



MIDDLE POMERANIAN SCIENTIFIC SOCIETY
OF THE ENVIRONMENT PROTECTION
ŚRODKOWO-POMORSKIE TOWARZYSTWO NAUKOWE
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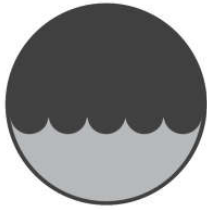
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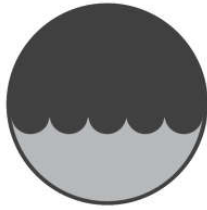
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ŚP
Prof. dr hab. inż.
TADEUSZ PIECUCH
04.06.1946–03.05.2018



Z głębokim żalem i bólem pożegnaliśmy zmarłego 3 maja 2018 roku prof. dr. hab. inż. Tadeusza Piecucha – redaktora naczelnego naszego Czasopisma.

Profesor Tadeusz Piecuch od 1971 roku był związany z Politechniką Śląską, następnie od 1978 roku z Politechniką Częstochowską i wreszcie od 1987 roku, aż do przejścia na emeryturę we wrześniu 2016 roku z Politechniką Koszalińską. Był członkiem komitetów naukowych i redakcyjnych, szeregu komisji i stowarzyszeń naukowych. Pełnił wiele odpowiedzialnych funkcji. Był Autorem monografii, książek, podręczników akademickich, publikacji naukowych oraz wdrożeń przemysłowych. Niezwykle istotna w Jego życiu była organizacja cyklicznej ogólnopolskiej konferencji naukowej pt.: „Kompleksowe i Szczegółowe Problemy Inżynierii Środowiska”. Przez wiele lat wychował liczne grono pracowników naukowych, którzy kontynuują i rozwijają Jego prace badawcze. W sferze dydaktycznej wypromował wielu magistrów i inżynierów. Profesor Tadeusz Piecuch był także wielkim społecznikiem i wybitnym działaczem sportowym.

Na obraz będący wspomnieniem człowieka składają się między innymi: pochodzenie, opowieść życia, rodzina, powołanie życiowe, charakter, ale i nasze spotkania z Nim. Każdy ocenia to inaczej, z własnego punktu widzenia ale wobec profesora Tadeusza Piecucha we wszystkich ocenach jesteśmy zgodni. Pełniąc swoją życiową misję – był człowiekiem wytrwałym, wielkiej pracowitości i sumienności, nie poddawał się nigdy, nie zakładał niepowodzenia i nie mówił, że nie podoła. Niewątpliwie zapamiętamy Go jako człowieka wymagającego, ciągle realizującego nowe pomysły i inicjatywy.

Żegnamy Cię Panie Profesorze, dziękujemy, że był Pan z nami. Cześć Twojej pamięci.

Redakcja



Application of the Mathematical Statistics for the Evaluation of the Waste Incineration Process

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1. Introduction

The sharp increase in the amounts and in the variety of available products on the market causes also an increase in the amounts of different packaging's and other elements that come with any given product. The large amounts of communal waste stem from different anthropomorphic activities and from different aspects of human consumption cause an increased demand for effective waste disposal, either by incineration, separation, recycling or by organic processing.

The technology of the incineration systems developed over years and currently reached state, when this form of waste disposal can be environmentally friendly, with the added value of produced thermal energy (Parobek & Paluš 2016, Pavlas et al. 2011). The acquired thermal energy can be then used for heating purposes, or be transformed into electrical energy. An efficient incinerator is not only assessed by the amount of thermal energy utilization but also by the levels of emissions and quality of the ash it produces (Goh et al. 2000). The thermal energy has some significant advantages, such as the greatly reduced volume of waste, the disposal of fungi, bacteria and germs, and the production of thermal power. There are however also some disadvantages in terms of environmental impacts such as the production of various toxic gases. As it is highly unlikely that there should be occur any significant decrease in the amount

of available products on the market, also the rate of consumption will not cease, thus one can safely forecast that there will be an increased demand for efficient waste disposal by incineration. Therefore, it is important to pay to environmental protection aspects of waste disposal in incineration facilities. As the future development in this area can only be estimated based on the statistics and conditions from the previous years, it is appropriate to apply mathematical and statistical analysis.

This appears to indicate a problem that is related to the effective use of means of mathematical statistics for the needs solutions for reducing the environmental impacts of waste incineration process in the concrete region and thus ensure sustainable environmental development in the region.

Under the process of waste incineration one can understand a production system with its components, facilities with its flows (Fontanili et al. 2000, Gottinger 1986, Sangmin et al. 1994). Due to large variations of waste types and difficulties in feed characterization (physical, chemical and thermal properties), the incineration process meets great challenges in a smooth operation, with substantial fluctuations of gas temperatures within the system (Belevi & Langmeier 2000, Lombardi et al. 2013, Noguchi et al. 2000, Yang et al. 2002). The aim within this case study is to set up the system of waste incineration in a way, where the negative effects of its activities and the associated environmental impacts are minimal. In ideal case there would be no negative impacts whatsoever. The aim of this case study is to discuss the use of principles of mathematical statistics for the management of waste incineration processes in the context of environmental protection. Not less important is the combination of these three approaches within one cohesive methodological framework to achieve the most efficient waste incineration process within the region of interest and thus, to ensure in practice a long-term sustainable development of the environment.

2. Theoretical base

2.1. Logistics and mathematical statistics in environment

To achieve the highest production performance by maximizing the efficiency, the logistics at the strategic, tactical and operational level defines and proposes actions that lead to the desired results using all available means of science and technology, economics and computer

science. The aim of logistics is to create a single, integrated, optimized material flow that can be created by connecting the various parts of the system so that a continuous exchange of goods and services can be provided. Logistics is gradually evolving and at the same time the views on its scope and level of influence is evolving (Straka 2013). The process of waste management is important for the health of the public and aesthetic and environmental reasons (Rushton 2003, Sahlin et al. 2004, Šomplák et al. 2014). The waste processing and disposal and the streamlined processing flows performance can be provided by the means of reverse logistics (Abdessalem et al. 2012, Pokharel & Mutha 2009, Sheu 2008).

When planning waste management, it is important to know that the choice of waste treatment method affects processes outside the waste management system (Eriksson et al. 2005). In waste treatment processes different materials and products are usually mixed (Finnveden 1999).

With these options available, different systems investigators are able to better understand the details of the operation within the system and to address them in terms of effective utilization of business resources.

The possibility for impacts of waste incineration solution is application of mathematical modelling (Hellweg et al. 2011, Luo et al. 2008, Yang et al. 2004). Gaussian least squares method is one of the basic methods for data processing. So called theoretical regression, that is the relation of one value to another, or the dependence of one variable (dependent), to another variable (independent), can be obtained from the currently measured, observed data, values pairs x_i, y_i , arranged for $V \{x_i, y_i\}_n$. Regression analysis is a very popular, effective and applicable tool for identifying dependencies between the examined variables. In this article this method will be applied to determine the dependence between the amount of waste incinerated and quantity of steam and the amount of heat produced. The advantage of this method is its versatility, considering it makes it possible to calculate the most appropriate parameter values (Aczel 1989, Ryu et al. 2004, Yeomans et al. 2003).

2.2. Data for mathematical statistics waste incineration analysis

For realization of a statistics analysis of the waste incineration process within a concrete region is necessary to prepare and carry out a thorough analysis of the given system. The waste incineration plant in question can be classified as an industry in the area of the chemical processing. The input into the system is formed by hauling thousands of tons

of communal waste from the city of Kosice Region and from Kosice – surroundings. The main activity of the company is the disposal of imported waste, by separation, sorting and the actual incineration.

Based on the results of the system analysis, in this case represented by the waste processing company one can derive the following findings:

- Every year, 83,000 tons of waste get imported into the company, that first goes through a several levels of separation.
- The first separation is intended to separate the plastics, electrical components and wood from imported waste. The total volume of imported waste is composed of 19% of the plastic and electrical components; of up to 10.00% wood in a variety of forms. The rest is represented by more than 71% of miscellaneous municipal waste.
- The second phase of separation occurs during the waste incineration phase, right after the actual burning. The resulting product of the incineration process and the subsequent separation consists of about 3% of ash, 90% of incinerated waste and about 7% are gases that arise in the process of waste incineration. The gases then pass through the filtration process, where the total volume of the flue gases consists of 65% steam and 35% of other emissions.
- The third phase of separation relates to the separation of the resulting burned material and is focused on separating metals from the remaining solid burned material. There is about 2% of metal in the charred mass, and the remaining 98% is a clean clinker.

