the amount of required work mode change of boilers and conducted measurements on real industrial-heating objects. The studies were performed on the real objects of URAN SPB and TERA companies. During the experimental works one examined the influence of quantitive and qualitive ratio of distributing the air into combustion zone as well as boiler power on the emission of CO and NO_x. The studies were conducted on identical steam boilers DKVR-20-13 equipped with various fan burners: GMGB-5,6, GMGm-5 and GMG-7. The achieved results of experimental research were set with the previously elaborated mathematical model in order to determine the adequacy rate of achieved results (fig. 1–2). The credible approximating dependence that determined the experimental data was made up by the function including the determination coefficient above 0.95. The values of approximating factors for the particular measurements were set in the table (1–4).

Słowa kluczowe:
modelowanie naukowe, aproksymacja, stężenie, spalania, badania naukowe

Keywords:
scientific modeling, aproximation, concentration, combustion, scientific research

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Zrównoważone gospodarowanie ściekami na przykładzie obszarów wiejskich

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1. Wstęp

Znaczny dopływ ładunku związków azotu i fosforu za pośrednictwem rzek m.in. z Polski przyczynia sie do eutrofizacji wód Morza Bałtyckiego. Szacuje się, że ok. 75% ogólnego ładunku azotu i aż 95–99% ogólnego ładunku fosforu jest doprowadzane do Bałtyku w odpływie rzecznym. Pozostałość pochodzi z atmosfery. Około 25% ładunku azotu pochodzi z depozycji atmosferycznej, która jest drugim istotnym źródłem zanieczyszczenia Bałtyku. Długi czas wymiany wód Bałtyku wynoszący od 25–30 lat powoduje, że tylko bezpośrednie działania w jego zlewni mogą przyczynić sie do poprawy jakości jego wód [8, 11, 12, 23].

Wśród dziewięciu państw usytuowanych w rejonie Morza Bałtyckiego, Polska odprowadza największy ładunek związków azotu i fosforu. Podejmowane działania w ostatnich latach znacznie ograniczyły jego dopływ. W okresie ostatnich 20 lat ładunek azotu ogólnego odprowadzany z terytorium naszego kraju do wód Morza Bałtyckiego uległ obniżeniu o ok. 43,0%, a ładunek fosforu o ok. 62% [9]. Pomimo to odprowadzane ładunki związków biogennych z obszaru Polski wciąż są zbyt wysokie. Aktualnie odprowadzany ładunek rzekami spływającymi z terytorium Polski wynosi odpowiednio: 120 tys. ton N_{og}/rok i 5 tys. ton P_{og}/rok, co stanowi 20% ogólnego ładunku odprowadzanego do Bałtyku. Natomiast ładunek odprowadzany ze ściekami oczyszczonymi z komunalnych oczyszczalni ścieków jest prawie 10-krotnie niższy [8].

Zanieczyszczenie wód powierzchniowych jest wywołane przede wszystkim nieuporządkowaną gospodarką ściekowo-osadową obszarów wiejskich. Wg GUS [10] w 2012 roku odsetek osób korzystających z sieci wodociągowej wynosił 76,2%, natomiast do sieci kanalizacyjnej podłączonych było zaledwie 29,4% ludności obszarów wiejskich. W wielu miejscach budowa sieci kanalizacyjnej jest nieuzasadniona pod względem ekonomicznym i środowiskowym.

Realizacja Krajowego Programu Zagospodarowania Ściekami spowodowała szereg działań związanych z budową i modernizacją dotychczasowych obiektów oczyszczania ścieków. Pomimo, że liczba oczyszczalni ścieków stale rośnie, wciąż bardzo dużo gospodarstw nie ma możliwości podłączenia do komunalnych oczyszczalni. Jednym z elementów, który mógłby uporządkować gospodarkę komunalną, szczególnie na terenach niezurbanizowanych, jest zastosowanie przydomowych oczyszczalni ścieków (POŚ), np. z wykorzystaniem technologii hydrofitowej. Nowe rozwiązania wykorzystujące tę technologię umożliwiają zagospodarowanie ścieków, co wynika nie tylko z możliwości ich oczyszczania, ale również zagospodarowania osadów ściekowych w warunkach lokalnych.

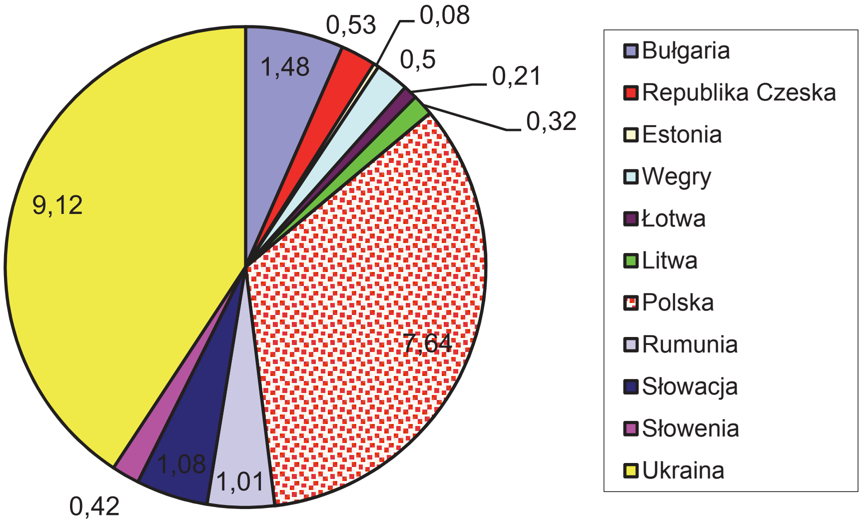
W pracy podano charakterystykę sanitacji obszarów wiejskich w Polsce na tle krajów Europy Środkowej i Wschodniej oraz najnowsze przykłady zagospodarowania ścieków i osadów w systemach wykorzystujących technologie hydrofitowe.

2. Gospodarka wodno-ściekowa obszarów wiejskich

W krajach Europy Środkowej i Wschodniej prawie 30% populacji (odpowiednio 42 mln ludności) zamieszkuje miejscowości, gdzie liczba mieszkańców jest poniżej 2000. Zaledwie ok. 9,0% ludności tych terenów jest podłączonych do komunalnych oczyszczalni ścieków.

Pomimo, że w Polsce liczba komunalnych oczyszczalni ścieków wynosi 3157 i jest najwyższa na obszarze Środkowo-Wschodniej Europy, to jednak tylko 64,0% ludności odprowadza do nich ścieki. Szacuje się, że aż 7,64 mln osób nie ma możliwości podłączenia się do komunalnych oczyszczalni ścieków (rys. 1).

W Polsce na jeden kilometr sieci kanalizacyjnej przypada 400 mieszkańców miast, a jedynie 74 mieszkańców wsi [2]. Przyjmuje się, że budowa kanalizacji jest technicznie i ekonomicznie uzasadniona, gdy na 1 km jej długości przypada mniej niż 120 osób, a na terenach objętych szczególną ochroną prawną mniej niż 90 osób [25]. Dlatego dla wielu rejonów wiejskich rozbudowa sieci kanalizacyjnej jest ekonomicznie i technicznie nieuzasadniona.



Rys. 1. Ludność bez możliwości podłączenia do komunalnej oczyszczalni ścieków, opracowane na podstawie [13]
Fig. 1. The population without the possibility of connecting to municipal wastewater treatment plant, on the basis of [13]

W przypadku braku możliwości podłączenia się do sieci komunalnych konieczne jest stosowanie kanalizacji bezodpływowej, np. zbiorników bezodpływowych, tzw. szamb lub przydomowych oczyszczalni ścieków.

Liczba zbiorników bezodpływowych, które są przeznaczone do gromadzenia nieczystości ciekłych uległa zmniejszeniu w ostatnich latach, ze względu na wysokie koszty eksploatacji. W 2012 roku ich liczba wynosiła 2 318 tys. (podczas gdy w 2009 roku – 2 433 tys.) [10]. Wg Kundziewicza i Miłaszewskiego [17] całkowity koszt budowy i eksploatacji zbiorników bezodpływowych jest niemal 2-krotnie wyższy niż w przypadku POŚ.

W ostatnich latach w Polsce odnotowano znaczny wzrost liczby nowych POŚ z 62 000 w roku 2009 do 126 164 w roku 2012 [10]. Szacuje się, że zrównoważenie gospodarki ściekowo-osadowej będzie związane z budową kolejnych 700 tys. obiektów obsługujących ok. 3,8 mln mieszkańców [21].

Dotychczas wykazano, że usuwanie zanieczyszczeń ze ścieków na obszarach wrażliwych na eutrofizację wymaga stosowania Hybrydowych Systemów Hydrofitowych (HSH) złożonych ze złóż z pionowym i poziomym przepływem ścieków [21].

Badania przeprowadzone przez zespół pracowników z Politechniki Gdańskie [6, 21, 22] w ramach projektu norweskiego NORWET wykazały, że obiekty te charakteryzują się wysoką efektywnością usuwania zanieczyszczeń, pod warunkiem prawidłowego eksploatowania i funkcjonowania m.in. osadników gnilnych oraz przestrzegania zalecanych obciążeń hydraulicznych oraz ładunków materii organicznej i związków azotu.

Przydomowe oczyszczalnie ścieków definiowane są zazwyczaj jako obiekty obsługujące do 50 mieszkańców. Ich maksymalna przepustowość w Polsce wynosi 5 m^3/d wg Prawa Wodnego [27] i 7,5 m^3/d wg Prawa Budowlanego [28]. Oczyszczalnie lokalne przeznaczone są do oczyszczania ścieków pochodzących od 50 do 2000 mieszkańców. Wg Rozporządzenia Ministra Środowiska z dn. 24 lipca 2006 [26] ścieki odprowadzane, do wód płynących, z tych obiektów powinny spełniać następujące warunki: $BZT_5 \leq 40$ mgO_2/dm^3, ChZT ≤ 150 mgO_2/dm^3, zawiesina ogólna ≤ 50 mg/dm^3. Dodatkowo, gdy ścieki odprowadzane są do wód stojących lub na obszarach szczególnie wrażliwych na eutrofizację (obecnie cały obszar Polski) należy zapewnić stężenie $N_{og} \leq$ 30 mg/dm^3 oraz $P_{og} \leq 5{,}0$ mg/dm^3. W tych warunkach HSH, ze względu na prostą budowę i eksploatację, zapewniają skuteczne usuwanie związków biogennych i stanowią konkurencje dla systemów konwencjonalnych.

Odpowiednio skonstruowane i eksploatowane systemy hydrofitowe są również wykorzystywana do odwadnia i stabilizacji osadów ściekowych pochodzących zarówno z konwencjonalnych oczyszczalni ścieków, jak również z POŚ. Metoda ta polega na stosowaniu wielowarstwowych zalewów osadów ściekowych (o niskiej zawartości suchej masy 0,5–1%) najczęściej w specjalnie zbudowanych obiektach naziemnych lub podziemnych zasiedlonych trzciną (*Phragmites australis*) [16, 18].

3. Metodyka badań

W ramach badań monitorowano w województwie pomorskim pracę lokalnych systemów hydrofitowych przeznaczonych do biologicznego oczyszczania ścieków (pochodzących od 15 do 750 mieszkańców) po wstępnym mechanicznym ich oczyszczaniu w osadnikach gnilnych. Obiekty znajdowały się w Darżlubiu k. Pucka, w Wieszynie, Wiklinie i Sarbsku k. Słupska oraz w Schodnie k. Kościerzyny [6].

Analizowano również 9 hybrydowych przydomowych oczyszczalni ścieków (POŚ) wybudowanych w 2009 roku na terenie gminy Stężyca w ramach projektu NORWET. Obiekty te pracowały w trzech konfiguracjach.

Przeprowadzono również badania jakości osadów ściekowych stabilizowanych w systemach hydrofitowych pracujących w warunkach lokalnych. Stabilizacji poddawano osady ściekowe pochodzące z konwencjonalnych oczyszczalni ścieków, zlokalizowanych w Helsinge, Rudkobing, Nakskov, Vallo k. Kopenhagi (w poszczególnych obiektach znajdowało się 8–10 kwater, które zasilano osadami pochodzącymi od 9 000 do 40 000 OLM (Obliczeniowa Liczba Mieszkańców), czas eksploatacji wynosił od 7–15 lat) oraz z oczyszczalni ścieków zlokalizowanej w Gniewinie w woj. pomorskim (w obiekcie znajduje się 6 kwater zasilanych osadami pochodzącymi od 24 000 mieszkańców; czas eksploatacji 2 lata) [1,5,16].

W analizowanych oczyszczalniach pobierano próbki ścieków doprowadzanych i odprowadzanych z uwzględnieniem czasu zatrzymania ścieków w monitorowanych obiektach badań [5, 6]. W pobranych próbkach wykonywano pomiary stężeń zawiesiny ogólnej, materii organicznej (BZT_5 i ChZT) oraz azotu ogólnego i fosforu ogólnego. Zastosowane procedury badań są zgodne z Polskimi Normami i zaleceniami podanymi w Rozporządzeniu Ministra Środowiska z dnia 24 lipca 2006 [26].

W celu określenia współzależności liniowej zmiennych zastosowano współczynnik korelacji Pearsona (r) przy założeniu, że dla $| r | < 0,2$ występuje brak związku liniowego, dla wartości 0,2–0,4 istnieje słaba zależność (w tych badaniach traktowana jako nieistotna zależność), dla wartości 0,4–0,7 występuje umiarkowana zależność, natomiast dla wartości z zakresu 0,7–0,9 zależność jest silna, a dla $| r | > 0,9$ bardzo silna.

W osadach ściekowych stabilizowanych metodą hydrofitową wykonano oznaczenie zawartości suchej masy i materii organicznej oraz stężeń azotu ogólnego i fosforu ogólnego. Wszystkie oznaczenia wykonano zgodnie z obowiązującymi Polskimi Normami [17].

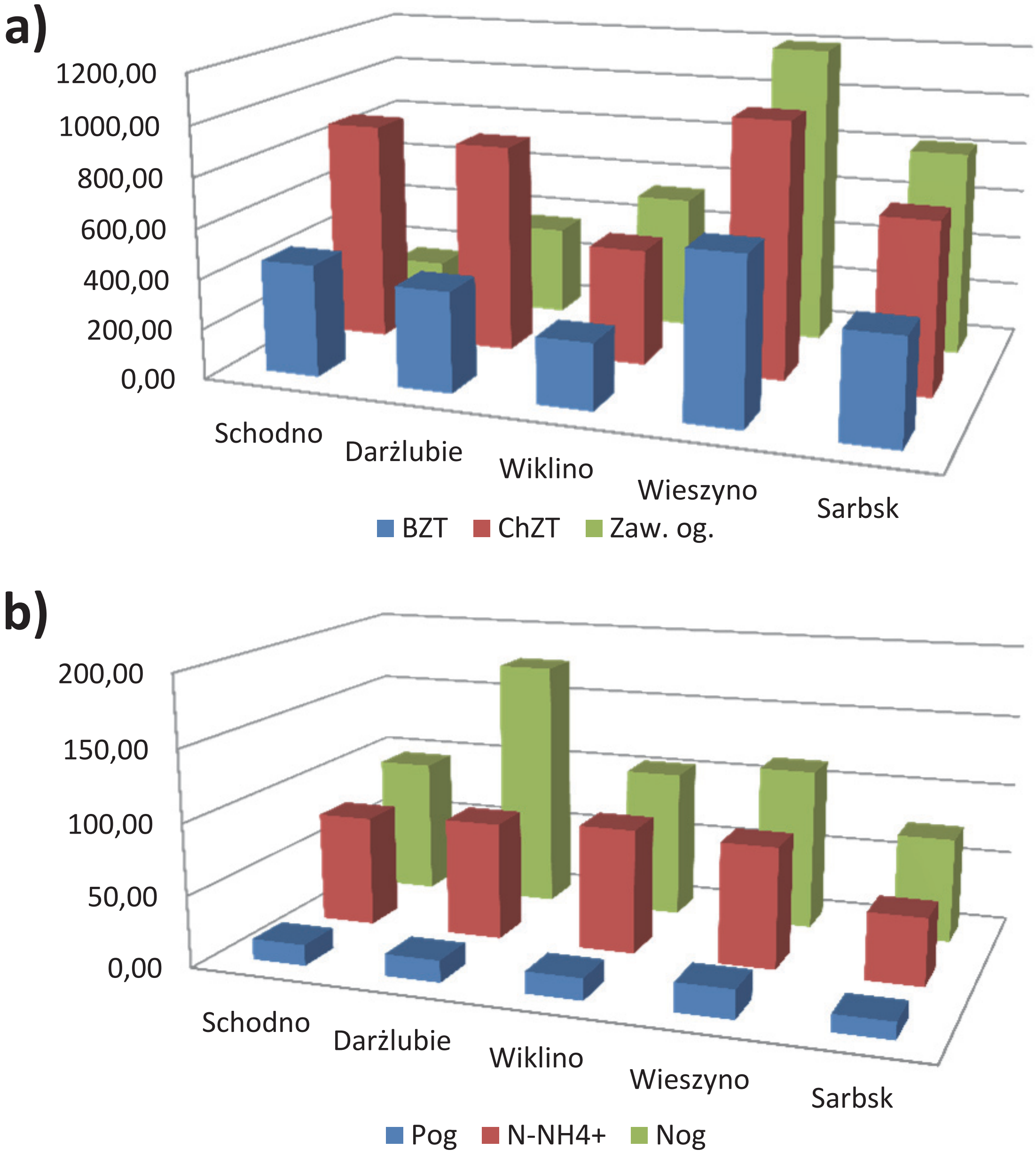
4. Wyniki badań i ich omówienie

4.1. Lokalne oczyszczalnie hydrofitowe

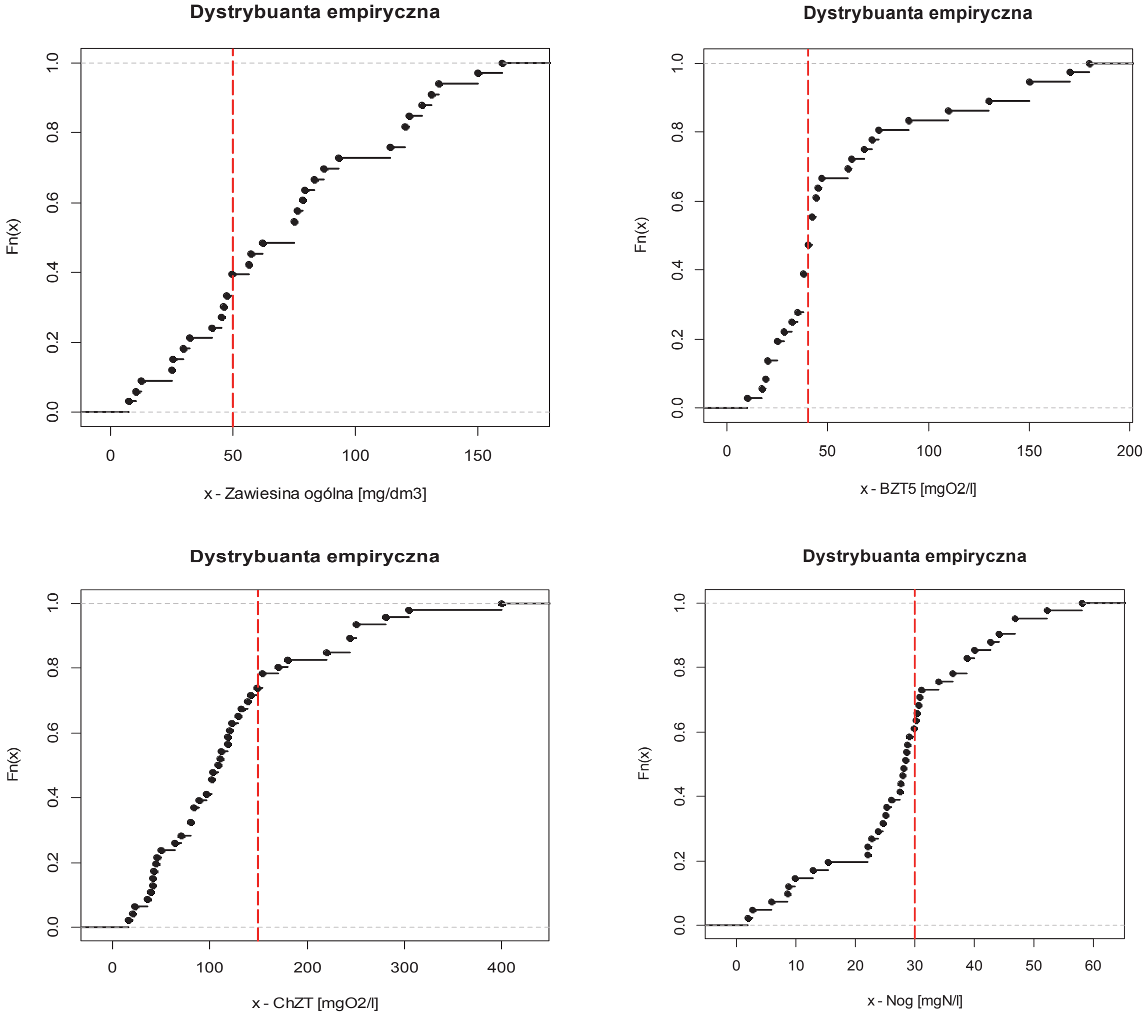
Na rysunku 2 przedstawiono charakterystykę jakości ścieków doprowadzanych do analizowanych HSH. Jakość ścieków odprowadzanych do środowiska przedstawiono na rysunku 3 z podaniem dystrybuanty rozkładu Weibulla dla poszczególnych stężeń analizowanych zanieczyszczeń.

Jakość ścieków doprowadzanych do analizowanych obiektów różniła się znacznie. Obiekt w Wieszynie zasilany był ściekami o najwyższych stężeniach zanieczyszczeń. Wysokie stężenie zawiesiny ogólnej oraz materii organicznej w ściekach doprowadzanych do pierwszego złoża w tym obiekcie potwierdza niewłaściwą eksploatację osadnika gnilnego. Natomiast ścieki doprowadzane do oczyszczalni w Schodnie charakteryzowały się dużą zmiennością. Bardzo wysokie stężenia materii organicznej doprowadzane do obiektów w Darżlubiu i Schodnie były spowodowane dopływem gnojowicy z obszarów przylegających do oczyszczalne. Stężenia zanieczyszczeń w ściekach doprowadzanych były bardzo wysokie, co może wskazywać na nieefektywną pracę osadników wstępnych w tych obiektach. W konsekwencji analizowane obiekty zasilane były ściekami o wyższych ładunkach zanieczyszczeń niż te, które zostały przyjęte w projektach budowlanych. Przekładało się to na ich niższą efektywność usuwania charakterystycznych zanieczyszczeń (rys. 3).

Zaledwie 40% analizowanych próbek (co dopowiada 153 dobom w roku kalendarzowym) spełniało wymogi, co do wartości stężenia zawiesiny ogólnej w oczyszczonych ściekach (rys. 3a). Podczas prowadzonego monitoringu stwierdzono, że większość złóż hydrofitowych pracujących w pierwszym stopniu analizowanych HSH uległa kolmatacji wskutek doprowadzania zbyt dużych stężeń materii organicznej w postaci zawiesinowej lub /i nieprawidłowo zaprojektowanego systemu rozprowadzania ścieków. W konsekwencji tworzyły się uprzywilejowane strefy przepływu ścieków np. doprowadzane ścieki płynęły po powierzchni, co spowodowało zmniejszenie skuteczności usuwania zawiesiny ogólnej. Dla materii organicznej (BZT_5 i ChZT) oraz azotu ogólnego wskaźniki niezawodności zmieniały się od 60 do 80 % (rys. 3 b-d). Zaobserwowano bardzo dobrą niezawodność pracy analizowanych HSH dla azotu ogólnego i ChZT (303 i 292 dni w roku, odpowiednio) i nieco niższą dla BZT$_5$ wynoszącą 219 dni w roku.



Rys. 2. Średnie wartości stężeń charakterystycznych zanieczyszczeń w ściekach doprowadzanych do analizowanych obiektów a) BZT, ChZT i zawiesina ogólna, b) P_{og}, N_{og} i $N\text{-}NH_4^+$
Fig. 2. Average values of specific pollutant concentrations in wastewater supplied to the analyzed objects a) BOD, COD and total suspended solids, b) P_{og}, N_{og} and $N\text{-}NH_4^+$



Rys. 3. Dystrybuanta empiryczna rozkładu stężeń zanieczyszczeń w ściekach oczyszczonych w analizowanych HSH dla: (a) zawiesiny og., (b) BZT_5, (c) ChZT, (d) N_{og}

Fig. 3. The empirical distribution function of pollutant concentrations in treated wastewater in analyzed objects for: (a) suspended solids, (B) BOD_5, (c) COD, (d) N_{tot}

Dotychczas oczyszczalnie hydrofitowe były stosowane w drugim stopniu oczyszczania ścieków do 2000 mieszkańców. Ostatnio budowane są też obiekty oczyszczające ścieki bytowe, pochodzące nawet od 3500 mieszkańców. Odpowiedni dobór technologii, uwzględniający zastosowanie wielostopniowych złóż ze zmiennym poziomym i pionowym przepływem ścieków, pozwolił na zmniejszenie jednostkowej powierzchni nawet do 1,7 m^2/OLM. Jest to znacznie mniejsza powierzchnia w porównaniu do dotychczas zalecanych 5 m^2/OLM [7].

4.2. Przydomowe oczyszczalnie hydrofitowe

Najbardziej popularnymi, dotychczas wykorzystywanymi urządzeniami POŚ są drenaże rozsączające i filtry piaskowe. Mniej popularne są złoża biologiczne i reaktory z osadem czynnym. Zasadniczą wadą drenażu rozsączającego jest duże zapotrzebowanie na powierzchnię, wynoszące od 20 do 60 m^2/M, brak możliwości kontrolowania jakości oczyszczonych ścieków oraz zagrożenie zanieczyszczenia wód podziemnych. W przypadku filtrów piaskowych konieczne jest stosowanie drogiego, płukanego i sortowanego piasku do wypełnienia złoża, a przy niekorzystnym nachyleniu terenu konieczność użycia pompy. Często również występuje problem z przykrymi zapachami. Reaktory z osadem czynnym mogą zapewnić skuteczne usuwanie materii organicznej oraz związków azotu i fosforu. Jednak koszt budowy oraz oczyszczania ścieków jest wyższy, a ich eksploatacja wymaga fachowej obsługi oraz zabezpieczenia serwisu urządzeń. Złoża biologiczne mogą być umieszczone w zbiorniku o konstrukcji podobnej do osadnika gnilnego. Obiekty te potrzebują jednak długiego czasu rozruchu i są energochłonne [3, 21, 24].

Stosunkowo nową metodą wykorzystywaną w POŚ są wielostopniowe systemy hydrofitowe. Zasadniczą zaletą tej technologii jest prosta budowa, łatwa eksploatacja oraz naturalny wygląd. Dodatkowo wg Kundziewicza i Miłaszewskiego [15] koszty eksploatacji tego typu oczyszczani są najniższe w porównaniu z innymi urządzeniami stosowanymi w POŚ.

W Polsce pierwsze przydomowe oczyszczalnie ścieków wykorzystujące metodę hydrofitową pojawiały sie w latach dziewięćdziesiątych ubiegłego wieku. Były to obiekty z poziomym przepływem. Dopiero w roku 2004 w Polsce zaczęto stosować hydrofitowe oczyszczalnie jednostopniowe z pionowym przepływem ścieków. Po pilotowych obiektach wybudowanych w rejonie Gdańska i Wrocławia [20], wdrażanie tego typu obiektów rozpoczęto na Podlasiu. Obecnie funkcjonuje tam ponad 60 takich oczyszczalni.

W ramach projektu "Innowacyjne rozwiązanie gospodarki ściekowo-osadowej dla terenów niezurbanizowanych" w lipcu 2009 wybudowano na terenie gm. Stężyca na Kaszubach dziewięć oczyszczalni hydrofitowych. Zastosowano 3 konfiguracje urządzeń:

- I konfiguracja – osadnik wstępny o przedłużonym czasie zatrzymania (5–6 dni), następnie złoże typu VF i staw,
- II konfiguracja – osadnik wstępny, następnie 2 sekwencyjnie pracujące złoża typu VF I i VF II oraz staw,
- III konfiguracja – osadnik wstępny, prefiltr wypełniony materiałem pollytag, następnie złoże typu HF i staw [21].

W każdej konfiguracji wybudowano 3 obiekty.

Badania obiektów hydrofitowych podzielono na dwa okresy badawcze. Pierwszy okres stanowiły lata 2010–2011 (prowadzone zarówno w okresie wegetacyjnym, jak i pozawegetacyjnym). Drugi okres odnosił sie do badań prowadzonych w latach 2012–2013 (uwzględniających jedynie okres pozawegetacyjny). Uzyskane wyniki skuteczności usuwania zanieczyszczeń w wyżej wymienionych obiektach podano w tabeli 1.

Tabela 1. Średnia skuteczność$^{*)}$ usuwania zanieczyszczeń w hydrofitowych POŚ w gm. Stężyca na Kaszubach, %
Table 1. The average efficiency$^{*)}$ of pollutants removal in hydrophite on-site WWTP in Stężyca in Kashubian region,%

Konfiguracja	Ob.	Parametr							
		I okres badań				II okres badań			
		Zaw. og	ChZT	N_{og}	P_{og}	Zaw. og	ChZT	N_{og}	P_{og}
I	1	68,2	84,1	70,6	68,2	93,5	91,5	82,3	21,2
	2	65,4	60,0	55,9	65,4	90,7	91,2	78,5	40,0
	3	29,1	53,1	55,6	29,1	82,0	86,3	75,0	5,6
II	1	67,8	68,6	75,9	67,8	79,9	81,5	73,8	1,9
	2	61,4	83,1	79,0	61,4	86,8	84,7	73,5	21,6
	3	64,0	78,6	54,3	64,0	91,3	76,5	77,8	13,7
III	1	57,6	79,9	49,7	57,6	83,7	85,5	63,6	30,1
	2	54,7	82,4	69,9	54,7	81,2	85,8	64,7	26,2
	3	50,0	83,3	55,8	50,0	87,0	85,9	68,8	37,4

*) *Skuteczność policzono jako* $(C_o–C_k)/C_k \cdot 100\%$*, gdzie* C_o *– stężenie na dopływie,* C_o *– stężenie na odpływie*

We wszystkich konfiguracjach stwierdzono najniższą skuteczność usuwania związków fosforu. Natomiast skuteczność usuwania zawiesiny ogólnej i materii organicznej (wyrażonej w ChZT) była wysoka i wynosiła ok. 90,0%. Stwierdzono również wysoką średnią skuteczność usuwania azotu ogólnego powyżej 60,0%.

Najwyższą skuteczność oczyszczania zapewniały obiekty pracujące w konfiguracji II. Działanie obiektów pracujących w konfiguracjach I i III było również efektywne.

Uzyskane wyniki porównano z efektywnością usuwania zanieczyszczeń w obiektach hydrofitowych analizowanych w literaturze (tabela 2).

Na podstawie analizy dotychczas funkcjonujących obiektów stwierdzono, że najniższą skutecznością usuwania materii organicznej charakteryzowały się obiekty z przepływem poziomym typu HF. Średnio skuteczność usuwania BZT_5 wynosiła od 45,8% do 78,7%. Skuteczność usuwania N_{og} była jeszcze niższa i wynosiła od 24,2% do 44,7%. Główną przyczyną słabej efektywności usuwania zanieczyszczeń była niewłaściwa eksploatacja osadników gnilnych oraz dopływ do złóż ścieków zawierających zawiesiny i tłuszcze. Powodowało to w niektórych przypadkach zmianę charakteru działania obiektów z obiektów z przepływem podpowierzchniowym na obiekty z przepływem powierzchniowym (typu SF – surface flow).

Znacznie wyższą skuteczność usuwania zanieczyszczeń uzyskano w obiektach hydrofitowych z przepływem pionowym. Średnia efektywność usuwania zawiesiny ogólnej wynosiła 86,0%, BZT_5 – 96,0%, a ChZT – 88,0%. Skuteczność usuwania związków biogennych w obiektach tego typu była znacznie niższa i wynosiła średnio 58,0% dla N_{og} i 31,0% dla P_{og}.

Najwyższą efektywność usuwania związków fosforu i azotu uzyskano w obiektach hybrydowych. Natomiast usuwanie materii organicznej oraz zawiesiny w tych obiektach było na poziomie efektywności uzyskanej w obiektach z przepływem pionowym.

Obiekty hydrofitowe z przepływem pionowym (VF) oraz obiekty hybrydowe (bez względu na zastosowaną konfiguracje charakteryzowały sie bardzo wysoką skutecznością usuwania zawiesiny ogólnej i materii organicznej (tabela 1 i 2). Znacznie niższa skuteczność usuwania materii organicznej występowała w obiektach z przepływem poziomym (HF).

Tabela 2. Średnia skuteczności usuwania zanieczyszczeń w obiektach hydrofitowych stanowiących POŚ
Table 2. The average removal efficiency in hydrophite objects as on-site WWTPs

Obiekt	Konfiguracja	Parametr					Źródło
		Zaw. og.	BZT_5	ChZT	N_{og}	P_{og}	
Wawrów, gm. Santok	HF	b.d.	66,8	b.d.	38,5	b.d.	Obarska-Pempkowiak i in. [19]
Gralewo, gm. Santok	HF	b.d.	64,2	b.d.	30,8	b.d.	Obarska-Pempkowiak i in. [19]
Małyszyn, gm. Mirzec	HF	b.d.	45,8	b.d.	44,7	b.d.	Obarska-Pempkowiak i in. [19]
Rokitno, gm. Rokitno	HF	b.d.	78,7	b.d.	24,2	b.d.	Obarska-Pempkowiak i in. [19]
Jamiłkowski, gm. Sokoły	VF	88,1	98,1	88,9	41,9	61,5	Gajewska i Obarska-Pempkowiak [4]
Stypółkowski, gm. Sokoły	VF	84,3	94,9	86,8	13,4	54,1	Gajewska i Obarska-Pempkowiak [4]
Dąbrowica (układ I), gm. Jastków	HF-VF	83,0	93,0	88,0	48,0	77,0	Jóźwiakowski [14]
Dąbrowicy (układ II), gm. Jastków	VF-HF	88,0	94,0	91,0	61,0	84,0	Jóźwiakowski [14]
Janowo, gm. Janowa	VF-HF	89,0	96,0	94,0	66,0	95,0	Jóźwiakowski [14]

b.d – brak danych*

Obiekty, w których zastosowano więcej niż jedno złoże hydrofitowe, charakteryzowały się zdecydowanie większą skutecznością usuwania związków biogennych. Najwyższą skuteczność usuwania związków azotu i fosforu uzyskano przy konfiguracji złóż VF-HF (tabela 1 i 2).

4.3. Stabilizacja osadów ściekowych w warunkach wiejskich

Osady ściekowe stanowią bardzo kłopotliwy produkt uboczny procesu oczyszczania ścieków. Powstają one zarówno w komunalnych oczyszczalniach ścieków, jak i POŚ. Wytwarzane osady są przyczyną pojawiania sie kolejnych problemów. Po pierwsze, ze względu na sanitację obszarów wiejskich i budowę wielu POŚ wzrasta ilość produkowanych osadów. Po drugie brak wystarczającej wiedzy oraz odpowiednich warunków i środków ich zagospodarowania zwłaszcza wtedy, gdy centralne komunalne oczyszczalnie ścieków są znacznie oddalone od gospodarstw wiejskich.

Rozwiązaniem problemów osadów ściekowych zarówno w POŚ, jak i małych oraz średnich oczyszczalniach ścieków mogłaby być technologia hydrofitowa do odwadniania i stabilizacji osadów ściekowych.

Efektywność działania tych systemów jest porównywalna z efektami uzyskiwanymi w urządzeniach mechanicznych np. prasach ciśnieniowych (gdzie zawartość suchej masy w odwadnianych osadach może wynosić nawet 40%) [15, 16, 18]. Dodatkowo koszt unieszkodliwiania osadów w systemach hydrofitowych jest stosunkowo niski i stanowi zaledwie 5–10% kosztów powszechnie stosowanych rozwiązań [15]. W odróżnieniu od tradycyjnych poletek ociekowych w systemach hydrofitowych następuje znaczna intensyfikacja wielu procesów biochemicznych, które powodują nie tylko bardziej intensywne odwadnianie osadów, lecz również w wyniku postępującej stabilizacji istnieje możliwość przekształcenia pozostałej materii w substancję humusową lub kompost.

W Polsce dotychczas wybudowano i eksploatowani kilka obiektów pilotowych opisanych przez Kołecką i Obarską-Pempkowiak [16] oraz Zwarę i Obarską-Pempkowiak [26]. Jednym z pierwszych obiektów wdrożonych w pełnej skali jest obiekt trzcinowy w Gniewinie. Porównanie jakości osadów ściekowych stabilizowanych w obiekcie trzcinowym w Polsce w ciągu 1 roku eksploatacji oraz czterech duńskich obiektów trzcinowych eksploatowanych w okresie od 7 do 15 lat podano w tabeli 3.

Na podstawie podanych wyników badań stwierdzono, że obiekt trzcinowy w Gniewinie charakteryzował się najniższą zawartością suchej masy, a także najwyższą zawartością materii organicznej. W obiektach z Danii wartości tych parametrów były bardziej do siebie zbliżone. Znaczne różnice w zawartości suchej masy i materii organicznej pomiędzy omawianymi obiektami wynikały przede wszystkim z czasu eksploatacji. Wysoka zawartość materii organicznej w osadach ściekowych świadczy o tym, że osady te nie zostały jeszcze ustabilizowane. Doświadczenia z eksploatacji obiektów duńskich wykazały, że konieczne jest długookresowe zatrzymanie osadów w obiektach, aby umożliwić pełną stabilizację.

Tabela 3. Jakość osadów ściekowych odwadnianych i stabilizowanych w obiektach trzcinowych
Table 3. The quality of sewage sludge dewatered and stabilized in reed bed systems

Parametr	Obiekty duńskie				Obiekt polski
	Helsinge	Rudkobing	Nakskov	Vallo	Gniewino
Sucha masa, %	20,7±2,6	29,3±3,5	23,6 ±2,9	26,1±2,7	11,8±2,4
Materia organiczna, % s.m.	41,1±2,9	42,0±2,3	44,1±2,0	46,0±4,3	57,1±11,5
Azot ogólny, %s.m	2,0±0,1	1,9±0,2	2,4±0,3	2,2±0,3	4,9±1,0
Fosfor ogólny, %s.m.	3,8±0,2	4,7±0,1	4,1±0,4	4,2 ±0,6	4,1±0,8

Stężenie fosforu ogólnego było we wszystkich obiektach na porównywalnym poziomie i było znacznie powyżej średnich wartości w porównaniu do osadach ściekowych odwadnianych w urządzeniach mechanicznych. Wg Bienia [1] wartości zmieniają się od 0 do 1,5% s.m. Stężenie azotu ogólnego w osadach z obiektu trzcinowego w Gniewinie było dwukrotnie wyższe niż dla osadów stabilizowanych z Danii. Uzyskane wartości były porównywalne z wartościami azotu ogólnego podawanymi przez Bienia [1] (wynoszącymi od 1,5 do 5,0% s.m.). Stosunkowo wysokie stężenia azotu w Gniewinie były spowodowane wysokim stężeniem związków azotu w oczyszczanych ściekach, co potwierdza dopływ nawozów organicznych w spływach powierzchniowych ze zlewni o charakterze rolniczym.

Uzyskane rezultaty potwierdzają, że analizowana metoda unieszkodliwiania i potencjalnego zagospodarowania osadów ściekowych w warunkach lokalnych stanowi alternatywę dla metod stosowanych w oczyszczalniach ścieków. W przypadku braku komunalnych oczyszczalni ścieków w warunkach wiejskich może znacznie obniżyć koszty związane z transportem osadów.

5. Wnioski

Na podstawie przeprowadzonych badań odnoszących się do najnowszych zastosowań zagospodarowania ścieków i osadów w systemach hydrofitowych sformułowano następujące wnioski:

1. Metoda hydrofitowa stanowi dobry przykład inżynierii ekologicznej, a jej zastosowanie w gospodarce komunalnej umożliwia zrównoważone gospodarowanie ściekami.
2. Lokalne systemy hydrofitowe można stosować w biologicznym stopniu oczyszczania ścieków do 3500 mieszkańców. Przy prawidłowej pracy osadników wstępnych obiekty te charakteryzują się dużą skutecznością usuwania zanieczyszczeń. Analizowane obiekty charakteryzowały sie wysokimi wskaźnikami niezawodności dla azotu ogólnego i ChZT.
3. Obiekty hydrofitowe dobrze sprawdzają się jako przydomowe oczyszczalnie ścieków. Największą skutecznością usuwania zanieczyszczeń charakteryzowały się obiekty hybrydowe.
4. Odpowiednio skonstruowane systemy trzcinowe zapewniają skuteczne odwadnianie i stabilizację osadów ściekowych. Przeprowadzone badania wykazały, że ustabilizowane osady stanowią bezpieczny produkt pod względem sanitarnym i chemicznym, a tym samym stanowią potencjalny nawóz organiczny, bogaty w związki azotu i fosforu, nadający się do rolniczego wykorzystania.

Literatura

1. **Bień J.:** *Osady ściekowe. Teoria i praktyka*. Wydawnictwo Politechniki Częstochowskiej. Częstochowa 2007.
2. **Błażejewski R.:** *Stan i możliwości rozwoju infrastruktury wodociągowo-kanalizacyjnej w Polsce*. Gaz, Woda i Technika Sanitarna. 2, 49–51 (2012).
3. **Brzostowski N., Hawryłyszyn M., Karbowski D., Paniczko S.:** *Przydomowe oczyszczalnie ścieków. Poradnik*. Podlaska Stacja Przyrodnicza Narwe. Białystok 2008.
4. **Gajewska M., Obarska-Pempkowiak H.:** *20 lat doświadczeń z eksploatacji oczyszczalni hydrofitowych w Polsce*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 11, 875–888 (2009).
5. **Gajewska M., Obarska-Pempkowiak H.:** *Efficiency of pollutant removal by five multistage 3 constructed wetlands in a temperate climate*. Environment Protection Engineering. 37(3), 27–37 (2011).

6. **Gajewska M., Wojciechowska E., Obarska-Pempkowiak H.:** *Najnowsze doświadczenia i aplikacje metody hydrofitowej w gospodarce komunalnej*. Gaz, Woda i Technika Sanitarna. 7, 264–268 (2014).
7. **Gajewska M.:** *Wpływ składu chemicznego ścieków i odcieków na specjację, konwersje i usuwanie azotu w oczyszczalniach hydrofitowych*. Wydawnictwo Politechniki Gdańskiej, Seria Monografie, nr 136, 2013.
8. GIOŚ (Główny Inspektorat Ochrony Środowiska): *Program Państwowego Monitoringu Środowiska na lata 2010–2012*. Warszawa 2009.
9. GIOŚ (Główny Inspektorat Ochrony Środowiska): R*aport o stanie środowiska w Polsce 2008*. Biblioteka Monitoringu Środowiska Warszawa 2010.
10. GUS (Główny Urząd Statystyczny): *Infrastruktura komunalna w 2012 r.*, Wyd. GUS. Warszawa 2013.
11. HELCOM: *Baltic facts and figures*, 2004. http://www.helcom.fi/environment2/nature/en_GB/facts
12. HELCOM: *The Fourth Baltic Sea Pollution Load Compilation (PLC-4).* Baltic Marine Environ. Protection Com. Proc. 93, 2004.
13. **Istenic D., Bodik I., Bulc T.:** *Barriers for implementation of treatment wetlands in central and Eastern Europe*. Environmental Science and Pollution Research. in press, 2015.
14. **Jóźwiakowski K., Mucha Z., Generowicz A., Baran S., Bielińska J.:** *The use of multi-criteria analysis for selection of technology for a household sewage treatment plant following the idea of sustainable development.* Archives of Environmental Protection. w druku, 2015.
15. **Kołecka K., Obarska-Pempkowiak H.:** *Operation of reed systems used to stabilisation of sewage sludge*. Polish Journal of Environmental Studies. 6, 60–69 (2009).
16. **Kołecka K., Obarska-Pempkowiak H.:** *Potential fertilizing properties of sewage sludge treated in the Sludge Treatment Reed Beds (STRB).* Water Science & Technology. 68(6), 1412–1418 (2013).
17. **Kundziewicz A., Miłaszewski R.:** *Analiza efektywności kosztowej indywidualnych systemów usuwania i oczyszczania ścieków.* Inżynieria Ekologiczna. 24, 174–183 (2011).
18. **Nielsen S.:** *Sludge drying reed beds*. Water Science and Technology. 48(5), 101–109 (2003).
19. **Obarska-Pempkowiak H., Gajewska M., Wojciechowska E., Ostojski A.:** *Oczyszczalnie w ogrodzie*. Wydawnictwo Seidel-Przywecki. Warszawa 2012.
20. **Obarska-Pempkowiak H., Gajewska M., Wojciechowska E.:** *Hydrofitowe oczyszczanie wód i ścieków.* PWN. Warszawa 2010.

21. **Obarska-Pempkowiak H., Kowalik P., Gajewska M., Tuszyńska A.:** *Oczyszczalnie hydrofitowe – doświadczenia i perspektywy rozwoju.* „Gospodarka wodno-ściekowa w regionach rolniczo-przemysłowych”. Zeszyty Naukowe Politechniki Białostockiej, 16, Wydawnictwo Politechniki Białostockiej, tom II, 192–202 (2003).
22. **Paruch A.M. Mæhlum T., Obarska-Pempkowiak H., Gajewska M., Wojciechowska E., Ostojski A.:** *Rural domestic wastewater treatment in Norway and Poland: experiences, cooperation and concepts on the improvement of constructed wetland technology.* Water Science and Technology. 63(4), 776–781 (2011).
23. **Pastuszak M.:** *Charakterystyka zlewiska Morza Bałtyckiego. Udział Polskiego rolnictwa w emisji związków azotu i fosforu do Bałtyku.* IUNG-PIB, Puławy. 17–37 (2009).
24. **Rosen P.:** *Przydomowe oczyszczalnie ścieków.* Centralny Ośrodek Informacji Budownictwa. Warszawa 2002.
25. Rozporządzenie Ministra Środowiska z 1 lipca 2010 r. w sprawie sposobu wyznaczania obszaru i granic aglomeracji, Dz.U. 2010, nr 137, poz. 922
26. Rozporządzenie Ministra Środowiska z dn. 24 lipca 2006, w sprawie warunków, jakie spełnić przy wprowadzeniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz.U. 2006, nr 137, poz. 984.
27. Ustawa z dn. 18 lipca 2001 Prawo wodne, Dz.U. 2001, nr 115, poz. 1229, tekst jednolity z dn. 10 stycznia 2012 Dz.U. 2012, nr 0, poz. 145.
28. Ustawa z dn. 27 marca 2003 r. Prawo budowlane Dz.U. 2003, nr 80, poz. 718
29. **Zwara W., Obarska-Pempkowiak H.:** *Polish experience with sewage sludge utilization in reed beds.* Water Science and Technology. 41(1), 65–68 (2000).

Sustainable Sewage Management in Rural Areas

Abstract

The Baltic Sea is highly susceptible to eutrophication. Among the nine countries located in the Baltic Sea catchment area Poland discharges the biggest load of nitrogen and phosphorus. Although in recent years this load has been significantly reduced, however it is still too high. No sustainable municipal management results in the decreasing water quality of the Baltic Sea contributing to the sea eutrophication.

The implementation of the National Programme for Development of Sewage caused a number of activities related to the construction and modernization of existing wastewater treatment plants.

Although the number of wastewater treatment plants has been constantly increasing, still a number of households do not have the possibility to connect to the municipal wastewater treatment plant, mainly for economic reasons. Although in Poland there is 3157 municipal wastewater treatment plants (the most in Central and Eastern Europe), only 64% of the population is connected to them. It is estimated that 7.64 million people do not have the possibility of connection to municipal wastewater treatment plants.

One of the solutions to wastewater management, especially in non-urbanized areas, are on-site wastewater treatment plants, for example treatment wetland systems. These technologies provide a sustainable solution of sewage and sludge management, since they can be used not only for treatment of wastewater, but also for dewatering and stabilization of produced sewage sludge

The article presents the results of research on local constructed wetlands for biological wastewater treatment (from 15 to 750 inhabitants) located in Darżlubie, Wieszyno, Wiklino, Sarbsk and Schodno as well as individual treatment wetlands representing 9 on-site wastewater treatment plants built in three different configurations in the municipality of Stężyca. There are also results of research from sludge treatment reed beds used for dewatering and stabilization of sewage sludge from municipal wastewater treatment plants located in Denmark (Helsinge, Rudkobing, Nakskov, Vallo) and in Poland (Gniewino).

Based on studies related to the latest examples of wastewater and sewage sludge management using treatment wetlands it has been shown that this method is a good example of ecological engineering. Local treatment wetland systems can be used as the second stage of wastewater treatment up to 3500 residents. With proper operation of primary tanks, these systems are characterized by high treatment efficiency. Treatment wetland systems can work as on-site wastewater treatment plants. The highest efficiency of pollutant removal was observed in the hybrid systems. Another facilities, constructed as reed beds or basins, are applied to effective dewatering and stabilization of sewage sludge. These facilities offer a sustainable solution of sludge management in local conditions.

Słowa kluczowe:
oczyszczanie ścieków, oczyszczalnie hydrofitowe, gospodarka wodno-ściekowa, sanitacja, zagospodarowanie osadów ściekowych

Keywords:
wastewater treatment, constructed wetlands, water and wastewater management, sanitation, sewage sludge management

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Metodologiczne aspekty badania substancji odorowych w otoczeniu oczyszczalni ścieków

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1. Wstęp

Monitorowanie wydzielających się substancji odorowych na terenie oczyszczalni ścieków, a szczególnie ich składu i propagacji w terenie, wymaga przeprowadzenia żmudnych operacji. Wykorzystuje się przy tym określone procedury, uwzględniające wszystkie czynniki wpływające na analizę, w tym pobieranie, utrwalanie i przygotowywanie próbek do badań oraz przeprowadzenie oznaczeń. Nie wszystkie rodzaje tych substancji należą do toksycznych. Tym niemniej ich obecność w powietrzu bywa uciążliwa dla ludzi. W przeszłości zazwyczaj pomijano takie oddziaływania. Rozpatrywano szczegółowo jedynie obecność niektórych gazów, powstających w znaczących stężeniach takich jak: metan, tlenki węgla, siarkowodór i amoniak. Obok wymienionych istnieje cała grupa związków chemicznych, których obecność w powietrzu decyduje o jego charakterystyce i uciążliwości [1–3].

Odory towarzyszą głównie procesom przebiegającym w początkowej fazie oczyszczania ścieków. Wrażenia zapachowe powodowane są obecnością szeregu odorantów, wydzielających się podczas rozkładu substancji organicznej. W pierwszej fazie należy liczyć się z zapachami gnilnymi, będącymi rezultatem procesów zachodzących w warunkach przemian tlenowo-beztlenowych. Wzrost temperatury w fazie termofilnej powoduje również szybki rozkład substancji organicznych m.in. do ditlenku węgla i wody. Deficyt tlenowy prowadzi wówczas do powstawania kolejnej grupy substancji zapachowych, w tym siarkowodoru i Amoniaku oraz związków organicznych zawierających azot i siarkę. Po zakończeniu rozkładu substancji organicznych natężenie emisji odorów maleje niemal do zera. Z wcześniejszych badań, prowadzonych na terenie państw Unii Europejskiej wynika, że w gazach odlotowych z oczyszczalni ścieków może znajdować się około 460 substancji identyfikowalnych. Uważa się, że około 100 substancji z tej grupy jest silnie zapachowych [1]. W ściekach poddawanych procesowi oczyszczania wyróżniono wówczas następujące grupy organicznych substancji zapachowych:

- kwasy tłuszczowe: propionowy, masłowy, walerianowy,
- alkohole: amylowy,
- aldehydy i ketony: 3-hydroksy-2-butanon (acetoina), 2,3-butanodion (biocetyl), aldehyd krotonowy, aldehyd walerianowy, aldehyd masłowy, aceton,
- związki azotu: pirydyna,
- związki siarki: metantiol (merkaptan metylowy), butantiol, sulfid dietylowy, oraz
- nieorganiczne: amoniak, siarkowodór.

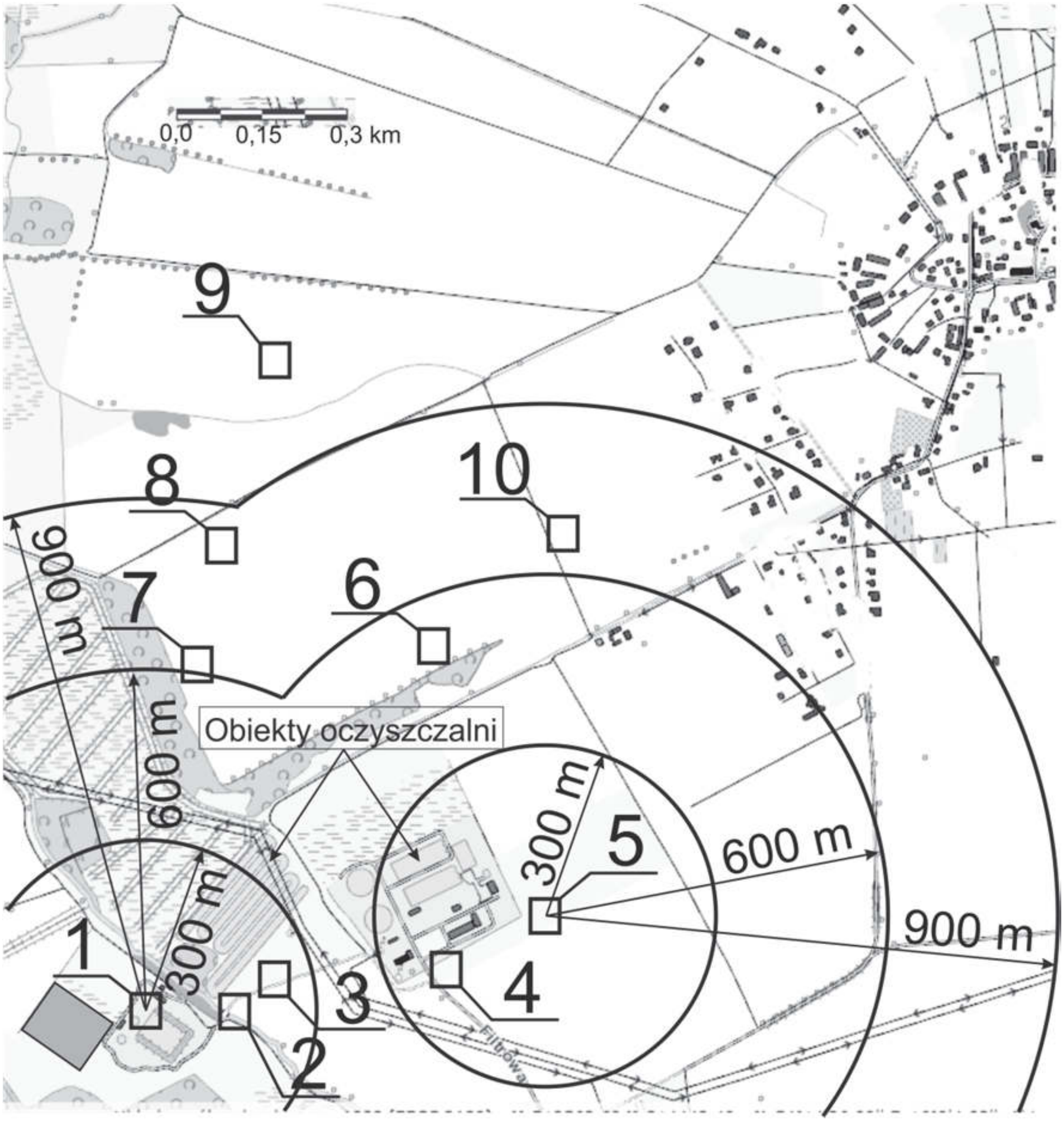
Szczegółowe badania tych związków prowadzono w niektórych krajach europejskich, stosując techniki sprzężone, będące połączeniem chromotografii gazowej i olfaktometrii. Metody te, aczkolwiek zaliczane do bardzo kosztownych, dają możliwość określenia niektórych cech zapachu charakterystycznego dla związku rejestrowanego przez odpowiedni detektor. W rezultacie można otrzymać tzw. osmogram, czyli pik węchowy odpowiadający intensywności wrażenia węchowego, a rodzaj zapachu podawany jest w formie opisowej. Na tej drodze zidentyfikowano, między innymi, HDMF (4,5-dimetylo-3-hydroksy-2(5H)-furanon), jeden z całej gamy związków, tworzący charakterystyczny zapach jako rezultat rozkładu związków organicznych obecnych w ściekach komunalnych oraz powstających osadach ściekowych [5,6].

Prowadzenie badań koncentracji odorantów w środowisku, jedynie przy pomocy sensorów elektronicznych, bywa zazwyczaj niewystarczające. Popełniane tu błędy oznaczeń wynikają głównie z ciągłych zmian stężenia odorantów w atmosferze, zmian kierunków wiatru, temperatury otoczenia, intensywności opadów, stanu równowagi atmosfery oraz topografii terenu. Jak dotychczas brak jest wyczerpujących aktów prawnych z tego zakresu. Stwarza to możliwość dowolnej interpretacji wrażeń zapachowych. Uważa się, że w tego typu badaniach winny być stosowane techniki sprzężone, wykorzystujące nowoczesne urządzenia elektroniczne (sensory elektroniczne) i tzw. badania eksperckie, bazujące na zespole osób charakteryzujących się zbliżonym progiem węchowej wyczuwalności, rozumianym jako stężenie progowe, przy którym zapach wyczuwa 50% reprezentatywnej populacji grupy ludzi. Za najważniejsze w tym zakresie uważa się techniki pomiarowe pozwalające oznaczać stężenie odorantów w środowisku oraz określić zależności intensywności zapachu od tych stężeń.

Problemy emisji odorantów w Polsce nie są administracyjnie uregulowane, ponieważ brak jest rozporządzeń wykonawczych do odpowiednich zapisów prawa. Istnieje jedynie norma określająca metodę pomiaru, jednak jej stosowanie zgodnie z polskim prawem jest dobrowolne [7–9]. W niniejszym opracowaniu uwzględniono wyniki badań prowadzonych na terenie oczyszczalni ścieków oraz wokół tego obiektu. Badania te wykonano tzw. metodą ekspercką, która pozwala na praktyczną ocenę uciążliwości odorantów i wpływ tych substancji na otoczenie [1].

2. Badania substancji odorowych w powietrzu metodą ekspercką

Badania zawartości odorantów na terenie i w otoczeniu oczyszczalni mechaniczno-biologicznej wykonano w latach 2013–2014. Pomiary odorantów w tym terenie prowadzono średnio 3 razy w ciągu miesiąca i każdorazowo w 10. charakterystycznych punktach, uwzględniających podstawowe procesy technologiczne oraz środowiskowe (rys. 1). Oceny uciążliwości zapachowej dokonywała 4-osobowa grupa ekspercka o odpowiednim doświadczeniu i o sprawdzonej wrażliwości sensorycznej [1,4,7]. W rezultacie wykonano 7200 serii badań. Korzystano przy tym z normy: ISO 5492, ISO 8589, ISO 1622 oraz wytycznych norm holenderskich i niemieckich. Zespół oceniający intensywność zapachową wokół obiektów oczyszczalni oraz rozprzestrzenianie się ich w atmosferze, zgodnie z Grupą Roboczą WG2 z Komisji Jakości Powietrza Europejskiego Komitetu Normalizacyjnego, pracował na podstawie określonej i mało zmiennej wrażliwości na zapach tzw. europejskiego wzorca – n-butanolu „Air quality – determination of odour concentration by dynamic olfactometr”, Pr EN, CEN TC264 (WG 2/N222/e-1998).



Rys. 1. Mapa oczyszczalni ścieków z zaznaczonymi punktami pomiarowymi oraz wyznaczonymi strefami uciążliwości zapachowej
Fig. 1. The map of sewage treatment plant with marked measuring points and appointed areas of smell onerousness

Poszczególne parametry pomiaru intensywności zapachowej odorantów w czasie oraz ich intensywność, oceniane przez 4. ekspertów (A,B,C,D) wg następującej skali zapachowej: 0 – niewyczuwalny, 1 – słaby, 2 – wyraźny, 3 – mocny.

Tabela 1. Przykładowe oceny pomiarów eksperckich intensywności zapachowej odorantów wykonane w punkcie nr 2 w maju 2014 r.
Table 1. Sample marks of expert measurement of odorant smell intensity done in point number 2 in May 2014

Intensywność zapachu		0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
A	1 minuta		x				x			x				x			
	2 minuta		x				x			x				x			
	3 minuta	x					x			x				x			
	4 minuta		x			x				x				x			
	5 minuta		x				x			x					x		
sekunda minuty		15				30				45				60			

Intensywność zapachu		0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
B	1 minuta	x					x				x			x			
	2 minuta		x				x				x			x			
	3 minuta		x			x					x				x		
	4 minuta		x				x				x			x			
	5 minuta	x				x				x					x		
sekunda minuty		15				30				45				60			

Intensywność zapachu		0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
C	1 minuta	x				x				x				x			
	2 minuta		x				x				x			x			
	3 minuta		x				x				x			x			
	4 minuta		x				x			x				x			
	5 minuta	x					x				x				x		
sekunda minuty		15				30				45				60			

Intensywność zapachu		0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
D	1 minuta	x				x				x					x		
	2 minuta		x				x				x				x		
	3 minuta	x				x					x			x			
	4 minuta		x			x					x			x			
	5 minuta		x			x					x				x		
sekunda minuty		15				30				45				60			

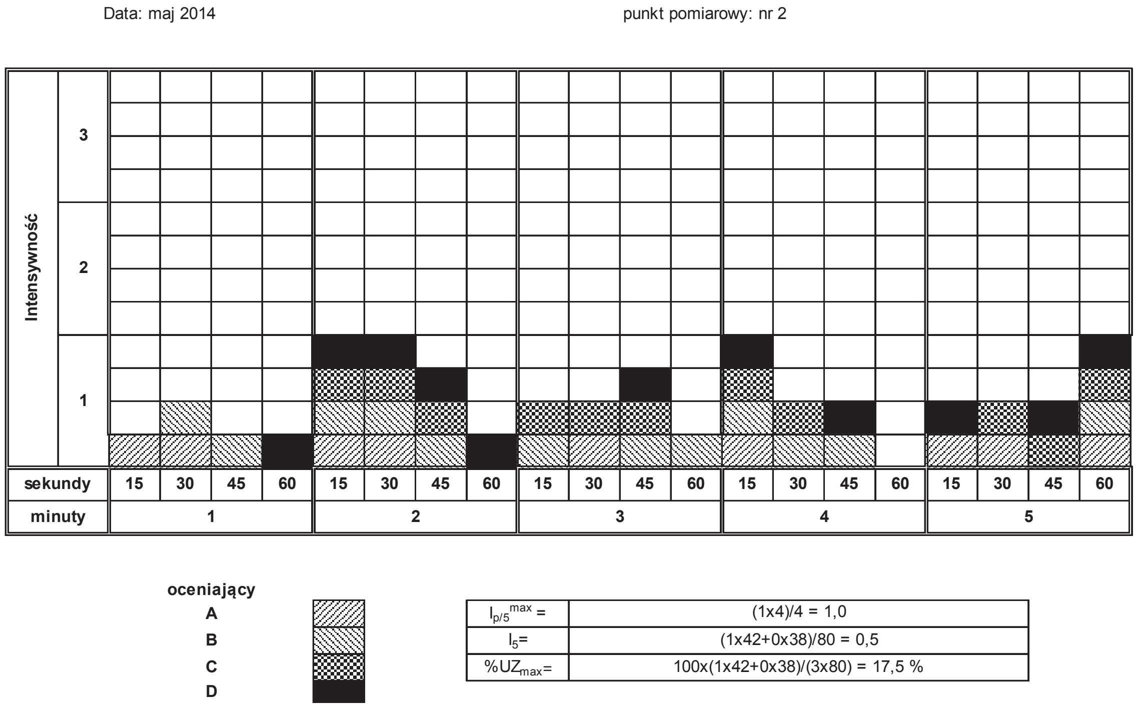
Opracowane wyniki tych badań zestawiono w tabeli 2. Na podstawie indywidualnych ocen intensywności zapachów zespołu eksperckiego opracowano zbiorcze karty wyników badań charakteryzujące zapachową jakość powietrza na ocenianym obszarze kontrolnym w okresie 5-minutowym.

Tabela 2. Średnia intensywność maksymalna uciążliwości zapachowej rejestrowana w czasie pięciominutowego okresu kontroli $I_{p/5}^{maks}$ oraz podstawowe parametry statystyczne
Table 2. Average max intensity of smell noxiousness registered in 5 minute period of control $I_{p/5}^{maks}$and basic statistic parameters

Miesiąc i rok pomiaru	Punkty pomiarowe									
	1	2	3	4	5	6	7	8	9	10
lip-13	0,75	1,00	0,75	0,75	0,75	0,50	1,00	0,00	0,00	0,00
sie-13	0,75	0,00	0,00	0,00	0,00	0,75	0,50	0,50	0,00	0,25
wrz-13	0,75	0,75	0,75	0,00	0,75	0,00	1,00	0,00	0,00	0,50
paź-13	0,75	0,75	0,00	0,00	1,00	1,00	1,00	0,00	0,00	0,75
lis-13	1,00	0,75	1,00	0,75	0,75	0,75	0,75	0,50	0,50	0,50
gru-13	0,75	0,75	1,00	0,75	0,75	0,75	0,00	0,00	0,00	0,00
sty-14	1,00	1,00	1,00	0,75	0,75	1,00	1,00	0,00	1,00	0,00
lut-14	1,75	1,50	1,00	0,75	1,75	1,00	1,75	0,75	0,75	0,75
mar-14	1,50	2,00	1,00	0,00	2,75	0,00	0,00	0,00	0,00	0,00
kwi-14	1,00	1,00	1,25	1,75	1,50	1,00	1,00	0,75	1,00	0,75
maj-14	0,75	1,00	0,75	1,00	1,00	0,75	0,75	0,75	0,00	0,00
cze-14	1,25	1,25	0,75	0,00	1,25	1,50	1,00	1,50	1,25	1,50
Podstawowe parametry statystyczne										
Max	1,75	2,00	1,25	1,75	2,75	1,50	1,75	1,50	1,25	1,50
Min	0,75	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mediana	0,88	1,00	0,88	0,75	0,88	0,75	1,00	0,25	0,00	0,38
Średnia	1,00	0,98	0,77	0,54	1,08	0,75	0,81	0,40	0,38	0,42
Liczba pom.	12	12	12	12	12	12	12	12	12	12

Tabela 2 stanowi przykładową kartę, którą wypełnia zespół ekspertów. Ze względu na skład zespołu eksperckiego wyniki badań uwzględniały: 4 osoby x 5 minut x 4 oceny, co odpowiada 80. jednostkowym ocenom zapachu x 90 serii badań. W rezultacie uzyskano 7200 serii badań. Przykładowe wyniki pomiarów uciążliwości zapachowej w 2014 roku, w skali 4-stopniowej, w punkcie 4 ilustruje tabela 3.

Tabela 3. Przykładowe wyniki pomiarów uciążliwości zapachowej w formie graficznej (pkt. 2, maj 2014)
Table 3. Sample results of smell noxiousness in graphical form (point 2, May 2014)

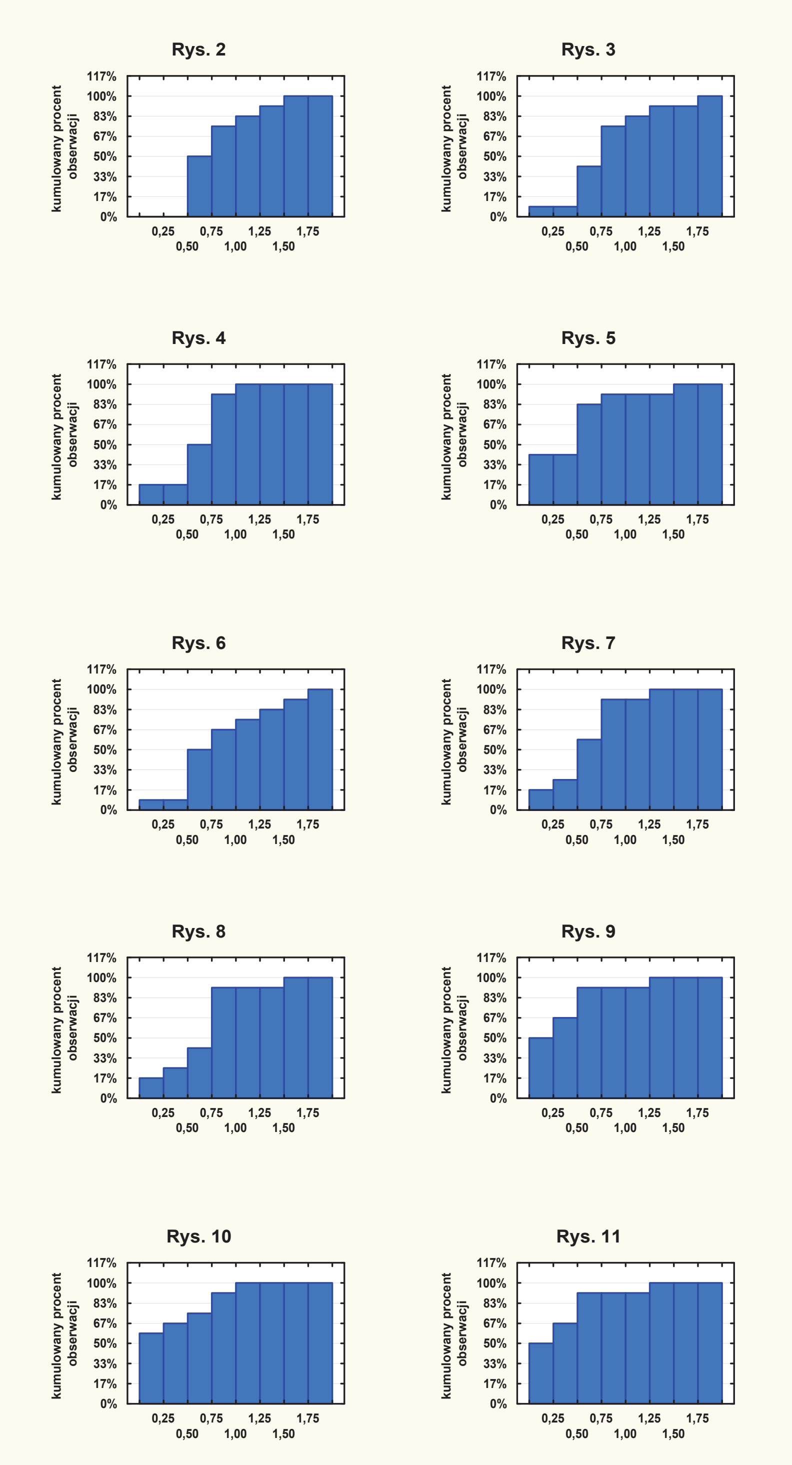


$I_{p/5}^{max}$ =	(1x4)/4 = 1,0
I_5=	(1x42+0x38)/80 = 0,5
$\%UZ_{max}$=	100x(1x42+0x38)/(3x80) = 17,5 %

W prowadzonych badaniach uwzględniono:

- położenie obszaru kontrolnego,
- datę wykonania badań,
- warunki meteorologiczne danego obszaru,
- kierunki wiatru,
- warunki środowiskowe ocenianego terenu.

Graficzną stronę wyników badań stanowią histogramy zbiorcze (rys. 2–11), na których naniesiono poziom uciążliwości zapachowej obliczony względem wartości maksymalnej $I_{p/5}$ ^{maks}.



Rys. 2–11. Histogramy pomiarów intensywności maksymalnej chwilowej $I_{p/5}^{max}$ odorantów w punktach: od 1 do 10

Fig. 2–11. Histograms of measurements of instantaneous max intensity $I_{p/5}^{max}$ of odorants in points: from 1 to 10

Zbiorcze wyniki badań średniej intensywności emisji zapachowych na terenie oczyszczalni ścieków zestawiono w tabeli 4.

Tabela 4. Zbiorcze wyniki badań średniej intensywności emisji zapachowych na terenie oczyszczalni ścieków
Table 4. Bulk experiments results of average intensity of smell emission in area of sewage treatment plant

Data badania	Intensywność zapachowa		
	$I_{p/5}^{maks}$	I_5	$\%UZ_{maks}$ [%]
Lipiec, 2013	0,0–1,00	0,0–0,4	0,0–13,0
Sierpień, 2913	0,0–0,75	0,0–0,3	0,0–10,0
Wrzesień, 2013	0,0–1,00	0,0–0,5	0,0–15,0
Październik, 2013	0,0–1,00	0,0–0,4	0,0–14,0
Listopad, 2013	0,0–1,00	0,0–0,5	2,5–16,0
Grudzień, 2013	0,0–1,00	0,0–0,5	0,0–16,0
Styczeń, 2014	0,0–1,00	0,0–0,6	0,0–21,0
Luty, 2014	0,0–1,75	0,2–1,0	7,0–35,0
Marzec, 2014	0,0–2,75	0,2–1,2	0,0–41,0
Kwiecień, 2014	0,75–1,75	0,2–0,7	0,54–24,0
Maj, 2014	0,0–1,00	0,0–0,4	0,0–17,5
Czerwiec, 2014	0,0–1,50	0,0–0,8	0,0–27,0

3. Analiza wyników badań eksperckich

Badania stopnia uciążliwości odorowej analizowanej oczyszczalni ścieków, prowadzone w okresie 12. miesięcy i wpływ tego obiektu na otoczenie, uwzględniające propagację substancji odorowych w powietrzu, wskazują na potrzebę precyzyjnego określenia zasięgu obszaru ograniczonego użytkowania tego terenu. Obserwacje (badania) prowadzone przez 4-osobowy zespół ekspercki wykazały, że zarówno w czasie, jak i w terenie będącym w bezpośrednim otoczeniu oczyszczalni ścieków, zmienia się koncentracja substancji odorowych (rys. 2–11). Oceny tej dokonano według opisanej wcześniej 4-stopniowej skali.

Jeżeli uwzględnimy parametr intensywności maksymalnej chwilowej $I_{p/5}^{maks}$ to tak zwany kumulowany procent obserwacji w skali zapachowej w punkcie 1 (rys. 2), stanowi od 50,0 do 75% obserwacji i dotyczy intensywności zapachowej poniżej progu wyczuwalności zespołu eksperckiego. W granicach od 75,0 do 83,0% obserwacji ocenia się jako intensywność zapachową słabą, natomiast powyżej 83,0% obserwacji intensywność tę można ocenić jako wyraźną. W punkcie 2 (rys. 3) intensywność zapachową kumulowaną, stanowiącą 41,7% obserwacji ocenia się jako niewyczuwalną, od 41,7 do 83,0% jako słabą, natomiast powyżej 83% jako wyraźną. W kolejnym punkcie 3. (rys. 4), kumulowana intensywność zapachowa, stanowiąca 50,0% obserwacji może być zaliczona do niewyczuwalnych, od 50,0 do 91,7% obserwacji jako słaba, natomiast powyżej 91,7% jako wyraźna. W punkcie 4. (rys. 5), kumulowana intensywność zapachowa jako niewyczuwalna stanowi 83% obserwacji, od 83,0 do 91,7% obserwacji jako słaba oraz powyżej 91,7% jako wyraźna. W kolejnym punkcie 5. (rys. 6) stwierdzono 67% obserwacji jako niewyczuwalną intensywność zapachową, od 67,0 do 91,7% jako słabą, natomiast powyżej 91,7% jako wyraźną. W punkcie 6. (rys. 7) można mówić o dwóch progach intensywności maksymalnej chwilowej. Pierwszy próg stanowi 91,7% obserwacji, w których intensywność zapachowa jest na poziomie niewyczuwalnym oraz powyżej 91,7% obserwacji jako intensywność zapachową wyraźną. Identyczne zjawisko obserwowano w punktach 7. (rys. 8), 8. (rys. 9) i 9. (rys. 10). W punkcie 10. (rys. 11) stwierdzono 3 progi intensywności zapachowej. Pierwszy dotyczył 67% obserwacji i został przez ekspertów zaliczony do intensywności niewyczuwalnej. Drugi próg odpowiadał 91,7% obserwacji i został zaliczony do intensywności jako slaby, natomiast trzeci próg stanowiący powyżej 91,7%j obserwacji zespół ekspertów uznał jako intensywność zapachową wyraźną. Zespół ten w żadnym z analizowanych przypadków nie zidentyfikował, w okresie prowadzonych obserwacji intensywność zapachową odorantów jako mocną, dla której intensywność maksymalna chwilowa $\mathbf{I_{p/5}^{maks}}$ byłaby wyższa od 2,0, zgodnie z tab. 3.

Zbiorcze wyniki badań średniej intensywności emisji zapachowych na terenie oczyszczalni ścieków w poszczególnych miesiącach 2013 i 2014 roku (tab. 4) mogą być pomocne do wyznaczenia strefy ochronnej wokół danego obiektu. Jak można zauważyć, wyniki te precyzują stopień zanieczyszczenia powietrza związkami odorantów. Badania eksperckie prowadzone w 10. charakterystycznych punktach obserwacyjnych (na terenie obiektu, w jego pobliżu oraz w pobliżu zabudowy mieszkalnej) (rys. 1) wykazały, że wysokie stężenie odorantów, najczęściej obserwowano w punktach 1–5, znaczące w punktach 6–8 oraz sporadyczne w punktach 9–10. W okresie badawczym 2013/14 roku zdecydowanie najbardziej odczuwalną obecność odorantów zanotowano w listopadzie i grudniu 2013 roku oraz w pierwszej połowie 2014 roku. Najwyższe stężenia substancji odorowych odnotowano w miesiącach: lutym, marcu, kwietniu i czerwcu 2014 roku, co było wynikiem awarii niektórych układów technologicznych i ich usytuowania na terenie oczyszczalni oraz zmian pogodowych. Wyraźne odczucia zapachowe stwierdzono też w miesiącach jesiennych 2013 roku. Były one odczuwalne szczególnie w bliskiej odległości od stacji wirówek oraz w pobliżu punktu zlewnego ścieków oraz krat, natomiast nieco słabiej w bezpośredniej bliskości suszarni osadów ściekowych.

4. Podsumowanie

Z przeprowadzonych badań eksperckich wynika, że kumulacja substancji odorowych jest najwyższa na terenie obiektów oczyszczalni ścieków w pobliżu sekcji odwadniania osadów ściekowych. W znacznie mniejszym stopniu zapachy te koncentrowały się przy bramie wjazdowej na teren oczyszczalni oraz w pobliżu budynków biurowych. Bardzo intensywne wrażenie zapachowe obserwowano w strefie dopływu ścieków surowych oraz punktu zlewnego. Szczególne uciążliwości odorowe emitowane z terenu oczyszczalni obserwuje się w odległości około 300 m. W mniejszym stopniu uciążliwości te występowały w odległości około 500–600 m od głównych źródeł emisji. Sporadyczne zanieczyszczenia powietrza substancjami odorowymi występują również w odległości 900 m w terenie zagospodarowanym rolniczo i w pobliżu istniejącej zabudowy mieszkalnej. Tym samym strefa uciążliwości dla badanej oczyszczalni powinna wynosić 900 m (rys. 1).

Jak wynika z prowadzonych badań oraz konsultacji społecznych, wszelkie uciążliwości związane z eksploatacją oczyszczalni zależą od składu odorantów w otoczeniu tego obiektu, ich intensywności i częstości występowania w skali roku. Wymienione czynniki silnie korelują z kierunkami i siłą wiatru (bardzo często zmiennymi w obszarze badań), temperaturą oraz czynnikami geomorfologicznymi. Bardzo korzystną rolę pełni tu zadrzewienie terenu. Badania intensywności zapachowej odorantów z wykorzystaniem metody eksperckiej winny być uzupełniane o badania olfaktometryczne.

Symbolika oznaczeń

$I_{p/5}^{maks}$ – poziom uciążliwości zapachowej, obliczony względem wartości maksymalnej,

I_5 – intensywność średnia uciążliwości zapachowej odniesiona do 5. min. okresu kontroli,

$\%UZ_{maks}$ – intensywność maksymalna chwilowa (poziom uciążliwości zapachowej obliczony względem wartości maksymalnej UZ_{maks}).

Literatura

1. **Kośmider J.**, **Mazur-Chrzanowska B., Wyszyński B.:** *Odory*. Wydawnictwo Naukowe PWN 2002.
2. **Sówka I.:** *Metody identyfikacji odorotwórczych gazów emitowanych z obiektów przemysłowych.* Monografie nr 55. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2011.
3. **Szynkowska. M., Wojciechowska E., Węglińska A., Paryjczak T.:** *Odory. Aktualny problem w ochronie środowiska.* Przemysł chemiczny. 6, 712–720 (2009).
4. **Brudniak A., Dębowski M., Zieliński M.:** *Określenie zapachowego oddziaływania wybranej oczyszczalni ścieków na tereny objęte opracowaniem planu zagospodarowania przestrzennego.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1759-1771 (2013).
5. **Kulig A., Lelicińska-Serafin K., Podedworna J., Sinicyn G, Heidrich Z., Czyżkowski B.:** *Charakterystyka i ocena oddziaływania zapachowego źródeł odorantów w gospodarce ściekowej i odpadowej w Polsce na podstawie badań ankietowych*. Chemik. 11, 414–420 (2009).
6. **Szklarczyk M.:** *Metody pomiaru stężenia zapachu.* Przegląd Komunalny. 11, 111–113 (2005).
7. PN-EN 13725:2007 „Jakość powietrza. Oznaczanie stężenia zapachowego metodą olfaktometrii dynamicznej”.
8. **Rutkowski J.:** *Unormowania formalno-prawne zapachowej jakości powietrza atmosferycznego.* Przegląd Komunalny. 10, 72–75 (2005).
9. **Friedrich M., Kośmider J., Terebecki P., Mizerna-Nowotna P.:** *Odour Abatement of Waste Gases from Sludge Thickeners in Wastewater Treatment Plant Using Bioscrubber*. Chemical Engineering Transactions. 40, 205–210 (2014).

Methodological Aspects of Odorous Substances Measurement in the Vicinity of a Sewage Treatment Plant

Abstract

Problems of emission of odorants in Poland are not regulated administratively, because there are no regulations to appropriate law records. Still, there is a norm that defines method of measurement, however using it according to polish law is voluntary.

The present study is based on the results of measurements carried out at a sewage treatment plant and around that object. Studies were performed using so called expert method that allows practical assessment of nuisance and impact of odorous substances on the environment.

Measurements of odorants contents at mechanical-biological sewage treatment plant and in its vicinity were carried out in the years 2013–2014. Measurements of odorants were taken on average 3 times per month and each time in 10 characteristic points, taking into account the basic technological and environmental processes (Fig. 1). Assessment of odour nuisance was made by group of 4 experts with relevant experience and proven sensory sensitivity. Individual parameters of odour intensity measurements in time were rated by 4 experts (A, B, C, D) according to the following odour scale: 0 – imperceptible, 1 – weak, 2 – distinct, 3 – strong.

Particular odorous nuisance emitted from the area of sewage treatment was observed at a distance of about 300 m. Nuisance observed at the distance of approximately 500–600 meters from the main sources of emissions was much smaller. Sporadic air pollution with odorous substances are also found in the distance of 900 m in developed agriculturally area and near existing residential development. Thus, nuisance zone of examined sewage treatment plant should be 900 m (Fig. 1). Results of this study and public consultation prove that all nuisance related to the operation of sewage treatment plant depend on composition of odorants in vicinity of the plant, their intensity and frequency of appearing during year. Those factors strongly correlate with directions and wind speed (very variable in the studied area), temperature and geomorphological factors. Very beneficial has here tree coverage of the area. Research odour intensity with the use of expert method should be supplemented with olfactometric measurements.

Słowa kluczowe:
odory, metoda ekspercka, uciążliwość oczyszczalni ścieków

Keywords:
odours, expert metod, niusance of sewage treatment plant

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Zastosowanie sorpcji i zaawansowanego utleniania do usuwania fenoli i ich pochodnych z roztworów wodnych

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1. Wstęp

Jednym z kluczowych zadań stojących przed inżynierią środowiska jest szeroko rozumiana ochrona środowiska, a w tym ograniczanie emisji zanieczyszczeń oraz ich usuwanie/unieszkodliwianie i ograniczanie ich rozprzestrzeniania. Jest to szczególnie ważne w odniesieniu do zanieczyszczeń organicznych takich jak: węglowodory alifatyczne i aromatyczne, fenole i ich pochodne, chlorowcopochodne, w tym pestycydy, wielopierścieniowe węglowodory aromatyczne (WWA), aldehydy, ketony, kwasy, detergenty, tłuszcze, barwniki itp. Związki te charakteryzują się wysoką toksycznością, trwałością w środowisku, zdolnością do przemieszczania się a jednocześnie ulegających biokumulacji w organizmach żywych. Zgodnie z danymi Chemical Abstract System (CAS) z 2013 r. liczba związków chemicznych dostępnych w obrocie handlowym wynosi 68 852 967 z czego większość stanowią związki organiczne wykorzystywane powszechnie do produkcji tworzyw sztucznych, materiałów, farb, lakierów, rozpuszczalników, smarów, leków, kosmetyków i wielu innych wyrobów [18].

Źródłem obecności zanieczyszczeń organicznych w środowisku są ścieki zarówno komunalne jak i przemysłowe praktycznie ze wszystkich gałęzi przemysłu. Zgodnie z danymi GUS [66] w Polsce powstaje rocznie około 8945,3 hm^3 ścieków z czego 7698,7 hm^3 to odpływy z zakładów. Przepustowość 1132 oczyszczalni ścieków przemysłowych wynosi 5919,7 dm^3/d. Przedstawione dane wskazują na skalę problemu, jaki stanowią ścieki przemysłowe o złożonym i zróżnicowanym składzie chemicznym zawierające głównie trudno rozkładalne związki organiczne.

Coraz wyższe wymagania stawiane ściekom oczyszczonym odprowadzanym do wód lub do ziemi [68] wymuszają ciągłe udoskonalania procesu ich oczyszczania. Z uwagi na znaczną ilość związków organicznych o zróżnicowanych właściwościach fizykochemicznych do ich usuwania ze ścieków konieczne jest stosowanie, a często nawet łączenie, wielu metod takich jak biodegradacja, koagulacja, filtracja, sorpcja, utlenianie, wymiana jonowa jak również technologie membranowe [7,40,69]. Stosowane obecnie metody oczyszczania ścieków mają swoje zalety jak również liczne ograniczenia, zarówno w odniesieniu do skuteczności usuwania poszczególnych grup zanieczyszczeń jak i kosztów inwestycyjnych i eksploatacyjnych.