In terms of the overall process of waste incineration some additional stations must be mentioned:

- One of such stations is the detection and measurement of waste humidity level. If the waste is too wet, it is necessary to reduce the overall waste moisture by mixing it with dry wood material. For this purpose, separated wood waste is used acquired from the imported communal waste. If necessary, this dry wood is added into the wet waste mixture. The amount of wood material that needs to be added into the waste mixture depends on the overall level of the annual rainfall. If there is a wet year with heavy rainfall, then more wood must be added. If there is a dry year, the wooden material needs to be added only occasionally. Overall, it can be stated that from the total volume of imported waste, 70% consists of dry waste without the

need to add wood material and 30% consists of moist or wet waste, where there is a need to add dry wood into mixture, due to the high humidity levels.

- The second stations that must mentioned, follows the process of burning and magnetic separation. The incinerated waste is a hot material, called bottom ash or clinker. This clinker must be cooled by adding water. For this activity about 10,000 m³ of water are used per year. The cooled clinker is then stored in a landfill within the company premises.

3. Case study

3.1. Application of mathematical statistics for analyse of waste incineration

For long-term materials and energy recovery from waste it is necessary to monitor the amount of imported waste, for example by using time series analysis. The aim of the time series analysis is mostly to design a model. The model analysis primarily enables to understand the mechanics of data, where it is possible to determine for example the seasonal trends in the volumes of imported waste. Seasonal effects are caused either by direct or indirect causes. The seasonal component in this particular case has its origin in the alternation of four seasons throughout the year. The understanding of time series model enables to predict the future development of the system. The Figure 1 shows the cause of a long-term seasonal effect on the amounts of imported waste for a period of nine years (KOSIT 2015, Malindžáková 2015).

Referring to the seasonal fluctuation in the quantity of imported waste it is important to also discuss the incineration process. In terms of incineration performance of the plant, it is important to notice disposal / theoretical capacity of the boiler (DCB / TCB), hourly amount of waste incinerated (HWI) in relation to the total quality of waste incinerated (TQWI) (Fig. 2-10). The facility capacity reached in 2007 in the months of April 77.22%, in May 86.56%, in June to 98.19% in July 66.53% of available capacity. These capacities were significantly above the long term average calorific values. The actual facility capacity in August 2007 reached 45.97%, while the calorific value reached 12.21 GJ.Mg⁻¹ which approaches the maximum technical limit for this facility (12.25 GJ.Mg⁻¹).

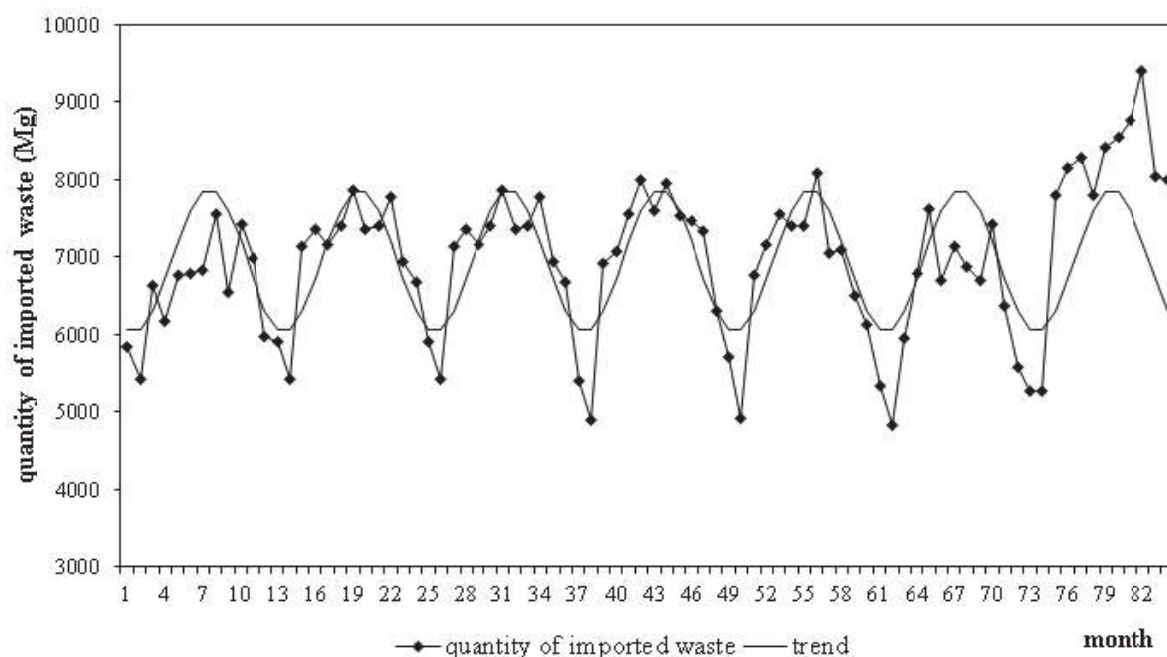


Fig. 1. Analysis of the seasonal component within the time series of the amounts of imported waste for the time period between the years 2007-2015

Rys. 1. Analiza komponentu sezonowego w ramach szeregów czasowych ilości importowanych odpadów w latach 2007-2015

In September 2007, the operational capacity dropped to 32.50%, whilst at the same time the waste calorific value was slightly reduced. The operational capacity reduction was actually caused by the boiler shutdown during major planned maintenance downtime (Fig. 2). The maximum calorific value (10.94 GJ.Mg^{-1}) in September 2008 indicates that dried waste, such as dry wood chips and leaves were burned. In September 2008, operational capacity was utilized to 79.72%, whilst the amount of incinerated waste was at 8.4 Mg.h^{-1} , but at the same time the calorific value of the waste was considerably above the average value (Fig. 3).