Przykładem ścieków, których oczyszczanie wciąż nastręcza wiele problemów, są ścieki pochodzące z przemysłu włókienniczo-tekstylnego, farbiarskiego i poligraficznego, zawierające w swoim składzie barwniki, fenole, wielopierścieniowe węglowodory aromatyczne, detergenty, kwasy nieorganiczne, silne utleniacze stosowane jako środki wybielające, a także kleje oraz alkalia [12]. Dane literaturowe jak i wdrożone rozwiązania [12,13,16,29,31,36,41,57,60,63,75,81] wskazują, że w odniesieniu do tych ścieków coraz większa uwagę zwraca się na możliwość wykorzystania do usuwania związków organicznych procesu sorpcji jak również pogłębionego utleniania AOP (Advanced Oxidation Processes). Takie postępowanie jest zgodne z Dyrektywą IPPC (Integrated Pollution Prevention and Control) [57] mającą na celu zintegrowane zapobieganie i ograniczanie emisji zanieczyszczeń z przemysłu, gdzie wymagane jest stosowanie Najlepszych Dostępnych Technik BAT (Best Available Techniques). Zalecane minimalne wymagania dotyczące BAT opisane w Dokumentach Referencyjnych BAT BREFs (BAT Reference Notes) dotyczące oczyszczania ścieków obejmują:

- określanie charakterystyki różnych strumieni ścieków powstających w danym procesie,
- poddawanie zanieczyszczonych strumieni ścieków najbardziej odpowiedniemu dla nich procesowi oczyszczania,
- zapobieganie przedostawaniu się do systemów biologicznego oczyszczania ścieków takich składników ścieków, które mogłyby zakłócić prawidłowe funkcjonowanie tych systemów,

- usuwanie ze strumienia ścieków frakcji nie ulegającej biodegradacji, przy użyciu odpowiednich metod przed poddaniem (lub zamiast poddania) ich ostatecznemu oczyszczaniu biologicznemu,
- rozdzielanie ścieków u źródła według rodzaju i ilości zawartych w nich zanieczyszczeń, przed zmieszaniem z innymi strumieniami ścieków.

W odniesieniu do ścieków włókienniczych, farbiarskich, poligraficznych, o złożonym składzie chemicznym, w celu zapewnienia skutecznego ich oczyszczania proponuje się procesy zintegrowane. Polega to na łączeniu oczyszczania biologicznego, fizycznego i chemicznego z oczyszczaniem trzeciego stopnia, polegającym np. na adsorpcji na węglu aktywnym, który jest następnie spalany lub na oczyszczaniu przy użyciu wolnych rodników ($OH^{\bullet}$, $O_2^{\bullet -}$, $CO_2^{\bullet -}$) [57].

2. Budowa i właściwości sorpcyjne węgli aktywnych

Spośród dostępnych sorbentów największe znaczenie i zastosowanie ma węgiel aktywny. Wykorzystanie sorpcyjnych właściwości węgla aktywnego sięga czasów prehistorycznych. Już starożytni hindusi filtrowali wodę przez węgiel drzewny, a Hipokrates i Pliniusz Starszy opisali pierwsze zastosowania do celów medycznych. Na początku XIX wieku odbarwiające właściwości węgli aktywnych zostały wykorzystane w przemyśle cukrowniczym w Anglii. Na początku XX wieku zaczęto produkować węgle aktywne na skalę przemysłową z wykorzystaniem aktywacji parowej i chemicznej, a od 1929 roku datuje się ich wykorzystanie w procesie oczyszczania wody pitnej. Podczas pierwszej wojny światowej w Rosji zastosowano granulowane węgle aktywne w sprzęcie ochrony dróg oddechowych. Węgle te otrzymywano na bazie skorup orzecha kokosowego drogą aktywacji parowej. Przemysłowa produkcja granulowanych węgli aktywnych, głównie na bazie skorup orzecha włoskiego, rozwinęła się po II wojnie światowej. Węgle te charakteryzowały się rozwiniętą strukturą porowatą i dobrymi właściwościami mechanicznymi, co sprawiło, że obszar ich zastosowania był coraz szerszy [2,16,17,36].

Szerokie i wciąż rosnące wykorzystanie węgli aktywnych pociąga za sobą coraz większą ich produkcję. Zgodnie z danymi Roskill Reports [67] światowe zużycie węgli aktywnych w 2007r. wyniosło ok. 650 tys.

ton, a przewiduje się że w 2015 r. będzie wynosiło 1,36 Mt, co wynika z rosnącego wykorzystania węgli aktywnych w procesach oczyszczania wody, ścieków i gazów jak również jako katalizatorów i nośników katalizatorów.

Obecnie węgle aktywne otrzymywane są w procesie termicznego i/lub chemicznego rozkładu substancji zawierających znaczne ilości węgla pierwiastkowego. Na skalę przemysłową sorbenty te są otrzymywane na drodze karbonizacji i aktywacji węgla kamiennego, brunatnego, torfu, półkoks lub koksu, ale również z pestek moreli i łupin migdałowych, skorup kokosa włoskiego jak również łupin orzecha [16,17]. W zależności od właściwości surowca wyjściowego zmienia się technologia produkcji węgla aktywnego, jego właściwości, pojemność sorpcyjna, a tym samym zastosowanie i cena.

Struktura porowata węgli aktywnych decydująca o właściwościach sorpcyjnych, ukształtowana jest przez system wzajemnie powiązanych porów. W zależności od wielkości promienia pory te dzielą się na [2,17,28,74]:

- mikropory – na które przypada zasadnicza część powierzchni właściwej węgli i dlatego odgrywają one podstawową rolę w procesie sorpcji, w czasie którego zapełniają się objętościowo,
- mezopory – w których zachodzi kondensacja kapilarna par adsorbowanych substancji, a przy niższych ciśnieniach adsorpcja mono- i polimolekularna,
- makropory – które w procesach adsorpcji i katalizy pełnią rolę „arterii transportowych”.

Istotną zaletą węgli aktywnych jako sorbentów jest to, że można w dość szerokim zakresie modyfikować ich strukturę poprzez dobór odpowiednich surowców, lepiszczy, parametrów karbonizacji i aktywacji.

Budowa chemiczna powierzchni węgli aktywnych ukształtowana jest zasadniczo przez dwa rodzaje grup funkcyjnych [2,15,17,24]:

- grupy o charakterze kwasowym, takie jak karboksylowe, fenolowe, karbonylowe, laktonowe, bezwodnikowe,
- grupy funkcyjne o charakterze zasadowym.

Obecność powierzchniowych grup funkcyjnych decyduje przede wszystkim o jonowymiennych właściwościach węgli aktywnych, ale ma również wpływ na ich właściwości adsorpcyjne, elektrochemiczne, katalityczne, utleniająco-redukujące oraz hydrofobowo-hydrofilowe. Adsorbenty węglowe są ze swej natury adsorbentami o stosunkowo dużej hydrofobowości, a poddane procesowi utleniania znacznie poprawiają swoje zdolności adsorpcyjne względem polarnych adsorbatów takich jak: alkohole, kwasy organiczne, estry, aminy oraz względem wody [15,17, 36,37,47,48].

Budowa chemiczna powierzchni węgli ma istotne znaczenie przy ich zastosowaniu jako sorbentów, do pochłaniania związków organicznych zawierających wiązania nienasycone, jak i kationów metali z roztworów wodnych oraz katalizatorów i nośników katalizatorów. Wynika to z faktu, że oddziaływanie wiązań wielokrotnych, jak i kationów metali z powierzchnią węgla aktywnego to suma oddziaływań z elektronami π węgla oraz z grupami funkcyjnymi o silnych właściwościach donorowo-akceptorowych [2,37,48]. Oddziaływania te prowadzą do wzrostu donorowych właściwości kationu metalu. Im mocniejsze jest to oddziaływanie, tym silniej wiązane są substancje.

Jednym z najważniejszych obszarów wykorzystania węgli aktywnych, gdzie zużywa się ponad 23% produkcji, jest oczyszczanie wód i ścieków [2,16,26,59]. Zagadnienia dotyczące zastosowania węgli aktywnych do usuwania zanieczyszczeń organicznych (wielopierścieniowych węglowodorów aromatycznych, chlorowcopochodnych organicznych, pestycydów, detergentów, kwasów humusowych, fenoli i chlorofenoli, ropopochodnych) jak również nieorganicznych np. jonów metali, cyjanków, azotanów były i nadal są przedmiotem dużego zainteresowania badaczy, czego efektem jest niezwykle bogata w tym zakresie literatura [15–17, 26–28,36,37,40,42,47,48,50–53,55,58,59,67,69,71,74,77–79].

3. Sorpcja fenoli na węglach aktywnych

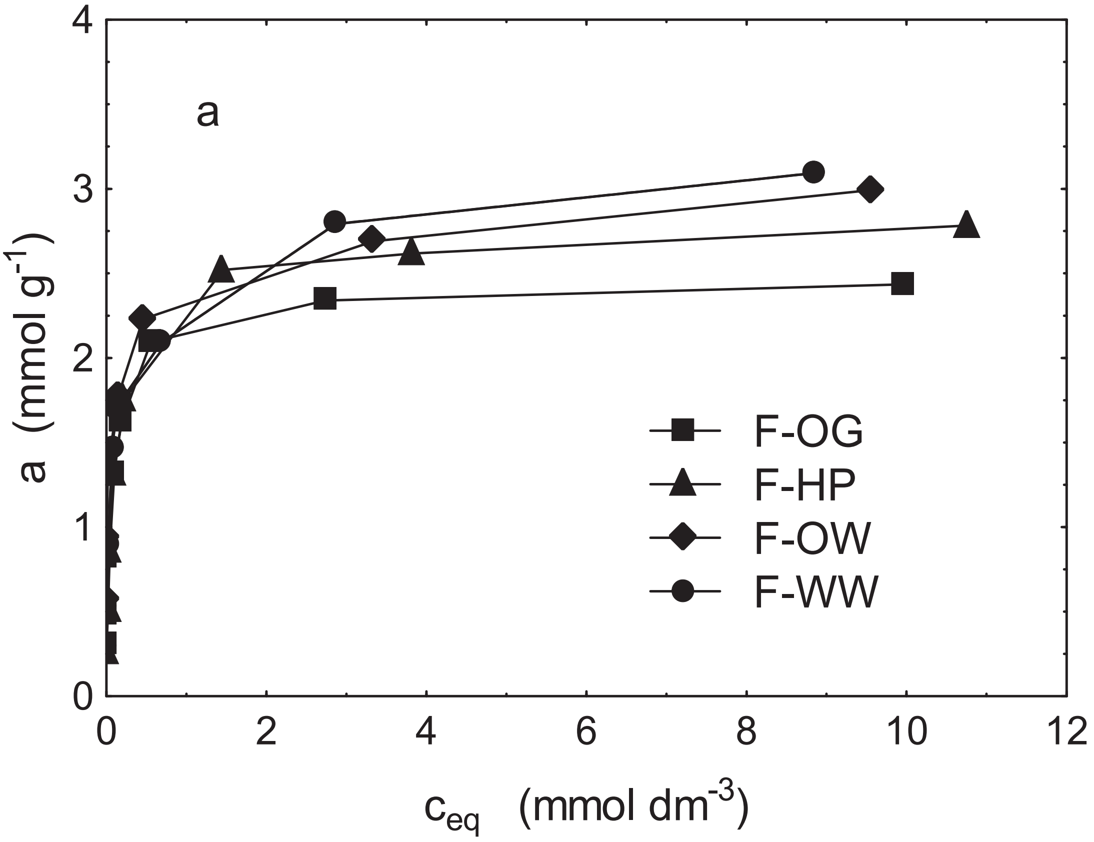
Wśród licznych badań poświęconych tematyce sorpcji substancji organicznych na węglach aktywnych wiele uwagi poświęca się sorpcji fenoli i chlorofenoli. Wynika to z faktu, że fenol i jego pochodne takie jak metylofenole, chlorofenole i dimetylofenole stanowią znaczącą grupę zanieczyszczeń, które niezmiennie obecne są w ściekach pochodzących z przemysłu chemicznego, produkcji tworzyw sztucznych, barwników i farb oraz z koksowni i przemysłu petrochemicznego. Niektóre z tych związków pochodzą również ze źródeł naturalnych w efekcie beztlenowego rozkładu materii organicznej i są uwalniane do wód powierzchniowych i podziemnych. Jednak głównym źródłem tych związków w środowisku są działania antropogeniczne.

Liczne badania sorpcji fenoli i ich pochodnych na węglach aktywnych pozwoliły na wyjaśnienie mechanizmu sorpcji tych substancji i znalezienie zależności pomiędzy wielkością sorpcji a strukturą porowatą i chemizmem powierzchni węgli [42,52,53,55,58,71,77–79]. W badaniach Moreno-Castilla [58] wykazano, że zdolność adsorpcyjna węgla aktywnego zależy od wielkości powierzchni właściwej, porowatości węgla, rozpuszczalności związków fenolu i hydrofobowości podstawników. Stwierdzono, że relatywne powinowactwo fenoli wobec powierzchni węgla związane jest z tworzeniem oddziaływań między elektronami typu π w cząsteczce adsorbatu oraz na powierzchni sorbentu oraz donorowo-akceptorowych kompleksów pomiędzy miejscami zasadowymi na powierzchni węgla, a pierścieniem organicznym. Magne i Walker [55] analizując mechanizm sorpcji fenoli na węglach aktywnych zwrócili uwagę, że sorpcja fenoli obejmuje zarówno sorpcję fizyczną jak i chemisorpcję. Ta ostatnia rośnie wraz z czasem i temperaturą adsorpcji, co wskazuje, że część fizycznie zaadsorbowanego fenolu ulegała następnie chemisorpcji przy czym chemisorpcja była hamowana obecnością tlenowych grup powierzchniowych. Wyniki te znalazły potwierdzenie w pracach opisanych w przeglądowej publikacji Bansal i Goyal [2] oraz w badaniach Lorenc-Grabowskiej i in. [50,51], Terzyka i Rychlickiego [77–79], Madeły i in. [52,53], Ksycińskiej-Rębiś i in. [42], jak również w pracach współautorskich Świątkowskiego [27,44,45,71]. Z badań tych wynika, że zarówno właściwości chemiczne adsorbowanego związku jak i rodzaj chemicznych ugrupowań powierzchniowych węgla aktywnego jest czynnikiem determinującym zdolności adsorpcyjne z roztworów względem fenoli. Adsorpcja fenoli i ich pochodnych jest zależna nie tylko od wielkości powierzchni i mikroporowatej struktury węgli aktywnych, ale również od obecności tlenowych grup funkcyjnych na powierzchni węgli oraz wartości pH zawiesiny węgiel-roztwór. Z faktu, że adsorpcja fenoli na węglu jest częściowo nieodwracalna i wymaga wysokiej energii, wynika, że mają miejsce silne oddziaływania donorowo-akceptorowe z tlenowymi grupami powierzchniowymi o charakterze z zasadowym (powierzchnia węgla działa jako donor elektronów, a pierścień aromatyczny substancji sorbowanej jako akceptor). Obecność silnie elektronoakceptorowej grupy nitrowej w fenolu zwiększa donorowo-akceptorowe interakcje pierścienia z powierzchnią węgla. Adsorpcja ta wzrasta wraz z obniżeniem kwasowości powierzchni. Negatywny wpływ powierzchniowych grup tlenowych został przypisany osłabieniu π-elektronowych wiązań warstw grafitowych jako efekt obniżenia sił przyciągania van der Wallsa. Jednocześnie kwasowe grupy funkcyjne, które są objętościowo duże, blokują wejście do wąskich mikroporów, co powoduje w rezultacie spadek adsorpcji. Ponadto dookoła polarnych, kwaśnych grup powierzchniowych gromadzą się cząsteczki wody również redukujące zdolność adsorpcyjną węgli.

Wpływ chemizmu powierzchni węgla aktywnego na jego zdolności sorpcyjne względem pochodnych fenolu był przedmiotem badań prowadzonych przez Biniaka i in. [14]. Analizowano wpływ działania ozonu na właściwości fizykochemiczne węgla aktywnego F-300 świeżego i poddanego chemicznej modyfikacji oraz na zmianę zdolności sorpcyjnych względem p-chlorofenolu. W celu wyeliminowania wpływu substancji mineralnych na zdolności sorpcyjne jak i podatność na utlenianie, węgiel ten został wstępnie poddany działaniu stężonych kwasów HF i HCl. Stwierdzono, że efektem utlenienia powierzchni węgla aktywnego zarówno ozonem jak i nadtlenkiem wodoru jest zasadniczo zmiana charakteru chemicznego powierzchni węgla wyrażona wzrostem kwasowości, przy niewielkich zmianach struktury porowatej.

Przedstawione na rysunku 1 izotermy sorpcji p-chlorofenolu na węglu aktywnym F-300 po jego wstępnym płukaniu wodą destylowaną F-WW oraz po utlenieniu: gazowym O_3 (F-OG), O_3 rozpuszczonym w wodzie (F-OW) oraz nadtlenkiem wodoru (F-HP) wskazują, że utlenienie powierzchni węgla aktywnego skutkuje niewielkim obniżeniem zdolności sorpcyjnych.

Pojemność sorpcyjna węgla F-WW względem p-chlorofenolu kształtuje się na poziomie ok. 3 mmol/g i praktycznie nie ulega zmianie gdy węgiel ten pozostawał w kontakcie z ozonem rozpuszczonym w roztworze wodnym. Niewielkie zmniejszenie pojemności sorpcyjnej do poziomu ok. 2,9 mmol/g obserwuje się w efekcie działania nadtlenku wodoru na powierzchnię węgla F-WW. Największe zmiany skutkujące zmniejszeniem się pojemności sorpcyjnej względem p-chlorofenolu obserwuje się w przypadku działania ozonem w fazie gazowej na węgiel aktywny F-WW. Sorpcja tego związku na węglu aktywnym F-OG wynosi ok. 2,2 mmol/g, co oznacza, że jest o około 30% niższa niż węgla wyjściowego podczas gdy zmniejszenie się powierzchni właściwej jak i objętości mikroporów nie przekracza 3%. Potwierdza to wcześniejsze spostrzeżenia, że obok struktury porowatej węgla aktywnego, na wielkość sorpcji p-chlorofenolu istotny wpływ mają chemiczne właściwości tak adsorbentu jak i adsorbatu przekładające się na oddziaływania dyspersyjne oraz donorowo-akceptorowe.



Rys. 1. Izotermy sorpcji p-chlorofenolu na węglu aktywnym F-300 po jego wstępnym płukaniu wodą destylowaną F-WW oraz po utlenieniu: gazowym O_3 (F-OG), O_3 rozpuszczonym w wodzie (F-OW) oraz nadtlenkiem wodoru (F-HP). Oznaczenie osi: a – wielkość sorpcji, mmol g^{-1}; c_{eq} – stężenie równowagowe, mmol dm^{-3} [14]

Fig. 1. The sorption isotherms of p-chlorophenol on activated carbon F-300 after its initial flushing with distilled water F-WW and after oxidation: with gaseous O_3 (F-OG), with O_3 in aqueous solution(F-OW) and with hydrogen peroxide (F-HP). Axis labels: a - sorption, mmol g-1, c_{eq} – equilibrium concentration, mmol dm^{-3} [14]

Badania wpływu chemizmu powierzchni wynikające z wpływu obecności metali takich jak Cu (II) i Fe (II) na powierzchni węgla aktywnego na skuteczność sorpcji fenolu przedstawiono w pracy [20]. Badano sorpcję fenolu (Ph) na świeżym węglu aktywnym F-300 (F-300-Ph), na węglu aktywnym F-300 z zaadsorbowanymi wcześniej jonami Fe(II) i Cu(II) (F-300-Cu-Ph, F-300-Fe-Ph) oraz sorpcję jonów metali Cu(II) i Fe(II) na węglu z zaadsorbowanym wcześniej fenolem (F-300-Ph-Cu, F-300-Ph-Fe) jak również równoczesną sorpcję fenolu i jonów metali (F-300-(Cu/Ph), F-300-(Fe/Ph)). Węgiel aktywny F-300, powszechnie stosowany jako sorbent zanieczyszczeń organicznych i nieorganicznych, charakteryzuje się rozwiniętą strukturą porowatą (powierzchnia właściwa 965 m^2/g, objętość porów 0,87 cm^3/g) i umiarkowaną kwasowością powierzchni (0,57mmol/g).Wyznaczona zdolność sorpcyjna świeżego węgla F-300 względem fenolu wynosi 180 mg/g, względem jonów Cu(II) wynosi 12 mg/g i jonów Fe(II) i wynosi 5,5 mg/g (tabela 1). Jednocześnie stwierdzono, że zaadsorbowane wcześniej jony Cu(II) nie wpływają na zmniejszenie sorpcji fenolu, a wpływ jonów Fe(II) był bardzo mały. Wyniki te wskazują, że jony metali sorbują się na innych centrach aktywnych niż fenol, ale również aktywnie uczestniczą w tym procesie. Jest to zgodne z danymi literaturowymi [2,47] wskazującymi, że sorpcja metali zachodzi na kwasowych grupach tlenowych na powierzchni węgla aktywnego natomiast sorpcji fenolu sprzyja obecność grup funkcyjnych o charakterze zasadowym. Jednocześnie obecność metali zapewnia wysoką zdolność sorpcyjną węgla aktywnego względem fenolu dzięki interakcji donorowo-akceptorowej metal – elektrony π pierścieni aromatycznych, pomimo tego, że część powierzchni węgla aktywnego jest już zajęta. Natomiast sorpcja jonów metali na węglu aktywnym z zaadsorbowanym fenolem jest mniejsza i wynosi dla Cu(II) 8 mg/g, a dla Fe(II) 5 mg/g. To wskazuje, że zaadsorbowane cząsteczki fenolu z uwagi na swoją wielkość zasłaniają centra aktywne zdolne do sorpcji jonów metali albo zmieniają charakter chemiczny powierzchni węgla aktywnego. Sorpcja z mieszaniny jon metalu-fenol (F-300-(Cu/Ph) i F-300-(Fe/Ph)) jest zdecydowanie mniejsza i wynosi dla Fe(II) 6 mg/g, dla Cu(II) 4 mg/g, a dla fenolu 110 mg/g. Fakt ten można wyjaśnić wynikiem konkurencji w obszarze dyfuzyjnym jak i występowaniem oddziaływań donorowo-akceptorowych fenol-jon metalu w roztworze.

Tabela 1. Ocena zdolności sorpcyjnej świeżego węgla aktywnego F-300 względem wybranych jonów metali i fenolu z roztworu wodnego w zależności od kolejności sorbowanych substancji [20]
Table 1. The assessment of sorption properties of activated carbon F-300 in relation to selected metal ions and phenol from the aqueous solution depending on the order of the absorbed substances [20]

Symbol próbki węgla aktywnego F-300 – składnik sorbowany jako pierwszy – składnik sorbowany jako drugi, (sorpcja z mieszaniny)	Zdolność sorpcyjna węgla względem wybranego jonu, mg/g	Zdolność sorpcyjna węgla względem fenolu, mg/g
F-300	–	180
F-300-Cu-Ph	12,0	180
F-300-Fe-Ph	5,5	170
F-300-Ph-Cu	8,0	180
F-300-Ph-Fe	5,0	180
F-300-(Cu/Ph)	4,0	110
F-300-(Fe/Ph)	6,0	110

Wysoka zdolność sorpcyjna węgli aktywnych względem fenoli i ich pochodnych oraz wyjaśniony mechanizm sorpcji wskazuje na możliwość wykorzystania tych sorbentów w procesach oczyszczania wód i ścieków. Należy również zauważyć, że zastosowanie tych sorbentów jest kosztowne zarówno z uwagi na cenę węgli aktywnych, koszty instalacji jak i koszty eksploatacji z uwzględnieniem problemu unieszkodliwiania zużytych węgli. Ponadto należy uwzględnić fakt, że w ściekach przemysłowych występuje mieszanina różnych związków organicznych a tym samym skuteczność sorpcji wybranych substancji może być ograniczona z uwagi i możliwość występowania sorpcji konkurencyjnej oraz obecność zawiesin. Z tego też względu analizuje się inne metody usuwania związków organicznych z wód i ścieków, w tym utlenianie związków organicznych w szczególności z wykorzystaniem tzw. pogłębionego utleniania (AOP).

4. Zaawansowane utlenianie związków organicznych

Dane literaturowe [3–6,12,13,29,31,32,41,49,57,60,63,75,76,81, 82] wskazują, że najbardziej rokującą metodą usuwania substancji organicznych, w szczególności trudno biodegradowalnych, jest ich chemiczna degradacja z wykorzystaniem metod określanych wspólnym terminem Advanced Oxidation Processes (AOP) oznaczającym pogłębione lub zaawansowane utlenianie. Metody te obejmują:

- termolizę zanieczyszczeń w wodzie nadkrytycznej,
- utlenianie nadtlenkiem wodoru H_2O_2 oraz H_2O_2/UV,
- utlenianie odczynnikiem Fentona Fe^{2+}/H_2O_2 oraz Fe^{2+}/H_2O_2/UV,
- ozonolizę w układach O_3/UV, O_3/H_2O_2, O_3/UV/H_2O_2,
- utlenianie fotokatalityczne TiO_2/UV.

Wspólną cechą tych metod jest utlenianie praktycznie wszystkich związków organicznych do CO_2, H_2O i związków nieorganicznych za pomocą generowanego w roztworze rodnika hydroksylowego $OH^•$ o wysokim potencjale utleniającym wynoszącym 2,8V. Mechanizm tworzenia rodników hydroksylowych i utleniania związków organicznych w roztworze wodnym jak i zaadsorbowanych na węglach aktywnych, na przykładzie reakcji Fentona można przedstawić następująco [5]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^•$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^•$$
$$Fe^{3+} + HO_2^• \rightarrow Fe^{2+} + H^+ + O_2$$
$$OH^• + H_2O_2 \rightarrow H_2O + HO_2$$
$$OH^• + Fe^{2+} \rightarrow Fe^{3+} + OH^-$$
$$OH^• + RH \rightarrow \text{produkty przejściowe utlenienia} \rightarrow CO_2 + H_2O$$

Należy podkreślić, że rodniki hydroksylowe mogą być również generowane w obecności innych kationów metali (M^{n+}), a sam proces przebiega podobnie jak w reakcji Fentona:

$$Me^{n+} + H_2O_2 \rightarrow Me^{n+1} + OH^- + OH^•$$

W przypadku reakcji foto-Fentona pod wpływem promieniowania UV zachodzi reakcja:

$$H_2O_2 + h\nu \rightarrow 2OH^•$$

i jednocześnie następuje fotoredukcja jonów Fe^{3+} do Fe^{2+} z utworzeniem rodników $OH^•$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^• + H^+$$

Powstające w ten sposób jony Fe^{2+} mogą w dalszym ciągu reagować z H_2O_2, generując nowe rodniki $OH^{\bullet}$ czego skutkiem może być zwiększenie efektywności procesu degradacji zanieczyszczeń.

O skuteczności utleniania związków organicznych w warunkach reakcji Fentona decyduje dawka nadtlenku wodoru i jonów żelaza(II) oraz ich wzajemny stosunek, odczyn, czas reakcji oraz rodzaj utlenianej substancji. Zarówno nadmiar nadtlenku wodoru jak i jonów żelaza(II) skutkuje wygaszaniem rodników, a tym samym obniżeniem wydajności reakcji utleniania. Optymalny zakres pH dla reakcji Fentona wynosi od 3 do 5 [3–6,32,49,76,82]. Wzrost pH układu reakcyjnego powoduje szybki rozkład H_2O_2, przypuszczalnie na kłaczkach powstałego wodorotlenku żelaza(III), a tym samym zmniejsza się ilość powstających rodników hydroksylowych. Natomiast gdy wartość pH roztworu jest mniejsza od 3 jony wodorowe niszczą rodniki $OH^{\bullet}$ zgodnie z reakcją:

$$OH^{\bullet} + H^{+} + e^{-} \rightarrow H_2O$$

Optymalny zakres temperatury powstawania rodników hydroksylowych zawiera się w granicach od 293 do 313K. W temperaturze powyżej 313K obserwuje się szybki rozkład nadtlenku wodoru na tlen i wodę, co jest niekorzystne z punktu widzenia efektywności utleniania związków organicznych.

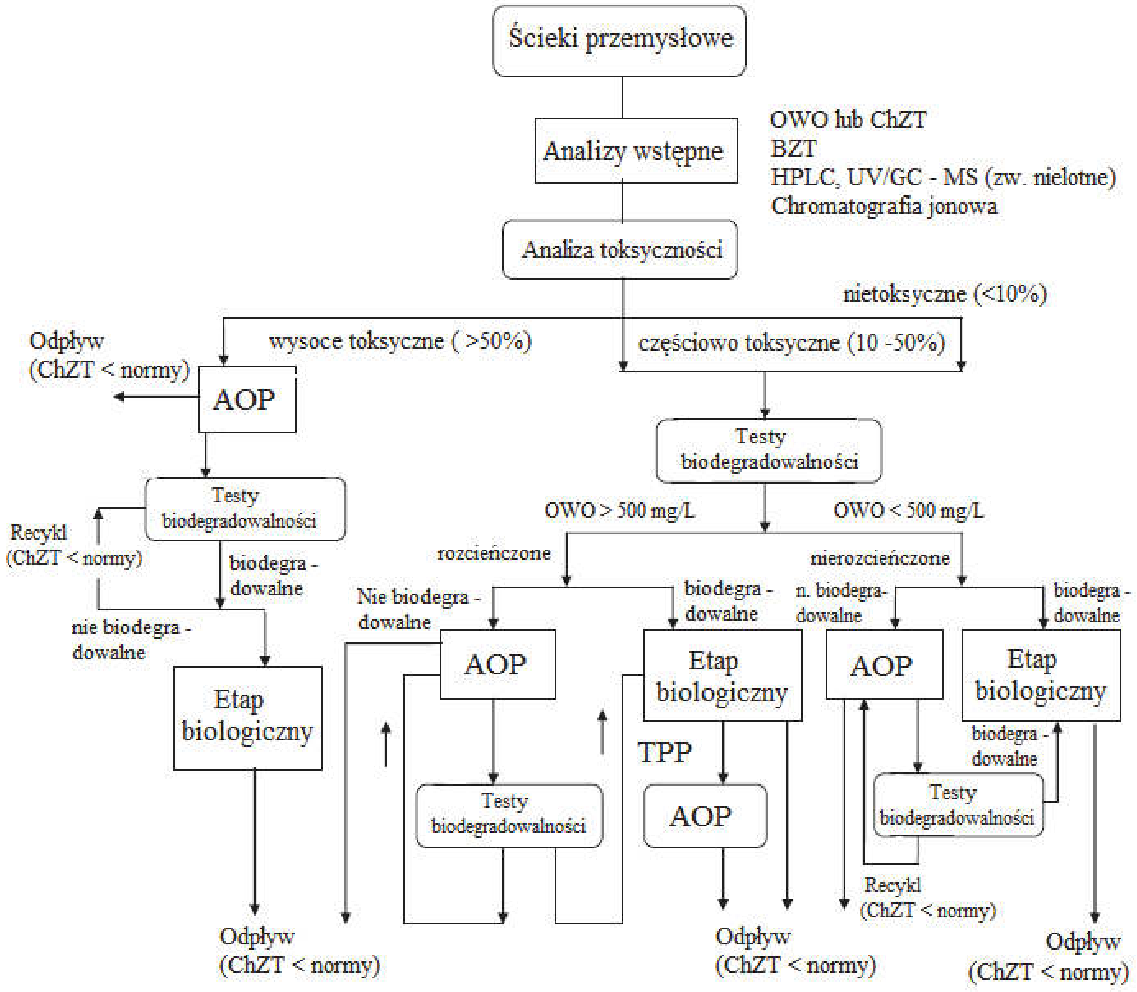
Wykazano, że spośród wymienionych czynników destrukcji zanieczyszczeń organicznych w ściekach, najskuteczniejszym jest odczynnik Fentona [3–6,12,29,31,32,41,49,63,76,82]. W optymalnych warunkach odczynnik Fentona utlenia wiele złożonych związków organicznych z efektywnością przekraczającą 90%. Na uwagę zasługuje prostota prowadzenia reakcji Fentona w porównaniu do innych metod generowania wysokoreaktywnych rodników hydroksylowych, nie wymagająca stosowania specjalistycznego oprzyrządowania (np. lamp UV, generatorów ozonu). Ponadto, produktami końcowymi samej reakcji Fentona są woda, tlen i wodorotlenek żelaza, które nie obciążają środowiska wodnego rozpuszczonymi zanieczyszczeniami. Zachodząca jednocześnie z procesami utleniania koagulacja zanieczyszczeń dodatkowo zwiększa efektywność usuwania zanieczyszczeń. Natomiast jedną z wad utleniania związków organicznych z wykorzystaniem reakcji Fentona jest konieczność końcowej korekty odczynu ścieków.

Wzrost skuteczności oczyszczania ścieków metodami AOP można uzyskać przez sekwencyjne połączenie procesów fizycznych, chemicznych i biologicznych. Właściwe rozwiązanie projektowe powinno łączyć najkorzystniejsze ekonomicznie procesy oczyszczania oraz zapewnić wysoką skuteczność degradacji zanieczyszczeń. Należy również zwracać uwagę na powstawanie toksycznych, pośrednich produktów rozkładu oraz zmianę charakteru zanieczyszczeń w trakcie procesu utleniania. Przykładowy schemat strategii wyboru najlepszej technologii oczyszczania ścieków przemysłowych z uwzględnieniem metod AOP przedstawili Oller Malato i Sánchez-Pérez (rysunek 2) [60].

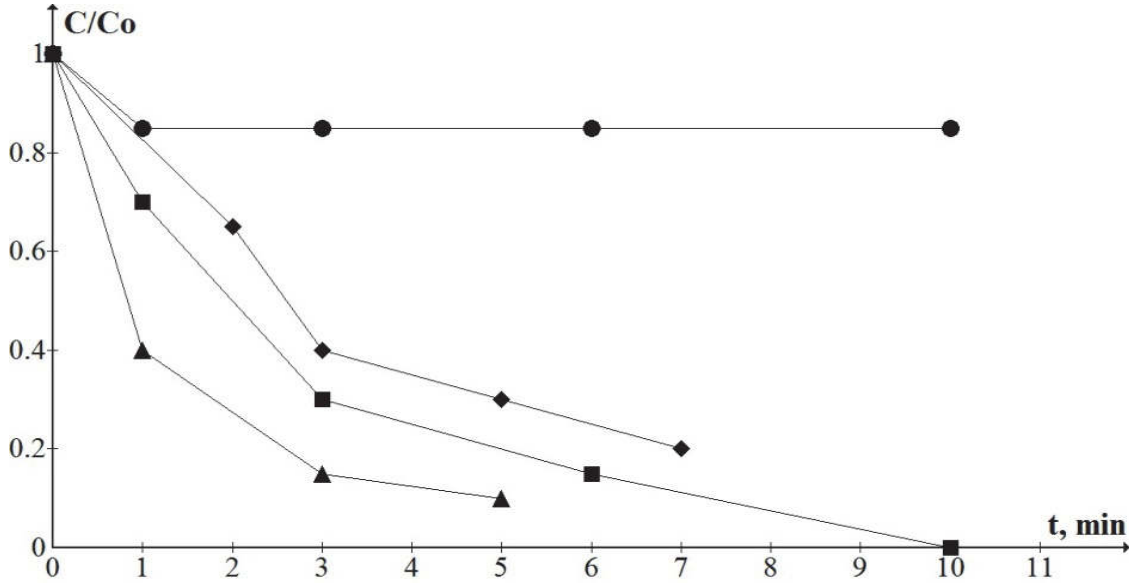
5. Utlenianie fenoli z wykorzystaniem AOP

Jak wykazano w pracach [8,25,39,43,46,56,62,65,70,75] fenole i ich pochodne łatwo i gwałtownie ulegają utlenianiu zarówno przez ozon jak i w warunkach reakcji Fentona. Utlenianie fenolu przebiega wielostopniowo z powstawaniem produktów pośrednich kolejno utlenianych (chinony, difenole, kwas mukonowy, kwas glioksalowy, kwas szczawiowy, kwas mrówkowy, glioksal) o coraz mniej złożonych cząsteczkach. Szybkość rozkładu fenolu rośnie ze spadkiem wartości pH i wzrostem stężenia czynników utleniających. Jednak należy zwrócić uwagę, że pośrednie produkty utleniania mogą wykazywać większą toksyczność niż związek wyjściowy. Przykładowo nadtlenek wodoru w obecności promieniowania UV wykorzystano do degradacji związków fenolowych obecnych w ściekach z tłoczenia oliwy [9,10], uzyskując prawie 90% redukcję zanieczyszczeń organicznych przy całkowitym ich odbarwieniu.

W pracy [64] analizowano kinetykę rozkładu p-chlorofenolu pod wpływem czynników utleniających z wykorzystaniem H_2O_2, H_2O_2/UV, Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV. Przedstawione na rysunku 3 wyniki wskazują, że nadtlenek wodoru jest zbyt słabym czynnikiem utleniającym aby spowodować rozkład p-chlorofenolu i tym samym doprowadzić do usunięcia z roztworu. Natomiast w obecności rodników hydroksylowych $OH^{\bullet}$, które generowane są z nadtlenku wodoru w obecności promieniowania UV, jak również w środowisku reakcji Fentona i foto-Fentona obserwuje się praktycznie natychmiastowy rozkład p-chlorofenolu. W przyjętych warunkach w ciągu pierwszych pięciu minut reakcji następuje utlenienie ok. 90% p-chlorofenolu obecnego w roztworze. Skutkiem utlenienia tego związku jest wzrost kwasowości roztworu (pH ok. 3,2), co jest zgodne z danymi literaturowymi [39,46]. Wykazano bowiem, że utlenienie p-chlorofenolu przebiega poprzez rozerwanie pierścienia aromatycznego, utlenienie grupy hydroksylowej do karboksylowej, a następnie dalszą mineralizację do produktów końcowych CO_2 i HCl.



Rys. 2. Strategia wyboru najlepszej technologii oczyszczania przemysłowych ścieków bio- lub niebiodegradowalnych [60]
Fig. 2. The selection strategy of the best technology for the treatment of bio- and nonbiodegradable industrial sewage [60]



Rys. 3. Porównanie szybkości rozkładu p-chlorofenolu pod wpływ czynników utleniających:
● – H_2O_2, ♦ – H_2O_2/UV, ■ – Fe^{2+}/H_2O_2, ▲ – Fe^{2+}/H_2O_2/UV [64]
Fig. 3. The comparison of decomposition velocity of p-chlorophenol under the impact of oxidants:
● – H_2O_2, ♦ – H_2O_2/UV, ■ – Fe^{2+}/H_2O_2, ▲ – Fe^{2+}/H_2O_2/UV [64]

6. Wykorzystanie sorpcji i utleniania do usuwania pochodnych fenoli

Zarówno sorpcja jak i utlenienie metodami AOP związków organicznych, w tym fenoli, obok istotnych zalet (wysoka wydajność i skuteczność) mają również wady. Do wad tych zaliczyć należy np.: problem unieszkodliwiania zużytych sorbentów czy też znaczne zużycie utleniaczy i zwiększenie ilości ścieków. W celu wykorzystania zalet tak sorpcji jak i zaawansowanego utleniania, a ograniczenia ich wad, rozważa się możliwość połączenia obu tych procesów. W tym przypadku usuwanie zanieczyszczeń realizowane jest jako proces dwu- lub jednoetapowy. W pierwszym przypadku usuwanie związków organicznych obejmuje sorpcję, a następnie utlenianie zaadsorbowanych substancji, z wykorzystaniem AOP, skutkujące równoczesną regeneracją węgla aktywnego. Natomiast w drugim przypadku mówi się o symultanicznym procesie sorpcji i utlenienia związków organicznych. W tak realizowanym procesie, jak wykazano w pracach Toledo [80] i Huanga [31,32], węgiel aktywny równocześnie pełni funkcję sorbenta związków organicznych jak i katalizatora tworzenia rodników hydroksylowych odpowiedzialnych za utlenianie substancji organicznych zarówno roztworze jak i zaadsorbowanych na węglu aktywnym. Proces ten przebiega zgodnie z reakcjami [80]:

$$AC - OH + H_2O_2 \rightarrow AC - OOH + H_2O$$
$$AC - OOH + H_2O_2 \rightarrow AC - OH + H_2O + O_2$$
$$AC + H_2O_2 \rightarrow AC^+ + OH^- + \underline{OH^\bullet}$$
$$AC^+ + H_2O_2 \rightarrow AC + HO_2^\bullet + H^+$$
$$HO^\bullet + RH \rightarrow \text{produkty utlenienia } (CO_2 + H_2O + \ldots..)$$

W obecności węgla aktywnego, w środowisku nadtlenku wodoru, ulegają utlenieniu związki organiczne, które nie są utleniane przez sam nadtlenek wodoru. To wskazuje na istotną rolę węgla aktywnego w generowaniu rodników hydroksylowych odpowiedzialnych za utlenianie związków organicznych.

Przydatność symultanicznego procesu sorpcji i utlenienia w oczyszczaniu ścieków farbiarskich wykazano w pracy Santosa i in. [72]. Badano kinetykę odbarwiania roztworów różnych barwników kwasowych, zasadowych i reaktywnych, przy zastosowaniu trzech różnych procesów: adsorpcji na węglu aktywnym, niekatalitycznego utleniania H_2O_2 i utlenianiu z H_2O_2 w obecności węgla aktywnego. Wykazano, że zarówno utlenianie H_2O_2 jak i sorpcja na węglu aktywnym są mało skutecznymi metodami usuwania barwników z roztworu wodnego. Natomiast w przypadku połączenia sorpcji i utlenienia obserwuje się synergiczny efekt skutkujący wzrostem efektywności odbarwiania roztworu. Wykazano, że chemizm powierzchni węgla aktywnego ma znaczenie na przebieg tego procesu. Sorpcja barwnika wzrasta wraz z zasadowością węgla aktywnego, natomiast odczyn roztworu nie ma zasadniczo wpływu na kinetykę tego procesu.

W badaniach Ince i in. [35] wykazano, że jeśli sorpcja fenolu i utlenianie z wykorzystaniem H_2O_2/UV przebiega równocześnie, to skuteczność usuwania wynosi 87,5%. Natomiast gdy węgiel był najpierw nasycany, a następnie poddawany regeneracji, uzyskano 92,5% redukcję zanieczyszczeń.

Jans i Hoigne [38] zaobserwowali, że rozkład ozonu na rodniki $HO^\bullet$ w obecności węgla aktywnego jest poprzedzany przez adsorpcję ozonu na węglu aktywnym. Ze względu na elektrofilowe właściwości cząsteczki ozonu mogą mieć większe powinowactwo w stosunku do węgli zasadowych, które są charakteryzowane przez obecność zdelokalizowanych elektronów π na płaszczyznach podstawowych. Stwierdzono, że istnieje związek pomiędzy zasadowością węgla i jego katalityczną rolą w procesie rozkładu ozonu na rodniki hydroksylowe.

Wyjaśnienie związku między właściwościami węgli aktywnych, a skutecznością ich działania w symultanicznym procesie sorpcji i utleniania przedstawiono w pracy [64]. Oceny zdolności katalitycznych węgli aktywnych w stosunku do rozkładu nadtlenku wodoru dokonano poprzez analogię do procesu dechloracji tj. reakcji węgla aktywnego z wolnym chlorem lub kwasem chlorowym (I) (HClO) w roztworze wodnym. Reakcja pomiędzy tymi utleniaczami, a węglem aktywnym opisana jest równaniem podanym przez Magee [54]:

$$C^{\bullet} + HOCl \rightarrow CO^{\bullet} + H+ + Cl^{-}$$

gdzie $C^{\bullet}$ oznacza centra aktywne na powierzchni węgla aktywnego, odpowiedzialne za rozkład, czyli centra katalityczne, a efektem końcowym jest utworzenie utlenionych obszarów $CO^{\bullet}$. W efekcie reakcji $C^{\bullet}$ z utleniaczem prawdopodobnie jako produkt pośredni powstaje $CHOCl^{\bullet}$ ulegający rozkładowi zgodnie z równaniem:

$$CHOCl^{\bullet} \rightarrow CO^{\bullet} + H+ + Cl$$

Do oceny zdolności katalitycznych węgli aktywnych w reakcji dechloracji, wykorzystywana jest liczba dechloracji oznaczająca wysokości warstwy węgla aktywnego w kolumnie o średnicy 40 mm wystarczającej do obniżenia stężenia wolnego chloru o połowę z roztworu o stężeniu 5 mg/L. Im mniejsza grubość warstwy węgla aktywnego, tym lepsze zdolności do dechloracji posiada dany węgiel aktywny.

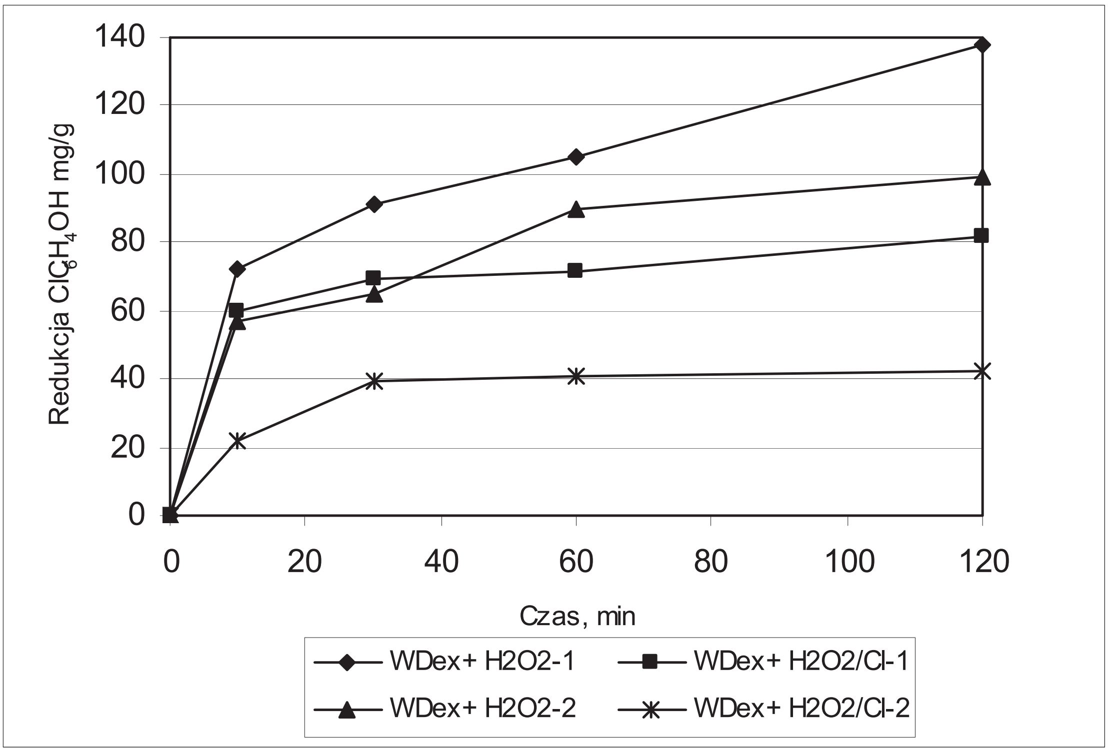
Zakładając analogiczny przebieg reakcji rozkładu nadtlenku wodoru na powierzchni węgla aktywnego z utworzeniem rodników hydroksylowych zgodnie z równaniami:

$$AC^{\bullet} + H_2O_2 \rightarrow AC^{+} + OH^{-} + OH^{\bullet}$$
$$AC^{+} + H_2O \rightarrow AC + HO^{\bullet} + H^{+}$$

przyjęto, że liczba dechloracji może być z powodzeniem wykorzystana do oceny przydatności węgli aktywnych do usuwania zanieczyszczeń organicznych poprzez ich symultaniczną sorpcję i utlenienie. Wykazano, że za przebieg reakcji rozkładu nadtlenku wodoru z utworzeniem rodników hydroksylowych odpowiedzialne są centra zasadowe (najprawdopodobniej centra zasadowe Lewis`a). Natomiast centra kwasowe (grupy kwasowe) odpowiedzialne za przyłączanie elektronów redukują zdolności katalityczne węgli aktywnych.

W oparciu o wyniki badań, prowadzone z wykorzystaniem węgli aktywnych o zróżnicowanych zdolnościach sorpcyjnych, przedstawione w pracach [21,22,64] wykazano, że im lepszy sorbent i bardziej zasadowy węgiel, a jednocześnie charakteryzujący się mniejszą liczbą dechloracji i większą liczbą jodową, tym efektywniej przebiega usuwanie zanieczyszczeń organicznych z roztworu wodnego w symultanicznym procesie sorpcji i utleniania. Z uwagi na to, że zarówno sorpcyjne jak i katalityczne właściwości węgli aktywnych są ważne można wnioskować, że procesy sorpcji i utleniania zachodzą równocześnie, a substancja musi być zaadsorbowana aby była utleniona. Spośród badanych węgli aktywnych najlepsze zdolności sorpcyjne w stosunku do fenoli i ich pochodnych oraz właściwości katalityczne posiadał węgiel aktywny WDex o największej zasadowości i najlepszej zdolności do dechloracji. Stwierdzono również, że efektem kontaktu utleniacza z węglem aktywnym jest zarówno zmiana struktury porowatej (w szczególności zmniejszenie powierzchni właściwej) jak i chemizmu powierzchni (wzrost kwasowości) pod wpływem rodników hydroksylowych. Na skutek utlenienia węgle aktywne zmieniają zarówno swoje zdolności sorpcyjne względem poszczególnych związków organicznych, jak i katalityczne, co nie jest korzystne z punktu widzenia możliwości ich wykorzystania w symultanicznym procesie usuwania związków organicznych drogą sorpcji i/lub utleniania.

Szczegółowe badania dotyczące usuwania p–chlorofenolu z roztworu w obecności węgla aktywnego WDex oraz nadtlenku wodoru opisano w pracy [19]. Skuteczność procesu oceniano na podstawie zmian stężenia p-chlorofenolu jak i ilości jonów chlorkowych, których obecność w roztworze wskazuje na jego utlenienie (WDex + H_2O_2/Cl-1, WDex + H_2O_2/Cl-2). Analizując otrzymane wyniki badań, przedstawione na rysunku 3, stwierdzono, że w układzie reakcyjnym węgiel aktywny-nadtlenek wodoru WDex/H_2O_2-1 w czasie trwania reakcji wynoszącym 10 min obserwuje się 31% ubytek p-chlorofenolu (72 mg/g). Z tej ilości utlenieniu ulega 83% (na co wskazuje ilość pojawiających się w roztworze jonów chlorkowych) a pozostała część (17%) usuniętego p-chlorofenolu pozostała zaadsorbowana na węglu aktywnym. Wydłużenie czasu reakcji do 30 min skutkuje usunięciem 91 mg/g p-chlorofenolu z czego 76% uległo utlenieniu a reszta została zaadsorbowana na węglu.



Rys. 4. Porównanie ilości usuniętego z roztworu p-chlorofenolu na 1 g węgla aktywnego WDex w obecności nadtlenku wodoru w dwóch kolejnych cyklach WDex/H_2O_2 -1 i WD extra/H_2O_2-2 z ilością utlenionego p-chlorofenolu oszacowanego na podstawie stężenia jonów Cl^- w roztworze WD extra/H_2O_2/Cl-1 i WDex/H_2O_2/Cl-2 [19]

Fig. 4. The comparison of the amount of p-chlorophenol removed from the solution for 1 g of activated carbon WDex in the presence of hydrogen peroxide at two consecutive stages WDex/H_2O_2 -1 and WD extra/H_2O_2-2 with the amount of oxidised p-chlorophenol determined from the concentration of Cl^- ions in the solution WD extra/H_2O_2/Cl-1 and WDex/H_2O_2/Cl-2 [19]

Wykorzystując pozostały po pierwszym etapie badań węgiel aktywny ponownie do usuwania kolejnej porcji p-chlorofenolu z roztworu w obecności H_2O_2 (wyniki oznaczone jako WDex/H_2O_2-2 i WDex/H_2O_2/Cl-2 na rysunku 4) stwierdzono zdecydowanie niższą skuteczność tego procesu. Ilość usuniętego p-chlorofenolu jest ok. 35% niższa niż w pierwszym cyklu, co można wyjaśnić częściowym zablokowaniem powierzchni węgla zaadsorbowanym i nieutlenionym p-chlorofenolem.

Analiza przebiegu reakcji wskazuje, że w powtórnym symultanicznym procesie udział usuwania p-chlorofenolu z roztworu poprzez sorpcję jest większy i po 120 minutach wynosi 57%. Uzyskane wyniki wskazują, że w zadanych warunkach zachodzi zarówno sorpcja jak i utlenianie substancji ale ilość utleniacza była zbyt mała aby utlenić całość adsorbatu. Przeprowadzone badania uzupełniające, w których w celu utlenienia zaadsorbowanego p-chlorofenolu wykorzystano reagent Fentona wykazały, że i w tym przypadku nie uzyskuje się całkowitej regeneracji węgla aktywnego. Niemniej jednak należy podkreślić, że niezależnie od zastosowanego czynnika utleniającego możliwe było ponowne wykorzystanie węgla aktywnego, a ilość skutecznie usuniętego z roztworu p-chlorofenolu była większa niż w przypadku gdyby prowadzono tylko sorpcję czy też tylko utlenianie jako procesy jednostkowe.

7. Wykorzystanie AOP do utleniania zaadsorbowanych związków organicznych

Przydatność procesu utleniania związków organicznych z wykorzystaniem rodników hydroksylowych powstających na powierzchni węgla aktywnego potwierdzają badania regeneracji zużytych węgli aktywnych nasyconych związkami organicznymi. Jedną z pierwszy prac były badania Shende i Mahajani [73], którzy z powodzeniem wykorzystali mokre utlenianie powietrzem do regeneracji węgla aktywnego nasyconego barwnikami. W pracach Toledo i in. [80] oraz Hulinga i in. [33,34] wykorzystano odczynnik Fentona do regeneracji węgli aktywnych nasyconych związkami organicznymi z grupy chloroorganicznych i eterów. Badania Toledo i in. [80] obejmowały regenerację węgla aktywnego nasyconego chlorobenzenem. W pracy zaobserwowano, że reagent Fentona był bardzo wydajny w utlenianiu zaadsorbowanych na powierzchni węgla aktywnego związków organicznych. W warunkach reakcji tzn. przy stosunku molowym związek organiczny/H_2O_2/Fe wynoszący 1/25/0.6, w temperaturze pokojowej, zaobserwowano po 2 godz. reakcji konwersję 100% tetra-chloroetylenu, 99% chloroformu, 99% 1,2-dichloropropanu, 90 % chlorobenzenu. Badania mechanizmu rozkładu zaadsorbowanych substancji jednoznacznie wskazują że węgiel aktywny promuje dekompozycję H_2O_2 poprzez formowanie rodników $OH^\bullet$ w sąsiedztwie zaadsorbowanych związków organicznych powodując ich mineralizację.

Interesujące badania dotyczące regeneracji węgla aktywnego nasyconego eterem tert-butylometylowym MTBE zostały przedstawione przez Hulinga i in. [33]. Stwierdzono, że wydajność regeneracji w przypadku węgla aktywnego nasyconego eterem MTBE (0,21 mg/g)wynosiła 91%. Co więcej stwierdzono, że zwiększona po regeneracji ilość żelaza poprawia zdolności sorpcyjne węgla. Jednocześnie zaobserwowano, że w układzie reakcyjnym nie pojawiły się produkty uboczne utleniania MTBE odczynnikiem Fentona (tert-butyloaceton i aceton) jakie występują w przypadku gdy reakcja ta zachodzi w roztworze wodnym bez udziału węgla aktywnego.

Przedstawione przez Georgia i Kopinke [30] wyniki badań nad wpływem nadtlenku wodoru na właściwości węgla aktywnego oraz wydajność regeneracji węgli nasyconych trichloroetylenem (TCE), eterem metylo-tertbutylowym (MTBE) oraz 2,4,5-trichlorofenolem (TCP) wskazują, że rozkład H_2O_2 w obecności/na powierzchni węgla aktywnego zachodzi zgodnie z kinetyką reakcji I rzędu. Zmniejszenie szybkości rozkładu H_2O_2 w przypadku węgli nasyconych została przypisana zmniejszeniu się ilości miejsc aktywnych na powierzchni węgla niezbędnych do tego procesu. Wykazano, że miejscami tymi mogą być zarówno powierzchniowe grupy funkcyjne jak i obecność metali/heteroatomów.

Badania dotyczące usuwania fenolu zaadsorbowanego na węglu aktywnym z wykorzystaniem zaawansowanego utleniania były prowadzone przez Álvareza i in. [1]. Wykazano, że efektem działania ozonu jest regeneracja węgli aktywnych nasyconych fenolem przy czym o skuteczności regeneracji decydują właściwości węgla aktywnego, co potwierdza ich katalityczną rolę w tym procesie.

W badaniach [23,24] poświęconych poszukiwaniu skutecznej metody usuwania związków organicznych z powierzchni zużytego katalizatora Pallad/węgiel aktywny (Pd/AC) zaproponowano utlenienie zanieczyszczeń organicznych wykorzystując metody pogłębionego utleniania. Wykazano, że skuteczną metodą regeneracji katalizatora jest utlenianie zaadsorbowanych związków organicznych za pomocą mieszaniny O_3/H_2O_2 i następnie redukcji związków palladu 9głównie tlenków) do wolnego Pd za pomocą wodoru. Na przykładzie testowej reakcji redukcji kwasu cynamonowego wykazano, że katalityczna aktywność zregenerowanego katalizatora jest porównywalna do aktywności katalizatora świeżego i może być on z powodzeniem stosowany w reakcjach uwodornienia.

8. Podsumowanie

Coraz wyższe wymagania stawiane oczyszczonym ściekom przemysłowym wymuszają stosowania coraz skuteczniejszych metod oczyszczania. Zróżnicowany i zmieniający się skład tych ścieków, wprowadzanie wciąż nowych substancji sprawia, że konwencjonalne metody oczyszczania nie są wystarczająco skuteczne i poszukuje się wciąż nowych rozwiązań. Ze względów ekonomicznych powinny to być rozwiązania proste, nie wymagające rozbudowanych instalacji, zapewniające odpowiedni stopień redukcji zanieczyszczeń w krótkim czasie, a jednocześnie tanie. Wśród szeregu rozwiązań coraz więcej uwagi poświęca się wykorzystaniu do tego celu zarówno sorpcji, jak i metod pogłębionego utleniania (AOP). Zainteresowanie tymi metodami wynika z ich wysokiej skuteczności usuwania związków organicznych z roztworów wodnych. Cechą charakterystyczną metod AOP jest generowanie w środowisku reakcji wysoce reaktywnych rodników hydroksylowych OH^* reagujących praktycznie ze wszystkimi związkami organicznymi powodując ich rozkład na prostsze cząsteczki lub prowadząc do całkowitego utlenienia. Natomiast sorpcja, szczególnie sorpcja na węglach aktywnych, jest jedną z najskuteczniejszych metod usuwania związków organicznych poprzez ich fizykochemiczne oddziaływanie z powierzchnią sorbentu, co jest wynikiem rozbudowanej struktury porowatej oraz właściwości chemicznych powierzchni.

Jak wykazano, na przykładzie fenoli zarówno zaawansowane utlenianie związków organicznych, szczególnie z wykorzystaniem reagenta Fentona, jak i usuwanie tych substancji drogą sorpcji na węglach aktywnych jest dobrze rozpoznane, opisane w literaturze i znajduje zastosowanie na skalę przemysłową. Niemniej jednak metody te mają również swoje ograniczenia. Poważną wadą metod AOP jest stosowanie znacznych ilości utleniaczy jak i możliwość powstawania produktów pośrednich utlenienia, co w konsekwencji prowadzi do zwiększenia ilości ścieków oraz dodatkowych kosztów. Natomiast zastosowanie węgli aktywnych napotyka na duże trudności z uwagi na ich cenę, koszty instalacji jak i koszty eksploatacji z uwzględnieniem unieszkodliwiania zużytych węgli.

Korzystną alternatywą dla regeneracji zużytych węgli aktywnych wykorzystywanych jako sorbenty zanieczyszczeń organicznych z roztworów wodnych poprzez utlenianie zaadsorbowanych substancji jest bezpośrednie utlenianie substancji organicznych z wykorzystaniem AOP w obecności węgli aktywnych. W tym przypadku równocześnie zachodzi proces sorpcji-utleniania-regeneracji węgla aktywnego, przy czym węgiel aktywny pełni w tym procesie zarówno rolę sorbentu jak i katalizatora reakcji rozkładu nadtlenku wodoru z utworzeniem rodników hydroksylowych $OH^{\bullet}$. Wykazano, że usuwanie związków organicznych z roztworów wodnych z wykorzystaniem węgli aktywnych oraz czynników utleniających zaliczanych do AOP jest procesem skuteczniejszym, niż gdyby procesy utleniania i sorpcji realizowane były oddzielnie. O przydatności węgli aktywnych do usuwania związków organicznych w symultanicznym procesie decydują zarówno ich właściwości sorpcyjne jak i katalityczne. Węgle aktywne powinny mieć charakter zasadowy, dużą powierzchnię właściwą i objętość porów oraz liczbę jodową, a także wysoką zdolność dechloracji.

Literatura

1. **Alvarez, P.M., Beltran, F.J., Gomez-Serrano, V., Jaramillo, J. and Rodriguez E.M.:** *Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol*, Water Res., 38, 2155–2165 (2004).
2. **Bansal R.Ch., Goyal M.:** *Activated Carbon Adsorption.* Taylor & Francis Group. Baca Raton - London - New York - Singapore (2005).
3. **Barbusiński K.:** *Intensyfikacja procesu oczyszczania ścieków i stabilizacji osadów nadmiernych z wykorzystaniem odczynnika Fentona*, Wyd. Politechniki Śląskiej, Gliwice (2004).
4. **Barbusiński K., Majewski J.:** *Discoloration of azo dye Acid Red 18 by Fenton reagent in the presence of iron powder,* Polish J. Environ. Studies, 12, 151–155 (2003).
5. **Barbusiński K.:** *Modyfikacje reakcji Fentona z zastosowaniem nadtlenków wapnia i magnezu,* Studia – Rozprawy – Monografie, Prace Naukowe Głównego Instytutu Górnictwa, 869, Katowice (2006).
6. **Barbusiński K.:** *Oczyszczanie ścieków przemysłowych metodami katalitycznymi z wykorzystaniem nadtlenku wodoru,* Chemik, 2, 31–36 (2001).
7. **Barkiewicz B., Umiejewska K.:** *Oczyszczanie ścieków przemysłowych*, Wydawnictwo Naukowe PWN (2010).
8. **Bayarri B., Gonzalez O., Maldonado I., Gimenez J., Esplugas S.:** *Comparative study of 2,4-dichlorophenol degradation with different advanced oxidation processes*, J. Sol. Energy Eng., 129, 60–67 (2006).

9. **Benitez F. J, Beltrán-Heredia J., González T., Real F.:** *Kinetics of the elimination of vanillin by UV radiation catalyzed with hydrogen peroxide,* Fresen. Environ. Bull., 7, 726–733 (1998).
10. **Benitez F. J., Beltrán-Heredia J., Acero J. L.:** *Oxidation of vanillic acid as a model of polyphenolic compounds in dive oil waste waters III. Combined UV radiation hydrogen peroxide oxidation,* Toxicol. Environ. Chem., 56, 199–210 (1996).
11. **Bezak-Mazur E., Adamczyk D.:** *Adsorpcja barwników na świeżym i zregenerowanym węglu WD-extra*, Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 13, 951–971 (2011).
12. **Bilińska L., Ledakowicz S.:** *Możliwości wykorzystania technik pogłębionego utleniania – AOP do oczyszczania ścieków włókienniczych (barwiarskich) w warunkach przemysłowych,* Informator Chemika Kolorysty, 17, 21–35 (2011).
13. **Biń A.K., Zieliński J.:** *Chemiczna degradacja zanieczyszczeń w ściekach przemysłowych,* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 2, 383–405 (2000).
14. **Biniak S., Trykowski G., Pakuła M., Świątkowski A., Malinowska Z., Popiel S.:** *Effects of ozone dissolved in water on physicochemical properties of activated carbon applied in drinking water treatment,* Adsorp. Sci.Technol., 28, 521–531 (2010).
15. **Boehm H.P.:** *Chemical identification of surface groups*, Adv.Catalysis, 16, 179–274 (1966).
16. **Buczek B., Czepirski L.:** *Adsorbenty węglowe – surowce, otrzymywanie, zastosowanie*, Gospodarka Surowcami Mineralnymi, 17, 29–61 (2001).
17. **Charmisinof P.N.:** *Carbon adsorption handbook*, Ann Arbor Science Publishers Inc., (1978)
18. Chemical Abstract System Registry, American Chemical Society (2014).
19. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Applying the combined processes of sorption and oxidation to remove organic compounds from an aqueous environment using the example of p-chlorophenol*, Ecol. Chem. Eng. A., 19, 275–286 (2012).
20. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Assessing the influence of the presence of heavy metals adsorbed on activated carbon on the efficiency of degradation of phenol using selected oxidizing agents,* Ecol. Chem. Eng. S, 19, 249–257 (2012).
21. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Badania nad usuwaniem barwnych związków organicznych ze ścieków z przemysłu włókienniczego*, Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 15, 901–913, 2013.

22. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Sorptive and catalytic properties of activated carbon used for the removal of crystal violet from an aqueous solution in the presence of hydrogen peroxide,* Ecol. Chem. Eng. A., 17, 1423–1433 (2010).
23. **Dąbek L., Świątkowski A., Dziaduszek J.:** *Regeneracja zużytych katalizatorów pallad-węgiel aktywny*, Patent 215431, 25.03.2013r.
24. **Dąbek L., Świątkowski A., Dziaduszek J.:** *Usuwanie substancji dezaktywujących z powierzchni zużytego katalizatora węgiel aktywny-Pd*, Przem. Chem., 86, 2–4 (2007).
25. **De Luis A., Lombraña J. I., Varona F., Menéndez A.:** *Kinetic study and hydrogen peroxide consumption of phenolic compounds oxidation by Fenton's reagent*, Korean J. Chem. Eng., 26, 48–56 (2009).
26. **Dębowski Z.:** *Kryteria doboru węgla aktywnego do oczyszczania wody*, Prace Naukowe Głównego Instytutu Górnictwa, 792, Katowice (1994).
27. **Deryło-Marczewska A., Błachnio M., Marczewski A.W., Świątkowski A., Tarasiuk B.:** *Adsorption of selected herbicides from aqueous solutions on activated carbon*, J. Therm. Anal. Calorim., 101, 785–794 (2010).
28. **Dubinin M.M.:** *Adsorption properties and microporous structure of carbonaceous adsorbents*, Carbon, 25, 593–598 (1987).
29. **Fung P.C., Poon C.S., Chu C.W., Tsui S.M.:** *Degradation kinetics of reactive dye by UV/H2O2/US process under continuous mode operation*, Water Sci. Technol., 44, 67–72 (2001).
30. **Georgi A., Kopinke F.D.:** *Interaction of adsorption and catalytic reactions in water decontamination processes. Part I: Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon*, Appl.Catal.B-Environmental, 58, 9–18 (2005).
31. **Huang H. H., Lu M. C., Chen J. N., Lee C. T.:** *Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons*, Chemosphere, 51, 935–943 (2003).
32. **Huang Y.H., Chou S., Perng M.G., Huang G.H., Cheng S.S.:** *Case study on the bioeffluent of petrochemical wastewater by electro-Fenton method*, Water Res., 39, 145–149 (1999).
33. **Huling S.G., Jones P.K., Ela W.P., Arnold R.G.:** *Repeated reductive and oxidative treatments on granular activated carbon*, J.Environ.Eng., 131, 287–297 (2005).
34. **Huling, S.G., Jones, P.K., Ela, W.P., Arnold R.G.:** *Fenton-driven chemical regeneration of MTBE-spent GAC*, Water Res., 39, 2145–2153 (2005).
35. **Ince N. H., Apikyan I. G.:** *Combination of activated carbon adsorption with lightenhanced chemical oxidation via hydrogen peroxide*, Water Res., 34, 4169–4176 (2000).
36. **Jankowska H., Świątkowski A., Choma J.:** *Węgiel aktywny,* WNT, Warszawa (1985).

37. **Jankowska H., Świątkowski A., Sarostin L., Ławrinienko-Omiecynska J.:** *Adsorpcja jonów na węglu aktywnym*, Wydawnictwo PWN, Warszawa (1991)
38. **Jans U., Hoigne J.:** *Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals,* Ozone Sci. Eng., 20, 67–90 (1998).
39. **Karci A., Arslan-Alaton I., Olmez-Hanci T., Bekbolet M.:** *Transformation of 2,4-dichlorophenol by H_2O_2/UV-C, Fenton and photo-Fenton processes: Oxidation products and toxicity evolution*, J. Photochem. Photobiol., A 230, 65–73 (2012).
40. **Koziorowski B.:** *Oczyszczanie ścieków przemysłowych,* WNT, Warszawa (1980).
41. **Krzemińska D., Neczaj E., Parkitna K.:** *Zastosowanie reakcji Fentona do wspomagania biologicznego oczyszczania ścieków z przemysłu mleczarskiego,* Rocznik Ochrona Środowiska (Annual Set The Environment Protection), 15, 2381–2397 (2013).
42. **Ksycińska-Rębiś E., Lach J, Okoniewska E.:** *Wpływ modyfikacji węgla aktywnego na jego zdolności sorpcyjne w stosunku do fenolu,* V Konferencja Naukowo-Technicza Węgiel aktywny w ochronie środowiska i przemyśle, Politechnika Częstochowska, 160–168, Białowieża (2006).
43. **Kucharska M., Naumczyk J.:** *Degradation of selected chlorophenols by advanced oxidation processes*, Environment Protection Engineering, 35, 47–55 (2009).
44. **Kuśmierek K., Sankowska M., Świątkowski A.:** *Kinetic and equilibrium studies of simultaneous adsorption of monochlorophenols and chlorophenoxy herbicides on activated carbon,* Desalin. Water Treat., 52, 178–183 (2014).
45. **Kuśmierek K., Świątkowski A., Syga P., Dąbek L.:** *Influence of chlorine atom number in chlorophenols molecules on their adsorption on activated carbon*, Fresenius Environ. Bull., 23, 947–951 (2014).
46. **Kuśmierek K., Świątkowski A.:** *Usuwanie 4-chlorofenolu z wody metodami pogłębionego utleniania opartymi na nadtlenku wodoru*, Przem. Chem., 91, 2422–2424 (2012).
47. **Lach J., Okoniewska E., Stepnia L., Ociepa-Kubicka A.:** *The influence of modification of activated carbon on adsorption of Ni(II) and Cd(II),* Desalin. Water Treat., 52, 3979–3986 (2014).
48. **Lach J.:** *Wpływ sposobu modyfikacji węgli aktywnych na adsorpcję metali ciężkich*, Wyd. Politechniki Częstochowskiej, (2011).
49. **Ledakowicz S., Olejnik D., Perkowski j., Segota H.:** *Wykorzystanie procesów pogłębionego utleniania do rozkładu niejonowego środka powierzchniowo czynnego Tryton X-114*. Przem. Chem., 80, 453–459 (2001).

50. **Lorenc-Grabowska E., Gryglewicz G., Diez M.A.:** *Kinetics and equilibrium studies of phenol adsorption on nitrogen-enriched activated carbons*, Fuel, 114, 235–243 (2013).
51. **Lorenc-Grabowska E., Gryglewicz G., Machnikowski J.:** *p-chlorophenol adsorption on activated carbons with basic surface properties*, Appl. Surf. Scie., 256, 4480–4487 (2010).
52. **Madeła M., Dębowski Z.:** *Sorpcja fenolu ze ścieków koksowniczych na granulowanych węglach aktywnych,* V Konferencja Naukowo-Technicza Węgiel aktywny w ochronie środowiska i przemyśle, Politechnika Częstochowska, 145–151, Białowieża (2006).
53. **Madeła M., Okoniewska E.:** *Badania bioregeneracji węgla aktywnego nasyconego fenolem,* V Konferencja Naukowo-Technicza Węgiel aktywny w ochronie środowiska i przemyśle, Politechnika Częstochowska, 152–159, Białowieża (2006).
54. **Magee V.:** *The Application o f Granular Active Carbon f or Dechlorination of Water Supplies,* Proc. Soc. Water Treat. Exam., 5, 17–40 (1956).
55. **Magne P., Walker P.L. Jr.:** *Phenol adsorption on activated carbons: Application to the regeneration of activated carbons polluted with phenol*, Carbon, 24, 101–107 (1986).
56. **Methatham T., Lu M.C., Ratanatamskul C.:** *Removal of 2,4-dichlorophenol as herbicide's by-product by Fenton's reagent combined with an electrochemical system*, Desalin. Water Treat., 32, 42–48 (2011).
57. **Mikułka M.:** (pod red.), *Charakterystyka technologiczna przemysłu włókienniczego w Unii Europejskiej*, Ministerstwo Środowiska, dostępne na stronie www.ippc.mos.gov.pl, Warszawa (2003).
58. **Moreno-Castilla C.:** *Adsorption of organic molecules from aqueous solutions on carbon materials,* Carbon, 42, 83–94 (2004).
59. **Nawrocki J., Bitozor S.:** red., *Uzdatnianie wody. Procesy chemiczne i biologiczne*, PWN, Warszawa-Poznań (2000).
60. **Oller I., Malato S., Sánchez-Pérez J. A.:** *Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination - A review,* Sci. Total Environ., 409, 4141–66 (2011).
61. **Paillard H.:** *Process for the oxidation of organic micropollutants in water using the O_3 /H_2O_2 combination,* US 5364537 A (1994).
62. **Pera-Titus M., Garcia-Molina V., Banos M., Jimenez J., Esplugas S.:** *Degradation of chlorophenols by means of advanced oxidation processes: a general review*, Appl. Catal. B: Environ., 47, 219–256 (2004).
63. **Pérez M., Torrades F., Domènech X., Peral J.:** Fenton and photo-Fenton oxidation of textile effluents, Water Research, 36, 2703–2710 (2002).
64. **Picheta-Oleś A.:** *Usuwanie wybranych związków organicznych ze ścieków przemysłowych przy symultanicznym prowadzeniu sorpcji i pogłębionego utleniania*, Politechnika Świętokrzyska (2014).

65. **Rastogi, A., Al-Abed, S.R., Dionysiou, D.D.:** *Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols*, Water Res., 43, 684–694 (2009).
66. Rocznik Statystyczny Rzeczpospolitej Polskiej 2014 , Zakład Wydawnictw Statystycznych Warszawa, ISSN 1506-0632
67. Roskill Reports Expanding the World`s Knowledge of Metals and Minerals Markets, 2013
68. Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014r. r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz.U.2014 nr 0 poz. 1800 2014.12.31
69. **Rüffer H., Rosenwinkel K.-H.:** *Oczyszczanie ścieków przemysłowych,* Poradnik Wyd. Pierwsze, Ofic. Wyd. Projprzem-EKO Bydgoszcz (1998).
70. **Sanchis S., Polo A.M., Tobajas M., Rodriguez J.J., Mohedano A.F.:** *Degradation of chlorophenoxy herbicides by coupled Fenton and biological oxidation*, Chemosphere, 93, 115–122 (2013).
71. **Sankowska M., Świątkowski A.:** *Kinetic and equilibrium studies of simultaneous adsorption of monochlorophenols and chlorophenoxy herbicides on activated carbon*, Desalin.Water Treat., 2013 (DOI: 10.1080/19443994. 2013.780984).
72. **Santos V.P., Pereira M.F.R., Faria P.C.C., Órfão J.J.M.:** *Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons*, J.Hazard.Mater., 162, 736–742 (2009).
73. **Shende, R.V., Mahajani, V.V.:** *Wet oxidative regeneration of activated carbon loaded with reactive dye*, Waste Manage., 22, 73–83 (2002).
74. **Stoeckli H.F.:** *Microporous carbons and their characterization: The present state of the art*, Carbon, 28, 1–6 (1990).
75. **Świderska R., Czerwińska M., Kutz R.:** *Utlenianie zanieczyszczeń organicznych za pomocą odczynnika Fentona.* Zesz. Nauk. Politechniki Koszalińskiej, 22, 1–12, Koszalin (2005).
76. **Tao Zhou, Teik-Thye Lim, Xiaohua Lu, Yaozhong Li, Fook-Sin Wong:** *Simultaneous degradation of 4CP and EDTA in a heterogene-ous Ultrasound/Fenton like system at ambient circumstance,* Sep. Purif. Technol., 68, 367–374 (2009).
77. **Terzyk A.P., Rychlicki G., Gauden P.A., Kowalczyk P.:** *The effect of carbon surface chemical composition on the mechanism of phenol adsorption from aqueous solutions*, (in:) Water Encyclopedia,Volume Oceanography; Meteorology; Physics and Chemistry; Water Law; and Water History Art and Culture, Willey 404–408 (2005).

78. **Terzyk A.P., Rychlicki G.:** *Mechanizmy adsorpcji fenoli roztworów wodnych na węglach aktywnych*, VII Krajowa Konferencja Naukowa „Węgiel Aktywny w Ochronie Środowiska i Przemyśle", Politechnika Częstochowska, 120–127, Białowieża (2006).
79. **Terzyk AP, Wiśniewski M, Gauden PA, Rychlicki G, Furmaniak S.:** *Carbon surface chemical composition in para-nitrophenol adsorption determined under real oxic and anoxic conditions,* J. Colloid_Interface Sci., 320, 40–51 (2008).
80. **Toledo L.C., Silva A.C.B., Augusti R., Lago R.M.:** *Application of Fenton's reagent to regenerate activated carbon saturated with organochloro compounds,* Chemosphere, 50, 1049–1054 (2003).
81. **Wąsowski J., Piotrowska A.:** *Rozkład organicznych zanieczyszczeń wody w procesach pogłębionego utleniania,* Ochrona Środowiska, 85, 27–32 (2002).
82. **Zarzycki R**. (red.): *Zaawansowane techniki utleniania w ochronie środowiska.* Polska Akademia Nauk, Łódź (2002).

Application of Sorption and Advanced Oxidation Processes for Removal of Phenols from Aqueous Solutions

Abstract

The removal of organic contaminants such as aliphatic and aromatic hydrocarbons, phenols and related compounds, halogenated compounds, polycyclic aromatic hydrocarbons, aldehydes, ketones, acids, detergents, fats, dyes etc. from water and sewage is still an interesting and significant problem in environmental engineering. Both household and industrial waste is a source of organic contaminants in the environment. Higher and higher requirements regarding treated waste that is directed to water or the ground require constant development of the waste treatment process. The literature data and implemented solutions indicate that more and more attention is now paid to the use of sorption and advanced oxidation processes for the removal of organic compounds.

The highest significance and application among available sorbents has activated carbon. The sorption properties of activated carbon are dependent on its porous structure, produced by the system of interconnected macro-, meso- and micropores as well as the chemical composition of the surface resulting from the presence of oxygen functional groups. Activated carbon is especially useful as sorbents of phenol and chlorophenol. It has been shown that the adsorption ability of activated carbon depends on the specific surface area, porosity and surface chemical composition. High affinity of phenol to the surface of activated carbon is related to the creation of donor-acceptor complexes between alkaline locations on the sorbent's surface and the aromatic ring. Oxidation of

activated carbon's surface leading to increased acidity lowers the sorption capacity of activated carbon. While the presence of metals increases the sorption capacity of activated carbon in relation to phenol due to the donor-acceptor interaction of metal-electrons of π aromatic ring in the phenol particle.

Another method of successful oxidation of phenols is their oxidation especially with the AOP methods (Advanced Oxidation Processe)s. A characteristic feature of these methods is oxidation of generally all organic compounds to CO_2, H_2O and inorganic compounds with the use of the hydroxyl radical OH^* (generated in the solution) of extremely high oxidising potential of 2,8 V. Phenols and the related compounds quite easily undergo oxidation, especially with Fenton and photo-Fenton reactions

Both sorption and oxidation of organic compounds (including phenols) with AOP methods have advantages (high output and efficiency) and disadvantages (treatment of used sorbents, significant use of oxidants and increased sewage volume). In order to focus on the advantages of sorption and advanced oxidation while limiting their disadvantageous effect a combination of these two processes is considered. In this case the removal of contaminants is arranged as a two- or one-stage process. In the first one the removal of organic compounds covers sorption and then oxidation of the adsorbed substances with the use of AOP, which leads to a simultaneous regeneration of activated carbon. While in the latter case simultaneous sorption and oxidation of organic compounds is considered. In these both cases activated carbon acts as a sorbent of organic compounds and catalyst in the production of hydroxyl radicals OH^* which are responsible for oxidation of organic compounds both in the solution and adsorbed on the activated carbon. It has been proven that in the presence of activated carbon in the environment of hydrogen peroxide, oxidation occurs of such organic compounds that do not undergo oxidation with the same oxidant in the aqueous solution. The applicability of activated carbon for the simultaneous removal of organic compounds is dependent on both their sorption and catalytic properties. Activated carbon should be alkaline, have high specific volume, pores' volume, iodine number and significant dechlorination ability.

The applicability of oxidation of organic compounds with the use of hydroxyl radicals created on the surface of activated carbon for regeneration of the used sorbents has also been proven.

Słowa kluczowe:
fenol, chlorofenol, węgiel aktywny, utlenianie, rodnik hydroksylowy

Keywords:
phenol, chlorophenol, activated carbon, oxidation, hydroxyl radicals

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Zmniejszenie uciążliwości zapachowych oczyszczalni ścieków w Tychowie

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1. Wstęp

Eksploatacja obiektów związanych z gospodarką ściekową wiąże się z emisją uciążliwych zapachowo odorów. Dotyczy to przede wszystkim większości oczyszczalni ścieków, punktów zlewnych ścieków dowożonych, jak i sanitarnych instalacji kanalizacyjnych [4].

Odoranty dopływają do oczyszczalni wraz ze ściekami, jak i powstają wtórnie na jej terenie podczas procesów oczyszczania ścieków i przeróbki osadów ściekowych. Badania wykazały, że emisja odorantów następuje na każdym etapie oczyszczania ścieków, tj. w miejscu dopływu ścieków do oczyszczalni, na kratach, w przepompowniach ścieków surowych, w piaskownikach, odtłuszczaczach, osadnikach wstępnych i komorach osadu czynnego, złożach biologicznych, a także w miejscach turbulentnego przepływu ścieków i składowania biomasy. Takimi miejscami są min. składowiska skratek, piasku, tłuszczu, stacje odwadniania, suszenia i gromadzenia osadów [4].

Odory pochodzenia ściekowego zawierają liczne gazy nieorganiczne, jak: siarkowodór (H_2S), amoniak (NH_3), dwutlenek węgla (CO_2), azot (N), wodór (H), tlen (O_2) oraz opary substancji organicznych, które powstają w procesach mikrobiologicznych: aldehydy, kwasy organiczne, ketony itp. Najbardziej uciążliwym dla otoczenia odorem jest siarkowodór [4].

Nieprzyjemne zapachy stwarzają nie tylko poczucie dyskomfortu, lecz także mogą być przyczyną negatywnych objawów psychosomatycznych, takich jak rozdrażnienie, bóle głowy, nudności, trudności z koncentracją, utratę łaknienia, trudności z zasypianiem i szereg innych niekorzystnych objawów [5, 17].

Brak w Polsce unormowań prawnych, dotyczących jakości powietrza oraz oddziaływania uciążliwych zapachowo substancji, przyczynia się do podejmowania badań nad odorami w zespołach badawczych rożnych instytucji, min. w Politechnice Szczecińskiej, Politechnice Lubelskiej, Politechnice Łódzkiej, Politechnice Wrocławskiej, Politechnice Warszawskiej, Uniwersytecie Warmińsko-Mazurskim w Olsztynie, a także Politechnice Koszalińskiej [2, 3, 6–13, 15, 16, 18, 19].

W Katedrze Techniki Wodno-Mułowej i Utylizacji Odpadów Politechniki Koszalińskiej od kilku lat prowadzone są badania nad maskowaniem nieprzyjemnych zapachów, czyli zastępowaniem zapachu niepożądanego przyjemniejszym. Jako środki maskujące wykorzystywane są naturalne olejki eteryczne, pozyskiwane ze świeżych surowców roślinnych w procesie destylacji parą wodną.

Najważniejszym celem prowadzonych badań było znalezienie optymalnych warunków prowadzenia procesu odwadniania komunalnych osadów ściekowych na wirówce dekantacyjnej ALFA LAVAL, typ ALDEC 30, zainstalowanej na terenie oczyszczalni ścieków w Tychowie, a także zmniejszenie uciążliwości pracy obsługi tej wirówki poprzez zastosowanie do procesu odwadniania olejku eterycznego z pomarańczy jako częściowego substytutu flokulantów.

2. Metodyka badań

2.1. Odwadnianie komunalnych osadów ściekowych

Proces odwadniania komunalnych osadów ściekowych badano na wirówce dekantacyjnej ALFA LAVAL, typ ALDEC 30 na terenie Oczyszczalni Ścieków w Tychowie.

Parametrami stałymi procesu odwadniania były:

- prędkość wirowania n [obr/min] – $n = 2400$ obr/min,
- dawka C [dm^3/m^3] – $C = 76{,}3$ dm^3/m^3.

Parametr zmienny niezależny procesu odwadniania:

- x_1– udział olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki $C = 76{,}3$ dm^3/m^3 $U_{O/F}$ [%] – przyjęto: $U_{O/F1}$ = [0%/100%], $U_{O/F2}$ = [25%/75%], $U_{O/F3}$ = [50%/50%], $U_{O/F4}$ = [75%/25%].

Parametry zmienne zależne (wynikowe) procesu odwadniania:

- y_1 – zawartość wody w osadzie W [%],
- y_2 – zawartość suchej masy w odcieku β [mg/dm^3],
- y_3 – stężenie zapachu olejku eterycznego z pomarańczy w odwirowanym osadzie c_{od} [ou_E/m^3].

Bezpośrednio po pobraniu próbek w czasie do 1h od chwili pobrania, oznaczano parametry fizyczne osadu, tworzącego nadawę do procesu odwadniania, tj.: pH [-], temperaturę [^{o}C], barwę, strukturę, zapach, zawartość wody W_N [%] i zawartość suchej masy β_N [mg/dm^3]. Próbki były przechowywane w lodówce w temperaturze 4^{o}C. Próbki pobrano z wylotu osadu na wirówce dekantacyjnej ALFA LAVAL, typ ALDEC 30, będącej własnością Oczyszczalni Ścieków w Tychowie.

2.2. Charakterystyka osadu ściekowego

Do badań użyto ściek zawiesinowy o następującej charakterystyce:

- pH: 7,3,
- temperatura: 20°C,
- barwa: czarna,
- struktura osadu: jednolita, trudno opadający, zawiesinowy,
- zapach: gnilny,
- zawartość wody W_N: 97,89%,
- zawartość suchej masy β_N: 21023,60 mg/dm^3.

2.3. Charakterystyka polimeru kationowego ZETAG® 9048FS

Proces odwadniania w przemysłowej wirówce dekantacyjnej ALFA LAVAL, typ ALDEC 30 na terenie Oczyszczalni Ścieków w Tychowie wspomagany był poprzez dawkowanie polimeru kationowego o nazwie handlowej ZETAG® 9048FS o stężeniu rzeczywistym roztworu 0,48%.

W tabeli 1 przedstawiono informacje na temat podstawowych właściwości fizycznych i chemicznych flokulanta ZETAG® 9048FS użytego do badań.

Tabela 1. Charakterystyka flokulanta ZETAG® 9048FS [1]
Table 1. Characteristics of ZETAG® 9048FS flocculant [1]

Stan skupienia/forma	emulsja
Kolor	kremowy, prawie biały
Zapach	charakterystyczny dla oleju mineralnego
Wartość pH	ok. 4
Temperatura zapłonu	> 93°C
Gęstość	ok. 1,0 g/cm^3 (20°C)
Rozpuszczalność w wodzie	rozpuszczalny
Lepkość dynamiczna	ok. 1.500 mPa.s
Niebezpieczeństwo eksplozji	produkt nie jest wybuchowy
Mieszalność z wodą	miesza się

2.4. Charakterystyka olejku eterycznego z pomarańczy

Do badań procesu mechanicznego odwadniania komunalnych osadów ściekowych w skali przemysłowej wykorzystano naturalny olejek eteryczny z pomarańczy, który zakupiono w Fabryce Substancji Zapachowych „POLLENA-AROMA" Sp. z o.o.

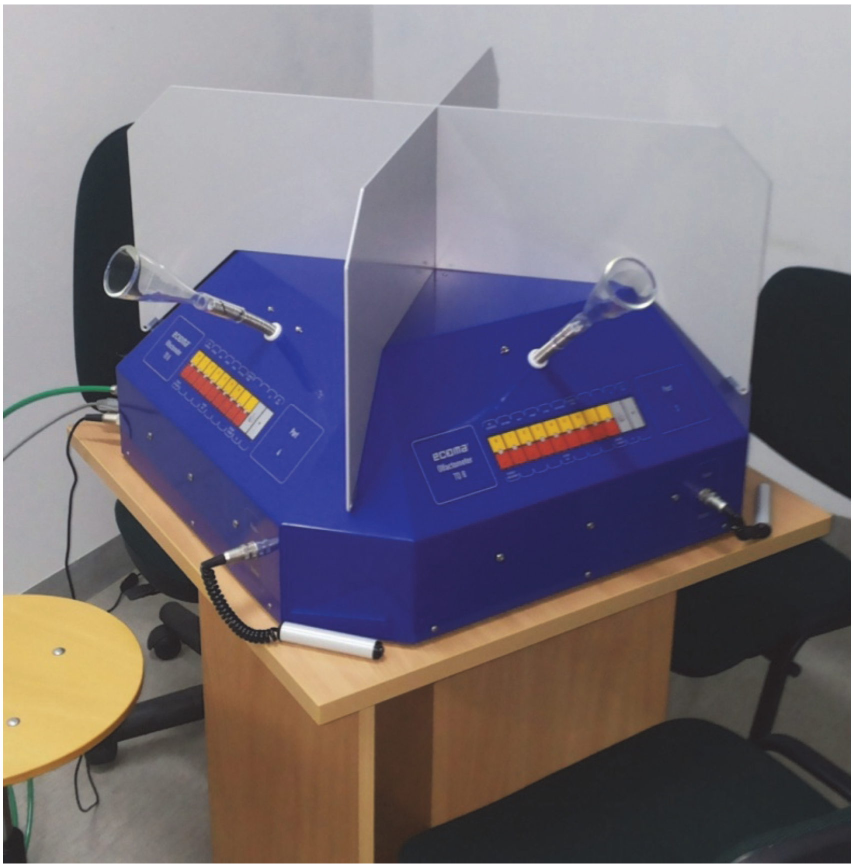
Informacje na temat podstawowych właściwości fizyczno-chemicznych olejku eterycznego z pomarańczy zastosowanego do badań przedstawiono w tabeli 2.

Tabela 2. Charakterystyka olejku eterycznego z pomarańczy [20]
Table 2. Characteristics of orange essential oil [20]

Wygląd	Ciecz
Barwa	Żółta do czerwonożółtej
Zapach	Pomarańczowy
Gęstość d_{20}^{20}	0,844 g/cm^3
Współczynnik załamania światła n_D^{20}	1,4730
Skręcalność α_D^{20}	+ 96,4°
Liczba kwasowa	-
Liczba estrowa	-
Rozpuszczalność w etanolu	-
Zawartość związków karbonylowych	1,2%

2.5. Pomiar stężenia zapachowego olejku eterycznego w odwodnionym osadzie

Bezpośrednio po poborze próbki były przewożone do laboratorium, gdzie dokonywano oznaczenia stężeń zapachowych. Pomiar wykonywany był metodą olfaktometrii dynamicznej zgodnie z wytycznymi opisanymi w PN-EN 13725:2007 [14] przy użyciu czterostanowiskowego olfaktometru T08 (rysunek 1) wraz z niezbędnym oprzyrządowaniem. Zespół pomiarowy składał się z operatora oraz czterech probantów, wyselekcjonowanych zgodnie z wytycznymi zawartymi w normie, przy użyciu n-butanolu jako substancji odniesienia. Zgodnie z normą badania były prowadzone w wyciszonym i odizolowanym pomieszczeniu o stabilnych warunkach temperaturowych i oświetleniowych.



Rys. 1. Olfaktometr T08
Fig. 1. Olfactometer T08

Podczas pomiaru próbka gazu z odwirowanego osadu podłączana była do olfaktometru, a zadaniem probantów było sygnalizowanie, czy wyczuwają zapach w prezentowanym strumieniu gazów. Gazy rozcieńczane były bezwonnym powietrzem w sposób dynamiczny. Początkowe rozcieńczenie zostało dobrane tak, aby nie było możliwe stwierdzenie obecności zapachu. Prezentowane rozcieńczenia były malejące. Wśród prezentowanych prób znajdowały się tzw. „ślepe próbki” lub „zerowe próby”, w których zamiast zapachu było prezentowane czyste, bezwonne powietrze. Olfaktometr był połączony z komputerem z zainstalowanym specjalnym oprogramowaniem. Jeden pomiar składał się z czterech serii pomiarowych. Zebrane w komputerze wyniki zostały obliczone jako wynik pomiaru zespołowego ($Z_{ite,pan}$) – średnia geometryczna ze wszystkich pomiarów indywidualnych. Była to jednocześnie wartość stężenia odorów w danej próbce (c_{od}) wyrażona w europejskich jednostkach zapachowych w metrze sześciennym (ou_E/m^3) zgodnie z PN-EN 13725:2007 [14].

3. Opis i analiza wyników badań

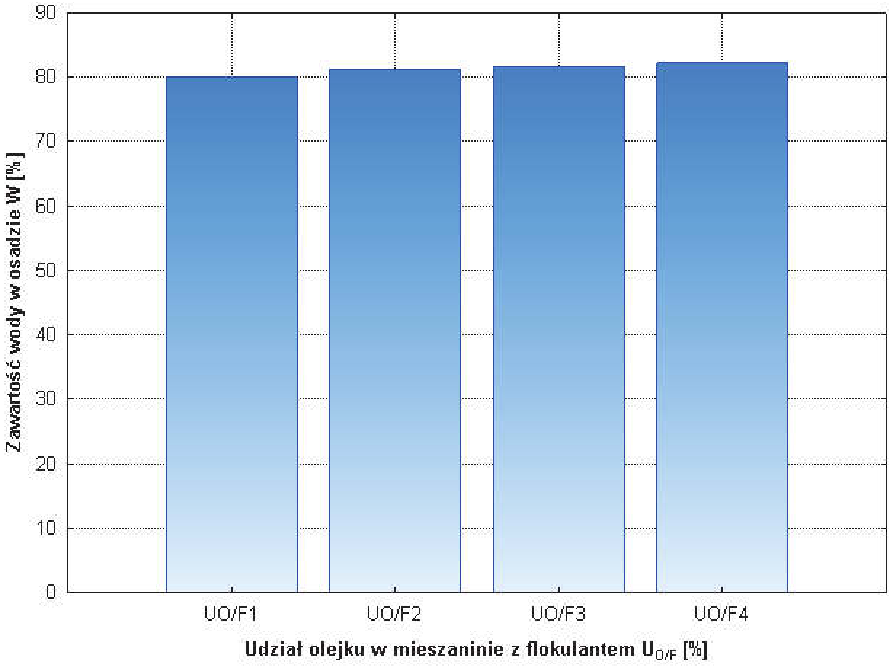
W tabeli 3 przedstawiono wyniki badań wpływu udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki C = 76,3 dm^3/m^3 na zawartość wody w osadzie W [%] i zawartość suchej masy w odcieku β [mg/dm^3]:

- **Udział $U_{O/F1}$** – 0% olejku z pomarańczy (0 dm^3) + 100% flokulanta ZETAG® 9048FS (76,3 dm^3)/m^3,
- **Udział $U_{O/F2}$** – 25% olejku z pomarańczy (19,1 dm^3) + 75% flokulanta ZETAG® 9048FS (57,2 dm^3)/m^3,
- **Udział $U_{O/F3}$** – 50% olejku z pomarańczy (38,15 dm^3) + 50% flokulanta ZETAG® 9048FS (38,15 dm^3)/m^3,
- **Udział $U_{O/F4}$** – 75% olejku z pomarańczy (57,2 dm^3) + 25% flokulanta ZETAG® 9048FS (19,1 dm^3)/m^3.

Tabela 3. Wyniki badań wpływu udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki $C = 76,3$ dm^3/m^3 na zawartość wody w osadzie W [%] i zawartość suchej masy w odcieku β [mg/dm^3]

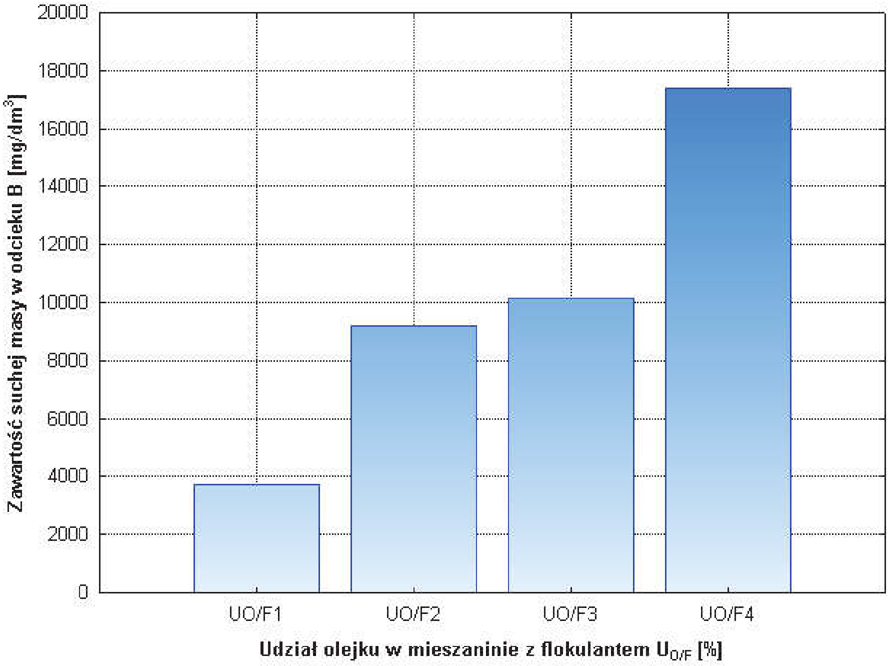
Table 3. Results of tests on influence of orange essential oil in mixture with ZETAG® 9048FS flocculant $U_{O/F}$ [%] in dose $C = 229$ dm^3/3 m^3 on water content in sediments W [%] and solids concentration in effluent β [mg/dm^3]

Udział $U_{O/F}$ [%]	Zawartość wody w osadzie W [%]	Zawartość suchej masy w odcieku β [mg/dm^3]
$U_{O/F1}$	80,07	3741,54
$U_{O/F2}$	81,14	9203,12
$U_{O/F3}$	81,62	10176,60
$U_{O/F4}$	82,27	17412,68



Rys. 2. Wpływ udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki $C = 76,3$ dm^3/m^3 na zawartość wody w osadzie W [%]

Fig. 2. Influence of orange essential oil in mixture with ZETAG® 9048FS flocculant $U_{O/F}$ [%] in dose $C = 229$ dm^3/3 m^3 on water on water content in sediments W [%]



Rys. 3. Wpływ udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki C = 76,3 dm^3/m^3 na zawartość suchej masy w odcieku β [mg/dm^3]

Rys. 3. Influence of orange essential oil share in the mixture with ZETAG® 9048FS flocculant $U_{O/F}$ [%] for dose C = 229 $dm^3/3\ m^3$ on solids concentration in effluent β [mg/dm^3]

W tabelach 4 i 5 przedstawiono wyniki badań wpływu udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki C = 76,3 dm^3/m^3 na stężenie zapachu olejku w odwirowanym osadzie c_{od} [ou_E/m^3].

Ogólnie stężenie nieprzyjemnego zapachu osadu ściekowego wynosi c_{od} = 11794 [ou_E/m^3].

Tabela 4. Dane do obliczania wyniku pomiaru stężenia zapachowego (metoda tak/nie)
Table 4. Data for calculation of result of odour concentration measurement (method yes/no)

Nr dawki	Nr próbki	Nr serii	Z_{tak1}	Z_{tak2}	Z_{tak3}	Z_{tak4}	Z_{ITE1}	Z_{ITE2}	Z_{ITE3}	Z_{ITE4}	$\bar{Z}_{ITE,pan}$	ΔZ_1	ΔZ_2	ΔZ_3	ΔZ_4
$U_{O/F1}$	1	1	16384	32768	32768	2048	23170	46341	46341	2896	11094	2,1	4,2	4,2	-3,8
		2	16384	16384	2048	16384	23170	23170	2896	23170		2,1	2,1	-3,8	2,1
		3	8192	8192	2048	4096	11585	11585	2896	5793		1,0	1,0	-3,8	-1,9
		4	16384	8192	4096	2048	23170	11585	5793	2896		2,1	1,0	-1,9	-3,8
	2	1	16384	16384	8192	4096	23170	23170	11585	5793	13193	1,8	1,8	-1,1	-2,3
		2	16384	8192	16384	8192	23170	11585	23170	11585		1,8	-1,1	1,8	-1,1
		3	8192	16384	16384	4096	11585	23170	23170	5793		-1,1	1,8	1,8	-2,3
		4	8192	8192	8192	4096	11585	11585	11585	5793		-1,1	-1,1	-1,1	-2,3
	3	1	4096	16384	16384	8192	5793	23170	23170	11585	11094	-1,9	2,1	2,1	1,0
		2	16384	16384	2048	4096	23170	23170	2896	5793		2,1	2,1	-3,8	-1,9
		3	8192	8192	8192	8192	11585	11585	11585	11585		1,0	1,0	1,0	1,0
		4	8192	16384	8192	2048	11585	23170	11585	2896		1,0	2,1	1,0	-3,8
$U_{O/F2}$	1	1	2048	4096	1024	2048	2896	5793	1448	2896	3298	-1,1	1,8	-2,3	-1,1
		2	2048	8192	512	2048	2896	11585	724	2896		-1,1	3,5	-4,6	-1,1
		3	4096	4096	1024	4096	5793	5793	1448	5793		1,8	1,8	-2,3	1,8
		4	4096	4096	1024	2048	5793	5793	1448	2896		1,8	1,8	-2,3	-1,1
	2	1	4096	8192	4096	4096	5793	11585	5793	5793	5312	1,1	2,2	1,1	1,1
		2	4096	8192	4096	4096	5793	11585	5793	5793		1,1	2,2	1,1	1,1
		3	4096	8192	1024	1024	5793	11585	1448	1448		1,1	2,2	-3,7	-3,7
		4	4096	8192	4096	1024	5793	11585	5793	1448		1,1	2,2	1,1	-3,7
	3	1	4096	4096	2048	2048	5793	5793	2896	2896	4277	1,4	1,4	-1,5	-1,5
		2	4096	4096	4096	2048	5793	5793	5793	2896		1,4	1,4	1,4	-1,5
		3	2048	8192	4096	2048	2896	11585	5793	2896		-1,5	2,7	1,4	-1,5
		4	4096	4096	1024	2048	5793	5793	1448	2896		1,4	1,4	-3,0	-1,5

Tabela 4. cd.
Table 4. cont.

Nr dawki	Nr próbki	Nr serii	Z_{tak1}	Z_{tak2}	Z_{tak3}	Z_{tak4}	Z_{ITE1}	Z_{ITE2}	Z_{ITE3}	Z_{ITE4}	$\bar{Z}_{ITE,pan}$	ΔZ_1	ΔZ_2	ΔZ_3	ΔZ_4
$U_{O/F3}$	1	1	2048	4096	2048	2048	2896	5793	2896	2896	6049	-2,1	-1,0	-2,1	-2,1
		2	4096	16384	4096	2048	5793	23170	5793	2896		-1,0	3,8	-1,0	-2,1
		3	8192	16384	4096	1024	11585	23170	5793	1448		1,9	3,8	-1,0	-4,2
		4	8192	16384	4096	2048	11585	23170	5793	2896		1,9	3,8	-1,0	-2,1
	2	1	4096	8192	1024	1024	5793	11585	1448	1448	4871	1,2	2,4	-3,4	-3,4
		2	4096	16384	2048	2048	5793	23170	2896	2896		1,2	4,8	-1,7	-1,7
		3	4096	4096	2048	2048	5793	5793	2896	2896		1,2	1,2	-1,7	-1,7
		4	2048	4096	4096	16384	2896	5793	5793	23170		-1,7	1,2	1,2	4,8
	3	1	2048	8192	2048	4096	2896	11585	2896	5793	4871	-1,7	2,4	-1,7	1,2
		2	2048	8192	2048	4096	2896	11585	2896	5793		-1,7	2,4	-1,7	1,2
		3	8192	8192	1024	4096	11585	11585	1448	5793		2,4	2,4	-3,4	1,2
		4	4096	8192	1024	8192	5793	11585	1448	11585		1,2	2,4	-3,4	2,4
$U_{O/F4}$	1	1	4096	8192	8192	8192	5793	11585	11585	11585	6597	-1,1	1,8	1,8	1,8
		2	2048	16384	2048	8192	2896	23170	2896	11585		-2,3	3,5	-2,3	1,8
		3	2048	8192	2048	4096	2896	11585	2896	5793		-2,3	1,8	-2,3	-1,1
		4	2048	8192	4096	4096	2896	11585	5793	5793		-2,3	1,8	-1,1	-1,1
	2	1	1024	8192	2048	4096	1448	11585	2896	5793	5312	-3,7	2,2	-1,8	1,1
		2	4096	4096	2048	8192	5793	5793	2896	11585		1,1	1,1	-1,8	2,2
		3	2048	8192	2048	8192	2896	11585	2896	11585		-1,8	2,2	-1,8	2,2
		4	4096	16384	4096	1024	5793	23170	5793	1448		1,1	4,4	1,1	-3,7
	3	1	2048	8192	4096	2048	2896	11585	5793	2896	6889	-2,4	1,7	-1,2	-2,4
		2	4096	8192	8192	16384	5793	11585	11585	23170		-1,2	1,7	1,7	3,4
		3	2048	8192	4096	8192	2896	11585	5793	11585		-2,4	1,7	-1,2	1,7
		4	4096	8192	2048	4096	5793	11585	2896	5793		-1,2	1,7	-2,4	-1,2

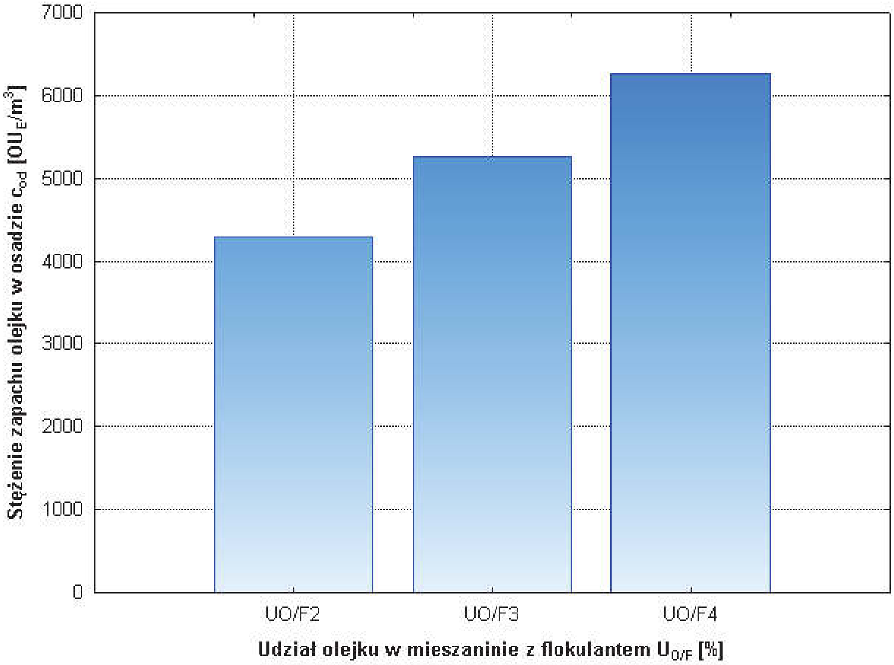
Z_{tak1}, Z_{tak2}, Z_{tak3}, Z_{tak4} – stopień rozcieńczenia na progu wyczuwalności 50% [-];
Z_{ITE1}, Z_{ITE2}, Z_{ITE3}, Z_{ITE4} – ocena progu indywidualnego, wyrażona jako stopień rozcieńczenia [-]; $\bar{Z}_{ITE,pan}$ – średnia geometryczna ocen progu indywidualnego Z_{ITE} dla wszystkich uprawnionych członków zespołu po powtórnej weryfikacji [-];
ΔZ_1, ΔZ_2, ΔZ_3, ΔZ_4 – parametr weryfikacji zespołu [-]

Na podstawie wartości stopnia rozcieńczenia do progu zespołowego $\bar{Z}_{ITE,pan}$ wyznaczono stężenia zapachowe w badanych próbkach:

- Udział $U_{O/F1}$, próbka nr 1: $\bar{Z}_{ITE,pan} = 11094$,
  stąd $c_{od} = 11094 \cdot 1\ ou_E/m^3 = 11094\ ou_E/m^3$,
- Udział $U_{O/F1}$, próbka nr 2: $\bar{Z}_{ITE,pan} = 13193$,
  stąd $c_{od} = 13193 \cdot 1\ ou_E/m^3 = 13193\ ou_E/m^3$,
- Udział $U_{O/F1}$, próbka nr 3: $\bar{Z}_{ITE,pan} = 11094$,
  stąd $c_{od} = 11094 \cdot 1\ ou_E/m^3 = 11094\ ou_E/m^3$,
- Udział $U_{O/F2}$, próbka nr 1: $\bar{Z}_{ITE,pan} = 3298$,
  stąd $c_{od} = 3298 \cdot 1\ ou_E/m^3 = 3298\ ou_E/m^3$,
- Udział $U_{O/F2}$, próbka nr 2: $\bar{Z}_{ITE,pan} = 5312$,
  stąd $c_{od} = 5312 \cdot 1\ ou_E/m^3 = 5312\ ou_E/m^3$,
- Udział $U_{O/F2}$, próbka nr 3: $\bar{Z}_{ITE,pan} = 4277$,
  stąd $c_{od} = 4277 \cdot 1\ ou_E/m^3 = 4277\ ou_E/m^3$,
- Udział $U_{O/F3}$, próbka nr 1: $\bar{Z}_{ITE,pan} = 6049$,
  stąd $c_{od} = 6049 \cdot 1\ ou_E/m^3 = 6049\ ou_E/m^3$,
- Udział $U_{O/F3}$, próbka nr 2: $\bar{Z}_{ITE,pan} = 4871$,
  stąd $c_{od} = 4871 \cdot 1\ ou_E/m^3 = 4871\ ou_E/m^3$,
- Udział $U_{O/F3}$, próbka nr 3: $\bar{Z}_{ITE,pan} = 4871$,
  stąd $c_{od} = 4871 \cdot 1\ ou_E/m^3 = 4871\ ou_E/m^3$,
- Udział $U_{O/F4}$, próbka nr 1: $\bar{Z}_{ITE,pan} = 6597$,
  stąd $c_{od} = 6597 \cdot 1\ ou_E/m^3 = 6597\ ou_E/m^3$,
- Udział $U_{O/F4}$, próbka nr 2: $\bar{Z}_{ITE,pan} = 5312$,
  stąd $c_{od} = 5312 \cdot 1\ ou_E/m^3 = 5312\ ou_E/m^3$,
- Udział $U_{O/F4}$, próbka nr 3: $\bar{Z}_{ITE,pan} = 6889$,
  stąd $c_{od} = 6889 \cdot 1\ ou_E/m^3 = 6889\ ou_E/m^3$.

Tabela 5. Wyniki badań wpływu udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki C = 76,3 dm^3/m^3 na stężenie zapachu olejku w osadzie c_{od} [ou_E/m^3]
Table 5. Results of tests on influence of orange essential oil in mixture with ZETAG® 9048FS flocculant $U_{O/F}$ [%] in dose C = 229 $dm^3/3\ m^3$ on odour concentration in sediments c_{od} [ou_E/m^3]

Udział $U_{O/F}$ [%]	Wartość średnia stężenia zapachu olejku w osadzie c_{od} [ou_E/m^3]
$U_{O/F2}$	4296
$U_{O/F3}$	5264
$U_{O/F4}$	6266



Rys. 4. Wpływ udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS $U_{O/F}$ [%] dla dawki C = 76,3 dm^3/m^3 na stężenie zapachu olejku w osadzie c_{od} [ou_E/m^3]
Fig. 4. Influence of orange essential oil share in mixture with ZETAG® 9048FS flocculant $U_{O/F}$ [%] in dose C = 229 $dm^3/3\ m^3$ on odour concentration in sediments c_{od} [ou_E/m^3]

W oczyszczalni ścieków w Tychowie badano zawartość wody w osadzie po procesie wirowania w zależności od udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3, przy stałej prędkości wirowania 2400 obr/min. Wyniki badań przedstawiono w tabeli 3 i na rysunku 2. Analiza wyników badań pozwala stwierdzić, że zwiększanie udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 powoduje wzrost zawartości wody w osadzie o 2,2%. Najniższą zawartość wody w osadzie uzyskano przy udziale $U_{O/F1}$ (0% olejku z pomarańczy (0 dm^3) + 100% flokulanta ZETAG® 9048FS (76,3 dm^3)), tj. 80,07%. Natomiast najwyższą zawartość wody w osadzie odnotowano przy udziale $U_{O/F4}$ (75% olejku z pomarańczy (57,2 dm^3) + 25% flokulanta ZETAG® 9048FS (19,1 dm^3)), tj. 82,27%. 25 % udział olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 spowodował wzrost zawartości wody w osadzie o 1,07%. Wzrost zawartości wody można tłumaczyć tym, że olejek z pomarańczy ma gorsze właściwości flokulujące w porównaniu do flokulanta ZETAG® 9048FS, czyli nie łączy tak dobrze wszystkich drobnych cząstek koloidalnych zawiesiny w większe aglomeraty, które znacznie lepiej podlegają oddziaływaniu siły odśrodkowej, przyspieszając w ten sposób sedymentację.

Kolejnym parametrem wynikowym jaki badano po procesie odwadniania w zależności od udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3, przy stałej prędkości wirowania 2400 obr/min była zawartość suchej masy w odcieku. Wyniki badań przedstawiono w tabeli 3 i na rysunku 3. Obserwacja wyników badań pozwala stwierdzić, że zwiększanie udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 powoduje również wzrost zawartości suchej masy w odcieku o 13671,14 mg/dm^3. Najniższą wartość zawartości suchej masy w odcieku uzyskano przy udziale $U_{O/F1}$ (0% olejku z pomarańczy (0 dm^3) + 100% flokulanta ZETAG® 9048FS (76,3 dm^3)), tj. 3741,54 mg/dm^3. Natomiast najwyższą wartość zawartości suchej masy w odcieku odnotowano przy udziale $U_{O/F4}$ (75% olejku z pomarańczy (57,2 dm^3) + 25% flokulanta ZETAG® 9048FS (19,1 dm^3)), tj. 17412,68 mg/dm^3. 25 % udział olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 spowodował wzrost zawartości suchej masy w odcieku o 5461,58 mg/dm^3. Wzrost zawartości suchej masy w odcieku można tłumaczyć tym, że olejek w porównaniu do flokulanta nie łączy tak dobrze wszystkich drobnych cząstek koloidalnych zawiesiny w większe aglomeraty, które w ten sposób szybciej ulegają procesowi sedymentacji. Część drobnych cząstek osadu przenika do odcieku wraz z olejkiem, ponieważ gęstość olejku jest mniejsza od gęstości wody i wypływa on na powierzchnię odcieku.

Ostatnim parametrem wynikowym jaki badano po procesie odwadniania w zależności od udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3, przy stałej prędkości wirowania 2400 obr/min było stężenie zapachu olejku eterycznego z pomarańczy w osadzie. Wyniki badań przedstawiono w tabelach 4, 5 i na rysunku 4. Analiza wyników badań pozwala stwierdzić, że zwiększanie udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 powoduje wzrost stężenia zapachu olejku w osadzie o 1970 ou_E/m^3. Najniższą wartość stężenia zapachu olejku w osadzie uzyskano przy udziale $U_{O/F2}$ (25% olejku z pomarańczy (19,1 dm^3) + 75% flokulanta ZETAG® 9048FS (57,2 dm^3)), tj. 4296 ou_E/m^3. Natomiast najwyższą wartość stężenia zapachu olejku w osadzie odnotowano przy udziale $U_{O/F4}$ (75% olejku z pomarańczy (57,2 dm^3) + 25% flokulanta ZETAG® 9048FS (19,1 dm^3)), tj. 6266 ou_E/m^3. 25 % wzrost udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 spowodował wzrost stężenia zapachu olejku w osadzie o 968 ou_E/m^3. Największy wzrost stężenia zapachu olejku w osadzie odnotowano przy udziale $U_{O/F4}$ (75% olejku z pomarańczy (57,2 dm^3) + 25% flokulanta ZETAG® 9048FS (19,1 dm^3)). Wzrost stężenia zapachu olejku w osadzie można tłumaczyć tym, że wraz ze zwiększaniem udziału olejku eterycznego z pomarańczy w mieszaninie z flokulantem ZETAG® 9048FS dla dawki C = 76,3 dm^3/m^3 zwiększa się jego objętość w odwodnionym osadzie, a tym samym wzrasta czas skutecznej neutralizacji nieprzyjemnych zapachów w odwirowanym osadzie.

3. Wnioski

Na podstawie przeprowadzonych badań i ich analizy można wyciągnąć następujące wnioski:

1. Olejek eteryczny z pomarańczy stanowi skuteczny, dobry flokulant, który można stosować jako wspomaganie w procesie sedymentacji odśrodkowej.

2. Działanie olejku eterycznego z pomarańczy jest niewiele mniej skuteczne, a więc nieco gorsze dla jakości odwadniania osadów w wirówce dekantacyjnej niż flokulanta ZETAG® 9048FS.
3. Nieco gorsza jakość odwadniania osadu (nieco wyższa zawartość wody w osadzie) oraz wyższa zawartość suchej masy w odcieku, jak to stwierdzono w wyniku badań – jest od strony technologicznej do przyjęcia; osad utrzymuje nadal konsystencję transportabilną, a odciek jest zawracany do obiegu oczyszczalni.
4. W rezultacie przeprowadzonych badań mając na uwadze zarówno dobre jakościowo odwadnianie osadów z równoczesnym, częściowym, ale wyraźnym i odczuwalnym obniżeniem uciążliwości odorów wydzielających się z osadów, przyjmuje się i zaleca do aplikacji dawkowanie równoczesne obydwu odczynników, tj. flokulanta ZETAG® 9048FS 50% oraz olejku eterycznego z pomarańczy także 50% udziału objętościowego.
5. Dozowanie olejku eterycznego z pomarańczy ma tę ważną zaletę, że zmniejsza w pewnym stopniu ogromną uciążliwość zapachową odwodnionych osadów.
6. Oczywiście ewentualne zastosowanie olejku eterycznego zwiększy koszt zastosowania łącznie obydwu flokulantów, ale musimy się liczyć z tym, że ochrona środowiska, tu powietrza, po prostu kosztuje.
7. Celowe jest prowadzenie dalszych badań nad zastosowaniem olejków z innych roślin jako flokulantów w szeroko rozumianych procesach techniki wodno-mułowej, a także prowadzenia prac nad ekonomiczną produkcją olejków z odpadów z uwzględnieniem logistyki ich wydzielania na etapie selekcji odpadów, bądź też ich pozyskiwania z zakładów przetwórstwa owocowego.

Literatura

1. **BASF** Karta charakterystyki flokulanta ZETAG® 9048FS (ID nr 304-80318/SDS_GEN_PL/PL.
2. **Brudniak A., Dębowski M., Zieliński M.:** *Określenie zapachowego oddziaływania wybranej oczyszczalni ścieków na tereny objęte opracowaniem planu zagospodarowania przestrzennego.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1759–1771 (2013).
3. **Czerwiński J., Ozonek J.:** *Elimination of odorous in off-gases from food production by means of ozone.* Chemical Engineering Transactions. 15, 177–182 (2008).

4. **Dymaczewski Z.:** *Poradnik eksploatatora oczyszczalni ścieków.* Praca zbiorowa, Wydanie III. Wydawca Polskie Zrzeszenie Inżynierów i Techników Sanitarnych, Poznań 2011.
5. **Kośmider J., Krajewska B.:** *Determining Temporary Odour Concetration under Field Conditions – Comparison of Methods.* Polish Journal of Environmental Studies. 16(2), 215–225 (2007).
6. **Kośmider J., Mazur-Chrzanowska B., Wyszyński B.:** *Odory.* Wydawnictwo Naukowe PWN, Warszawa 2012.
7. **Kośmider J.:** *Uciążliwość zapachowa. Klasyfikacja terenów i źródeł emisji zanieczyszczeń powietrza.* Archiwum Ochrony Środowiska. 1–2, 31–41 (1994).
8. **Kowalczyk A., Piecuch T., Andriyevska L.:** *Zastosowanie olejku eterycznego z sosny do maskowania uciążliwych zapachów wydzielających się w procesie mechanicznego odwadniania komunalnych osadów ściekowych.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 807–822 (2013).
9. **Kowalczyk A., Piecuch T.:** *Zastosowanie olejku eterycznego z pomarańczy do maskowania nieprzyjemnych zapachów powstających podczas odwadniania komunalnych osadów ściekowych.* Inżynieria Ekologiczna. 25, 124–134 (2011).
10. **Kulig A., Lelicińska-Serafin K., Podedworna J., Sinicyn G., Heidrich Z., Czyżkowski B.:** *Identyfikacja, inwentaryzacja i charakterystyka źródeł odorantów w gospodarce komunalnej w Polsce* [w:] **Szynkowska M., Zwoździak J.:** *Współczesna problematyka odorów,* 14–53. Wydawnictwo Naukowo-Techniczne, Warszawa 2010.
11. **Kulig A.:** *Źródła i oddziaływanie odorantów emitowanych z obiektów gospodarki ściekowej.* Przegląd Komunalny. 11, Zeszyty Komunalne, 99–103 (2005).
12. **Ozonek J., Jahołkowski, Czerwiński J.:** *Ograniczenie uciążliwości zapachowej w zakładach utylizacji odpadów zwierzęcych.* Przemysł Chemiczny. 88(5), 544–547 (2009).
13. **Ozonek J., Szulżyk-Cieplak J., Czerwiński J.:** *Ograniczenie emisji odorów z wód popłucznych przemysłu cukrowniczego z wykorzystaniem zjawiska kawitacji hydrodynamicznej.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 11, 1054–1062 (2009).
14. PN-EN 13725:2007 *„Jakość powietrza. Oznaczanie stężenia zapachowego metodą olfaktometrii dynamicznej”.*
15. **Sówka I.:** *Metody identyfikacji odorotwórczych gazów emitowanych z obiektów przemysłowych.* Monografie Nr 55. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2011.

16. **Szklarczyk M., Zwoździak J., Sówka I.:** *Przemysłowe źródła emisji zapachów* [w:] **Szynkowska M., Zwoździak J.:** *Współczesna problematyka odorów.* 54–85. Wydawnictwo Naukowo-Techniczne, Warszawa 2010.
17. **Szklarczyk M.:** *Odory w oczyszczalniach ścieków.* Wodociągi-Kanalizacja. 10, 30–33 (2007).
18. **Szynkowska M., Wojciechowska E., Węglińska A., Paryjczak T.:** *Katalizatory stosowane w reakcji utleniania związków złowonnych.* Przemysł Chemiczny. 87(8), 834–843 (2008).
19. **Szynkowska M., Wojciechowska E., Węglińska A., Paryjczak T.:** *Odory. Aktualny problem w ochronie środowiska.* Przemysł Chemiczny. 88(6), 712–720 (2009).
20. Świadectwo badania olejku eterycznego z pomarańczy Nr 81/12.

Reduction of Odorous Noxiousness of Sewage Treatment Plant in Tychowo

Abstract

The most important aim of the study was to find the optimum conditions of the process of dewatering of sewage sludge using decanter centrifuge, and also reduce noxiousness of the centrifuge service, by applying orange essential oil as a partial substitute of flocculants.

The tests were performed at sewage treatment plant in Tychowo where dewatering process of sewage sludge is carried using decanter centrifuge ALFA LAVAL, type ALDEC with application of different proportions of orange essential oil mixed with ZETAG® 9048FS flocculant for dose $C = 76.3\ dm^3/m^3$. Water content in the sediment, dry matter content in effluent and concentration of orange essential oil odour in dewatered sediments were assessed.

Conducted tests proved that orange essentials oil is a efficient, good flocculant, which may be used as an addition do centrifugal sedimentation process. Addition of orange essential oil has a substantial advantage: it causes the decrease of odorous noxiousness of dewatered sediments.

The experiments were conducted on-site in the sewage treatment plant in the centrifuge station. Analysis of odorous noxiousness was conducted in the laboratory using samples collected on-site. Odorous noxiousness was assessed by determination of oudour concentration. Measurements were made using method of dynamic olfactometry according to standard PN-EN 13725:2007 [14] on four station olfactometer T08 (figure 1) equipped with all necessary apparatus. One measurement consisted of four series. Computer software colleted all the measurements results and calculated result of the measurement team ($Z_{ite,\ pan}$) –geometric mean of all individual measurements. This value is at the

same time the concentration of odour in the sample (c_{od}), expressed in european odorous units per cubic meter (o_{uE}/m^3) in accordance with PN-EN 13725:2007 [14].

As a result of conducted tests, taking into account good quality of dewatering of sludge with simultaneous, partial, but clear and noticeable reduction of noxious odours emitted from the sediments, both reagents are recommended for dosage that is ZETAG® 9048FS flocculant and orange essential oil, both 50% of the dose volume.

It is advisable to conduct further research on the use of essential oils from other plants as flocculants in the broadly defined processes of water and sludge technology, as well as conducting works on the economic production of essential oils form waste materials, also including the logistics of their separation at the selection of waste stage, or their acquisition from fruit processing plants.

Słowa kluczowe:
odory, zapach, olejki eteryczne, flokulant, osady ściekowe, odwadnianie

Keywords:
odours, scent, essential oils, flocculant, sewage sludge, dewatering

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Regeneracja żywic polimerowych stosowanych do frakcjonowania naturalnych substancji organicznych

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1. Wstęp

Usuwanie naturalnych substancji organicznych z wody (ang. *natural organic matter* – NOM) jest jedną z najważniejszych operacji w technologii oczyszczania wody, m. in. ze względu na konieczność zmniejszenia ryzyka powstawania podczas chlorowania ubocznych produktów dezynfekcji [6, 11, 13]. Obniżenie zawartości tych związków do wymaganego poziomu wiąże się z koniecznością prowadzenia szczegółowych badań nad nimi i opracowywaniem nowych, efektywnych technik ich usuwania. Naturalne substancje organiczne stanowią niejednorodną mieszaninę składników o bardzo zróżnicowanych właściwościach. Można je podzielić na 3 frakcje: hydrofobową, hydrofilową oraz transfilową [16]. Określenie wielkości i masy cząsteczkowej substancji organicznych jest niezwykle skomplikowane, co wynika ze złożoności składu chemicznego i rozbudowanej struktury przestrzennej cząstek tych substancji. Chemiczna struktura naturalnych związków organicznych do tej pory nie została jeszcze dokładnie określona [10].

Ze względu na złożoność naturalnych substancji organicznych, istotnym zagadnieniem jest rozdzielenie tych składników na poszczególne frakcje, które następnie można poddać szczegółowym analizom. Rozdziału NOM można dokonać zarówno metodami chemicznymi (strącanie, ekstrakcja, chromatografia adsorpcyjna) jak i fizycznymi (elektroforeza, filtracja membranowa, chromatografia wykluczająca SEC, ultrawirowanie) [2]. Obecnie powszechnie stosowaną metodą rozdziału związków organicznych jest metoda opracowana przez Leenheera i Huffmana [8] oraz Malcolma i MacCarthyego [9], wykorzystująca zjawisko adsorpcji poszczególnych frakcji NOM na niejonowych makroporowatych żywicach syntetycznych. Poprzez korektę odczynu wody wpływa się na rozpuszczalność lub hydrofobowość poszczególnych frakcji NOM, co pozwala na preferencyjną ich adsorpcję na żywicach polimerowych o różnych właściwościach. Metoda ta była wielokrotnie modyfikowana przez szereg badaczy. Obecnie najczęściej stosuje się procedurę opracowaną przez Chow i in. [3], wykorzystującą żywice typu XAD. W procedurze tej wykorzystuje się zjawisko adsorpcji fizycznej (siły van der Wallsa, oddziaływania dipolowe) oraz chemicznej (poprzez wiązania jonowe) poszczególnych frakcji NOM na odpowiednich materiałach sorpcyjnych. Zazwyczaj do tego celu stosuje się adsorbenty polimerowe Supelite DAX-8, Amberlite XAD-4 oraz silnie zasadową żywicę anionowymienną Amberlite IRA-958 lub inne o analogicznych właściwościach. Ich zastosowanie do izolacji naturalnych substancji organicznych było także przedmiotem badań polskich naukowców [5, 12].

Użycie makroporowatych sorbentów DAX-8 i XAD-4 pozwala rozseparować NOM na frakcje hydrofobową i hydrofilową, zaś użycie w dalszym etapie żywicy anionowymiennej pozwala dokonać dalszego rozdziału na składniki o charakterze kwasowym, zasadowym i obojętnym.

Dzięki zastosowaniu tego typu żywic można frakcjonować NOM na 4 grupy substancji [3]:

- kwasy silnie hydrofobowe (ang. *very hydrophobic acids*, VHA) – adsorbowane przez żywicę DAX-8,
- kwasy słabo hydrofobowe (ang. *slightly hydrophobic acids*, SHA) – adsorbowane przez żywicę XAD-4,
- substancje hydrofilowe obdarzone ładunkiem (ang. *hydrophilic charged*, CHA) – wiązane przez żywicę IRA-958,
- substancje hydrofilowe obojętne (ang. *hydrophilic neutral*, NEU) – niesorbowane przez żadną z użytych żywic.

Stosowana procedura frakcjonowania polega na przepuszczaniu próbki wody przez szeregowo połączone kolumny wypełnione różnymi żywicami (rys. 1) [15]. Frakcja VHA adsorbowana jest przez żywicę DAX-8, frakcja SHA – przez żywicę XAD-4, frakcja CHA – przez żywicę

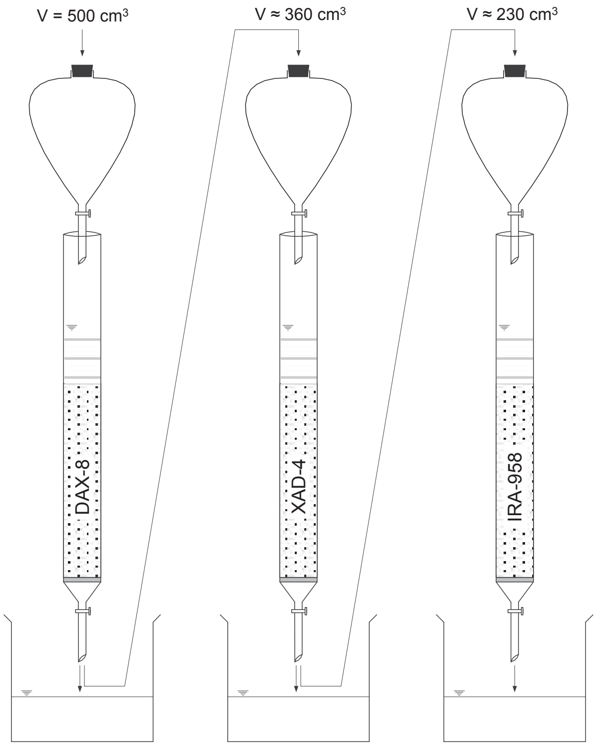
IRA-958, zaś frakcja NEU nie jest sorbowana przez żadną z użytych żywic. Próbkę wody o objętości 500 cm^3, po filtracji przez membranę o średnicy porów 0,45 µm i zakwaszeniu przy użyciu HCl do pH 2, należy przepuszczać przez kolumnę wypełnioną żywicą DAX-8. 30 cm^3 przesączu jest odrzucane, a kolejne 100 cm^3 próby pobierane w celu oznaczenia stężenia rozpuszczonego węgla organicznego (RWO). Pozostała ilość wody przepuszczana jest przez kolumnę z żywicą XAD-4. Analogicznie jak wcześniej, 30 cm^3 przesączu jest odrzucane i następnie 100 cm^3 filtratu jest pobierane w celu oznaczenia stężenia RWO. Do przesączu z kolumny zawierającej żywicę XAD-4, przed filtracją przez złoże zawierające żywicę IRA-958, dodawany jest roztwór NaOH, w celu podniesienia wartości odczynu do pH 8. 30 cm^3 filtratu z trzeciej kolumny jest odrzucane i następnie pobierana jest próba w celu oznaczenie stężenia RWO. Zawartość poszczególnych frakcji NOM wyznacza się z zależności:

$$\mathrm{VHA} = \mathrm{RWO}_{\mathrm{surowe}} - \mathrm{RWO}_{\mathrm{filtrat\ DAX\text{-}8}} \tag{1}$$

$$\mathrm{SHA} = \mathrm{RWO}_{\mathrm{filtrat\ DAX\text{-}8}} - \mathrm{RWO}_{\mathrm{filtrat\ XAD\text{-}4}} \tag{2}$$

$$\mathrm{CHA} = \mathrm{RWO}_{\mathrm{filtrat\ XAD\text{-}4}} - \mathrm{RWO}_{\mathrm{filtrat\ IRA\text{-}985}} \tag{3}$$

$$\mathrm{NEU} = \mathrm{RWO}_{\mathrm{filtrat\ IRA\text{-}985}} \tag{4}$$



Rys. 1. Schemat układu do frakcjonowania NOM
Fig. 1. NOM fractionation set-up

Z punktu widzenia wiarygodności uzyskanych efektów frakcjonowania na sorbentach bardzo istotnym zagadnieniem jest także skuteczność ich regeneracji przed kolejnym użyciem. Regenerację żywic, mające na celu zdesorbowanie zatrzymanych cząsteczek NOM, jedynie przy użyciu 0,1 n NaOH nie gwarantuje 100% regeneracji, gdyż neutralne hydrofobowe makrocząsteczki, niezależnie od odczynu, pozostają niepolarne i nie będą wymywane. Uważa się, że przywrócenie pierwotnej zdolności sorpcyjnej żywic możliwe jest jedynie poprzez ekstrakcję metodą Soxhleta [7]. Problematykę regeneracji niejonowych sorbentów opisali m.in. Anielak i wsp. [1].

Wobec powyższych ograniczeń należy stwierdzić, że o przydatności stosowanych żywic do przeprowadzenia procedury frakcjonowania NOM decyduje także możliwy do osiągnięcia stopień ich regeneracji [4]. W związku z tym przeprowadzono badania mające na celu ocenę skuteczności regeneracji żywic typu Supelite DAX-8, Amberlite XAD-4 oraz Amberlite IRA-958 oraz porównanie uzyskanych skuteczności pod kątem sposobu prowadzenia procesu regeneracji.

2. Materiały i metody badawcze

Do przeprowadzenia badań nad regeneracją żywic wykorzystywanych do frakcjonowania naturalnych substancji organicznych użyto 3 różnych sorbentów: Supelite DAX-8 (Supelco), Amberlite XAD-4 oraz Amberlite IRA-958 (Rohm&Haas). W tabelach 1 i 2 przedstawiono podaną przez producentów charakterystykę zastosowanych w badaniach żywic.

Tabela 1. Charakterystyka żywic Amberlite [17, 18]
Table 1. Properties of Amberlite polymeric resins [17, 18]

Nazwa żywicy	Amberlite XAD-4	Amberlite IRA-958
Postać fizyczna	białe, półprzezroczyste ziarna	białe, nieprzezroczyste, sferyczne ziarna
Typ	makroporowata, polistyrenowa, niepolarna	makroporowata, poliakrylowa, silnie zasadowa
Higroskopijność, %	54–60	66–72
Rozmiar cząstek, µm	490–690	630–850
Porowatość, cm^3/cm^3	$\geq 0{,}5$	$\geq 0{,}5$
Powierzchnia właściwa, m^2/g	725	brak danych

Tabela 2. Charakterystyka adsorbentu polimerowego Supelite DAX-8 [19]
Table 2. Properties of Supelite DAX-8 polymeric adsorbent [19]

Nazwa żywicy	Supelite DAX-8
Postać fizyczna	białe, półprzezroczyste ziarna
Typ	makroporowata, poliakrylowa
Średni rozmiar porów, nm	22,5
Przybliżona objętość porów, cm^3/g	0,79
Powierzchnia właściwa, m^2/g	160

Procedura frakcjonowania NOM realizowana była w 3 szklanych kolumnach laboratoryjnych o wysokości 20 cm i średnicy wewnętrznej 13 mm, zawierających po 15 cm^3 odpowiedniej żywicy. Zakres przeprowadzonych badań obejmował przygotowanie żywicy do pracy poprzez regenerację wstępną, wysycanie złoża sorpcyjnego naturalnymi substancjami organicznymi oraz właściwą regenerację złoża.

Procedura przygotowania adsorbentów polimerowych Supelite DAX-8, Amberlite XAD-4 oraz Amberlite IRA-958 obejmowała wstępne oczyszczanie świeżych żywic, polegające na mieszaniu przez godzinę z metanolem klasy HPLC, następnie przez godzinę z acetonitrylem oraz w końcowym etapie przez taki sam czas z wodą redestylowaną [3]. Najdrobniejsze ziarna żywic usuwano przez dekantację.

Do wysycenia żywic wykorzystano wodę z Odry oraz roztwór modelowy powstały po zmieszaniu wody wodociągowej (po dechloracji – barbotaż powietrzem) i wody zawierającej naturalne substancje organiczne, którą pobrano ze strumienia wypływającego z Wielkiego Torfowiska Batorowskiego w Górach Stołowych. Zawartość związków organicznych we wszystkich roztworach określono poprzez pomiar intensywności barwy (absorbancja przy długości fali 350 nm), absorbancji UV przy długości fali 254 nm oraz stężenia rozpuszczonego węgla organicznego (RWO). Pomiary spektrofotometryczne wykonano przy użyciu spektrofotometru HITACHI U-1900, zaś stężenie RWO oznaczano przy użyciu analizatora HACH IL550 TOC-TN. Temperatura wszystkich roztworów badawczych wynosiła 20°C. Charakterystykę badanych roztworów zawierających NOM przedstawiono w tabeli 3.

Każdą z badanych żywic wysycano 3-krotnie: świeżą, po jednokrotnej regeneracji i po dwukrotnej regeneracji. Podczas wysycania mierzono barwę, absorbancję UV przy długości fali 254 nm i stężenie RWO, sporządzając na podstawie wyników izoplany. Procedura wysycania żywic trwała aż do momentu stwierdzenia w odcieku takich samych parametrów jakościowych jak w roztworze zasilającym.

Tabela 3. Właściwości badanych roztworów
Table 3. Properties of examined solutions

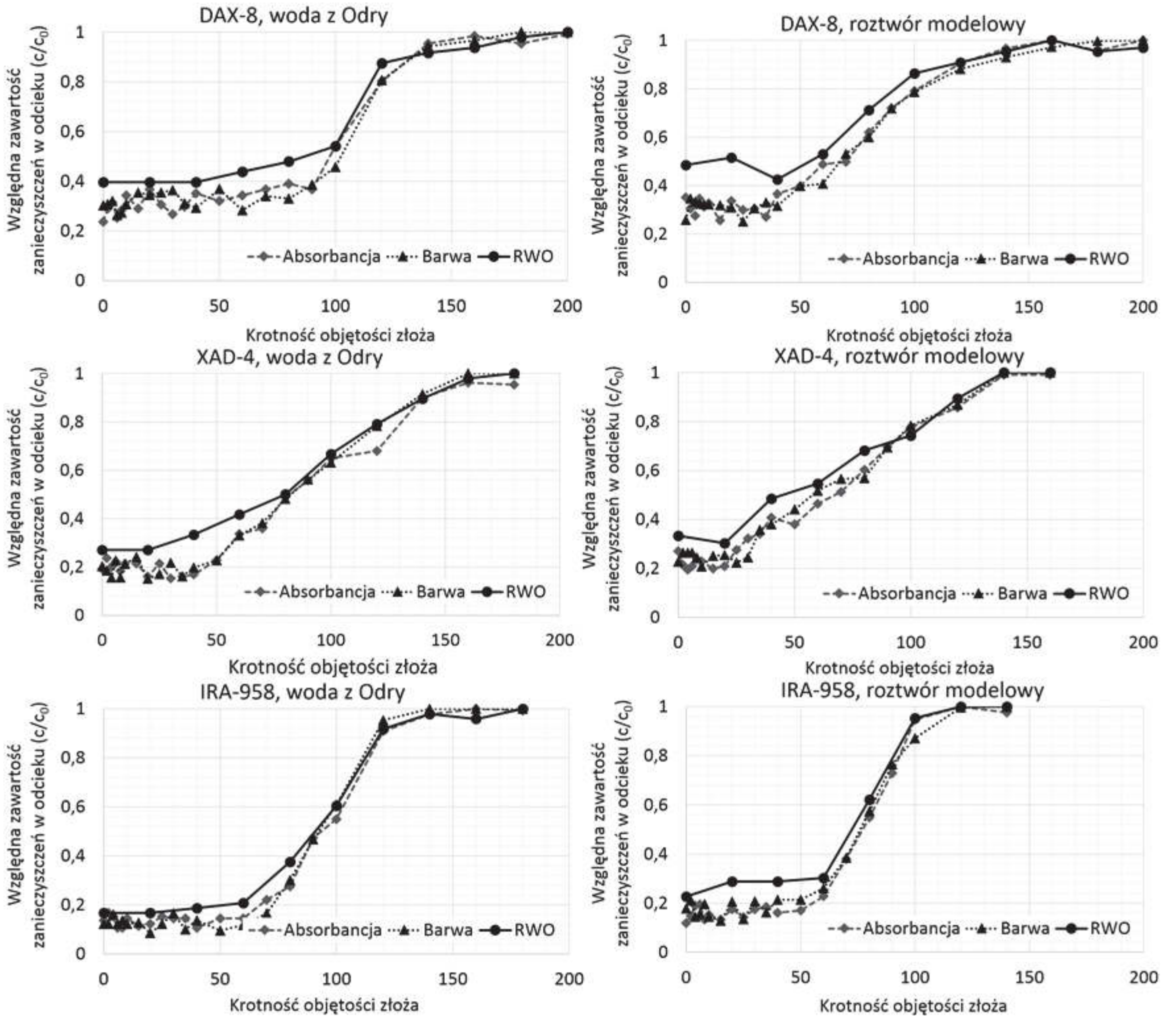
Typ roztworu	Absorbancja UV, cm^{-1}	Barwa, g Pt/m^3	RWO, g C/m^3	Przewodność, µS/cm
Woda z Odry	0,131	21,2	4,8	1540
Roztwór modelowy	0,211	32,7	6,6	645

Proces regeneracji żywic typu Supelite DAX-8, Amberlite XAD-4 oraz Amberlite IRA-958 prowadzono w układzie przepływowym dwoma metodami. Pierwsza z nich była zgodna z procedurą przygotowania żywic opracowaną przez Chow i in. [3] i polegała na mieszaniu żywicy z metanolem klasy HPLC, następnie acetonitrylem i wodą destylowaną, każde przez 1 h. Na zakończenie usuwano najdrobniejsze ziarna żywicy przez dekantację. Natomiast w drugiej metodzie, podczas regeneracji żywice były przemywane kolejno: wodą redestylowaną, 0,1 n NaOH, 0,1 n HCl, 0,1 n NaOH. Reagenty te użyto w celu desorpcji z żywic kwasów organicznych (NaOH) i związków organicznych hydrofobowych o charakterze zasadowym (HCl) oraz ponownie wodą redestylowaną aby wypłukać pozostałości NaOH przed dalszą regeneracją. Ten etap regeneracji zbliżony był do procedury użytej przez Smith'a i Alqabany [14]. Następnym etapem było przemywanie żywic kolejno: metanolem, acetonitrylem, ponowne metanolem w celu wymycia substancji organicznych obojętnych hydrofobowych, a na zakończenie wodą redestylowaną aby pozbyć się resztek zastosowanych wcześniej reagentów. Doboru roztworów wykorzystanych w drugiej metodzie dokonano w oparciu o zalecenia producentów żywic oraz charakter związków obecnych w roztworach badawczych. Strumień przepływu czynników regenerujących przez złoże wynosił 6 cm^3/min (tj. 0,4 objętości złoża na minutę) przez taki sam czas dla każdego z roztworów regenerujących, przy czym sprawdzono 4 różne czasy: 1 h (metoda 1 h), 2 h (metoda 2 h), 3 h (metoda 3 h) i 4 h (metoda 4 h).

Skuteczność procesu regeneracji określono na podstawie porównania izoplan otrzymanych podczas wysycania z izoplaną wyznaczoną dla świeżej żywicy.

3. Wyniki i ich omówienie

Wstępne badania, mające na celu określenie przebiegu procesu sorpcji w warunkach przepływowych, przedstawiono na rysunku 2. Wykonane badania wykazały, że w każdym przypadku w początkowych minutach prowadzenia procesu wartości intensywności barwy, absorbancji UV i stężenia RWO w odcieku utrzymywały się na stałym poziomie, następnie rosły aż do osiągnięcia wartości takich jak w wodzie surowej. Ważnym jest fakt, że żadna z żywic nie sorbowała zanieczyszczeń w 100%. Ponadto, dla wszystkich testowanych żywic oraz dla obu badanych roztworów zaobserwowano, że frakcje NOM, odpowiedzialne za barwę i absorbancję UV były w równym stopniu zatrzymywane przez żywice, natomiast stopień zmniejszenia zawartości rozpuszczonego węgla organicznego był zauważalnie mniejszy. Przykładowo, dla wody z Odry, odpowiednio dla świeżych żywic DAX-8, XAD-4 i IRA-958 uzyskano w pierwszych minutach procesu obniżenie barwy o 69%, 81%, 88%, absorbancji o 70%, 80%, 87% i stężenia RWO o 58%, 72%, 80%. W trakcie przepuszczania pierwszych 40 objętości złoża (600 cm^3) stężenie RWO po każdej z kolumn było stabilne co pozwoliło określić ilość substancji organicznych zatrzymywanych przez każdą z żywic: DAX-8 była odpowiedzialna za obniżenie RWO o 58%, XAD-4 o 15%, IRA-958 o 9%, zaś pozostałe 20% RWO nie zostało zasorbowane przez żadną z żywic. Natomiast dla roztworu modelowego, obniżenie wskaźników po kolejnych kolumnach adsorbentów polimerowych (DAX-8, XAD-4, IRA-958) wynosiło: 74%, 77%, 82% (barwa), 65%, 73%, 88% (absorbancja) oraz 52%, 67%, 77% (RWO). Z pierwszych 600 cm^3 roztworu modelowego, żywica DAX-8 usunęła 55% RWO, XAD-4: 8%, IRA-958: 10%. Pozostałe 26% RWO nie adsorbowała żadna żywica. Całkowitą pojemność sorpcyjną określono z różnicy pomiędzy ilością naturalnych substancji organicznych w wodzie surowej (mierzonej jako rozpuszczony węgiel organiczny), a ilością tych związków nie zasorbowanych przez żywicę (tabela 4). Badania nie wykazały znaczącego wpływu typu roztworu na tak obliczoną pojemność sorpcyjną żywic.



Rys. 2. Izoplany sorpcji naturalnych substancji organicznych na żywicach typu DAX-8, XAD-4 i IRA-958 (świeże żywice, c – zawartość zanieczyszczeń w odcieku, c_0 – zawartość zanieczyszczeń w roztworze badawczym)
Fig. 2. Breakthrough curves of natural organic matter adsorption using DAX-8, XAD-4 and IRA-958 resins (raw resins, c – effluent contaminants content, c_0 – raw water contaminants content)

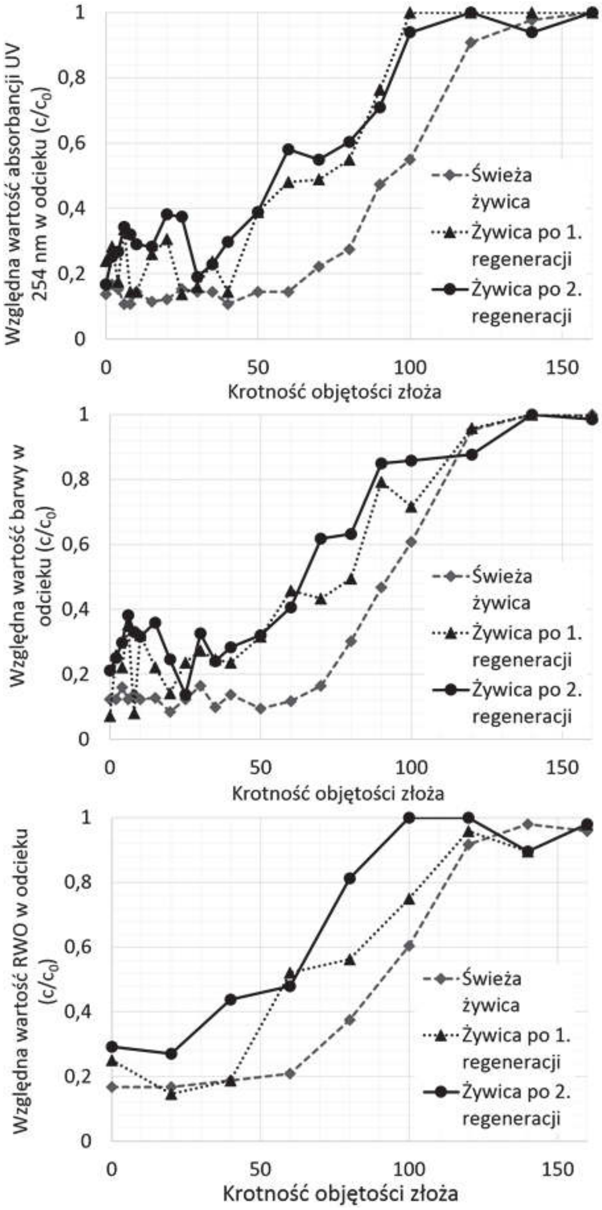
Tabela 4. Całkowita pojemność sorpcyjna żywic w zależności od typu roztworu
Table 4. Resin sorption capacity depending on solution type

Żywica	Pojemność sorpcyjna, mg C / cm^3	
	Woda z Odry	Roztwór modelowy
DAX-8	0,297	0,305
XAD-4	0,024	0,027
IRA-958	0,044	0,046

Przeprowadzone badania nad skutecznością regeneracji żywic jonowymiennych, celem przywrócenia złożu jego pierwotnej zdolności sorpcyjnej, pozwoliły na porównanie dwóch metod regeneracji. Analiza uzyskanych wyników (rys. 3) pozwoliła stwierdzić, że metoda regeneracji zgodna z procedurą przygotowania żywic opracowaną przez Chow i in. [3] nie pozwalała przywrócić żywicom ich pierwotnej zdolności sorpcyjnej. Łatwo można było zauważyć, że każda kolejna regeneracja powodowała obniżenie całkowitej pojemności sorpcyjnej badanych żywic w stosunku do odpowiednich frakcji naturalnych substancji organicznych. Zastosowanie drugiej metody regeneracji (przemywanie żywic kolejno wodą redestylowaną, 0,1 n NaOH, 0,1 n HCl, 0,1 n NaOH, wodą redestylowaną, metanolem, acetonitrylem, metanolem, wodą redestylowaną) pozwoliło na pełną regenerację badanych żywic (rys. 4). Przywrócenie ich pierwotnej zdolności sorpcyjnej osiągnięto zarówno podczas pierwszej jak drugiej regeneracji. Uzyskane po procesie regeneracji izoplany świadczą o tym, że podczas czyszczenia żywic nie zmieniły się ich właściwości. Wyparty adsorbat z ziaren żywicy był systematycznie usuwany z kolumny, dzięki czemu ziarna żywicy miały ciągły kontakt z czystym roztworem regeneracyjnym.

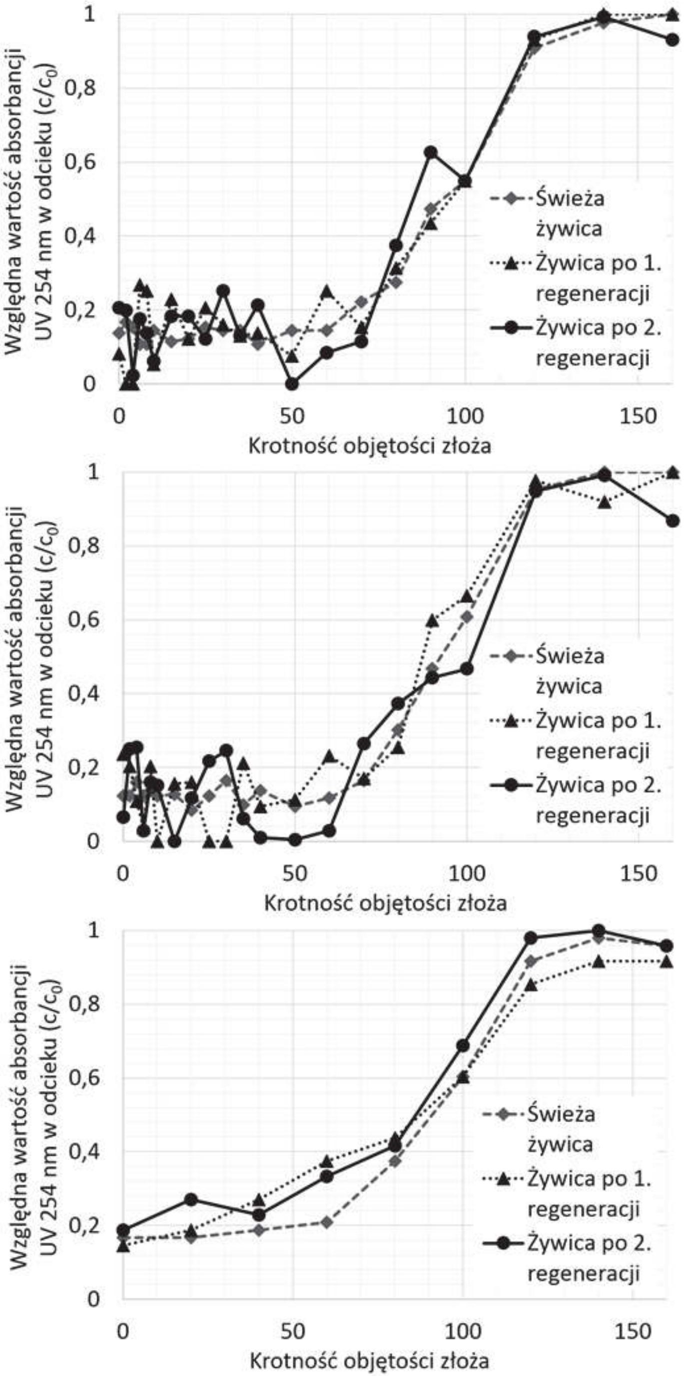
Zbadano również wpływ czasu kontaktu żywic z poszczególnymi reagentami stosowanymi do ich regeneracji na jej skuteczność przy zastosowaniu metody pozwalającej na przywrócenie całkowitej pojemności sorpcyjnej badanych żywic. Analizowany czas kontaktu z każdym z reagentów wynosił 1, 2, 3 i 4 h. Przedstawione na rysunku 5 wyniki badań jednoznacznie pokazują, że skuteczność rosła wraz z wydłużaniem czasu regeneracji przy użyciu poszczególnych reagentów. Prowadzenie regeneracji metodą 1h (przepłukiwanie żywicy przez 1 h przy użyciu kolejnych reagentów) skutkowało uzyskaniem, przykładowo dla roztworu modelowego i żywicy DAX-8, pojemności sorpcyjnej żywicy 0,245 mg C/cm^3 dla jednokrotnej regeneracji i 0,230 mg/cm^3 dla dwukrotnej regeneracji, zaś zastosowanie metody 2h pozwoliło na uzyskanie pojemności, odpowiednio 0,297 mg C/cm^3 i 0,267 mg C/cm^3.

Zauważono także, iż optymalny czas trwania poszczególnych etapów regeneracji dla badanych żywic wynosi 3h, zaś dalsze jego wydłużanie nie powodowało wzrostu skuteczności odzyskiwania właściwości sorpcyjnych żywic. Efekt ten zaobserwowano dla każdej z testowanych żywic oraz dla obu badanych roztworów. W przypadku żywicy IRA-958 stwierdzono, że niemal całkowitą pierwotną zdolność sorpcyjną uzyskano już przy zastosowaniu metody 2h, co mogło wynikać z charakteru tej żywicy.

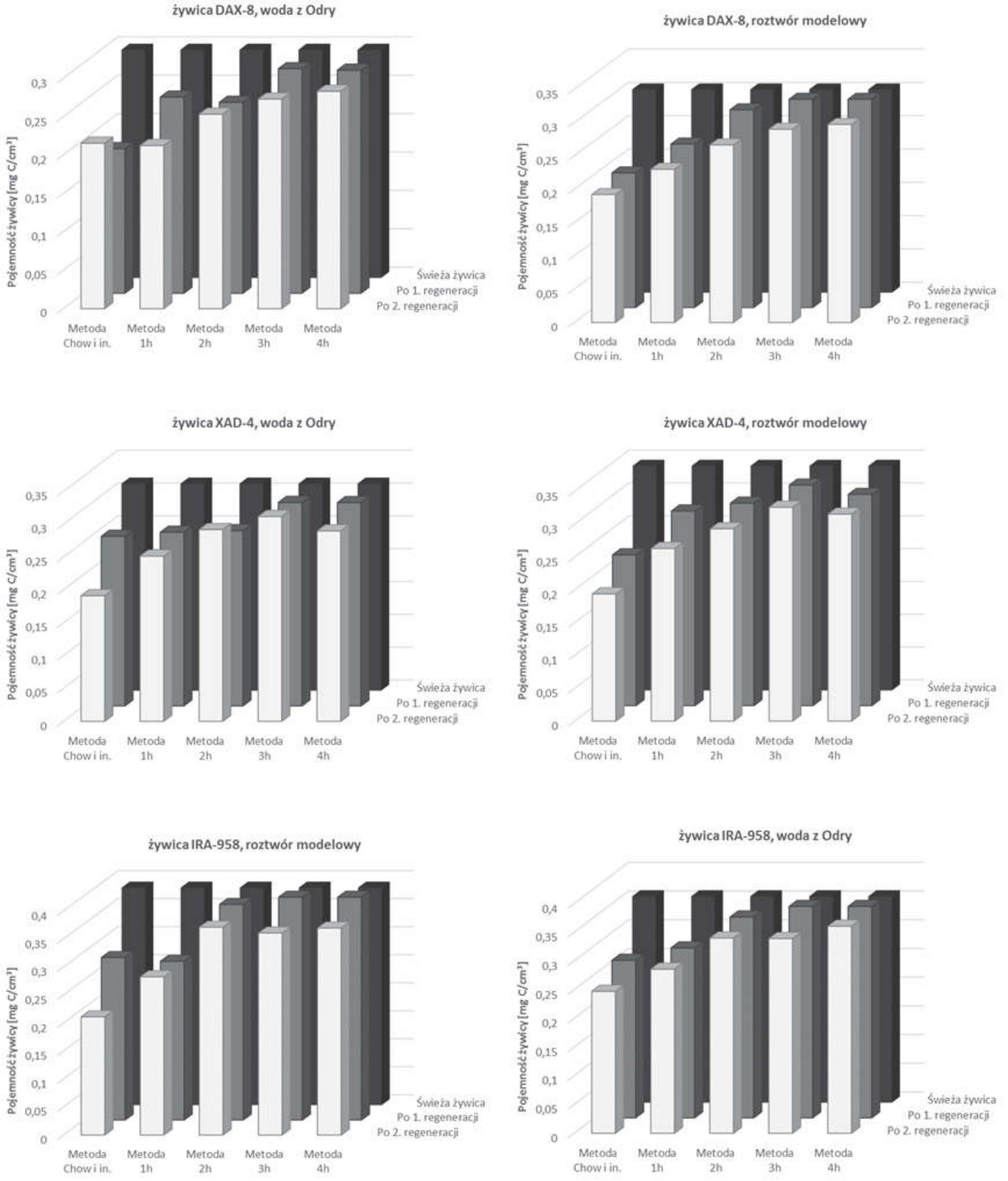


Rys. 3. Izoplany sorpcji naturalnych substancji organicznych z wody z Odry na żywicy typu IRA-958 regenerowanej metodą Chow i in. [3] (c – zawartość zanieczyszczeń w odcieku, c_0 – zawartość zanieczyszczeń w roztworze badawczym)

Fig. 3. Breakthrough curves of natural organic matter adsorption from Odra river water with the use of IRA-958 resin regenerated using Chow et al. method [3] (c – effluent contaminants content, c_0 – raw water contaminants content)



Rys. 4. Izoplany sorpcji naturalnych substancji organicznych z wody z Odry na żywicy typu IRA-958 (3 h kontaktu żywicy z każdym z reagentów)
(c – zawartość zanieczyszczeń w odcieku, c_0 – zawartość zanieczyszczeń w roztworze badawczym)
Fig. 4. Breakthrough curves of natural organic matter adsorption from Odra river water with the use of IRA-958 (3 h contact time with each of reagents)
(c – effluent contaminants content, c_0 – raw water contaminants content)



Rys. 5. Wpływ metody regeneracji żywicy na pojemność żywicy mierzonej jako ilość zaadsorbowanego RWO
Fig. 5. Influence of applied regeneration method on resin capacity measured as an amount of adsorbed dissolved organic carbon

4. Wnioski

Przeprowadzone badania nad oceną skuteczności regeneracji makroporowatych żywic typu DAX-8, XAD-4 oraz IRA-958, wykorzystanych do frakcjonowania naturalnych substancji organicznych, pozwoliły na sformułowanie następujących wniosków:

- metoda opracowana przez Chow i in. [3] nie pozwalała na całkowite przywrócenie żywicom ich pierwotnej zdolności sorpcyjnej,
- zastosowanie opracowanej przez autorki metody regeneracji, tj. przemywanie żywic kolejno wodą redestylowaną, 0,1 n NaOH, 0,1 n HCl, 0,1 n NaOH, wodą redestylowaną, metanolem, acetonitrylem, metanolem, wodą redestylowaną, pozwoliło na całkowitą regenerację badanych żywic, zarówno podczas pierwszej jak i drugiej ich regeneracji,
- skuteczność regeneracji żywic zaproponowaną metodą rośnie wraz z wydłużaniem czasu ich kontaktu z czynnikami regenerującymi,
- optymalny czas kontaktu badanych żywic z poszczególnymi czynnikami regenerującymi wynosił 3 h, zaś dalsze jego wydłużanie nie powodowało wzrostu skuteczności regeneracji.

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Literatura

1. **Anielak P., Janio K., Jankowski J.:** *Removal of Chlorophenoxy Acid Derivatives from Wastewaters.* Chemistry for the Protection of the Environment Environmental Science Research. 42, 789–796 (1991).
2. **Chow A.T., Dahlgren R.A., Gao S.:** *Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: a review.* Journal of Water Supply Research and Technology. 54, 475–507 (2005).
3. **Chow Ch.W.K., Fabris R., Drikas M.:** *A rapid fractionation to characterize natural organic matter for the optimization of water treatment process.* Journal of Water Supply: Research and Technology – AQUA. 53, 85–92 (2004).
4. **Gu B., Brown G. M., Maya L., Lance M. J., Moyer B. A.:** *Regeneration of perchlorate (ClO_4^-) – loaded anion exchange resins by a novel tetrachloroferrate ($FeCl_4^-$) displacement technique.* Environmental Science Technology. 35, 3363–3368 (2001).

5. **Grzybowski W., Pempkowiak J.:** *Application of Amberlite XAD resins to the isolation of substances from sea water*. Oceanologia. 33, 105–109 (1992).
6. **Kowal A.L., Świderska-Bróż M.:** *Oczyszczanie wody. Podstawy teoretyczne i technologiczne, procesy i urządzenia*. PWN. Warszawa, 2007.
7. **Leenheer J.A.:** *Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters*. Environmental Science and Technology. 15, 578–587 (1981).
8. **Leenheer J.A., Huffman Jr. E.W.D.:** *Classification of organic solutes in water by using macroreticular resins*. Journal Research US Geological Survey. 4, 737–751 (1976).
9. **Malcolm R.L., MacCarthy P.:** *Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water*. Environment International. 18, 597–607 (1992).
10. **Matilainen A., Gjessing E. T., Lahtinen T., Hed L., Bhangar A., Sillanpaa M.:** *An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment*. Chemosphere. 83, 1431–1442 (2011).
11. **Matilainen A., Sillanpaa M.:** *Removal of natural organic matter from drinking water by advanced oxidation processes*. Chemosphere. 80, 351–365 (2010).
12. **Rajca M.:** *NOM fouling mechanism during ultrafiltration*. ACEE Architecture Civil Engineering Environment. 4, 113–120 (2011).
13. **Singer P.:** *Control of Disinfection By-Products in Drinking Water*. Journal of Environmental Engineering. 120, 727–744 (1994).
14. **Smith E. H., Alqabany A. A.:** *Fractionation of natural organic matter in the Nile River: Implications for treated water quality*. Water Science and Technology. 59, 1989–1997 (2009).
15. **Vieira R. F., Berenguel A. T., Silva M. A., Vilaca J. S., Domingues V. F., Figueiredo S. A.:** *Natural organic matter fractionation along the treatment of water for human consumption.* Global NEST Journal. 14, 399–406 (2012).
16. **Zularisam A.W., Ismail A.F., Salim M. R., Sakinah M., Ozaki H.:** *The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes*. Desalination. 212, 191–208 (2007).
17. *Amberlite® XAD4 Industrial Grade Polymeric Adsorbent, Product Data Sheet*, http://www.dow.com/assets/attachments/business/process_chemicals/amberlite_xad/amberlite_xad4/tds/amberlite_xad4.pdf [data dostępu: 2015-03-15]

18. *Product Data Sheet, Amberlite® IRA958 Cl Industrial Grade Strong Base Anion Exchanger*, http://www.dow.com/assets/attachments/business/ier/ie-r_for_industrial_water_treatment/amberlite_ira958_cl/tds/amberlite_ira958_cl.pdf [data dostępu: 2015-03-15]
19. *Supelco, Resins & Media*, http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Supelco/Brochure/1/supelco-13-resins-media.pdf [data dostępu: 2015-03-15]

Regeneration of XAD Resins Used for Natural Organic Matter Fractionation

Abstract

Natural organic matter (NOM) removal plays important role in water treatment due to their ability to form disinfection by-products. Due to NOM complexity, it is crucial to separate it into fractions and then subject them to the detailed analysis. Organic contaminants are heterogeneous mixture of various organic compounds of diverse properties and could be divided into 3 fractions: hydrophobic, hydrophilic and transphilic. Currently, the common NOM fractionation method was proposed by Chow et al. This method employs XAD resins to fractionate NOM. One of decisive factors, when it comes to their usability, is the possibility to regenerate it. In this connection evaluation of XAD resin regeneration methods efficiency was performed. Supelite DAX-8, Amberlite XAD-4 and Amberlite IRA-958 nonionic macroporous resins were used in the experiments. Experiments included resin preparation by initial regeneration, resin saturation with NOM and final resin regeneration. Experiments were carried out on the model solution and surface water taken from Odra River (Poland). Regeneration was conducted in a column system with the use of two methods. The first one was in accordance with Chow et al. procedure. The second one comprised of successive resin rinsing with redistilled water, 0.1 n NaOH, 0.1 n HCl, 0.1 n NaOH, redistilled water, methanol, acetonitrile, methanol and redistilled water. Preliminary research that were conducted in order to evaluate sorption performance in column system revealed that in all cases same schema could be observed: in few initial minutes, UV 254 nm absorbance, colour and dissolved organic carbon concentration in column effluent was constant, then started rising until reaching feed solution values. It is noticeable that none of the resins adsorbed all contaminants at any time. Subsequent experiments has shown that developed by Chow et al. method of saturated resins regeneration was not able to restore their initial sorptive capacity. Regeneration procedure developed by paper authors allowed full regeneration of NOM saturated resin, even after second saturation-regeneration cycle. Influence of regeneration time on resin sorption capacity restoration efficiency was also observed: longer regeneration resulted in better results. The best effects of resin regeneration was observed for 3 h contact time with each regenerant solution.

Słowa kluczowe:
naturalne substancje organiczne, żywice typu XAD, regeneracja

Keywords:
natural organic matter, XAD resins, regeneration

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Analiza kosztów funkcjonowania przydomowych oczyszczalni ścieków

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1. Wstęp

Na terenach bez kanalizacji zbiorczej zagospodarowanie ścieków bytowo-gospodarczych odbywa się poprzez gromadzenie ścieków w zbiornikach bezodpływowych i ich wywóz do punktu zlewnego lub poprzez unieszkodliwianie ścieków w przydomowych oczyszczalniach. W ostatnich latach w Polsce nastąpił znaczący wzrost liczby tego typu obiektów [8], jednak wciąż jest ona niewystarczająca, szczególnie z uwagi na zagrożenia, wynikające z eksploatacji tzw. szamb, wciąż powszechnie stosowanych na terenach nieskanalizowanych [7].

Zarówno system kanalizacji bezodpływowej, jak i przydomowe oczyszczalnie ścieków są kapitałochłonne – w pierwszym przypadku należy uwzględnić wysokie opłaty, związane z cyklicznym odbiorem ścieków, podczas gdy koszty inwestycyjne są niskie. Użytkowanie oczyszczalni wiąże się z większymi nakładami inwestycyjnymi, jednak niższe są koszty eksploatacji.

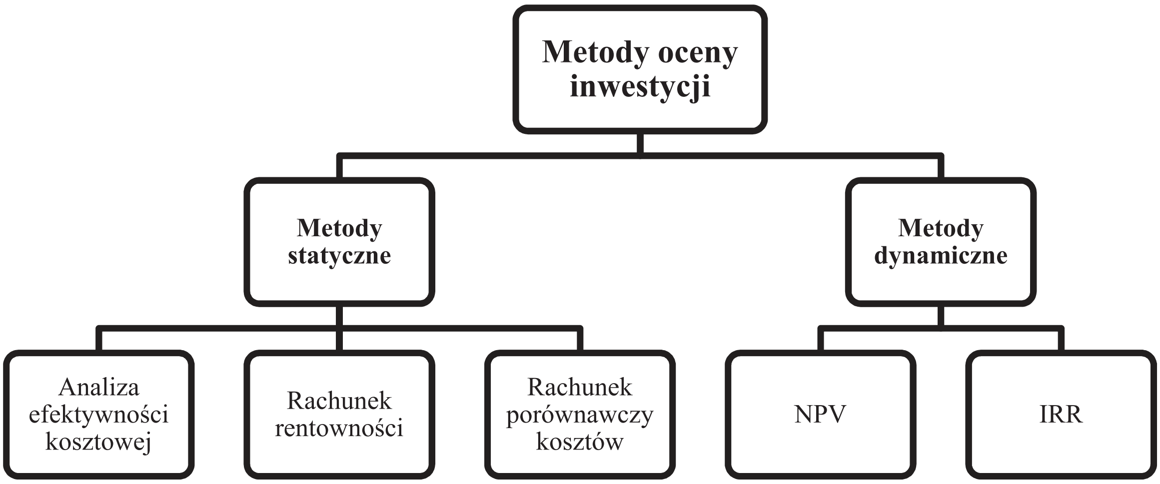
Producenci i dystrybutorzy urządzeń i systemów do oczyszczania niewielkich ilości ścieków oferują wiele rozwiązań technologicznych. Wybór optymalnego układu w konkretnym przypadku nie jest sprawą łatwą. Jednym z podstawowych kryteriów przydatności danego systemu są aspekty ekonomiczne. W pracy porównano pod kątem ekonomicznym trzy wybrane układy oczyszczalni przydomowych. Analizowane systemy są oferowane przez firmę HABA i charakteryzują się odmiennymi rozwiązaniami technologicznymi. Są to: układ z drenażem rozsączającym, oczyszczalnia biologiczna SBR oraz oczyszczalnia hydrobotaniczna.

2. Procedury określania kosztów funkcjonowania oczyszczalni

2.1. Metody oceny inwestycji

Podstawą przeprowadzenia porównawczej analizy ekonomicznej poszczególnych systemów oczyszczania ścieków jest przyjęcie jednakowych metod pomiaru składników kosztów inwestycyjnych i eksploatacyjnych. Dokonanie oceny inwestycji wiąże się z oszacowaniem korzyści, wynikających z przeprowadzonych prac, a w przypadku rozpatrywania kilku wariantów – z wyborem tego najbardziej opłacalnego. Istnieją różne metody oceny inwestycji w zależności od autora, jednak ogólnie można je podzielić na metody statyczne i dynamiczne. Podstawowa klasyfikacja została przedstawiona na rysunku 1.

Metody statyczne oceny inwestycji polegają na statystycznym opracowaniu danych, dotyczących poszczególnych kosztów, a następnie na porównaniu ich w czasie. Zaliczane są do metod niedyskontowych, nieuwzględniających szeregu czynników (np. inflacji). Ponadto nie uwzględniają całego okresu trwania projektu, obejmując wąską jego część. Praktyczne wykorzystanie metod statycznych ogranicza się do inwestycji, w których nakłady i efekty są niewielkie, bądź ma miejsce podczas wyboru inwestycji, nie wymagających złożonych obliczeń.



Rys. 1. Podział metod oceny inwestycji. Oprac. własne na podstawie [5,6,9]
Fig. 1. Methods assessment of the investment. Own calculations based on [5, 6,9]

Metody dynamiczne, bardziej złożone niż statyczne, są dokładniejsze i umożliwiają uwzględnienie większej liczby czynników (np. zmienności wartości pieniądza w czasie). Ponadto – w odróżnieniu od metod statycznych – obejmują cały okres inwestycji.