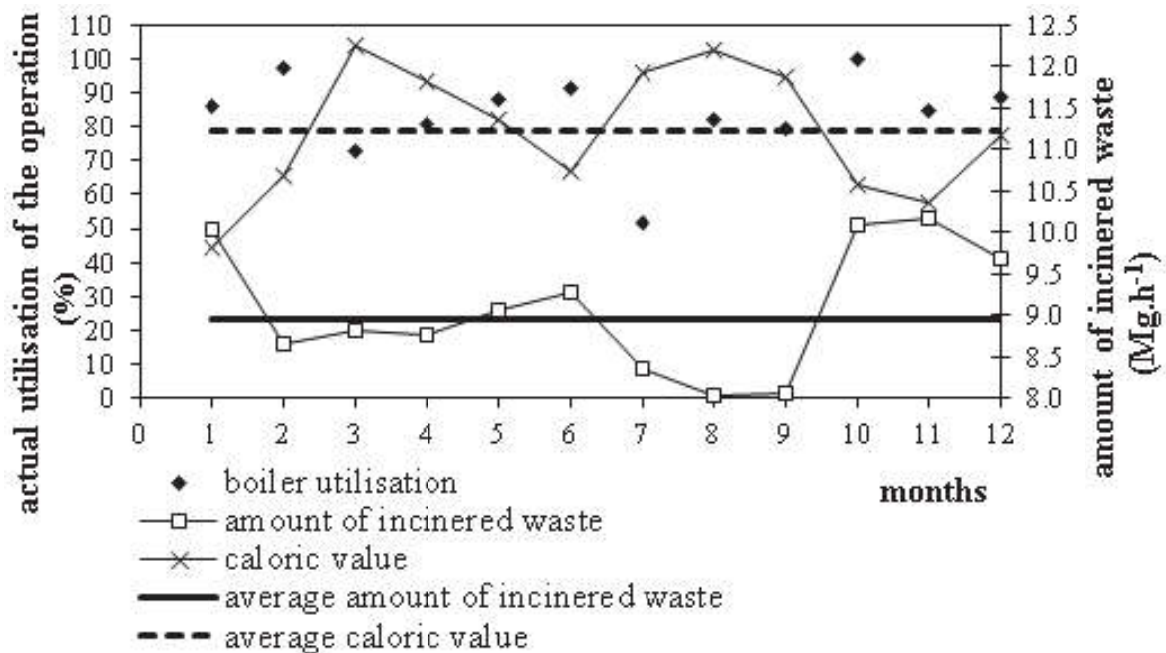


Fig. 2. The relationship between the operation use of TQWI in 2007

Rys. 2. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2007

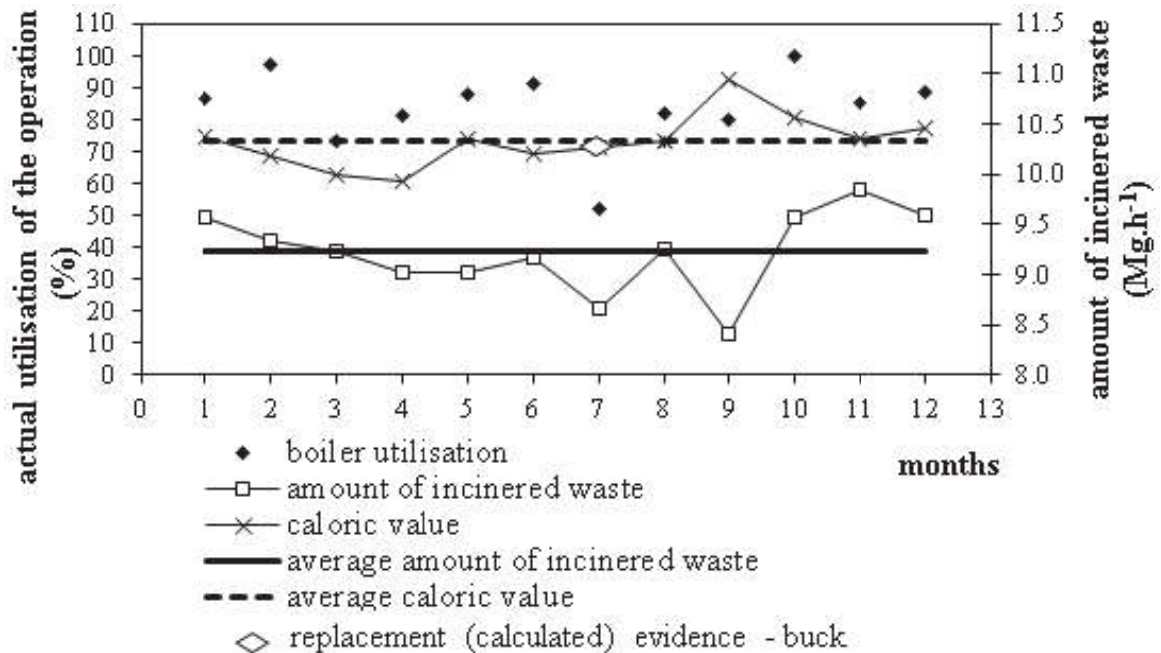


Fig. 3. The relationship between the operation use of TQWI in 2008

Rys. 3. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2008

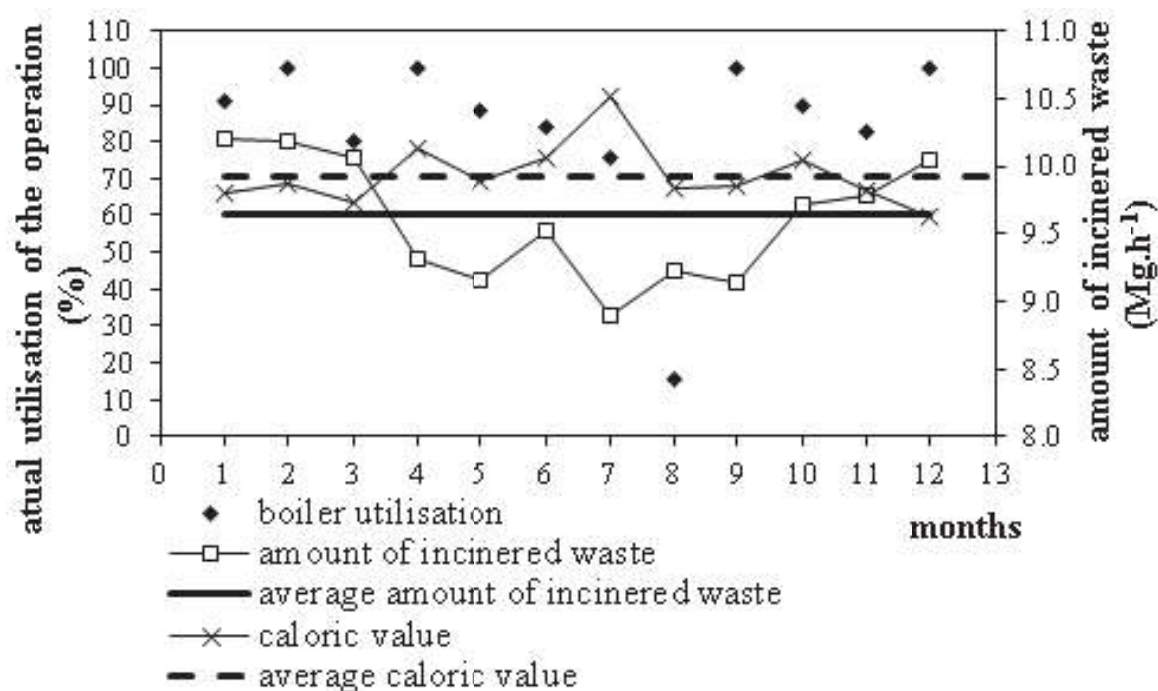


Fig. 4. The relationship between the operation use of TQWI in 2009

Rys. 4. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2009

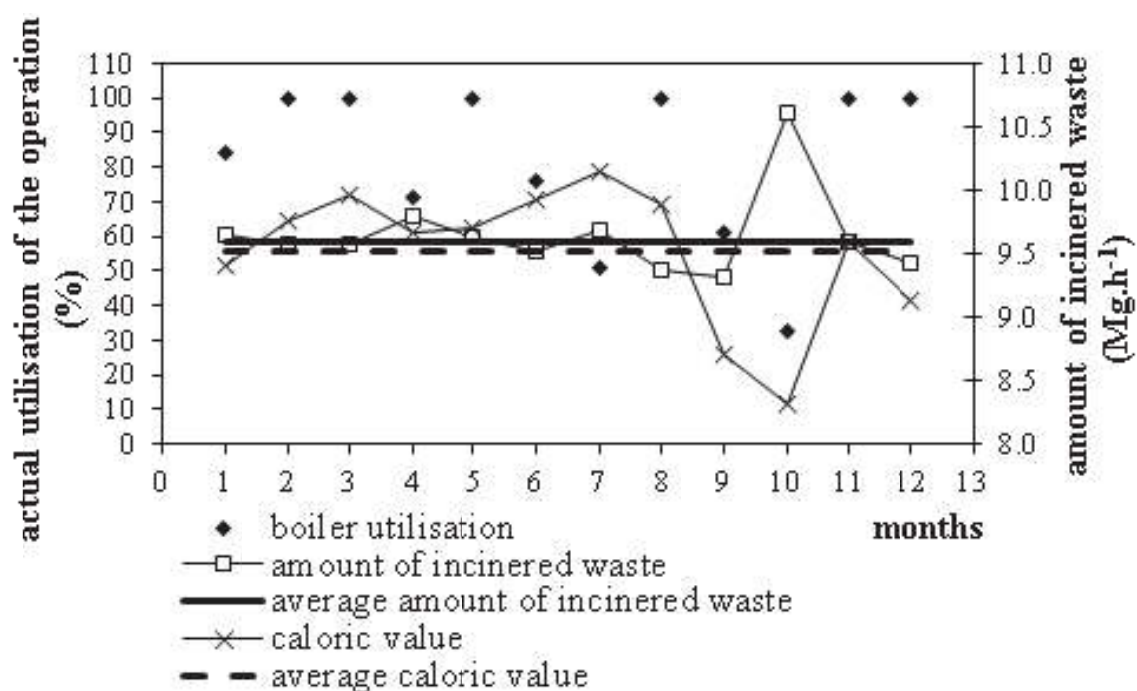


Fig. 5. The relationship between the operation use of TQWI in 2010

Rys. 5. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2010

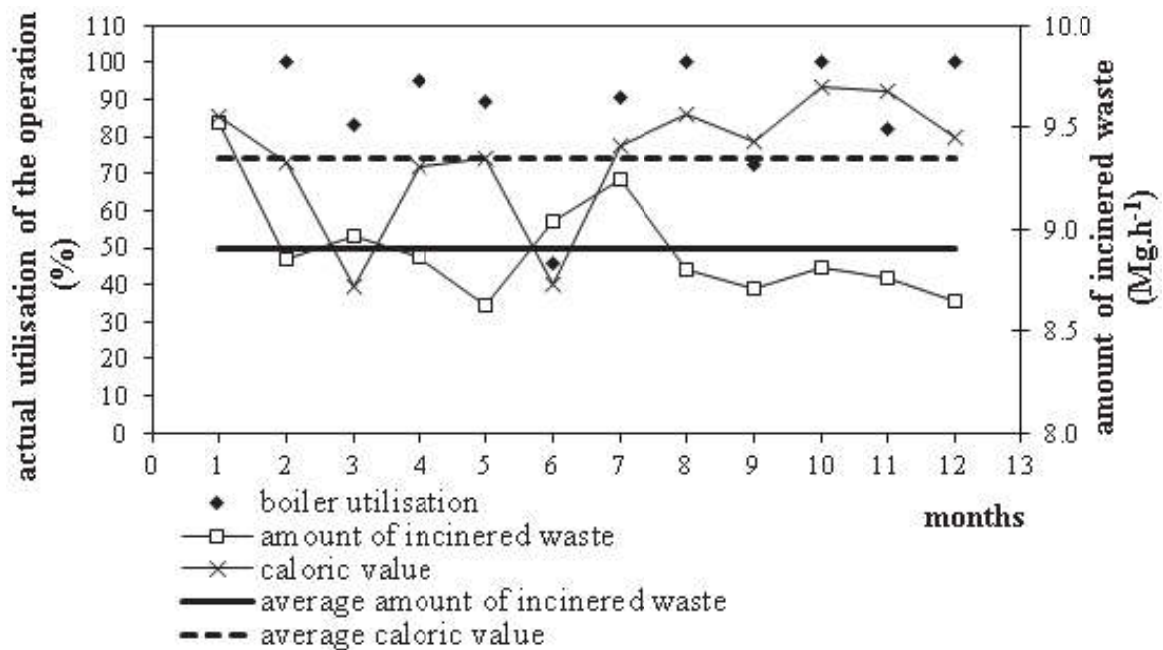


Fig. 6. The relationship between the operation use of TQWI in 2011

Rys. 6. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2011

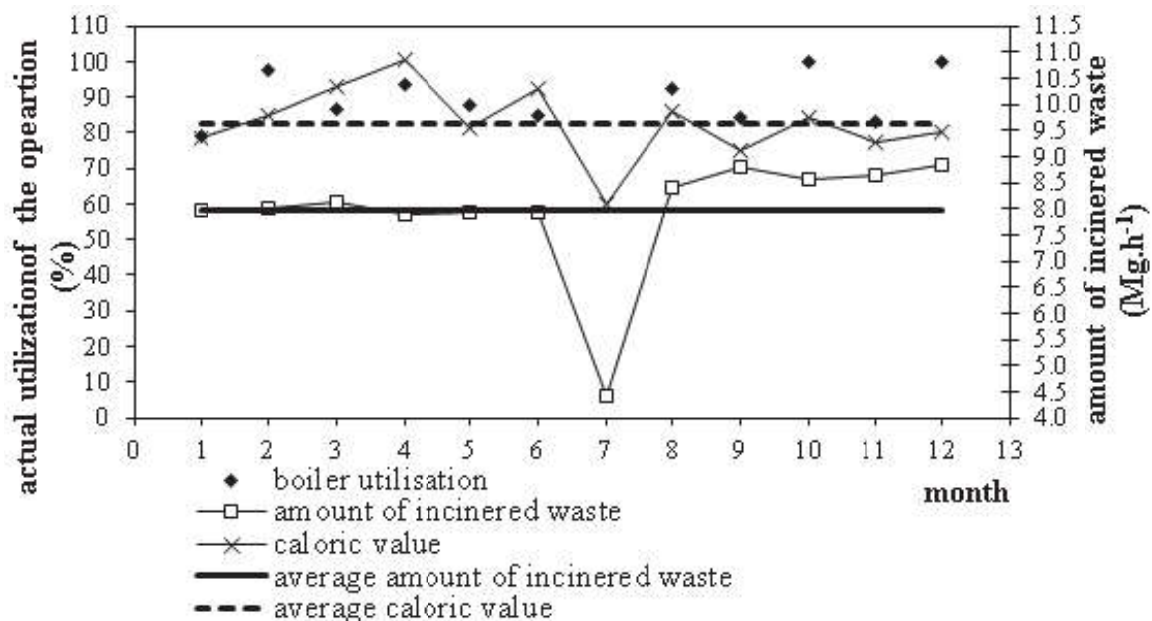


Fig. 7. The relationship between the operation use of TQWI in 2012

Rys. 7. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2012

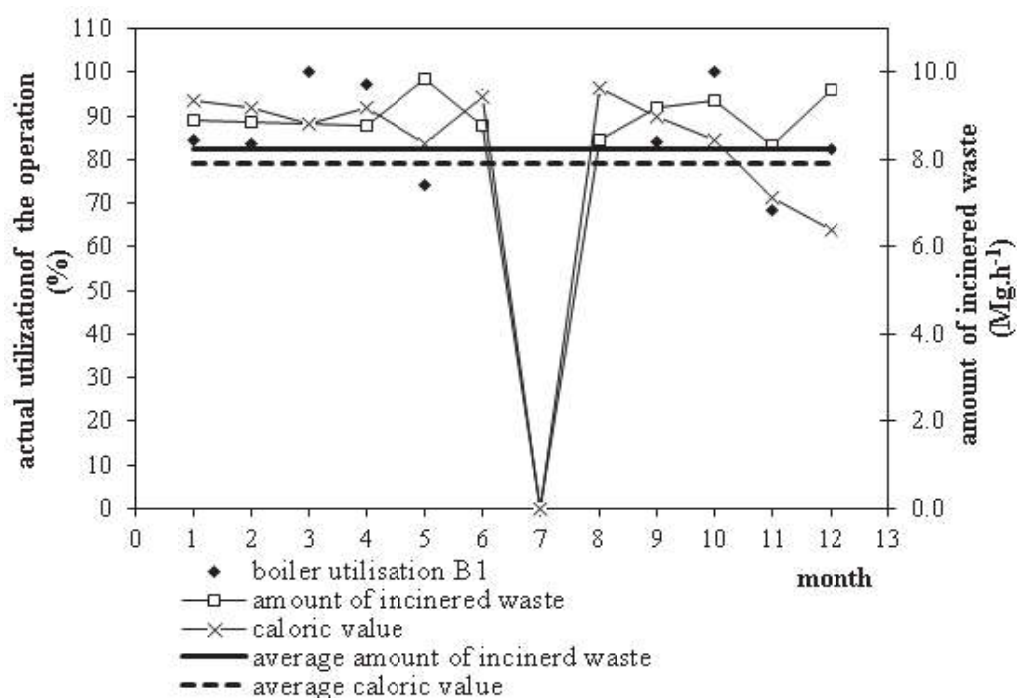


Fig. 8. The relationship between the operation use of TQWI in 2013

Rys. 8. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2013

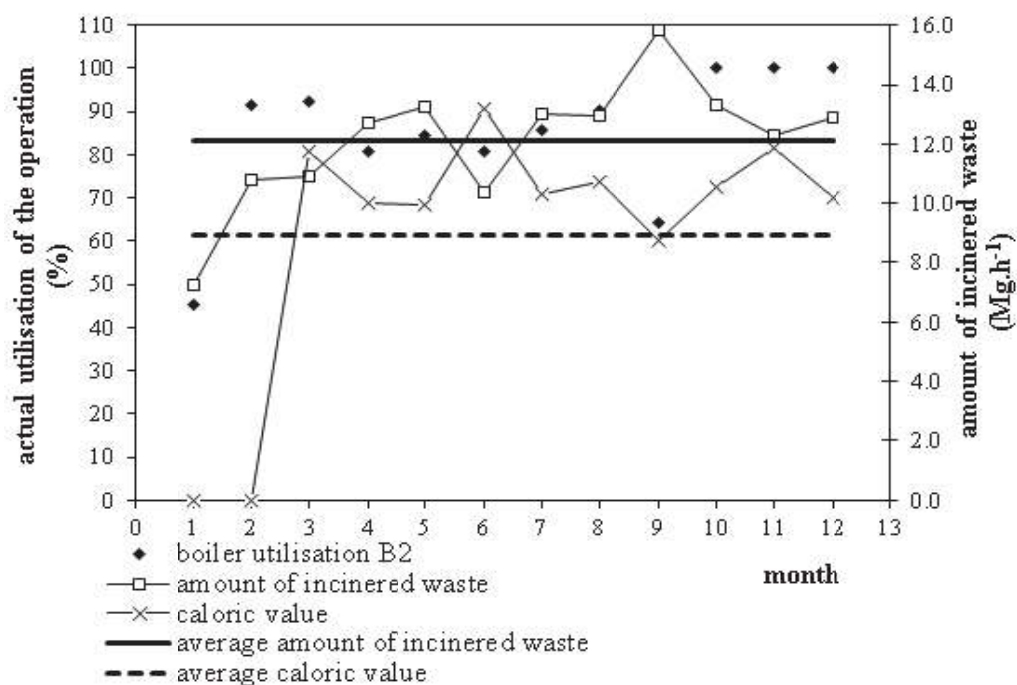


Fig. 9. The relationship between the operation use of TQWI in 2014

Rys. 9. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2014

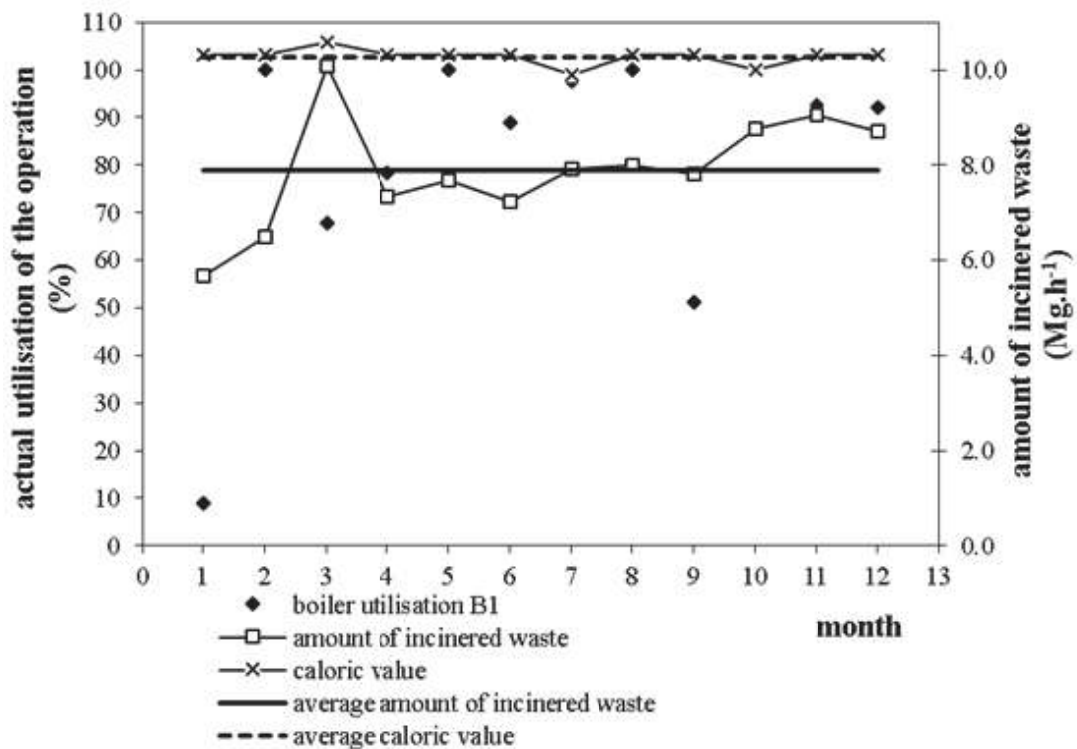


Fig. 10. The relationship between the operation use of TQWI in 2015

Rys. 10. Zależność między operacyjnym wykorzystaniem a całkowitą jakością spalanych odpadów w roku 2015

During 2009 the operational capacity was utilised in the months of April to 100% in May to 88.17%, in June to 83.75% and in July to 75.81%, but the calorific value during these months was significantly above the average calorific values. Due to the fact that in August 2009, the incinerator boiler maintenance took place, the operational capacity dropped significantly at the time, down to 15.32%, while the calorific value of the waste was slightly below average calorific values. Paradoxically, in September 2009, the operational capacity has been utilized to 100%, but the calorific value of the waste was only little different from the calorific value of the previous month, when operational capacity was limited to merely 15.32% of full production capacity (Fig. 4).

In Figure 5 it can be seen that in October 2010 the operation worked at 32.80% of available capacity, while the amount of waste incinerated in the month was 10.61 Mg.h⁻¹ and the calorific value was significantly below the average calorific value. This observation can be explained by the fact that the incinerator underwent maintenance at the time. It can be observed that the operational capacity in 2011 (Fig. 6) was utilised to 100%

during February, August, October and December, while the calorific value in these months was also above average calorific value. Operating capacity has decreased significantly in June, down to 45.83%, when the calorific value was slightly below the average calorific value.

In August 2011 the operational capacity has been utilized to 100%, but the calorific value was slightly above average.

The 2012 results (Fig. 7) show significantly below average amounts of incinerated waste. In July the boiler reached only 5.91% of available capacity, which was due to the boiler maintenance. Given the fact that the operation reached 86.83% in March, 93.61% in April, and 84.72% in June, the average calorific value has reached above average calorific value. In 2012 the operation was utilised to 100% only during 2 months, namely during October and in December.

The operation utilisation in July 2013 (Fig. 8) was at 0.00%, as in that month a complete shutdown was ordered for the boiler K1, due to the maintenance reasons. Only during the last months of 2013 the K1 boiler ran at 100%. K1 boiler was then shut down and subjected to reconstruction.