Budowę przydomowej oczyszczalni ścieków należy zaliczyć do przedsięwzięć, nie generujących wpływów z inwestycji. Stąd w celu dokonania oceny tego typu przedsięwzięcia należy zastosować taką metodę, w której efektów inwestycji nie da się zmierzyć. Za efekt, uzyskiwany w tego typu przedsięwzięciach, może zostać uznana ilość oczyszczonych ścieków w skali czasu. Z drugiej strony jako efekt można przyjąć tzw. straty uniknione, możliwe do oszacowania w sytuacji braku inwestycji. M.in. autorzy [6] podkreślają, że podstawą prawidłowego porównania poszczególnych rozwiązań indywidualnych systemów oczyszczania ścieków jest doprowadzenie nakładów inwestycyjnych oraz eksploatacyjnych do kosztów jednostkowych. Podzielenie rocznych kosztów oczyszczania przez ilość oczyszczonych ścieków umożliwia uzyskanie jednakowej podstawy do porównań. Według autorów [6] najlepszą metodą jest analiza efektywności kosztowej, będąca modyfikacją metody CBA, czyli analizy kosztów i efektów. Uzasadniając prezentowane powyżej stanowisko autorzy zwracają uwagę na fakt, że w jednostkach pieniężnych mierzone są jedynie koszty, natomiast ocenie wartościującej nie podlegają efekty. Metoda zakłada ocenę inwestycji w sposób uproszczony, uwzględniając zarówno poniesione nakłady inwestycyjne, jak i koszty eksploatacji.

Inne stanowisko, w kwestii wyboru najlepszej metody oceny technologii oczyszczalni przydomowej z ekonomicznego punktu widzenia, reprezentują autorzy [2]. Korzystają oni przede wszystkim z metody NPV, przyporządkowanej do metod dynamicznych (wg klasyfikacji na rysunku 1).

Określenie wartości bieżącej netto polega na obliczeniu zdyskontowanych przepływów gotówki w kolejnych latach inwestycji. Według autorki [1] dyskontowanie przepływów pieniężnych sprowadza się do określenia różnicy pomiędzy wpływami i wydatkami pieniężnymi, poniesionymi na nakłady inwestycyjne, sprowadzonymi do wspólnego mianownika, co pozwala na precyzyjne i czytelne porównania.

Pierwszymi czynnościami, zmierzającymi do określenia NPV, są: ustalenie nakładów inwestycyjnych oraz rocznych całkowitych kosztów eksploatacyjnych, które będą dyskontowane na dzień przeprowadzania analizy. Wartość bieżąca netto określana jest wzorem:

$$\boldsymbol{NPV = I + a \times K_e} \tag{1}$$

gdzie:
I – nakłady inwestycyjne [zł],
a – współczynnik dyskontujący,
K_e – roczne koszty eksploatacji [zł/rok].

Niezbędne jest także określenie wartości współczynnika dyskontującego, umożliwiającego przeliczenie wartości rocznych kosztów eksploatacyjnych do wartości na dzień inwestycji. Współczynnik dyskontujący obliczony jest z zależności:

$$\boldsymbol{a = \sum_{t=1}^{n} \frac{1}{(1+p)^t}} \tag{2}$$

gdzie:
n – liczba lat eksploatacji oczyszczalni ścieków [lata],
p – stopa dyskontowa,
t – liczba okresów.

Po obliczeniu przepływów pieniężnych, w przypadku rozpatrywania kilku wariantów indywidualnych systemów oczyszczania ścieków, za najkorzystniejszą należy uznać inwestycję, dla której wartość NPV jest najniższa – zgodnie z sugestią autora [2].

2.2. Określenie nakładów inwestycyjnych

Nakłady inwestycyjne w przypadku oczyszczalni przydomowej uzależnione są przede wszystkim od przyjętej technologii oczyszczania, szczególnie na etapie biologicznym. Układy mniej złożone, takie jak drenaż rozsączający czy oczyszczalnia hydrobotaniczna, cechują się niższymi kosztami inwestycyjnymi niż np. układ z biocenozą zawieszoną lub osiadłą czy system hybrydowy. Najbardziej kapitałochłonne rozwiązania oczyszczania ścieków związane są z biologicznymi systemami oczyszczania, do których zalicza się złoża biologiczne oraz komory osadu czynnego. Zwiększone nakłady inwestycyjne wiążą się m.in. z dodatkowymi elementami instalacji, w tym aparaturą utrzymującą optymalne warunki dla mikroorganizmów w strefie biologicznej. Ważnym aspektem dotyczącym niezbędnych nakładów inwestycyjnych jest charakterystyka ilościowo-jakościowa ścieków oraz warunki terenowe w miejscu lokalizacji oczyszczalni. Istotne są: dostępna powierzchnia, warunki gruntowo-wodne oraz układ przestrzenny, decydujący m.in. o zastosowaniu najdroższych tu pomp, podnoszących ścieki na większą wysokość. Przykład szczegółowej analizy kosztów inwestycyjnych dla oczyszczalni hydrobotanicznej przedstawiono w pracy [13]. Autorka w swoim opracowaniu wykazała także, że przy budowie systemu oczyszczania ścieków dla całej wsi, niższe nakłady inwestycyjne będą poniesione przy budowie indywidualnych systemów oczyszczania ścieków w porównaniu z systemami zbiorowymi.

2.3. Koszty eksploatacyjne

Do podstawowych kosztów eksploatacyjnych należą okresowe przeglądy instalacji, wykonywane przez wyspecjalizowane firmy. Częstotliwość przeglądów jest uzależniona od rodzaju instalacji, jednak zasadniczo przyjmuje się je przeprowadzać raz w roku [3]. Obok przeglądów technicznych, z użytkowaniem oczyszczalni wiąże się również okresowe usuwanie osadów i kożucha, zebranych w wyniku sedymentacji oraz flotacji zanieczyszczeń w osadniku gnilnym. Ilość osadów oraz częstotliwość ich usuwania uzależniona jest od przyjętej pojemności części fermentacyjnej osadnika gnilnego, parametrów ilościowych i jakościowych dopływających ścieków, a także od przyjętej technologii oczyszczania w kolejnym etapie (uwzględnienie osadów nadmiernych, kierowanych do osadnika z części biologicznej). Koszty, związane z pobieraniem oraz transportem osadów, uzależnione są przede wszystkim od uwarunkowań lokalnych. Wywóz osadów, najczęściej raz na rok lub raz na dwa lata, powinien być wykonywany przez służby asenizacyjne, które przetransportują osady np. do oczyszczalni ścieków. Koszty eksploatacyjne to także usuwanie zanieczyszczeń z filtrów doczyszczających osadników wstępnych oraz przepłukiwanie instalacji czystą wodą. Te ostatnie czynności często nie są uwzględniane w kalkulacji kosztów, gdyż eksploatator może je wykonać samodzielnie (zwykle co 2–3 miesiące) [10]. Do podstawowych kosztów eksploatacyjnych należą także koszty energii elektrycznej, uzależnione od wielkości oczyszczalni, zastosowanej technologii oraz warunków terenowych. Zużycie energii generowane będzie głównie przez pompy oraz systemy napowietrzania ścieków. Obok wyżej wymienionych, do kosztów eksploatacyjnych zalicza się również koszty, związane z badaniami jakości oraz ilości konkretnych zanieczyszczeń w ściekach, odprowadzanych z oczyszczalni do odbiornika. Częstotliwość poboru próbek, zakres badań oraz dopuszczalne wartości wskaźników zanieczyszczeń w ściekach, odprowadzanych do wód i do ziemi, określa Rozporządzenie Ministra Środowiska [12]. Badania są przeprowadzane przez wyspecjalizowane laboratoria. Ich koszt uzależniony jest od przyjętego zakresu badań oraz jednostki, w której są one wykonywane i waha się od 200 do 300 złotych rocznie. W przypadku zastosowania oczyszczalni hydrofitowych może wystąpić konieczność wymiany roślinności wskutek jej zniszczenia (np. w wyniku suszy, mrozów lub chorób roślin). Praktycznie do wymiany roślinności dochodzi jednak bardzo rzadko. Podobnie jak w przypadku oczyszczalni roślinnych, przy niewłaściwej eksploatacji złóż biologicznych oraz komór osadu czynnego może dojść do zniszczenia zasiedlającej je biocenozy. W takim przypadku konieczne jest odbudowanie osadu czynnego czy też kolonii bakterii na złożu biologicznym poprzez specjalne startery. Powtórne szczepienie bakterii jest incydentalne i nie można go zaliczyć do typowych kosztów eksploatacyjnych. Do innych kosztów tzw. incydentalnych można zaliczyć koszty napraw urządzeń oraz wymiany zbiorników (np. nieszczelnych). Najczęściej awariom ulegają pompy, wymagające okresowych przeglądów i doboru, właściwego dla ilości pompowanych ścieków. W przypadku drenaży rozsączających należy uwzględnić koszty okresowego (co 5 lat) czyszczenia układu z uwagi na jego kolmatację, a w dłuższym okresie eksploatacji (od 10 do 15 lat) nawet jego wymiany.

Analiza ekonomiczna oczyszczalni przydomowych powinna uwzględniać amortyzację, tj. zużywanie się danego środka trwałego podczas jego normalnej eksploatacji. W przypadku POŚ taką eksploatacją jest oczyszczanie ścieków wraz z ich odprowadzeniem do odbiornika. Według rozporządzenia [11] przydomowe oczyszczalnie ścieków sklasyfikowane są w grupie 2, obejmującej „obiekty inżynierii lądowej i wodnej”. Roczny procent amortyzacji takich obiektów to 10%, przy czym podstawą amortyzacji jest wartość całej oczyszczalni przydomowej, podwyższona o wartość urządzeń, nie mogących działać samodzielnie. Ponadto należy uwzględnić wszystkie dodatkowe koszty, poniesione do dnia rozpoczęcia użytkowania instalacji.

3. Porównanie wybranych rozwiązań oczyszczalni przydomowych pod względem ekonomicznym

Ocenie ekonomicznej poddano trzy systemy oczyszczania ścieków, oferowane przez firmę HABA, charakteryzujące się odmiennymi rozwiązaniami technologicznymi.

System typu DT składa się z osadnika gnilnego oraz układu drenażowego, rozprowadzającego ścieki do gruntu za pomocą tuneli. Tunele zbudowane są z półkolistych kształtek na wspornikach, w których ułożone są dreny. Otwory, umieszczone po bokach tuneli umożliwiają odpływ ścieków i dalszą ich infiltrację do gruntu.

Oczyszczalnia z reaktorem sekwencyjnym typu SBR – Primo charakteryzuje się 24 godzinnym cyklem pracy. Układ wyposażony został w przepompownię ścieków, umożliwiającą podniesienie ścieków w przypadku znacznego obniżenia terenu. Ścieki oczyszczone, w zależności od warunków lokalnych, mogą zostać odprowadzone do gruntu lub do cieku wodnego.

System typu ORS to oczyszczalnia hydrobotaniczna z re cyrkulacją. W pierwszym etapie oczyszczania ścieki trafiają do osadnika gnilnego, wyposażonego w filtr doczyszczający. Drugi etap realizowany jest w filtrze piaskowo-roślinnym z matami rozsączającymi, wyposażonymi w drenaż umożliwiający recyrkulację ścieków. Filtr zasypany jest korą, na której sadzi się roślinność hydrofilną. Ostatnim elementem instalacji jest staw (odprowadzenie ścieków oczyszczonych). Dzięki recyrkulacji możliwe jest podwójne oczyszczenie ścieków na drugim stopniu oczyszczania.

Ceny porównywanych oczyszczalni przyjęto w oparciu o dane katalogowe firmy HABA, znajdujące się na stronie internetowej (rok 2014) [4]. Zamieszczone w pracy obliczenia zostały dokonane na podstawie opracowania [6]. Założono, że z oczyszczalni korzystać będzie 5 osób, generujących łącznie 0,75 [m^3] ścieków na dobę (przyjęto średnią dobową ilość ścieków na osobę równą 0,15 [m^3]). Przyjęto stopę dyskontową r = 5% w skali roku.

Niezbędne nakłady inwestycyjne dla poszczególnych typów oczyszczalni zestawiono w tabeli 1.

Tabela 1. Nakłady inwestycyjne dla wybranych oczyszczalni. Opracowanie własne na podstawie cen producenta na rok 2014 [4]; data dostępu: 10.02.2014
Table 1. Investment costs of selected wastewater treatment plants. Own calculations based on producer prices for the year 2014 [4]; access date: 10/02/2014

Typ oczyszczalni	DT	ORS	SBR-PRIMO
Nakłady inwestycyjne [zł]	4300,00	6150,00	8610,00

Wielkość kosztów eksploatacyjnych dla każdego z analizowanych rozwiązań technologicznych przedstawiono w tabeli 2.

Tabela 2. Koszty eksploatacyjne dla wybranych rozwiązań technologicznych. Opracowanie własne na podstawie cenników producentów, firm usługowych oraz dostawcy energii elektrycznej
Table 2. Operating costs for different wastewater treatment plants. Own study based on producer, service companies and electricity supplier tariff

Lp.	Rodzaj kosztów eksploatacyjnych	Typ oczyszczalni		
		DT	ORS	SBR-PRIMO
1	Okresowa konserwacja układu	492,00	492,00	492,00
2	Badania jakości oczyszczania	250,00	250,00	250,00
3	Wywóz osadu	140,00	140,00	140,00
4	Biopreparaty	136,00	56,00	56,00
5	Dosadzanie roślinności	-	150,00	-
6	Czyszczenie stawu	-	100,00	-
7	Energia elektryczna	-	17,00	17,00
Suma		**1018,00**	**1205,00**	**955,00**

Koszty energii elektrycznej przyjęto w oparciu o cennik operatora Energa obrót – 0,61 [zł/kWh] oraz o zużycie prądu dla analizowanych rozwiązań, określone przez producenta na poziomie 0,1 [kWh/m^3] (wg autora mogą być zaniżone – praca pomp). Przy $Q_{dśr}$=0,75 [m^3/d] roczne koszty energii elektrycznej zostały obliczone wg wzoru:

$$\mathbf{E.elektr.} = (\mathbf{0,75 \times 365})\left[\frac{\mathbf{m^3}}{\mathbf{d}}\right] \times \mathbf{0,1}\left[\frac{\mathbf{kWh}}{\mathbf{d}}\right] \times \mathbf{0,61}\left[\frac{\mathbf{zł}}{\mathbf{kWh}}\right] \cong \mathbf{17(zł)} \qquad (3)$$

Sumaryczne koszty oczyszczania ścieków

Dla określenia sumarycznych kosztów oczyszczania ścieków zostały obliczone:

- współczynnik stopy zwrotu z inwestycji α (dla 25 lat eksploatacji):

$$\boldsymbol{\alpha} = \frac{\mathbf{0{,}05(1+0{,}05)^{25}}}{\mathbf{(1+0{,}05)^{25}-1}} = \mathbf{0{,}071}\ [-] \tag{4}$$

- roczne koszty oczyszczania:

– dla systemu HABA typu DT z drenażem tunelowym:

$$\boldsymbol{K_r} = \mathbf{4300 \times 0{,}071 + 1018 = 1323{,}30}\left(\frac{\boldsymbol{zł}}{\boldsymbol{rok}}\right) \tag{5}$$

– dla systemu HABA typu ORS (o. gruntowo-roślinna):

$$\boldsymbol{K_r} = \mathbf{6150 \times 0{,}071 + 1205 = 1641{,}65}\left(\frac{\boldsymbol{zł}}{\boldsymbol{rok}}\right) \tag{6}$$

– dla systemu typu SBR-PRIMO:

$$\boldsymbol{K_r} = \mathbf{8610 \times 0{,}071 + 955 = 1566{,}31}\left(\frac{\boldsymbol{zł}}{\boldsymbol{rok}}\right) \tag{7}$$

- nośnik kosztów:

$$\boldsymbol{K_r} = \mathbf{4300 \times 0{,}071 + 1018 = 1323{,}30}\left(\frac{\boldsymbol{zł}}{\boldsymbol{rok}}\right) \tag{8}$$

- jednostkowe koszty oczyszczania:

– dla systemu z drenażem tunelowym:

$$\boldsymbol{k_r} = \frac{\mathbf{1323{,}30}}{\mathbf{273{,}75}} = \mathbf{4{,}83}\left[\frac{\frac{\boldsymbol{zł}}{\boldsymbol{m^3}}}{\boldsymbol{rok}}\right] \tag{9}$$

– dla oczyszczalni gruntowo-roślinnej:

$$\boldsymbol{k_r} = \frac{\mathbf{1641{,}65}}{\mathbf{273{,}75}} = \mathbf{6{,}00}\left[\frac{\frac{\boldsymbol{zł}}{\boldsymbol{m^3}}}{\boldsymbol{rok}}\right] \tag{10}$$

– dla oczyszczalni SBR-PRIMO:

$$\boldsymbol{k_r} = \frac{\mathbf{1566{,}31}}{\mathbf{273{,}75}} = \mathbf{5{,}72}\left[\frac{\frac{\boldsymbol{zł}}{\boldsymbol{m^3}}}{\boldsymbol{rok}}\right] \tag{11}$$

Zestawienie zbiorcze wszystkich kosztów, związanych z zakupem i eksploatacją każdej z analizowanych oczyszczalni, w tym wartości rocznych kosztów oczyszczania ścieków, stanowi tabela 3.

Tabela 3. Koszty roczne wybranych systemów. Źródło: opracowanie własne
Table 3. Annual costs of selected systems. Source: own study

Lp.	Składniki kosztów [zł]	Rodzaj oczyszczalni		
		DT	ORS	SBR-PRIMO
1	Nakłady inwestycyjne	4300,00	6150,00	8610,00
2	Roczne koszty eksploatacyjne	1018,00	1205,00	955,00
3	Roczne koszty oczyszczania	1323,30	1641,65	1566,31
4	Koszt oczyszczania 1 m^3 ścieków	4,83	6,00	5,72

4. Podsumowanie i wnioski

Układy technologiczne oczyszczalni przydomowych wymagają różnych nakładów inwestycyjnych. Dane liczbowe, zawarte w tabeli 1, wskazują, że spośród analizowanych rozwiązań najbardziej kapitałochłonna jest oczyszczalnia biologiczna typu SBR-PRIMO. W jej przypadku na realizację inwestycji należy przeznaczyć 8610,00 zł. Znaczący wpływ na wielkość tych kosztów mają niezbędne w układzie technologicznym dodatkowe urządzenia, m.in. dmuchawy i pompy. Najmniejszych nakładów finansowych na zakup (4300,00 zł) wymaga układ z drenażem tunelowym. Nakłady inwestycyjne są dla tego układu dwukrotnie niższe niż dla oczyszczalni typu SBR. Decydujący jest w tym przypadku brak dodatkowych urządzeń, m.in. pompowni czy systemu napowietrzania ścieków. Zakup trzeciego z analizowanych rozwiązań, tj. oczyszczalni gruntowo-roślinnej, wiąże się z poniesieniem nakładów inwestycyjnych w wysokości 6150,00 zł. Koszty te są prawie 1500 zł niższe niż w przypadku oczyszczalni SBR, jednak zdecydowanie wyższe (o 1850 zł) od najtańszego układu z drenażem tunelowym.

Porównując koszty, związane z użytkowaniem poszczególnych systemów oczyszczania ścieków (tabela 2), należy zauważyć, że najniższymi kosztami eksploatacyjnymi (955,00 [zł/rok]) charakteryzuje się oczyszczalnia SBR. Jednocześnie jest to rozwiązanie, wymagające najwyższych nakładów inwestycyjnych. W przypadku oczyszczalni z drenażem tunelowym zależność jest inna – układ wymaga najniższych nakładów inwestycyjnych, jednak koszty eksploatacyjne są relatywnie wysokie. Jednak najwyższych kosztów eksploatacyjnych wymaga oczyszczalnia gruntowo-roślinna, co jest przede wszystkim związane ze specyfiką tego rozwiązania. Podczas użytkowania systemu należy uwzględnić dodatkowe czynności zwiększające koszty, np. gdy wystąpi konieczność dosadzania roślin czy czyszczenia stawu..

Istotne dla oceny ekonomicznej oczyszczalni przydomowych jest porównanie kosztów oczyszczania ścieków dla poszczególnych układów technologicznych. Przeprowadzone obliczenia wykazały, że najniższymi rocznymi kosztami oczyszczania 1m^3 ścieków charakteryzuje się oczyszczalnia z drenażem tunelowym HABA typu DT. Spośród trzech ujętych w pracy systemów najwyższe koszty oczyszczania ścieków generuje oczyszczalnia gruntowo-roślinna HABA typu ORS. Koszty te są ponad 25% wyższe niż koszty, obliczone dla oczyszczalni tunelowej.

Literatura

1. **Czerska J.:** *Metody oceny efektywności projektów inwestycyjnych*. Skrypt Politechniki Rzeszowskiej. 2002.
2. **Heidrich Z., Stańko G.:** *Leksykon przydomowych oczyszczalni ścieków*. Wyd. Seidel-Przywecki Sp. Z o.o. Warszawa 2007.
3. http://www.aquatechnika.com.pl.
4. http:// www. haba .pl.
5. **Krzemińska D.:** *Finanse Przedsiębiorstw*. WSB. Poznań 2005.
6. **Kundziewicz A., Miłaszewski R.:** *Analiza efektywności kosztowej indywidualnych systemów usuwania i oczyszczania ścieków.* Inżynieria Ekologiczna. 24 (2011).
7. **Nowak R.:** *Kanalizacja bezodpływowa – potencjalne i realne zagrożenie dla środowiska przyrodniczego*. Gaz, Woda i Technika Sanitarna. 6 (2012).
8. **Nowak R.:** *Stan gospodarki ściekowej na terenach wiejskich na przykładzie powiatu koszalińskiego*. CHEMIK. 10(68) (2014).
9. **Pastusiak R.:** *Ocena efektywności inwestycji.* Wyd. CDW. Warszawa 2010.
10. *Przydomowe oczyszczalnie ścieków – poradnik.* Ekoprom. Białystok 2008.
11. Rozporządzenie Rady Ministrów z dnia 10.12.2010 r. w sprawie Klasyfikacji Środków Trwałych (KŚT) [Dz. U. 2010 nr 242, poz. 1622].

12. Rozporządzenie Ministra Środowiska z dnia 18 listopada 2014 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego [Dz. U. 2014 poz. 1800].
13. **Skoczko I.:** *Ekonomiczna analiza rozwiązań oczyszczalni ścieków dla wsi przy rozproszonej zabudowie*. Gaz, Woda i Technika Sanitarna. 6 (2012).

Analysis of Operating Costs of Domestic Sewage Treatment Plants

Abstract

The economics aspects of the operation of household wastewater treatment plants are discussed in the paper. Three selected individual wastewater treatment systems offered by HABA are presented, such as (1) system with drainage tunnel (HABA DT), (2) treatment plant of SBR type (HABA SBR PRIMO) and (3) constructed wetland wastewater treatment plant (HABA ORS). In the work the analytical procedures for determining the costs are presented. Next, a comparative economics analysis of these systems is carried out. The level of annual costs as well as unit costs of wastewater disposal and treatment are determined for these systems. The annual unit cost in presented small sewage treatment facilities ranged from 4.83 to 6.00 zł per m^3. The calculations showed that the lowest annual cost of wastewater treatment is characterized by a system with drainage tunnel. Of the three systems included in the work of the highest costs of wastewater treatment plant generates system HABA ORS.

Słowa kluczowe:
oczyszczanie ścieków, przydomowe oczyszczalnie ścieków,
ocena ekonomiczna

Keywords:
wastewater treatment, domestic sewage treatment plants, economic analysis

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Adsorpcja ołowiu na modyfikowanym węglu aktywnym ROW 08 Supra

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1. Wstęp

Ołów jest jednym z bardziej toksycznych metali, co wiąże się z jego kumulowaniem w organizmach żywych [19]. W przypadku wody do spożycia dopuszczalne jego stężenie wynosi 0,01 mg/dm^3 (Dz.U. nr 72 poz. 466). Znajduje się w bardzo wielu produktach codziennego użytku np.: akumulatorach kwasowo-ołowianych, farbach, olejach, nawozach fosforowych, elektronice. Jest emitowany do środowiska również ze ściekami. Jego dopuszczalna zawartość w ściekach wprowadzanych do wód lub ziemi wynosi 0,1 mg/dm^3 dla ścieków z przemysłu ciepłowniczego i 0,5 mg/dm^3 dla ścieków z pozostałych gałęzi przemysłu (Dz. U. nr 27 poz. 169). Może być usuwany z wody i ścieków przez chemiczne strącanie, elektrochemiczną redukcję, wymianę jonową, biosorpcję, elektrofiltarcję, procesy membranowe oraz adsorpcję [9, 23]. Wybór metody usuwania jonów ołowiu zależy od wielu czynników (stężenia, formy, obecności innych zanieczyszczeń, pH, zastosowania wody po usunięciu jonów ołowiu), jednak adsorpcja na węglu aktywnym jest procesem coraz szerzej stosowanym. Coraz częściej poszukiwane są tanie (często odpadowe) surowce do produkcji sorbentów węglowych skutecznych w adsorpcyjnym usuwaniu Pb(II), np. łupiny orzecha kokosowego [11, 22], trociny [5], wytłoczki trzciny cukrowej [27], pestki owoców [17], łupiny orzechów [3, 26]. Istotnym z punktu zastosowania węgli aktywnych w stacjach uzdatniania wody jest ich przebadanie również pod względem adsorpcji jonów metali ciężkich. Dlatego też komercyjne węgle aktywne analizowane są również pod kątem adsorpcji potencjalnych zanieczyszczeń m.in. metali ciężkich. Przeprowadzane są również różnego rodzaju modyfikacje zwiększające skuteczność usuwania jonów metali ciężkich w tym ołowiu [1, 2, 15, 18, 20, 25].

Skuteczna adsorpcja jonów metali ciężkich, w tym ołowiu zależy od wielkości powierzchni właściwej, od struktury porowatej, a przede wszystkim od chemicznej budowy powierzchni węgla aktywnego i obecności innych zanieczyszczeń [7, 8, 10, 21, 24]. Równie ważne są warunki prowadzenia procesu adsorpcji np. wartość pH lub/i temperatura roztworu w jakim ten proces zachodzi.

Celem niniejszej pracy była ocena wpływu wysokotemperaturowej modyfikacji węgla aktywnego, prowadzonego w piecu obrotowym oraz na stanowisku SEOW (Stanowisko elektrycznego ogrzewania węgla), w którym wykorzystano podgrzewanie węgla podczas przepływu prądu przez złoże węglowe. Przenalizowano również stopień dopasowania różnych form izotermy Langmuira i izotermy Freundlicha do uzyskanych wyników. Innym analizowanym zagadnieniem była ocena wpływu wartości pH roztworu i jego temperatury na skuteczność adsorpcji jonów Pb(II).

2. Materiał i metodyka badań

2.1. Materiał badań

Do badań wykorzystano węgiel aktywny ROW 08 Supra. Charakterystykę podstawowych właściwości, fizycznych, chemicznych w tym adsorpcyjnych wyjściowego węgla aktywnego zamieszczono w tabeli 1. Grupy funkcyjne oznaczono i zinterpretowano, stosując metodykę Bohema [6]. Przed modyfikacją węgiel przemywano kilkakrotnie wodą destylowaną i suszono w temperaturze 140ºC.

Węgiel aktywny był modyfikowany w piecu obrotowym i stanowisku do elektrycznego ogrzewania węgla aktywnego [14]. Modyfikację w piecu obrotowym prowadzono w ciągu 1 godziny w temperaturze 400ºC i 800ºC, przy stałym przepływ pary wodnej, dwutlenku węgla i powietrza. Wyjściowy węgiel aktywny oznaczono jako R0, a zmodyfikowany odpowiednio: R/400/CO_2, gdzie liczba 400 oznaczała temperaturę modyfikacji w °C, CO_2, H_2O lub AIR określają gazy użyte do modyfikacji (odpowiednio dwutlenek węgla, parę wodną, powietrze).

Tabela 1. Właściwości fizyczne i chemiczne węgla aktywnego R0 (PN-83/C-97555)
Table 1. Physical and chemical properties of activated carbons R0 (PN-83/C-97555)

Wskaźnik	Wartość	Promień kapilar, nm	Objętość kapilar, cm^3/g
Masa nasypowa, g/dm^3	417	<1,5	0,250
Nasiąkliwość wodna, cm^3/g	0,97	1,5–15	0,240
Powierzchnia właściwa, m^2/g	890	15–150	0,309
pH wyciągu wodnego	8,6	150–1500	0,3197
Własność adsorpcyjne wobec:		1500–7500	0,017
- błękitu metylenowego, LM	34	0–7500	1,134
- jodu, LI, mg/g	760		
- fenolu*, mg/g	53,8		

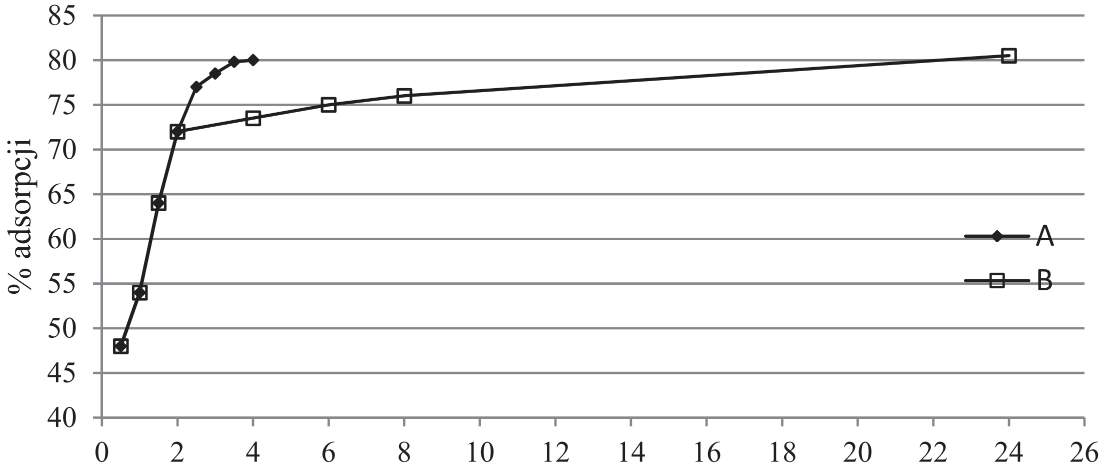
**Badania sorpcji fenolu prowadzono z roztworu o objętości 0,25 dm^3 o stężeniu 250 mg/dm^3 z dodatkiem 1 g węgla aktywnego*

Druga część próbki węgla została zmodyfikowana na stanowisku SEOW. W tym wypadku próbki węgla ogrzewa się do 400°C ± 20ºC. Schemat tego stanowiska oraz szczegółowe sposoby modyfikacji zostały przedstawione w pracy [14]. W odniesieniu do wyników poprzednich badań dotyczących Cr(III), stwierdzono, że węgiel aktywny uzyskany z kolejnych wysokości reaktora różnił się właściwościami adsorpcyjnymi. Dlatego do badania adsorpcji Pb(II) węgiel aktywny pobieranego tylko z tych części reaktora, które wykazały najwyższe właściwości adsorpcyjne wobec Cr (III). Modyfikacja węgla aktywnego na stanowisku SEOW polegała na ogrzewaniu złoża węglowego podczas przepływu prądu, a następnie chłodzeniu złoża powietrzem lub ditlenkiem węgla.

Węgle modyfikowane na tym stanowisku oznaczono według następującego kodu: R/400E+80/80AIRd – gdzie R oznacza wyjściowy węgiel aktywny ROW 08 Supra, 400E – ogrzewanie węgla na stanowisku SEOW do temperatury 400°C, +80 – przepływ gazu podczas nagrzewania przez reaktor z węglem aktywnym w dm^3/h, 80AIR (CO_2) – ilość gazu (powietrza lub ditlenku węgla) przepływającego podczas chłodzenia złoża w dm^3/h, miejsce poboru próbki węgla: d – z dolnej części reaktora, ś – ze środkowej części reaktora, g – z górnej części reaktora.

2.2. Pomiary właściwości adsorpcyjnych

Adsorpcję jonów ołowiu prowadzono w warunkach statycznych z roztworów $Pb(NO_3)_2$ o stężeniu Pb(II): 20, 50, 70, 90, 100, 150, 200, 250, 300, 350, 400, 450, 500 mmol/m^3. Przedstawione wyniki badań są średnią z trzech pomiarów. Adsorpcję prowadzono z roztworu o objętości 0,25 dm^3, do którego dodawano 1 g węgla aktywnego. W celu ustalenia czasu niezbędnego do osiągnięcia równowagi adsorpcji oceniono dwa sposoby kontaktu roztworów z węglem aktywnym (rysunek 1). W pierwszym (zależność A) roztwór z węglem aktywnym mieszano przez 4 godziny. Pomiary stężeń wykonywano z częstotliwością 30 min. W drugim przypadku (zależność B) roztwór z węglem aktywnym mieszano przez 2 godziny i pozostawiono na 2, 4, 6, 22, 46 i 70 h. Na rysunku 1 nie przedstawiono stężeń po upływie 48 i 72 godzin z powodu niewielkich różnic w wartościach uzyskanych stężeń. Po 24 godzinach i 72 godzinach różnice w stężeniach były mniejsze od 1%. Równowagę adsorpcji osiągnięto po 3 h mieszania, ale taki sam efekt obserwowano po 2 h mieszania i 22 h kontaktu statycznego. W badaniach użyto drugiego sposobu (czyli 2 h mieszania i 22 h kontaktu statycznego). Po tym okresie czasu mierzono stężenie końcowe.



Rys. 1. Wpływ czasu kontaktu na adsorpcję Pb (II): A – mieszanie
B – mieszanie 2 h i pozostawienie na 2, 4, 6 lub 22 h
Fig. 1. Effect of contact time on adsorption of Pb(II): A – stirred,
B – stirred 2 h and left for 2, 4, 6 or 22 h

Badania wpływu temperatury na efektywność adsorpcji prowadzono z użyciem łaźni wodnej z mechanicznym wytrząsaniem. Pomiary prowadzono w temperaturze 20, 30 i 40±2°C.

Pomiary stężeń ołowiu wykonano na atomowym spektrometrze emisyjnym z plazmą wzbudzoną indukcyjnie (ICP).

2.3. Modele opisu sorpcji w warunkach statycznych

Do opisu wyników badań w warunkach statycznych wykorzystano równania izoterm Freundlicha (1) i Langmuira (2):

$$Q = K_F \cdot C_e^{\frac{1}{n}} \tag{1}$$

$$Q = \frac{Q_{,m} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{2}$$

gdzie:
Q – pojemność adsorpcyjna,
K_F i n – stałe równania Freundlicha,
C_e – stężenie równowagowe,
Q_m i K_L – stałe równania Langmuira.

Z postaci liniowych izoterm Freundlicha (3) oblicza się stałe równania.

$$\log Q = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

Stałe Langmuira wyznaczono z kilku liniowych form równań (4–8) [12].

Langmuir-forma 1 – stałe Q_m i K_L obliczono z zależności $\frac{1}{Q}$ od $\frac{1}{C_e}$

$$\frac{1}{Q} = \left(\frac{1}{K_L \cdot Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m} \tag{4}$$

Langmuir-forma 2 – stałe Q_m i K_L obliczono z zależności $\frac{C_e}{Q}$ od C_e

$$\frac{C_e}{Q} = \left(\frac{1}{Q_m}\right) \cdot C_e + \frac{1}{K_L \cdot Q_m} \tag{5}$$

Langmuir-forma 3 – stałe Q_m i K_L obliczono z zależności Q od $\frac{Q}{C_e}$

$$Q = \left(\frac{-1}{K_L}\right)\frac{Q}{C_e} + Q_m \tag{6}$$

Langmuir-forma 4 – stałe Q_m i K_L obliczono z zależności $\frac{Q}{C_e}$ od Q

$$\frac{Q}{C_e} = (-K_L)Q + K_L \cdot Q_m \tag{7}$$

Langmuir-forma 5 – stałe Q_m i K_L obliczono z zależności $\frac{1}{C_e}$ od $\frac{1}{Q}$

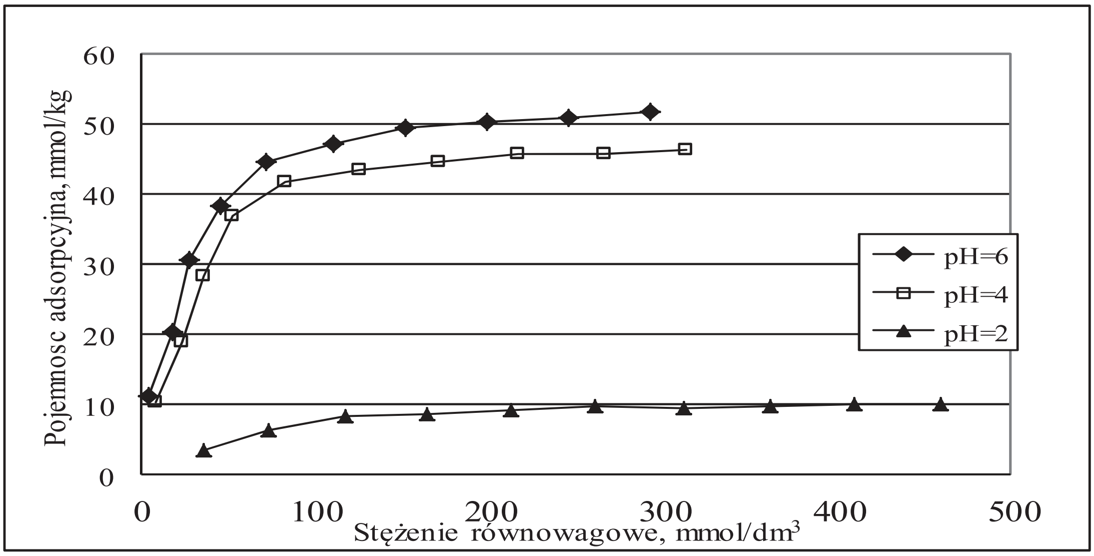
$$\frac{1}{C_e} = (K_L \cdot Q_m)\frac{1}{Q} - K_L \tag{8}$$

Stałe izoterm oraz wartości R^2 obliczono z użyciem programu Statistica IV.

3. Wyniki badań i ich dyskusja

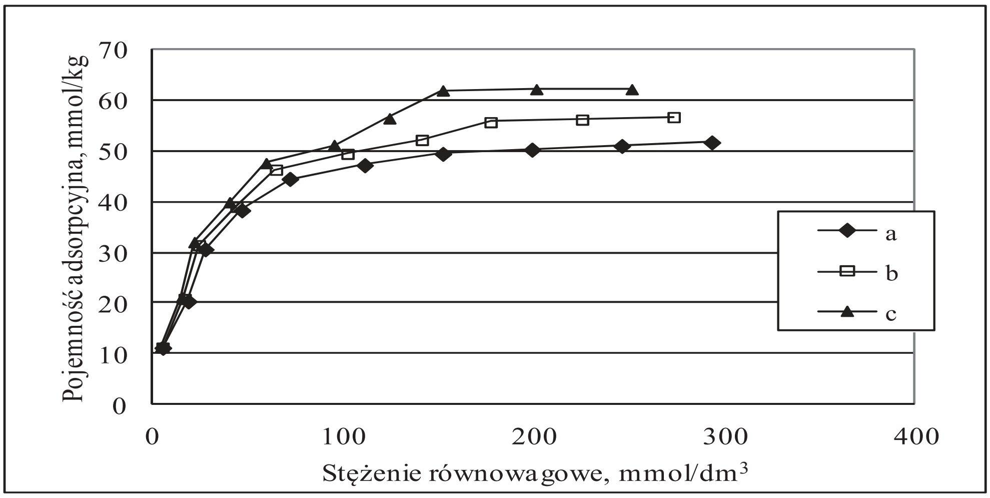
3.1. Wpływ pH i temperatury na adsorpcję ołowiu(II)

W pierwszym etapie badań oceniono wpływ pH roztworu na wyniki adsorpcji. Analizowano adsorpcję z roztworów o pH 2, 4 i 6 (rysunek 2). Wartość pH roztworu z jednej strony może mieć wpływ na formę jonu ołowiu z drugiej na dysocjację grup funkcyjnych na powierzchni węgla aktywnego. W takich warunkach (pH od 2 do 6) ołów występuje jako jon Pb^{2+} [4]. Grupy funkcyjne obecne na powierzchni węgli aktywnych są najistotniejsze przy usuwaniu jonów metali ciężkich w tym ołowiu [21, 24]. W badaniach potwierdzono bardzo istotny wpływ pH na wyniki adsorpcji. Najkorzystniej adsorpcja zachodziła przy pH = 6, a bardzo niskie pojemności adsorpcyjne otrzymano wówczas gdy pH roztworu wynosiło 2. Tak niskie wartości adsorpcji ołowiu z silnie kwaśnych roztworów mogą być wynikiem konkurencyjności jonów Pb^{2+} i H^+. W dalszych badaniach adsorpcję prowadzono z roztworów o pH = 6.



Rys. 2. Wpływ pH roztworu na adsorpcję Pb(II) na węglu aktywnym R0 (temp. 20°C)
Fig. 2. Effect of pH on the Pb(II) adsorption capacity on the activated carbon R0 (temp. 20°C)

Przeanalizowano również wpływ temperatury roztworu na wielkość adsorpcji jonów ołowiu (rysunek 3). Adsorpcję prowadzono dla roztworów o temperaturze 20, 30 i 40°C. Im wyższa temperatura roztworu tym adsorpcja Pb(II) była większa, chociaż uzyskane różnice nie są duże.



Rys. 3. Wpływ temperatury roztworu na adsorpcję Pb(II) na węglu aktywnym R0 (pH 6): a) 20°C, b) 30°C, c) 40°C
Fig. 3. Effect of temperature on the adsorption of Pb(II) on the activated carbon R0 (pH 6): a) 20°C, b) 30°C, c) 40°C

3.2. Wpływ modyfikacji węgla aktywnego na adsorpcję ołowiu(II)

Węgiel R0 modyfikowano w piecu obrotowym lub na stanowisku SEOW. Izotermy adsorpcji Pb(II) przedstawiono na rysunku 4. Zmodyfikowane węgle aktywne w większości przypadków lepiej adsorbują jony ołowiu niż wyjściowy R0. Wyraźnie większą pojemnością charakteryzują się węgle modyfikowane na SEOW. Ołów był adsorbowany najskuteczniej na węglu R/400E/80AIRgdś. Był to węgiel modyfikowany na stanowisku SEOW w najprostszym układzie: gaz modyfikujący – powietrze, jeden cykl nagrzewanie-chłodzenie, niewielki przepływ powietrza tylko w fazie chłodzenia – 40 dm^3/h. Uzyskana maksymalna pojemność adsorpcyjna przekracza 90 mmol/kg podczas gdy dla wyjściowego R0 wynosi 51 mmol/kg. Pozostałe węgle modyfikowane na SEOW również charakteryzowały się znacznie większą pojemnością adsorpcyjną niż węgiel wyjściowy. W przypadku węgli aktywnych modyfikowanych w piecu obrotowym większą adsorpcję jonów ołowiu otrzymano tylko dla węgli R/400/H2O, R/800/CO2, R/800/H2O.

Biorąc pod uwagę pojemność adsorpcyjną badanych węgli zostały uszeregowane w następujący sposób:

R/400E/40AIRgśd > R/400E+80/80CO2dś ≈ R/400E/80CO2dś > R/800/CO2 > R/400E+40/40AIRgś ≈ R/400E/40CO2dś > R/400E+40/40CO2dś > R/400/H2O > R/800/H2O > R0 > R/400/AIR > R/400/CO2

Mechanizmy wiązania jonów Pb(II) na powierzchni węgli aktywnych wiązane są z obecnością ugrupowań tlenowych. Według Rao i in. (2008) wiązanie Pb(II) na polarnych funkcyjnych grupach (C=O, S=O, –OH) na powierzchni węgli aktywnych odbywa się zgodnie z dwoma mechanizmami [21]:

$$Pb^{2+} + 2P^{-} \Leftrightarrow PbP_2 \tag{9}$$

lub

$$Pb^{2+} + 2HP^{-} \Leftrightarrow PbP_2 + 2H^{+} \tag{10}$$

gdzie:

P^{-} i HP^{-} to polarne grupy funkcyjne na powierzchni węgla [21].

Świątkowski i in. przebadali adsorpcję ołowiu na zasadowych oraz kwasowych węglach aktywnych i zaproponowali następujący schemat adsorpcji [25]:

- na amfoterycznych i zasadowych węglach aktywnych:

$\geqslant C: + Pb^{2+} \rightarrow \geqslant C : Pb^{2+}$ (Cπ-kation interakcje) (11)

- dodatkowo na zasadowych węglach aktywnych:

$> C{-}OH + Pb^{2+} + 3H_2O \rightarrow\, > COPbOH + 2H_3O^+$ (12)

$> C{-}O^{-*} + Pb^{2+} + 2H_2O \rightarrow\, > C{-}O{-}PbOH + H_3O^+$ (13)

$> N: + Pb^{2+} + 2H_2O \rightarrow\, > N{-}Pb(H)^+ + H_3O^+$ (14)

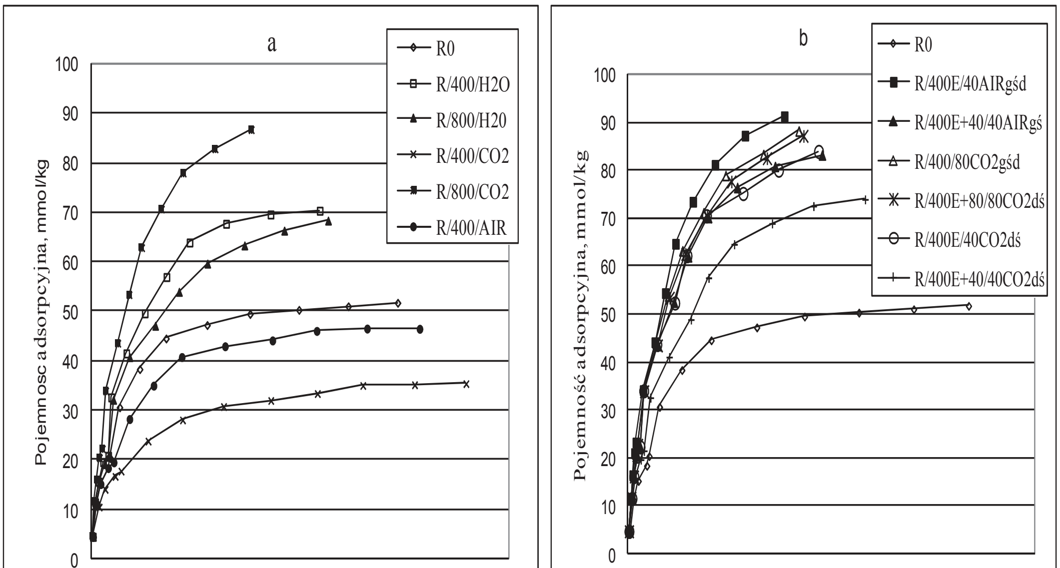
- na utlenionym „kwaśnym” węglu aktywnym:

$> C{-}COOH + Pb^{2+} + H_2O \rightarrow\, > C{-}O{-}COOPb^+ + H_3O^+$ (15)

$(> C{-}COOH)_2 + Pb^{2+} + 2H_2O \rightarrow (> C{-}COO)_2Pb + 2H_3O^+$ (16)

$> C{-}OH + Pb^{2+} + H_2O \rightarrow\, > C{-}OPb^+ + H_3O^+$ (17)

Obok wymiany jonowej i kompleksowania ołów może być usuwany na węglach w wyniku depozycji tlenków i wodorotlenków.



Rys. 4. Izotermy adsorpcji Pb(II) na modyfikowanych węglach z grupy R0 Węgle modyfikowane w piecu obrotowym, b) węgle modyfikowane na SEOW
Fig. 4. Adsorption isotherms for Pb(II) on modified activated groups of R0, carbons modified in rotary furnace, b) carbons modified in SEOW

W związku z przedstawionymi mechanizmami adsorpcji jonów ołowiu przebadano liczba grup funkcyjnych metodą Bohema (tabela 2). Można zauważyć, że różnorodność mechanizmów odpowiedzialnych za adsorpcję ołowiu nie pozwala na jednoznaczne określenie grup funkcyjnych, które mają determinujący wpływ na skuteczność adsorpcji jonów ołowiu. Węgiel aktywny adsorbujący najwięcej jonów ołowiu charakteryzuje się dużą (ale nie największą) liczbą grup kwasowych, a jedną z niższych grup zasadowych. Uszeregowanie węgli aktywnych ze względu na ilość grup zasadowych lub kwasowych nie pokrywa się z uszeregowaniem ze względu na pojemności adsorpcyjne w odniesieniu do jonów ołowiu. Przedstawione różnorodne mechanizmy adsorpcji ołowiu powodują brak możliwości oceny węgli aktywnych tylko na podstawie np. liczba grup funkcyjnych.

Tabela 2. Liczba grup funkcyjnych na wyjściowym i utlenionych węglach aktywnych oznaczanych metodą Bohema

Table 2. The number of surface functional groups in initial R0 and modified activated carbon determined by means of the Boehm method

Węgiel	Grupy funkcyjne, mmol/g					
	pK	pK	pK	pK	ΣB	ΣA
	<6,37	6,37–10,75	10,75–15,74	15,74–20,58	zasadowe	kwasowe
R0	0,063	0,12	0,409	0,021	0,434	0,592
R/400E/40AIRgśd	0,190	0,084	0,341	0,068	0,356	0,615
R/400E+/40AIRgś	0,156	0,098	0,330	0,000	0,366	0,584
R/400E/80CO2gśd	0,135	0,146	0,288	0,029	0,332	0,569
R/400E+80/80CO2dś	0,097	0,130	0,287	0,008	0,480	0,514
R/400/40CO2dś	0,168	0,028	0,358	0,000	0,330	0,554
R/400E+40/40CO2dś	0,134	0,146	0,307	0,006	0,407	0,586
R/400/CO2	0,128	0,030	0,369	0,081	0,394	0,527
R/400/AIR	0,238	0,114	0,393	0,000	0,563	0,745
R/400/H2O	0,213	0,075	0,392	0,000	0,351	0,680
R/800/CO2	0,056	0,000	0,150	0,108	0,442	0,206
R/800/H2O	0,000	0,042	0,228	0,006	0,448	0,270

Modyfikacja węgli aktywnych na stanowisku SEOW jest nie tylko bardziej skuteczna, ale również kilkakrotnie mniej energochłonna w porównaniu z wysokotemperaturową modyfikacją w piecu obrotowym [14]. Inną zaletą jest brak istotnej zmiany wielkości powierzchni właściwej w wyniku takiej modyfikacji, co jest korzystne ponieważ często oprócz jonów np. metale ciężkie w roztworach znajdują się również niezdysocjowane związki organiczne (tabela 3).

Tabela 3. Powierzchnia właściwa wyjściowego i modyfikowanego węgla aktywnego R0
Table 3. The surface area of initial R0 and modified activated carbon

Parametr	R0	R/400EI/40AIRdśg	R/400EI+40/40AIRdśg	R/400EI/40CO2dś	R/400EI+40/40CO2dś	R/400EI/80CO2dśg	R/400EI+80/80CO2dś
Powierzchnia właściwa S_{BET}, m^2/g	890	905	915	914	907	902	938

3.3. Izotermy adsorpcji

Otrzymane wyniki adsorpcji ołowiu na wyjściowym i utlenionych węglu aktywnych opisano równaniami izotermy Freundlicha i Langmuira. Stałe izoterm Frendlicha i Langmuira można uzyskać z prostoliniowych postaci równań. W przypadku izotermy Langmuira istnieje 5 różnych prostoliniowych postaci (4–8). Stałe otrzymane z tych zależności różnią się między sobą. Również współczynniki korelacji nie są jednakowe. Najlepsze dopasowanie wyników (najwyższy R^2) otrzymano dla prostoliniowej postaci I, II i V izotermy Langmuira. Najwyższe wartości współczynnika Q_m, a najniższe K_L otrzymano dla zależności II i IV tej izotermy. Porównano dopasowanie izotermy Freundlicha i Langmuira do uzyskanych wyników pomiarowych i stwierdzono, że izoterma Langmuira lepiej je opisuje, szczególnie gdy do wyznaczenia stałych wykorzystuje się prostoliniową formę I (zależność $1/Q$ od $1/C_e$), II (zależność C_e/Q od C_e) lub IV (zależność Q/C_e od Q).

Tabela 4. Parametry równań izoterm Langmuira i Freundlicha dla modyfikowanych węgli aktywnych w piecu obrotowym
Table 4. Coefficients equations of Freundlich and Langmuir for the carbons modified in rotary furnace

Parametr	Węgiel aktywny					
	R	R/400/H2O	R/800/H2O	R/400/CO2	R/800/CO2	R/400/AIR
Izoterma Langmuira						
Forma I						
K_L, m^3/mmol	0,0438	0,0338	0,0352	0,0748	93,46	0,0519
Q_m, mmol/kg	53,76	76,92	69,44	30,86	0,0378	45,45
R	0,992	0,987	0,991	0,998	0,989	0,984
Forma II						
K_L, m^3/mmol	0,0400	0,0297	0,0266	0,0372	105,26	0,0380
Q_m, mmol/kg	56,5	82,64	79,37	38,02	0,03	51,28
R^2	0,998	0,993	0,995	0,998	0,994	0,998
Forma III						
K_L, m^3/mmol	0,0421	0,0341	0,0329	0,0577	0,0367	0,0464
Q_m, mmol/kg	55,46	77,99	73,12	34,27	96,28	48,1
R^2	0,922	0,885	0,905	0,901	0,905	0,930
Forma IV						
K_L, m^3/mmol	0,0388	0,0302	0,0298	0,0519	0,0332	0,0431
Q_m, mmol/kg	57,37	82,85	76,80	35,38	101,54	49,57
R^2	0,922	0,885	0,905	0,901	0,905	0,930
Forma V						
K_L, m^3/mmol	0,0427	0,0317	0,034	0,0732	0,0359	0,0521
Q_m, mmol/kg	54,69	80,96	71,18	31,13	97,31	45,18
R^2	0,992	0,987	0,991	0,988	0,989	0,995
Izoterma Freundlicha						
K_F, mmol/kg	4,99	4,72	4,50	4,54	5,37	4,85
1/n	0,46	0,56	0,55	0,38	0,60	0,44
R^2	0,917	0,946	0,925	0,948	0,965	0,880

Tabela 5. Parametry równań izoterm Langmuira i Freundlicha dla węgli modyfikowanych na stanowisku SEOW
Table 5. Coefficients equations of Freundlich and Langmuir for the carbons modified carbons modified in SEOW

Parametr	Węgiel aktywny					
	R/400E/40AIRgśd	R/400E+40/AIRgś	R/400E/80CO2gśd	R/400E+80/80CO2dś	R/400E/40CO2dś	R/400E+40/40CO2dś
Izoterma Langmuira						
Forma I						
K_L, m^3/mmol	0,0496	0,0454	0,0489	0,0524	0,0535	0,0471
Q_m, mmol/kg	90,91	81,30	85,4700	78,125	74,07	67,11
R^2	0,999	0,997	0,968	0,998	0,995	0,994
Forma II						
K_L, m^3/mmol	0,0361	0,0327	0,0349	0,0330	0,0317	0,0289
Q_m, mmol/kg	109,89	99,01	104,17	103,09	99,01	86,95
R^2	0,995	0,996	0,997	0,996	0,996	0,994
Forma III						
K_L, m^3/mmol	0,0420	0,0366	0,0400	0,0389	0,0383	0,0367
Q_m, mmol/kg	102,14	94,05	97,67	95,68	92,44	78,61
R^2	0,962	0,945	0,970	0,957	0,937	0,908
Forma IV						
K_L, m^3/mmol	0,0404	0,0346	0,0389	0,0372	0,0359	0,0333
Q_m, mmol/kg	104,28	97,05	99,23	97,90	95,64	82,47
R^2	0,962	0,945	0,970	0,957	0,937	0,908
Forma V						
K_L, m^3/mmol	0,0486	0,0459	0,0486	0,0507	0,0525	0,0463
Q_m, mmol/kg	92,52	80,37	85,96	80,44	75,02	67,91
R^2	0,999	0,998	0,997	0,998	0,995	0,994

Tabela 5. cd.
Table 5. cont.

Parametr	Węgiel aktywny					
	R/400E/40AIRgśd	R/400E+40/AIRgś	R/400E/80CO2gśd	R/400E+80/80CO2dś	R/400E/40CO2dś	R/400E+40/40CO2dś
Izoterma Freundlicha						
K_F, mmol/kg	6,24	5,49	5,97	5,73	5,59	4,95
1/n	0,60	0,59	0,59	0,60	0,58	0,56
R^2	0,970	0,963	0,968	0,972	0,964	0,968

4. Podsumowanie

Uzyskane wyniki badań potwierdziły istotny wpływ warunków prowadzenia procesu (temperatury i pH roztworu) na adsorpcję jonów ołowiu na węglu aktywnym ROW 08 Supra. W przypadku adsorpcji z roztworów o pH 2, 4 i 6 najwyższe pojemności uzyskano dla pH 6 (ponad 50 mmol/kg), a bardzo niskie gdy pH wynosiło 2 (około 10 mmol/kg). Przebadano adsorpcję z roztworu o temperaturze 20, 30 i 40°C i stwierdzono, że im wyższa temperatura tym większa skuteczność adsorpcji.

Przedstawiona w pracy modyfikacja węgli aktywnych może mieć wpływ na adsorpcję Pb (II). Obie metody modyfikacji węgla podane w pracy (sposób konwencjonalny w piecu obrotowym i przy użyciu elektrycznego ogrzewania węgla na stanowisku SEOW) mają pozytywny wpływ na wielkość adsorpcji Pb (II). Spośród wielu sposobów modyfikacji najkorzystniejsza ze względu na adsorpcję jonów Pb(II) jest modyfikacja podczas elektrycznego ogrzewania węgla do 400^{o}C i chłodzeniu powietrzem w ilości 40 dm^3/h (R/400E/40AIRgśd). Wszystkie otrzymane sorbenty w wyniku modyfikacji na stanowisku SEOW charakteryzowały się zwiększoną adsorpcją Pb(II). W przypadku modyfikacji w piecu obrotowym wyższe pojemności adsorpcyjne uzyskano tylko dla niektórych węgli aktywnych (modyfikowanych w 800^{o}C).

Praca została przygotowana w ramach Badań statutowych
BS_PB- 401-301-12.

Literatura

1. **Abdel-Nasser A., El-Hendawy A.A.:** *The role of surface chemistry and solution pH on the removal of Pb2+ and Cd2+ ions via effective adsorbents from low-cost biomass*. J. Hazard. Mater., 167, 260–267 (2009).
2. **Ahn C.K., Park D., Woo S.H., Park J.M.:** *Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactans*. J. Hazard. Mater., 164, 1130–1136 (2009).
3. **Ahmedna M., Marshall W.E., Husseiny A.A., Rao R.M., Goktepe I.:** *The use of nutshell carbons in drinking water filters for removal of trace metals,* Water Res., 38, 1062–1068 (2006).
4. **Aroua M.K., Yin C.Y., Lim F.N., Kan W.L., Daud W.M.A.W.:** *Effect of impregnation of activated carbon whit chelating polymer on adsorption kinetics of* Pb^{2+}. J. Hazard. Mater., 166, 1526–1529 (2009).
5. **Ayyappan R., Carmalin A.S., Swaminathan K., Sandhya S.:** *Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes.* Process. Biochem., 40, 1293–1299 (2005).
6. **Boehm H.P.:** *Some aspects of the surface chemistry of carbon blacks and other carbons.* Carbon, 32, 759–769 (1994).
7. **Dąbek L., Ozimina E., Picheta-Oleś A.:** *Assessing the influence of the presence of heavy metals adsorbed on activated carbon on the efficiency of degradation of phenol using selected oxidizing agents.* Soc. Ecological and Chemistry Engineering S; 19(2):249–257 (2012).
8. **Dąbek L., Kulig E.:** *Sorpcja jonów ołowiu(II) na węglu aktywnym w obecności kwasów humusowych.* Inż. Ochr. Środ., 3, 409–414 (2000).
9. **Gercel Ö., Gercel H.F.:** *Adsorption of lead(II) ions from aqueous solutions by activated carbon prepared from biomass plant material of Euphorbia rigida.* Chem. Eng. J., 132, 289–297 (2007).
10. **Giraldo-Gutierrez L., Moreno-Pirajan J.C.:** *Pb(II) and Cr(VI) adsorption from aqueous solution on activated carbons obtained from sugar cane husk and sawdust*. J. Anal. Appl. Pyrolysis, 81, 278–284 (2008).
11. **Goel J., Kadirvelu K., Rajagopal C., Garg V.K.:** *Removal of lead(II) by adsorption using treated granual activated carbon: batch and column studies.* J. Hazard. Mater., 125, 211–220 (2005).

12. **Hamdaoui O., Naffrechoux E.:** *Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon.* J. Hazard. Mater., 147, 381–394 (2007).
13. **Khezami L., Capart R.:** *Removal of chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies.* J. Hazard. Mater., B123, 223–231 (2005).
14. **Lach J.:** *Wpływ sposobu modyfikacji węgli aktywnych na adsorpcję metali ciężkich*. Seria Monografie 197, Wyd. P. Cz., Częstochowa 2011.
15. **Lach J., Ociepa E., Stępniak L.:** Sorpcja *metali ciężkich na utlenionych węglach.* Inż. Ochr. Środ., 9/2, 161–171 (2006).
16. **Lach J., Okoniewska E., Stępniak L., Ociepa E.:** *Wpływ pola ultradźwiękowego na adsorpcję kationów kadmu.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15(3), 2142–2157 (2013).
17. **Malik D.J., Strelko V., Streat M., Puziy A.M.:** *Characterisation of novel modified active carbons and marine algal biomass for the selective adsorption of lead.* Water Res., 36, 1527–1538, (2002).
18. **Nadeem M., Shabbir M., Abdullah M.A., Shah S.S., McKay G.:** *Sorption of cadmium from aqueous solution by surfactant-modified carbon adsorbents.* Chem. Engineering J., 148, 365–370 (2009).
19. **Ociepa-Kubicka A., Ociepa E.:** *Toksyczne oddziaływanie metali ciężkich na rośliny, zwierzęta i ludzi.* Inż. Ochr. Środ. 15(2) (2012).
20. **Okoniewska E., Lach J., Stępniak L., Ociepa E.:** *Modyfikacja węgli aktywnych z wykorzystaniem pola ultradźwiękowego.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15(1), 2563–2572 (2013).
21. **Rao M., Rao G.P., Seshaiah K., Chudary N.V., Wang M.C.:** *Activated carbon from Ceiba pentandra hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions.* Waste Manage., 28, 849–858 (2008).
22. **Sekar M., Sakthi V., Rengaraj S.:** *Kinetics and equillibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell.* J. Coll. Interf. Sci., 279(2), 307–313 (2004).
23. **Singh C.K., Sahu J.N., Mahalik K.K., Mohanty C.R., Mohan B.R., Meikap B.C.:** *Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid.* J. Hazard. Mater., 153, 221–228 (2008).
24. **Świątkowski A., Pakuła M., Biniak S., Walczyk M.:** *Influence of the surface chemistry of modified activated carbon on its electrochemical behaviour in the presence of lead(II) ion.* Carbon, 9, 42, 3057–3069 (2004).

25. **Walczyk M., Świątkowski A., Pakuła M., Biniak S.:** *Electrochemical studies of the interaction between a modified activated carbon surface and heavy metal ions.* J. Appl. Electrochem., 35, 123–130 (2005).
26. **Wilson K., Yang H., Seo C.W., Marshall W.E.:** *Select metal adsorption by activated carbon made from peanut shells.* Bioresource Technol., 97, 2266–2270 (2006).
27. **Zhang K., Cheung W.H., Valis M.:** *Roles of physical and chemical properties of activated carbon in the adsorption of lead ions.* Chemosphere, 60, 1129–1140 (2005).

Adsorption of Lead on ROW 08 Supra Modified Activated Carbon

Abstract

The presented work is aimed at comparing two types of gaseous modification: conventional with the use of external source of energy (heat) and originally developed method with Joule heat generated during the flow of electrical current through a carbon bed. Conventional modification of ROW 08 Supra activated carbon was conducted in a rotary furnace in the atmosphere of (1) steam and carbon dioxide at temperature of 400 and 800°C and (2) air at the temperature of 400°C. The modification of activated carbon in the electric heating experimental system (referred to as SEOW) occurred in the process of heating of activated carbon during the flow of electric current through the carbon bed up to 400°C, followed by cooling down with the air or carbon dioxide. Both methods for modification of activated carbons allowed for increasing adsorption capacity towards ions Pb(II). The advantage of heating the activated carbon with the electric heating experimental system (SEOW) required far less energy than in case of conventional method (up to many fold).

In case of modified carbon ROW 08 Supra, the increased adsorption efficiency was obtained for coals modified at 800°C and the carbon modified at 400°C with the participation of water vapor. As a result of modification of the SEOW carbons for all analyzed activated carbons, the adsorption percentage increased. Among all the modified activated carbon, the highest adsorption capacity has been given to carbon modified to SEOW through heating it to 400°C and air cooling as well.

The results are described by the means of Freundlich and Langmuir isotherm. In order to determine the coefficients of Langmuir isotherm, five different rectilinear forms were used. Among the analyzed issues the best fit to the experimental results obtained for the I Langmuir isotherms (the highest values of the coefficients R^2).

The impact of pH and temperature on the effectiveness within the adsorption solution of Pb (II) was also analyzed. The most effective adsorption of lead from solutions of pH 2, 4, and 6 occurred at the highest pH, but the differences between the adsorption solution at pH 6 and pH 8 has been low. Within the adsorption from solutions having a pH of 2 a very little adsorption of lead was observed. Furthermore the size of adsorption of solutions at 20, 30 and 40°C was analyzed as well. What has been found is that through increasing the temperature the efficiency of the adsorption process within Pb (II) is raised.

Słowa kluczowe:
adsorpcja, ołów, izoterma Langmuira

Keywords:
adsorption, lead, Langmuir isotherm

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Instrumenty zarządzania w ochronie środowiskowej

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> *Problem z Ziemią polega*
> *na tym, że jakiś czas temu*
> *przestano ją produkować*
> Mark Twain

1. Wstęp

Odkrycie oraz poznanie właściwości promieniotwórczości w latach trzydziestych XX w. umożliwiło wykorzystanie jej między innymi w medycynie. Funkcjonowanie w ochronie zdrowia podmiotów medycyny nuklearnej powoduje „*korzystanie ze środowiska*", które oprócz obowiązków prawnych, związane jest z koniecznością ponoszenia określonych kosztów ochrony środowiska. Warunkiem członkostwa w Unii Europejskiej – UE było dostosowanie polskiego systemu prawnego do obowiązującego prawa unijnego we wszystkich dziedzinach – *acquis communataire*, będących fundamentem zrównoważonego rozwoju, opierającym się na:

- działaniach zapobiegawczych,
- likwidacji powstałych szkód w środowisku, zwłaszcza u źródeł ich powstawania oraz
- zasadzie pokrywania kosztów szkód przez sprawcę.

Akcesja do UE wzmogła zainteresowanie się problematyką szeroko rozumianego bezpieczeństwa [21] podmiotów medycyny nuklearnej oraz wpływu na środowisko. Umiejętność skutecznego procesu prognozowania, projektów świadczonych usług zdrowotnych, daje kadrze medycznej możliwość dokonywania racjonalnych wyborów procesów diagnostyczno-terapeutycznych. Natomiast, podstawą procesu ochrony radiologicznej w diagnostyce aparaturowe i środowiska naturalnego w świadczeniu usług zdrowotnych, jest postępowanie zgodne z aktualną wiedzą oraz budową kompleksowych systemów bezpieczeństwa poprzez:

- uzasadnienie narażenia – prognozowana korzyść zdrowotna powinna być większa niż ewentualne skutki uboczne,
- optymalizację procesu wykorzystania właściwości izotopów promieniotwórczych oraz
- limitowanie dawek indywidualnych.

Szpital jako miejsce diagnostyki oraz leczenia, jest również miejscem powstawania różnych zagrożeń.

Celem artykułu jest identyfikacja źródeł zagrożeń i czynników determinujących bezpieczeństwo stanowisk pracy w podmiotach medycyny nuklearnej. Od sposobu w jaki zostanie przeprowadzona ocena, zależy skuteczność funkcjonującego w szpitalach publicznych (podmiotach medycyny nuklearnej) systemu zarządzania ochroną środowiska, a w szczególności ochrona życia i zdrowia pracowników – *life and health of wolkers*.

Badaniom poddano próbę 8 975 (7,33% ogółu lekarzy), z 104 (20,43% ogółu szpitali publicznych) wybranych z bazy adresowej REGON[1], funkcjonujących w trzech, losowo wybranych województwach warmińsko-mazurskim, pomorskim oraz wielkopolskim (18,75% ogółu województw), oznaczonych w dalszych rozważaniach, analogicznie, jako *A*, *B*, oraz C, w okresie od stycznia 2007r. do grudnia 2011r. (w przyjętych cyklach rocznych), za pomocą autorskiego kwestionariusza. Na 250 ankiet wysłanych, otrzymano zwrotnie 203 poprawnie wypełnionych ankiet. Biorąc pod uwagę relatywnie wysoką zwrotność na poziomie 81,20% oraz to, że struktura zarówno zbiorowości respondentów, jak i podmiotów publicznych jest zbliżona, można stwierdzić, iż uzyskane

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[1] 509 szpitali publicznych bez MON oraz MSW: Stan na dzień 31.12.2007r.

wyniki badania ankietowego są reprezentatywne dla całej populacji szpitali publicznych w Polsce, przynajmniej w zakresie ujawnionym w rejestrze REGON. Populacja badanych jest zgodnie z założeniami procedury badawczej – podobna, aczkolwiek odnotowano tylko niewielkie różnice w liczebności szpitali publicznych, będących wynikiem przemian w ochronie zdrowia.

2. Identyfikacja ryzyka w procesie świadczenia usług z zakresu medycyny nuklearnej

Identyfikacja zagrożeń – *identification of risks* może odbywać się na podstawie istotnych informacji zgromadzonych w procesie wywiadu środowiskowego. O ryzyku w procesie diagnostyczno-terapeutycznym mówimy wówczas, kiedy jednoznacznie można określić istniejące zagrożenia oraz oszacować prawdopodobieństwo wystąpienia. W przeciwnym wypadku – kiedy jeden lub oba z ww. elementów są nieznane – mamy do czynienia z niepewnością [14]. Pojęcie ryzyka jest wykorzystywane w analizie sytuacji decyzyjnych, których przyszły rezultat nie jest znany, lecz istnieją przesłanki do przewidywania możliwych i prawdopodobnych stanów rzeczy [19]. Takie podejście wydaje się mieć również zastosowanie do analizy sytuacji decyzyjnych w procesie świadczenia usług z zakresu diagnostyki radiologicznej. Wykorzystując dostępne dane, doświadczenie oraz wiedzę uczestników zespołu diagnostyczno-terapeutycznego, można przewidywać pewne stany rzeczy i korzystając z tej wiedzy kształtować rzeczywistość w sposób pozwalający na redukcję ryzyka w różnych jego aspektach. Aby jednak ograniczać ryzyko [13], należy je najpierw zdefiniować – ustalić czym jest, jakie są jego źródła zarówno dla samego prosumenta jak i środowiska naturalnego, w których elementach systemu może się pojawić i zakłócić jego funkcjonowanie. Ocena ryzyka w procesie świadczenia usług z zakresu medycyny nuklearnej przebiega w następujących etapach:

- identyfikacja zagrożenia,
- korzyść zdrowotna-skutki uboczne,
- ocena narażenia oraz
- charakterystyka występującego ryzyka.

Pierwszym etapem w ocenie ryzyka jest identyfikacja zagrożeń, która pozwoli określić kategorie ryzyka. Analizując te kwestię, należy brać pod uwagę istotę systemu szpitalnego, w tym przypadku pracowni medycyny nuklearnej, zadania jakie ma realizować oraz występujące w nim ograniczenia. Ryzyko procesu świadczenia usług diagnostyczno-terapeutycznych z punktu widzenia istotnych zagrożeń, należy rozpatrywane jako ryzyko:

- *ludzkie*, rozumiane jako utrata zdrowia – cierpienie fizyczne oraz psychiczne spowodowane przez istotne zdarzenia występujące w procesie świadczenia usług diagnostyczno-terapeutycznych,
- *środowiskowe*, rozumiane jako presja systemu oddziałów medycyny nuklearnej na środowisko naturalne – emisje związane np. z procesami unieszkodliwiania odpadów radioaktywnych lub niekontrowaną emisję odpadów do środowiska oraz
- *finansowe*, rozumiane jako zmiana kosztów funkcjonowania systemu, czyli koszty gromadzenia odpadów, transportu oraz unieszkodliwiania ponadto, koszty spraw odszkodowawczych.

Wiedza o ryzyku występującym w procesach świadczenia usług z zakresu medycyny nuklearnej, pozwala na odpowiednie kształtowanie systemu, tak aby poziom bezpieczeństwa osiągnął akceptowalny poziom. W niniejszych rozważaniach przyjęto, że wiedza w połączeniu ze statystykami dotyczącymi jakości funkcjonowania pracowni radiologicznych, jest kluczem do redukcji ryzyka decyzyjnego, we wszystkich jego aspektach – środowiskowym, ludzkim oraz ekonomicznym.

3. Zarządzanie ryzykiem medycznym w radiologii istotą audytu klinicznego świadczonych usług

Medyczna koncepcja ryzyka ukierunkowana jest na pierwotne i wtórne czynniki utrzymania ludzkiego życia. O czynniku wyzwalającym ryzyko można mówić wtedy, kiedy istnieje związek między przyczyną i skutkiem oraz kiedy ten związek przyczynowy jest dostatecznie silny. Usunięcie przyczyny może spowodować niewystąpienie choroby lub złagodzenie jej przebiegu. Ustawa [17] definiuje ryzyko radiacyjne jako prawdopodobieństwo wystąpienia określonego szkodliwego efektu zdrowotnego w wyniku narażenia na promieniowanie jonizujące. Implementacja istotnych elementów analizy ryzyka w audycie klinicznym [6] w ramach procedur radiologicznych przyczynić się może do wzrostu jakości świadczonych usług, bezpieczeństwa pacjentów oraz redukcji odpadów niebezpiecznych do środowiska.

Zarządzanie ryzkiem oraz zapewnianie istotnej jakości procesu świadczonych usług w pracowniach medycyny nuklearnej obejmuje ryzyko występujące na wszystkich etapach decyzyjnych, począwszy od momentu planowania, poprzez realizację poszczególnych subprocesów, aż do zakończenia wykonania usługi. Agencja Atomistyki [15] zdefiniowała następujące rodzaje skutków pojawiających się błędów w realizacji procedur radioterapeutycznych:

- *incydent*: niezamierzone wydarzenie inicjujące prekursory wypadków radiacyjnych i zagrożeń – źródło szkodliwych konsekwencji punktu widzenia ochrony środowiska lub bezpieczeństwa uczestników zdarzenia,
- *zagrożenie*: zdarzenie, które może nastąpić w wyniku sekwencji rzeczywistych zdarzeń, ale nie doszło do skutku ze względu na panujące w tym czasie warunki,
- *wypadek radiacyjny*: awarie urządzeń lub inne nieszczęśliwe wydarzenia, których następstwa są istotne z punktu widzenia ochrony środowiska lub bezpieczeństwa i skutków zdrowotnych dla pacjenta.

Jako uzupełnienie powyższej stratyfikacji należy również przytoczyć definicje medycznego wypadku radiologicznego [18] dla wszystkich rodzajów ekspozycji medycznej:

- *medycznym wypadkiem radiologicznym w radioterapii* jest w szczególności niezamierzona różnica między całkowitą przepisaną dawką promieniowania jonizującego a dawką rzeczywiście zaaplikowaną w trakcie całego cyklu radioterapii, zwiększająca ryzyko powikłań u pacjenta, z utratą życia włącznie, lub spadku wyleczalności.
- *wypadkiem w radioterapii* jest również napromienienie niewłaściwego pacjenta, a także błędna anatomicznie lokalizacja obszaru napromienienia oraz niewłaściwy rozkład dawki, w tym przy użyciu nieprawidłowego typu wiązki lub energii wiązki oraz niewłaściwego produktu radiofarmaceutycznego, a także niewłaściwe frakcjonowanie, jeżeli prowadzą one do nieosiągnięcia założonych efektów terapeutycznych lub odległych w czasie ciężkich następstw zdrowotnych.

Podstawową formą zabezpieczenia przed pojawianiem się niekontrolowanych zdarzeń radiacyjnych w procesie świadczenia usług radiologicznych, jest stworzenie oraz regularne aktualizowanie międzynarodowych wytycznych opartych na zasadach „*medycyny opartej na faktach*" – *evidence based medicine – EBM* wraz z wymaganiami dla sprzętu oraz kontroli dozymetrycznej. Standardy postępowania, wytyczne oraz procesy nadzoru i kontroli powinny być weryfikowane przez niezależne profesjonalne, multidyscyplinarne zespoły partycypujące w tych procedurach [10].

4. Instrumenty procesu redukcji ryzyka zagrożeń środowiskowych

System zarządzania środowiskowego zgodnego z normą ISO 14001:2005, to istotna część kompleksowego systemu zarządzania, obejmująca strukturę organizacyjno-funkcjonalną, odpowiedzialność, zasady postępowania, procedury, procesy wdrażania i utrzymywania polityki środowiskowej oraz zarządzania pracowniami radiologicznymi, obejmujące szeroko rozumianą ochronę środowiska z równoczesnym zachowaniem jakości i ekonomiki procesu świadczenia usług z zakresu medycyny nuklearnej. Idea zarządzania środowiskowego bardziej motywuje całość personelu niż komercyjne aspekty związane z systemami zapewnienia jakości [8]. Wymaga to jednak od kadry postawy dowodzącej, że dbałość o środowisko jest częścią strategii oraz oceną oddziaływań na obecny i przyszły stan środowiska naturalnego. Ponadto, bieżące analizy cyklu życia procesów (diagnostyczno-terapeutycznych) pozwalają na uzyskanie istotnych informacji na temat źródeł największych zagrożeń środowiskowych [1] oraz możliwości wdrożenia działań naprawczo-zapobiegawczych – redukcji ryzyka decyzyjnego w procesie świadczenia usług. Celem wdrożenia kompleksowego systemu ochrony środowiska opartego na normach ISO serii 14000, jest zapewnienie bezpiecznego stosowania źródeł promieniotwórczych przy jak najmniejszym i możliwym do zaakceptowania poziomie ryzyka dla pacjentów oraz środowiska naturalnego.

Natomiast implementacja zasad kultury ochrony radiologicznej to nie tylko poprawa bezpieczeństwa personelu szpitalnego, ale również poprawa poczucia bezpieczeństwa pacjentów: *Kultura ochrony radiologicznej to sposób, w jaki ochrona radiologiczna jest regulowana, zarządzana, wykonywana, kultywowana i postrzegana w miejscach pracy, medycynie i życiu codziennym i odzwierciedla nastawienie, wierzenia, zro-*

zumienie, cele i wartości wspólne, uznawane przez pracowników, lekarzy, inspektorów i ogół społeczeństwa, w odniesieniu do ochrony radiologicznej [9].

Do kultury ochrony radiologicznej odnoszą się także ogólne zasady kultury bezpieczeństwa, czyli zasady Deminga, według których: *właściwi ludzie, wykonują właściwe rzeczy we właściwym czasie z właściwym nastawieniem i po uzasadnionych kosztach*. Wizualizacją definicji kultury bezpieczeństwa jest: „*Sposób, w jaki postępujemy, kiedy nikt nie patrzy*". Natomiast Międzynarodowe Stowarzyszenie Ochrony Radiologicznej – *International Radiation Protection Associacion – IRPA* sformułowało istotne zadania kształtujące rozwój kultury ochrony radiologicznej poprzez:

- przejrzystość istotnych zasad ochrony radiologicznej,
- rozpowszechnianie wiedzy na temat ryzyka związanego z ochroną radiologiczną,
- rozbudzenie poczucia odpowiedzialności wśród kadry zarządzającej oraz medycznej za pacjenta oraz środowisko naturalne,
- zapewnienie jakości oraz skuteczności ochrony radiologicznej,
- wdrożenia działań na rzecz zwiększenia poczucia procesu bezpieczeństwa prosumentów jak również środowiska naturalnego.

W niniejszych rozważaniach przyjęto, że wiedza na temat ochrony środowiska naturalnego oraz ochrony radiologicznej – świadomość społeczna, ewoluuje w czasie, podobnie jak inne zjawiska kulturowe. Podsumowując, kultura ochrony radiologicznej to ogół wiedzy naukowej, technicznej, etycznej oraz zachowań zgodnych z regułami ograniczonego zaufania.

Integracja programów ochrony środowiska jako narzędzi proekologicznej polityki oddziałów medycyny nuklearnej pozwala na opracowywane metod redukcji ilości oraz szkodliwości odpadów, kosztów inwestycyjnych oraz eksploatacji systemu.

5. Ubezpieczenie ekologiczne jako istotny instrument finansowy ochrony środowiska naturalnego

Pogłębiająca się degradacja środowiska naturalnego, spowodowanego działalnością człowieka wywołuje zauważalne zmiany klimatyczne. Przeciwdziałanie procesowi destrukcji następuje poprzez stosowanie różnego rodzaju instrumentów prawno-finansowych m.in. ubezpieczeń ekologicznych, których istotnym celem jest ochrona środowiska naturalnego. W latach 80–90 ubiegłego wieku wprowadzono prawno-instytucjonalne rozwiązania określające formy oraz zakres odpowiedzialności cywilnej za straty oraz szkody środowiskowe zawarte m.in. w ustawie:

- japońskiej z 1988r. o kompensacji szkód zdrowotnych,
- amerykańskiej z 1988 wprowadzającej system ubezpieczeń obowiązkowych,
- niemieckiej ustawie z 1991 o odpowiedzialności cywilnej za oddziaływania środowiskowe (pełny zakres szkód środowiskowych będących wynikiem oddziaływań produkcyjnych) oraz regulacjach
- prawnych Hiszpanii i Holandii precyzujących szczegółowo odpowiedzialność cywilną w dziedzinie gospodarowania materiałami niebezpiecznymi oraz wszelkiego rodzaju odpadami [18].

Kwerenda literatury przedmiotu pozwoliła na przyjęcie określenia, że odpowiedzialność ekologiczna pracowni medycyny nuklearnej to również przeciwdziałanie tzw. ryzyku publicznemu – *public hazard* poprzez instrumenty ekonomiczne, które obligują do skutecznego wykorzystywania posiadanych zasobów poprzez uiszczanie dodatkowych opłat za:

- emisję zanieczyszczeń do środowiska – protokół z Kioto (kraje członkowskie UE od 2012r. uiszczają kary za przekroczenie dopuszczalnych limitów np. CO_2),
- dokonywanie istotnych zmian w środowisku naturalnym oraz
- przekraczanie wymagań ochrony środowiska oraz
- subwencje dla przedsięwzięć proekologicznych ponadto
- ekologiczne opłaty produktowe, jak również
- ubezpieczenia ekologiczne [22].

Ubezpieczenia ekologiczne są istotnym instrumentem ekonomiczno-finansowym, w przypadku zawierania kompleksowej umowy ubezpieczenia typu *all risks* jednoznacznie określających przedmiot ubezpieczenia. Natomiast w polskim systemie ubezpieczeń wyłącza się szkody powstałe wskutek [12] oddziaływania:

- energii jądrowej, promieni laserowych, promieniowania jonizującego, pola magnetycznego oraz elektromagnetycznego i skażenia radioaktywnego oraz

- powstałe wskutek powolnego działania czynnika termicznego, chemicznego, biologicznego i
- wskutek oddziaływania azbestu, formaldehydu lub dioksyn.

Przeprowadzone autorskie badania[2], analiza danych[3] oraz aktów prawnych pozwala na przyjęcie stwierdzenia, że w Polsce nie podejmuje się kompleksowego rozwiązania problemu ubezpieczeń ekologicznych, natomiast:

- proces zarządzania ryzykiem ekologicznym nie jest traktowany jako jeden z elementów kompleksowego zarządzania szpitalami publicznymi – pracowniami medycyny nuklearnej – 38,3%, a
- wykup polisy, to zdaniem kadry zarządzającej szpitalami publicznymi – pracowni medycyny nuklearnej zbędny wydatek – 63,7%.

W niniejszych rozważaniach przyjęto również, że wyodrębnienie ubezpieczeń ekologicznych (w formie jednolitego aktu prawnego) może stanowić podstawę nie tylko społecznej odpowiedzialności pracowni medycyny nuklearnej, ale również co jest istotne – prawnej. Ponadto, kadra całego szpitala publicznego powinna kształtować standardy oraz budować *goodwill* łańcucha proekologicznych wartości świadczonych usług radiologicznych, uzupełniając go o edukację etyczną oraz obywatelską [7] w zakresie ochrony środowiska naturalnego.

6. Rekomendacje i wnioski

Poprawa jakości, bezpieczeństwa procesu świadczonych usług z zakresu medycyny nuklearnej należy prowadzić w oparciu o monitorowanie oraz dokonywanie pomiaru funkcjonowania m.in.:

- wskaźników jakości,

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[2] Badania przeprowadzono na terenie województwa warmińsko-mazurskiego, pomorskiego oraz wielkopolskiego. Tematyka badań obejmowała społeczno-ekonomiczne czynniki funkcjonowania 104 (20,43%) ogółu szpitali publicznych. Uzyskano również istotne wypowiedzi w zakresie ochrony środowiska naturalnego od 8975 członków kadry medycznej (7,33% ogółu zatrudnionych lekarzy) w okresie od stycznia 2007 do grudnia 2011roku.

[3] Dane KNUiFE za 2007r.: na OC 500mln PLN – 12% rynku ubezpieczeń dla firm, przeliczając to na zawarte umowy – 400 tys. (9%), gdzie np. OC pojazdów 25% rynku w ujęciu wartościowym i około 28,6% w ujęciu zawartych umów.

- wyników audytów wewnętrznych i zewnętrznych – podstawa działań naprawczo-zapobiegawczych.

Podmioty medycyny nuklearnej w swojej polityce środowiskowej deklarują świadczenie usług radiologicznych, dążąc do zapewnienia wysokiej jakości, przy jednoczesnym ścisłym respektowaniu zasad ochrony środowiska. Powyższe działania są podejmowane poprzez:

- przestrzeganie obowiązujących wymagań prawnych w zakresie ochrony środowiska,
- wykorzystywanie wszelkich możliwości korzystnego oddziaływania na środowisko,
- zapobieganie zanieczyszczeniom,
- zarządzanie wytwarzanymi odpadami poprzez ograniczanie ich ilości, bezpieczne dla środowiska ich magazynowanie oraz unieszkodliwianie oraz
- zmniejszanie zużycia nośników energii i
- zachęcanie dostawców oraz podwykonawców do działań zgodnych z wymogami ochrony środowiska opartych na normach ISO serii 14000a,
- umiejętność przewidywania jest istotnym elementem sukcesu uczestników interdyscyplinarnego zespołu diagnostyczno-terapeutycznego oraz zapewnienia zrównoważonego w oparciu o normy ISO 26000:2010 [2] porządkujące obszar zrównoważonego rozwoju pracowni medycyny nuklearnej.