In the January 2014 (Fig. 9) a new boiler was put into operation (boiler K2) designated for the incineration of municipal waste. The efficiency of the K2 boiler during the initial period (January) was 45.43%. In the coming months the utilisation of the K2 boiler was at about 90%. The new boiler K2 reached the 100% capacity in the months of October, November and December 2014. As paradox one can mention the month of September 2014, when the amount of waste incinerated was $15.84 \text{ Mg}_w \cdot \text{h}^{-1}$, but the calorific value of waste reached only $8.72 \text{ GJ} \cdot \text{Mg}^{-1}$.

The beginning of 2015 (Fig 10) was for the incineration of municipal waste particularly difficult because there was a serious malfunction of the turbine in the boiler K2. Due to a major breakdown, the boiler K2 was shut down and it was necessary to carry out the general maintenance. The company responded immediately by launching the original reconstructed boiler K1. The values for the quantity of the incinerated waste were within the range from $5.68 \text{ Mg}_w \cdot \text{h}^{-1}$ to $10.08 \text{ Mg}_w \cdot \text{h}^{-1}$. On the other hand, the calorific value of the waste in the corresponding month of 2015 was stable, fluctuating around the average number of $10.27 \text{ GJ} \cdot \text{Mg}^{-1}$.

Given the importance of the relation between the quantity of heat and of the generated steam to the heating value, a graph was created showing the long term relationship of these three essential characteristics

(Fig. 11). Since the company does not have data for the generated heat and steam for the year 2007, in Figure 11 this part of the trend shows no values. The downward trend of the calorific value was probably the result of wear and tear in the sheath inside the boiler. This has resulted in a downward trend in production of heat and steam produced from 2009.

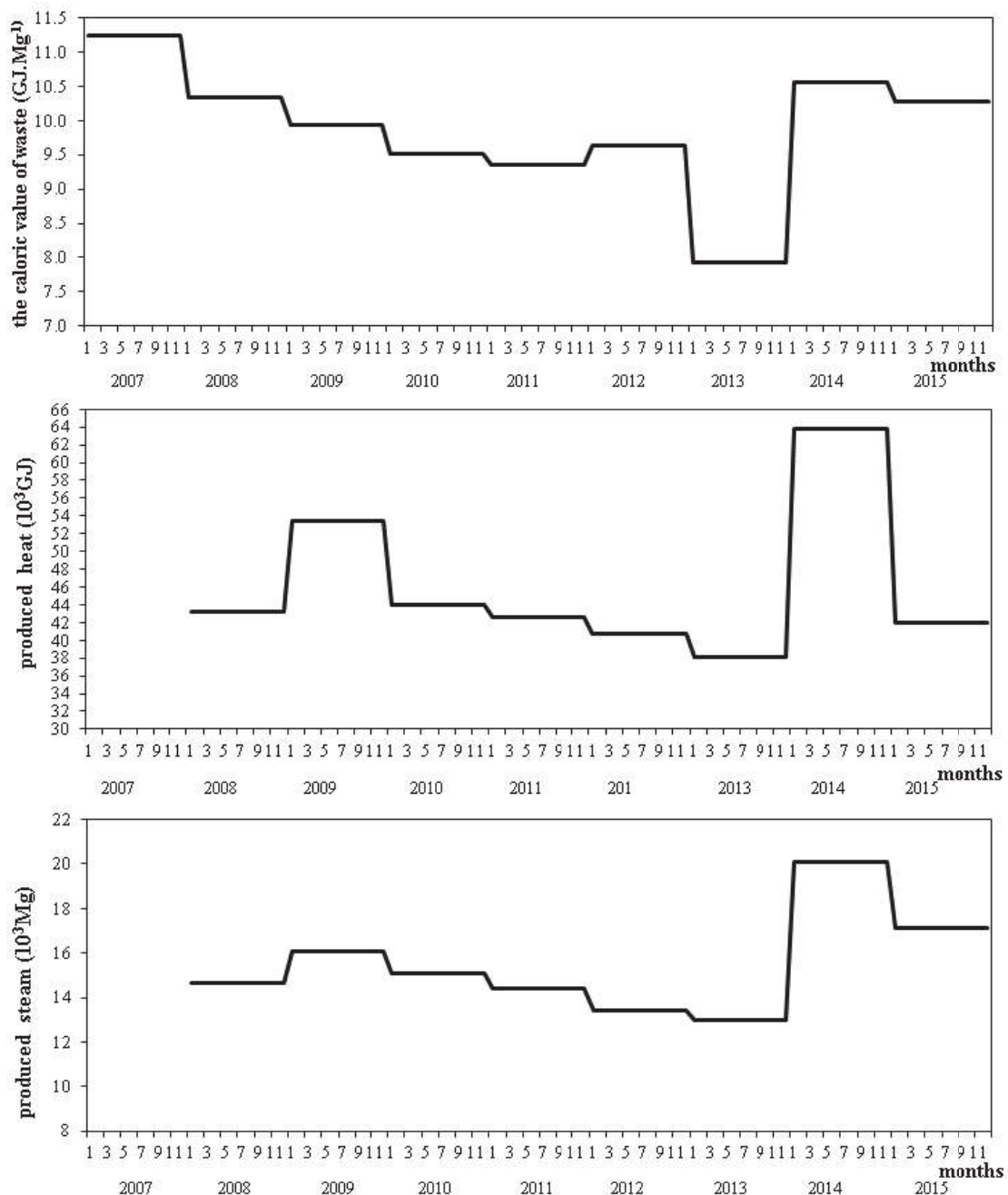


Fig. 11. The production of heat and of steam in relation to the net calorific values
Rys. 11. Produkcja ciepła i pary w stosunku do wartości kalorycznych netto

3.2. Statistics data for Gaussian least squares method

The steam resulting from the incineration of municipal waste can be used to produce heat and electricity in steam and gas turbines. For the model calculation of the relation between the incinerated waste amount and the steam quantity produced, the Gaussian least squares method was applied.

This method is considered to be the basic working method for data processing. The basic methods of Gaussian least squares principle (Chatfield 2003, Fischer 1995, MATH 2013) can be expressed as follows (1)(2)(3):

$$ZY = \sum_{i=1}^n dy_i^2 = \sum_{i=1}^n (Y_i - y_i)^2 = \sum_{i=1}^n (a_0 + a_1 \cdot x_i - y_i)^2 \quad (1)$$

$$\frac{\partial Z}{\partial a_0} = 2 \sum_i (a_0 + a_1 \cdot x_i - y_i) = 0 \quad (2)$$

$$\frac{\partial Z}{\partial a_1} = 2 \sum_i (a_0 + a_1 \cdot x_i - y_i) \cdot x_i = 0 \quad (3)$$

$$\begin{bmatrix} n & \sum x_i \\ \sum x_i & \sum x_i^2 \end{bmatrix} \cdot \begin{bmatrix} a_0 \\ a_1 \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum x_i \cdot y_i \end{bmatrix}$$

$$(X^T \cdot X) \cdot a = (X^T \cdot y) \Rightarrow \text{normal system of equations} \quad \begin{bmatrix} \hat{a}_0 \\ \hat{a}_1 \end{bmatrix} = \hat{a} = (X^T \cdot X)^{-1} \cdot (X^T \cdot y)$$

The calculation of the Pearson correlation coefficient (4):

$$r_{xy} = r_{yx} = r = \frac{\text{COV}_{xy}}{s_x \cdot s_y} \quad (4)$$

where:

cov_{xy} – the mixed dispersion of x and y

s_x – standard deviation for the variable x ,

s_y – standard deviation for the variable y .

The relationship between the amount of incinerated waste $\{x_i\}$ and quantity of steam $\{y_i\}$ is expressed by the theoretical mode (5):

$$Y = 1434.3 + 2.3661 \cdot x \quad (5)$$

Its strength is also reflected by the Pearson correlation coefficient. The resulting correlation coefficient $r_{xy} = 0.82$ confirms that among the variables being monitored is a very strong linear relationship – with the growing values of the incinerated waste quantity, in proportion also the values for a quantity of generated steam grow which can be demonstrated by the “correlation scissors” that are almost closed (Fig. 12).

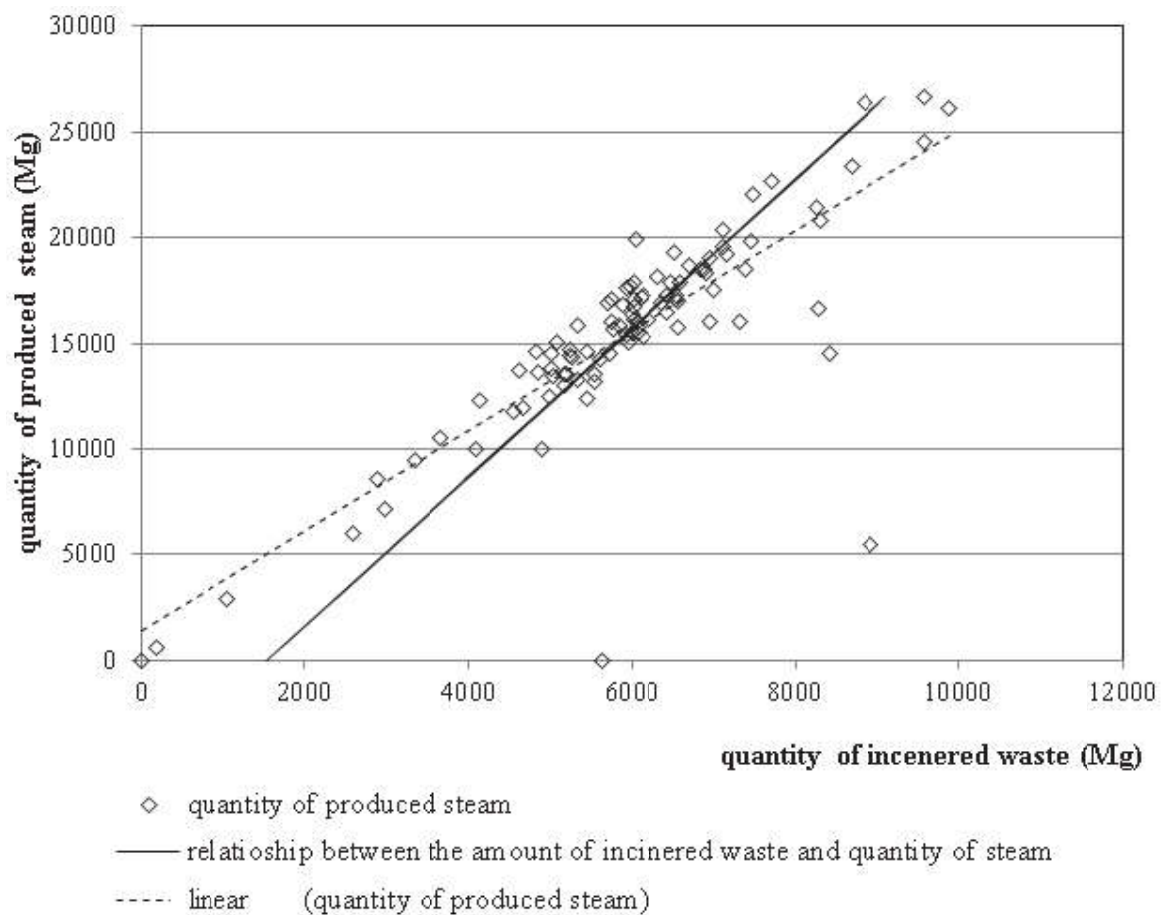


Fig. 12. The relationship between the amount of incinerated waste and the quantity of steam

Rys. 12. Zależność między ilością spalanych odpadów a ilością pary

It is also possible to calculate the model depending on the amount of waste incinerated and the amount of heat produced. This model can be expressed by the formula (6):

$$Y = 17.437 + 0.0048 \cdot x \quad (6)$$

The Pearson correlation coefficient $r_{xy} = 0.54$ indicates that there is a moderate linear relationship, presented by a direct proportion between the values of incinerated waste quantity and the quantity values of produced heat (Fig. 13).