W ramach procedur radiologicznych realizowane są zadania z zakresu diagnostyki obrazowej i radiologii zabiegowej, szacowane są czynniki ryzyka związane ze skutkami użycia promieniowania jonizującego w stosunku do uzyskanych efektów diagnostyczno-terapeutycznych zarówno dla pacjenta jak i środowiska naturalnego. Ryzyko błędu w realizacji procedur radioterapeutycznych skutkuje efektami postradiacyjnymi, wpływającymi w istotny sposób na jakość życia i powodującymi zgon pacjenta jak również skażenie środowiska naturalnego. W wyniku analizy zdarzeń oraz czynników stworzono mapy ryzyka, na podstawie których WHO, opracowała profil ryzyka dla każdego etapu procedury radioterapeutycznej [16]:

- W pracowniach medycyny nuklearnej, bezpieczeństwo personelu stanowi priorytetową kwestię, niezbędna jest identyfikacja istotnych czynników zagrożeń występujących na danym stanowisku pracy oraz konieczność propagowania wiedzy na temat ryzyka związanego z wykonywanymi procedurami oraz implementacją istotnych działań korygująco-zapobiegawczych.
- Wdrożony system zarządzania środowiskowego zgodny z normą ISO 14001:2005 jest strategicznym narzędziem w procesie redukcji wpływu pracowni diagnostyczno-terapeutycznych na środowisko. Ze względu na istniejący stan środowiska oraz ograniczone zasoby naturalne, konieczne wydaje się dokonywanie ekologicznej analizy cyklu życia procesów świadczenia usług z zakresu medycyny nuklearnej, co umożliwi sterowanie działaniami środowiskowymi oraz kontrolowanie funkcjonowania oddziałów diagnostyki radiologicznej w obszarze ochrony środowiska.

W związku z powyższym, celowe wydaje się prowadzenie dalszych, interdyscyplinarnych badań pozwalających na szersze określenie skali zagrożeń związanych nie tylko z ochroną środowiska, ale również personelu w miejscu pracy poprzez powołanie zespołów interdyscyplinarnych, których zadaniem byłoby wypracowanie standardów oraz procedur przeciwdziałających występowaniu negatywnych czynników psychofizycznych na stanowiskach pracy w oddziałach medycyny nuklearnej.

7. Podsumowanie

Ochrona środowiska naturalnego w szpitalnych oddziałach diagnostyczno-terapeutycznych to całokształt działań prowadzących do zapobiegania narażaniu na promieniowanie jonizujące personelu oraz pacjentów m.in. poprzez:

- licencjonowanie oraz nadzór działalności medycznej związanej z narażeniem na promieniowanie jonizujące i
- ograniczaniu narażenia na to promieniowanie.

Wynika to m.in. z właściwości poszczególnych właściwości substancji promieniotwórczych, gdzie podczas procesu diagnostyczno-terapeutycznego dochodzi do uszkodzenia *DNA* obecnego w czynnikach chorobotwórczych. Reakcja organizmu pacjentów uwarunkowana jest przenikalnością promieniowania oraz cech osobniczych, takich jak np.: wiek, płeć, wrażliwość osobnicza, równowaga hormonalna i inne [11].

Postęp technologiczny w zakresie aparatury diagnostyczno-terapeutycznej sprawił, iż ryzyko skażenia środowiska jest skutecznie redukowane poprzez wdrażanie rekomendacji Międzynarodowej Komisji Ochrony Radiologicznej – *International Commmission of Radiological Protection – ICRP* oraz wytycznych *MAEA*. Istotnym czynnikiem zagrożenia jest również promieniowanie rozproszone, zwiększające ryzyko uszkadzania tkanek zdrowych osób przemywających w zasięgu działania np. powstawania zaćmy [4]. Metody oraz techniki ochrony radiologicznej stosowanej aparatury diagnostyczno-terapeutycznej różnią się w zależności od rodzaju oraz źródeł [20] promieniowania, oparte są m.in. na:

- wykorzystywaniu nowoczesnych rozwiązań konstrukcyjnych w dziedzinie radiologii,
- skutecznym korzystaniu ze środków indywidualnej ochrony osobistej,
- ustaleniu oraz przestrzeganiu indywidualnych dawek dla personelu,
- wymaganiach aktualnie obowiązujących przepisów oraz wyznaczaniu osoby odpowiedzialnej za audyt radiologiczny podmiotów.

Na podstawie analizy uzyskanych odpowiedzi stwierdzono również, że do podstawowych celów realizowanych przez badane oddziały medycyny nuklearnej należy również:

- ograniczenie zużycia zasobów naturalnych – właściwe, odpowiedzialne składniki – *responsible ingredients* w procesie świadczenia usług z zakresu diagnostyki obrazowej,
- zmniejszenie emisji zanieczyszczeń do powietrza, jako wynik modernizacji instalacji,
- ograniczenie ilości odpadów poprzez wprowadzenie np. cyfrowej obróbki obrazów.

Natomiast skuteczność realizowania celów oraz zadań środowiskowych jest relatywnie niska. Poddano analizie 65 zaplanowanych celów w okresie 2007–2010 – 70% zrealizowano, co świadczy o braku skutecznego zarządzania w zakresie ochrony środowiska oraz niezrozumieniu wymagań normy ISO 14001 (pomimo posiadania certyfikatu); 21% celów nie zostało zrealizowanych ze względu na brak środków finansowych, a 9% niezrealizowanych celów zostało określonych jako trudne do realizacji. Stwierdzono również, że cele bardzo często są mylone z zadaniami (co również świadczy o braku zrozumienia normy) oraz że oddziały diagnostyczno-terapeutyczne – szpitale publiczne, choć deklarują brak środków finansowych, nie wykazują jednocześnie potrzeby pozyskiwania środków na realizację celów oraz zadań z zewnętrznych źródeł finansowania np. poprzez uczestnictwo w *PPP* [3].

Wyniki badań wskazują, że najniższe efekty środowiskowe (mniejsze od planowanych) uzyskano w zakresie redukcji odpadów niebezpiecznych, oraz ilości odprowadzanych ścieków, najlepsze natomiast w obniżaniu emisji zanieczyszczeń do powietrza. Zmniejszenie zużycia energii, wody i ciepła w ciągu roku było większe od planowanego. W zależności od szpitala publicznego, opłaty środowiskowe zmniejszyły się o 4,6%, a opłaty eksploatacyjne zmalały o 6,8% natomiast 31% zadeklarowało, ze wdrożenie systemu zarządzania środowiskowego zwiększyło ich obciążenie finansowe do 18%, co jest spowodowane głównie kosztami realizacji zadań środowiskowych i opłatami za audyty nadzoru. Badanie ankietowe wykazało, że:

- 89% szpitali publicznych poza systemem zarządzania środowiskowego ma wdrożone również inne systemy (najczęściej zarządzania jakością według ISO 9001:2008),
- 14% nie przestrzega obowiązku zgłoszenia się w odpowiednim terminie do jednostki certyfikującej w celu przeprowadzenia audytu kontrolnego, potwierdzającego poprawne funkcjonowanie systemu i zgodność z wymaganiami (17,4 % podmiotów, które wdrożyły system przed 2003 r., nie ma przeprowadzonego audytu nadzoru),
- oddziały medycyny nuklearnej deklarują, że nieuzyskanie zamierzonych efektów środowiskowych związane jest przede wszystkim z brakiem środków finansowych, ale jednocześnie tylko 29,7 % z nich wystąpiło o środki finansowe do instytucji zewnętrznych (większość je otrzymała – były to głównie dotacje).

Podsumowując badania, stwierdzono, że systemy zarządzania środowiskowego wdrożone w szpitalach publicznych są mało efektywne oraz wymagają podjęcia działań korygujących. Bardzo niepokojący jest brak troski o utrzymanie certyfikatu (brak audytów nadzoru), jak również niska aktywność, jeżeli chodzi o pozyskiwanie środków finansowych. Przykład 29,7% szpitali, które zdecydowały się na poszukiwanie finansowania zewnętrznego wskazuje relatywnie wysoką skuteczność takich działań.

Analiza uzyskanych wyników wykazała, że jednym z istotnych problemów związanych z występowaniem czynników szkodliwych w pracowniach diagnostyczno-terapeutycznych – środowisku pracy jest nie tylko brak należytej uwagi, jaką szpitalna kadra zarządzająca zwraca na ocenę skażenia radiologicznego oraz zasady doboru indywidualnych środków ochrony radiologicznej, ale także niska świadomość personelu odnośnie zagrożeń występujących w miejscu pracy. Ma to szczególne znaczenie ze względu na fakt, iż coraz powszechniej pojawiają się zagrożenia nowe, poza biologicznymi, chemicznymi i fizycznymi.

Natomiast brak standardów radiologicznych spójnych ze standardami skażeń substancjami chemicznymi, prowadzi do istotnego spadku zaufania prosumentów.

Ponadto, przeprowadzone badania wskazują również, że zdanie to podziela większość przedstawicieli środowiska medycznego. Stwierdzają oni także, że stan dostosowania podmiotów ochrony zdrowia do wymagań dyrektyw UE wdrażanych do polskiego prawa jest na ogół relatywnie wysoki.

Literatura

1. **Adamczyk W.:** *Ekologia Wyrobów. Jakość. Cykl życia. Projektowanie.* PWE, Warszawa 2004.
2. **Bachorski-Rudnicki M., Kroik J.:** *ISO 26000.* Problemy Jakości. 7, 8 (2011).
3. **Bober B.:** *The Idea Public-Private Partnership as a Chance for the Infrastructure of the Private Hospital.* [w:] Integration in management. (red.) E. Skrzypek, Wyd. UMCS, Lublin 2012.
4. **Chodick G., Bekiroglu N.:** *Risk of cataract after exposure to low doses of Ionizing radiation: A 20-Year prospective cohort study among US radiologic technologists.* Am. J. Epidemiol. 68(6), 620–631 (2008).
5. KNUiFE
6. Dyrektywa Rady 97/43/Euratom z dnia 30.06.1997 w sprawie ochrony zdrowia osób fizycznych przed niebezpieczeństwem wynikającym z promieniowania jonizującego związanego z badaniami medycznymi uchylająca dyrektywę 84/466/Euratom. Dziennik Urzędowy L-180 z 09.07.97 określa audyt kliniczny w jednostkach stosujących promieniowanie jonizujące w celach medycznych (radioterapii, diagnostyce obrazowej, medycynie nuklearnej) jako systematyczną kontrolę lub przegląd medycznych procedur radiologicznych.

7. **Filek J.:** *Przyczyny małego zainteresowania ideą CSR w Polsce.* [w:] Społeczna odpowiedzialność biznesu w małych i średnich przedsiębiorstwach, (red.) Bąk M., Kulawczuk P., IBnDiPP, EQUAL. Warszawa 2008.
8. **Gierzyńska-Dolna M., Konodyba-Szymański B.:** *Wybrane problemy ochrony środowiska w powiększonej UE*. [w] II Ogólnopolska Konferencja Quality-2004, Doświadczenia i efekty funkcjonowania systemów zarządzania jakością w przedsiębiorstwach. Częstochowa 2004.
9. **Golnik N., Tulik P.:** *IRPA initiative on radiation protection culture*. Pol. J. Med. Phys. Eng. 7(1), 1–12 (2011).
10. **Kaczmarek T.T.:** *Ryzyko i zarządzanie ryzykiem – Ujęcie interdyscyplinarne*. Difin. Warszawa 2008.
11. **Martin C.J., Sutton D.G.:** *The radiobiology/radiation protection interface in healthcare*. J. Radiol. Prot. 29(2A), A1–A20 (2009).
12. Ogólne warunki ubezpieczenia odpowiedzialności cywilnej dla klienta korporacyjnego, uchwała Nr UZ/385 z dnia 21 lipca 2005r. Zarządu Powszechnego Zakładu Ubezpieczeń S.A., ze zmianami ustalonymi Uchwała Nr UZ/464/2005 z dnia 21 września 2005r. Zarządu Powszechnego Zakładu Ubezpieczeń S.A.
13. **Olkiewicz M.:** *Ograniczanie ryzyka i niepewności w działalności MSP – wyniki z badań.* [w] Natura i uwarunkowania ryzyka (red) I. Staniec. Wyd. Politechnika Łódzka. Łódź 2014.
14. **Połoński M., Pruszyński K.:** *Interdyscyplinarny charakter nauki o ryzyku.* Materiały konferencyjne Zarządzanie ryzykiem w przedsiębiorstwie. Ciechocinek 2006.
15. Prawo atomowe z dn. 24.02.2006 r. (Dz. U. 2006 r., nr 52)
16. *Radiotherapy risk profile.* Technical Manual. WHO 2008.
17. Rozporządzenie Ministra Zdrowia z dn. 18.02.2011r. w sprawie warunków bezpiecznego stosowania promieniowania jonizującego dla wszystkich rodzajów ekspozycji medycznej (Dz. U. z dn. 9.03.2011 r. nr 51, poz. 265).
18. **Rutkowska M.:** *Ecological Insurance in Poland as instrument of environmental Policy*. [w:] Hradecke` Ekonomicke Dny 2006, Podnikani a rozwoj regionu. Univerzita Hradec Kralove-Gaudeamus, Hradec Kralove 2006.
19. **Sienkiewicz P.:** *Analiza ryzyka w zarządzaniu projektami systemów.* Zeszyty Wojskowego Instytutu Technicznego Uzbrojenia. 95, 9–18 (2005).
20. **Singer G.:** *Occupational radiation exposure to the surgeon*. Am. J. Acad. Orthop. Surg. 13(1), 69–76 (2005).
21. **Szopa T.:** *Niezawodność i bezpieczeństwo*. Oficyna Wydawnicza Politechniki Warszawskiej. Warszawa 2009.
22. **Tucker M.:** *Climate change and the insurance industry: the cost of increased risk and the impetus for action*. Ecological Economics. 22, 85–96 (1997).
23. Ustawa Prawo atomowe z dn. 12.03.2004 r. (Dz. U. 2004 r., nr 70, poz. 632).

Management Instruments in Environmental Protection

Abstract

The article presents the instruments for the assessment of environmental protection – the risk of nuclear medicine in the entities. Streamlining of processes in health care entities is the determinant of the concept of process management. It is based on the implementation of significant changes in the course of diagnostic and therapeutic processes, which result in their efficiency is raised (a measure of the cost and time), flexibility (the ability to process an adequate response of the body of the patient). Analyses show that the implementation of a comprehensive process approach to risk management and environmental protection can bring many tangible benefits to operators of nuclear medicine. Where the process of elimination of risk is not possible, they should be restricted, and the risk of residual control. Development of systems for environmental protection and risk assessment is never ending – is doomed to evolution. Factor causing this situation is the fact that they reflect the diagnostic and therapeutic subprocesses managing the process of providing medical services, they are also an expression of the attitude of the medical community conditioned the current state of knowledge.

Słowa kluczowe:
ryzyko, zarządzanie, medycyna nuklearna, ochrona środowiska

Keywords:
risk, management, nuclear medicine, environmental protection

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Analiza efektywności kosztowej różnych wariantów technologicznych przydomowych oczyszczalni ścieków

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1. Wstęp

Według danych Głównego Urzędu Statystycznego w 2013 roku z sieci wodociągowej korzystało 76,6% ludności wsi, a z sieci kanalizacyjnej zaledwie 30,9% [5]. Niski stopień skanalizowania terenów niezurbanizowanych, przy jednocześnie wysokim stopniu zwodociągowania, stwarza istotne zagrożenie dla środowiska, a także pogarsza warunki życiowe ludności [22]. Stwarza również bariery w rozwoju tych terenów [13].

Przyjmuje się, że budowa sieci kanalizacyjnej jest uzasadniona finansowo i technicznie, gdy na 1 km jej długości przypada nie mniej niż 120 osób, a w szczególnych okolicznościach nie mniej niż 90 [17]. W pozostałych przypadkach należy stosować kanalizację bezodpływową lub oczyszczać ścieki w miejscu ich powstania za pomocą przydomowych oczyszczalni ścieków. Sposób odprowadzania i oczyszczania ścieków zależy od struktury zabudowy i może być różny w poszczególnych częściach miejscowości bądź gminy [1].

Według wielu autorów [6, 8, 11], średnioroczne koszty ponoszone przez użytkowników przydomowych oczyszczalni ścieków są niższe w porównaniu z kosztami gromadzenia nieczystości ciekłych w szczelnych zbiornikach bezodpływowych i ich okresowego wywożenia do zbiorczych oczyszczalni ścieków. W większości opracowań brakuje jednak informacji na temat struktury nakładów inwestycyjnych ponoszonych na budowę poszczególnych rodzajów przydomowych oczyszczalni ścieków, a także rodzaju kosztów eksploatacji ujętych w kalkulacji. Pomijane są także warunki gruntowo-wodne, znacznie wpływające na wielkość nakładów inwestycyjnych. W efekcie potencjalni użytkownicy, kierujący się przy doborze oczyszczalni zwykle kryterium ekonomicznym, nie znają wielkości całkowitych kosztów ani warunków, jakie muszą być spełnione w celu uzyskania wymaganej efektywności technologicznej [19].

Celem artykułu jest ocena efektywności kosztowej różnych rozwiązań technologicznych przydomowej oczyszczalni ścieków zaprojektowanej dla czteroosobowego gospodarstwa domowego, położonego na gruncie o dobrej przepuszczalności i wodach gruntowych na najmniejszej głębokości 3,5 m p.p.t. Analizie poddano koszty budowy i eksploatacji siedmiu następujących wariantów technologicznych przydomowej oczyszczalni ścieków: drenażowej, z tunelami rozsączającymi, z pakietami rozsączającymi, hydrofitowej, z komorą osadu czynnego, ze złożem biologicznym oraz oczyszczalni hybrydowej. Uwzględniono wszystkie możliwe sposoby odprowadzania ścieków oczyszczonych, czyli drenaż rozsączający, tunele rozsączające i pakiety rozsączające, studnię chłonną i oczko wodne. Obliczone koszty zestawiono także z kosztami budowy i eksploatacji szczelnego zbiornika bezodpływowego.

Za wskaźnik będący miarą całkowitego kosztu ponoszonego przez użytkownika przyjęto średnioroczny koszt oczyszczania ścieków. Zależy on od wielkości nakładów inwestycyjnych i kosztów eksploatacji oczyszczalni, a także zakładanego okresu jej eksploatacji i stopy dyskontowej, uwzględnianych w wartości współczynnika odzysku kapitału. Zgodnie z założeniami analizy efektywności kosztowej, przeprowadzono ją przy założeniu jednakowego we wszystkich przypadkach efektu użytkowego, za który przyjęto ilość oczyszczonych ścieków. W analizie tej pomija się kryteria jakości ścieków oczyszczonych, a także pozostałe efekty inwestycji [12].

2. Materiały i metody

2.1. Charakterystyka gospodarstwa domowego

Gospodarstwo domowe, dla którego jest projektowana przydomowa oczyszczalnia ścieków, znajduje się na terenie gminy Augustów w województwie podlaskim. Działka o powierzchni 800 m^2 jest położona na obrzeżach miasta bez dostępu do sieci kanalizacyjnej, a ścieki są tymczasowo gromadzone w zbiorniku bezodpływowym i wywożone do zbiorczej oczyszczalni. Plan zagospodarowania przestrzennego dopuszcza na tym terenie budowę przydomowych oczyszczalni ścieków. Prace hydrogeologiczne wykazały, iż na działce występują grunty niespoiste (piaski średnioziarniste), charakteryzujące się dobrą przepuszczalnością, a maksymalny poziom wód gruntowych wynosi 3,5 m p.p.t.

Z posadowionego na działce podpiwniczonego budynku mieszkalnego kanalizacja wewnętrzna jest wyprowadzona na głębokości 0,8 m p.p.t. W budynku na stałe mieszkają 4 osoby, a średnie roczne zużycie wody wynosi $Q_r = 90$ m^3. Zakładając 5% wskaźnik bezzwrotnego zużycia wody, średniodobową ilość powstających ścieków szacuje się na $Q_{dśr}$=0,25 m^3/d, a maksymalną Q_{dmax} = 0,50 m^3/d (przyjmując wskaźnik nierównomierności dobowej N_d = 2,00).

2.2. Charakterystyka poszczególnych wariantów technologicznych oczyszczalni

Poniżej opisano sposób wykonania poszczególnych wariantów technologicznych przydomowej oczyszczalni ścieków. W celu uzyskania porównywalnych wyników przyjęto następujące założenia:

- zastosowanie przepompowni wstępnej;
- wykorzystanie dwukomorowego osadnika gnilnego o pojemności 2 m^3, wyposażonego w kosz filtracyjny, z wyjątkiem oczyszczalni kontenerowych (z komorą osadu czynnego, ze złożem biologicznym i hybrydowej), wyposażonych fabrycznie w osadnik gnilny;
- przykrycie dna wykopu pod osadnik, przepompownie i oczyszczalnie kontenerowe 10 cm warstwą piasku stabilizowanego cementem, w celu zabezpieczenia przed wyporem przy okresowo podwyższonym poziomie wód gruntowych;
- połączenie urządzeń rurami PVC Ø110;
- wentylacja przez obejście z wywiewką wyprowadzoną 0,6 m ponad górną krawędź okien i drzwi zewnętrznych.

W kalkulacji kosztów natomiast założono:

- uwzględnienie cen katalogowych polskich producentów, których produkty mają wymagane atesty i dopuszczenia;

- uwzględnienie realnych lokalnych stawek robocizny (pracownicy: 15 zł/h, koparka: 120 zł/h) i godzinowego wymiaru prac ustalonego z firmą wykonawczą;
- przyjęcie kosztu transportu kruszywa z najbliższej żwirowni oddalonej o 30 km (stawka transportu: 4 zł/km – droga liczona w obie strony);
- transport własny pozostałych materiałów i urządzeń;
- przyjęcie kosztu pracy wykwalifikowanego personelu do okresowej obsługi i kontroli pracy oczyszczalni znajdujących się na terenie gminy (30 zł/h);
- uwzględnienie maksymalnej stawki za wywóz osadów z przydomowej oczyszczalni ścieków określonej w uchwale Rady Gminy Augustów (49 zł/m^3 brutto), a w przypadku nieczystości ciekłych średniej ceny oferowanej przez podmioty świadczące usługi w zakresie opróżniania zbiorników bezodpływowych na terenie gminy (20 zł/m^3 brutto).

Oczyszczalnia z drenażem rozsączającym

Oczyszczalnia z drenażem rozsączającym, dzięki stosunkowo niskim kosztom budowy i eksploatacji, jest w wielu gminach w Polsce dominującym rozwiązaniem [7]. Ze względu na ograniczoną możliwość poboru próbek ścieków oczyszczonych, w wielu państwach europejskich jego stosowanie zostało zabronione. Budowa oczyszczalni z drenażem rozsączającym jest możliwa tylko na gruntach o bardzo dobrej, dobrej i średniej przepuszczalności. Zabronione jest jej stosowanie na gruntach nieprzepuszczalnych. Ponadto wymagane jest zachowanie odległości min. 1,5 m od najwyższego użytkowego poziomu wód gruntowych. W innym przypadku konieczna jest budowa kopca filtracyjnego.

W kalkulacji kosztów przyjęto, że oczyszczalnia składa się z przepompowi wstępnej, osadnika gnilnego, przepompowni właściwej i drenażu rozsączającego w układzie otwartym. Drenaż tworzą 3 ciągi o długości 13 m każdy, ułożone w rozstawie 1,5 m. Rury drenażowe są ułożone ze spadkiem 1% w wykopie o szerokości 50 cm i głębokości 1 m, wypełnionym 35 cm warstwą kruszywa o granulacji 16–32 mm przykrytą geowłókniną, a następnie gruntem rodzimym. Ciągi drenażowe są zakończone wentylacją w postaci rur PVC z wywiewką usytuowaną 0,5 m n.p.t.

W tabeli 1 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni z drenażem rozsączającym. W kosztach robocizny uwzględniono 30 roboczogodzin, a w kosztach sprzętu 10 godzin pracy koparki, a także koszt transportu 12 ton kruszywa. W kosztach eksploatacji uwzględniono koszty: energii elektrycznej pobieranej przez pompy w przepompowniach, wywozu osadów z osadnika gnilnego (1 na rok) i zakupu biopreparatów. Założono, że okresowe przeglądy i czyszczenie kosza filtracyjnego osadnika gnilnego będą wykonywane przez użytkownika oczyszczalni.

Tabela 1. Koszty budowy i eksploatacji oczyszczalni z drenażem rozsączającym (poziom cen z 2014 r.)
Table 1. Investment and operating costs of drainage treatment plant (2014 price level)

Oczyszczalnia z drenażem rozsączającym		
1. nakłady inwestycyjne	8 547 zł	
a) materiały	6 657 zł	78%
b) robocizna	450 zł	5%
c) sprzęt	1 200 zł	14%
d) transport	240 zł	3%
2. roczne koszty eksploatacji	340 zł	

Źródło: opracowanie własne

Oczyszczalnia z tunelami rozsączającymi

W kalkulacji kosztów założono zastosowanie tuneli rozsączających zamiast tradycyjnego drenażu, zachowując opisany powyżej osadnik i przepompownie. Sposób ich montażu, a także wymagania co do przepuszczalności gruntu i odległości od poziomu wód gruntowych pozostają niezmienne. Dwa ciągi tuneli o długości 11 m każdy są ułożone w rozstępie 1,5 m ze spadkiem 1%, w wykopie o głębokości 1 m i szerokości 1,4 m, pokrytym 10 cm warstwą podsypki ze żwiru płukanego. Tunele są przykryte geowłókniną i przysypane warstwą gruntu rodzimego. W odróżnieniu od tradycyjnego drenażu, tunele zaprojektowano w układzie zamkniętym, tj. ciągi połączono studzienką zamykającą z wentylacją w postaci rur PVC z wywiewką usytuowaną 0,5 m n.p.t.

W tabeli 2 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni z tunelami rozsączającymi. W porównaniu z oczyszczalnią z tradycyjnym drenażem rozsączającym, zastosowanie tuneli podwyższa koszty materiałów, ale obniża koszty transportu kruszywa. Pozostałe składowe kosztów budowy i eksploatacji są takie same.

Tabela 2. Koszty budowy i eksploatacji oczyszczalni z tunelami rozsączającymi (poziom cen z 2014 r.)
Table 2. Investment and operating costs of drainage – tunnels treatment plant (2014 price level)

Oczyszczalnia z tunelami rozsączającymi		
1. nakłady inwestycyjne	10 606 zł	
a) materiały	8 836 zł	84%
b) robocizna	450 zł	4%
c) sprzęt	1 200 zł	11%
d) transport	120 zł	1%
2. roczne koszty eksploatacji	340 zł	

Źródło: opracowanie własne

Oczyszczalnia z pakietami rozsączającymi

W kalkulacji kosztów założono zastosowanie pakietów rozsączających, zamiast tradycyjnego drenażu lub tuneli, zachowując opisany powyżej osadnik i przepompownie. Sposób ich montażu, a także wymagania co do przepuszczalności gruntu i poziomu wód pozostają niezmienne. Zastosowano 4 pakiety rozsączające ułożone w jednym ciągu, ze spadkiem 1% w wykopie o szerokości 40 cm i głębokości 1 m. Na pakietach są ułożone główne rury drenażowe PVC Ø110, do których podłączono rury boczne. Na końcu ciągu została zastosowana wentylacja w postaci rur PVC Ø110, zakończona wywiewką usytuowaną 0,5 m n.p.t.

W tabeli 3 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni z pakietami rozsączającymi. W porównaniu z poprzednimi oczyszczalniami drenażowymi, zmianie ulega koszt materiałów. Pozostałe składowe kosztów budowy i eksploatacji są takie same, przy czym nie występują tu koszty transportu żwiru.

Tabela 3. Koszty budowy i eksploatacji oczyszczalni z pakietami rozsączającymi (poziom cen z 2014 r.)
Table 3. Investment and operating costs of drainage panels treatment plant (2014 price level)

Oczyszczalnia z pakietami rozsączającymi		
1. nakłady inwestycyjne	7 834 zł	
a) materiały	6 184 zł	79%
b) robocizna	450 zł	6%
c) sprzęt	1 200 zł	15%
2. roczne koszty eksploatacji	340 zł	

Źródło: opracowanie własne

Oczyszczalnia hydrofitowa

Zastosowanie złóż hydrofitowych w Polsce jest coraz bardziej powszechne ze względu na ich dużą odporność na nierównomierność dopływu ścieków i temperaturę, a także prostą obsługę [16]. Oprócz oczyszczania ścieków bytowych i komunalnych, złoża te znajdują również zastosowanie, m. in. do odwadniania osadów ściekowych [14], oczyszczania odcieków ze składowisk odpadów [23], czy też zmniejszania obciążenia oczyszczalni poprzez podczyszczanie nieczystości ciekłych [20] lub oczyszczanie odcieków z przeróbki osadów [3]. W złożach o pionowym podpowierzchniowym przepływie (VF-CW), wysokie efekty oczyszczania utrzymują się przez wiele lat [21].

W odróżnieniu od oczyszczalni drenażowych, oczyszczalnia hydrofitowa może być stosowana na każdym gruncie i niezależnie od poziomu wód gruntowych, przy czym oba czynniki wpływają na wybór sposobu odprowadzania ścieków oczyszczonych, a także głębokość posadowienia oczyszczalni. W kalkulacji kosztów przyjęto, że oczyszczalnia składa się przepompowni wstępnej, osadnika gnilnego, przepompowni właściwej i złoża hydrofitowego o powierzchni 12 m^2. Częściowo zagłębione złoże uszczelniono folią basenową i folią kubełkową. Zgodnie z zaleceniami [4, 2] wypełniono je wyłącznie materiałem mineralnym: na dnie zastosowano kamienie o granulacji 60–100 mm (grubość warstwy 15 cm), następnie żwir płukany 12,5-25 mm (grubość warstwy 30 cm) i piasek 0,1–2 mm (grubość warstwy 15 cm). Drenaż rozsączający z rur PVC Ø110, połączony ze studzienką rozdzielczą, składa się z dwóch ciągów o długości 3,5 m każdy. Drenaż zbierający, ułożony w warstwie kamieni, składa się również z dwóch ciągów o długości 3,5 m każdy, łączących się w studzience zbierającej. Wentylację obu drenaży zapewniają pionowe rury PVC Ø110 mm zakończone wywiewką. Zgodnie z zaleceniami [2] złoże zasadzono zakupionymi sadzonkami trzciny pospolitej (*Phragmites australis*).

W tabeli 4 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni hydrofitowej. W kosztach robocizny uwzględniono 40 roboczogodzin, w kosztach sprzętu 16 godzin pracy koparki, a także koszt transportu 14 ton kruszywa. W kosztach eksploatacji uwzględniono koszty: energii elektrycznej pobieranej przez pompy w przepompowniach oraz wywozu osadów z osadnika gnilnego (1 na rok). Założono, że okresowe przeglądy i czyszczenie kosza filtracyjnego osadnika gnilnego będą wykonywane przez użytkownika oczyszczalni.

Tabela 4. Koszty budowy i eksploatacji oczyszczalni hydrofitowej (poziom cen z 2014 r.)
Table 4. Investment and operating costs of constructed wetlands (2014 price level)

Oczyszczalnia hydrofitowa			
1. nakłady inwestycyjne		8 964 zł	
a)	materiały	6 084 zł	68%
b)	robocizna	600 zł	7%
c)	sprzęt	1 920 zł	21%
d)	transport	360 zł	4%
2. roczne koszty eksploatacji		103 zł	

Źródło: opracowanie własne

Oczyszczalnia ze złożem biologicznym

Oczyszczalnie ze złożem biologicznym przez wiele lat były w Polsce powszechnie stosowane do oczyszczania małych ilości ścieków na terenach wiejskich. W latach dziewięćdziesiątych XX wieku, podwyższenie wymagań prawnych w zakresie usuwania związków biogennych spowodowało wyparcie tej technologii przez urządzenia osadu czynnego. Zmiana przepisów i udoskonalenie technologii złóż biologicznych sprawiło, że są one obecnie znów chętnie stosowane zarówno w małych zbiorczych, jak też przydomowych oczyszczalniach ścieków [9]. Ich zaletą jest niewielkie zapotrzebowanie terenu, odporność na nierównomierność obciążeń hydraulicznego i ładunkiem zanieczyszczeń, a także niższe w porównaniu do technologii osadu czynnego zużycie energii. Oczyszczalnie te mogą być stosowane niezależnie od rodzaju gruntu i poziomu wód gruntowych, przy czym oba te czynniki wpływają na wybór sposobu odprowadzania ścieków oczyszczonych. W kalkulacji kosztów założono, że oczyszczalnia składa się z czterokomorowego złoża biologicznego z wydzielonym osadnikiem wstępnym, przed którym zamontowano przepompownię wstępną.

W tabeli 5 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni ze złożem biologicznym. W kosztach robocizny uwzględniono 20 roboczogodzin, a w kosztach sprzętu 8 godzin pracy koparki. W kosztach eksploatacji uwzględniono koszty: energii elektrycznej pobieranej przez pompę w przepompowni oraz przez złoże biologiczne, wywozu osadów z osadnika gnilnego (1 na rok) oraz okresowej zewnętrznej obsługi oczyszczalni (przyjęto 1h/miesiąc).

Tabela 5. Koszty budowy i eksploatacji oczyszczalni ze złożem biologicznym (poziom cen z 2014 r.)
Table 5. Investment and operating costs of biological filter treatment plant (2014 price level)

Oczyszczalnia ze złożem biologicznym		
1. nakłady inwestycyjne	11 484 zł	
a) materiały	10 224 zł	89%
b) robocizna	300 zł	3%
c) sprzęt	960 zł	8%
2. roczne koszty eksploatacji	561 zł	

Źródło: opracowanie własne

Oczyszczalnia z komorą osadu czynnego

Efektywna technologicznie i kosztowo w dużych oczyszczalniach metoda osadu czynnego, przeniesiona na grunt przydomowych oczyszczalni ścieków nie zawsze daje oczekiwane efekty [10]. Obsługa oczyszczalni z komorą osadu czynnego wymaga fachowej wiedzy, a zatem konieczne jest zatrudnienie dochodzącej obsługi do okresowego nadzoru jej pracy. Podobnie jak oczyszczania ze złożem biologicznym, oczyszczalnia z komorą osadu czynnego zajmuje mało miejsca. Może być stosowana na każdym gruncie i niezależnie od poziomu wód gruntowych, przy czym oba czynniki wpływają na wybór sposobu odprowadzania ścieków oczyszczonych. W kalkulacji kosztów przyjęto zastosowanie reaktora kompaktowego, składającego się z osadnika wstępnego, komory osadu czynnego i osadnika wtórnego. Przed oczyszczalnią znajduje się przepompownia wstępna.

W tabeli 6 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni z komorą osadu czynnego. W kosztach robocizny uwzględniono 20 roboczogodzin, a w kosztach sprzętu 8 godzin pracy koparki. W kosztach eksploatacji uwzględniono koszty: energii elektrycznej pobieranej przez reaktor i przepompownię, wywozu osadów ściekowych (2 razy w roku), biopreparatów oraz okresowej zewnętrznej obsługi oczyszczalni (przyjęto 2h/miesiąc).

Tabela 6. Koszty budowy i eksploatacji oczyszczalni z komorą osadu czynnego (poziom cen z 2014 r.)
Table 6. Investment and operating costs of activated sludge treatment plant (2014 price level)

Oczyszczalnia z komorą osadu czynnego		
1. nakłady inwestycyjne	11 676 zł	
a) materiały	10 416 zł	89%
b) robocizna	300 zł	3%
c) sprzęt	960 zł	8%
2. roczne koszty eksploatacji	1 123 zł	

Źródło: opracowanie własne

Oczyszczalnia hybrydowa

Oczyszczalnia hybrydowa stanowi połączenie technologii osadu czynnego i złóż biologicznych. Łączy wysoką efektywność osadu czynnego, z większą odpornością złóż biologicznych na zmieniające się obciążenie hydrauliczne i obciążenie ładunkiem zanieczyszczeń [15]. Warunkiem pełnego wykorzystania możliwości tej oczyszczalni jest zapewnienie okresowego nadzoru wyspecjalizowanej obsługi, przy czym zakres jej prac jest mniejszy niż w przypadku oczyszczalni z komorą osadu czynnego. Podobnie jak trzy poprzednie oczyszczalnie, może być ona stosowana na każdym gruncie i niezależnie od poziomu wód gruntowych, przy czym oba czynniki wpływają na wybór sposobu odprowadzania ścieków oczyszczonych. W kalkulacji kosztów założono zastosowanie kompaktowej oczyszczalni, poprzedzonej przepompownią wstępną. Oczyszczalnia składa się z dwukomorowego osadnika gnilnego o pojemności 2,5 m^3, wyposażonego w filtr szczelinowy, a także bioreaktora o pojemności 2,5 m^3 z przegrodą dzielącą zbiornik na dwie strefy: osad czynny i złoże biologiczne.

W tabeli 7 zestawiono informacje o kosztach budowy i eksploatacji oczyszczalni hybrydowej. W kosztach robocizny uwzględniono 20 roboczogodzin, a w kosztach sprzętu 8 godzin pracy koparki. W kosztach eksploatacji uwzględniono koszty: energii elektrycznej pobieranej przez przepompownię oraz oczyszczalnię, wywozu osadów ściekowych i obumarłej błony biologicznej (2 razy na rok) oraz okresowej zewnętrznej obsługi oczyszczalni (przyjęto 1 h/miesiąc).

Tabela 7. Koszty budowy i eksploatacji oczyszczalni hybrydowej (poziom cen z 2014 r.)
Table 7. Investment and operating costs of hybrid treatment plant (2014 price level)

Oczyszczalnia hybrydowa		
1. nakłady inwestycyjne	14 607 zł	
a) materiały	13 347 zł	91%
b) robocizna	300 zł	2%
c) sprzęt	960 zł	7%
2. roczne koszty eksploatacji	809 zł	

Źródło: opracowanie własne

2.3. Sposoby odprowadzania ścieków oczyszczonych

Ścieki oczyszczone mogą być odprowadzane do wód, gruntu i atmosfery. Najczęściej ich odbiornikiem jest grunt, do którego są odprowadzane za pomocą drenażu, pakietów i tuneli rozsączających lub studni chłonnej. Stosując oczko wodne zasiedlone roślinnością wodną i wodnolubną, ścieki oczyszczone są odprowadzane do atmosfery przez odparowanie i ewapotranspirację. Można je także wykorzystać do podlewania trawników. W okresie niskich temperatur, oczko wodne może zamarznąć, dlatego warto za nim przewidzieć odcinek drenażu.

Wybierając sposób odprowadzania ścieków oczyszczonych, należy uwzględnić konieczność zachowania odległości minimum 1,5 m od najwyższego użytkowego poziomu wód gruntowych, a także przepuszczalność gruntu. Na gruntach nieprzepuszczalnych jedyną możliwość odprowadzania ścieków oczyszczonych stanowi odparowanie w oczku wodnym.

W kalkulacji kosztów przyjęto sposób montażu drenażu rozsączającego, tuneli i pakietów rozsączających zgodny ze wcześniejszym opisem, przy czym ich długość jest o połowę mniejsza niż w przypadku, gdy są one stosowane jako urządzenie do biologicznego oczyszczania ścieków (czyli: 2 ciągi drenażu po 10 m, ciąg tuneli o długości 11 m, 2 pakiety). We wszystkich przypadkach w kosztach robocizny uwzględniono 10 roboczogodzin, w kosztach sprzętu 5 godzin pracy koparki. W przypadku drenażu i tuneli rozsączających uwzględniono dodatkowo koszt transport kruszywa.

W kalkulacji studni chłonnej założono zastosowanie studni w kształcie dzwonu o średnicy u podstawy d=1,3 m, z nadstawką i pokrywą. Umieszczono ją w poszerzonym wykopie o szerokości 1,7 m, pokrytym 1 m warstwą żwiru płukanego o granulacji 16-32 mm. Zapewniono również jej wentylację poprzez rury PVC Ø110 zakończone wywiewką położoną 0,5 m n.p.t. W kosztach robocizny uwzględniono 8 roboczogodzin, w kosztach sprzętu 3 godziny pracy koparki, a w kosztach transportu koszt transportu 4 ton kruszywa.

W przypadku oczka wodnego założono, że jego głębokość wynosi 0,7 m, a powierzchnia 6 m^2. Jego dno jest uszczelnione geomembraną 1 mm, a boki obsadzone roślinnością wodnolubną. W kosztach robocizny uwzględniono 8 roboczogodzin, w kosztach sprzętu 3 godziny pracy koparki.

W tabeli 8 zestawiono informacje o kosztach budowy poszczególnych rozwiązań. Do tych kosztów należy doliczyć koszt prac hydrogeologicznych, poprzedzających decyzję o wyborze sposobu odprowadzenia ścieków oczyszczonych, sięgający 300–500 zł.

Tabela 8. Koszty budowy systemu odprowadzania ścieków oczyszczonych (poziom cen z 2014 r.)
Table 8. Costs for construction of a system for discharge of treated sewage (2014 price level)

1. Drenaż rozsączający		
nakłady inwestycyjne	1486 zł	
a) materiały	616 zł	42%
b) robocizna	150 zł	10%
c) sprzęt	600 zł	40%
d) transport	120 zł	8%
2. Tunele rozsączające		
nakłady inwestycyjne	2467 zł	
a) materiały	1597 zł	65%
b) robocizna	150 zł	6%
c) sprzęt	600 zł	24%
d) transport	120 zł	5%
3. Pakiety rozsączające		
nakłady inwestycyjne	1139 zł	
a) materiały	389 zł	34%
b) robocizna	150 zł	13%
c) sprzęt	600 zł	53%
4. Studnia chłonna		
nakłady inwestycyjne	1954 zł	
a) materiały	1354 zł	69%
b) robocizna	120 zł	6%
c) sprzęt	360 zł	19%
d) transport	120 zł	6%
5. Oczko wodne		
nakłady inwestycyjne	955 zł	
a) materiały	475 zł	50%
b) robocizna	120 zł	12%
c) sprzęt	360 zł	38%

Źródło: opracowanie własne

2.4. Zbiornik bezodpływowy

Alternatywą do budowy przydomowej oczyszczalni ścieków jest gromadzenie nieczystości ciekłych w zbiorniku bezodpływowym i ich okresowe wywożenie do zbiorczej oczyszczalni ścieków w Augustowie. W kalkulacji kosztów założono zastosowanie dwukomorowego zbiornika bezodpływowego o pojemności 8 m^3, opróżnianego ze średnią częstotliwością raz w miesiącu. Zbiornik zamontowano na podsypce z piasku stabilizowanego cementem, a jego wentylację zapewnia obejście z wywiewką wyprowadzoną 0,6 m ponad górną krawędź okien i drzwi.

W tabeli 9 zestawiono informacje o kosztach budowy i eksploatacji tego zbiornika. W kosztach robocizny uwzględniono 15 roboczogodzin, a w kosztach sprzętu 5 godzin pracy koparki. W kosztach eksploatacji uwzględniono koszty okresowego wywozu nieczystości ciekłych do zbiorczej oczyszczalni ścieków (20 zł/m^3 brutto).

Tabela 9. Koszty budowy i eksploatacji zbiornika bezodpływowego (poziom cen z 2014 r.)
Table 9. Investment and operating costs of a holding tank (2014 price level)

Zbiornik bezodpływowy		
1. nakłady inwestycyjne	7 948 zł	
d) materiały	7 123 zł	90%
e) robocizna	225 zł	3%
f) sprzęt	600 zł	7%
2. roczne koszty eksploatacji	1 920 zł	

Źródło: opracowanie własne

2.5. Metodyka wyznaczania całkowitego średniorocznego kosztu oczyszczania ścieków

Całkowity średnioroczny koszt oczyszczania ścieków jest obliczany ze wzoru [12]:

$$K_r = I\alpha + K_e \qquad (1)$$

gdzie:
K_r – całkowity średnioroczny koszt oczyszczania ścieków [zł/rok],
I – nakłady inwestycyjne [zł],

α – współczynnik zwrotu kapitału [rok^{-1}],
K_e – koszty eksploatacji (bez amortyzacji) [zł/rok].

Jak zatem wynika ze wzoru (1) całkowity średnioroczny koszt oczyszczania ścieków (K_r) zależy od nakładów inwestycyjnych (I), kosztów eksploatacji (K_e), a także opisanego równaniem (2) współczynnika zwrotu kapitału:

$$\alpha = \frac{r(1+r)^n}{(1+r)^n - 1} \tag{2}$$

gdzie:
α – współczynnik zwrotu kapitału [rok^{-1}],
r – stopa dyskontowa [rok^{-1}],
n – kalkulacyjny okres eksploatacji [lata].

Założony okres eksploatacji wszystkich oczyszczalni wynosi n = 20 lat. Stopę dyskontową przyjęto na poziomie r = 5%. W nakładach inwestycyjnych uwzględniono sumę kosztów ponoszonych na budowę urządzeń do oczyszczania ścieków, a także systemu odprowadzania ścieków oczyszczonych. Podane koszty eksploatacji dotyczą całego układu.

3. Wyniki i dyskusja

W tabeli 10 zestawiono wyniki obliczeń wielkości nakładów inwestycyjnych, rocznych kosztów eksploatacji i całkowitego średniorocznego kosztu oczyszczania w poszczególnych wariantach oczyszczalni, uwzględniając różne sposoby odprowadzania ścieków oczyszczonych.

Średnioroczny koszt gromadzenia nieczystości ciekłych w szczelnym zbiorniku bezodpływowym i ich wywożenia do zbiorczej oczyszczalni ścieków w Augustowie wynosi 2 556 zł/rok. Średnioroczny koszt oczyszczania ścieków w oczyszczalni przydomowej, zależnie od zastosowanej technologii i sposobu odprowadzania ścieków oczyszczonych, waha się od 896 zł/rok do 2 255 zł/rok i wynosi średnio 1 627 zł/rok. Jest tym samym niemal dwukrotnie niższy od kosztów budowy i eksploatacji szczelnego zbiornika bezodpływowego. Należy jednak przy tym zaznaczyć, iż relacja tych kosztów w istotny sposób zależy od ceny wywozu nieczystości ciekłych, które są w skali kraju bardzo zróżnicowane.

Tabela 10. Zestawienie nakładów inwestycyjnych, kosztów eksploatacji i całkowitych średniorocznych kosztów oczyszczania ścieków w zależności od technologii i sposobu odprowadzania ścieków oczyszczonych (poziom cen z 2014 r.)

Table 10. Comparison of investment, operating and total annual costs of sewage treatment depending on the technology and system of treated sewage discharge (2014 price level)

Wariant technologiczny oczyszczalni		Układ odprowadzający ścieki oczyszczone				
		drenaż rozsączający	tunele rozsączające	pakiety rozsączające	studnia chłonna	oczko wodne
Nakłady inwestycyjne [zł]		1 486	2 467	1 139	1 954	955
z drenażem rozsączającym	8 547	–	–	–	–	–
z tunelami rozsączającymi	10 606	–	–	–	–	–
z pakietami rozsączającymi	7 834	–	–	–	–	–
hydrofitowa	8 964	10 450	11 431	10 103	10 918	9 919
ze złożem biologicznym	11 484	12 970	13 951	12 623	13 438	12 439
z komorą osadu czynnego	11 676	13 162	14 143	12 815	13 630	12 631
hybrydowa	14 607	16 093	17 074	15 746	16 561	15 562
Zbiornik bezodpływowy	7 948					
Roczne koszty eksploatacji [zł/rok]						
z drenażem rozsączającym	340	–	–	–	–	–
z tunelami rozsączającymi	340	–	–	–	–	–
z pakietami rozsączającymi	340	–	–	–	–	–
hydrofitowa	–	103	103	103	103	103
ze złożem biologicznym	–	561	561	561	561	561
z komorą osadu czynnego	–	1 123	1 123	1 123	1 123	1 123
hybrydowa	–	809	809	809	809	809
Zbiornik bezodpływowy	1 920					

Tabela 10. cd.
Table 10. cont.

Wariant technologiczny oczyszczalni		Układ odprowadzający ścieki oczyszczone				
		drenaż rozsączający	tunele rozsączające	pakiety rozsączające	studnia chłonna	oczko wodne
Całkowity średnioroczny koszt oczyszczania ścieków [zł/rok]						
z drenażem rozsączającym	1 023	–	–	–	–	–
z tunelami rozsączającymi	1 188	–	–	–	–	–
z pakietami rozsączającymi	966	–	–	–	–	–
hydrofitowa	–	939	1 017	911	976	896
ze złożem biologicznym	–	1 599	1 677	1 571	1 636	1 556
z komorą osadu czynnego	–	2 176	2 255	2 149	2 214	2 134
hybrydowa	–	2 096	2 175	2 069	2 134	2 054
Zbiornik bezodpływowy	2 556					
Jednostkowy średnioroczny koszt oczyszczania ścieków [zł/m^3/rok]						
z drenażem rozsączającym	11	–	–	–	–	–
z tunelami rozsączającymi	13	–	–	–	–	–
z pakietami rozsączającymi	11	–	–	–	–	–
hydrofitowa	–	10	11	10	11	10
ze złożem biologicznym	–	18	18	17	18	17
z komorą osadu czynnego	–	24	25	24	24	23
hybrydowa	–	23	24	23	23	23
Zbiornik bezodpływowy	28					

Źródło: opracowanie własne

Spośród analizowanych rozwiązań technologicznych oczyszczalni ścieków, najniższych nakładów inwestycyjnych wymaga oczyszczalnia z pakietami lub drenażem rozsączającym. Najtańszy sposób odprowadzania ścieków oczyszczonych stanowi oczko wodne, a najdroższy tunele rozsączające. Najniższymi kosztami eksploatacji charakteryzuje się oczyszczalnia hydrofitowa, a najwyższymi zbiornik bezodpływowy, oczyszczalnia z komorą osadu czynnego i oczyszczalnia hybrydowa. Stosunkowo wysokie są także koszty eksploatacji oczyszczalni drenażowych i ze złożem biologicznym. Najniższym średniorocznym kosztem charakteryzuje się oczyszczalnia hydrofitowa z odprowadzaniem ścieków oczyszczonych do oczka wodnego, a najwyższym oczyszczalnia hybrydowa z odprowadzaniem ścieków oczyszczonych do gruntu za pomocą tuneli rozsączających. Wnioski z analizy przeprowadzonej przez innych autorów są podobne [8, 11, 18]. W pracy otrzymano jednak wyższe średnioroczne koszty oczyszczania ścieków we wszystkich oczyszczalniach, co wynika z uwzględniania, zwykle pomijanych składowych kosztów, takich jak zakup kruszywa, praca ludzi i sprzętu przy budowie oczyszczalni czy też koszt okresowych przeglądów przeprowadzanych przez wykwalifikowaną obsługę. Są to koszty bez których nie da się osiągnąć wymaganych efektów w zakresie jakości ścieków oczyszczonych odprowadzanych do odbiornika.

4. Wnioski

Z przeprowadzonej analizy efektywności kosztowej różnych rozwiązań technologicznych przydomowych oczyszczalni ścieków można wyciągnąć następujące wnioski:

1. Całkowity średnioroczny koszt oczyszczania ścieków w obiektach przydomowych jest średnio niemal dwukrotnie niższy od kosztu ponoszonego w przypadku budowy i eksploatacji szczelnego zbiornika bezodpływowego, przy czym relacja ta w dużej mierze zależy od zróżnicowanych w skali kraju kosztów opróżniania zbiorników bezodpływowych.
2. Najwyższy udział w nakładach inwestycyjnych, ponoszonych na budowę przydomowych oczyszczalni ścieków stanowią materiały (średnio 83%) i koszty wynajęcia sprzętu (średnio 12%). W przypadku systemu odprowadzania ścieków oczyszczonych koszty te stanowią odpowiednio średnio 52% i 35%.
3. Spośród analizowanych rozwiązań technologicznych, najniższych nakładów inwestycyjnych wymaga oczyszczalnia drenażowa z pakietami lub drenażem rozsączającym. Najniższe koszty eksploatacji występują w przypadku oczyszczalni hydrofitowej. Najbardziej efektywnym pod względem ekonomicznym rozwiązaniem, charakteryzującym

się najniższym całkowitym średniorocznym kosztem oczyszczania ścieków, jest oczyszczalnia hydrofitowa z odprowadzeniem ścieków oczyszczonych do oczka wodnego. Wnioski z analizy mogą się różnić w przypadku przyjęcia innych zestawień materiałowych, w tym modeli oczyszczalni kontenerowych, a także stawek pracy ludzi i kosztów wynajęcia sprzętu.

Literatura

1. **Boruszko D., Piotrowski P., Miłaszewski R.:** *Ocena ekonomicznej efektywności komunalnej oczyszczalni ścieków w gminie Sokoły*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 1086–1097 (2013).
2. **Cooper P.F.:** *What can we learn from old wetlands? Lessons that have been learned and some that may have been forgotten over the past 20 years*. Desalination, 246, 11–26 (2009).
3. **Dąbrowski W., Wiater J.:** *The Possibility of Dairy WWTP Load Decreasing by Using Separate Constructed Wetland for Effluents from Sludge Processing Treatment*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 823–834 (2013).
4. **Environmental Protection Agency:** *Constructed Wetlands Treatment of Municipal Wastewater. Manual*. EPA Report 625/R-99-010, Cincinnati, Ohio 2000.
5. **Główny Urząd Statystyczny**: *Infrastruktura Komunalna* (2014).
6. **Goleń M., Maśloch G., Warężak T., Ziółkowski T.:** *Ekonomika gospodarki ściekowej na wsi. Poradnik dla gminy oraz mieszkańców terenów niezurbanizowanych*. Oficyna Wydawnicza Szkoły Głównej Handlowej w Warszawie, Warszawa 2011.
7. **Grygorczuk-Petersons E.H.:** *Ocena funkcjonowania przyzagrodowych oczyszczalni ścieków na terenie wybranej gminy Zielonych Płuc Polski*. Inżynieria Ekologiczna, 24, 32–37 (2011).
8. **Heidrich Z., Stańko G.:** *Leksykon przydomowych oczyszczalni ścieków*. Wydawnictwo „Seidel-Przywecki" Sp. z o.o., Warszawa 2007.
9. **Ignatowicz K., Puchlik M.:** *Złoża biologiczne jako alternatywa oczyszczania małych ilości ścieków*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 13, 1385–1404 (2011).
10. **Jóźwiakowski K., Marzec M.:** *Problemy funkcjonowania przydomowych oczyszczalni ścieków z osadem czynnym – badania wstępne*. Przegląd Naukowy, Inżynieria i Kształtowanie Środowiska, 2 (34), 163–171 2006.

11. **Kundziewicz A., Miłaszewski R.:** *Analiza efektywności kosztowej indywidualnych systemów usuwania i oczyszczania ścieków*. Inżynieria Ekologiczna, 24, 174–183 2011.
12. **Miłaszewski R.:** *Ekonomika ochrony wód powierzchniowych*, Wydawnictwo Ekonomia i Środowisko, Białystok 2003.
13. **Ministerstwo Rolnictwa i Rozwoju Wsi:** *Założenia do strategii zrównoważonego rozwoju wsi i rolnictwa*. Warszawa 2010.
14. **Kołecka K., Obarska-Pempkowiak H.:** *The quality of sewage sludge stabilized for a long time in reed basins*. Environment Protection Engineering, 34(3), 13–20 (2008).
15. **Krzanowski S., Wałęga A.:** *Effectiveness of organic substance removal in household conventional activated sludge and hybrid treatment plants*, Environment Protection Engineering, 34(3), 5–12 (2008).
16. **Obarska-Pempkowiak H., Gajewska M., Wojciechowska E.:** *Efficiency of Wastewater Treatment in Single-Family Constructed Wetlands in Kaszuby Lake District*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 81–95 (2013).
17. *Rozporządzenie Ministra Środowiska z dnia 22 lipca 2014 r. w sprawie sposobu wyznaczania obszaru i granic aglomeracji* (Dz. U. 2014 poz. 995).
18. **Skoczko I.:** *Economic analysis of options for sewage treatment plant*. Teka Kom. Ochr. Kszt. Środ. Przyr. – OL PAN, 7, 5–11 (2010).
19. **Skoczko I.:** *Ekonomiczna analiza rozwiązań oczyszczalni ścieków dla wsi przy rozproszonej zabudowie*, Gaz, Woda i Technika Sanitarna, 6, 271–275 (2012).
20. **Tomczuk B., Dąbrowski W.:** *New applications of hydrophyte method in environmental protection*: W: Environment Alterations - research and protection methods (ed. J. Koc), 8, 171–184 (2011).
21. **Warężak T., Sadecka Z., Myszograj S., Suchowska-Kisielewicz M.:** *Skuteczność oczyszczania ścieków w oczyszczalni hydrofitowej typu VF-CW*, Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 1243–1259 (2013).
22. **Wiater J.:** *Ocena świadomości ekologicznej gminy Choroszcz*, Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 13, 653–680 (2011).
23. **Wojciechowska E.:** *Removal of persistent organic pollutants from landfill leachates treated in three constructed wetland systems*, Water Science and Technology, 68(5), 1164–1172 (2013).

Cost-effectiveness Analysis of Different Technological Variants of Single-house Sewage Treatment Plants

Abstract

The cost-effectiveness of a range of variants of single-house sewage treatment plants is analyzed in the article. They include plants with drainage pipe, with package drainage, with tunnel drainage, constructed wetlands, activated sludge chamber, biological filter and a hybrid plant. The analysis focuses on different ways of discharging treated wastewater, i.e. drainage pipe, package drainage, tunnel drainage, pond and soakaway. Selection of the most financially efficient system was made on the basis of the minimal rate of the average annual treatment cost. The total cost was compared with the construction costs as well as the operating costs of a holding tank.

The analysis shows that, on the average, the total average annual cost of single-house sewage treatment facilities is almost 2-times lower than the cost incurred on the construction and operations of a holding tank. This ratio, however, depends largely on different prices for emptying a tank. Materials (avg. 83%) and equipment rental (avg. 12%) constitute the greatest share of the investment costs incurred on the construction of sewage treatment plants.

Among the analyzed sewage treatment plant technologies the lowest investment outlays are required for drainage pipes and packages as well as constructed wetlands. The lowest treated sewage discharge costs are generated by ponds, whereas the highest by tunnel drainage. The lowest operation costs are generated by constructed wetlands, whereas the highest by holding tank, activated sludge chambers and hybrid plants. The most cost effective, characterized by the lowest average total annual cost, is constructed wetland with discharge by a pond. The greatest average annual cost of wastewater treatment is generated by hybrid plants with treated wastewater discharged into the ground by drainage tunnels.

The conclusions of analysis carried out by other authors are similar to those presented in this paper. However, the presented research shows that the average annual outlays for wastewater treatment for all plants are greater. This is because additional cost factors, such as the purchase of gravel, human costs, equipment expenditures or maintenance of periodic inspections carried out by qualified personnel, were taken into account. These are costs without which it is impossible to achieve the required quality of treated sewage.

Słowa kluczowe:
efektywność kosztowa, przydomowe oczyszczalnie ścieków,
warianty technologiczne

Keywords:
cost effectiveness, single-house sewage treatment plants, technological variants

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Projekt CIVITAS RENAISSANCE w Szczecinku w kontekście założeń zrównoważonego rozwoju

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1. Wstęp

Zrównoważony rozwój stanowi dziś cel priorytetowy polityki Unii Europejskiej, wynikający z objętego przez nią następującego celu strategicznego: „stać się najbardziej konkurencyjną i dynamiczną, opartą na wiedzy gospodarką świata, zdolną do zrównoważonego rozwoju gospodarczego, zapewniającego więcej lepszych miejsc pracy oraz większą spójność socjalną” [2]. Pojawiające się tu pojęcie zrównoważonego rozwoju oznacza konsekwencje we wszelkich obszarach aktywności państwa i na wszystkich szczeblach administracji. Przedsięwzięcia podejmowane przez samorządy powinny mieć zatem ów walor przewodni: być spójne z wytycznymi zrównoważonego rozwoju. Oznacza to jednak różnorodność aspektów, które warto by przedstawić.

2. Wytyczne zrównoważonego rozwoju

Cytując za L. Pawłowskim powszechnie uznawaną definicję zrównoważonego rozwoju, pochodzącą z raportu ONZ „*Nasza Wspólna Przyszłość*” stworzonego w 1978 roku przez tzw. Komisję Brundtland, „zrównoważony rozwój Ziemi to rozwój, który zaspokaja podstawowe potrzeby wszystkich ludzi oraz zachowuje, chroni i przywraca zdrowie i integralność ekosystemu Ziemi, bez zagrożenia możliwości zaspokojenia potrzeb przyszłych pokoleń i bez przekraczania długookresowych granic pojemności ekosystemu Ziemi” [6]. W literaturze istnieje wiele modyfikacji przytoczonej definicji, mnożących się wraz z upowszechnianiem tej idei[8]. Wszystkie one jednak opierają się na godzeniu interesów trzech obszarów, tj. ekonomii, społeczeństwa i środowiska.

Skutki, jakie mają nieść działania prowadzone zgodnie z tą koncepcją znalazły też swój wyraz w Strategii Zrównoważonego Rozwoju dla Unii Europejskiej. „Rozwój zrównoważony oferuje Unii Europejskiej pozytywną, długoterminową wizję społeczeństwa, które jest zamożniejsze i bardziej sprawiedliwe i które obiecuje czystsze, bezpieczniejsze i zdrowsze środowisko”[2]. Odwołania do zrównoważonego rozwoju są również podstawą wytycznych Narodowych Strategicznych Ram Odniesienia, wyznaczających ramy realizacji założeń polityki unijnej w Polsce [5]. Odwołania do tej koncepcji znaleźć też można w rdzennie polskich aktach prawnych, począwszy od najważniejszego z nich – Konstytucji RP, która w art. 5 stanowi: „Rzeczpospolita Polska […] zapewnia ochronę środowiska, kierując się zasadą zrównoważonego rozwoju”[3].

Skutkiem działań zgodnych z koncepcją rozwoju zrównoważonego jest tzw. dobrostan obywateli, osiągnięty bez umniejszania szans na rozwój przyszłych pokoleń [7]. Stąd inicjatywy podejmowane na różnych szczeblach administracji państwa, jak również te, będące w gestii innych podmiotów (organizacji non-profit, przedsiębiorstw, instytucji ochrony zdrowia, kultury, sportu, edukacji, pomocy społecznej itd.), uwzględniają owe założenia w swoich działaniach, zwłaszcza, jeśli środki na ich realizację pochodzą z unijnego budżetu. W dokumencie wiodącym, unijnej strategii wzrostu na lata 2010–2020, pod nazwą Europa 2020, założono bowiem 3 priorytety rozwoju, obejmujące szeroki kontekst społeczno-środowiskowo-ekonomiczny [10]. Pierwszy z nich, *rozwój inteligentny*, to działania ukierunkowane na osiąganie lepszych wyników w:

- innowacji – poprawa warunków finansowania badań i innowacji,
- edukacji – poprawa wyników systemów kształcenia i atrakcyjności szkolnictwa wyższego,
- społeczeństwie cyfrowym – upowszechnianie szybkiego interentu.

Drugi, *rozwój zrównoważony* zakłada działania w obszarach:

- klimat, energia i mobilność – zmniejszenie udziału emisji węgla, większe wykorzystanie odnawialnych źródeł energii, modernizację transportu, propagowanie efektywności energetycznej,
- konkurencyjność – poprawa otoczenia biznesu i warunków dla rozwoju przedsiębiorczości i konkurencyjności przedsiębiorstw.

Rozwój sprzyjający włączeniu społecznemu, to natomiast:

- zatrudnienie i umiejętności – zwiększanie mobilności siły roboczej, podnoszenie kwalifikacji zawodowych, a w efekcie podniesienie stopy zatrudnienia w Europie,
- walka z ubóstwem – zapewnienie spójności społecznej i terytorialnej, tak, aby upowszechnić korzyści płynące ze wzrostu gospodarczego i zatrudnienia.

Zgodnie z tymi wytycznymi, odwołania do koncepcji zrównoważonego rozwoju znaleźć można w każdym dokumencie, określającym zasady korzystania z unijnego wsparcia. Są to zarówno wytyczne do wdrażania programów pomocowych na szczeblu krajowym, jak też instrumenty wdrażania tzw. wspólnotowego programu lizbońskiego. Przykładem jest 7 Program Ramowy w zakresie badań i rozwoju technologicznego (7PR). Również jego priorytety odwołują się do synergicznego wsparcia europejskiej działalności badawczej przy założeniu pozytywnego wpływu na rozwój społeczny, kulturalny i gospodarczy państw Unii [1].

3. CIVITAS RENAISSANCE – założenia projektu

Jednym z projektów realizowanych wśród Programów Ramowych jest inicjatywa *CIVITAS* zainaugurowana na początku 2002 roku w ramach 5PR jako *CIVITAS I*. Łącznie, w dotychczasowych 4 edycjach programu zaplanowano do realizacji piętnaście niezależnych projektów, w które zaangażowało się 69 miast z 22 krajów Europy. Wszystkie projekty mają własne priorytety i przewidziane do realizacji działania. Są one jednak spójne z nadrzędnym celem postawionym przed całym programem, którym jest czysty, efektywny energetycznie, harmonijny i zrównoważony transport miejski [4].

Miasto Szczecinek uczestniczyło w *CIVITAS* w komponencie *RENAISSANCE*, realizowanym od września 2008 roku do końca 2012 roku. Główne założenia *RENAISSANCE* skupiają się na zmniejszeniu uciążliwości ruchu drogowego w aglomeracjach miejskich poprzez zastosowanie nowoczesnych rozwiązań technologicznych oraz realizowanie działań zmierzających do ochrony środowiska naturalnego. W ramach projektu w Szczecinku wdrażane było 10 działań:

1.6. Flota minibusów (zakup ekologicznych minibusów i budowa myjni ekologicznej),
2.3. Rozwój transportu wodnego (uruchomienie rejsów tramwajem wodnym, budowa przybrzeżnej infrastruktury),
2.4. Modernizacja przystanków autobusowych,
3.6. Strategia rozwoju zrównoważonego transportu,
4.6. Promocja transportu publicznego i rowerowego (szereg imprez organizowanych z inicjatywy CIVITAS lub przy jego współudziale),
5.5. Podniesienie poziomu bezpieczeństwa pieszych i ruchu ulicznego,
6.6. System wypożyczalni rowerów i riksz,
6.7. Rozbudowa tras rowerowych,
8.5. Monitoring ruchu drogowego,
8.6. Rozwój monitoringu ruchu na przejściach w pobliżu szkół.

Celem wymienionych działań było podniesienie świadomości ekologicznej mieszkańców Szczecinka, wzrost atrakcyjności transportu miejskiego i poszerzenie oferty alternatywnych sposobów przemieszczania się. Miało to prowadzić do zmiany zachowań komunikacyjnych użytkowników dróg i bardziej intensywnego wykorzystania ekologicznych środków transportu. Działania miały być przy tym korzystne dla środowiska naturalnego oraz efektywne kosztowo. Mimo nacisku na rezultaty z obszaru ochrony środowiska, zakładany wkład projektu miał być więc, zgodnie z zasadą zrównoważonego rozwoju, odczuwalny we wszystkich trzech obszarach, a zatem również społecznym i ekonomicznym.

4. CIVITAS RENAISSANCE – aspekty środowiskowe, społeczne i ekonomiczne

Zgodnie z celem projektu, działania podjęte w ramach *CIVITAS* miały prowadzić do korzystnych zmian w obszarze ochrony środowiska naturalnego. Wiele z przyjętych mierników realizacji celów dotyczyło więc wykazania ograniczenia negatywnego wpływu na środowisko, jak również zmian w świadomości mieszkańców w kierunku zachowań proekologicznych. W związku z tym podejmowano szereg badań, mających dostarczyć informacji na ten temat.[1] Pomiary obejmowały badanie czynników wskazujących na kondycję środowiska naturalnego, ale też badania opinii publicznej oraz mierniki ekonomiczne dotyczące rentowności podejmowanych przedsięwzięć. Należały do nich, między innymi:

- poziom emisji zanieczyszczeń powietrznych w mieście i nad wodą oraz stężenie pyłów w powietrzu;
- pomiary natężenia hałasu (efektem prac była mapa hałasu dla miasta Szczecinka, będąca podstawą konstruowania strategii zrównoważonego transportu w mieście, której cel określono jako „budowa zrównoważonego, dostępnego i zintegrowanego transportu”[9]. Jej efektem docelowym ma być „odciążenie” obszarów miasta o najintensywniejszym ruchu ulicznym i, co za tym idzie, najwyższym poziomie hałasu);
- ocena jakości infrastruktury transportowej miasta;
- monitoring prędkości i zbieranie danych o liczbie wypadków i kolizji drogowych;
- badania ankietowe opinii publicznej dotyczące świadomości ekologicznej i poziomu akceptacji podejmowanych działań;
- zbieranie informacji o kosztach inwestycyjnych oraz eksploatacyjnych taboru różnych gałęzi transportu miejskiego;
- liczenie rowerów na ścieżkach i przed szkołami.

Osiągnięte efekty świadczą o powodzeniu projektu, zwłaszcza w jego obszarze środowiskowym. Zanotowano spadek emisji zanieczyszczeń do atmosfery, wynikający z użytkowania nowych, ekologicznych minibusów, w miejsce dotychczasowego taboru konwencjonalnego (rysunek 1 i 2). Z czasem można spodziewać się też dalszego ograniczania zanieczyszczeń, czego podstawą jest planowane stopniowe wycofywanie przestarzałych środków komunikacji z użytkowania.

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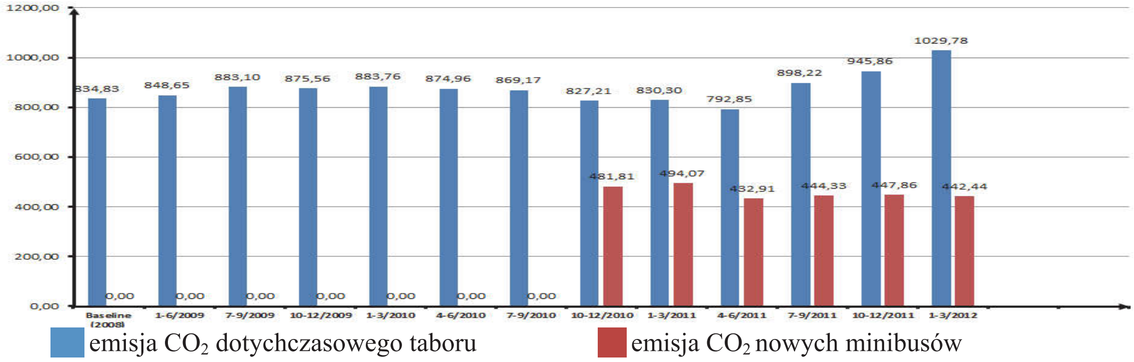
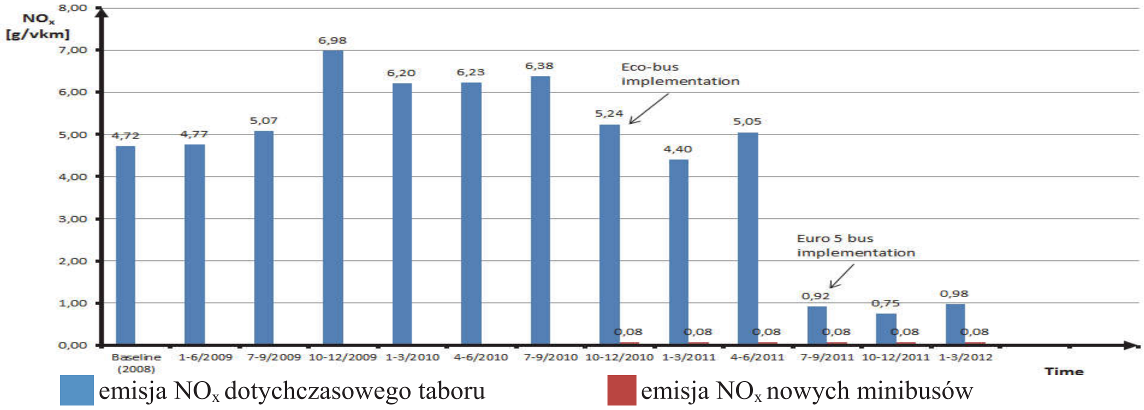
[1] Badania, których wyniki prezentowane są w niniejszym artykule, zostały wykonane przez zespół ewaluacyjny projektu *CIVITAS RENAISSANCE*, kierowany przez prof. T. Heese, składający się z pracowników Politechniki Koszalińskiej, a wśród nich autorki niniejszego artykułu.

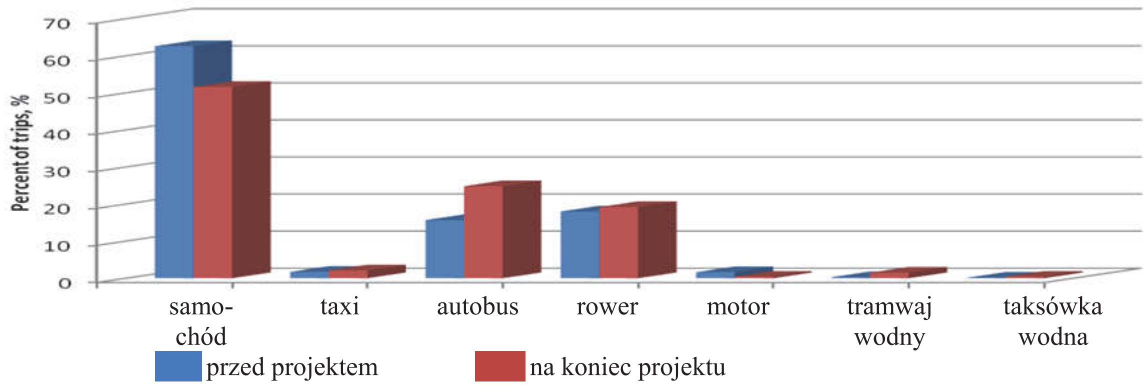


Rys. 1. Emisja CO_2 2008–2012 (średnio w kwartale)
Fig. 1. CO_2 emissions 2008–2012 (in average by quarter)

Aspekty społeczne projektu należy rozpatrywać w dwojakim sensie. Podstawowy kontekst wynikający z jego celów i założeń dotyczy zmiany zachowań transportowych mieszkańców Szczecinka. Tu na znaczące wyniki trzeba zapewne poczekać nieco dłużej, bowiem zmiany w świadomości i utartych schematach postępowania są procesem długotrwałym. Jednak już na koniec projektu zaobserwowano właściwe tendencje w zachowaniach mieszkańców. W ciągu czterech lat jego trwania spadło użytkowanie samochodu prywatnego na rzecz autobusów miejskich i rowerów (rysunek 3).

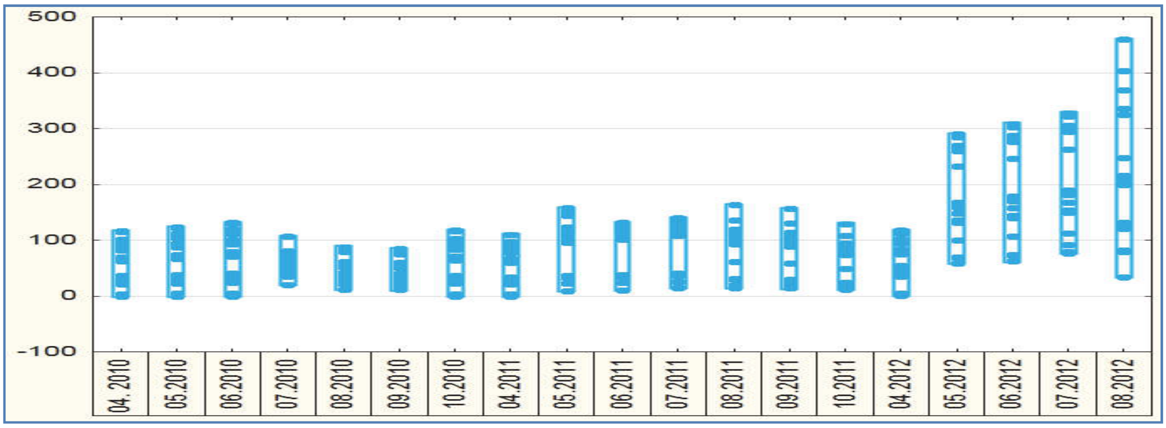


Rys. 2. Emisja NO_x 2008–2012 (średnio w kwartale)
Fig. 2. NO_x emissions 2008–2012 (in average by quarter)

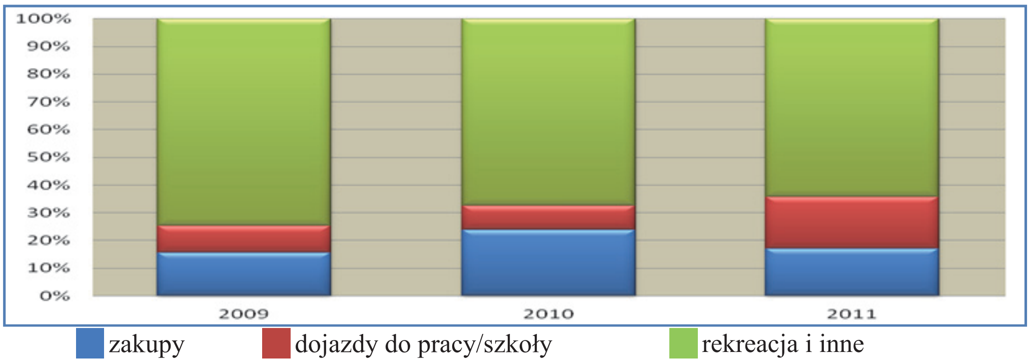


Rys. 3. Wykorzystanie środków transportu
Fig. 3. The use of means of transport

Zanotowano też znaczny wzrost liczby rowerów na ścieżkach (rysunek 4). Za tak duży wzrost popularności jazdy rowerem odpowiada, w przekonaniu badaczy, nie tyle prowadzona akcja edukująca (działanie 4.6.), co raczej istotne zwiększenie długości tras rowerowych w mieście (działanie 6.7.), łącznie o ponad 6 km. Nie bez znaczenia jest też uruchomiona wypożyczalnia rowerów i riksz (działanie 6.6.), oddająca do dyspozycji użytkowników 50 sztuk rowerów w 5-ciu punktach wypożyczeń. Zaobserwowano też zmianę w wykorzystaniu roweru. W dalszym ciągu podstawowym celem jego użytkowania jest rekreacja, jednak proporcje te, w trakcie trwania projektu, stopniowo zmieniały się na korzyść dojazdów do pracy/szkoły oraz po zakupy (rysunek 5).



Rys. 4. Ilość rowerów na ścieżkach w latach 2010–2012 (w miesiącu)
Fig. 4. Number of bikes on the bike paths in the years 2010–2012 (per month)

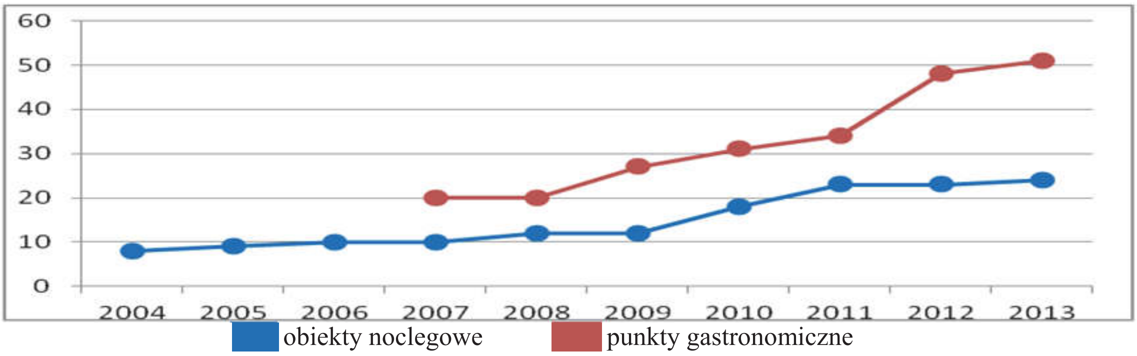


Rys. 5. Procentowe użycie rowerów dla różnych aktywności (w latach)
Fig. 5. Proportional bike use for different activities (in years)

Drugim, ważnym aspektem społecznym zrównoważonego rozwoju, wynikającym z projektu, jest jakość życia mieszkańców Szczecinka. Poza oczywistymi korzyściami, wynikającymi z ograniczania emitowanych do atmosfery zanieczyszczeń, projekt przynosi też korzystne efekty, niejako uboczne, związane ze wzrostem atrakcyjności miasta (dla turystów i mieszkańców). Podjęte w ramach *CIVITAS* inicjatywy korzystnie wpłynęły na estetykę miasta (działania 2.3., 2.4) , wzbogaciły jego infrastrukturę (działania 1.6, 2.3, 6.6, 6.7), podniosły odczuwany poziom bezpieczeństwa mieszkańców (działania 2.4, 8.5, 8.6), dostarczyły wydarzeń pozwalających atrakcyjnie spędzić czas w mieście (działanie 4.6).

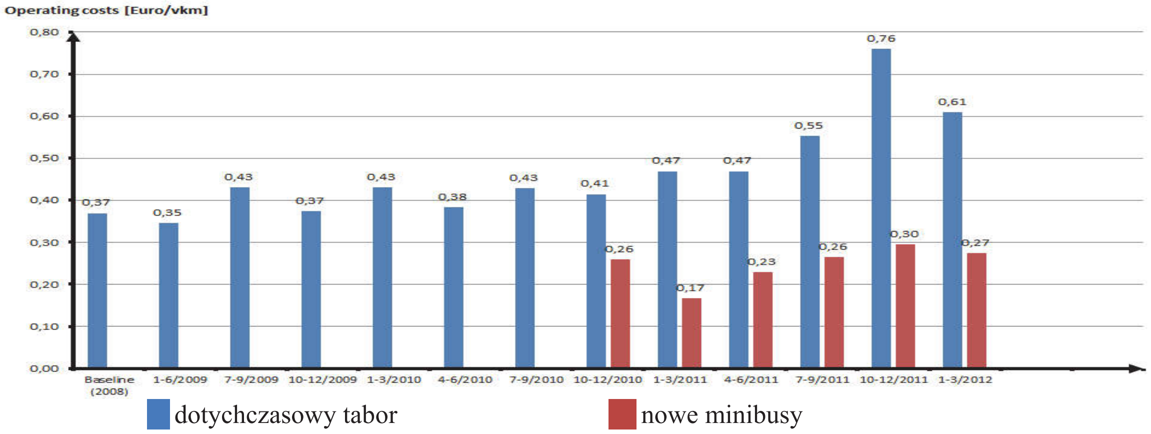
Powyższe rezultaty miały też skutek pośredni: zaobserwowano dynamiczny rozwój rynku usług turystycznych w Szczecinku (rysunek 6). Zapewne nie jest to jedynie efekt działań samego projektu, jednak trudno nie zauważyć, że ów rozwój zbiega się w czasie z okresem jego realizacji. Ponadto, wzrost atrakcyjności miasta przekłada się na wzrost zainteresowania nim wśród turystów, a zatem i ożywienie gospodarcze w tej branży.

Najmniej korzystnie wypadają w projekcie wskaźniki ekonomiczne. Podjęcie nowych działań wiązało się bowiem, także z podniesieniem kosztów eksploatacji. Wzrost kosztów operacyjnych taboru Komunikacji Miejskiej w Szczecinku miał związek z zakupem nowych minibusów (rysunek 7) i uruchomieniem tramwaju wodnego. Pamiętać jednak należy, że równocześnie przyniosło to dodatkowe dochody (rysunek 8), wynikające z większej liczby pasażerów (por. rysunek 3). Wzrost kosztów nie wynika ponadto, li tylko ze zwiększenia liczebności środków komunikacji. Jest też rezultatem starzenia się posiadanych autobusów i stąd rosnących kosztów ich utrzymania (np. usuwanie awarii), co odzwierciedla rysunek 7.

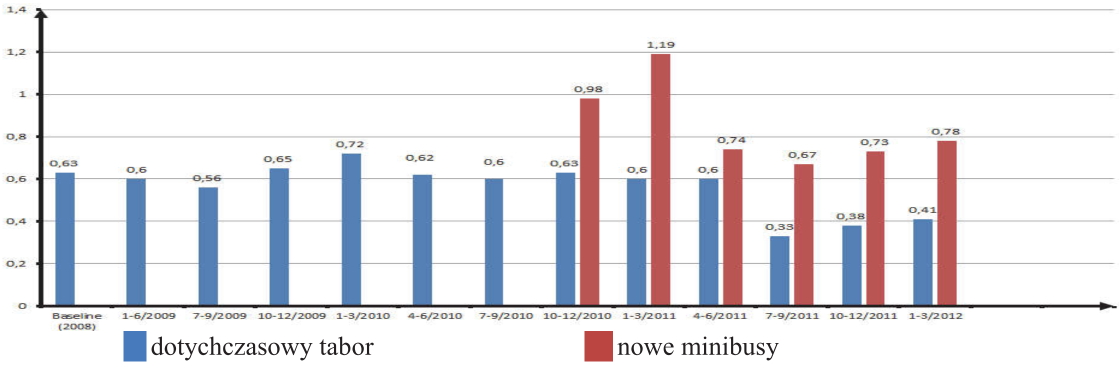


Rys. 6. Liczba obiektów noclegowych i gastronomicznych w Szczecinku
Fig. 6. Number of hotels and restaurants in Szczecinek

Kolejna inwestycja – uruchomienie rejsów tramwajem wodnym, do końca projektu nie osiągnęła rentowności, czego jedną z przyczyn był ich sezonowy (z uwagi na klimat) charakter. Ponadto, tramwaj wodny, w zamiarze autorów projektu, miał pełnić funkcję alternatywnego środka transportu, tymczasem, dla użytkowników pozostał raczej atrakcją turystyczną, z której korzystanie zdeterminowane było nie tylko dogodną porą roku ale i ładną pogodą. Z faktu traktowania go jako atrakcji wynikała też sporadyczność użytkowania tego środka transportu.