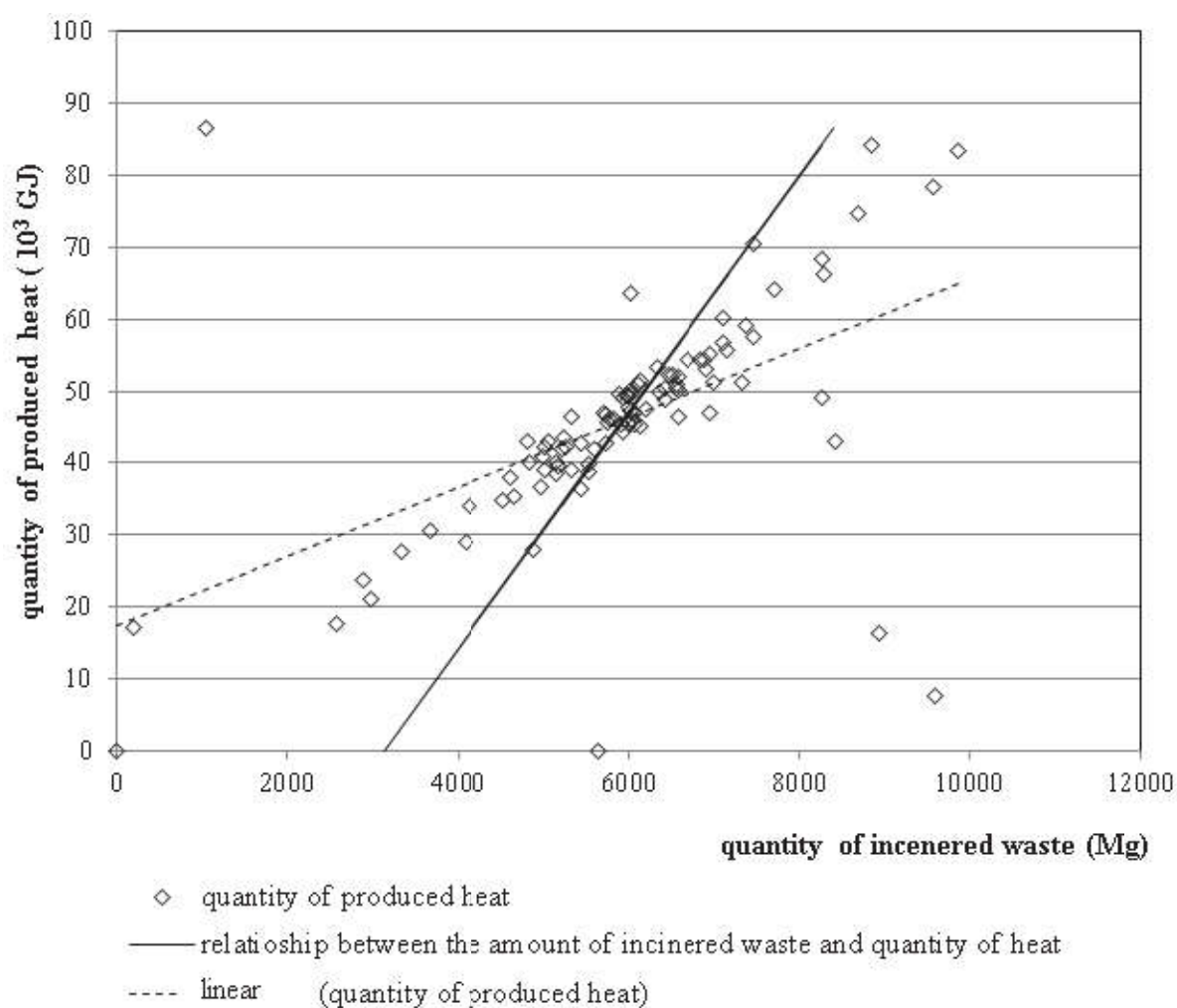


Fig. 13. The relation between the amount of waste incinerated and the amount of produced heat

Rys. 13. Zależność między ilością spalanych odpadów a ilością produkowanego ciepła

4. Conclusions

Many research studies show that the adverse environmental impacts can be minimized by reducing the amount of waste production (whether within industrial or municipal sector), and in this way reduce also the related emissions release. An essential step in waste reduction is the use of green materials as well as its secondary recovery, starting with the separation of waste.

Currently within the case study company, the operating costs are mainly affected by the composition of the input material for incineration, the amount of waste, the amount of used fuel and the amount of natural gas needed to support the burning process. This indicates that a cost reduction is possible by ensuring a thorough separation of input materials. This was achieved by raising awareness among the population towards the sorting and secondary recovery of municipal waste, which indirectly affected also the total cost of fuel (less waste means fewer trips for waste transport vehicles) and also the costs of the actual incineration process due to a smaller amount of natural gas used. Therefore, throughout the entire product life cycle from raw material acquisition through production, use, disposal at the end of product life, including the recycling and the final disposal (from cradle to grave) it is important to perform efficient sorting of related waste such as the product packaging.

The results of this years of research for this case study show that the correct operation setting of the waste processing, utilising the principle of logistics and modern technologies, whilst adhering to current legislation for the field of waste can lead to achieving a sustainable development of the environment within the given region.

The results of mathematical statistics show that there is a direct relationship between the amount of incinerated waste (negative aspect) and the production of electricity (positive), but also the amount of heat produced (positive) and the amount of produced flue gas and ash (negative aspect).

The environmental assessment is an important step in building and implementing Environmental Management System (EMS), which consists of the development and evaluation of the analysis followed by the adoption of measures to remedy the deficiencies. The aim of the analysis of the environmental situation within the region of the case study

company is a fact-finding in the field of protection of environment that affects the production and non-production operations, and should be monitored:

- the manufacturing practice compliance of the company with the current legislation,
- the status of operational documentation,
- the status of internal and external communications in the area of the environmental protection,
- the responsibilities and liabilities between departments and employees.

Despite the amount of obtained results, there are still open question and topics for further research such as:

- What influence can have the combination of a climate change and the continuous waste incineration process on the population in the region?
- Will make the technological developments in the future possible to recover up to 100% of waste without the need of incineration?

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Zastosowanie statystyk matematycznych do oceny procesu spalania odpadów

Streszczenie

W artykule omówiono wpływ procesów spalania odpadów na środowisko w danym regionie za pomocą statystyk matematycznych. Obszar zainteresowania niniejszego studium przypadku uwzględnia aspekty praktycznego za-

stosowania powyższych metod i zasad w celu zmniejszenia wpływu na środowisko procesu spalania odpadów w konkretnym regionie. Współczynnik korelacji Pearsona $r_{xy} = 0,54$ wskazuje, że istnieje umiarkowana liniowa zależność, wprost proporcjonalna, między ilością spalonych odpadów a ilością wytworzonego ciepła. Wyniki analizy statystycznej pokazują, że spalarnia w ciągu jednego roku generuje około 15 266 ton odzyskanych elementów plastikowych i elektrycznych, około 590 000 GJ energii, około 199 000 ton pary, 287 ton innych emisji przy zaledwie 3 miligramach dioksyn. Statystyka matematyczna służy do analizy, a następnie dostosowania i udoskonalenia procesu spalania odpadów w celu osiągnięcia pożądanych wartości parametrów, w szczególności wartości opałowej, ilości wytwarzanego ciepła i pary oraz zanieczyszczeń powietrza.

Wyniki statystyki matematycznej pokazują, że istnieje bezpośredni związek między ilością spalanych odpadów (aspekt negatywny) a produkcją energii elektrycznej (aspekt pozytywny), ale także ilością wytworzonego ciepła (aspekt pozytywny) i ilością wytworzonych gazów spalinowych i popiołów (aspekt negatywny).

Oceny środowiskowe są ważnym krokiem w budowaniu i wdrażaniu Systemu Zarządzania Środowiskiem, który polega na opracowaniu i ocenie analizy, a następnie przyjęciu środków mających zaradzić niedociągnięciom. Celem analizy sytuacji środowiskowej w regionie firmy ze studium przypadku jest ustalenie stanu faktycznego w zakresie ochrony środowiska, które ma wpływ na działalność produkcyjną i nieprodukcyjną. To powinno być monitorowane zgodnie z praktyką produkcyjną firmy oraz obowiązującym ustawodawstwem, stanem dokumentacji operacyjnej, stanem komunikacji wewnętrznej i zewnętrznej w zakresie ochrony środowiska, odpowiedzialności między działami i pracownikami.

Abstract

The article deals with the research on the impacts of waste incineration processes on the environment within a particular region by the means of mathematical statistics. The area of interest for this case study considers the aspects of practical application of using the above methods and principles in order to reduce the environmental impacts of waste incineration process in the concrete region. The Pearson correlation coefficient $r_{xy} = 0.54$ indicates that there is a moderate linear relationship, presented by a direct proportion between the values of incinerated waste quantity and the quantity values of produced heat. The statistics results show that the incineration during a one-year period produces about 15,266 tons of plastic and electrical components, and will release about 590,000 GJ of energy and about 199,000 tons of steam and 287 tons of other emissions with only 3 milligrams of dioxins. The mathematical statistics

is used to analyse, and subsequently adjust and improve the waste incineration process in order to achieve the desired parameter values, specifically the calorific values, the amount of heat produced, and the amount of generated steam and air pollutants.

The results of mathematical statistics show that there is a direct relationship between the amount of incinerated waste (negative aspect) and the production of electricity (positive), but also the amount of heat produced (positive) and the amount of produced flue gas and ash (negative aspect).

The environmental assessments are an important step in building and implementing Environmental Management System (EMS), which consists of the development and evaluation of the analysis followed by the adoption of measures to remedy the deficiencies. The aim of the analysis of the environmental situation within the region of the case study company is a fact-finding in the field of protection of environment that affects the production and non-production operations, and should be monitored the manufacturing practice compliance of the company with the current legislation, the status of operational documentation, the status of internal and external communications in the area of the environmental protection, the responsibilities and liabilities between departments and employees.

Słowa kluczowe:

spalanie odpadów, ocean wpływu na środowisko, statystyki matematyczne, analiza, dane

Keywords:

waste incineration, environmental impacts evaluation, mathematical statistics, analysis, data



The Determination of the Maximum Runoff in the Representative and Experimental Hydrographical Basin of Sebes River (Banat, Romania)

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1. Introduction

The Romanian natural and climatic factors, together with the irrational human activities (massive deforestation, lack of hygiene in the forest exploitation areas etc.) lead to the creation of potential torrential conditions, disturbances in the hydrological regime of most watercourses, leading in most of the times to considerable damage.

The runoff represents the movement of water across the earth's surface owing to the force of gravity and which are influenced many geographic factors (Maftai et al. 2015).

Many methods to estimate runoff exist (Haan et al. 1982, Chow et al. 1988). Runoff volume or rate estimation involves estimating the amount of rainfall exceeding infiltration and initial abstractions, which must be satisfied before the occurrence of runoff. Infiltration excess runoff can be estimated using different techniques.