Rys. 7. Koszty operacyjne taboru Komunikacji Miejskiej w Szczecinku (średnio w kwartale)
Fig. 7. Operating costs of Komunikacja Miejska Szczecinek (in average by quarter)



Rys. 8. Przychody taboru Komunikacji Miejskiej w Szczecinku (w kwartale)
Fig. 8. Revenues of Komunikacja Miejska Szczecinek (by quarter)

Również wypożyczalnia rowerów i riksz przyniosła nie w pełni zadowalające rezultaty. Po początkowym (w 2009 roku), dużym zainteresowaniu wypożyczeniami i niewielkim wzroście jeszcze w następnym roku, już w 2011 liczba ta spadła. Analizując problem, można wskazać na dwie główne przyczyny takiego stanu. Zapewne przyczyną początkowej dużej popularności wypożyczalni, a następnie jej spadku było zainteresowanie nowością, które z czasem, gdy wypożyczalnia spowszedniała, osłabło. Drugi powód natomiast, dotyczący tylko riksz, to fakt, że, do końca trwania projektu zarządca wypożyczalni – Szczecinecka Lokalna Organizacja Turystyczna borykała się z problemem organizacyjnym udostępniania riksz użytkownikom (sposób zatrudniania kierowców riksz, sposób naliczania i kasowania opłat itd.). Skutkiem tych problemów była czasowa niedostępność riksz w wypożyczalni. Z drugi jednak strony, bardzo duże zainteresowanie rowerami w wypożyczalni przerosło ich podaż i stało się dla władz miasta podstawą decyzji o ich dokupieniu.[2]

5. Podsumowanie

Mimo, że nie wszystkie działania szczecineckiego *CIVITASu* uwieńczone zostały zadowalającymi rezultatami, sam projekt oceniono jako sukces władz miasta i partnerów uczestniczących w jego realizacji. Dodatkowym, nieanalizowanym, ale nie dającym się przecenić efektem

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[2] Z przyczyn obiektywnych, nie można w tym opracowaniu zaprezentować wszystkich danych, zebranych w toku trwania projektu oraz analiz i wyników przeprowadzonych badań. Stąd też intencją autorki było wskazanie kluczowych osiągnięć projektu, istotnych przy tym z uwagi na poruszaną w artykule tematykę.

projektu jest przy tym upowszechnienie wizerunku Szczecinka w Polsce, ale przede wszystkim, wśród krajów uczestniczących w *CIVITAS*. Stał się też, w jakimś sensie, wytyczną dla dalszego rozwoju Szczecinka i kontynuacji jego osiągnięć.

Mimo zakończenia działań, wpływ dokonań *CIVITAS RENAISSANCE* na miasto trwa nadal. Wyraża się on w zachowaniach mieszkańców i roli, jaką odegrał w popularyzacji ekologicznych środków transportu, w decyzjach władz o dalszych kierunkach rozwoju Szczecinka, w nieocenionym wręcz rozgłosie, jaki przyniósł miastu w Polsce i poza jej granicami, we wzroście zadowolenia mieszkańców z miejsca, w którym żyją. Jego rezultaty (zwłaszcza te miękkie) wykraczają daleko poza założone cele projektu, oscylujące, wydawałoby się, wyłącznie wokół zagadnień z zakresu ochrony środowiska, dając tym samym dowód zrównoważonego rozwoju obszaru jego wdrażania.

Literatura

1. *Decyzja nr 1982/2006/WE Parlamentu Europejskiego i Rady z dnia 18 grudnia 2006 r. dotycząca Siódmego Programu Ramowego Wspólnoty Europejskiej w zakresie badań, rozwoju technologicznego i demonstracji (2007–2013).*
2. *Komunikat Komisji. Zrównoważona Europa dla Lepszego Świata: Strategia Zrównoważonego Rozwoju Unii Europejskiej*. Bruksela 2001.
3. *Konstytucja RP*, Dz. U. z 1997 r. Nr 78, poz. 483.
4. Oficjalna strona Programu *CIVITAS*, www.civitas.eu,
5. **Pawłowski L.:** *Rola monitoringu środowiska w realizacji zrównoważonego rozwoju*, Rocznik Ochrona Środowiska (Annual Set the Environment Protection) 13, 2011.
6. *Polska. Narodowe Strategiczne Ramy Odniesienia 2007–2013 wspierające wzrost gospodarczy i zatrudnienie. Narodowa Strategia Spójności.* Ministerstwo Rozwoju Regionalnego. Warszawa 2007.
7. *Polska 2030. Wyzwania rozwojowe.* Kancelaria Prezesa Rady Ministrów. Warszawa 2009.
8. **Stanny M., Czarnecki A.:** *Zrównoważony rozwój obszarów wiejskich Zielonych Płuc Polski. Próba analizy empirycznej*. Instytut Rozwoju Wsi i Rolnictwa PAN, Warszawa 2011.
9. *Strategia Transportowa Miasta Szczecinek na lata 2010–2020*, Szczecinek 2010.
10. Oficjalna strona Komisji Europejskiej. *Strategia Europa 2020*, http://ec.europa.eu/europe2020/europe-2020-in-a-nutshell/priorities/sustainable-growth/index_pl.htm

CIVITAS RENAISSANCE Project in Szczecinek in the Context of Sustainable Development

Abstract

Sustainable development is now a primary objective of the European Union's policies. Its rules, which require consistency of three areas: economy, society and the environment are the basis of EU guidelines for the use of aid programs. One of them is the *CIVITAS* program, along with the component *RENAISSANCE*, in which participated town Szczecinek. The program was implemented in 10 measures, including the purchase of eco minibuses and introduction of ecological car wash, launch of waterbus cruises, the construction of waterside infrastructure, modernization of public bus stops, launch of bike and rickshaws rental, expansion of bike paths, improvement of pedestrians and traffic safety, promotion of environmentally friendly transport behaviour and the creation of sustainable transport development strategy.

The project had the positive results in all three areas of sustainable development (but not every activity reached an expected level). As the result of the environment protection action the noise map was produced, which formed the basis for constructing a sustainable transport strategy for the town. Another effect of the implemented environmental program is decreased pollution emission resulting from the use of new minibuses and eco car wash. Further reduction of emissions is expected in the future on account of changes in residents transport habits – by moving away from car use to public transport and bicycles. It is also the social effect of the project. Already towards the end of the project, reduced use of private cars in favor of more environment friendly transport including significant increase in the number of bikes on the bike paths, was noticed. There was also recorded a change in the use of bicycles - increased role of cycling in commuting to work, school and when shopping. The second effect of the project is improvement of life quality in Szczecinek. These is due to reduced pollution levels and also rise in the attractiveness of the town, which is a consequence of the enhanced esthetic of the town, upgraded infrastructure, improved residents perception of security and boosted public entertainment offers providing options for attractive outings.

The economic indicators have the lowest grades in the project. The reason for the above is fact that undertaken developments required an increase in operating costs like expansion of the minibuses fleet or launching the waterbus cruises. However, at the same time owing to greater numbers of passengers additional revenues were recorded. As yet, waterbus has not reached break-even due to its seasonality and approach to it as a tourist attraction rather than means of transport. Also, bicycles and rickshaws rental outcome was not fully satisfactory. After the initial high interest, in the third year of the project decline was noted. However, one of the reasons for decline is the management problems within Rental Company.

The results of the project have also additional effects: publicity of Szczecinek in Poland and Europe and the impact on local government decisions regarding the further development directions of the town. It goes far beyond the project's goals concerning environmental protection, thereby proving sustainable development of implementation area.

Słowa kluczowe:
zrównoważony rozwój, transport w miastach, *CIVITAS*

Keywords:
sustainable development, transport in cities, *CIVITAS*

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Projektowane zalesienia w gminie Tarnowo Podgórne w świetle koncepcji korytarzy ekologicznych

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1. Wstęp

Planowanie przestrzenne może być rozpatrywane jako jeden z instrumentów ochrony środowiska, zwłaszcza w świetle intensywnego rozwoju infrastrukturalnego i społeczno-gospodarczego. Racjonalne zagospodarowanie przestrzeni jest niezbędne dla zapewnienia właściwej dynamiki rozwoju w kontekście potrzeb człowieka i potrzeb środowiska naturalnego. Coraz częściej zauważa się, że racjonalne dla rozwoju korzystnych zależności w układzie człowiek – środowisko jest przeznaczanie specjalnych terenów dla potrzeb przyrody. Doskonałym przykładem takich działań jest powiększanie areału kompleksów leśnych – zalesienie ponad 600 tys. ha, (Programu Zwiększania Lesistości Powiatu Poznańskiego, 2007). Mimo podejmowania korzystnych działań w ujęciu planowania przestrzennego, negatywnym i często pomijanym skutkiem dynamicznego rozwoju jest postępująca fragmentacja środowiska naturalnego. Izolacja obszarów cennych przyrodniczo uruchamia procesy stanowiące poważne zagrożenie dla różnorodności biologicznej i stabilności ekosystemów. Istotną kwestią jest nie tylko tworzenie dokumentów planistycznych wskazujących przestrzenne rozmieszczenie obszarów cennych przyrodniczo i preferowanych pod zalesienia, ale także zadbanie o niepogarszanie stanu siedlisk przyrodniczych oraz stworzenie realnych możliwości utrzymania integralności i powiązań między poszczególnymi fragmentami tych siedlisk. Doskonałym instrumentem, pożądanym z punktu widzenia właściwego kształtowania przestrzeni i krajobrazu, zapewniającego przepływ materii organicznej i nieorganicznej między różnymi biotopami, rozmieszczonymi najczęściej w sposób mozaikowy pośród ośrodków bytności człowieka jest koncepcja sieci korytarzy ekologicznych. Korytarze ekologiczne są to struktury przestrzenne, które umożliwiają rozprzestrzenianie się gatunków pomiędzy obszarami węzłowymi oraz terenami do nich przylegającymi [3]. Połączenia między węzłami przyrodniczymi powinny być wdrożone w procesy planowania przestrzennego z uwzględnieniem ich ochrony prawnej i administracyjnej co umożliwi zachowanie łączności ekologicznej między siedliskami w skali regionu, kraju i Europy [7].

2. Cel i zakres pracy

Stworzenie przestrzennego modelu korytarzy ekologicznych z uwzględnieniem istniejących i projektowanych obszarów leśnych było częścią autorskiego projektu koncepcji zalesień dla gminy Tarnowo Podgórne przedstawionej w pracy Zydronia i Bobera [10].

Celem pracy było opracowanie propozycji utworzenia sieci korytarzy wraz ze wskazaniem lokalizacji węzłów poprzez rozpoznanie istniejących oraz projektowanych w świetle koncepcji zalesień i uwarunkowań środowiskowych w gminie Tarnowo Podgórne.

Badaniami objęto obszar gminy Tarnowo Podgórne z uwzględnieniem przyległych kompleksów leśnych.

3. Metodyka i materiał badawczy

Podczas prac wykorzystano materiały źródłowe pozyskane z Wydziału Zagospodarowania Przestrzennego gminy Tarnowo Podgórne oraz Regionalnej Dyrekcji Lasów Państwowych w Poznaniu [A2, A5].

Analiza zaprojektowanej w systemie informacji przestrzennej (SIP) programu ArcGIS (pakiet ArcView SU 9.3, nr lic. 418533504) koncepcji zalesień, przedstawionej w postaci warstw obszarów o zdefiniowanych atrybutach środowiskowych (uwarunkowaniach przyrodniczych) oraz rekomendowanych do zalesień na podstawie wytycznych w zgromadzonych dokumentach [A1, A4, A6, A7] pozwoliła na wyznaczenie sieci węzłów i korytarzy ekologicznych poprzez zastosowanie wskazań praktycznych [5] oraz metody ilościowej i jakościowej sieci połączeń ekologicznych. Prace pozwoliły na określenie stopnia funkcjonalności struktury powiązań oraz stabilności ekologicznej wybranego fragmentu krajobrazu, w tym wypadku obszaru gminy Tarnowo Podgórne.

Dla oceny modelu sieci wykorzystano podstawowe wskaźniki stosowane w metodzie oceny stabilności fragmentu krajobrazu według kryterium sieci połączeń.

Wskaźnik α – przyjmujący wartość z przedziału (0,1), określający stosunek między rzeczywistą a maksymalnie możliwą liczbą pętli w modelu sieci połączeń. Wskaźnik β – przyjmujący wartość z przedziału (0,3), określający stopień rozczłonkowania węzłów w modelu oraz ilość pętli w badanym obszarze. Wskaźnik γ – przyjmujący wartość z przedziału (0,1), określający stosunek liczby ciągów ekologicznych do maksymalnej ich liczby, która mogła by wystąpić w układzie o tej samej liczbie węzłów ekologicznych.

Na podstawie opracowanej koncepcji oraz uwarunkowań przyrodniczych gminy wykonany został schematyczny rysunek przedstawiający rozmieszczenie kompleksów określonych mianem leśnych węzłów ekologicznych oraz wyznaczenie możliwych połączeń między nimi pod postacią leśnych korytarzy ekologicznych.

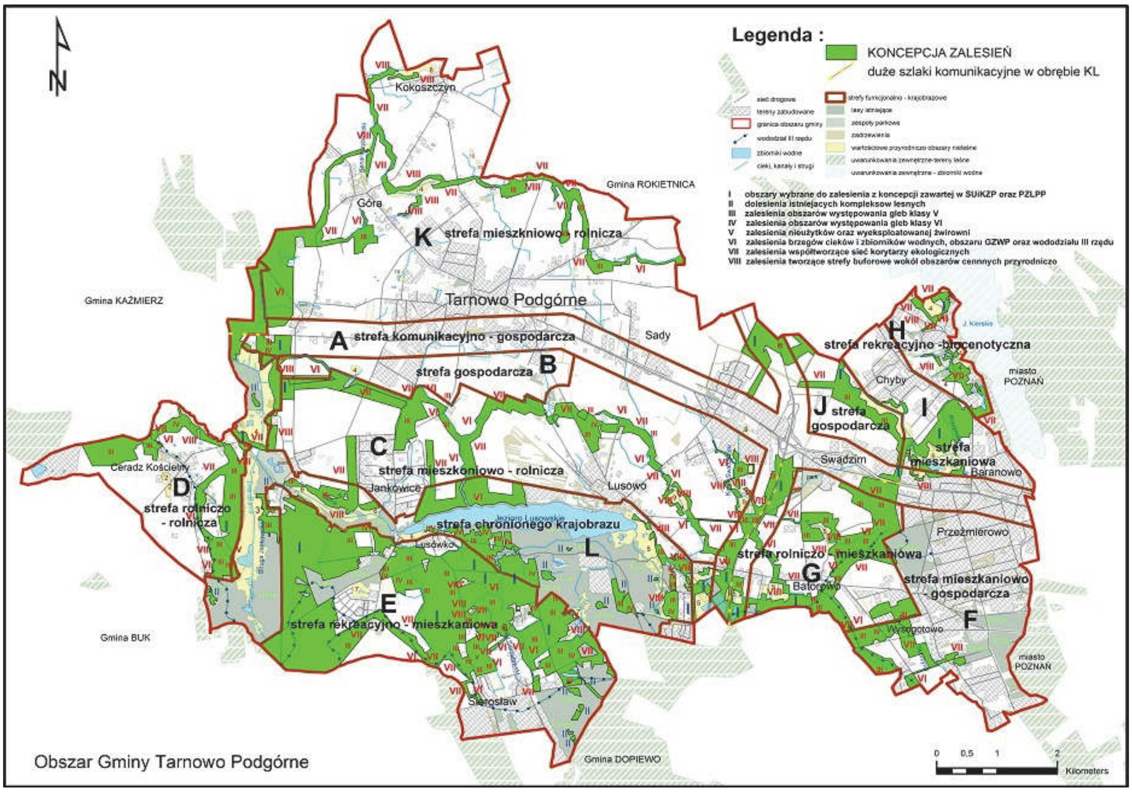
Na podstawie zgromadzonych informacji w programie graficznym GIMP (GIMP 2.Ink) opracowany został graficzny schemat modelu węzłów ekologicznych wraz z siecią połączeń korytarzy ekologicznych.

4. Charakterystyka obszaru badań

Gmina Tarnowo Podgórne zlokalizowana jest w środkowej części województwa wielkopolskiego, a jej obszar zajmuje powierzchnię 101,4 km^2. Gmina graniczy od wschodu z miastem Poznaniem oraz z gminami Dopiewo, Rokietnica, Buk i Kaźmierz. Wraz z innymi gminami powiatu poznańskiego gmina Tarnowo Podgórne tworzy obszar metropolitarny miasta Poznania, co przejawia się w modelu zagospodarowania przestrzeni i jego funkcjach [10].

Lasy w obszarze gminy stanowią powierzchnię około 792,2 ha (7,8% powierzchni gminy). Zalesienia ujęte w projektowanej koncepcji stanowią powierzchnię około 2 324, 9 ha (22,9% pow. gminy). Dobór obszarów wskazanych do zalesienia jest efektem zestawienia uwarunkowań przyrodniczych takich jak: występowanie gleb najsłabszych, warunki hydrograficzne, występowanie obszarów przyrodniczo cennych, dolesień istniejących kompleksów, z wytycznymi zawartymi w odpowiednich dokumentach. Zgodnie z wytycznymi w sprawie ustalenia granicy rolno leśnej 19,03% całości koncepcji (ok. 442,43 ha) to kompleksy leśne zaplanowane w celu utworzenia stabilnej sieci połączeń ekologicznych w strukturze lasów gminy [10].

Lasy istniejące oraz projektowane obejmują łącznie obszar ok. 3117 ha co stanowi wzrost lesistości do poziomu 30,7% powierzchni gminy (rys. 1).

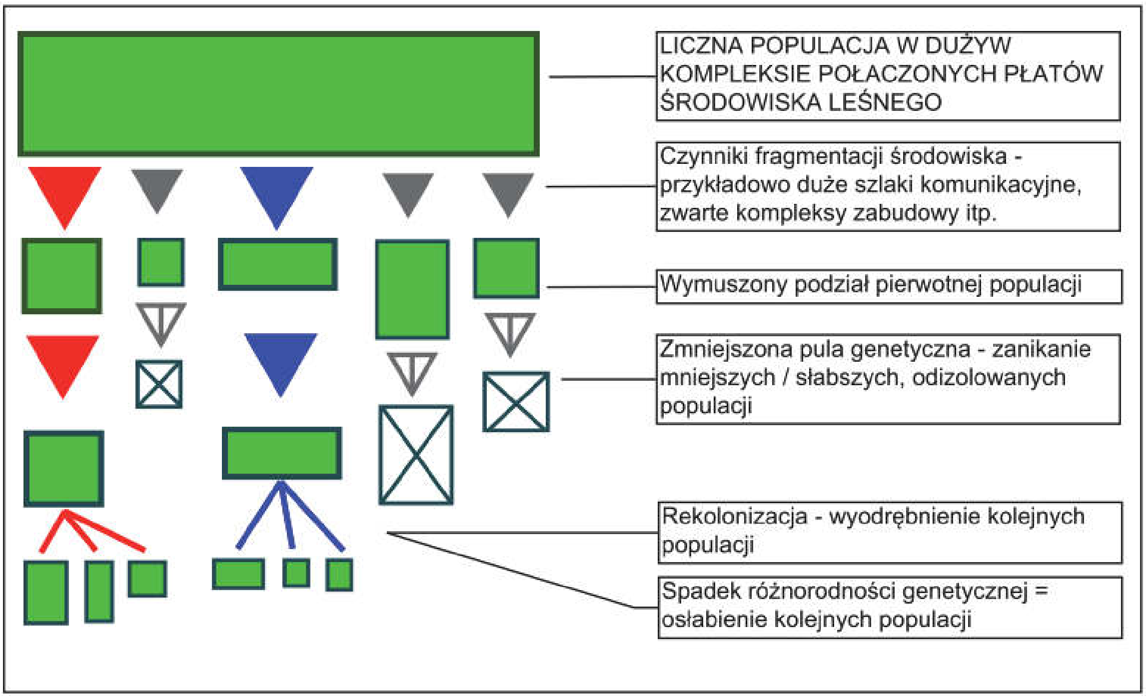


Rys. 1. Koncepcja zalesień dla gminy Tarnowo Podgórne wraz z istniejącym układem przestrzennym
Fig. 1. The concept of Tarnowo Podgorne afforestation together with the existing spatial layout

5. Wyniki badań

5.1. Problematyka fragmentacji środowiska leśnego na terenie gminy Tarnowo Podgórne

Istotnym aspektem dla zapewnienia prawidłowego funkcjonowania złożonego ekosystemu leśnego jest zapewnienie odpowiednich dla niego warunków przestrzennych. Najczęściej w ujęciu planowania przestrzennego przejawem tego jest względna ochrona kompleksów istniejących oraz sporadyczne dolesienia izolowanych areałów. Niestety pomijane są aspekty łączności ekologicznej [6].



Rys. 2. Schematyczny model wpływu fragmentacji środowiska na zanikanie I zmniejszenie różnorodności genetycznej wśród modelowej populacji zwierząt leśnych
Fig. 2. A schematic model of the impact of habitat fragmentation on the disappearance and reduction of genetic diversity among populations of the model forest animals

Spośród zagrożeń spowodowanych działalnością ludzką najgroźniejsze dla występowania i liczebności zwierząt jest zabudowa i fragmentacja siedlisk [9]. Fragmentacja i izolacja środowisk leśnych ma nie tylko niekorzystny wpływ na liczebność ale także na różnorodność genetyczną i zdolności przystosowawcze populacji roślin, zwierząt i grzybów co przekłada się bezpośrednio na spadek różnorodności biologicznej i możliwości przetrwania gatunku w obrębie biotopu leśnego. Przykład populacji gatunku zwierząt leśnych, dla których pojawiające się w przestrzeni niekorzystne czynniki fragmentacji i skutecznej izolacji ukazuje mechanizm stopniowego zanikania gatunku na danym obszarze w kontekście spadku różnorodności genetycznej. Brak wymiany genów między osobnikami tego samego gatunku w odizolowanych płatach leśnych przyczynia się wraz z czynnikami losowymi, takimi jak choroby czy odstrzał do osłabienia i zanikania populacji. Nawet w przypadku wystąpienia zjawiska rekolonizacji – ponownego zasiedlania izolowanych kompleksów przez przedstawicieli populacji, które przetrwały zmiany przestrzenne – ogólny poziom zmienności genetycznej może okazać się w przyszłości zbyt niski dla zapewnienia przetrwania na danym obszarze (rys. 2) [6].

W gminie Tarnowo Podgórne największe kompleksy leśne położone są w części południowo-zachodniej (ok. 630 ha) i południowo-wschodniej (ok. 126,6 ha). Pozostałe obszary leśne występują pod postacią małych, rozrzuconych mozaikowo płatów w całej gminie (łącznie około 39,5 ha). Część centralna oraz północna odznaczają się zerową lesistością [10].

Dodatkowym zagrożeniem sprzyjającym fragmentacji środowiska leśnego jest występowanie dużych stref funkcjonalno-przestrzennych przeznaczonych pod terenochłonne inwestycje przemysłowe i gospodarcze – strefa B, J oraz zwarte kompleksy różnego rodzaju zabudowy mieszkaniowej w strefach I, F, C, stanowiących duże utrudnienie dla przepływu informacji genetycznej miedzy izolowanymi płatami lasu (rys. 1).

Szczególnie niesprzyjający jest układ komunikacyjny w gminie – strefa A. Dwa duże szlaki komunikacyjne dzielą jej obszar na cztery części – ze wschodu na zachód jest to droga krajowa nr 92: Terespol – Warszawa – Świecko oraz Zachodnia Obwodnica Poznania: Złotkowo – autostrada A2, przecinająca gminę z północy na południe. Oba szlaki stanowią poważne ograniczenie w funkcjonowaniu projektowanych korytarzy ekologicznych. Drogi o dwóch pasach ruchu w każdym z kierunków, odizolowane barierkami i ekranami akustycznymi w niektórych miejscach stanowią barierę zaporową dla większości gatunków zwierząt, dla pozostałych są zagrożeniem sprzyjającym wzrostowi śmiertelności w wyniku kolizji z pojazdami [8]. Obecny układ lasów sprzyja występowaniu negatywnych reperkusji dla populacji leśnych w izolowanych enklawach związanych bezpośrednio z fragmentacją środowiska przyrodniczego (rys. 1).

5.2. Analiza przestrzenna projektowanej sieci korytarzy ekologicznych

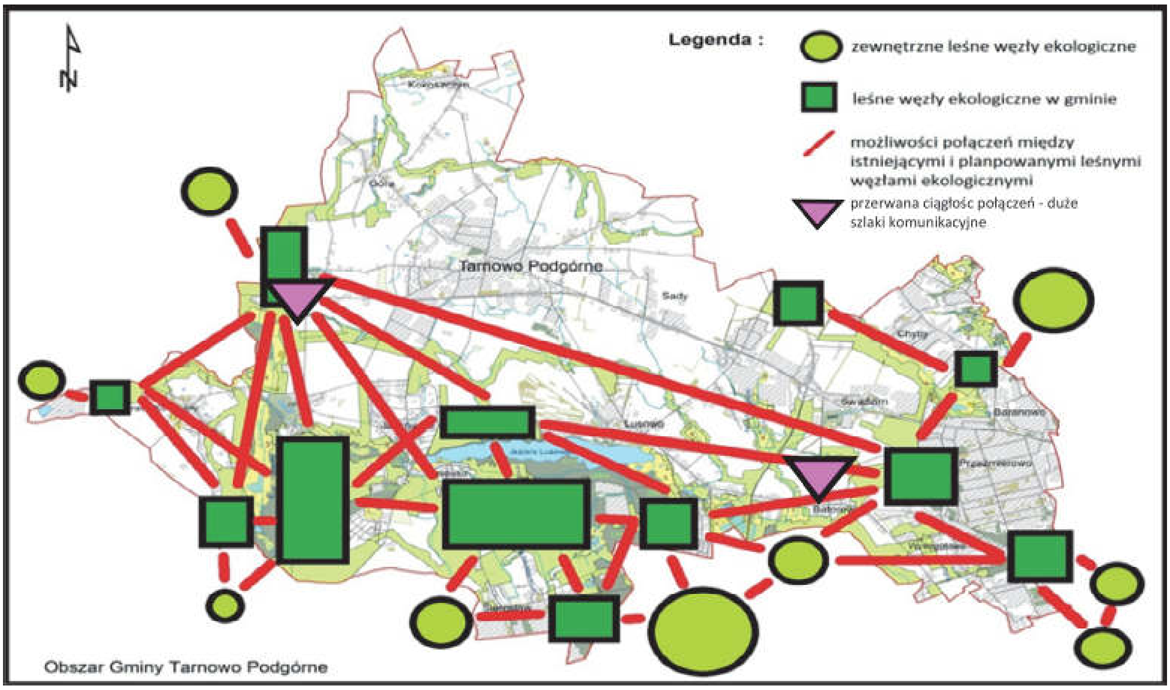
Dla zachowania ciągów ekologicznych umożliwiających migrację zwierząt, ochrony istniejących obszarów cennych przyrodniczo, wprowadza się obszary zapewniające łączność poprzez przestrzenne i pasmowe korytarze ekologiczne na zasadzie hierarchicznej o znaczeniu krajowym (k), regionalnym (r), i lokalnym (l), [2]. Korytarze ekologiczne jako trasy przemieszczania materii, energii oraz informacji biologicznej między węzłami ekologicznymi są istotnym elementem opracowanej koncepcji. Najważniejszym zagrożeniem dla funkcjonowania korytarzy ekologicznych jest przerywanie ich ciągłości przez infrastrukturę liniową (drogi i linie kolejowe) oraz wylesienie powierzchni i rozwój obszarów zabudowanych, a przede wszystkim chaotyczna zabudowa terenów wiejskich [3]. Ujęcie układu płatów i korytarzy ekologicznych pod względem krajobrazowym jest istotne dla zapewnienia prawidłowego funkcjonowania środowiska przyrodniczego w aspekcie stosunków wodnych, klimatycznych i geodynamicznych [1]. Układ przestrzenny zalesień istniejących oraz projektowanych tworzy w obszarze gminy sieć korytarzy ekologicznych. Dla prawidłowego funkcjonowania sieci ciągów ekologicznych istnieje konieczność zlikwidowania najpoważniejszych barier antropogenicznych. Najbardziej znaczącymi ogranicznikami w ciągłości sieci korytarzy ekologicznych są duże ciągi komunikacyjne przebiegające w obrębie istniejących lasów i projektowanych zalesień. W projektowanym układzie korytarzy ekologicznych wskazano miejsca nieciągłości, spowodowane przebiegiem największych szlaków drogowych, w obrębie których powinna powstać stosowna infrastruktura przejść dla zwierząt, zgodna z właściwymi wytycznymi, umożliwiająca drożność sieci powiązań ekologicznych w obszarze gminy (rys. 3).

Zgodnie z metodą ilościowej i jakościowej oceny sieci połączeń ekologicznych określającej stopień funkcjonalności struktury powiązań oraz stabilność ekologiczną badanego obszaru obliczono [4], że współczynnik α określający kryterium stosunku określonych w modelu pętli wynikających z połączeń do ich maksymalnej możliwej ilości we wskazanym układzie obliczony według wzoru:

$$\frac{\mathrm{E} - \mathrm{V} + 1}{2\mathrm{V} - 5} = \frac{17}{37} = 0{,}46 \qquad (1)$$

gdzie:
V – 21 (liczba węzłów),
E – 37 (liczba połączeń),

jest równy wartości liczbowej 0,46, co oznacza, że zaprojektowane połączenia realizują niemal połowę wszystkich możliwości. Im wartość współczynnika większa tym więcej jest ścieżek między płatami.



Rys. 3. Schemat struktury sieci korytarzy ekologicznych w świetle opracowanej koncepcji zalesień
Fig. 3. Schematic structure of the network of ecological corridors in the light of the concept developed afforestation

Trzeci brany pod uwagę wskaźnik γ, określający stosunek liczby ciągów ekologicznych do maksymalnej ich liczby, która mogła by wystąpić w układzie o tej samej liczbie węzłów, obliczony według wzoru:

$$\frac{E}{3(V-2)} = \frac{37}{57} = 0{,}65 \qquad (2)$$

gdzie:
V – 21 (liczba węzłów),
E – 37 (liczba połączeń)

wyrażony wielkością na poziomie wartości liczbowej 0,65 oznacza, że w planowanej sieci korytarzy ekologicznych wykorzystana została ponad połowa wszystkich możliwości połączeń między węzłami. Im większa wartość wskaźnika tym długość poszczególnych połączeń między płatowych jest krótsza.

6. Podsumowanie

Dla zapewnienia prawidłowego funkcjonowania przestrzeni w układzie środowisko – człowiek istnieje potrzeba, oprócz zabezpieczenia areałów ekosystemów zbliżonych do naturalnych, konieczność uwzględnienia łączności biologicznej między kompleksami leśnymi. Doskonałym instrumentem dla tych celów jest wdrażanie w koncepcjach zagospodarowania przestrzennego korytarzy ekologicznych, które zapewniają możliwość migracji zwierzyny i wymianę genów pomiędzy populacjami. Prawidłowo funkcjonująca sieć powiązań ekologicznych przeciwdziała zmniejszeniu różnorodności genetycznej wśród metapopulacji poszczególnych gatunków leśnych a co za tym idzie przeciwdziała obniżeniu różnorodności biologicznej i stabilizuje ekosystemy leśne. Wprowadzenie korytarzy ekologicznych wpływa też korzystnie na różnorodność krajobrazu. Analiza zaprojektowanej struktury korytarzy ekologicznych w kontekście metody ilościowej i jakościowej fragmentu krajobrazu wskazuje, że wszystkie badane wskaźniki mieszczą się w wyznaczonych w metodzie przedziałach, a ich interpretacja dowodzi jednoznacznie, że zaprojektowana sieć korytarzy ekologicznych będzie spełniać swoje funkcje przyrodnicze i krajobrazowe w sposób wystarczający oraz stabilny.

Najważniejszym ograniczeniem w funkcjonowaniu projektowanych korytarzy ekologicznych w gminie Tarnowo Podgórne jest przerywanie ich ciągłości przez infrastrukturę liniową (drogi i linie kolejowe) oraz wylesienie powierzchni i rozwój obszarów zabudowanych, a przede wszystkim chaotyczna zabudowa terenów wiejskich.

Literatura

Akty prawne i dokumenty

A1. Krajowy Program Zwiększania Lesistości – Aktualizacja 2003, Warszawa, maj 2003 r.

A2. Opracowanie ekofizjograficzne podstawowe dla gminy Tarnowo Podgórne, Poznań 2004

A3. Plan Urządzania Lasu Nadleśnictwa Konstantynowo na okres od 1 stycznia 2008 r. do 31 grudnia 2017 r., Biuro Urządzania Lasu i Geodezji Leśnej, Poznań 2008 r.

A4. Program Zwiększania Lesistości Powiatu Poznańskiego, Warszawa, grudzień 2007

A5. Studium Uwarunkowań i Kierunków Zagospodarowania Przestrzennego Gminy Tarnowo Podgórne, Tarnowo Podgórne, 2011 r.

A6. Ustawa o przeznaczeniu gruntów rolnych do zalesienia z dnia 8 czerwca 2001 r.

A7. Wytyczne dotyczące ustalania granicy rolno-leśnej, 2003 r.

Książki i artykuły

1. **Ciszewska A., Giedych R.:** *Możliwości i ograniczenia zastosowania koncepcji płatów i korytarzy ekologicznych w planowaniu miejscowym*. Problemy Ekologii Krajobrazu, tom XVI, Wydawnictwo SGGW, Warszawa 2004.
2. **Czerniak A., Górna M.:** *Restytucja korytarzy ekologicznych w Wielkopolskim Parku Narodowym*. Zeszyty Naukowe nr 23 Wydziału Budownictwa i Inżynierii Środowiska Politechniki Koszalińskiej, Koszalin – Darłówko 2007.
3. **Czerniak A., Górna M.:** *Funkcjonalność przejść górnych dla zwierząt*. Bogucki Wydawnictwo Naukowe, Poznań 2010.
4. **Obidziński A., Żelazo J.:** *Inwentaryzacja i waloryzacja przyrodnicza*. Wydawnictwo SGGW, Warszawa 2007.
5. **Skolud P.:** *Zalesienia gruntów rolnych i nieużytków – poradnik właściciela*. Centrum Informacyjne Lasów Państwowych, Warszawa 2006.
6. **Jędrzejewski W., Ławerszczuk D.:** *Ochrona łączności ekologicznej w Polsce.* Materiały konferencji międzynarodowej „Wdrażanie korytarzy ekologicznych w Polsce”, Zakład badania ssaków PAN, Białowieża 2009.
7. **Kistowski M., Pchanek M.:** *Natura 2000 w planowaniu przestrzennym – rola korytarzy ekologicznych*. Wydawnictwo Ministerstwa Środowiska, Warszawa 2009.
8. **Kurek R.:** *Ochrona dziko żyjących zwierząt przy inwestycjach drogowych w Polsce*, Bystra 2008.
9. **Okarma H., Tomek A.:** *Łowiectwo*. Wydawnictwo Edukacyjno Naukowe H_2O, Kraków 2008.
10. **Zydroń A., Bober Ł.:** *Opracowanie koncepcji zalesień dla gminy Tarnowo Podgórne.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 2942–2961 (2013).

Concept of Ecological Corridors in the Light of Afforestation Planned for the Tarnowo Podgorne Municipality

Abstract

An important element to be taken into account when designing the afforestation of Tarnowo Podgorne municipality was to create a model of ecological corridors, taking into account existing and planned natural forest areas. Analysis of the concept of afforestation and conditions allowed to determine the existing network nodes and corridors through the use of quantitative and qualitative methods of organic interconnection network and determine the degree of functional chain structure and ecological stability in the community. For the evaluation of the network model used in the basic indicators used in the method of assessing the stability of part of the landscape in order of network connections. Designed structure of ecological corridors indicates that all test indicators are within the ranges set by the method, and their interpretation proves unequivocally that the designed network will fulfill their natural functions. The proposed concept is characterized by the attention to the behavior of spatial order with regard to the functionality of other forms of land use space. Although the community is not in any formal way affiliated with the Nature 2000 network the structure of ecological corridors is the result of the development of the concept shows a high degree of functionality and stability as part of the assessment of the stability of the landscape in order of network connections.

Słowa kluczowe:
planowanie przestrzenne, obszary ochrony przyrody, gmina

Keywords:
spatial planning, nature conservation areas, commune

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Zrównoważony rozwój krajów Unii Europejskiej. Typologia krajów w kontekście Strategii Europa 2020

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1. Wstęp

Kraje Unii Europejskiej od lat dążą do przekształcenia gospodarki unijnej w najbardziej konkurencyjną, opartą na zasobach wiedzy, gospodarkę na świecie [4,5,9,10,12]. Podkreśla się, że dalszy rozwój społeczno-gospodarczy krajów europejskich (ale i nie tylko) może być uzyskany przez przyszłe pokolenia tylko wtedy, gdy zostanie zachowana koherencja pomiędzy trzema składowymi rozwoju tj. środowiskiem naturalnym, społeczeństwem i gospodarką [6]. To „ewolucyjne" podejście do czynnika środowiskowego w procesach gospodarowania wynika z faktu, że globalny rynek wykorzystuje globalne środowisko naturalne i rozwój zrównoważony jest warunkiem niezbędnym nowego paradygmatu w ekonomii [11].

Poszukująca nowoczesnych czynników wzrostu gospodarczego, Europa, stymulujących jej konkurencyjność i innowacyjność, aktualnie wykorzystuje koncepcję rozwoju, pozwalającego odblokować jej potencjał rozwojowy. Kluczowym czynnikiem sprawczym rozwoju społeczno-gospodarczego w tym modelu gospodarki są czynniki związane z zasobem wiedzy, wśród których w szczególności wymienia się inwestycje w innowacje, rozwój zasobów ludzkich i wysokie technologie, nakłady na sferę badawczo-rozwojową oraz współpracę gospodarki z ośrodkami naukowo-badawczymi [3,1,2,7]. Obok inteligentnego wzrostu (*ang. smart growth*), opartego na wiedzy i innowacjach oraz działań sprzyjających włączeniu społecznemu (*ang. inclusive growth*), model ten promuje wzrost zrównoważony (*ang. sustainable growth*), czyli zakłada transformację w kierunku gospodarki niskoemisyjnej oraz efektywne korzystanie z zasobów naturalnych, promuje efektywność energetyczną i wykorzystanie odnawialnych źródeł energii [13].

Powyższe priorytety rozwojowe stworzyły podstawę do podjętej w niniejszym artykule typologii i klasyfikacji krajów europejskich w oparciu o syntetyczny wskaźnik zrównoważonego rozwoju oszacowany na podstawie wybranych cech opisujących zmiany w filarach: środowisko-gospodarka –społeczeństwo. Filary te stanowią ramy programu reform dla krajów europejskich – Strategia Europa 2020 [14]. W artykule podjęto próbę uzyskania odpowiedzi na pytanie o kierunki zmian w poziomie zrównoważonego rozwoju w krajach europejskich zachodzących na przestrzeni lat 2004–2012, a także zidentyfikowania czynników determinujących uzyskiwany przez poszczególne kraje poziom zrównoważonego rozwoju. Do weryfikacji przyjęto założenie a zmniejszającym się dystansie rozwojowym pomiędzy krajami UE oraz o czynnikach ekonomicznych, jako silnie determinujących poziom zrównoważonego rozwoju.

2. Metoda i zakres danych

W badaniach międzynarodowych stosowane są różne wskaźniki i mierniki wykorzystywane do pomiaru i oceny zróżnicowania w rozwoju społeczno-gospodarczego krajów. Najbardziej popularne, aczkolwiek niedoskonałe w swojej konstrukcji to PKB, a także wykorzystywany do oceny rozwoju społecznego HDI. W niniejszym artykule podjęto próbę stworzenia systetycznego wskaźnika, który bazuje na wskaźnikach (cechach) aktualnie wytypowanych przez Komisję Europejską do oceny zrównoważonego rozwoju krajów UE, ujętych w programie Strategia Europa 2020. Uwzględnia on w swojej konstrukcji trzy filary: gospodarkę, społeczeństwo oraz czynnik, często pomijany w innych analizach porównawczych, mianowicie czynnik środowiskowy.

W celu określenia poziomu rozwoju osiągniętego przez kraje UE w ramach strategii Europa 2020[1] zastosowano porządkowanie liniowe w oparciu o metodę sum standaryzowanych wartości oraz w efekcie przyporządkowano każdemu z krajów względny wskaźnik poziomu rozwoju

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[1] Badaniem objęto 29 krajów europejskich, wybór państw do analizy uwarunkowany był dostępnością danych. Spośród analizowanych 29 krajów europejskich Norwegia nie jest członkiem UE. Chorwacja w momencie zbierania danych nie była członkiem UE.

opisujący łączny stopień realizacji założeń strategii Europa. Polega ona na sumowaniu zestandaryzowanych uprzednio wartości uwzględnionych cech, wśród których cechy będące destymulantami przekształcono, mnożąc ich wartości przez -1. Zmienną syntetyczną opisującą ogólny poziom zaawansowania krajów w realizacji założeń strategii Europa 2020 przekształcono wg następującej formuły [8]:

$$W_i = \frac{\sum_{j=1}^{k} z_{ij}}{\sum_{j=1}^{k} \max_i \{z_{ij}\}} \tag{1}$$

gdzie:

$z_{ij} = x_{ij} + \left| \min_i \{x_{ij}\} \right|$ oraz x_{ij} *oznacza wartość cechy j dla kraju o numerze i.*

Otrzymano w ten sposób wskaźnik względnego poziomu rozwoju. Przyjmuje on wartości z przedziału <0,1>, przy czym większa wartość oznacza obiekt lepszy pod względem kryterium ogólnego.

Klasyfikacji krajów dokonano w oparciu o hierarchiczną procedurę aglomeracyjną Warda opisaną za pomocą następującego schematu [8]:

1. Każdy obiekt traktuje się jako grupę jednoelementową.
2. W macierzy odległości wyszukuje się odległości minimalnej.
3. Najbliższe obiekty łączy się w jedną grupę dwuelementową.
4. Wyznacza się odległości nowo utworzonej grupy od wszystkich pozostałych grup.
5. Powtarza się kroki 2–5 aż do momentu, gdy wszystkie obiekty utworzą jedną grupę.

W metodzie Warda, będącej jednym z wariantów metody hierarchicznego grupowania, odległość między grupami obiektów wyznacza się wg następującego wzoru [8]:

$$d_{ir} = \frac{N_i + N_p}{N_i + N_r} d_{ip} + \frac{N_i + N_q}{N_i + N_r} d_{iq} - \frac{N_i}{N_i + N_r} d_{pq} \tag{2}$$

gdzie:

$d_{pq} = \min_{i,j} \{d_{ij}\}$,

d_{ij} – odległości euklidesowe między klasyfikowanymi obiektami,

d_{ip} – odległości między jedną z dwóch grup łączonych na danym etapie procedury zawierającą N_p elementów a pozostałymi grupami (niełączonymi na danym etapie), których liczba wynosi N_i.
D_{iq} – odległości między drugą z grup łączonych na danym etapie procedury liczącą N_q elementów a pozostałymi N_i grupami.
Nr – liczba elementów w nowo utworzonej grupie.

Tabela 1. Charakterystyki wyjściowe przyjęte do badania
(dane za 2004 i 2012) [15]
Table 1. Output characteristics adopted for testing (2004; 2012) [15]

Kraj	X1		X2		X3		X4		X5	
	Destymulanta		Stymulanta		Stymulanta		Destymulanta		Stymulanta	
	2012	2004	2012	2004	2012	2004	2012	2004	2012	2004
Belgia	12	13,1	67,2	65,6	2,24	1,86	21,6	21,6	4,1	1,9
Bułgaria	12,5	21,4	63	60,1	0,64	0,49	49,3	61,3	13,8	9,2
Czechy	5,5	6,3	71,5	70,1	1,88	1,2	15,4	19,6	9,4	6
Dania	9,1	8,8	75,4	77,6	2,99	2,48	19	16,5	23,1	14,9
Niemcy	10,6	12,1	76,7	68,8	2,92	2,5	19,6	18,4	12,3	5,2
Estonia	10,5	13,1	72,1	70,6	2,18	0,85	23,4	26,3	25,9	18,4
Irlandia	9,7	13,1	63,7	71,5	1,72	1,23	29,4	24,8	6,7	2,4
Grecja	11,4	14,7	55,3	64	0,69	0,55	34,6	30,9	11,6	7,1
Hiszpania	24,9	32	59,3	65,2	1,3	1,06	28,2	25	15,1	8,3
Francja	11,6	12,1	69,3	69,5	2,26	2,16	19,1	19,8	11,5	9,3
Chorwacja	4,2	5,4	55,4	59,6	0,75	1,05	32,3	30,7	15,7	15,2
Włochy	17,6	22,9	61	61,5	1,27	1,09	29,9	26,4	11,5	5,1
Cypr	11,4	20,6	70,2	74,9	0,47	0,37	27,1	25,3	5,4	2,7
Łotwa	10,6	14,7	68,1	69,3	0,66	0,42	36,2	46,3	33,1	32,8
Litwa	6,5	10,5	68,5	69	0,9	0,75	32,5	41	20,3	17,3
Luxemburg	8,1	12,7	71,4	67,7	1,51	1,63	18,4	16,1	2,9	0,9
Węgry	11,5	12,6	62,1	62,1	1,3	0,88	32,4	32,1	9,1	4,4
Malta	22,6	42,1	63,1	57,9	0,84	0,51	22,2	20,2	0,4	0
Holandia	8,8	14,1	77,2	74,9	2,16	1,93	15	16,7	4,3	1,8
Austria	7,6	9,5	75,6	70,8	2,84	2,24	18,5	17,5	30,9	22,8
Polska	5,7	5,6	64,7	57,3	0,9	0,56	26,7	45,3	10,4	7
Portugalia	20,8	39,4	66,5	72,6	1,5	0,74	25,3	27,5	24,9	19,3
Rumunia	17,4	22,4	63,8	63,5	0,42	0,39	41,7	45,9	21,4	17
Słowenia	4,4	4,3	68,3	70,4	2,8	1,39	19,6	18,5	18,8	16,1
Słowacja	5,3	6,8	65,1	63,7	0,82	0,51	20,5	32	9,7	6,7
Finlandia	8,9	10	74	72,2	3,55	3,45	17,2	17,2	31,8	29
Szwecja	7,5	9,2	79,4	77,4	3,41	3,58	18,2	16,9	46,8	38,7
Wlk. Brytania	13,6	12,1	74,2	75	1,72	1,67	24,1	24,8	3,8	1,2
Norwegia	14,8	4,7	79,9	78,2	1,66	1,57	13,8	15,8	65	58,6

Do oszacowania syntetycznego wskaźnika rozwoju Europa 2020 przyjęto dane roczne pozyskane z Eurostatu opisane dla takich obszarów definiujących główne założenia dla tej strategii. Są to następujące cechy:

- X_1 zatrudnienie – wskaźnik zatrudnienia osób w przedziale wiekowym 20–64 lata,
- X_2 sfera badawczo-rozwojowa – wskaźnik opisany jako wielkość nakładów na B+R jako % PKB,
- X_3 edukacja – wskaźnik opisany jako udział osób w wieku 18–24 lata przedwcześnie kończących naukę,
- X_4 ubóstwo i wykluczenie społeczne – wskaźnik określający udział osób zagrożonych ubóstwem lub wykluczeniem społecznym,
- X_5 emisja CO_2 – udział energii ze źródeł odnawialnych w końcowym zużyciu energii brutto.

Zakres czasowy badania objął dwa momenty czasowe: rok 2004 i 2012.

3. Rezultaty badań

Uzyskana hierarchia pozwoliła pogrupować kraje na pięć różnych klas, względnie homogenicznych wewnętrznie, pod względem poziomu syntetycznego wskaźnika rozwoju społeczno-gospodarczego Europa 2020. Wyniki typologii wskazują, że zarówno w 2012 jak i 2004 najwyższym poziomem rozwoju cechowały się kraje skandynawskie (tj. Szwecja, Norwegia, Finlandia) uzyskujące najwyższe wartości wskaźnika. Najgorzej w ocenie wypadły Bułgaria i Rumunia, stosunkowo najmłodsze państwa w strukturach unijnych, a także Malta oraz kraje południa Europy: Hiszpania, Grecja, Włochy (por. tabela 2).

Oceniając pozycję Bułgarii i Rumunii w uzyskanej typologii należy podkreślić, że pomimo faktu, iż w klasyfikacji kraje te wydają się być podobne pod względem poziomu rozwoju, to jednak sytuacja tych gospodarek jest zdecydowanie odmienna. Przede wszystkim Bułgaria pozostając na ostatnim miejscu i tak poprawiła wynik wskaźnika rozwoju o prawie 34 p.p. w stosunku do 2004 r. Ta pozytywna zmiana widoczna jest w samej tylko wartości wskaźnika syntetycznego. Potwierdzają to także wartości cech cząstkowych przyjęte do badania. Jednak o tak niskiej pozycji tego kraju zadecydować mógł czynnik związany ze sferą społeczną. Bułgaria nadal notuje jeden z najwyższych w Europie wskaźników zagrożenia ubóstwem (tabela 1). Ponadto nie bez znaczenia wydaje się być niski udział wydatków na B+R (liczony jako % od PKB). Należy także podkreślić, że i Bułgaria i Rumunia notują najniższy wskaźnik PKB (w 2012 roku odpowiednio 47 i 49 proc. średniej unijnej, a w 2004 było to zaledwie odpowiednio 32 i 33 proc. średniej unijnej), co bezpośrednio wpływa na wielkość kwot przekazywanych na powyższy cel.

Oceniając sytuację Rumunii, zaobserwowano wyraźne zahamowanie procesu rozwojowego w tym kraju. Czynnikiem sprawczym tej sytuacji mógł być, podobnie jak w przypadku Bułgarii, jeden z najniższych nakładów na sferę B+R oraz największe w Europie zagrożenie ubóstwem i towarzyszący biedzie wysoki udział osób nie kontynuujących nauki.

Odmienną specyfiką charakteryzuje się Malta. O ile w sferze społecznej i ekonomicznej sytuacja tego kraju nie odbiega znacząco od innych krajów sklasyfikowanych w tej samej grupie, to jednak brak w 2004 r., a później w 2012 r. śladowy udział wykorzystania energii niekonwencjonalnej mógł przyczynić się do stosunkowo niskiej oceny Malty na tle innych krajów. W kraju tym nastąpił także przyrost wskaźnika osób zagrożonych ubóstwem (por. tabela 1).

Ciekawie przedstawiają się wyniki dla Polski, dla której szacowana wartość wskaźnika rozwoju miała największy przyrost (o prawie 48%) w stosunku do pozostałych analizowanych krajów. Z pewnością na wynik ten wpływ miało ograniczenie liczby osób zagrożonych ubóstwem o ok. 50% (był to obok Rumunii i Bułgarii jeden z najwyższych wskaźników w 2004 r.). Poprawa warunków życia z pewnością była konsekwencją dynamicznego rozwoju Polski w tym okresie. Ponadto Polska może pochwalić się jednym z najniższym wskaźników osób przedwcześnie kończących naukę, na co wpływ może mieć obowiązek szkolny i bezpłatne studia. Nie można tutaj jednak mówić o prostej zależności z jakością nauczania, co pozostaje poza obszarem monitoringu strategii.

Przypatrując się bliżej sytuacji krajów, które osiągnęły w 2012 roku gorsze wyniki w stosunku do 2004 r., można uznać, że nie bez wpływu pozostawała ogólna niespokojna sytuacja gospodarcza na światowych rynkach. Spośród 29 analizowanych krajów aż w 16 zanotowano niższy niż w 2004 roku wskaźnik rozwoju społeczno-gospodarczego. Ponadto w trzynastu krajach nastąpił spadek zatrudnienia, więc nie jest zaskoczeniem, że jednocześnie w czternastu krajach wzrósł udział osób żyjących na granicy ubóstwa socjalnego, jako bezpośredni efekt utraty dochodów i konieczności ograniczenia wydatków na bieżącą konsumpcję. Analizując także dynamikę PKB stwierdzono, iż większość krajów zanotowała wyhamowanie wzrostu gospodarczego utrzymujące się także w 2012 r. (por. rysunek 1). Co prawda nie był to jednoroczny epizod, spowolnienie gospodarcze a nawet kryzys odczuwalne były na światowych rynkach począwszy od 2007 r.

Zebrany materiał pozwolił na podjęcie próby oceny zbadania zależności pomiędzy badanymi cechami. Badania wykazały, że występuje stosunkowo silna dodatnia zależność pomiędzy wskaźnikiem zatrudnienia a wydatkami na B+R (r = 0,679). Równie silna, ale ujemna zależność występuje pomiędzy zagrożeniem socjalnym a zatrudnieniem (r = -0,676) i sferą B+R (r = -0,687)[2].

Wykorzystanie energii niekonwencjonalnej w ocenie poziomu rozwoju ocenić należy za element istotny. Czynnik środowiskowy wykazuje największą współzależność ze wskaźnikiem zatrudnienia (r = 0,445), także stwierdzono dodatnią zależność, ale o mniejszej sile występującą względem nakładów na sferę B+R. Ujemną współzależność zaobserwowano w korelacji z liczbą osób przedwcześnie kończących naukę oraz liczbą osób zagrożonych ubóstwem. Wszystkie te zależności ocenić należy za prawidłowe[3]. Cztery kraje o najwyższym poziomie rozwoju jednocześnie posiadają najwyższych udział wykorzystania energii niekonwencjonalnej, przy czym Norwegia dwukrotnie więcej niż Finlandia i Austria.

Mając na uwadze powyższe współzależności określające siłę i kierunek pomiędzy badanymi cechami należy uznać aktualne starania rządów państw UE do zwiększenia wydatków na sferę B+R za jak najbardziej uzasadnione. Pierwszych siedem państw cechujących się najwyższym wskaźnikiem rozwoju jednocześnie ponosi największe nakłady na sferę badawczo-rozwojową. Wśród państw, które wydają najmniej na naukę i badania jest Polska. Poza naszym krajem mniej niż 1 proc. PKB na te cele przeznaczają: Litwa, Malta, Słowacja, Chorwacja, Grecja, Łotwa, Bułgaria, Cypr i Rumunia. Jest to zdecydowanie nadal zbyt mało by zwiększyć innowacyjność tych gospodarek. Obecnie kraje kojarzone z przewagą technologiczną mają nakłady znacznie wyższe niż nasz cel krajowy na 2020 rok. Dla przykładu: Korea Południowa w 2010 r. miała

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[2] Pozostałe współzależności pomiędzy badanymi cechami wykazują mniejszą siłę

[3] Uzyskane wyniki korelacji wykazują podobną, ale jednak większą współzależność w 2012 roku aniżeli w 2004.

nakłady równe 3,74% PKB, USA 2,88% PKB, Niemcy 2,82% PKB, Finlandia 3,87% PKB, Wielka Brytania 1,77% PKB. Najwięcej w naukę i innowacje inwestują także Szwecja (ok. 3,5% PKB), a także Dania, Austria i Słowenia (ok. 3% PKB).

Przechodząc do typologii krajów dokonanej w 2004 roku w oparciu o szacowany syntetyczny wskaźnik rozwoju, wytypowano pięć klas: pierwsza i druga to zbiory trzyelementowe, o najwyższym i wysokim poziomie rozwoju. Dominują tutaj kraje skandynawskie (Szwecja, Norwegia, Finlandia) a także Dania, Austria i Słowenia. Grupowanie to właściwie obejmuje państwa podobne i ze względu na lokalizację jak i poziom życia, poza Słowenią, która jest stosunkowo młodym członkiem struktur unijnych. Norwegia pozostaje poza strukturami UE. Najliczniejsze klasy zaś to trzecia (9 krajów) i czwarta (10 krajów), obejmująca kraje o średnim poziomie rozwoju. Skrajną piątą grupę tworzą cztery kraje cechujące się najniższym w badanym roku poziomem rozwoju, w tym dwa (Polska i Malta), formalnie zostały członkami UE w 2004, a dwa kolejne (Rumunia i Bułgaria) uzyskały członkostwo dopiero trzy lata później (por. tabela 2).

Typologia krajów przeprowadzona dla 2012 roku pozwoliła wyodrębnić, podobnie jak dla 2004 roku, pięć grup krajów, zróżnicowanych względem siebie, ale stosunkowo jednorodnych (podobnych wewnętrznie). Ponadto otrzymane grupy krajów są bardziej wyrównane liczebnie w stosunku do poprzedniego okresu. Kolejność państw w pierwszej dziesiątce właściwie pozostaje w układzie bardzo podobnym jak w 2004 roku. Dominujący udział mają kraje skandynawskie i Europy zachodniej. Również, analogicznie jak w 2004 r., w piątej i czwartej grupie zaszeregowania dominują kraje Europy środkowo-wschodniej i południowej, czyli cechujące się najniższym poziomem rozwoju zrównoważonego (por. tabela 2).

Oceniając poziom rozwoju w oparciu o oszacowany syntetyczny wskaźnik rozwoju zaobserwowano, że ogólnie, pozytywne zmiany w poziomie rozwoju zaszły w trzynastu krajach (czyli mniej niż połowie badanych obiektów). Widoczne jest także mniejsze zróżnicowanie w poziomie rozwoju badanych krajów w roku w 2012 stosunku do 2004 roku. Różnica pomiędzy wskaźnikiem szacowanym dla najbardziej i najsłabiej rozwiniętego kraju (Szwecji i Bułgarii) w 2012 r. wyniosła 0,63, podczas gdy w 2004 r. różnica ta wyniosła 0,71.

Tabela 2. Wskaźnik rozwoju społeczno-gospodarczego strategia Europa 2020. Hierarchia krajów [opracowanie własne]
Table 2. Indicator of socio-economic development strategy Europe 2020. Hierarchy of countries [own elaboration]

Lp.	2012	Wartość wskaźnika	Grupy[4]	Lp	2004	Wartość wskaźnika	Grupy[5]
1	Sweden	0,86560321	1	1	Sweden	0,88499	1
2	Norway	0,79451098		2	Norway	0,881349	
3	Finland	0,77149134		3	Finland	0,789791	
4	Austria	0,74602278		4	Denmark	0,734996	2
5	Denmark	0,70756639	2	5	Austria	0,685056	
6	Slovenia	0,66945385		6	Slovenia	0,629934	
7	Germany	0,65707477		7	Netherlands	0,600001	3
8	Netherlands	0,63537409		8	Germany	0,596985	
9	Czech Republic	0,6242235		9	France	0,59279	
10	Estonia	0,60822651	3	10	Czech Republic	0,561631	
11	France	0,55530778		11	United Kingdom	0,557664	
12	Luxembourg	0,53703875		12	Luxembourg	0,527686	
13	Belgium	0,49308999		13	Estonia	0,526713	
14	Slovakia	0,48987955		14	Ireland	0,501432	
15	United Kingdom	0,48611895	4	15	Belgium	0,499912	
16	Lithuania	0,47437728		16	Croatia	0,453243	4
17	Poland	0,45273604		17	Lithuania	0,45059	
18	Latvia	0,44232861		18	Latvia	0,447386	
19	Ireland	0,4225344		19	Cyprus	0,439295	
20	Portugal	0,41477249		20	Slovakia	0,410853	
21	Cyprus	0,39589661		21	Portugal	0,394133	
22	Croatia	0,3737549		22	Greece	0,379778	
23	Hungary	0,36064732	5	23	Hungary	0,378074	
24	Italy	0,31576551		24	Italy	0,358159	
25	Greece	0,2722931		25	Spain	0,357871	
26	Malta	0,26669934		26	Poland	0,306499	5
27	Spain	0,25762276		27	Romania	0,295349	
28	Romania	0,25670339		28	Malta	0,198762	
29	Bulgaria	0,23701852		29	Bulgaria	0,177762	

Kraje sklasyfikowane w pierwszej, drugiej oraz grupie trzeciej pod względem osiągniętego poziomu rozwoju (poza Estonią, Słowenia i Słowacją, Czechami) wypracowują jednocześnie PKB na poziomie wyższym niż średnia unijna. Ciekawymi przypadkami, niedającymi się opisać szablonem, są kraje: Estonia, Słowenia, Czechy, Słowacja, które na tle krajów

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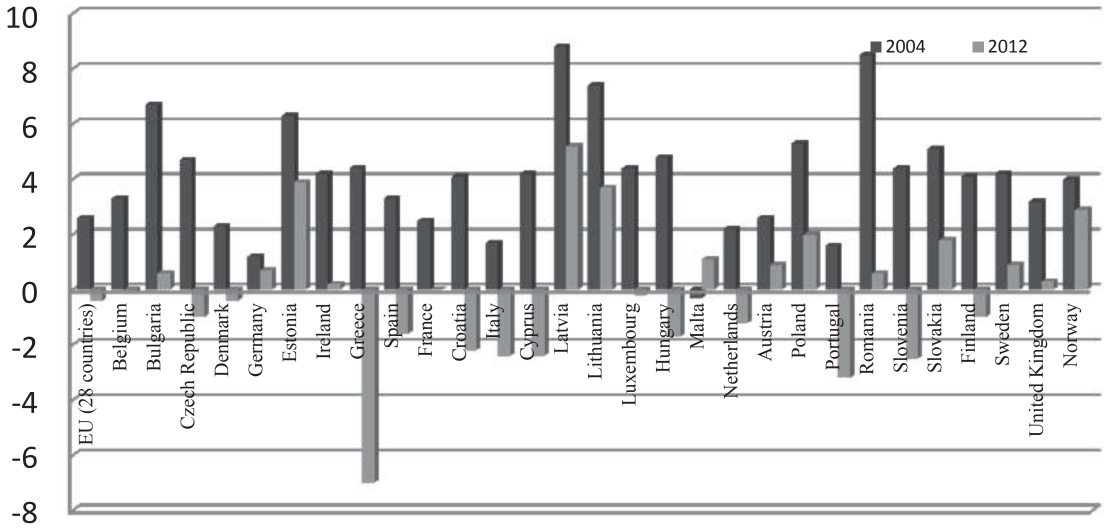
[4] Rozpiętość klas 0,125717, przedziały o równej rozpiętości
[5] Rozpiętość klas 0,141446, przedziały o równej rozpiętości

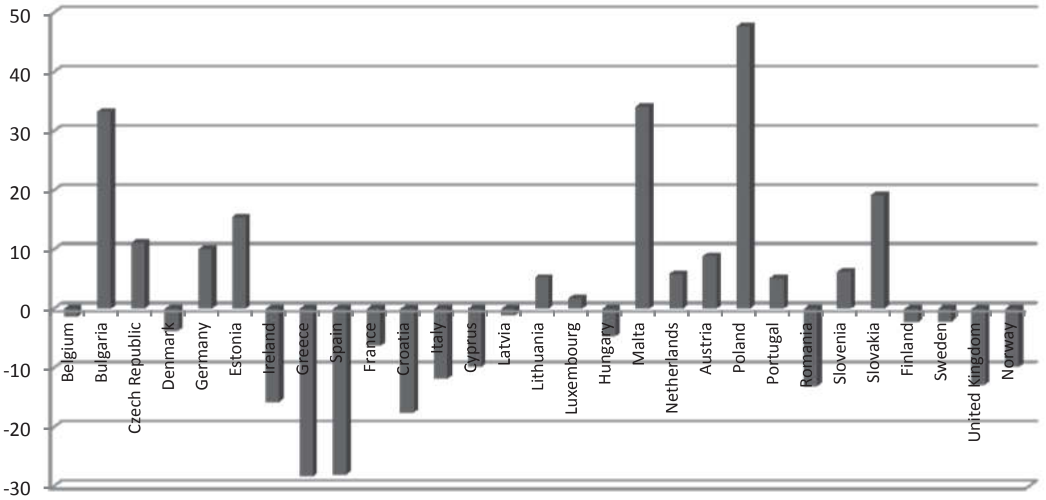
Europy środkowo-wschodniej osiągają zdecydowanie wyższe wyniki, jednocześnie wypracowując swój PKB na poziomie niższym niż średnia unijna. Podjęta próba stwierdzenia zależności statystycznie istotnej pomiędzy uzyskanym poziomem wskaźnika rozwoju a wielkością PKB wykazała, iż pomiędzy badanymi cechami zachodzi dodatnia korelacja o średnim natężeniu (r = 0,55 w 2012 r. i r = 0,49 w 2004 r.), zatem można przyjąć za słuszne twierdzenie, że im kraj wypracowuje większy PKB (tutaj mierzony jako % średniej unijnej dla 28 krajów) tym wyższy uzyskuje wskaźnik rozwoju (por. rysunek 1).



Rys. 1. Dynamika PKB (%) w 2004 i 2012 r. [opracowanie własne na podstawie 15]
Fig. 1. GDP growth rate (%) in 2004 and 2012 [own elaboration based on 15]

Oceniając dynamikę zmian w poziomie wskaźnika rozwoju, które zaszły w 2012 roku w stosunku do 2004, największe pozytywne zmiany zaobserwowano w Polsce, na Malcie, Słowacji, w Bułgarii i Estonii (rysunek 2). Przyglądając się bardziej szczegółowo sytuacji w tych krajach zaobserwowano bardzo wyraźne zmiany w kształtowaniu się poszczególnych cech przyjętych do badania i tak np. w przypadku Polski na postęp ten wpłynąć mógł wzrost wskaźnika wykorzystania energii odnawialnej (prawie o 49%), wskaźnika zatrudnienia (o 13%) i znaczący spadek ubóstwa (o prawie 42%). Malta zanotowała poprawę głównie w sferze edukacji ograniczając liczbę osób przedwcześnie kończących naukę prawie o 46%, także zmiany zaszły na rynku pracy, gdzie zanotowano wzrost zatrudnienia o 9% oraz w sferze wykorzystania energii niekonwencjonalnej. Bułgaria zanotowała zmiany porównywalne do Malty. Nastąpiła redukcja ubóstwa o 19,5% oraz liczby osób kończących przedwcześnie edukację o prawie 40%. Estonia i Słowacja zainwestowały głównie w sferę B+R (odpowiednio 156% i 60%)oraz wykorzystanie energii niekonwencjonalnej (odpowiednio o 41% i 45%).

Najbardziej dramatyczny spadek w poziomie rozwoju zaobserwowano głównie w Grecji i Hiszpanii (po 28%), a także w Chorwacji, Irlandii, Rumunii oraz Wielkiej Brytanii. Polska wyraźnie poprawiła efektywność w realizacji celów rozwojowych, co znalazło swoje pozytywne konsekwencje w przesunięciu z klasy piątej do klasy czwartej oraz wyraźnej poprawie wartości wskaźnika rozwoju w 2012 r. o prawie 48%.

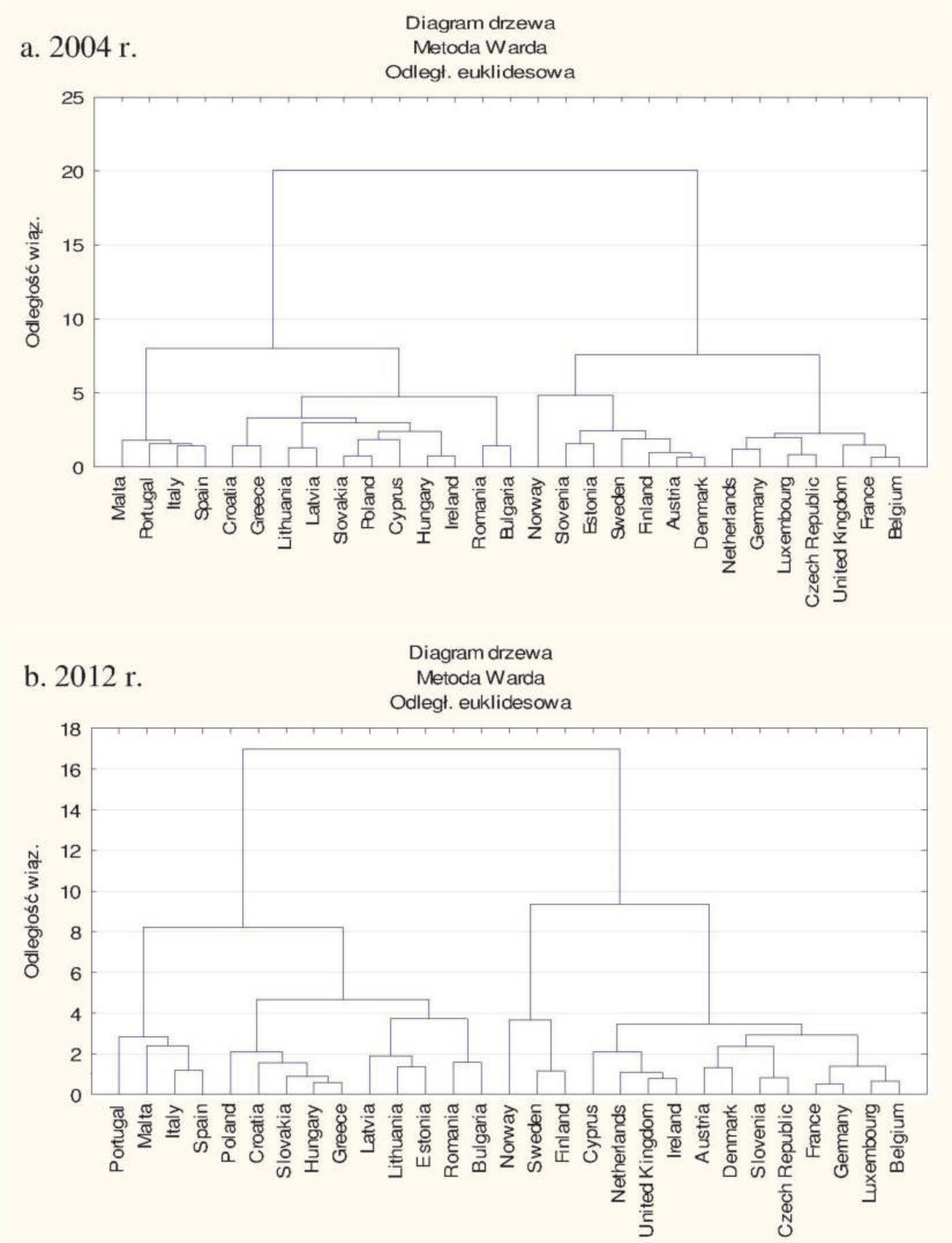


Rys. 2. Zmiany w poziomie wskaźnika zrównoważonego strategia Europa 2020 (2004 = 100%) [opracowanie własne]

Fig. 2. Changes of sustainable development indicator Europe 2020 (2004 = 100%) [own elaboration]

5. Grupowanie państw metodą Warda

Zastosowanie metody Warda, opisanej powyżej procedury, pozwoliło na dokonanie pogrupowania krajów podobnych pod względem analizowanych cech, co umożliwiło podjęcie próby określenia podstawowych własności (tych grup) krajów w kontekście czynników determinujących ich zrównoważony rozwój. Poniższe wykresy ilustrują wzajemne absolutne odległości poszczególnych krajów lub ich podgrup nazywane odległościami wiązań oraz odległości względne stanowiące procent odległości maksymalnej. W klasyfikacji krajów wykonanej na podstawie danych dotyczących 2004 roku maksymalna odległość wiązań wyniosła 16,99. W 2012 roku na skutek zróżnicowanego tempa rozwoju poszczególnych krajów pod względem analizowanych kryteriów maksymalna odległość wiązań wzrosła do 20,05 (por. rysunek 3).



Rys. 3. Efekty grupowania krajów metodą Warda [opracowanie własne]
Fig. 3. The effects of grouping countries by Ward [own elaboration]

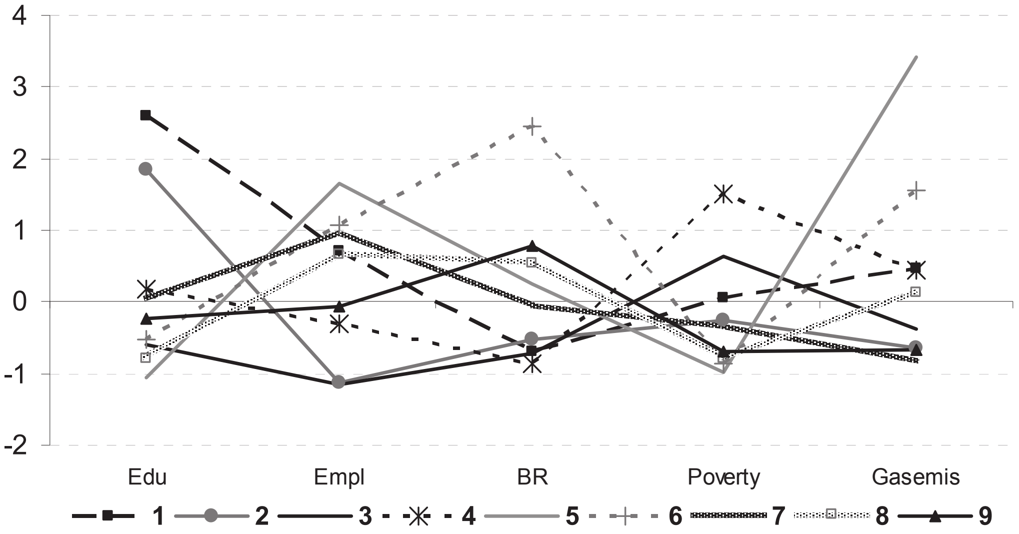
W efekcie zastosowania metody Warda można otrzymać kilka klasyfikacji różnych pod względem ilości otrzymanych grup oraz stopnia ich jednorodności. Oczywiście większa liczba skupień oznacza jednocześnie mniejsze odległości wewnątrz tych skupień. Dla 2004 roku odcinając „gałęzie drzewa" na poziomie 3,73 (22% odległości maksymalnej) otrzymujemy 5 skupień, natomiast dla 2012 roku odcinając gałęzie na relatywnie podobnym poziomie 4,77 (24% maksymalnej odległości) otrzymana liczba skupień wynosi 6.

W grupowaniu przeprowadzonym dla 2004 roku o relatywnie dużej liczbie 9 skupień odległość wiązań nie przekroczyła wielkości 2,41 (nieco ponad 14% odległości maksymalnej). W podobnym grupowaniu dla 2012 roku maksymalna odległość wewnątrz skupień wyniosła trochę więcej niż w 2004 roku, gdyż niecałe 2,44, co stanowiło jednak mniejszy odsetek odległości maksymalnej wynoszący 12,2%. Na skutek tego grupowania otrzymano jednocześnie mniejszą o jedno liczbę skupień. Mimo wzrostu odległości maksymalnej między skupieniami w 2012 roku niektóre kraje „przybliżyły się do siebie", dzięki czemu można było wyodrębnić 8 grup.

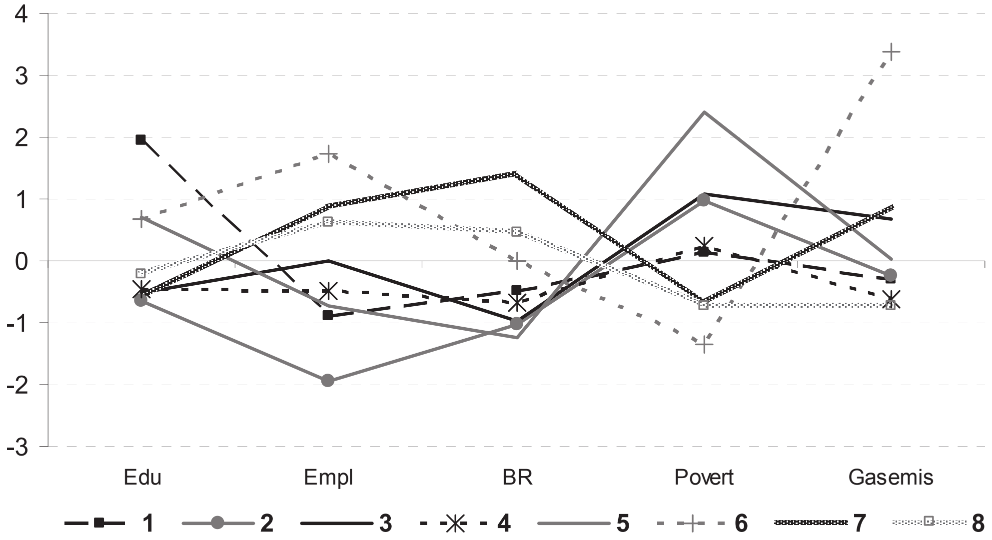
Tabela 3. Klasyfikacja krajów – efekty grupowania 2004 i 2012 [opracowanie własne]
Table 3. Classification of countries 2004 and 2012 [own elaboration]

Grupa	Kraje 2004	Grupa	Kraje 2012
1	Portugal	1	Portugalia, Malta, Włochy, Hiszpania
2	Malta, Italy, Spain	2	Chorwacja, Grecja
3	Poland, Croatia, Slovakia, Hungary, Greece	3	Łotwa, Litwa
4	Latvia, Lithuania, Estonia, Romania, Bulgaria	4	Slovakia, Poland, Cyprus, Hungary, Ireland
5	Norway	5	Romania, Bulgaria
6	Sweden, Finland	6	Norway
7	Cyprus, Netherlands, United Kindom, Ireland	7	Slovenia, Estonia, Sweden, Finland, Austria, Denmark
8	Austria, Denmark, Slovenia, Czech Republic	8	Netherlands, Germany, Luxembourg, Czech Republic, United Kindom, France, Belgium
9	France, Germany, Luxembourg, Belgium		

Średnie poziomy badanych cech zaprezentowano również na wykresie, jednak w celu zachowania przejrzystości wykresu oraz ilustracji względnych relacji średnich poziomów badanych zmiennych w wyodrębnionych grupach, zastosowano tutaj średnie wartości zmiennych standaryzowanych.



a. 2004



b. 2012

Rys. 4. Wartości średnie poszczególnych wskaźników [opracowanie własne]
Fig. 4. The average values of each indicator for groups of countries [own elaboration]

W 2004 roku grupami cechującymi się najlepszą sytuacją pod względem badanych cech były grupa 5 i 6, przy czym „grupa piąta" stanowiła specyficzną grupę jednoelementową zawierającą tylko Norwegię. W Norwegii zaobserowano najwyższy średni poziom energii odnawialnej, najwyższe zatrudnienie, najniższy odsetek osób przedwcześnie kończących naukę oraz jednocześnie najmniejsze zagrożenie ubóstwem.

Jedynie pod względen nakładów na badania i rozwój kraj ten uplasował się na jednej ze środkowych pozycji. Natomiast grupa 6 (Szwecja i Finlandia) odznaczała się średnio najwyżymi nakładami na badania i rozwój, bardzo wysokimi poziomami energii odnawialnej oraz zatrudnienia (drugimi po Norwegii), bardzo niskim (drugim po Norwegii) poziomem zagrożenia ubóstwa, oraz jednym z niższych w Europie udziałe osób przedwcześnie kończących naukę.

Portugalia stanowiąca jednoelementową grupę o numerze 1 wyróżniała się w 2004 roku najwyższym udziałem osób przedwcześnie kończących naukę i jednym z najniższych poziomów nakładów na badania i rozwój, przy dość wysokim poziomie zatrudnienia. W grupie drugiej również odnotowano bardzo wysoki odsetek osób przedwcześnie kończących naukę, przy jednocześnie bardzo niskim poziomie zatrudnienia, oraz relatywnie niskim (podobnie jak w Portugalii) poziomie nakładów na badania i rozwój. W tej grupie, trochę inaczej niż w Portugalii, średnio na bardzo niskim poziomie utrzymywał się odsetek energii odnawialnej. Natomiast nieco niżej od Portugalii kształtował się tam średni poziom zagrożenia ubóstwem.

Najwyższym poziomem zagrożenia ubóstwem odznaczała się w 2004 roku grupa 4 (Łotwa, Litwa, Estonia, Rumunia, Bułgaria). Jednocześnie średnio najmniższe w tych krajach były wydatki na badania i rozwój przy dość zadawalającym poziomie odsetka energii odnawialnej.

Na drugim miejscu pod względem poziomu zagrożenia ubóstwem uplasowała się grupa 3, do której obok Chorwacji, Słowacji, Węgier i Grecji zaklasyfikowała się również Polska. W tej grupie podobnie jak w grupie 2 jest wyjątkowo niski poziom zatrudnienia oraz bardzo niski poziom nakładów na badania i rozwój. Jedynym pozytywnym aspektem/zjawiskiem w tejgrupie był jeden z niższych odsetków przedwcześnie kończących naukę.

Grupa 7 (Cypr, Holandia, Wlk. Brytania i Irlandia) podobnie jak grupa 2 i 9 (Francja, Niemcy, Luxemburg i Belgia) cechują się stosunkowo jednym z najniższych poziomów wykorzystania energii odnawialnej. W grupie 8 (Holandia, Niemcy, Luxemburg, Czechy, Wlk. Brytania, Francja, Belgia) występuje stosunkowo najniższe zagrożenie ubóstwem oraz najmniejszy udział osób przedwcześnie kończących edukację. Natomiast zatrudnienie kształtuje się na poziomie niższym, a wydatki na sferę B+R na poziomie wyzszym niż państw w grupie 7.

Efekty grupowania dla 2012 r. kształtują się nieco odmiennie niż w 2004 r., zarówno co do liczebności poszczególnych grup jak i klasyfikacji państw w poszczególnych grupach. Generalnie otrzymano 8 grup. Wyodrębniono dwa skupienia wyróżniające się lepszym niż średnim poziomem zatrudnienia i udziałem energii odnawialnej. Norwegia (grupa 6) stanowiąca jednoelementowy zbiór wyróżniała się spośród wszystkich analizowanych grup najwyższym udziałem energii odnawialnej, najniższym udziałem osób zagrożonych obóstwem, najwyższym zatrudnieniem i nieco wyższym niż srednio udziałem osób kończących przedwcześnie naukę. Podobnie jak w grupowaniu z 2004 r. sytuacja państw tej grupy była najkorzystniejsza. Grupa 7 (Słowenia, Estonia, Szwecja, Finlandia, Austria, Dania), to grupa o relatywnie korzystnej sytaucji względem pozostałych sześciu grup. W stosunku do grupy 6 cechuje się lepszą sytuacją w sferze edukacji i zdecydowanie wyższymi nakładami na sferę badawczo-rozwojową.

Najgorsza sytuacja pod względem badanych cech występowała w grupie drugiej (Chorwacja, Grecja) i piątej (Rumunia, Bułgaria).

Ciekawe wnioski nasuwają się na podstawie analizy wiązań na poziomie odległości 10. Na jej podstawie wyłoniono dwie wyraźnie zróżnicowane pod względem poziomu zrównoważonego rozwoju grupy państw dla obu momentów czasowych. Można zaobserować charakterystyczny podział na dwa skupiska krajów „biedniejszych i bogatszych”. W grupie krajów bogatszych skupiającej 14 państw (za wyjątkiem Czech, Estonii i Słowenii oraz Norwegii) są to kraje tworzące rdzeń UE, uzyskujące PKB p.c. powyżej średniej unijnej. Drugie skupienie liczące 15 państw to zdecydowanie uboższe kraje europejskie, głównie są to nowi członkowie UE oraz cztery państwa południa Europy (Grecja, Włochy, Hiszpania, Portugalia), będące w strukturach unijnych już od lat 80. (a Włochy od 1952 r.), ale borykające się w ostatnich latach z poważnymi problemami gospodarczymi (głównie rosnącym zadłużeniem, brakiem stabilności finansów publicznych). Wyraźnie zarysowuje się tutaj podział państw w oparciu o kryterium historyczno-polityczno-geograficzne dla państw byłego bloku wschodniego, a także podział na linii kryterium bogata północ – biedne południe, mający także swoje wyjaśnienie w teoriach ekonomicznych. Opisywany efekt był zauważalny w obu badanych momentach czasowych (w 2004 i 2012 r.).

Podejmując próbę zweryfikowania siłę czynników determinujących poziom systetycznego wskaźnika rozwoju zastosowano równanie regresji. Okazało się, że w 2012 r. najsilniej determinującym czynnikiem była cecha związana z aktywnością rynku pracy, w 75% objaśniająca poziom wskaźnika rozwoju. Równie silnie opisującą wskaźnik rozowju okazała się być cecha, informująca o wysokości nakładów na sferę badawczo-rozwojową (R^2 = 71%). Liczba osób zagrożonych ubóstwem w 61% wyjaśniała poziom wskaźnika rozwoju. Pozostałe cechy: liczba osób przedwcześnie kończących naukę oraz element środowiskowy wydają się mieć słabszą moc wyjaśniającą (odpowiednio R^2 = 25 i R^2 =32%)[6].

5. Podsumowanie

Przeprowadzona hierarchia i klasyfikacja państw krajów europejskich pod względem osiągniętego wskaźnika zrównoważonego rozwoju pozwala przyjąć kilka wniosków.

Bazując na trzech filarach (sferze społecznej, gospodarczej i środowiskowej), stwierdza się, że dystans rozwojowy pomiędzy krajami europejskimi zmniejsza się. Badanie przeprowadzono w dwunastoletnim interwale czasowym, co w kontekście uzyskanych wyników potwierdza, że proces wyrównywania dysproporcji rozwojowych jest procesem wieloletnim i powolnym. Na dzień dzisiejszy silne zróżnicowanie przestrzenne krajów Europy pod względem rozwoju nadal się utrzymuje, pomimo niekwestionowanych zmian zachodzących w słabiej rozwiniętych krajach europejskich.

Przeprowadzone analizy pozwalają na wyodrębnienie trzech grup państw (zarówno w uzyskanej hierarchii jak i metodą grupowania): kraje skandynawskie oraz kraje tzw. rdzenia UE, charakteryzujące się najwyższym poziomem życia i najlepszą sytuacją gospodarczą. Zmiany zachodzące w tych krajach jednak cechują się stosunkowo niską dynamiką, co jest cechą charaketrystyczną dla dojrzałych gospodarek. Druga grupa krajów to kraje byłego „bloku wschodniego" z rozszerzenia UE w 2004 (poza Maltą), znajdujące się aktualnie na drodze doganiania bogatszych sąsiadów. Charakteryzują się stosunkowo wysoką dynamiką

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[6] Podjęta próba oceny czynników determinujących wskaźnik rozwoju w 2004 r. wskazuje podobną prawidłowość, o nieco niższej sile wyjaśniającej badanych cech.

zmian, głównie w sferze społecznej. Zmiany te ocenić należy pozytywnie. Trzecia grupa to kraje będące w strukturach UE od lat, kraje południowej Europy (głównie Hiszpania, Grecja, Włochy), w których progresu nie zaobserwowano lub był on znikomy. Zważywszy na wyniki analizy statystycznej wskazującej, że cechy składowe komponentu gospodarczego (głównie zatrudnienie i nakłady na sferę badawczo-rozwojową) najsilniej determinują poziom wskaźnika rozwoju, można domniemywać, że ze względu na malejącą w badanym okresie aktywność rynku pracy, będącej efektem kryzysu gospodarczego, w tych krajach zmiany rozwojowe były słabo zauważalne lub nie zaszły w ogóle.

Należy podkreślić, iż wyłonione grupy są niejednorodne wewnętrznie, co oznacza, że wykazują zróżnicowanie w przyjętych do badania cechach w obszarze środowisko-gospodarka-społeczeństwo. Cechują się także zróżnicowanym tempem zmian w badanym okresie (2004 i 2012), oraz różnym poziomem syntetycznego wskaźnika rozwoju.

Analizując zmiany w poziomie rozwoju krajów europejskich w dwóch momentach czasowych (2004 i 2012 r.) zaobserwowano widoczny proces odrabiania zaległości rozwojowych przez kraje Europy środkowo-wschodniej, wśród których liderem jest Polska. Zmiany zachodzące w tym kraju są najbardziej dynamiczne. Równie dynamiczne, pozytywnie oceniane zmiany zaobserwoano w Czechach, Estonii i Słowenii, które to kraje znajdują się na wyższym niż Polska poziomie rozwoju. Także w krajach o najniższym poziomie rozwoju tj. Bułgaria i Malta zachodzą równie bardzo dynamiczne, korzystne zmiany, przede wszystkim sferze socjalnej, jednak nie zmienia to faktu, iż poziom rozwoju w tych krajach na tle innych krajów europejskich jest stosunkowo niski.

Podjęta próba zidentyfikowania głównej cechy (z obszaru: środowisko, gospodarka, społeczeństwo) determinującej poziom syntetycznego wskaźnika rozwoju nie pozwoliła wskazać spośród badanych cech jednej, szczególnie silnej determinanty. Aż trzy z pięciu cech poddanych weryfikacji (dwie z filaru gospodarka i jedna z filaru społeczeństwo) porównywalnie silnie wyjaśniają wartość wskaźnika. Mniejsze znaczenie okazał się mieć komponent środowiskowy.

Podsumowując rozważania o poziomie spójności rozwoju zrównoważonego krajów eropejskich, stwierdzić należy, iż jest on jeszcze wysoce niezadowalający, szczególnie z punktu widzenia słabiej rozwiniętych gospodarek (głównie najmłodszych członków UE).

Literatura

1. **Anselin L., Varga A., Acs Z.:** *Local Geographic Spillovers between University Research and High Technology Innovations.* Journal of Urban Economics. 42(3), 422–448 (1997).
2. **Antonelli, C.:** *The microdynamics of technological change*, London, Routledge 1999.
3. **Bercovitz J., Feldman M.:** *Entrepreneurial Universities and Technology Transfer: A Conceptual Framework for Understanding Knowledge-Based Economic Development,* The Journal of Technology Transfer. 31(1), 175–188 (2006).
4. **Figel J., Rodrigues M.J.:** *Strategy of the Europe AT the turn of the Century, Knowledge- Based State and Economy*, Tallin, The State Chancellery of the Republic Estonia, 16–36 (2004).
5. **Foray D., Lundvall B.A.:** *The Knowledge Based Economy: From the Economics of Knowledge to the Learning Economy*, in Employment and Growth in the Knowledge-based Economy, OECD, Paris 1996.
6. **Giovannini E., Linster M.:** *Measuring sustainable development.* Achievements and challenges. OECD (2005).
7. **Nonaka, I. Takeuchi H.:** *The Knowledge Creating Company*, Oxford University Press, Oxford 1995.
8. **Nowak E.:** *Metody taksonomiczne w klasyfikacji obiektów społeczno-gospodarczych*, PWE, Warszawa, 80 (1990).
9. **Rodrigues M.J.:** *European Policies For A Knowledge Economy*. Cheltenham: Edward Elgar (2004).
10. **Rodrigues M.J.:** *The New Knowledge Economy in Europe*: *A Strategy for International Competitiveness and Social Cohesion.* Edward Elgar, Cheltenham 2003.
11. **Spychalski G.:** *Wyzwania kryzysowe na tle ewolucji kapitalizmu z uwzględnieniem uwarunkowań środowiskowych.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection), 15, 780–792 (2013).
12. **Stiglitz J.:** *Knowledge in the Modern Economy.* “Economics of the Knowledge Driven Economy”, DTI & CERP, London 1999.
13. Europa 2020. Strategia na rzecz inteligentnego i zrównoważonego rozwoju sprzyjającego włączeniu społecznemu, Komisja Europejska Bruksela, 3.3.2010 KOM(2010) 2020 wersja ostateczna za: http://www.mg.gov.pl.
14. Europa efektywnie korzystająca z zasobów – inicjatywa przewodnia strategii „Europa 2020” Komunikat Komisji do Parlamentu Europejskiego, Rady, Europejskiego Komitetu Ekonomiczno -Społecznego i Komitetu Regionów, Komisja Europejska, Bruksela, dnia 26.1.2011, KOM(2011) 21 wersja ostateczna, za: http://www.eur-lex.europa.eu.
15. Eurostat za: http://ec.europa.eu/eurostat/data/database.

EU Countries Socio-Economic Development in the Context of Europe 2020 Strategy

Abstract

This article discusses important and current issues of sustainable development of the EU countries in the context of the Europe 2020 strategy (a strategy for smart, sustainable and inclusive growth).

The main objective of this article is to prepare hierarchy and classification of the EU countries (including Norway and Croatia), showing the degree of core indicators implemented as described in the framework of the Europe 2020 strategy. Authors attempt to isolate groups of the EU countries which present similar development levels on the basis of accepted development indicators. It was attempts to determine:

- the level of sustainable development EU countries (based on synthetic indicator),
- trends in changing of sustainable development level EU countries,
- the main factors determining the level of sustainable development level EU countries.

Based on estimated indicators following assumptions were verified: the development distance between EU countries has steadily decreased and the economical factors are the most strongly determining factors of sustainable development.

Selected methods of multivariable objects hierarchy and classification have been used in the study. In order to measure the level of sustainable development of the EU countries, linear ordering has been applied based on the standardized sums method. As a result, a relative level indicator of development has been assigned to each country.

The classification of the EU countries has been made mainly according to the Ward hierarchical agglomeration procedure. Thus, groups of countries appeared have been similar in terms of analyzed characteristics. It allowed an attempt to determine basic features of these countries' groups in terms of factors determining their development.

Analysis will be carried out in spatial and time dimension as a part of the research. The subject of spatial analysis will be the EU countries, in particular their socio-economic development indicators as described in the Europe 2020 strategy framework. The time range of the study includes 2004 and 2012. Eurostat has been the main data source.

Based on the obtained results, it has turned out that the development distance between European countries has been reduced. Analyzing changes of the level of the European countries development in 2004 and 2012 has showed visible process of catching-up development by countries in Central and Eastern Europe (with the leading position of Poland).

Strong spatial differentiation of the European countries in terms of socio-economic development persists still. Analyzes have allowed to distinguish three groups of countries (both in the resulting hierarchy and grouping method): the Scandinavian countries and the countries of the so-called "the core of the EU", characterized by the highest level of life and the best economic situation. The second group of countries, called "Eastern bloc" of the enlargement of the EU in 2004 (except Malta), that are currently on the way of approximating their richer neighbours. They characterized by relatively high growth, mainly in the social sphere. The third group consists of countries that are in the structures of the EU for years, the countries of southern Europe (mainly Spain, Greece and Italy), in which the progress has not been observed or has been negligible.

As many as three out of five features under examination (two of economy pillar and one of the society pillar) comparatively strongly explain the level of sustainable development indicator. It was proven that an environmental component was of less importance.

Słowa kluczowe:
zrównoważony rozwój, hierarchia, klasyfikacja, Unia Europejska,
strategia Europa 2020

Keywords:
sustainable development, hierarchy, classification, EU countries,
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Analiza możliwości pozyskiwania krytycznych surowców mineralnych

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1. Wstęp

W 2008 r. Komitet ds. Kopalin Krytycznych dla Gospodarki Stanów Zjednoczonych przedstawił definicję surowców krytycznych, która została również przyjęta przez kraje Unii Europejskiej. Wg tej definicji surowce krytyczne to „kopaliny/surowce narażone na ryzyko zachwiania lub przerwania płynności podaży i dostaw, dla których deficyt ten może mieć poważne skutki ekonomiczne dla całej gospodarki".

Pierwszy kompleksowy raport i wstępna lista tych surowców została opublikowana w 2010 r. w opracowaniu pt.: „Critical raw materials for the EU – Report of the Ad-hoc Working Group on defining critical raw materials. EU Commissision Enterprise and Industry" [8].

W dokumencie tym przeprowadzono m. in. analizę krytyczności, opierając się na trzech grupach kryteriów, tj.:

- gospodarczo-ekonomiczne skutki ograniczenia podaży,
- ryzyko ograniczenia (zachwiania lub przerwania) podaży,
- „ryzyko środowiskowe", związane z ograniczeniami możliwości produkcji w poszczególnych krajach, wynikające z wymogów prawnych w zakresie ochrony środowiska naturalnego (utrzymanie standardów jakości środowiska, minimalizacja zagrożeń).

Ocenę tę przeprowadzono dla 41 wytypowanych surowców mineralnych, uwzględniając 10-letni horyzont czasowy, czyli:

- metalicznych: aluminium, antymon, beryl, chrom, cynk, gal, german, ind, kobalt, lit, magnez metaliczny, mangan, molibden, nikiel, niob, pierwiastki ziem rzadkich, platynowce, ren, rudy miedzi, rudy żelaza, srebro, tantal, tellur, tytan, wanad, wolfram,
- niemetalicznych: baryt, bentonit, boksyty, borany, diatomit, fluoryt, gips, gliny ceramiczne wraz z kaolinem, grafit, magnezyt, perlit, piaski kwarcowe, surowce skaleniowe, talk, wapienie.

Według Raportu Zespołu popyt na te minerały i metale będzie rósł ze względu na wzrost gospodarczy krajów rozwijających się, a także pojawienie się nowych innowacyjnych technologii. Surowce te wykorzystywane są na przykład do produkcji: kolektorów słonecznych, samochodów elektrycznych, telefonów komórkowych, produkcji telewizorów LCD itd.

W wyniku przeprowadzonej analizy podzielono surowce wstępnie na trzy grupy o różnym stopniu krytyczności. Za najbardziej krytyczne, dla gospodarki Unii Europejskiej, uznano 14 surowców o ważnym znaczeniu ekonomicznym, tj.: antymon, beryl, kobalt, fluoryt, gal, german, grafit, ind, magnez metaliczny, niob, platynowce, pierwiastki ziem rzadkich, tantal i wolfram), charakteryzujące się przede wszystkim wysokim ryzykiem niedoboru lub braku podaży, które wynikają z ograniczonej ilości źródeł ich pozyskiwania i podaży. Większość spośród zaliczonych do tej grupy surowców jest niezbędna dla rozwoju nowych technologii [8,14,15].

Przedstawiona lista surowców krytycznych jest propozycją, która może ulec modyfikacji w wyniku dalszych prac Grupy ds. Podaży Surowców Mineralnych.

Pozostałe spośród 41 analizowanych surowców wykazują w mniejszym stopniu znamiona niedoboru lub deficytu podaży.

Grupa ds. Podaży Surowców Mineralnych, w dalszych swych pracach przyjmie dłuższą perspektywę czasową, rzędu 20 lat, obejmującą pełny cykl inwestycyjny, od poszukiwania złoża, poprzez jego rozpoznanie do udostępnienia i uzyskania pierwszej produkcji surowca. Ponadto zasób surowców krytycznych w krajach europejskich zmniejsza się. Przez wiele lat zaprzestano poszukiwania nowych złóż i dodatkowo maleje możliwość dostępności terenu, związana z rozwojem budownictwa oraz wymaganiami ochrony przyrody i krajobrazu. Wysokie ryzyko niedoboru lub braku podaży surowców krytycznych wynika również z ograniczonej ilości źródeł ich pochodzenia i podaży, zdominowanej przez:

- Chiny – pierwszego światowego producenta: antymonu, berylu, fluorytu, pierwiastków ziem rzadkich, galu, germanu, indu, magnezu metalicznego, grafitu,
- Rosję – tradycyjnego światowego lidera w produkcji platynowców,
- Brazylię – głównego producenta i dostawę niobu i tantalu,
- Kongo – wiodącego światowego dostawcę surowców kobaltu [7,13,14].

Kompleksowa ocena potencjału surowcowego krajów Unii Europejskiej oraz identyfikacja tzw. surowców krytycznych, (niezbędnych dla jej harmonijnego i zrównoważonego rozwoju gospodarczego oraz postępu technologicznego) jest jednym z priorytetów polityki surowcowej Unii Europejskiej [14,15].

2. Technologie pozyskiwania surowców krytycznych

W wyniku analizy technologii, sporządzonej na podstawie dostępnej literatury [1,4–6,11–13], stwierdzono, że najbardziej powszechną metodą pozyskiwania surowców krytycznych jest przeróbka polimetalicznych rud, które są nośnikami wielu metali. Proces przeróbki rud znalazł zastosowanie w odniesieniu do następujących surowców: beryl, kobalt, wolfram oraz fluoryt.

Rudy poddaje się przeróbce w celu: polepszenia składu chemicznego, a także ujednolicenia koncentratów pod względem właściwości chemicznych oraz fizyko-chemicznych.

Ponieważ wydobywane rudy najczęściej nie nadają się do bezpośredniego wykorzystania, istotnym procesem jest wielostopniowe wzbogacanie rud. Wzbogacanie rud metali podzielić można na: wzbogacanie mechaniczne oraz chemiczne.

W tabeli 1 przedstawiono zestawienie technologii chemicznej przeróbki i wzbogacania surowców krytycznych.

Tabela 1. Zestawienie technologii chemicznej przeróbki i wzbogacania surowców krytycznych
[źródło: opracowanie własne na podstawie [1,4–6,11–13]]
Table 1. Summary of chemical processing technology and enrichment of critical raw materials [source: own calculations based on [1,4–6,11–13]]

Surowiec	Technologia
beryl	– Flotacja kolektywna rud berylu w środowisku kwaśnym, – flotacja selektywna rud berylu w środowisku kwaśnym.
kobalt	– Flotacja selektywna rud Cu-Co, – flotacja kolektywno-selektywna rud Cu-Co, – flotacja kolektywno-selektywna rud Cu-Co-Fe, – wzbogacanie mieszanych siarczkowych i utlenionych rud Cu-Co, – wzbogacanie rud polimetalicznych, – wzbogacanie rud As-Co-Ni-Bi, – wzbogacanie rud As-Co-Ag.
wolfram	– Stadialne rozdrabnianie i wzbogacanie grubowpryśniętej rudy hübnerytowej i średniowpryśniętej rudy scheelitowej, – wzbogacanie rud wolframu w cieczach ciężkich, – wzbogacanie rud wolframu w osadzarkach, – wzbogacanie rud wolframu na stołach koncentracyjnych, – wzbogacanie grawitacyjne rud wolframu z zastosowaniem wzbogacalników zwojowych, – wzbogacanie grawitacyjne rud wolframu z zastosowaniem automatycznych stołów koncentracyjnych i flotograwitacji, – flotacja szlamów rudy hübnerytowej, – wzbogacanie flotograwitacyjne koncentratu siarczkowo-kasyterytowo-scheelitowego.
fluoryt	– Przeróbka kwarcowych rud fluorytowych, – przeróbka kwarcowych rud fluorytu zawierających galenę, – przeróbka grubo wpryśniętych węglanowych rud fluorytu zawierających galenę i sfaleryt, – przeróbka drobno wpryśniętych węglanowych rud fluorytu zawierających galenę i sfaleryt, – przeróbka rud barytowo-fluorytowych.

Surowiec	Technologia
magnez	– Elektrolityczna produkcja magnezu metalicznego, – produkcja magnezu metodą elektrolizy, – proces kalcynowania zawiesinowo-gazowego dolomitu i magnezytu jako proces obróbki wstępnej przy produkcji magnezu metalicznego, – produkcja magnezu pierwotnego z zastosowaniem procesu odwadniania.
antymon	– Metoda hydrometalurgicznego wydzielania złota i antymonu (ługowanie alkalicznego siarczku), – technologia przetwarzania koncentratów złotonośnego siarczku antymonu.
german	– Technologia otrzymywania metalicznego germanu, – technologia otrzymywania germanu metodą topienia sferycznego.
gal	– Otrzymywanie galu na drodze elektrolizy lub redukcji tlenku galu(III).
ind	– W procesie flotacji siarczkowych rud cynku i ołowiu ind przechodzi do koncentratu, następnie koncentrat przerabia się pirometalurgicznie. W otrzymanym pyle znajduje się ind, do 70% cynku i 20% ołowiu (w postaci związków), – proces wydzielania indu z pyłów – prażenie sulfatyzujące i ługowanie spieku wodą, – pozostałe technologie chemicznej przeróbki i wzbogacania indu tj.: wymiana jonowa, ekstrakcja mieszaniną kwasów alkilofosforowych, elektroliza chlorku lub siarczanu(VI) indu(III), redukcja tlenku indu(III) wodorem lub cementacja za pomocą cynku lub glinu, rafinowanie.
niob i tantal	– Przeróbka koncentratów niobowo-tantalowych (spiekanie z sodą albo z wodorotlenkiem sodu oraz spiekanie z potażem lub z wodorotlenkiem potasu), – metody rozdziału niobu od tantalu: frakcjonowana krystalizacja związków kompleksowych, takich jak K_2TaF_7 i K_2NbOFs * H_2O, frakcjonowana destylacja chlorków albo fluorków, selektywna ekstrakcja fluorków niobu i tantalu trójbenzyloaminą albo kupferonem w chloroformie, selektywna redukcja chlorków niobu i tantalu za pomocą wodoru, selektywna wymiana na wymieniaczach jonowych.

Surowiec	Technologia
platynowce	– Metoda hydrometalurgiczna przerabiania koncentratu lub szlamu z elektrolizy niklu, – przeróbka koncentratu, uzyskiwanego jako szlam anodowy przy elektrorafinacji surowego niklu otrzymanego z rud kanadyjskich.
pierwiastki ziem rzadkich	– Otrzymywanie skandu z odpadów powstających przy przeróbce wolframitów, – przeróbka koncentratu monacytowego metodą kwaśną, – przeróbka koncentratu monacytowego metodą alkaliczną, – otrzymywanie lantanowców z fosfogipsów, – otrzymywanie lantanowców z luminoforów.

3. Występowanie, produkcja i zapotrzebowanie na surowce krytyczne

Na podstawie analizy literaturowej poniżej przedstawiono informacje dotyczące źródła występowania, produkcji oraz zapotrzebowania krajowego na surowce krytyczne [2,3,7,10].

3.1. Beryl

- *źródła występowania* – na Dolnym Śląsku (głównie w pegmatytach i granitach). Podwyższone zawartości berylu stwierdzono w popiołach z węgli kamiennych GZW (97 tys. Mg berylu),
- *produkcja* – w Polsce nie pozyskuje się rud berylu oraz nie produkuje się berylu metalicznego lub jego związków oraz stopów,
- *zapotrzebowanie krajowe* – pokrywane było do 2003 r. importem znacznych ilości berylu (2,2 Mg0 w postaci metalu i proszku, głównie z Chin i krajów Unii Europejskiej. Dane o obrotach surowcami berylu w latach 2008-2009 obroty nie były wykazywane w statystykach GUS. Obecnie importowane są zmienne ilości wyrobów z berylu (USA, Kazachstan i kraje Unii Europejskiej).

3.2. Kobalt

- *źródła występowania* – złoża rud kobaltu nie występują samodzielne. Jego obecność stwierdzono w złożach rud miedzi na Monoklinie Przedsudeckiej (zasoby szacunkowe 120,6 tys. Mg kobaltu, w tym w złożach eksploatowanych 96,1 tys. Mg oraz w pokładach węgla kamiennego w GZW (zasoby szacunkowe 400 tys. Mg). Średnią zawartość kobaltu w złożu rud miedzi szacuje się na ok. 60 ppm. Najwyższe koncentracje tego pierwiastka występują w rudzie łupkowej (śr. 460 ppm, maksymalnie do 3300 ppm kobaltu) oraz stropowej partii rudy piaskowej złoża Lubin - Małomice (śr. 350 ppm). Potencjalnym źródłem odzysku kobaltu w postaci proszku są odpady po przeróbce złomu kobaltonośnych stopów, stali szlachetnych oraz narzędzi do skrawania wykonanych z węglików spiekanych,

- *produkcja* – W 2009 r., wraz z urobkiem rud miedzi w kopalniach KGHM „Polska Miedź” S.A., wydobyto 1750 Mg kobaltu. Największe ilości tego metalu zawierała ruda eksploatowana w kopalni Lubin–Małomice (82–250 g kobaltu na każdy Mg urobku). W procesie wzbogacania od l30 do 930 ppm kobaltu przechodzi do koncentratów miedzi. W toku ich przeróbki metalurgicznej około 80% kobaltu jest tracone w żużlach konwertorowych, które zawierają 1–2% kobaltu,
- *zapotrzebowanie krajowe* –w całości pokrywane jest importem jego surowców. Saldo obrotów surowcami kobaltu w Polsce jest ujemne.

3.3. Wolfram

- *źródła występowania* – w 2008 r. udokumentowano złoże rud molibdenu z wolframem i miedzią typu porfirowego Myszków, którego zasoby wynoszą 550,8 mln Mg rudy zawierającej 238 tys. Mg wolframu. Złoże ma formę sztokwerku zawierającego okruszcowanie siarczkowo-tlenkowe, związane z waryscyjskim magmatyzmem granitoidowym.
- *produkcja* – w Polsce nie wydobywa się rud wolframu oraz nie produkuje surowców wolframu,
- *zapotrzebowanie krajowe* –pokrywane jest w całości importem jego surowców.

3.4. Fluoryt

- *źródła występowania* – w Polsce nie rozpoznano złóż fluorytu o znaczeniu ekonomicznym. Jego występowanie udokumentowano natomiast w głębszych partiach złoża barytu Stanisławów. Zasoby, wg stanu na 31 grudnia 2009 r., określono na 542 tys. Mg,

- *produkcja* – fluoryt nigdy nie był w Polsce produkowany. Niewielkie ilości kryolitu syntetycznego ok. l–2 tys. Mg/rok, są uzyskiwane w trakcie produkcji kwasu fosforowego(V) z fosforytów przez Zakłady Chemiczne „Siarkopol” Tarnobrzeg Sp. z o.o. Inne związki fluoru produkowane są przez krajowy przemysł chemiczny,
- *zapotrzebowanie krajowe* – w Polsce pokrywane jest importem, który ostatnio osiąga poziom 9,1–9,7 tys. Mg/rok. Na rynku krajowym dominują fluoryty metalurgiczne i ceramiczne (Meksyk), pozostałe fluoryty chemiczne pochodzą z Niemiec i Czech.

3.5. Magnez

- *źródła występowania* – potencjalnym źródłem do produkcji magnezu metalicznego są złoża dolomitów – nie są one jednak obecnie wykorzystywane,
- *produkcja* – w Polsce produkcja magnezu metalicznego z dolomitów nie została podjęta, pomimo opracowania i wdrożenia w skali ćwierćtechnicznej w latach 50-tych w Zakładach Metalurgicznych „Trzebinia” metody pozyskiwania tlenku magnezu i magnezu,
- *zapotrzebowanie krajowe* – pokrywane jest w całości importem, którego poziom po wzroście w 2007 r. do poziomu 5,4 tys. Mg, w latach 2008 i 2009 został ograniczony o 30%. Import magnezu odbywa się głównie z Chin (50–85%), Austrii, Czech, Holandii, Niemiec oraz Węgier i Rosji.

3.6. Antymon

- *źródła występowania* – w Polsce nie rozpoznano złóż rud antymonu a także innych rud antymonośnych,
- produkcja – w Polsce nie produkuje się półproduktów antymonu,
- *zapotrzebowanie krajowe* – pokrywane jest w całości importem głównie z Chin. W latach 2006–2007 import antymonu nieobrobionego wynosił ponad 140 Mg/rok, a w latach 2008–2009 spadł do poziomu ok. 60 Mg/rok. Natomiast w przypadku tlenków antymonu wynosił on w latach 2006–2007 ok. 1350 Mg/rok, by w następnych latach ustabilizować się na poziomie ok. 1000 Mg/rok.

3.7. Grafit

- *źródła występowania* – grafit tworzy nagromadzenia w postaci łupków grafitowych w okolicach Stronia Śląskiego. Natomiast wkładki skał grafitowych spotykane są koło Strzelina, Dzierżoniowa, Wałbrzycha i Bystrzycy Kłodzkiej. Grafit występuje w wielu różnych skałach metamorficznych (m.in. w łupkach krystalicznych Tatr Zachodnich),
- *produkcja* – z uwagi na niewielkie złoża grafitu, brak w Polsce wydobycia grafitu naturalnego. Szeroko natomiast stosowane są substytuty grafitu. Wyroby z węgli uszlachetnionych, produktów grafityzowanych i grafitu syntetycznego produkowane w Polsce głównie przez SGL Carbon Polska S.A. (Nowy Sącz i Racibórz). Zakład w Raciborzu, wytwarza szerokie spektrum wyrobów z grafitu i węgla, m.in. wyłożenia grafitowe do wielkich pieców, pieców elektrycznych i elektrolizerów glinu oraz katod grafitowych, natomiast zakład w Nowym Sączu specjalizuje się głównie w produkcji elektrod grafitowych. Elektrody węglowe oraz bloki katodowe trafiają do hut w Czechach, Słowacji, Niemczech, Norwegii i Turcji, podczas gdy grafity specjalne użytkowane są np. do produkcji baterii zasilających m.in. laptopy, a grafitowe ślizgi stosowane są w napędach lokomotyw i tramwajów. Produkcja grafitu syntetycznego wynosiła w 2005 r. ok. 50 tys. Mg, w 2008 ok. 66 tys. Mg, by spaść do poziomu ok. 53 tys. Mg w 2009 r. W latach 2007–2008 według danych GUS produkcja elektrod węglowych i pozostałych wyrobów z grafitu wynosiła ok. 70–80 tys. Mg, by spaść do poziomu 50 tys. Mg w 2009 r. z uwagi na kryzys w sektorze hutniczym,
- *zapotrzebowanie krajowe* – naturalny pokrywane jest w całości importem, którego poziom wahał się w ostatnich latach w przedziale 3–6 tys. Mg/rok.

3.8. German

- *źródła występowania* – german nie tworzy samodzielnych złóż. Występuje także w ilościach śladowych w rudach Zn-Pb złóż śląsko-krakowskich. Potencjalne zasoby w złożach wynoszą 40 Mg. Nie są one jednak obecnie wykorzystywane,

- *produkcja* – pomimo pozyskiwania i przetwarzania w latach ubiegłych germanonośnych rud Zn-Pb nie podjęto produkcji germanu w Polsce,
- *zapotrzebowanie krajowe* – pokrywane jest w całości nieregularnym importem germanu (nieobrobionego, odpadów i złomu, proszków) oraz ciągłym importem tlenków germanu w ilości od 17–34 Mg/rok (Francja, Wielka Brytania, Holandia, Chiny, Kanada, USA i Japonia). Notowany jest również import zmiennych ilości wyrobów z germanu.

3.9. Gal

- *źródła występowania* – potencjalne zasoby galu w nie zagospodarowanych dotychczas złożach rud cynkowo-ołowiowych śląsko-krakowskich zostały określone na ok. 120 Mg. Gal sporadycznie tworzy własne fazy mineralne, brak samodzielnych złóż. Znaczenie praktyczne mają domieszki galu jako składnika rozproszonego w złożach innych kopalin. Ponad 90% pierwotnego galu pozyskuje się w złożonych procesach elektrolitycznych, z tzw. czerwonych szlamów powstających w trakcie przerobu boksytów metodą Bayer'a na aluminę, a resztę otrzymuje się metodami chemicznymi z pyłów hutnictwa cynku,
- *produkcja* – pomimo pozyskiwania i przetwarzania w latach ubiegłych galonośnych rud cynkowo-ołowiowych nie podjęto produkcji galu w Polsce,
- *zapotrzebowanie krajowe* – pokrywane jest importem, głównie wyrobów elektronicznych i innych z jego udziałem. Import galu do 2007 r., w formie nie obrobionej, był sporadyczny, w 2008 r. wzrósł do 57 kg, a w 2009 spadł o połowę. Głównymi dostawcami są następujące kraje: Słowacja, Niemcy, USA, Francja, i Szwecja. W latach 2008–2009 był odnotowany reeksport do Białorusi.

3.10. Ind

- *źródła występowania* – złoża rud cynkowo-ołowiowych śląsko-krakowskich nie są indonośne. Źródłem indu są rudy cynku, cyny, ołowiu, wolframu, żelaza oraz piryty. Ind najczęściej jest pozyskiwany sposobami hydrometalurgicznymi z wypałków po prażeniu siarczkowych rud cynku w postaci silnie zanieczyszczonego indu czarnego. Wymaga to następnie oczyszczenia elektrochemicznego, destylacji próżniowej oraz rafinacji strefowej do indu metalicznego o czystości min. 99,97%,

- *produkcja* – ind w Polsce nie jest produkowany, podobnie jak surowce indonośne,
- *zapotrzebowanie krajowe* – jest pokrywane regularnym importem. Głównymi dostawcami są: Stany Zjednoczone; inni dostawcy to: Chiny, Belgia, Niemcy, Szwajcaria, Japonia i Wielka Brytania.

3.11. Niob

- *źródła występowania* – brak jest złóż kopalin niobu i realnych perspektyw na ich odkrycie,
- *produkcja* – surowce niobu nie są produkowane w Polsce,
- *zapotrzebowanie krajowe* – obroty niobem i renem są ujmowane w statystykach łącznie, jednak należy sądzić, że główna część obrotów przypada na niob. Najważniejszym surowcem niobu sprowadzanym do Polski jest żelazoniob. Wielkość importu jest zmienna i zależy od zapotrzebowania przemysłu stalowniczego.

3.12. Tantal

- *źródła występowania* – nie rozpoznano złóż kopalin tantalu i brak perspektyw na ich odkrycie. Podstawowymi źródłami tantalu są jego rudy oraz rudy tantalowo-niobowe, rudy niobu, rudy cyny, który wraz z niobem stanowi domieszkę, a także żużle tantalonośne hutnictwa cyny. Koncentraty tantalitowe (60% tlenku tantalu(V) i tlenku niobu(V)) wymagają skomplikowanej wstępnej obróbki chemicznej oraz metalurgicznej celem otrzymania metalicznego tantalu. Bezpośrednio uzyskuje się go z żużli tantalonośnych (zawierają 12–15% tlenku tantalu(V)) powstałych po przerobie hutniczym kasyterytu. Syntetyczny koncentrat tantalitu, zawiera 50% tlenku tantalu(V) i jest pozyskiwany z żużli odpadowych hutnictwa cyny,
- *produkcja* – odzysk tantalu z surowców wtórnych okresowo jest prowadzony w byłym zakładzie Unitra-Cemat w Skawinie.

  W 2006 r., największy producent tantalu – Australia, znacznie ograniczył produkcję, co doprowadziło do spadku wielkości produkcji o ponad 30%. Natomiast w latach 2007–2008 podaż światowa wzrosła niemal o 32%. Kryzys finansowy w 2009 r. doprowadził do 39% spadku produkcji światowej surowców tantalu,

- *zapotrzebowanie krajowe* – dostawy tantalu nieobrobionego i wyrobów z tantalu (sztaby, pręty, kształtowniki, druty, blachy, taśmy i folie) pochodziły z Niemiec i Austrii oraz z Chin, USA i krajów UE. Notuje się również reeksport odpadów, złomu i wyrobów z tantalu do Wielkiej Brytanii, Niemiec i Rosji.

3.13. Platynowce

- *źródła występowania* – źródłem pierwotnym platynowców są złoża rud miedzi na Monoklinie Przedsudeckiej. Platyna i pallad występują przeważnie w spągu łupka miedzionośnego. Platynowce tworzą minerały własne, a także domieszki w minerałach złota i w związkach niemetalicznych. Źródłami wtórnymi są głównie siatki katalityczno-wychwytujące, a także złom i odpady platynowców z innych zakładów produkujących wyroby z ich udziałem lub ich związki,
- *produkcja* – w cyklu technologicznym produkcji KGHM „Polska Miedź" S A. platynowce występujące głównie w rudzie łupkowej przechodzą kolejno do koncentratów rud miedzi, miedzi anodowej oraz szlamów anodowych po rafinacji miedzi, które są w całości przetwarzane w HM Głogów. W stosowanej tu technologii Boliden Kaldo prowadzi się procesy: elektrorafinacja srebra, ługowanie i strącanie złota oraz wydzielenie selenu. Otrzymywany jest szlam platynowo-palladowy zawierający 22–36% Pt i 12–22% Pd. Produkcja tego szlamu w ostatnich latach ustabilizowała się na poziomu 90–100 kg/rok. Szlamy te sprzedawane są głównie do Mennicy Państwowej S.A. w Warszawie, gdzie następuje rafinacja platynowców. Mniejsze ilości są użytkowane także przez POCH SA. w Gliwicach. Sporadycznie część produkcji kierowana jest na eksport. Platyna odzyskiwana jest również z roztworów odpadowych Wydziału Metali Szlachetnych w Legnickim Oddziale Instytutu Metali Nieżelaznych, a produktem końcowym jest koncentrat platyny zawierający ok. 30% tego pierwiastka.

  Platynowce rafinowane są wytwarzane głównie przez firmę Mennica-Metale Szlachetne Sp. z o.o. zarówno ze wspomnianych szlamów platynowo-palladowych, jak i ze złomów i odpadów platynowców (szczególnie siatki katalityczne i siatki katalityczno-wychwytujące z zakładów azotowych). Produkcja platyny ze szlamów szacowana jest na 25–30 kg/rok, a palladu na poziomie 15–20 kg/rok. Znacznie większa jest produkcja platyny, palladu, rodu i innych platynowców ze złomów. Łączna krajowa produkcja platynowców (surowych i proszków) wyniosła w 2007 r. 465 kg, w 2008 r. 381 kg, a w 2009 – 95 kg (dane za poprzednie lata nie są dostępne), w tym większość ze źródeł wtórnych,

- *zapotrzebowanie krajowe* – na najwyższym i stosunkowo stabilnym poziomie kilkuset-kilku tysięcy kilogramów na rok kształtują się obroty półproduktami platynowymi: sztabami, prętami i drutem platynowym. Obroty były bardzo zmienne, niekiedy przekraczając 100 kg/rok lub nawet 1000 kg/rok. Oficjalne obroty platynowcami, surowymi i ich półproduktami prowadzone są z krajami Europy Zachodniej i Środkowej oraz USA. Wobec znacznych wahań w poziomie obrotów poszczególnymi platynowcami ważne są także salda ich obrotów. Łączne saldo obrotów platynowcami w formie surowej lub półproduktów, tradycyjnie jest ujemne na poziomie kilku-kilkunastu milionów PLN/rok, choć wyjątkowo w latach 2005–2006 było ono dodatnie, a w 2009 r. dodatnie w zakresie obrotów półproduktami. Wartości jednostkowe obrotów poszczególnymi platynowcami w formie surowej lub półproduktów wahają się w bardzo szerokim zakresie, co wynika ze zróżnicowanej jakości towaru w obrębie danej pozycji.

3.14. Pierwiastki ziem rzadkich

- *źródła występowania* – złoża pierwiastków ziem rzadkich znajdują się na Dolnym Śląsku w okolicach Szklarskiej Poręby (do 0,5%) i Bogatyni (1,55% jako tlenki), i mają znaczenie mineralogiczne. Ważne gospodarczo są natomiast źródła wtórne, tzn. odpadowe fosfogipsy, importowane koncentraty apatytowe (0,8–1,0% tlenków pierwiastków ziem rzadkich) ze złóż masywu Chibińskiego w Rosji do produkcji kwasu fosforowego(V). Dobrze rozpoznane jest składowisko fosfogipsów przy ZCh Wizów, które zawiera 8,28 tys. Mg pierwiastków ziem rzadkich w suchym fosfogipsie,

- *produkcja* – pomimo, że badania nad pozyskiwaniem pierwiastków ziem rzadkich ze zwałowiska w Wizowie potwierdzają możliwość ich produkcji nie została jednak ona podjęta ze względów ekonomicznych.
- *zapotrzebowanie krajowe* – zaspokajane jest importem, głównie z Chin, krajów Europy Zachodniej, USA, a w latach 2007–2008 z Estonii. W okresie 2005–2009 w strukturze importu dominowały związki metali ziem rzadkich i ceru.

4. Podsumowanie i wnioski

Możliwości pozyskania surowców mineralnych zaliczanych do krytycznych są w Polsce niewielkie m. in. z następujących powodów: brak złóż o znaczeniu ekonomicznym (beryl, magnez, niob, kobalt i antymon, wolfram), brak perspektyw na odkrycie złóż niobu, tantalu i fluorytu czy współwystępowanie surowców z innymi metalami (niob, platyna, gal, ind, german). Natomiast złoża pierwiastków ziem rzadkich znajdujące się w okolicach Szklarskiej Poręby i Bogatyni mają znaczenie tylko mineralogiczne [2,3,5–7].

W Polsce beryl występuje na Dolnym Śląsku, głównie w pegmatytach i granitach. Natomiast potencjalnym źródłem do produkcji magnezu metalicznego są złoża dolomitów, które obecnie nie są wykorzystywane. Na Dolnym Śląsku znajdują się także złoża pierwiastków ziem rzadkich ale mają one tylko znaczenie mineralogiczne. W Polsce brak jest złóż kopalin niobu i realnych perspektyw na ich odkrycie. Surowce niobu nie są produkowane w Polsce. W Polsce nie rozpoznano także złóż kopalin tantalu i nie ma perspektyw na ich odkrycie. Udokumentowano złoże rud molibdenu z wolframem i miedzią typu porfirowego w okolicach Myszkowa, którego zasoby wynoszą 550,8 mln Mg rudy zawierającej 238 tys. Mg wolframu. Jednak w Polsce nie wydobywa się rud wolframu i nie produkuje surowców wolframu.

Źródłem pierwotnym platynowców są złoża rud miedzi, zawierające również kobalt. Złoża te znajdują się w Monoklinie Przedsudeckiej. Platynowce tworzą minerały własne, a także domieszki w minerałach złota i w związkach niemetalicznych. W Polsce nie występują samodzielne złoża rud kobaltu. W Polsce brakuje samodzielnych złóż galu. Potencjalne jego zasoby w nie zagospodarowanych dotychczas złożach rud cynkowo-ołowiowych śląsko-krakowskich zostały określone na ok. 120 Mg. Gal sporadycznie tworzy własne fazy mineralne. Gal jest składnikiem rozproszonym w złożach innych kopalin. Pomimo pozyskiwania i przetwarzania galonośnych rud cynkowo-ołowiowych nie podjęto do tej pory produkcji galu w Polsce. Natomiast źródłem indu są rudy cynku, cyny, ołowiu, wolframu, żelaza oraz piryty. Ind i surowce indonośne w Polsce nie są produkowane. German występuje tylko w ilościach śladowych w rudach Zn-Pb złóż śląsko-krakowskich. Jego potencjalne zasoby w złożach udokumentowanych określono na poziomie 40 Mg, które nie są one obecnie wykorzystywane. Pomimo pozyskiwania i przetwarzania germanonośnych rud Zn-Pb nie podjęto produkcji germanu w Polsce. W Polsce nie rozpoznano złóż rud Sb i jego rud antymonośnych. Nie produkuje się również surowców antymonu.

W Polsce nie rozpoznano złóż fluorytu o znaczeniu ekonomicznym. Jego występowanie udokumentowano natomiast w głębszych partiach złoża barytu Stanisławów. Do tej pory fluoryt nigdy nie był w Polsce produkowany. Natomiast inne związki fluoru produkowane są przez przemysł chemiczny w Polsce [2,3,5–7].

Niektóre z surowców krytycznych można pozyskać ze źródeł wtórnych. I tak, przykładowo szacuje się, że w popiołach z węgli kamiennych znajduje się 97 tys. Mg berylu jednak nie ma odpowiedniej technologii jego odzysku. Ważne gospodarczo są źródła wtórne pierwiastków ziem rzadkich. Są to odpadowe fosfogipsy pozostałe po przerobie słabo wzbogaconych, importowanych koncentratów apatytowych ze złóż masywu Chibińskiego w Rosji. Zawierają one 0,8–1,0% tlenków pierwiastków ziem rzadkich. Fosfogipsy te znajdują zastosowanie w produkcji kwasu fosforowego(V). Przy Zakładach Chemicznych Wizów znajduje się zwałowisko fosfogipsów, będącego źródłem pierwiastków ziem rzadkich. Pomimo, prowadzonych badań nad pozyskiwaniem tych pierwiastków ze zwałowiska ich produkcji jednak nie została ona podjęta. Źródłami wtórnymi platynowców są głównie siatki katalityczne, a także złom i odpady platynowców, z innych zakładów produkujących wyroby z ich udziałem lub ich związki. Zaobserwowano obroty złomem magnezu. Regularnie sprowadzane są również duże ilości magnezu w postaci proszków, opiłków, wiórów i granulek. Natomiast statystycznie nieuchwytne są obroty indem w masowo sprowadzanych wyrobach z przemysłu elektronicznego.

Potencjalnym źródłem odzysku kobaltu w postaci proszku są odpady po przeróbce złomu kobaltonośnych stopów, stali szlachetnych oraz narzędzi do skrawania wykonanych z węglików spiekanych. Ponad 90% pierwotnego galu pozyskuje się w złożonych procesach elektrolitycznych, z tzw. czerwonych szlamów powstających w trakcie przerobu boksytów metodą Bayer'a na aluminę, a resztę otrzymuje się metodami chemicznymi z pyłów hutnictwa cynku. Coraz większe znaczenie, jako źródło indu, zyskują surowce wtórne, głównie zużyte monitory, zawierające tlenek indocyny [3,5–7].

W 2012 r. odnotowano wzrost zapotrzebowania na antymon i kobalt. Zapotrzebowanie na te surowce wyrażono wielkością zużycia rzeczywistego lub pozornego w porównaniu do wielkości z lat 2008–2011. I tak, np.: dla antymonu zapotrzebowanie w Polsce wynosi +15%, a dla kobaltu +10% [1].

Zapotrzebowanie krajowe antymonu pokrywane jest w całości importem tlenków, antymonu nieobrobionego i proszków głównie z Chin. W latach 2006–2007 import antymonu nieobrobionego wynosił ponad 140 Mg/rok, natomiast w latach 2008–2012 wahał się w przedziale 48-70 Mg/rok. Natomiast w przypadku tlenków antymonu wynosił on w latach 2006–2007 ok. 1350 Mg/rok, a w latach 2008–2012 ustabilizował się na poziomie ok. 1000 Mg/rok z nieznacznym spadkiem w 2012 r. do wartości ok. 900 Mg/rok.

Wielkość importu kobaltu i jego surowców w całości jest pokrywana importem, co przestawiono w tabeli 2.

Tabela 2. Struktura importu kobaltu w latach 2005–2012
Table 2. Structure of imports of cobalt in the years 2005–2012

Wyszczególnienie	Struktura importu kobaltu w latach 2005–2012 [Mg]							
	2005	2006	2007	2008	2009	2010	2011	2012
surowce metaliczne kobaltu	25	40	57	39	39	34	33	33
tlenki i wodorotlenki kobaltu	134	62	18	37	14	18	110	15

Zapotrzebowanie na kobalt i jego surowce jest pokrywane dostawami z Belgii, Chin,. Finlandii, Francji, Holandii, Kanady, Niemiec, USA i Wielkiej Brytanii.

W 2012 r. zanotowano natomiast spadek zapotrzebowania na następujące surowce: magnez (-10%), german (-26%), pierwiastki ziem rzadkich (-28%), ind, tantal i wolfram (-86%) oraz niob (-100%). Brak danych nt. zapotrzebowania na beryl i platynowce [3].

Zapotrzebowanie krajowe na magnez metaliczny pokrywane jest w całości importem. Wielkość importu magnezu metalicznego w latach 2010–2012 ustabilizowała się na poziomie ok. 5 tys. Mg po 30% ograniczeniu go w latach 2008–2009. W latach 2010–2012 import surowców magnezu pochodził głównie z Chin (50–85%), Austrii, Czech, Holandii, Niemiec oraz Węgier i wahał się w granicach 4,8–5,7 tys. Mg. W 2012 r. największe dostawy surowców magnezu w ilości 3,3 tys. Mg pochodziły z Chin.

Zapotrzebowanie na german pokrywane jest w całości nieregularnym jego importem (głównie germanu nieobrobionego, odpadów i złomu, proszków) wahającym się w granicach kilku do kilkunastu kilogramów rocznie oraz ciągłym importem tlenków germanu w ilości od 17–34 Mg/rok. Kierunki importu tlenków germanu to głównie Francja, Wielka Brytania, Holandia oraz Chiny, Kanada, USA i Japonia.

Zapotrzebowanie na surowce pierwiastków ziem rzadkich zaspokajane jest importem. Główne kierunki importu to: Chiny, kraje Europy Zachodniej, USA, a w latach 2007–2008 z Estonii. W okresie 2005–2012 w strukturze importu dominowały związki metali ziem rzadkich i ceru. Wielkość importu tych surowców jest zmienna zwłaszcza dla związków metali ziem rzadkich oprócz ceru, co przedstawiono w tabeli 3.

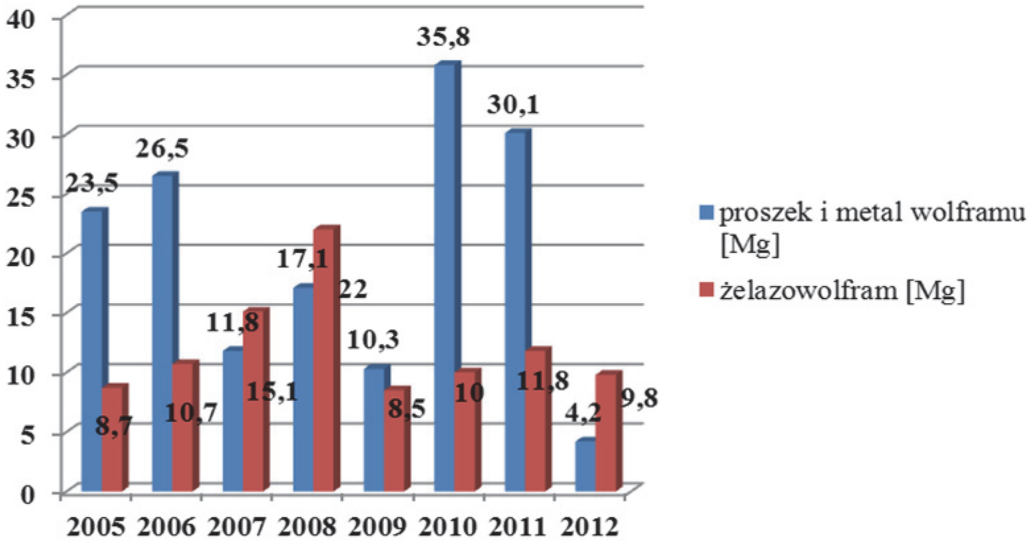
W latach 2005–2012 krajowe zapotrzebowanie na ind jest pokrywane regularnym importem z USA, Chin, Belgii, Niemiec, Szwajcarii, Japonii i Wielkiej Brytanii. W latach 2005–2008 import indu wzrósł z 13 kg do 77 kg, następnie nastąpił w 2009 r. spadek importu indu do 48 kg. W 2010 r. wartość importu indu osiągnęła wartość aż 20 Mg, a potem osiągnęła w 2012 r. poziom 9 kg.

Tabela 3. Struktura importu pierwiastków ziem rzadkich w latach 2005–2012
Table 3. Structure of imports of rare earths in the years 2005–2012

Rok	Struktura importu pierwiastków ziem rzadkich w latach 2005–2012 [Mg]							
	2005	2006	2007	2008	2009	2010	2011	2012
Metale ziem rzadkich, skand i itr (łącznie)	6,0	6,8	0,9	0,6	2,4	7,9	0,0	1,7
Związki metali ziem rzadkich (oprócz ceru)	39,0	29,9	62,7	57,6	15,6	47,5	21,0	12,4
Związki ceru	79,3	94,1	84,8	147,8	41,0	135,4	85,5	64,9

Zapotrzebowanie na wolfram pokrywane jest w całości importem proszku i metalu wolframu oraz żelazowolframu m.in. z: Chin, Niemiec, Wielkiej Brytanii oraz Rosji.

Na rysunku 1. przestawiono strukturę importu w latach 2005–2012 proszku i metalu wolframu oraz żelazowolframu.



Rys. 1. Struktura importu pierwiastków produktów wolframu w latach 2005–2012
Fig. 1. Structure of imports of products of tungsten in the years 2005–2012

Najważniejszym surowcem niobu sprowadzanym do Polski jest żelazoniob. Wielkość importu jest zmienna i zależy od zapotrzebowania przemysłu stalowniczego. W latach 2005–2012 kształtowała się na poziomie od 104 Mg w 2005 r. do 397 Mg w 2010 r. poprzez 377 Mg w 2007 r. i 379 Mg w 2012 r. Żelazoniob był importowany z Brazylii, Holandii.

Zapotrzebowanie krajowe berylu pokrywane było do 2003 r. importem ok. 2,2 Mg/rok berylu w postaci metalu i proszku, głównie z Chin i krajów Unii Europejskiej. W latach 2005–2009 dane obrotach berylu nie były wykazywane w statystykach GUS. W 2010 r. reeksportowano wyroby z berylu, przekraczający sześciokrotnie wielkość jego importu. Jedynym dostawcą berylu do Polski w latach 2010–2011 był Kazachstan, a w przypadku wyrobów z berylu głównymi dostawcami w ostatnich latach były kraje UE, USA i Kazachstan. Reeksport w 2010 r. był kierowany do Belgii i Szwajcarii.

Import tantalu jest niewielki, wg danych GUS, w 2006 r. wyniósł tylko 2 kg, w 2007 r. – 173 kg, a w 2008 r. – 18 kg. W latach następnych nie odnotowano importu tantalu. Import tantalu nieobrobionego i wyrobów z tantalu (sztaby, pręty, kształtowniki, druty, blachy, taśmy i folie) pochodził z Niemiec i Austrii oraz z Chin, USA i krajów UE. Odbywał się również reeksport odpadów, złomu i wyrobów z tantalu do Wielkiej Brytanii, Niemiec i Rosji.

Import platynowców do Polski w latach 2005–2012 był bardzo zmienny, co przedstawiono w tabeli 3. Głównymi kierunkami importu były Niemcy, Słowacja, USA i Wielka Brytania.

Tabela 4. Struktura importu platynowców w latach 2005–2012
Table 4. Structure of imports of platinum group metals in the years 2005–2012

Wyszczególnienie	Struktura importu platynowców w latach 2005–2012 [kg]							
	2005	2006	2007	2008	2009	2010	2011	2012
platynowce-surowe i proszki	2	7	102	126	45	37	41	675
platynowce-półprodukty	3378	1045	559	668	4770	2590	2092	618

Z powyższych rozważań można wyciągnąć wniosek, że zapotrzebowanie na surowce krytyczne jest pokrywane głównie importem. Na przestrzeni analizowanego okresu czasowego, w latach 2005–2012, zmienność importu dotyczyła m.in. platynowców, antymonu, magnezu, germanu, pierwiastków ziem rzadkich, indu czy niobu.

Prognozy gospodarcze na najbliższe lata wskazują na to, że związany z rozwojem nowych technologii wzrost zapotrzebowania na te surowce, będzie pokrywany importem gotowych wyrobów z berylu, galu, indu, germanu, niobu, tantalu i wolframu (Chiny oraz kraje Unii Europejskiej o większym potencjale przemysłowym) [2,8,4,14].

Literatura

1. bazy.uprp.pl – informacje nt. zgłoszeń patentowych .
2. *Bilans gospodarki surowcami mineralnymi Polski i świata 2009* (red. T. Smakowski, R. Ney, K. Galos). Wyd. IGSMiE PAN, Kraków, (2011).
3. **Biel K., Blaschke W., Witkowska-Kita B.:** *Surowce krytyczne – studium pozyskiwania w Polsce*. Monografia: Innowacyjne i przyjazne dla środowiska techniki i technologie przeróbki surowców mineralnych, Wyd. KOMAG Gliwice, 7–20 (2013).
4. **Blaschke W., Blaschke Z.:** *Mała encyklopedia technologii przeróbki kopalin,* Inżynieria Mineralna. Tom 20–22. Wyd. PTPK, Kraków 2011.
5. **Blaschke W., Blaschke Z.:** *Przeróbka mechaniczna, w Surowce Mineralne Świata* (red. A. Bolewski). Tom Al-Be-Li-Mg, Tom Ba-B-F-Sr, Tom Ni-Co, Tom Mo-W-Re-Sc, Wyd. Geologiczne, Warszawa, (1976,1978, 1984,1985).
6. **Brzyska W.:** *Lantanowce i aktynowce*. Wydawnictwa Naukowo-Techniczne, Warszawa 1987.
7. **Ciba J.:** *Mała encyklopedia pierwiastków*. Wydawnictwa Naukowo-Techniczne, Warszawa 1996.
8. *Critical raw materials for the EU – Report of the Ad-hoc Working Group on defining critical raw materials.* EU Commissision Enterprise and Industry. (2010).
9. **Gruszczyk H.:** *Nauka o złożach*. Wydawnictwo Geologiczne, Warszawa 1984.
10. **Kabata-Pendias A.:** *Biogeochemia pierwiastków śladowych*. Wydawnictwa Naukowe PWN, Warszawa 1993.
11. **Kijkowska J.:** *Sposób odzyskiwania lantanowców z fosfogipsu*. Opis patentowy Nr 129444, (1987).

12. **Kijkowska R., Mazanek Cz.:** *Otrzymywanie koncentratów ziem rzadkich z apatytu*. Praca zbiorowa „Pierwiastki ziem rzadkich – surowce technologiczne, zastosowanie". Wydawnictwa Naukowo-Techniczne, Warszawa 1990.
13. **Kowalczyk J., Mazanek Cz.:** *Ziemie rzadkie – problem zaspokajania potrzeb gospodarki narodowej*. Fizykochemiczne Problemy Mineralurgii (Physicochemical Problems of Mineral Processing), 19, 233–241 (1987).
14. **Radwanek-Bąk B.:** *Zasoby kopalin Polski w aspekcie oceny surowców krytycznych Unii Europejskiej*. Gospodarka Surowcami Mineralnymi (Mineral Resources Managment), 1 (27), 5–19 (2011).
15. **Smakowski T.:** *Surowce mineralne – krytyczne czy deficytowe dla gospodarki UE i Polski*. Zeszyty Naukowe IGSMiE PAN, 81, 59–68 (2011).

Analysis of the Possibility of Obtaining Critical Minerals

Abstract

In 2008 Committee on Critical Mineral Impacts of the U.S. Economy, presented a definition of critical raw materials, which was also adopted by the countries of the European Union. According to this definition the critical raw materials are "minerals / materials exposed to the risk of disrupting or interruption of the supply, for which this deficit can have serious economic consequences for the entire economy".

The most critical to the economy of the European Union were considered 14 raw materials of significant economic importance, (i.e.: antimony, beryllium, cobalt, fluorspar, gallium, germanium, graphite, indium, magnesium metal, niobium, platinum group metals, rare earths, tantalum and tungsten) characterized primarily by a high risk of shortage or lack of supply, which result from a limited number of sources of their acquisition. Most materials belonging to this group are essential for the development of new technologies. The above list of 14 critical raw materials is a proposal that can be modified as a result of the reduction of critical raw materials resources in European countries.

As a result of the literature analysis of identified technology it was found that the most recognizable way to enrich the individual raw materials is processing their ores, which are the carriers of many metals.

The ore is processed in order to improve the chemical composition, standardization of the ore in terms of chemical and physico-chemical properties, providing adequate size pieces of the ore.

Since the mined ore is usually not suitable for direct processing, multistage process of the ore enrichment is important. The enrichment of metal ores can be divided into: mechanical and chemical enrichment. The process of ore processing was applied to the following materials: beryllium, cobalt, tungsten and fluorite.

A comprehensive assessment of mineral potential of the European Union countries and the identification of the so-called critical raw materials necessary for its harmonious and sustainable economic development and technological progress, is one of the priorities of the EU's raw materials policy.

Słowa kluczowe:
surowce krytyczne, raport Komitetu UE, technologie pozyskiwania, produkcja, zapotrzebowanie

Keywords:
critical raw materials, EU Committee report, technology acquisition, production, demand

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Oczyszczanie ścieków ze stacji naprawy samochodów

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1. Wstęp – informacja literaturowa

Ścieki zaolejone jako ścieki poprodukcyjne pochodzą z różnych przemysłów (branż) i to determinuje ich charakter. Zatem, mogą to być po prostu ścieki miejskie, w których znajdują się substancje tłuszczowe [25], ścieki zawierające zużyte oleje smarowe, paliwa oraz oleje napędowe [3,9,11,12,14–16,34], ścieki zawierające oleje chłodząco-smarujące [42], ścieki z przemysłu spożywczego [32].

Zaolejone ścieki zawierają często także inne zanieczyszczenia z grupy związków chemii nieorganicznej oraz zanieczyszczenia stałe, które wpływają na ostateczny efekt oczyszczania. Do procesów, które są stosowane najczęściej dla oczyszczania ścieków zaolejonych należą m.in. biodegradacja, oczyszczanie mechaniczne polegające na zastosowaniu oddzielaczy tzw. lamelowych lub wypełnień kolumnowych, procesy mikrofiltracji na membranach [1,6,10,13,21,23], oczyszczanie ścieków na złożach hydrofitowych [2,5,7,17,27–31], oczyszczanie ścieków metodą osadu czynnego [8,18,20,22,24,25], w procesach filtracji grawitacyjnej, w tym biofiltracji [31], w procesie sorpcji [26,36], w procesie koagulacji [19], w procesie termokatalitycznego unieszkodliwiania ścieków zawierających oleje i detergenty [14], w procesach destabilizacji emulsji olejowych, metodami chemicznymi [33,37,38], oraz metodą flotacji [32,39].

W niniejszej publikacji przedstawione są badania rozpoznawcze możliwości podczyszczania ścieków będących nośnikiem głównie benzyny i oleju napędowego a więc takich, które powstają w każdym zakładzie usługowym naprawy samochodów oraz na stacjach benzynowych. Jest to ogromna ilość punktów usługowych, które co prawda w roboczym odniesieniu do jednej doby, nie produkują dużych ilości ścieków a wręcz odwrotnie ilości niewielkie, to jednak w skali kraju jest to ilość ogromna, która najczęściej odprowadzana jest do kanalizacji – niekoniecznie spełniająca warunki dla takich zrzutów, które to wytycza dana oczyszczalnia ścieków miejsko-gminna odbierająca te ścieki olejowo-benzynowe.

Na każdej stacji benzynowej i w każdym zakładzie naprawczym samochodów znajduje się na wyposażeniu sprężarka, a więc jest dostęp do strugi sprężonego powietrza.

Dlatego też autorzy podjęli rozważania nad koncepcją zastosowania procesu flotacji, celem podczyszczenia ścieków olejowo-benzynowych, jako mała instalacja podczyszczania ścieków, która mogłaby być zainstalowana w oddzielnym pomieszczeniu warsztatu samochodowego lub też stacji benzynowej. Niniejsza praca zawiera wstępne testy o charakterze pilotażowo-rozpoznawczym.

Badania laboratoryjne procesów flotacji przeprowadzono w dwóch niezależnych grupach badań tj. na ściekach modelowych a potem na ściekach rzeczywistych.

2. Badania własne – laboratoryjne

2.1. Badania procesu flotacji na ścieku modelowym

Badania procesu flotacji wykonano na flotowniku mechanicznym typu MECHANOBR.

W pierwszej serii badań spreparowano roztwór modelowy na bazie czystej wody tak, że w każdym dm^3 takiego roztworu znajdowało się 1 cm^3/dm^3 benzyny oraz 1 cm^3/dm^3 detergentu. Stosowanym w badaniach detergentem był płyn o nazwie handlowej LUDWIK GRUPA INCO, w którego skład wchodzą: 5–15% – środki anionowe powierzchniowo-czynne/anionic surfactants, 5% – amfoteryczne środki powierzchniowo czynne/amphoteric surfactants, konserwant/preservative (Methylchloroisothiazolinone, Methilisothiazolinone, 2-Bromo-2- Nitropropane-1,3-Diol), barwnik/dye (CI 9140, CI 42080), kompozycja zapachowa/perfume.

Wartością zawsze stałą był czas flotacji t = 3 min, natomiast wartością zmienną, tzw. niezależną, była ilość wprowadzanego oleju napędowego do 1 dm^3 takiego ścieku, odpowiednio: 1,0 cm^3/dm^3, 2,0 cm^3/dm^3 oraz 3,0 cm^3/dm^3 – tabela 1.

Tak spreparowane 3 różne ścieki odpowiadały tzw. wskaźnikowi ekstraktu eterowego, który charakteryzował roztwór przeznaczony do flotacji.

W tabeli 1 podano rezultat flotacji wszystkich trzech ścieków modelowych, natomiast w tabeli 2 podano wartość wskaźnika substancji rozpuszczonych SR, zarówno przed flotacją, jako parametr zmienny niezależny oraz po procesie flotacji, jako parametr zmienny zależny (wynikowy).

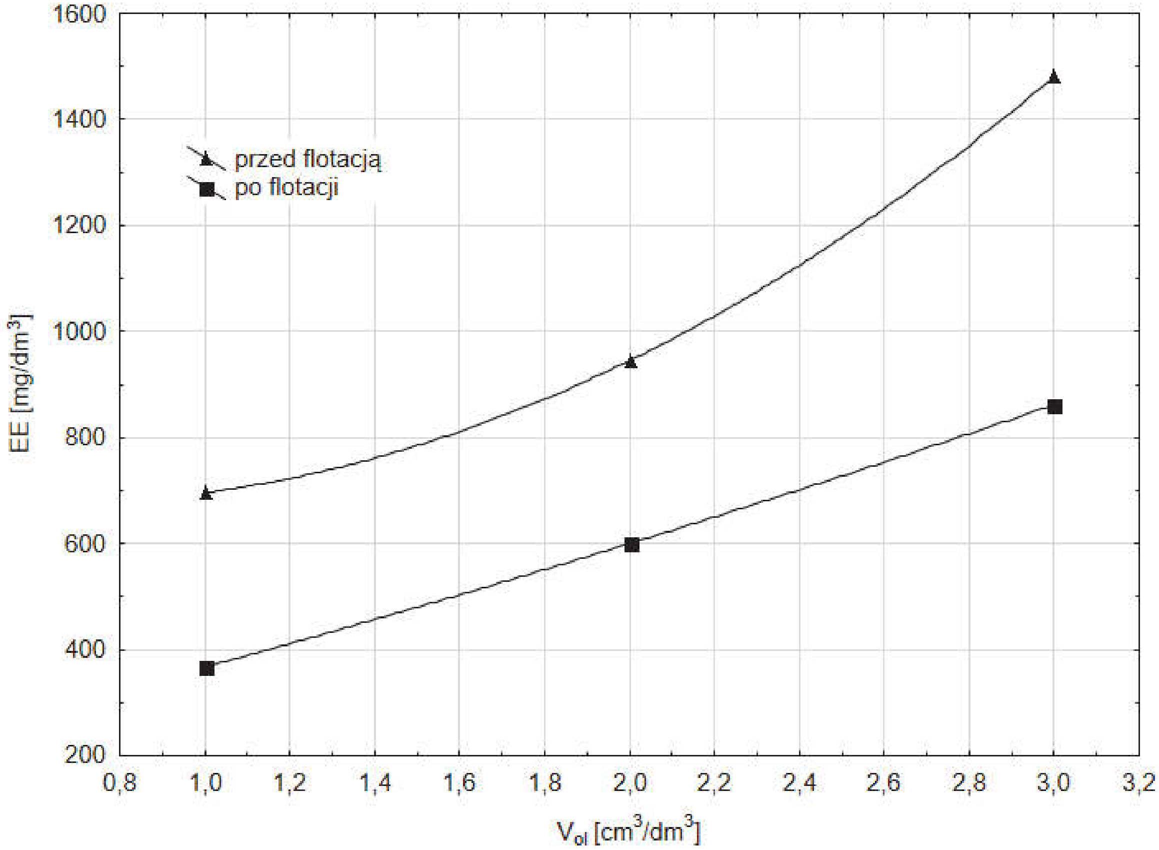
Rezultaty badań zawarte w tabeli 1 i 2 przedstawiono graficznie w formie wykresów na rysunku 1 oraz na rysunku 2.

Tabela 1. Wpływ stężenia oleju dodawanego do ścieku modelowego na wartość wskaźnika EE oznaczoną przed i po procesie flotacji
Table 1. Influence of concentration of oil added to model wastewater on EE value determined before and after the flotation process

Stężenie oleju dodawanego V_{ol} [cm^3/dm^3]	Ekstrakt eterowy EE [mg/dm^3]	
	przed flotacją	po flotacji
1,0	696	367
2,0	945	589
3,0	1481	862

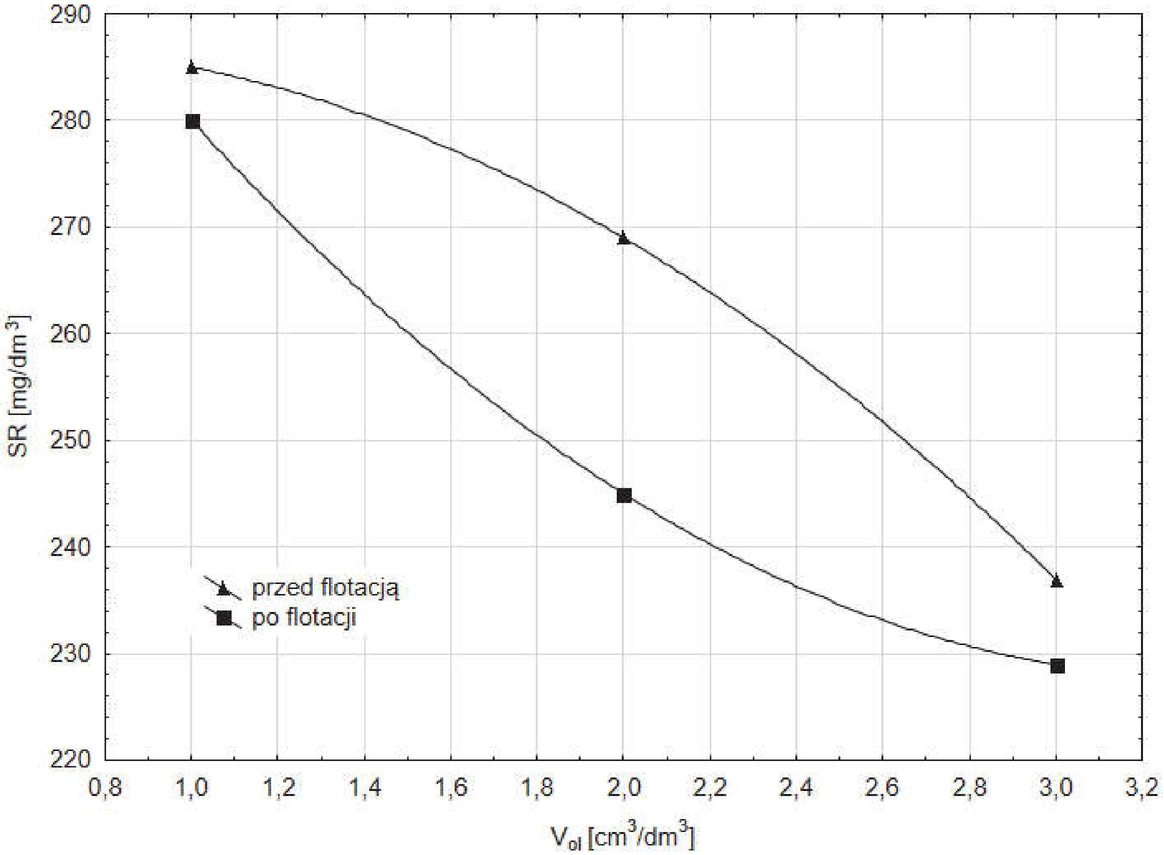
Tabela 2. Wpływ stężenia oleju dodawanego do ścieku modelowego na ilość substancji rozpuszczonych SR przed i po procesie flotacji
Table 2. Influence of concentration of oil added to model wastewater on amount of dissolved substances before and after the flotation process

Stężenie oleju dodawanego V_{ol} [cm^3/dm^3]	Ilość substancji rozpuszczonych SR [mg/dm^3]	
	przed flotacją	po flotacji
1,0	285	280
2,0	269	246
3,0	237	229



Rys. 1. Wpływ ilości oleju dodawanego do ścieku modelowego V_{ol} [cm^3/dm^3] na wartość wskaźnika EE [mg/dm^3]; wartości stałe – dawka benzyny V_b = 1 cm^3/dm^3, dawka detergentu V_d = 1 cm^3/dm^3, czas flotacji t = 3 min
Fig. 1. Influence of amount of oil added to model wastewater V_{ol} [cm^3/dm^3] on EE value [mg/dm^3]; constants – gasoline dose V_b = 1 cm^3/dm^3, detergent dose V_d = 1 cm^3/dm^3, flotation time t = 3 min

W drugiej serii badań na ściekach modelowych zmienną niezależną, zadawaną był czas flotacji zmieniany w granicach odpowiednio 1,0 min, następnie 3,0 min oraz 5,0 min oraz zmiennej dawce benzyny tj. 0,5 cm^3/dm^3, 1,0 cm^3/dm^3 oraz 1,5 cm^3/dm^3 w ścieku preparowanym. Zawsze stała była dawka detergentu 1 cm^3/dm^3, dawka oleju napędowego 2 cm^3/dm^3. Także zawsze stała była temperatura ścieku modelowego równa 20°C.



Rys. 2. Wpływ ilości oleju dodawanego do ścieku modelowego V_{ol} [cm^3/dm^3] na wartość wskaźnika SR [mg/dm^3]; wartości stałe – dawka benzyny $V_b = 1$ cm^3/dm^3, dawka detergentu $V_d = 1$ cm^3/dm^3, czas flotacji $t = 3$ min
Fig. 2. Influence of amount of oil added to model wastewater V_{ol} [cm^3/dm^3] on value of DS [mg/dm^3]; constants – gasoline dose $V_b = 1$ cm^3/dm^3, detergent dose $V_d = 1$ cm^3/dm^3, flotation time $t = 3$ min

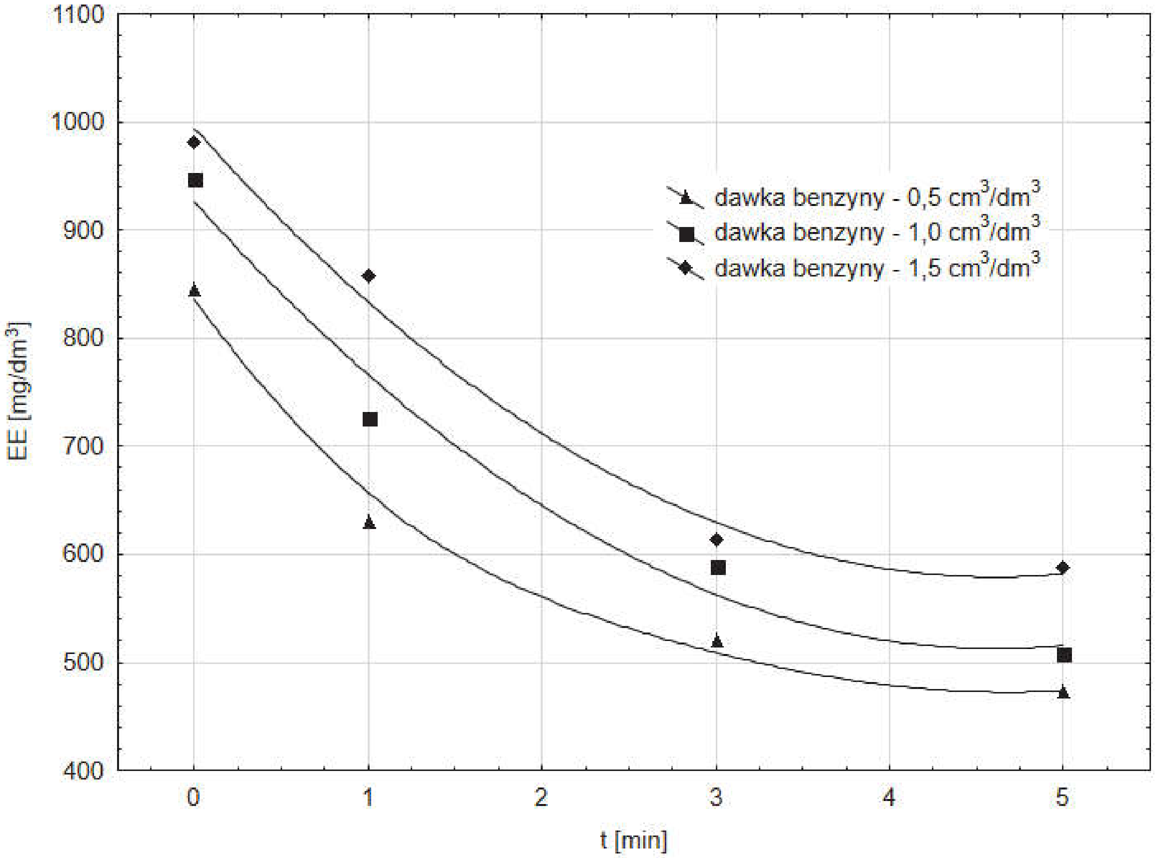
Zmienną wynikową przeprowadzonych badań tzw. zmienną zależną był wskaźnik ekstraktu eterowego EE po procesie flotacji a wyniki badań przedstawiono w tabeli 3 oraz podobnie wskaźnik substancji rozpuszczonych SR, których wyniki badań przedstawiono w tabeli 4. Rezultaty tych badań przedstawiono także graficznie na wykresach – rysunek 3 oraz rysunek 4.

Tabela 3. Wyniki badań procesu flotacji zaolejonych ścieków modelowych; wpływ czasu flotacji t [min] na wartość wskaźnika EE [mg/dm^3]
Table 3. Results of oily model wastewater flotation process; effect of flotation time t [min] on EE value [mg/dm^3]

Czas flotacji t [min]	Ekstrakt eterowy EE [mg/dm^3] przy dawce benzyny V_b [cm^3/dm^3]		
	0,5	1,0	1,5
0	845	947	981
1,0	630	727	858
3,0	521	589	613
5,0	473	508	587

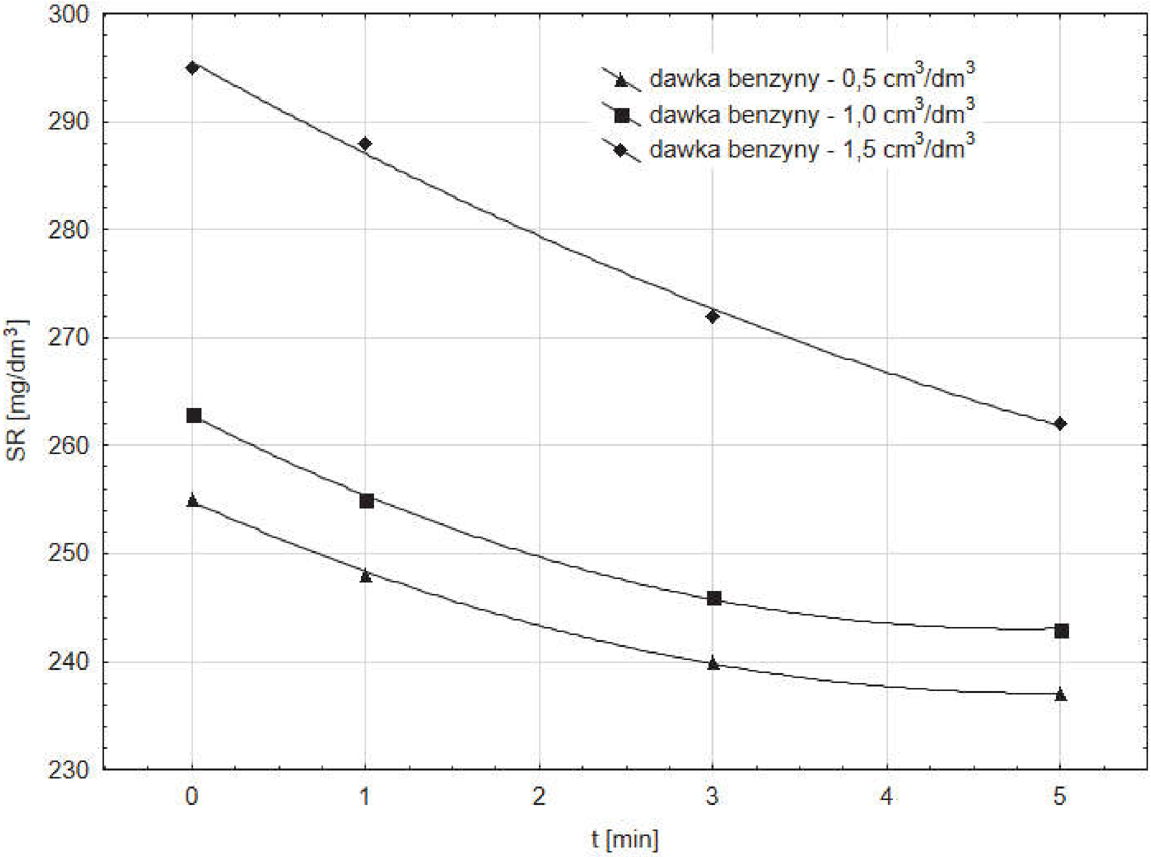
Tabela 4. Wyniki badań procesu flotacji zaolejonych ścieków modelowych; wpływ czasu flotacji t [min] na wartość wskaźnika SR [mg/dm^3]
Table 4. Results of oily model wastewater flotation process; effect of flotation time t [min] on SR value [mg/dm^3]

Czas flotacji t [min]	Substancje rozpuszczone SR [mg/dm^3] przy dawce benzyny V_b [cm^3/dm^3]		
	0,5	1,0	1,5
0,0	255	263	295
1,0	248	255	288
3,0	240	246	272
5,0	237	243	262



Rys. 3. Wpływ czasu flotacji t [min] na wartość wskaźnika EE [mg/dm^3]; wartości stałe – dawka oleju napędowego V_{ol} = 2 cm^3/dm^3, dawka detergentu V_d = 1 cm^3/dm^3, temperatura ścieków 20ºC

Fig. 3. Effect of flotation time t [min] on EE value [mg/dm^3]; constants – Diesel fuel dose V_{ol} = 2 cm^3/dm^3, dose of detergent V_d = 1 cm^3/dm^3, waste water temperature 20°C



Rys. 4. Wpływ czasu flotacji t [min] na wartość wskaźnika SR [mg/dm^3]; wartości stałe – dawka oleju napędowego $V_{ol} = 2$ cm^3/dm^3, dawka detergentu $V_d = 1$ cm^3/dm^3, temperatura ścieków 20°C

Fig. 4. Effect of flotation time t [min] on SR value [mg/dm^3]; constants – Diesel fuel dose $V_{ol} = 2$ cm^3/dm^3, dose of detergent $V_d = 1$ cm^3/dm^3, waste water temperature 20°C

2.2. Opis i analiza wyników badań na ściekach modelowych

Analiza wyników badań zawarta w tabeli 1 wskazuje, że wskaźnik ekstraktu eterowego EE w ścieku po procesie flotacji obniża się odpowiednio przy zawartości oleju w ścieku zadanym do flotacji w zakresie 1–3 cm^3/dm^3 – w przedziale około 365–860 mg/dm^3. Jest to obniżenie znaczące, aczkolwiek niewystarczające, aby uznać go za skuteczne. Warunki zrzutu do kanalizacji, jak wiadomo określa przedsiębiorstwo wodociągów i kanalizacji (miejskie, gminne), które często są różne dla oczyszczalni ścieków komunalnych, które są tym przedsiębiorstwom podległe. Natomiast warunki odprowadzania ścieków do wód lub do ziemi i w sprawie substancji szczególnie niebezpiecznych dla środowiska określa Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 roku Dziennik Ustaw 06.137.981. Odnośne Rozporządzenie ustala dopuszczalną wartość dla zrzutu ekstraktu eterowego do 50 mg/dm^3 a dla zawiesiny ogólnej 35 mg/dm^3.

Wyniki badań przedstawione na rysunku 1, wskazują, iż im więcej oleju napędowego znajduje się w ścieku nadanym do flotacji, tym efekt odolejania jest większy. Efekt określono na podstawie wartości wskaźnika EE po procesie wobec jego wartości przed procesem flotacji. Skuteczność flotacji w odolejaniu badanych ścieków modelowych wobec wskaźnika substancji rozpuszczonych SR pokazano w tabeli 2, gdzie wyniki badań wskazują, iż otrzymano obniżenie wartości tego wskaźnika stosunkowo niewielkie i mieści się ono w granicach od około 5 mg/dm^3 do około 24 mg/dm^3. Rezultaty badań zawarte w tabeli 2 oraz przedstawione graficznie na wykresie – rysunek 2, wskazują, że wraz ze wzrostem ilości oleju napędowego tworzącego ściek modelowy, wskaźnik substancji rozpuszczonych maleje i ta tendencja zachowana jest również po procesie flotacji.

Wyniki badań procesu flotacji modelowych ścieków zaolejonych, przy zmiennej dawce benzyny (tabela 3), wskazują, że wskaźnik EE wzrasta wraz z czasem flotacji gdy w ścieku jest więcej benzyny.

Przy zawartości benzyny ok. 0,5–1,5 cm^3/dm^3, wartość tego wskaźnika EE, zależnie od czasu flotacji, wzrasta od 115 mg/dm^3 do 136 mg /dm^3. Ważnym parametrem jest czas flotacji. Nie powinien być on zbyt krótki. Niski czas flotacji powoduje wyraźny efekt podniesienia wartości wskaźnika ekstraktu eterowego wobec tej wartości w ścieku nadanym. Na rysunku 3 widać, że czas równy 3 min. można przyjąć jako prawie optymalny.

Analiza wyników badań procesu flotacji ścieków zaolejonych pod kątem oceny wartości wskaźnika substancji rozpuszczonych SR przedstawiona w tabeli 4 wskazuje, że im więcej benzyny znajduje się w ściekach preparowanych, tym wartość wskaźnika substancji rozpuszczonych SR rośnie i to w przedziale zmian czasu flotacji od 1,0 do 5,0 min. o wartość przeciętnie ok. 25–30 mg/dm^3, jako przedział przeciętny tych różnic.

2.3. Badania procesu flotacji na ściekach rzeczywistych

Charakterystykę technologiczną ścieku surowego, a więc rzeczywistego, pobranego bezpośrednio z Zakładu X, przedstawia tabela 5.

W tabeli tej, obok wskaźników określanych dla ścieków modelowych tj. ekstraktu eterowego EE, oraz wskaźnika substancji rozpuszczonych SR, oznaczono także takie parametry, jak wskaźnik zawiesiny ogólnej ZO [mg/dm^3], chemiczne zapotrzebowanie tlenu ChZT [mg/dm^3] a także ogólny węgiel organiczny OWO [mg/dm^3].

Tabela 5. Zestawienie wyników badań podczyszczania ścieków rzeczywistych
Table 5. Results of real treat wastewater pre-treatment

Parametr	Rodzaj ścieków		Etap oczyszczania w procesach sedymentacji i sorpcji		
	surowe	po flotacji	dawka koagulanta $Al(SO_4)_3\cdot18H_2O$ K [mg/dm^3]		po sorpcji
			0,5	1,0	
pH [bzw]	8,0	8,0	7,5	7,5	6,0
SR [mg/dm^3]	1426	1246	1074	1026	404
ZO [mg/dm^3]	592	388	304	280	0
ChZT [mg/dm^3]	449	166	106	102	29
OWO [mg/dm^3]	526	408	357	334	55
EE [mg/dm^3]	420	162	134	117	13

Powyższe wskaźniki oznaczono także po procesie flotacji i pokazano je w tabeli 5. Proces flotacji trwał 10 min. Zatem, w przypadku flotacji ścieku surowego, ten czas flotacji jest wyraźnie większy niż w procesie flotacji ścieków modelowych.

Przeprowadzono bowiem najpierw badania wpływu czasu flotacji na efekt końcowy oczyszczania a wyniki badań w odniesieniu do wartości wskaźnika ekstraktu eterowego przedstawiono w tabeli 6, w której ujęto także wyznaczony paralelnie wskaźnik substancji rozpuszczonych SR.

Analiza wyników badań ścieków surowych wskazała, że efekty ich podczyszczania wyłącznie w procesie flotacji nie są zadawalające. Zatem dodatkowo przeprowadzono badania procesu koagulacji siarczanem glinu $Al_2(SO_4)_3\cdot18H_2O$ a potem po procesie sedymentacji zdekantowany ścieki doczyszczano w procesie sorpcji na węglu aktywnym w kolumnie o wysokości 1 m. Temperatura podczyszczanego ścieku wynosiła 20°C.

2.4. Opis i analiza wyników badań na ściekach rzeczywistych

Wyniki badań jakościowych, ścieków rzeczywistych w odniesieniu do spreparowanych ścieków modelowych wobec wskaźnika ekstraktu eterowego pokazują, że wartość tego parametru w ściekach modelowych była wyższa. W zależności od badanego ścieku wartość ta wahała się w granicach od około 487 do około aż 1481 mg/dm^3, gdy tymczasem pobrane i poddane badaniom podczyszczania ścieki rzeczywiste miały wartość wskaźnika ekstraktu eterowego EE = 420 mg/dm^3.

Należy też zwrócić uwagę, że ścieki modelowe, a więc te preparowane nie zawierały zawiesiny ogólnej a w ścieku rzeczywistym wskaźnik ten miał wartość 592 mg/dm^3.

Analiza wyników wskazuje, że proces flotacji poprawił wartość wskaźnika ekstraktu eterowego o 258 mg/dm^3; zauważmy jednak wydłużony czas flotacji, a więc wyższy niż czas 3 min., który był prawie optymalny dla ścieków modelowych. Pokazuje to wartość ekstraktu eterowego zapisana dla różnych czasów flotacji w tabeli 6.

Tabela 6. Wyniki badań wpływu czasu flotacji ścieku rzeczywistego na wartość wskaźnika ekstraktu eterowego EE [mg/dm^3] oraz wskaźnika substancji rozpuszczonych SR [mg/dm^3]
Table 6. Effect of time of flotation of real wastewater on EE value [mg/dm^3] and SR value [mg/dm^3]

Czas flotacji t [min]	Ekstrakt eterowy EE [mg/dm^3]	Substancje rozpuszczone SR [mg/dm^3]
0	420	1426
1	350	1401
3	278	1377
5	234	1343
10	162	1246

Oznaczenie wskaźnika substancji rozpuszczonych SR wskazuje na obniżenie jego wartości o około 220 mg/dm^3, ale po czasie flotacji aż 10 min.

Biorąc pod uwagę powyższą analizę, podczyszczone ścieki rzeczywiste w procesie flotacji, poddano następnie procesowi koagulacji siarczanem glinu przy dwóch jego różnych dawkach tj. 0,5 mg/dm^3 oraz 1,0 mg/dm^3.

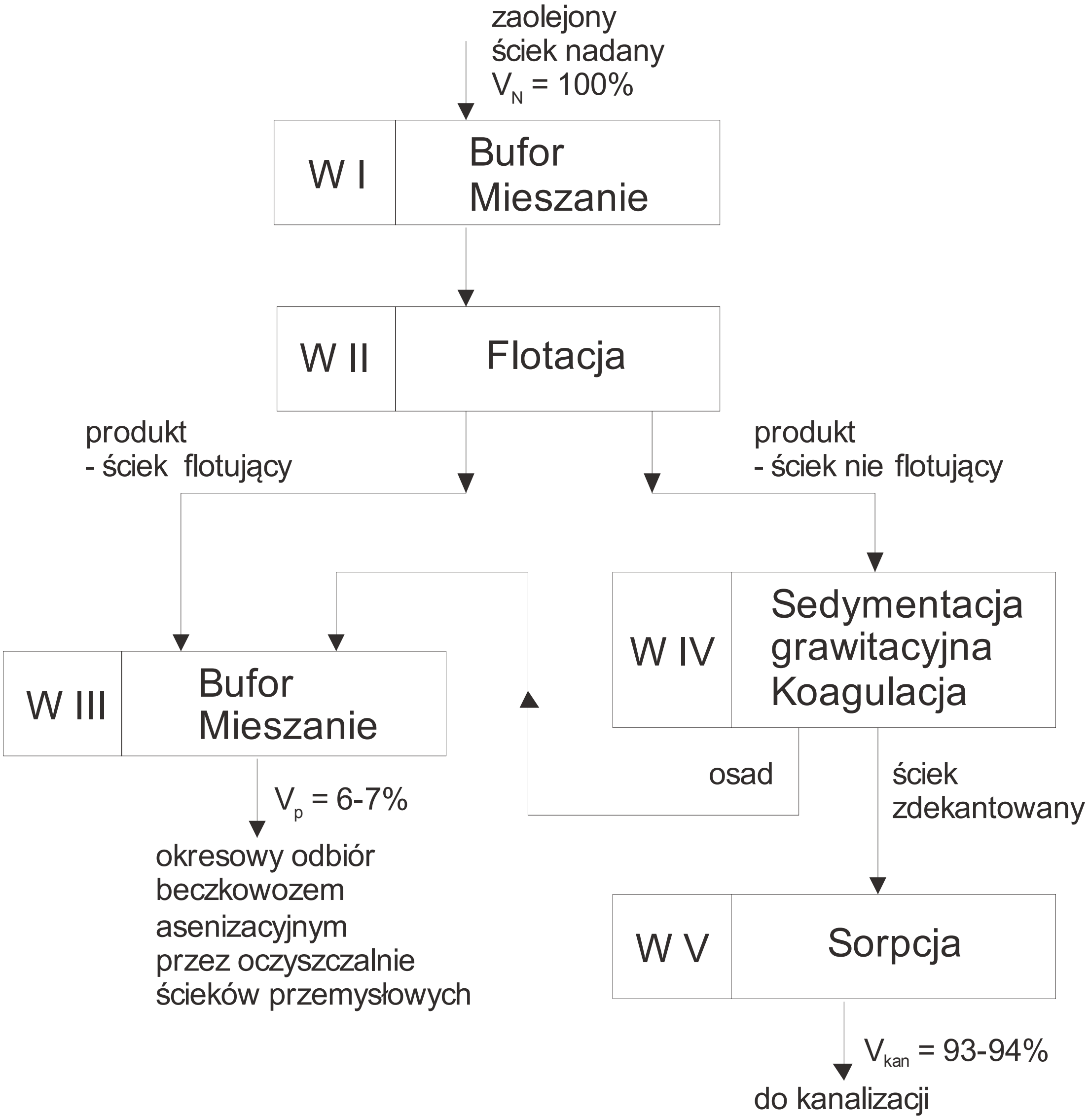
Analiza wyników zawartych w tabeli 5 wskazuje, ze wzrost dawki flokulanta powoduje po procesie sedymentacji niewielką poprawę wartości głównych wskaźników zanieczyszczeń w ścieku poflotacyjnym.

Dlatego też zdecydowano się przeprowadzić jeszcze proces sorpcji na węglu aktywnym, aby ścieki doczyścić do parametrów, które pozwalają na odprowadzanie ścieków do kanalizacji a więc w konsekwencji do oczyszczalni miejskiej ścieków komunalnych. Wyniki badań po procesie sorpcji pokazano w tabeli 5. Analiza wyników wskazuje na bardzo dobry efekt oczyszczania. Wartość ekstraktu eterowego EE wyniosła tylko 13 mg/dm^3 a wartość przykładowo wskaźnika zawiesiny ogólnej ZO była równa zero.

3. Propozycja małej instalacji podczyszczania ścieków na zapleczach samochodowych warsztatów mechanicznych

W związku z powyższą analizą wyników badań można rozważyć, nakładem niewielkich środków finansowych budowę małych instalacji podczyszczania ścieków pochodzących z warsztatów samochodowych lub stacji benzynowych. Przykładowy schemat pokazano na rysunku 5. Stację należy wyposażyć w pojemnik, w którym gromadzone są popłuczyny o wielkości dobranej zależnie od intensywności mycia i spłukiwania posadzek. Ten zbiornik powinien mieć charakter mieszalnika; węzeł I.

Zbiornik powinien być ulokowany podpoziomowo i mieć pojemność roboczą równą przynajmniej objętości ścieków z pojedynczego mycia i spłukiwania posadzki. Następnie z węzła I, raz na dobę, ściek byłby podawany do flotownika (węzeł II) z którego otrzymujemy dwa produkty; produkt flotujący (około 5–10% objętości ścieków nadanych, które musiałyby być magazynowane w oddzielnym zbiorniku i odbierane przez oczyszczalnie ścieków przemysłowych specjalnym beczkowozem asenizacyjnym). Wyflotowane oleje stanowią także apolarne odczynniki flotacyjne, stosowane do flotacji węgla [40,41]. Natomiast ścieki nieflotujące byłyby podawane do procesu sedymentacji grawitacyjnej wspomaganej koagulacją, po którym to procesie znowu otrzymuje się 2 produkty.



Rys. 5. Schemat blokowy technologiczny kieszonkowej instalacji podczyszczania ścieków ze stacji usług samochodowych i stacji benzynowej; V_N – procentowa objętość ścieków nadanych, V_p – procentowa objętość wydzielonych ścieków przemysłowych, V_{kan} – procentowa objętość ścieków do kanalizacji

Fig. 5. Block diagram of small installation for pre-treatment of wastewater from car service station and gas station; V_N – percentage volume of wastewater, V_p –percentage volume of industrial wastewater, V_{kan} – percentage volume of wastewater piped to sewage system

Powyższa propozycja i wyniki badań mają charakter wstępny i ewentualna możliwość kontynuacji tego typu prac pod kątem wdrożenia, musiałaby przede wszystkim znaleźć akceptacje właścicieli warsztatów samochodowych lub stacji benzynowych i to w takim odniesieniu, aby od razu zdecydowano się zbudować taką instalację i pracę jej zoptymalizować w trakcie prowadzonych na niej badań. W ramach tych badań należałoby określić żywotność danej kolumny sorpcyjnej, charakter stopniowej utraty jej pojemności sorpcyjnej oraz ilość wymian tej kolumny w określonym interwale czasu. Dlatego też proces łatwej flotacji ścieków zaolejonych, przy bezproblemowej dostępności do sprężonego powietrza a także towarzyszący mu proces sedymentacji grawitacyjnej wspomaganej koagulacją ewidentnie wydłuży czas pracy takiej kolumny. Zużyty węgiel aktywny, można spalić w mieszance w piecach MEC lub w spalarni odpadów. Wydaje się jednak, że takie ewentualne kontynuowanie badań aplikacyjnych, musiałoby być poparte pewnym interwencjonizmem w zakresie ogólnych wytycznych dotyczących odprowadzania ścieków przez wszystkie stacje benzynowe i wszystkie warsztaty samochodowe a więc po prostu powinny to regulować określone przepisy zmuszające do wdrażania nowych rozwiązań. Bez tego typu wytycznych, poza pojedynczymi przypadkami ewentualne wdrożenia nie będą miały miejsca, gdyż jest to zawsze jednak pewien wysiłek dla inwestora oraz pewien kłopot najpierw z zainwestowaniem, budową a potem eksploatacją takiej instalacji – ale próbować należy.

4. Podsumowanie – wnioski

Z przeprowadzonych badań rozpoznawczych oraz analizy wyników tych badań nasuwają się pewne ogólne wnioski.

1. Ścieki będące wynikiem prac usługowych samochodowych warsztatów mechanicznych a także stacji benzynowych są zanieczyszczone związkami ropopochodnymi i chociaż pojedynczy zakład odprowadza niewiele ścieków do kanalizacji, to jednak suma tych ścieków w skali kraju, każdego dnia jest ogromna – a przecież są to związki kancerogenne.
2. Proponowana do wdrożenia, mała instalacja ścieków zaolejonych, poprawi na pewno jakość ścieków codziennie wprowadzanych do kanalizacji.
3. Proces flotacji stanowiący pierwszy węzeł tej propozycji technologicznej instalacji nie podczyszcza ścieków w sposób bardzo dobry, ale wystarczająco zauważalny, a przez to pozwala wydłużyć żywotność działania ważnego węzła tej instalacji, tj. węzła sorpcji.

4. Badania powinny być kontynuowane na małej doświadczalnej instalacji zamontowanej w konkretnym zakładzie samochodowym lub stacji benzynowej.

Wykaz symboliki

ChZT – chemiczne zapotrzebowanie tlenu, mg/dm^3,
EE – ekstrakt eterowy, mg/dm^3,
K – dawka koagulanta, mg/dm^3,
OWO – węgiel organiczny, mg/dm^3,
pH – wskaźnik stężenia jonów wodorowych, bzw,
SR – substancje rozpuszczone, mg/dm^3,
t – czas trwania procesu, min,
V_{ol} – objętość wskaźnikowa oleju w ścieku preparowanym, cm^3/dm^3,
V_b – objętość wskaźnikowa benzyny w ścieku preparowanym, cm^3/dm^3,
V_d – objętość wskaźnikowa detergentu w ścieku preparowanym, cm^3/dm^3,
Z_O – zawiesina ogólna, mg/dm^3.

List of symbols

ChZT – chemical oxygen demand, mg/dm^3,
EE – ether extract, mg/dm^3,
K – coagulant dose, mg/dm^3,
OWO – total organic carbon, mg/dm^3,
pH – concentration of hydrogen ions, -,
SR – dissolved substances, mg/dm^3,
t – process duration of the, min,
V_{ol} – volume of oil in the model wastewater, cm^3/dm^3,
V_b –volume of gasoline in the model wastewater, cm^3/dm^3,
V_d – volume of Diesel fuel in the model wastewater, cm^3/dm^3,
Z_O – total suspended solids, mg/dm^3.

Literatura

1. **Beeskow T., Streger J.:** *Polymeric Membranes for Organophilic Nanofiltration.* Filtech 2007. International Conference and Exhibition for Filtration and Separation Technology Conference Proceedings II. 534–546 (2007).
2. **Berger T.:** *Mechanizmy usuwania zanieczyszczeń w oczyszczalniach hydrobotanicznych*. Inżynieria Środowiska. 8(1) (2003).

3. **Biernat:** *Problemy utylizacji zużytych olejów smarowych*. Paliwa oleje i smary w eksploatacji Eksplonaft Sp. z o.o. 7(54), 26–29 (1998).
4. **Boguski A.:** *Efektywność usuwania substancji tłuszczowych w układzie oczyszczania ścieków miejskich*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 10, 481–489 (2008).
5. **Bugajski P.:** *Hydrobotaniczne (hydrofitowe) oczyszczalnie ścieków*. III Konferencja Naukowo-Techniczna „Błękitny San", Dubiecko 2006, 93–99 (2006).
6. **Cheryan:** *Ultrafiltration and Microfiltration*. Handbook CRC Press United States 1998.
7. **Chmielowska A.:** *Hydrobotaniczne oczyszczalnie ścieków*. Wydawnictwo „Zielone Brygady". Kraków 2002.
8. **Chrzanowska M, Hupka J.; Szewczulak Ł.:** *Badania oczyszczania ścieków pożarniczych metoda osadu czynnego*. Inżynieria ekologiczna nr 8. Technologie odolejania gruntów, odpadów i ścieków. Wydawnictwo naukowe Gabriel Borowski. 96–102, Warszawa 2003.
9. **Ciesielczuk T, Rosik-Dulewska Cz, Nabzdyjak T.:** *Występowanie węglowodorów alifatycznych oraz wielopierścieniowych węglowodorów aromatycznych w wodach podziemnych na terenie magazynu paliw bazy lotniczej*. Ecological Chemistry and Engineering. 13 S4, 531–538 (2006)
10. **Cui Z.F., Muralidhara H.S.:** *Membrane Technology a practical guide to membrane technology and applications in food bioprocessing*. Amsterdam Butterworth – Heinemann. 213–254 (2010).
11. **Czerwiński J., Kurzac M., Tora B.:** *Utylizacja olejów przepracowanych*. Czysta energia – czyste środowisko. Małopolsko – Podkarpacki. Klaster czystej energii. 457–464 (2008).
12. **Dudek A.:** *Oleje smarowe Rafinerii Gdańskiej*. Wydawnictwo MET-PRESS. Gdańsk 1999.
13. **Gao W, Liang H., Ma Han M., Chen Z., Han Z., Li G.:** *Membrane fouling control in ultrafiltration technology for drinking water production. A Review*. Desalination. (1-3), 1–8 (2011).
14. **Garlicki S., Jasiński A.W.:** *Polski rynek olejów przepracowanych – zbiórka i przeróbka*. Paliwa, oleje i smary w eksploatacji EKSPLONAFT Sp. z o.o., 8(68), 25–28 (1999).
15. **Gomółka E.:** *Usuwanie i unieszkodliwianie zanieczyszczeń olejowych zawartych w ściekach*. Prace naukowe Politechniki Wrocławskiej. Seria Monografie 49 (19), Wydawnictwo Politechniki Wrocławskiej, Wrocław 1987.
16. **Gomółka E.:** *Usuwanie olejów ze ścieków*. Ochrona środowiska. Wyd. PZiTS. 463/1 (23), 39–43 (1985).

17. **Gwozdyak P.J., Globa L.I., Dmytrenko G.M.:** *Oczyszczanie zaolejonych ścieków przemysłowych i wód powierzchniowych hydrobiocenozami immobilizowanymi*. Materiały konferencyjne. AUZO 96 Gdańsk.
18. **Hartman L.:** *Biologiczne oczyszczanie ścieków.* Wydawnictwo Instalator Polski. Warszawa 1996.
19. **Karaś J, Winiarski A, Molenda J.:** *Wpływ wstępnej koagulacji na skuteczność usuwania zanieczyszczeń ze ścieków przemysłowych w procesie odwróconej osmozy*. Inżynieria i Ochrona Środowiska. 15(1), 33–40 (2012).
20. **Kiepurski J.:** *Efekty zastosowania kultur bakteryjnych do rozkładu ropopochodnych w istniejących układach środowiskowych*. Inżynieria Środowiska Nr 2. Technologie odolejania gruntów, odpadów, ścieków. Wydawnictwo Ekoinżynieria, Wysowa Zdrój, 97–101.
21. **Kołtuniewicz A.:** *Usuwanie emulsji ropopochodnych z wody na membranach ceramicznych*. Wydawnictwo Politechniki Wrocławskiej. Wrocław 1997.
22. **Kwapisz E.:** *Szlaki tlenowej biodegradacji węglowodorów ropy naftowej*. Biotechnologia. 2(73), 166–168 (2006).
23. **Laine J.M., Jacangelo J.G., Adhan S.:** *Membrne for microbiol removal*. Denver, CO AWWA Research Foundation and American Water Works Association. 1997.
24. **Małachowska-Jutsz A, Rudek J, Janosz W.:** *The effect of Ribwort (Plantago Lanceolata) and its Myrrorrhizas on the Growth of Microflora in Soil Contaminated with Used Engine Oil.* Archives of Environmental Protection. 37(1), 99–113 (2011).
25. **Mazur R., Nowakowski T.:** *Uwarunkowania decydujące o szybkości biodegradacji związków ropopochodnych*. Materiały krakowskiej konferencji młodych uczonych 2011. Kraków, Grupa naukowa PRO Futuro, Fundacja dla AGH (sympozja i konferencje). 6, 651–662 (2011).
26. **Michel M.M.:** *Sorpcja oleju na złożach mineralnych*. Przegląd naukowy Inżynieria i kształtowanie środowiska. SGGW. 1(33), 95–102 (2006).
27. **Obarska-Pempkowiak H., Gajewska M., Wojciechowska E.:** *Hydrofitowe oczyszczanie wód i ścieków*. Wydawnictwo Naukowe PWN, Warszawa 2010.
28. **Obarska-Pempkowiak H, Gajewska M, Arendacz M.:** *Oczyszczanie wód opadowych w obiektach hydrofitowych*. Gaz, Woda i Technika Sanitarna. wrzesień 2008.
29. **Obarska-Pempkowiak H., Wojciechowska E.:** *Zawartość wybranych metali ciężkich w makrofitach oczyszczalni hydrofilowej*. Gaz, Woda i Technika Sanitarna. wrzesień 2008.
30. **Obarska-Pempkowiak H.:** *Oczyszczalnie hydrofitowe.* Wydawnictwo Politechniki Gdańskiej. Gdańsk 2002.

31. **Obarska-Pempkowiak H.:** *Oczyszczanie ścieków metodą hydrobotaniczną z wykorzystaniem filtrów gruntowych i stawów ściekowych*. Rozprawy. Zeszyty Naukowe Politechniki Gdańskiej. Nr 489. Seria Budownictwo Wodne. 3, 96 (1992).
32. **Piecuch T., Dąbrowski T.:** *Badania podczyszczania ścieków w zakładach przetwórstwa ryb w procesie flotacji*. Zeszyty Naukowe Politechniki Białostockiej – seria Inżynieria Środowiska. 15(2001), 2001.
33. **Rogoś E.:** *Skuteczność destabilizacji emulsji olejowo-wodnych metodami chemicznymi*. Problemy eksploatacji. Instytut Technologii i Eksploatacji PIB. 1, 149–158 (2012).
34. **Rosik Dulewska Cz, Ciesielczuk T, Krysiński M.:** *Organic Pollutants in Groundwater in the Former Airbase*. Archives of Environmental Protection. 38(1), 27–34 (2012).
35. **Rubio J., Souzo M.L., Smith R.W.:** *Overview of flotation as a wastewater treatment technique minerals*. Engineering. 15, 139–155 (2002).
36. **Rutkowski M., Lipnicka D., Zych Z.:** *Badania możliwości wykorzystania sorbentów mineralnych i mineralno-węglowych do oczyszczania wód skażonych związkami chemicznymi*. Materiały Konferencyjne AUZO, Gdańsk 1996.
37. **Stępniak S.:** *Usuwanie zanieczyszczeń olejowych ze ścieków emulsyjnych nowoczesnymi preparatami chemicznymi*. Gaz, Woda i Technika Sanitarna. 11, 254–255 (1992).
38. **Stępniak S.:** *Emulsje olejowe i ścieki zaolejone*. Gaz, Woda i Technika Sanitarna. 9 (1991).
39. **Suschka J.:** *Flotacja w technologii oczyszczania ścieków*. Nowa Technika w Inżynierii Sanitarnej. Wodociągi i Kanalizacja. Wydawnictwo Arkady. Warszawa 1981.
40. **Wencheng Xia, Jianguo Yang.:** *Experimental design of oily bubbles in oxidized coal flotation.* Gospodarka Surowcami Mineralnymi. 29(4) (2013).
41. **Zechner V, Guziurek M, Fecko P.:** *Application of brown coal pyroliytic oils in black coal slurry flotation.* Gospodarka Surowcami Mineralnymi. 29(2) (2013).
42. **Zwierzycki W.:** *Oleje, paliwa i smary motoryzacji i przemysłu.* RN „GLIMAR” S.A. Gorlice 2001.

Treatment of Wastewater from Car Service Station

Abstract

The paper presents exploratory examinations on possibility of pre-treatment of wastewater containing gasoline and diesel fuel, that is wastewater "produced" in each car service and repair workshop and in gas station. It is a vast number of service points, which, though daily produce small amounts of wastewater but in the scale of the whole country amount of wastewater is substantial. Such wastewater is usually piped off into the sewage system. Often oily wastewater does not meet requirements set by local companies which own the municipal sewage treatment plants.

Therefore, authors made have undertaken considerations on the concept of use the flotation process for pre-treatment of wastewater containing oil and gasoline, as a small wastewater treatment plant that could be installed in a separate room of garage or gas station. Example diagram is shown in Figure 5.

This paper presents preliminary testing of a pilot-distinctive nature. Laboratory tests of flotation process were carried out in two independent study groups, ie. one with use of model wastewater and second with the use of real wastewater.

Conducted examinations and analysis of the results allow to draw certain conclusions:

1. Wastewater from car service stations, mechanical garages and also gas stations are contaminated with oil derived compound, and although individual garage produces small amounts of wastewater, the sum of all wastewater in the scale of the whole country each day is substantial.
2. Proposed small installation for pre-treatment of oily wastewater, when implemented In the car service station or gas station will improve quality of wastewater daily inputted to sewage system.
3. The flotation process which is the first node of proposed technological installation does not treat wastewater sufficiently, but noticeably, and thus it allows to extend the life of an important node of the installation, that is sorption process.
4. Research should be continued on a small experimental plant installed in the car or gas station.

Słowa kluczowe:
flotacja, ścieki zaolejone, podczyszczanie

Keywords:
Flotation, oily wastewater, pre-treatment

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Nowoczesne techniki i technologie inżynierii środowiska

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1. Wstęp

Wzrastające stale wymagania dotyczące ochrony środowiska przyrodniczego zachęcają do poszukiwań nowych efektywnych i ekonomicznie atrakcyjnych technologii oczyszczania ścieków, gazów i remediacji gruntów. Coraz częściej, odmiennie niż w przeszłości, w celu efektywnego usuwania zanieczyszczeń stosowane są technologie hybrydowe, łączące procesy biologiczne, chemiczne i fizyczne. W niniejszym przeglądzie omówione będą zarówno wybrane nowoczesne technologie inżynierii środowiska, jak i narzędzia badawcze pozwalające na sterowanie wybranymi procesami biologicznymi, które są zazwyczaj zasadniczym etapem wielu technologii środowiskowych.

2. Tlenowe granule drobnoustrojów

W konwencjonalnych systemach oczyszczania ścieków komory osadu czynnego są zespolone z osadnikami wtórnymi. Wadą tej metody jest miedzy innymi ograniczone obciążenie komór napowietrzania ładunkiem zanieczyszczeń. Bardzo wysokie obciążenie powoduje natomiast nadmierną podaż substratu, intensyfikując syntezę biomasy, jednocześnie ograniczając ilość utlenionych substancji. W konsekwencji stopień oczyszczenia ścieków jest niewystarczający oraz zwiększa się ilość odprowadzanego osadu nadmiernego. Dostrzegając ważność i złożoność tego problemu opracowywano systemy o zwiększonej retencji biomasy. Już w latach 90-tych podano pierwsze rozwiązania, gdzie biomasa immobilizowana była w postaci biofilmu na specjalnych nośnikach [19]. W tym czasie prężnie rozwinęły się również technologie beztlenowego oczyszczania ścieków w reaktorach UASB, gdzie mikroorganizmy utrzymywane są w dolnej części reaktora w postaci zawieszonej warstwy o specyficznej, granulkowatej strukturze. Po analizie procesów zachodzących w reaktorach UASB podjęto próbę opracowania technologii otrzymywania granulowanych form drobnoustrojów w warunkach aerobowych, która zakończyła się pozytywnie [38].

Tlenowe granule o kompaktowej i gęstej strukturze, dużej bioróżnorodności oraz o doskonałych właściwościach sedymentacyjnych wykorzystuje się do oczyszczania ścieków zarówno o niskim, jak i wysokim obciążeniu ładunkiem zanieczyszczeń, do usuwania związków azotu i fosforu, a także toksycznych substancji. Ze względu na sukces jaki odniosła technologia granulowanego osadu w skali laboratoryjnej, sprawdzono jej wydajność w skali pilotowej. Pierwsza stacja pilotowa uruchomiana została we wrześniu 2003 roku w holenderskiej oczyszczalni ścieków w Ede, a w roku 2008 powstały pierwsze oczyszczalnie ścieków komunalnych w Portugalii (Freilas) i Południowej Afryce (Gansbaai) [65] Doświadczenia z pracy stacji pilotowych wykazały, że biologiczny rozruch reaktorów z granulowaną biomasą wymaga czasu od około 270 do nawet 400 dób, czyli znacznie dłużej niż w skali laboratoryjnej, gdzie czas formowania dojrzałych granul wynosi około 60 dób [31].

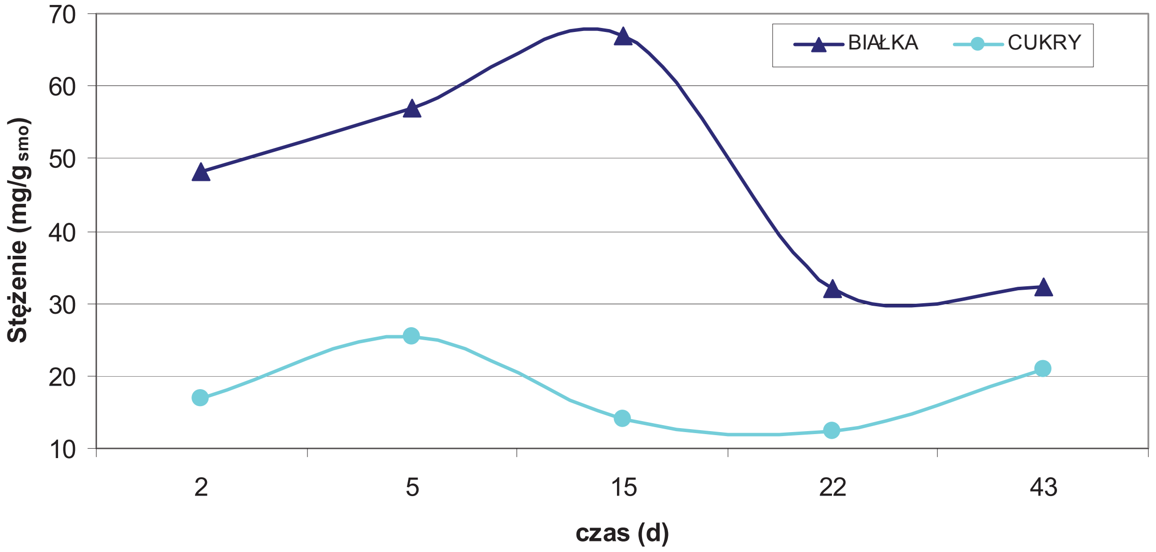
Procesowi biogranulacji sprzyja obecność polimerów zewnątrzkomórkowych (EPS), które są substancjami syntetyzowanymi, wydzielanymi i akumulowanymi na zewnątrz komórki. Kompozycja polimerów zewnątrzkomórkowych jest zmienna i zależy od rodzaju mikroorganizmów, a najogólniej podzielić je można na: polisacharydy, białka, DNA i produkty lizy komórek bakteryjnych [63]. EPS odgrywają ważną rolę w procesie biogranulacji, ponieważ pozwalają utrzymywać trójwymiarową i zintegrowaną strukturę granul osadu czynnego.

EPS występują w różnych formach bioagregatów, takich jak kłaczki osadu czynnego, biofilmy, granule tlenowe i beztlenowe. Jednakże ich stężenie w granulach osadu czynnego jest o wiele większe niż w konwencjonalnym osadzie czynnym [60].

W literaturze można spotkać różne, sprzeczne informacje dotyczące kompozycji EPS w biogranulach. Rezultaty niektórych badań wskazują, że najważniejszym komponentem granul są białka, a stosunek proteiny/polisacharydy (PN/PS) jest relatywnie stały podczas formowania granul osadu czynnego[44]. Inni badacze natomiast podają, że największą ilość stanowią polisacharydy, które uczestniczą w usieciowaniu polisacharydów i powodują uformowanie trójwymiarowej sieci [37]. Również obecność niektórych kationów wyraźnie sprzyja powstawaniu granul [26].

Najważniejszą rolę w formowaniu granul osadu czynnego odgrywa frakcja mocno związanych polimerów zewnątrzkomórkowych [25]. Rysunek 1 przedstawia wyniki zmiany zawartości poszczególnych komponentów polimerów zewnątrzkomórkowych tejże frakcji wraz z czasem biogranulacji. Obserwowano, że zawartość białek i w mniejszym stopniu polisacharydów wzrasta aż do momentu uformowania pierwszych granul o średnicy 0.4–2mm oraz gęstej i kompaktowej strukturze. Od 16 doby obserwuje się, że zawartość EPS spada, a od dnia 23 utrzymuje się na stałym poziomie.

Zgodnie z Li et al. [29] w momencie uformowania granul, ustala się równowaga pomiędzy procesami akumulacji a metabolizmem, czego rezultatem jest stała zawartość EPS w dojrzałych granulach.



Rys. 1. Zmiany frakcji mocno związanych EPS w czasie formowania tlenowych granul [25]
Fig. 1. Changes of the fractions of tightly bound EPS during the formation of aerobic granules [25]

Uwzględniając aktualny stan wiedzy dotyczący wykorzystania tlenowych granul mikroorganizmów, można stwierdzić, że:

- Zaletą procesów wykorzystujących granulowany osad jest przede wszystkim zmniejszenie wymiarów reaktorów, w których prowadzone są procesy. Dodatkowo zwiększa się czas retencji biomasy w układzie oraz stopień koncentracji biomasy, a poprzez to następuje poprawa efektów oczyszczania ścieków
- Formowanie granul osadu czynnego ściśle wiąże się z produkcją EPS. Mikroorganizmy produkują i akumulują EPS, aż do momentu uformowania stabilnych, gęstych granul.
- Bakterie znajdujące się w wewnętrznej strefie dojrzałych granul zużywają polimery zewnątrzkomórkowe jako dodatkowe źródło węgla, co pozwala im przeżyć i zachować aktywność.
- Polisacharydy są komponentem, który stabilizuje strukturę granul. Mikroorganizmy nie zużywają tych strukturalnych polisacharydów w swoich procesach metabolicznych.
- Białka są dominującą frakcją polimerów zewnątrzkomórkowych.

3. Proces częściowej nitryfikacji i Anammox

Procesy biologiczne, w których następuje usuwanie nieorganicznych związków azotowych podczas oczyszczania ścieków zarówno komunalnych, jak i przemysłowych, do niedawna sprowadzały się praktycznie do nitryfikacji i denitryfikacji. Procesy usuwania azotu są jednymi z najbardziej kosztownych w oczyszczaniu ścieków. Koszty te wynikają ze znacznego zapotrzebowania na energię (napowietrzanie) w procesie nitryfikacji. Energia przeznaczona na napowietrzenie w procesie osadu czynnego stanowi 60–70% całkowitego zużycia energii w oczyszczalni, co stanowi nawet 30% udział w całkowitych kosztach eksploatacji oczyszczalni ścieków. W przypadku ścieków zawierających wysokie stężenia związków azotowych ww. metody mogą być zakłócone poprzez hamowanie nitryfikacji wolnym amoniakiem oraz nieodpowiedni stosunek węgla organicznego do azotu, co w znacznym stopniu ogranicza biologiczną denitryfikację. Aby proces oczyszczania był najefektywniejszy, a jednocześnie niedrogi, poszukuje się alternatywnych metod oczyszczania ścieków. Taką alternatywą może być połączenie procesu częściowej skróconej nitryfikacji oraz odkrytego w latach 90-tych ubiegłego wieku, a przewidywany już od lat 70-tych [1], proces beztlenowego utleniania amoniaku, czyli Anammox (ang. Anaerobic Ammonium Oxidation). Usuwanie azotu w procesie częściowej nitryfikacji/Anammox pozwala zmniejszyć koszty napowietrzania a co za tym idzie zużycie energii o ponad 60%, ponadto nie ma też potrzeby zapewnienia węgla organicznego, a dodatkowo zmniejsza się emisję CO_2 o ok. 90% co ma duże znaczenie biorąc pod uwagę fakt, że dwutlenek węgla jest jednym z głównych gazów cieplarnianych. Warto też zaznaczyć, że w przeciwieństwie do nitryfikacji/denitryfikacji w procesie Anammox emisja tlenków azotu jest na bardzo niskim poziomie. Ze względu na brak konieczności dozowania zewnętrznego źródła węgla, proces charakteryzuje się małą szybkością wzrostu biomasy (0,08 zamiast prawie 1 g_{smo}/gN) co wpływa na relatywnie małą produkcję osadu, a tym samym powoduje zmniejszenie kosztów eksploatacyjnych [7, 40]. Proces częściowej nitryfikacji/Anammox może być realizowany w dwóch osobnych reaktorach [22, 66] lub w jednym reaktorze [2, 5], w którym proces częściowej nitryfikacji i Anammox przebiegają symultanicznie.

Sam proces Anammox polega na utlenianiu azotu amonowego do azotu gazowego z wykorzystaniem azotynów jako ostatniego akceptora elektronów. Opierając się na bilansie masowym, w pomiarach doświadczalnych, Strous i inni [58]zaproponowali następujące równanie stechiometryczne procesu:

$$\begin{aligned} NH_4^+ + 1{,}32 \cdot NO_2^- + 0{,}066 \cdot HCO_3^- + 0.13 \cdot H^+ \rightarrow 1{,}02 \cdot N_2 + \\ + 0{,}26 \cdot NO_3^- + 0{,}066 \cdot CH_2O_{0.5}N_{0,15} + 2{,}03 \cdot H_2O \end{aligned} \tag{1}$$

Głównym produktem beztlenowego usuwania azotu amonowego jest azot gazowy, jednak około 10% azotu w dopływie jest przekształcana do azotanów. Ogólny bilans azotu pokazuje stosunek molowy równy 1:1,32:0,26 dla przemian amoniaku, azotanów (III) i (V). Przypuszcza się, że część azotanów (III) jest utleniana do azotanów (V) w celu uwolnienia elektronów, które następnie są wykorzystywane do wiązania CO_2 [58].

Bakterie Anammox w systemach oczyszczalnia ścieków pozostają aktywne w szerokim zakresie temperatur (pomiędzy 10 a 43°C), z wartością optymalną na poziomie 37°C. Najnowsze doniesienia wskazują, że proces Anammox może być z powodzeniem zastosowany w układach pracujących w temperaturze poniżej 20°C [4]. Biorąc pod uwagę koszty związane z koniecznością utrzymania wysokiej temperatury w reaktorze, zasadne jest prowadzenie procesu w temperaturach znacznie niższych niż wartości zbliżone do optimum dla bakterii Anammox. Kolejnym parametrem mającym wpływ na przebieg procesu jest wartość pH. Strous [58] wykazał, że zakres pH dla procesu Anammox zawiera się w przedziale 6,7–8,3, z wartością optymalną, wynoszącą 8. Dodatkowo Egli i współpracownicy [12] obserwowali aktywność bakterii Anammox przy pH w zakresie 8,5–9,0. Proces Anammox jest hamowany przez obecność tlenu. Jest to jednak inhibicja odwracalna, co pokazały badania z przerywanym napowietrzaniem, dzięki czemu możliwe jest prowadzenie procesów częściowej nitryfikacji i Anammox w jednym reaktorze. Bakterie Anammox charakteryzują się bardzo wysokim powinowactwem do substratów, amoniaku i azotanów (III), dla których stała powinowactwa K_S jest poniżej 5 µM. Proces jest jednak hamowany przez azot azotanowy (III), chociaż w literaturze nie ma zgodności co do stężeń powodujących inhibicję procesu. Najczęściej podaje się że stężenia przekraczające 10 mM (140 mg/dm^3) powodują inhibicję procesu. Kiedy stężenie azotu azotanowego (III) przekracza 5 mM (70 mg/dm^3) przez dłuższy okres (12 h) aktywność procesu Anammox całkowicie zanika. Jednakże jego aktywność może zostać przywrócona poprzez dodawanie niewielkich ilości (ok. 50 µM) hydrazyny, która jest produktem pośrednim reakcji Anammox. Jednak ostatnie badania pokazują, że proces ten jest bardziej odporny na stężenia azotu azotanowego (III) niż przypuszczano i stężenie powodujące spadek szybkości procesu o połowę ($IC_{50)}$ wynosi nawet ponad 350 mg/dm^3 [6]. Dodatkowo, najnowsze badania wskazują, że zakłócenia w prawidłowym przebiegu tego procesu mogą być wynikiem wysokiego stężenie wolnego amoniaku, a prawdopodobne jest też, że wolny amoniak może wzmagać inhibicję powodowaną azotanami (III) [3, 21].

4. Zaawansowane procesy utleniania w oczyszczaniu ścieków

Termin *zaawansowane procesy utleniania* (ang. advanced oxidation processes, AOPs) obejmuje wszystkie procesy utleniania chemicznego, których mechanizm bazuje na reakcji z rodnikami hydroksylowymi ($HO^•$). Rodniki $HO^•$, ze względu na swój wysoki potencjał utleniający (E^O=2,7 V, pH=7,0) i nieselektywność reagowania ze związkami organicznymi i nieorganicznymi, przyczyniają się do rozkładu (całkowitego lub częściowego) większości zidentyfikowanych zanieczyszczeń antropogenicznych. Na podstawie danych literaturowych można przyjąć, że w środowisku wodnym, wartości stałych szybkości reakcji związków organicznych i nieorganicznych z rodnikami hydroksylowymi mieszczą się w przedziale 10^7–10^{10} l/mol·s [68].

Nie ma jednoznacznej klasyfikacji procesów zaliczanych do AOPs, jednakże można je podzielić na dwie zasadnicze grupy, tj. chemiczne i fotochemiczne. W chemicznych wolne rodniki generowane są w wyniku przemian związków utleniających, zachodzących w ściśle określonych warunkach. W procesach fotochemicznych, rodniki hydroksylowe powstają na skutek przemian określonych substancji, przy czym przemiany te indukowane są promieniowaniem fotochemicznym [13, 51, 73].

Zaawansowane procesy utleniania stosowane są już nie tylko w skali laboratoryjnej, jak miało to miejsce na początku lat 90. ubiegłego wieku, ale coraz częściej wykorzystywane są w skali pilotażowej [61], a nawet w skali technicznej [28]. W technologii oczyszczania ścieków, procesy AOPs mogą być skojarzone w technikami biologicznymi i mogą być one umiejscowione, tuż po osadnikach wstępnych (jako tzw. utlenianie wstępne) albo na końcu biologicznego stopnia oczyszczania ścieków, czyli po osadnikach wtórnych (tzw. doczyszczanie ścieków lub utlenianie końcowe) [42].

W przypadku łączenia technik AOPs z biologicznym oczyszczaniem ścieków (tzw. systemy hybrydowe), ich znaczenie w procesie oczyszczania ścieków ma ścisły związek z miejscem ich stosowania. I tak, celem utleniania wstępnego jest przede wszystkim częściowe utlenienie substancji biologicznie nierozkładalnych (lub trudno rozkładalnych) i doprowadzenie ich do postaci, w której będą mogły być już dalej rozłożone w procesach biologicznego oczyszczania ścieków. Natomiast celem doczyszczania ścieków jest usunięcie mikrozanieczyszczeń antropogenicznych, które nie są całkowicie usuwane w procesach biologicznego oczyszczania ścieków i mogą wraz ze ściekami oczyszczonymi przedostawać się do wód powierzchniowych, stanowiąc zagrożenie dla organizmów tam bytujących (tzw. detoksykacja ścieków). Zaawansowane procesy utleniania mają także znaczenie w instalacjach do oczyszczania ścieków przemysłowych. Jednakże wskazane jest, aby w przypadku stosowania tego typu rozwiązań, ChZT ścieków nie przekraczało wartości 5,0 g/l. Wynika to z tego, że wyższe stężenie ChZT powoduje wzrost kosztów zakupu reagentów niezbędnych do wygenerowania odpowiedniej ilości rodników hydroksylowych. Ponadto koszty energii elektrycznej są zbyt wysokie [52].

Należy wspomnieć, że procesy AOPs były skutecznie wykorzystywane do oczyszczania ścieków z przemysłu tekstylnego [27], celulozowo-papierniczego [72], koksowniczego [59] czy winiarsko-gorzelniczego [67]. W przypadku (oczyszczonych) ścieków bytowo-gospodarczych, zastosowanie technik bazujących na zaawansowanych procesach utleniania, pozwoliły na skuteczne usunięcie wybranych zanieczyszczeń antropogenicznych [14,15,17,24,70] Także w przypadku degradacji wybranych substancji zaliczanych do grupy biomimetyków hormonalnych, procesy AOPs wymieniane są jako potencjalne narzędzie, które może służyć do eliminacji tego typu zanieczyszczeń ze środowiska wodnego [11,16,45].

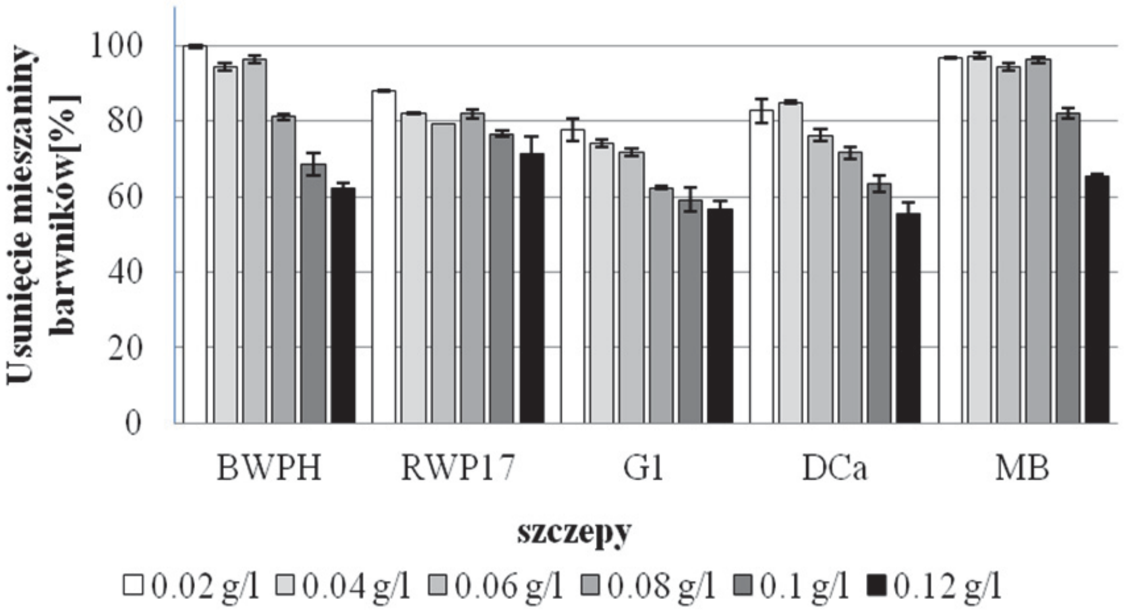
Pomimo faktu, że zaawansowane procesy utleniania w sposób zadawalający pozwalają na degradację trudno rozkładalnych zanieczyszczeń antropogenicznych w środowisku wodnym, trzeba pamiętać o tym, że są to technologie wymagające stosunkowo wysokich nakładów finansowych. Dlatego ich stosowalność należy rozpatrywać indywidualnie, w zależności od wymaganego efektu końcowego (zwiększenie biodostępności ścieków, detoksykacja, itd.). Mimo określonych mankamentów tych procesów, przede wszystkim z wysokich kosztów inwestycyjnych i eksploatacyjnych, coraz liczniejsze są publikacje potwierdzające różne możliwości zastosowania AOPs. Zatem należy uznać, że procesy te posiadają stosunkowo dobre perspektywy znacznie szerszego niż do tej pory, wykorzystania w skali technicznej.

5. Wykorzystanie grzybów w usuwaniu barwników

Grzyby stanowią istotny element ekosystemów lądowych, a także i wodnych. posiadają one specyficzne cechy, których pozbawione są inne mikroorganizmy. Między innymi są nielicznymi organizmami skutecznie degradującymi substancje lignino-celulozowych w środowisku. Zwłaszcza ta grupa cieszy się ogromnym zainteresowaniem badaczy, ze względu na swój system enzymatyczny. Grzyby te charakteryzują się mała specyficznością enzymatyczną (system związany z produkcją enzymów zaliczanych do lakaz i peroksydaz), dzięki któremu mogą degradować różnorodne ksenobiotyki takie jak: WWA, pestycydy, czy barwniki syntetyczne. Obecnie zwraca się duża uwagę na barwniki, ponieważ są one odporne na biodegradację w konwencjonalnych systemach oczyszczania ścieków opartych o metodę osadu czynnego. W tym przypadku różnorodne grzyby mogą zostać wykorzystane w dwojaki sposób – jako materiał adsorpcyjny, jak również do enzymatycznej biotransformacji substancji aromatycznych. Podkreśla się, że pomimo tego, iż proces adsorpcji jest szybki i wydajny, to właśnie proces biotransformacji ma w tym przypadku szczególnie duży dział w usuwaniu barwy [10,30]. Biosorpcja natomiast dotyczy głównie grzybów nieligninolitycznych, jak *Aspergillus niger* [18].

Grzyby mogą zostać wykorzystane zarówno do usuwania pojedynczych barwników [48], jak również ich mieszanin [49,50]. Na rysunku 2 przedstawiono efektywność dekoloryzacji mieszaniny zieleni brylantowej i błękitu Evansa (w stosunku 1:1) w zależności od stężenia składników w mieszaninie. Jak wskazują badania, zarówno szczepy zaliczane do grzybów zgnilizny drewna (BWPH i MB – *Pleurotus ostreatus*; RWP17 – *Polyporus picipes*), jak i inne gatunki (DCa – *Gloeophyllum odoratum*; G1 – *Fusarium oxysporum*) mają zdolność usuwania barwników z roztworów wodnych, a efektywność procesu zależy od rodzaju szczepu i stężenia substancji barwnych. Przykładowo, gdy stężenie barwników było w zakresie 0,02–1,2 g/l, efektywność usunięcia przekraczała 50% w ciągu 7 dni [31].

Na efektywność dekoloryzacji wpływają również warunki hodowli. Wstrząsanie prób pozwala na lepsze natlenienie, a także zwiększenie powierzchni kontaktu barwników z biomasą. Jak wskazują wyniki przedstawione w tabeli 1 wytrząsanie pozwoliło na zwiększenie efektywności dekoloryzacji w przypadku wszystkich badanych szczepów w zakresie od 12% (szczep MB) do ponad 27% (szczep G1). Prócz znacznego usunięcia barwy (90% w ciągu 96h w przypadku szczepu MB), korzystnym efektem procesu było również zmniejszenie zoo- i fitotoksyczności prób. Badania toksyczności wykazały, że próby po dekoloryzacji zaklasyfikowano jako toksyczne wobec *Daphnia magna* (III klasa toksyczności*)*, a także jako nietoksyczne (I klasa toksyczności) wobec *Lemna minor* (dekoloryzacja z udziałem szczepów BWPH, RWP17, G1 i MB hodowane w warunkach wytrząsania, w których dekoloryzacja była wyższa). Zatem w procesie uzyskano spadek zootoksyczności i fitotoksyczności odpowiednio o 2 i 3 klasy.



Rys. 2. Efektywność dekoloryzacji różnych stężeń mieszaniny barwników przez wybrane szczepy grzybów [49]
Fig. 2. Effectiveness of decolorization od different concentrations of the dyes mixture by selected fungal strains [49]

Tabela 1. Wyniki 96-h dekoloryzacji mieszaniny barwników (0.08g/l) w próbach wstrząsanych i statycznych oraz testów zoo- i fitotoksyczności [50]
Table 1. Results of 96-h decolourization of the dyes mixture (0.08 g/l) and zoo- and phytotoxicity tests [50]

Szczep	Próba	BWPH	RWP17	G1	DCa	MB	Kontrole
% usunięcie mieszaniny po 96h	wytrząsana	83.58	87.13	79.20	84.67	90.13	
	statyczna	67.50	71.00	51.93	65.61	78.00	
Klasa zootoksyczności	wytrząsana	III	III	III	III	III	V
	statyczna	III	III	III	III	III	
Klasa fitotoksyczności	wytrząsana	I	I	I	III	I	IV
	statyczna	I	I	III	III	II	

6. Hydrofitowe metody oczyszczania ścieków

Oczyszczalnie hydrofitowe są to systemy inżynierskie, których zasada działania opiera się na imitacji i intensyfikacji procesów usuwania zanieczyszczeń zachodzących w naturalnych mokradłach. W ciągu ostatnich trzech dekad stosowanie oczyszczalni hydrofitowych znacznie się upowszechniło. Układy te uznawane są obecnie za alternatywę wobec bardziej zaawansowanych technicznie rozwiązań w oczyszczaniu ścieków zwłaszcza w małych jednostkach osadniczych [71]. Perspektywiczne kierunki prac badawczych i rozwojowych dotyczących oczyszczalni hydrofitowych można podzielić w zależności od: rodzaju oczyszczanych ścieków, rodzaju zanieczyszczeń, sposobu intensyfikacji procesów oczyszczania ścieków, miejsca zastosowania i aspektów dodatkowych. W początkowych etapach rozwoju oczyszczalnie hydrofitowe były stosowane przede wszystkim do oczyszczania ścieków bytowo-gospodarczych, co nadal jest najczęstszym zastosowaniem tych układów [71]. Zastosowanie i badania dotyczące oczyszczalni hydrofitowych obejmują jednak również oczyszczanie innych rodzajów ścieków np. galwanizerskich [54], z produkcji wina, z produkcji sera, spływów powierzchniowych z terenów lotnisk oraz odcieków składowiskowych [36]. Badania i wykorzystanie oczyszczalni hydrofitowych koncentrowały się pierwotnie na usuwaniu związków organicznych, azotu i fosforu, jednak obecnie coraz większą uwagę poświęca się innym rodzajom zanieczyszczeń. Najnowsze doniesienia skupiają w coraz większym stopniu na usuwaniu takich zanieczyszczeń jak: pierwiastki (zwłaszcza metale, ale również antymon, selen, bor) [55, 56], nanocząstki metali [33], cyjanki [55] i mikrozanieczyszczenia organiczne (np. farmaceutyki i inhibitory korozji) [9, 36]. Jak wspomniano powyżej, jednym z aktualnych kierunków badawczych jest badanie możliwości zintensyfikowania procesów odpowiedzialnych za usuwanie związków organicznych, azotu i fosforu, jak również innych zanieczyszczeń.

Do najczęściej badanych i stosowanych metod zwiększania efektywności usuwania zanieczyszczeń w oczyszczalniach hydrofitowych należy recyrkulacja ścieków. Prowadzi to do zwiększenia usunięcie azotu całkowitego, ale wymaga większych nakładów energetycznych. Można tez stosować napowietrzanie złoża i zasilanie szarżowe w celu zwiększenia efektywności nitryfikacji. Inne możliwości to zastosowanie dżdżownic, nadtlenku wodoru [41] lub zmiennego kierunku przepływu ścieków w celu ograniczenia kolmatacji złoża, czy bioaugmentacja (zwłaszcza w przypadku usuwania zanieczyszczeń refrakcyjnych). Ciekawym rozwiązaniem jest wprowadzanie węgla organicznego (jako wypełnienia złoża lub substancji dodawanej do ścieków surowych) w celu intensyfikacji denitryfikacji lub usuwanie metali poprzez sprzężenie procesu redukcja siarczanów i wytrącanie ich w postaci siarczków) [57]. Również zastosowanie denitryfikacji autotroficznej, ograniczenie możliwości zamarzania złoża, zastosowanie materiałów o zwiększonej pojemności sorpcyjnej względem fosforu [46] są możliwymi do zastosowania sposobami modyfikacji procesu [71]. Ponadto do intensyfikacji usuwania zanieczyszczeń ze ścieków (głównie azotu i fosforu) proponuje się układy hybrydowe, czyli połączenie różnych typów oczyszczalni hydrofitowych. Spośród tych rozwiązań najbardziej popularnym układem jest połączenie złoża o przepływie pionowym i poziomym, co umożliwia prowadzenie nitryfikacji i denitryfikacji ścieków [69]. W praktyce istnieje jednak wiele konfiguracji układów hybrydowych, co uwarunkowane jest rodzajem ścieków, wymaganiami dotyczącymi jakości ścieków oczyszczonych i innymi czynnikami (np. warunki klimatyczne). Jednym z ciekawszych rozwiązań (również pod względem estetycznym) jest połączenie oczyszczania ze złożem (o przepływie pionowym lub poziomym) ze zbiornikiem z wyspą pływającą. Umożliwia to pobieranie substancji biogennych przez akumulację w biomasie roślinnej. W szerszym znaczeniu, układy hybrydowe mogą stanowić połączenie oczyszczalni hydrofitowej z innymi technologiami oczyszczania ścieków (np. z osadem czynnym) lub z takimi naturalnymi procesami jak np. fotodegradacja. Należy wspomnieć, że oczyszczalnie hydrofitowe oprócz zalet (efektywne usuwanie zanieczyszczeń) i znanych wad (np. zwiększone zapotrzebowanie powierzchni) mogą również zostać włączone w przestrzeń miejską. W zakresie tych zastosowań oczyszczalni hydrofitowych można wymienić takie rozwiązania jak zielone dachy, zielone ściany czy ogrody deszczowe [32].

7. Fitoremediacja gruntów wspomagana mikoryzacją roślin

Fitoremediacja to technologia w której wykorzystuje się naturalne zdolności roślin do pobierania i gromadzenia zanieczyszczeń lub do ich biodegradacji. Jest to metoda tania, ale dość długotrwała o efektywności zależnej od wielu czynników [43]. Można przyspieszyć jej przebieg przez wykorzystanie mikoryzy czyli zjawiska symbiozy pomiędzy żywymi komórkami korzeni roślin a niepatogenicznymi wysoko wyspecjalizowanymi grzybami zasiedlającymi glebę. Grzyby mikoryzowe mogą być wykorzystywane w procesie fitodegradacji, gdyż produkują one enzymy uczestniczące we wstępnych i pośrednich etapach rozkładu ksenobiotyków. Wpływa to korzystnie na dalszy rozkład zanieczyszczeń przez inne organizmy ryzosfery. Grzyby mikoryzowe można wykorzystać np. do intensyfikacji procesów fitoremediacji gruntów zanieczyszczonych substancjami ropopochodnymi [35]

Samoistna kolonizacja podłoża zanieczyszczonego wysokimi stężeniami węglowodorów jest procesem długotrwałym. Czas ten można skrócić przez wprowadzenie propagul grzybów mikoryzowych w formie inokulum. Grzyby stosowane do iniekcji powinny być izolowane z zanieczyszczonych gleb, gdyż są już zaadaptowane do tego rodzaju zanieczyszczeń, co gwarantuje ich przetrwanie i dalszy rozwój. Stopień rozkładu węglowodorów w gruncie zależy od rodzaju zastosowanej modyfikacji. Wykazano, iż najlepsze rezultaty uzyskuje się w procesie bioremediacji prowadzonej z wykorzystaniem roślin jednoliściennych oraz inokulantów grzybów mikoryzowych otrzymanych z gleb zanieczyszczonych.W badaniach stwierdzono, że symbioza grzybów mikoryzowych z roślinami jednoliściennymi powoduje zwiększenie stopnia usunięcia węglowodorów cztero-, pięcio- i sześciopierścieniowych średnio o 15% w porównaniu z konwencjonalnymi metodami [35].

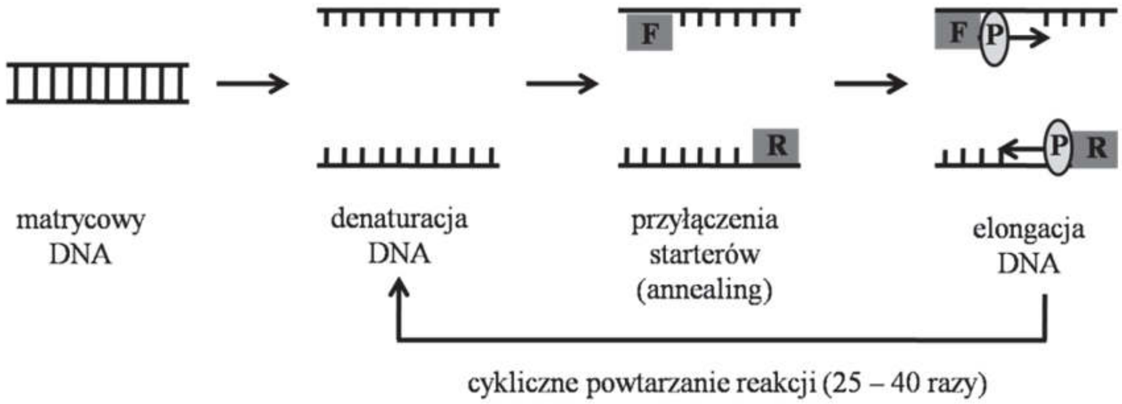
Generalnie można potwierdzić zwiększenie skuteczności oraz szybkości procesu bioremediacji gruntów zanieczyszczonych produktami ropopochodnymi dzięki uprawie roślin o rozbudowanych systemach korzeniowych sprzyjających rozwojowi mikroorganizmów ryzosferowych. W celu oceny jakości gruntów poddawanych oczyszczaniu z substancji ropopochodnych – oprócz analiz fizykochemicznych – wskazane są także badania ekotoksykologiczne uwzględniające wpływ zanieczyszczeń oraz ich metabolitów na organizmy wskaźnikowe.

8. Techniki biologii molekularnej w inżynierii środowiska

Bardzo ważnym aspektem zagadnień związanych z inżynierią i ochroną środowiska jest możliwość analizowania składu jakościowego i ilościowego zbiorowisk bakteryjnych, odpowiedzianych za procesy biotechnologiczne, takie jak bioremediację gruntów [64], oczyszczanie ścieków [34], czy kompostowanie. Ze względu na fakt, że wyhodowanie większości mikroorganizmów występujących w środowisku nie jest możliwe w laboratorium metodami klasycznej mikrobiologii, z pomocą przychodzą tu techniki biologii molekularnej.

Metody te można podzielić na dwie główne grupy: pośrednie – oparte na łańcuchowej reakcji polimerazy (PCR; ang. Polymerase Chain Reaction) i bezpośrednie, w których amplifikacja metodą PCR nie jest konieczna (należą tu m.in. metody hybrydyzacyjne i cytometria przepływowa) [23,77].

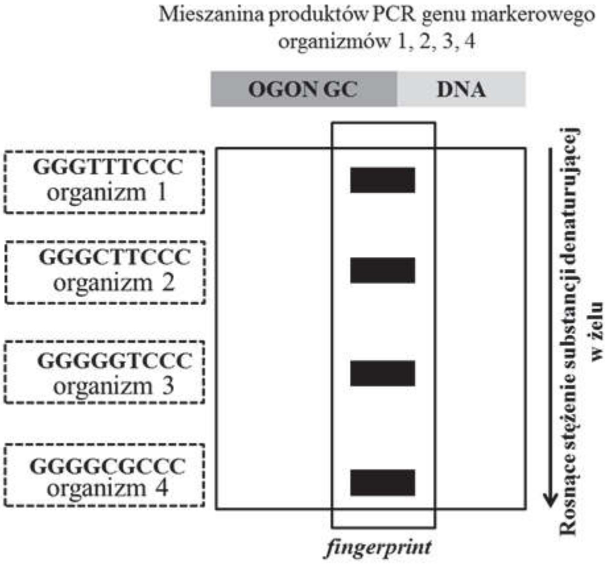
Technika PCR to reakcja enzymatyczna *in vitro*, naśladująca replikację DNA w komórce. Pozwala ona powielić w znacznej liczbie kopii ściśle określony fragment materiału genetycznego. Tak precyzyjny zakres amplifikacji jest możliwy dzięki zastosowaniu wysoce specyficznych starterów reakcji, flankujących określony region materiału genetycznego, który zostanie poddany kopiowaniu. Schemat reakcji przedstawiono na rysunku 3.



Rys. 3. Schemat reakcji PCR [74]
Fig. 3. PCR scheme [74]

Podstawowa reakcja PCR została wielokrotnie modyfikowana. Wśród ważniejszych modyfikacji z punktu widzenia monitoringu biocenoz bakteryjnych można wymienić reakcję PCR w czasie rzeczywistym (ang. Real Time PCR), która umożliwia ilościową analizę poszczególnych grup mikroorganizmów w próbce środowiskowej. Metoda ta jest często wykorzystywana w badaniach bakterii glebowych [20], czy osadu czynnego [8]. Drugą z ważnych odmian PCR jest połączenie tej reakcji z odwrotną transkrypcją (RT-PCR; ang. reverse transcriptase PCR), w której właściwa reakcja amplifikacji PCR poprzedzona jest syntezą cDNA (ang. complimentary DNA) na matrycy całkowitego RNA bakteryjnego izolowanego z próbki środowiskowej. RT-PCR jest stosowana do badań aktywności mikrobiocenoz w glebie, wodzie czy osadzie czynnym [53].

PCR nieodzownie łączy się z użyciem technik elektroforetycznych, z których na szczególną uwagę zasługuje elektroforeza w gradiencie czynnika denaturującego (DGGE; ang. Denaturing Gradient Gel Electrophoresis). Amplifikacja PCR prowadzona jest na całkowitym DNA wyizolowanym z próbki środowiskowej i pozwala na uzyskanie amplikonów o takiej samej długości, ale różnej sekwencji DNA (czyli fragmentów o innej temperaturze topnienia). Elektroforeza w gradiencie czynnika denaturującego – mocznika, powoduje, że amplikony PCR rozdzielają się w żelu przy różnej wartości stężenia denaturanta tzn. im wyższa temperatura topnienia fragmentu, tym produkt PCR przesunie się na większą odległość w żelu denaturującym[40,76]. W efekcie uzyskuje się tzw. fingerprint, czyli wzór prążkowy, obrazujący złożoność strukturalną zbiorowiska bakteryjnego (rysunek 4).



Rys. 4. Schemat elektroforezy w gradiencie denaturacji DGGE [74]
Fig. 4. Denaturing gradient gel electrophoresis (DGGE) scheme [74]

Wśród metod hybrydyzacyjnych największa popularnością w badaniach mikrobiocenoz cieszy się hybrydyzacja fluorescencyjna in situ (FISH; ang. Fluorescent in situ Hybridisation) [75]. Technika ta opiera się na zasadzie komplementarności kwasów nukleinowych. Krótkie fragmenty DNA (tzw. sondy oligonukleotydowe) są znakowane barwnikiem fluorescencyjnym i poddawane hybrydyzacji z badaną próbką środowiskową. Preparaty po hybrydyzacji są obserwowane w mikroskopie fluorescencyjnym lub konfokalnym, gdzie istnieje możliwość określenia liczebności poszczególnych grup bakteryjnych w materiale w stosunku do całkowitej liczby bakterii w próbce. Można to osiągnąć poprzez zastosowanie różnych barwników fluorescencyjnych [62].

9. Podsumowanie

Postęp w inżynierii środowiska obejmujący wszystkie jej obszary począwszy od uzdatniania wody, poprzez oczyszczanie ścieków, remediację gruntów, zagospodarowanie odpadów, aż do oczyszczania zanieczyszczonych gazów, następuje zazwyczaj w sposób wybiórczy i skokowy. Są takie obszary, gdzie stosowane technologie są dość niezmienne, ale widoczny jest znaczny rozwój rozwiązań technicznych, a z tym wiąże się istotne zwiększenie ich efektywności. Taka sytuacja wydaje się występować w uzdatnianiu wód i oczyszczaniu gazów. Natomiast w oczyszczaniu ścieków czy remediacji gruntów (rekultywacji gleb), obserwuje się intensywny rozwój nieznanych do niedawna technologii, a dotyczy to w szczególności procesów biologicznych. Związane to jest w dużym stopniu z rozwojem biologii, a w szczególności biologii molekularnej, co pozwala na nieosiągalne dotychczas precyzyjne rozpoznanie i identyfikację aktywnych populacji mikroorganizmów. Ponieważ obserwowany postęp następuje, jak już wzmiankowano, w sposób skokowy, można więc oczekiwać, że także w innych obszarach inżynierii środowiska takich jak np. inżynieria środowiska wewnętrznego, nastąpi podobny progres.

Literatura

1. **Broda E.:** *Two kinds of lithotrophs missing in nature*. Zeitschrift für allgemeine Mikrobiologie. 17 (6), 491–493 (1977).
2. **Cema G., Płaza E., Trela J., Surmacz-Górska J.:** *Dissolved oxygen as a factor influencing nitrogen removal rates in one-stage system with partial nitritation and Anammox process*. Water Science and Technology. 64(5), 1009–1015 (2011).
3. **Cema G., Schneider Y., Beier M., Rosenwinkel K-H.:** *Influence of Free Ammonia and Free Nitrous Acid on Anammox Activity*. In proceeding of: WEF/ IWA Nutrient Removal and Recovery 2013: Trends in Resources Recovery and Use, Vancouver, Kanada 2013.

4. **Cema G., Wiszniowski J., Żabczyński S., Zabłocka-Godlewska E., Raszka A., Surmacz-Górska J.:** *Biological nitrogen removal from landfill leachate by deammonification assisted by heterotrophic denitrification in rotating biological contactor (RBC)*. Water Science and Technology. 55(8–9), 35–42 (2007).
5. **Cema, G., Szatkowska, B., Plaza, E., Trela, J., Surmacz-Górska, J.:** *Nitrogen removal rates at a technical-scale pilot plant with the one-stage partial nitritation/Anammox process*. Water Science and Technology. 54(8), 209–217 (2006).
6. **Dapena-Mora A., Fernandez I., Campos J.L., Mosquera-Corral A.:** Méndez R, Jetten M.S.M. *Evaluation of Activity and Inhibition effects on Anammox process by batch tests based on nitrogen gas production*. Enzyme and Microbial Technology. 40(4), 859–865 (2007).
7. **De Clippeleir H., Yan X., Verstraete W., Vlaeminck S.E.:** *OLAND is feasible to treat sewage-like nitrogen concentrations at low hydraulic residence time*. Proceedings of the IWA/WEF Nutrient Recovery and Management, 9–12 January 2011, Miami, Florida. 1264–1274 (2011).
8. **Dionisi H. M., Harms G., Layton A.C., Gregory I. R., Parker J., Hawkins S.A., Robinson K. G., Sayler G. S.:** *Power Analysis for Real-Time PCR Quantification of Genes in Activated Sludge and Analysis of the Variability Introduced by DNA Extraction*. Applied and Environmental Microbiology. 69, 11, 6597–6604 (2003).
9. **Dordio A. V., Carvalho A. J. P.:** *Organic xenobiotics removal in constructed wetlands, with emphasis on the importance of the support matrix*. Journal of Hazardous Materials. 252, 272–292 (2013).
10. **Dos Santos A., Cervantes F.J., van Lier J.B.:** *Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology*. Bioresource Technology. 98, 2369–2385 (2007).
11. **Dudziak M.:** *Badania skuteczności usuwania mykoestrogenów z roztworów wodnych w zintegrowanym procesie sorpcja-rozkład fotokatalityczny-nanofiltracja*. Rocznik Ochrona Środowiska (Annual Set the Environment Protection) 15, 1929–1936 (2013).
12. **Egli K., Fanger U., Alvarez P.J.J., Siegrist H., van der Meer J.R., Zehnder A.J.B.:** *Enrichment and characterisation of an anammox bacterium from rotating biological contactor treating ammonium-rich leachate*. Archives of Microbiology. 175, 198–207 (2001).
13. **Esplugas S., Gimenez J., Contreras S., Pascual E., Rodrigez M.:** *Comparison of different advanced oxidation processes for phenol degradation*. Water Research. 36, 1034–1042 (2002).

14. **Felis E., Alder A.C., Surmacz-Gorska J., Miksch K.:** *Advanced oxidation of the polycyclic musk fragrances with using UV and UV/H_2O_2 processes*. Archives of Environmental Protection. 34, 13–23 (2008).
15. **Felis E., Marciocha D., Surmacz-Górska J., Miksch K**.: *Photochemical degradation of naproxen in the aquatic environment.* Wat. Sci. Tech. 55(12), 281–286 (2007).
16. **Felis E., Miksch K.:** *Nonylphenols degradation in the UV, UV/H_2O_2, O_3 and UV/O_3 processes – comparison of the methods and kinetic study*. Water Science and Technology. 71(3), 446–453 (2015).
17. **Felis E., Miksch K.:** *Removal of analgesic drugs from the aquatic environment using photochemical methods*. Water Science and Technology. 60, 2253–2259 (2009).
18. **Fu Y., Viraraghavan T.:** *Fungal decolorization of dye wastewater: a review*. Bioresource Technology. 79, 251–262 (2001).
19. **HeijnenJ.J., van Loosdrecht M. C. M. , Mulder A and Tijhuis L.:** *Formation of Biofilms in a Biofilm Air-Lift Suspension Reactor.* Water Science & Technology. 26(3–4), 647–654 (1992).
20. **Henry S., Baudoin E., López-Gutiérrez J., C., Martin-Laurent F., Brauman A., Philippot L.:** *Quantification of denitrifying bacteria in soils by nirK gene targeted real-time PCR.* Journal of Microbiological Methods. 59, 3, 327–335 (2004).
21. **Jaroszynski, L., Cicek, N., Sparling, R., Oleszkiewicz, J:**. *Impact of free ammonia on anammox rates (anoxic ammonium oxidation) in a moving bed biofilm reactor*. Chemosphere. 88(2), 188–195 (2012).
22. **Jeanningros Y., Vlaeminck S.E., Kaldate A., Verstraete W.:** *Fast start-up of a pilot-scale deammonification sequencing batch reactor form activated sludge inoculum*. Water Science and Technology. 61(6), 1393–1400 (2010).
23. **Katsanis S.H., Katsanis N.:** *Molecular genetic testing and the future of clinical genomics*. Nature Reviews Genetics. 14, 415–426 (2013).
24. **Klavarioti M., Mantzavinos D., Kassinos D.:** *Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes.* Environmental International. 35, 402–417 (2009).
25. **Kończak B., Fernandez I., Miksch K.:** *Evolución de los polímeros extracelulares de gránulos aerobios durante su formación en el reactor SBR.* Konfer. Proc.” 1st IWA National Young Water Professional Conference”, 16–18.06.2010, Barcelona 2010.
26. **Kończak B., Karcz J., Miksch K.:** *Influence of calcium, magnesium and iron ions on aerobic granulation.* Applied Biochemistry and Biotechnology. 174, 2910–2918 (2014).

27. **Ledakowicz S., Solecka M., Zylla R.:** *Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes.* Journal of Biotechnology. 89, 175–184 (2001).
28. **Legrini O.:** *Commercial scale advanced oxidation processes for TOC removal*. Programme and Executive Summaries of 6th IWA Specialist Conference on Oxidation Technologies for Water and Wastewater Treatment. Goslar, Germany, 7–9 May 2012.
29. **Li X-F., Li Y-J., Hua Z-Z., Du G-C. and Chen J.:** *Correlation between extracellular polymeric substances and aerobic biogranulation in membrane bioreactor*. Sep. Purif. Technol. 59, 26–33 (2008).
30. **Liu W., Chao Y., Yang X., Bao H., Qian S.:** *Biodecolorization of azo, anthraquinonic and triphenylmethane dyes by white-rot fungi and a laccase-secreting engineered strain.* Journal of Industrial Microbiology and Biotechnology. 31, 127–132 (2004).
31. **Liu Y-Q., Moy B., Kong Y-H., Tay, J-H.:** *Formation, physical characteristics and microbial community structure of aerobic granules in a pilot-scale sequencing batch reactor for real wastewater treatment.* Enzyme and Microbial Technology. 46(6), 520–525 (2010).
32. **Lovell S. T., Johnston D. M.:** *Designing landscapes for performance based on emerging principles in landscape ecology*. Ecology and Society. 14(1), 44 (2009).
33. **Lowry G.V., Espinasse B.P., Badireddy A.R., Richardson C.J., Reinsch B.C., Bryant L.D., Bone A.J., Deonarine A., Chae S., Therezien M., Colman B.P., Hsu-Kim H., Bernhardt E.S., Matson C.W., Wiesner M.R.:** *Long-term transformation and fate of manufactured Ag nanoparticles in a simulated large scale freshwater emergent wetland.* Environmental Science and Technology. 46, 13, 7027–7036 (2012).
34. **Łuczkiewicz A., Felis E., Ziembińska A., Gnida A., Kotlarska E., Olańczuk-Neyman K., Surmacz-Górska J.:** *Resistance of Escherichia coli and Enterococcus spp. to selected antimicrobial agents present in municipal wastewater*. Journal of Water and Health. 11, 4, 600–612 (2013).
35. **Małachowska-Jutsz A.:** *Mikoryzacja roślin a efektywność fitoremediacji gruntów zanieczyszczonych węglowodorami.* Zeszyty Naukowe Politechniki Śląskiej, nr 1782, Gliwice 2008.
36. **Miksch K., Cema G., Corvini P. F.-X, Felis E., Sochacki A., Surmacz-Górska J., Wiszniowski J., Żabczyński S.:** *R&D priorities in the field of sustainable remediation and purification of agro-industrial and municipal wastewater*. New Biotechnology. 32, 1, 128–132 (2015)

37. **Miksch K., Konczak B.:** *Distribution of Extracellular Polymeric Substances and their Role in Aerobic Granule Formation*. Chemical and Process Engineering. 33(4), 679–688 (2012).
38. **Morgenroth E., Sherden T., van Loosdrecht M.C.M., Heijnen J.J., Wilderer P.A.:** *Aerobic granular sludge in a sequencing batch reactor.* Wat. Res. 31, 3191–3194 (1997).
39. **Mulder A.:** *The quest for sustainable nitrogen removal technologies*. Water Science and Technology. 48(1), 67–75 (2003).
40. **Muyzer G., Smalla K.:** *Application of denaturing gradient gel electrophoresis (DGGE) and temperature gradient gel electrophoresis (TGGE) in microbial ecology*. Antonie van Leeuwenhoek 73, 127–141 (1998).
41. **Nivala J., Rousseau, D.:** *Reversing clogging in subsurface-flow constructed wetlands by hydrogen peroxide treatment: two case studies*. Water Science and Technology 59, 10, 2037–2046 (2009).
42. **Oller I., Malato S., Sanchez-Perez J. A.:** *Combination of advanced oxidation processes and biological treatments for wastewater decontamination – A review*. Science of Total Environment. 409, 4141–4166 (2011).
43. **Panz K., Miksch K.:** *Phytoremediation of explosives (TNT, RDX, HMX) by wild-type and transgenic plants.* Journal of Environmental Management. 113, 85–92 (2012).
44. **Park Ch., Novak J.T., Helm R.F., Ahn Y-O. and Esen A.:** *Evaluation of the extracellular proteins in full-scale activated sludges*. Water Res. 42, 3879–3889 (2008).
45. **Parsons S. (red.):** *Advanced oxidation processes for water and wastewater treatment*. IWA Publishing, London 2005.
46. **Paruch A., Mæhlum T., Obarska-Pempkowiak H., Gajewska M., Wojciechowska E., Ostojski A.:** *Rural domestic wastewater treatment in Norway and Poland: experiences, cooperation and concepts on the improvement of constructed wetland technology.* Water Science and Technology. 63(4), 776–781 (2014).
47. **Pignanelli S.:** *Laboratory diagnosis of Toxoplasma gondii infection with direct and indirect diagnostic techniques*. Indian Journal of Pathology and Microbiology. 54 (4), 786–789 (2011).
48. **Przystaś W., Zabłocka-Godlewska E., Grabińska-Sota E.:** *Biological Removal of Azo and Triphenylmethane Dyes and Toxicity of Process By-Products.* Water Air and Soil Pollution. 223, 1581–1592 (2012).
49. **Przystaś W., Zabłocka-Godlewska E., Grabińska-Sota E.:** *Effectiveness of dyes removal by mixed fungal cultures and toxicity of their metabolites.* Water Air and Soil Pollution. 224, 1534–1543 (2013).

50. **Przystaś W., Zabłocka-Godlewska E., Grabińska-Sota E.:** *Efficacy of fungal decolorization of a mixture of dyes belonging to different classes.* Brazilian Journal of Microbiology – zaakceptowany do publikacji 2015.
51. **Rey A., Carbajo J., Adán C., Faraldos M., Bahamonde A., Casas J.A., Rodriguez J.J.:** *Improved mineralization by combined advanced oxidation processes.* Chemical Engineering Journal. 174, 134–142 (2011).
52. **Rizzo L.:** *Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment.* Water Research, 45, 4311–4340 (2011).
53. **Selvaratnam S., Schoedel B.A., McFarland B.L., Kulpa C.F.:** *Application of reverse transcriptase PCR for monitoring expression of the catabolic dmpN gene in a phenol-degrading sequencing batch reactor*. Applied and Environmental Microbiology. 61, 11, 3981–3985 (1995).
54. **Sochacki A., Faure O., Guy B., Surmacz-Górska J.:** *Polishing of Real Electroplating Wastewater in Microcosm Fill-and-Drain Constructed Wetlands*. W: The Role of Natural and Constructed Wetlands in Nutrient Cycling and Retention on the Landscape (pod red. Jana Vymazala), Springer International Publishing Switzerland, 2015,
55. **Sochacki A., Surmacz-Górska J., Faure O., Guy B.:** *Microcosm fill-and-drain constructed wetlands for the polishing of synthetic electroplating wastewater*. Chemical Engineering Journal. 251C, 10–16 (2014).
56. **Sochacki A., Surmacz-Górska J., Faure O., Guy B.:** *Polishing of synthetic electroplating wastewater in microcosm upflow constructed wetlands: Effect of operating conditions*. Chemical Engineering Journal. 237, 250–258 (2014).
57. **Sochacki A., Surmacz-Górska J., Faure O., Guy B.:** *Polishing of synthetic electroplating wastewater in microcosm upflow constructed wetlands: Metals removal mechanisms*. Chemical Engineering Journal. 242, 43–52 (2014).
58. **Strous M., Heijen J. J., Kuenen J. G., Jetten M. S. M.:** *The sequencing batch bioreactor as a powerful tool for the study of slow growing anaerobic ammonium-oxidizing microorganisms*. Applied Microbiology and Biotechnology. 50, 589–596 (1998).
59. **Świderska-Dąbrowska R., Piaskowski K.:** *Wpływ charakteru zanieczyszczeń organicznych na efektywność ich utleniania w procesie Fentona.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 15, 1126–1142 (2013).
60. **Tay J.H., Liu Q.S. and Liu Y.:** *The role of cellular polysaccharides in the formation and stability of aerobic granules*. Lett. Appl. Microbiol. 33, 222–226 (2001).

61. **Ternes T. A., Joss A. (pod red.):** *Human Pharmaceuticals, Hormones and Fragrances: The challenge of micropollutants in urban water management*. IWA Publishing, London 2006.
62. **Thamdrup B., Dalsgaard T.:** *Production of N_2 through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments*. Applied and Environmental Microbiology. 68, 1312–1318 (2002).
63. **Tian Y.:** *Behaviour of bacterial extracellular polymeric substances from activated substances from activated sludge: a review*, Int. J. Environment and Pollution. 32(1), 78–89 (2008).
64. **Turek-Szytow J., Ziembińska A., Miksch K., Tekla P., Walawska B., Gluzińska J.:** *Evaluation of the impact of calcium peroxide on soil properties of permanently petroleum-polluted soils*. Przemysł Chemiczny. 91(6), 1209–1213 (2012).
65. **van der Roest H.F., de Bruin L.M.M., Gademan G., Coelho F.:** *Towards sustainable waste water treatment with Dutch Nereda® technology*, Water Practice & Technology. 6(3) (2011).
66. **Vázquez-Padín J., Fernádez I., Figueroa M., Mosquera-Corrala A., Campos J-L., Méndez R.:** *Applications of Anammoxnext term based processes to treat anaerobic digester supernatant at room previous temperature*. Bioresource Technology. 100(12), 2988–2994 (2009).
67. **Vilar V.J.P., Maldonado M.I., Oller I., Malato S., Boaventura R.A.R.:** *Solar treatment of cork boiling and bleaching wastewaters in a pilot plant*. Water Research. 43, 4050–4062 (2009).
68. **von Gunten U.:** *Review: Ozonation of drinking water: Part I. Oxidation kinetics and product formation*. Water Research. 37, 1443–1467 (2003).
69. **Vymazal J.:** *The use of hybrid constructed wetlands for wastewater treatment with special attention to nitrogen removal: a review of a recent development*. Water Research. 47(14), 4795–4811 (2013).
70. **Włodarczyk-Makuła M.:** *Zmiany ilościowe WWA w ściekach oczyszczonych podczas utleniania.* Rocznik Ochrona Środowiska (Annual Set the Environment Protection). 16, 1093–1104 (2011).
71. **Wu S., Kuschk P., Brix H., Vymazal J., Dong, R.:** *Development of constructed wetlands in performance intensifications for wastewater treatment: A nitrogen and organic matter targeted review.* Water Research. 57, 40–55 (2014).
72. **Yeber M.C., Rodriguez J., Freer J., Baeza J., Duran N., Mansilla H.D.:** *Advanced oxidation of a pulp mill bleaching wastewater.* Chemosphere. 39, 1679–1688 (1999).
73. **Zarzycki R. (red.):** *Zaawansowane techniki utleniania w ochronie środowiska.* Polska Akademia Nauk Oddział w Łodzi, Łódź 2002.

74. **Ziembińska-Buczyńska A.:** *Dynamika zmian bioróżnorodności zespołów bakterii biorących udział w przemianach związków azotu w złożu tarczowym oczyszczającym ścieki koksownicze*. Wydawnictwo Politechniki Śląskiej, Gliwice (w druku), 2015.
75. **Ziembińska A., Ciesielski S., Gnida A., Żabczyński S., Surmacz-Górska J., Miksch K.:** *Comparison of Ammonia-Oxidizing Bacterial Community Structure in Membrane-Assisted Bioreactors Using PCR-DGGE and FISH.* Journal of Microbiology and Biotechnology. 22(8), 1035–1043 (2012).
76. **Ziembińska A., Ciesielski S., Miksch K.:** *Ammonia oxidizing bacteria community in activated sludge monitored by denaturing gradient gel electrophoresis (DGGE).* Journal of General and Applied Microbiology. 55, 373–380 (2009).
77. **Ziembińska A., Ciesielski S., Wiszniowski J.:** *DGGE-based monitoring of bacterial diversity in activated sludge dealing with wastewater contaminated by organic petroleum compounds.* Archives of Environmental Protection. 36(4), 119–125 (2010).

Novel Methods and Technologies in Environmental Engineering

Abstract

The novel technologies used in environmental engineering were discussed in this paper – the formation of aerobic granules, the Anammox process, the advanced oxidation processes, the use of fungi for dyes decolorization, constructed wetlands, the soil phytoremediation supported by rhizosphere microorganisms and the use of molecular biology technique in environmental engineering.

The structure of granular sludge is influenced by EPS production. The average diameter and density of biogranules increase due to EPS production. Although polysaccharides are essential, proteins were found to be the predominant component of aerobic granular sludge. Compared to loosely bound EPS (LB-EPS), tightly bound EPS (TB-EPS) showed more significant correlations with granules formation. This investigation will contribute towards a better understanding of the behavior and composition of EPS in sequencing batch reactors.

The traditional nitrification and denitrification processes proceed well with typical municipal wastewater. Nevertheless, there are also nitrogen-rich wastewater streams like landfill leachate or reject waters from dewatering of digested sludge, for which traditional nitrification/denitrification can be generally ineffective due to free ammonia inhibition of nitrification and unfavorable biode-

gradable carbon content for denitrification. Because of high requirements for oxygen and the necessity for addition of external carbon source, treating such nitrogen-rich streams with nitrification/denitrification would become expensive and unsustainable. The least resources consuming pathway for the conversion of ammonium to nitrogen gas is a combination of partial nitrification and the Anammox process. The main advantages of this process compared to the conventional nitrification/denitrification are: low sludge production, decrease of the aeration costs by almost 60% (only half of the ammonia is oxidized to nitrite in the nitritation process without further oxidation to nitrate), and no need for external organic carbon source addition (Anammox process). Furthermore, anammox bacteria oxidize ammonium under anoxic conditions with nitrite as the electron acceptor, and converse energy for CO_2 fixation. Additionally, the biomass yield of the Anammox process is very low (0.08 kg VSS kg NH_4-N^{-1} in comparison to 1 kg VSS kg NH_4-N^{-1} in conventional nitrification/denitrification process) consequently, little sludge is produced. The low sludge production is another factor that contributes to the substantially lower operation costs compared to conventional denitrification systems.

Advanced oxidation processes (AOPs) are oxidative methods which are based on the generation of the hydroxyl radicals, which are very reactive and less selective than other oxidants. In the wastewater treatment technology, AOPs can be used in a combination with conventional biological techniques (so called hybrid processes), as pre- and post- treatment processes. The advanced oxidation processes have been used in order to increase the biodegradability and also detoxification of the wastewater.

The ability of fungi to degrade lignin-cellulose debris is well known. In addition to these natural molecules they may also degrade synthetic compounds, including synthetic dyes. High effectiveness of Evans blue and brilliant green mixture removal by all tested strains was demonstrated. The process was the most effective and fast in shaken conditions. Finally strain MB removed 90% of tested mixture in shaken samples after 96h. It was the best result reached among all the strains used in the experiment. High removal efficiency was accompanied by a decrease of toxicity (from V class to III class in test with *D. magna* and from IV class even to non-toxic in test with *L. minor*). The highest decrease of phytotoxicity was noticed in samples with shaken biomass in which the effect of dyes mixture elimination was the best. The research indicates very high potential of tested strains for decolorization and detoxification of dyes mixture.

Constructed wetlands are man-made system mimicking the process occurring in natural wetlands. These systems are considered to be an alternative to more technically advanced waste water treatment technologies. The development of constructed wetlands is envisaged to pursue the following directions grouped according to: the type of the waste water to be treated, target contaminants, treatment intensification methods, ancillary benefits and the locality.

Mycorrhiza fungi can be used for phytoremediation proccess. They support plant growth by lowering the stress caused by the lack of phosphorus and water. They produce enzymes participating in several stages of xenobiotics decomposition, which is helpful in their further biodegradation performed by the other rhisospherical organisms. The natural colonisation of PAHs contaminated soil is a long-term process. It could be shortend by adding fungal propagules as an inoculum to the soil. Fungi used for the injections should be isolated from PAHs contaminated soil. That guarantees their survival and development in the contaminated environment. The level of PAHs elimination from soil depends on a type of bioremediation modification used. It was shown that the best results are obtained with monocotylous plants combined with bacterial and fungal biopreparations obtained from contaminated soil. The symbiosis of mycorrhiza fungi with monocotylous plants caused ca. 40% increase of 3, 4, 5 and 30% of 6-ring hydrocarbons removal from soil in comparison with the conventional methods.

Important aspect of environmental protection and engineering is the possibility for qualitative and quantitative monitoring of complex microbial communities, responsible for biotechnological processes, such as: soil bioremediation, wastewater treatment or composting.

Due to the fact that most of the environmental bacteria cannot be grown in the laboratory conditions molecular techniques are widely used in environmental engineering. Among these methods the Polymerase Chain Reaction (PCR)-based and hybridization-based (such as Fluorescent in situ Hybridization; FISH) techniques are known to be the most useful.

Słowa kluczowe:
tlenowe granule, zewnątrzkomórkowe polimery, częściowa nitryfikacja, proces Anammox, zaawansowane procesy utleniania, systemy hybrydowe, oczyszczalnie hydrofitowe, dekoloryzacja barwników, bioremediacji gruntów, mikoryza roślin, techniki biologii molekularne, PCR, FISH

Keywords:
aerobic granules, granule formation, extracellular polymeric substances, partially nitrification, Anammox process, advanced oxidation processes, hybrid systems, constructed wetlands, decolorization, synthetic dyes, soil bioremediation, plant mycorrhization, molecular biology techniques, PCR, FISH