The Rational Formula estimates the peak runoff rate using remotely-sensed land use data and soils information to determine a runoff coefficient. The coefficient gives the percent of rainfall converted into runoff (Beven 2012).

In the hydrologic analysis for a drainage structure, many important, variable factors affect floods. The primary factors to be considered on a site-by-site basis include: precipitation type, amount, duration, in-

tensity, frequency and distribution; basin size and physiographic characteristics; soil type; vegetative cover; previous moisture condition; surface storage potential; and basin development potential (Virginia Department of Transportation 2002).

Studies focus on measures which increase water yield or enhance temporal water storage in small catchments are scarce. For this reason, it's important to consider the studies on larger scales of one similar hydrographical basin.

These measures have to be adapted to the conditions in small catchments and evaluated with regard to the aim of controlling maximum runoff. The measures, which must be taken, are varied and can take into account the following technical aspects: the effective volume, the time scale, the controllability and conflict potential.

Thus it's necessary to create an evaluation matrix which can be used to help draw up water resources management plans. Since actual concepts that integrate high discharges protection are inadequate, modelling tools and decision support systems that offer measures to control the maximum runoff need to be developed and refined.

The experimental and representative hydrological basin of Sebeş River, a tributary of Timiş River, is located in the south-west part of Romania, is part of European Network of Experimental and Representative Basins (ERB) and has a small surface (124 km²) (Fig. 1).

The role of the experimental hydrographical basins is to know the process of runoff formation in a small hydrological basin (surface < 150 km²) (Teodorescu 2003).

The flood formation in this hydrological basin is mainly linked to the climatic conditions to which other factors are added, such as: the geology, the soil through its temperature and humidity, the vegetation, the topography through the slope beds and the slopes, the shape and the surface of the hydrological basins, which influence formation time and water volume.

In order to determine the maximum flow in small hydrographical basins, such as the hydrographical basin of Sebeş River is, an important parameter is the runoff coefficient determined using the ARCGIS software, based on the Frevert tables, knowing the altitude, the slope, the land use cover, the soil texture and the rainfall intensity.

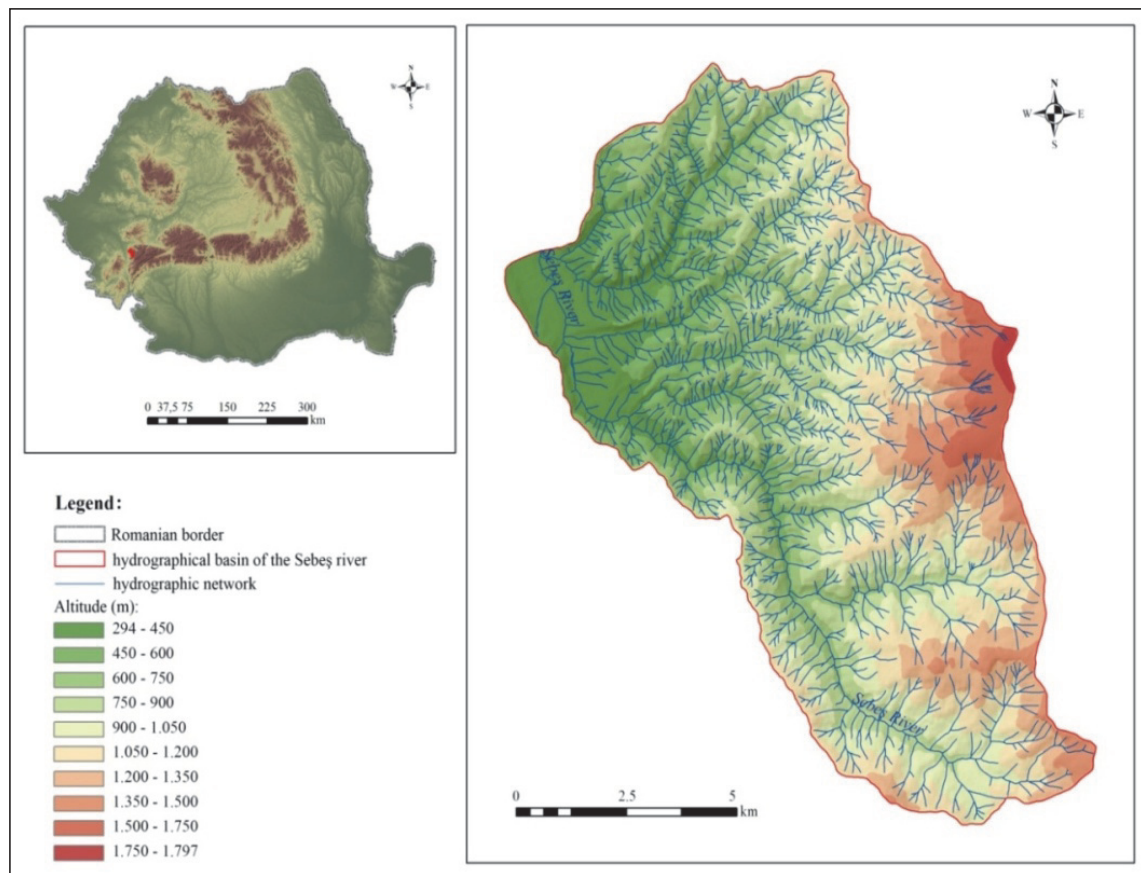


Fig. 1. The representative hydrographical basin of Sebeș River – localization within Romania

Rys. 1. Prezentacja hydrograficzna dorzecza rzeki Sebes – położenie w Rumunii

The runoff regime represents the variation of water flow over time, during several months, seasons, years or decades. This varies according to the determining and conditioning factors of the runoff, such as the atmospheric precipitations, the air temperature and humidity, the flash floods, the morphological and geological structure of the hydrographical basin, the soil structure, the land use cover etc. (Arba 2016).

2. Materials and methods

For the recorded flood in the Sebeș hydrological basin, which occurred during 9-13 January 2015, we used relevant climate data from two meteorological stations (Țarcu and Cuntu) and two rainfall stations (Borlova and Turnu Ruieni) within the basin.

This analysis required the building of a database with inputs required by the model which we built, both with information on the hydrological basin, found on the cartographic materials, such as: topographic and pedological maps, following the digital elevation model and the satellite images, regarding the land use cover and with climate data strings on heavy rains during 9-13 January 2015 (Table 1).

Table 1. Data sources and types used for the study

Tabela 1. Źródła i rodzaje danych użytych w badaniach

No.	Data source	Type	Attributes	Variable code
1	Land use cover	shp	Yes	<i>Crops</i>
2	Soils	shp	yes	<i>Heavy_texture</i> <i>Medium_texture</i> <i>Light_texture</i>
3	Soils	grid	yes	–
4	DEM (digital elevation model)	grid	yes	–
5	Rain intensity	grid	Yes	–
6	Hydrographical basin limit	shp	–	–

Because the runoff is routed through the basin along flow paths itself determined by the topography, this study uses the digital elevation model (DEM) both for viewing the altitude variation in the Sebeş hydrological basin, and for the hydrological analysis of the studied area.

The raster structure of this elevation model is usually used to derive topographic data for distributed hydrological models. So on the basis of the DEM, we determined the water flow direction and accumulation in order to delimit the hydrological basin analysed (Musa et al. 2015).

In order to calculate the maximum flow in small hydrological basins such as Sebeş hydrological basin we used one rational method, which is based on the runoff coefficient.

This method is an empirical relationship between the intensity of the rain and the maximum flow, proper for the estimation of the maximum flow in small hydrological basins with a surface of approximately 200 acres, where there are no important accumulations of water, and is calculated using the following relationship:

The rational method is often used, which is based on the runoff coefficient, to determine the maximum flow in small hydrological basins.

$$Q = k \cdot C \cdot F \cdot I \quad (1)$$

where:

Q – peak surface runoff in m³/s,

k – conversion coefficient in the metric system 16,67,

C – runoff coefficient,

F – total surface of the hydrographical basin in km²,

I – intensity of the rainfall in mm/min.

The leakage coefficient (C) from the first relation is determined as weighted average based on the specific leakage coefficients corresponding to the elementary surfaces from the representative and experimental hydrographical basin of Sebeș River with different types of land use:

$$C = \sum(c_i \cdot f_i) / F \quad (2)$$

where:

C – leakage coefficient,

c_i – specific coefficient,

f_i – elementary surface [km²],

F – total surface of the hydrographical basin [km²].

The runoff coefficient may have a value between 0 and 1; the zero value indicates that no rain fallen on the surface of the hydrological basin does not generate the maximum water flow, and the value of 1 indicates that all of the rain falling in the basin generates a maximum flow.

The rational method uses the rain intensity to render the average intensity of a rainfall with a specific frequency for a selected duration (Viessman et al. 1977).

Rainfall intensity is selected from an IDF curve (intensity – duration – frequency) generated from rainfall data collected in the local area (Fig. 2).

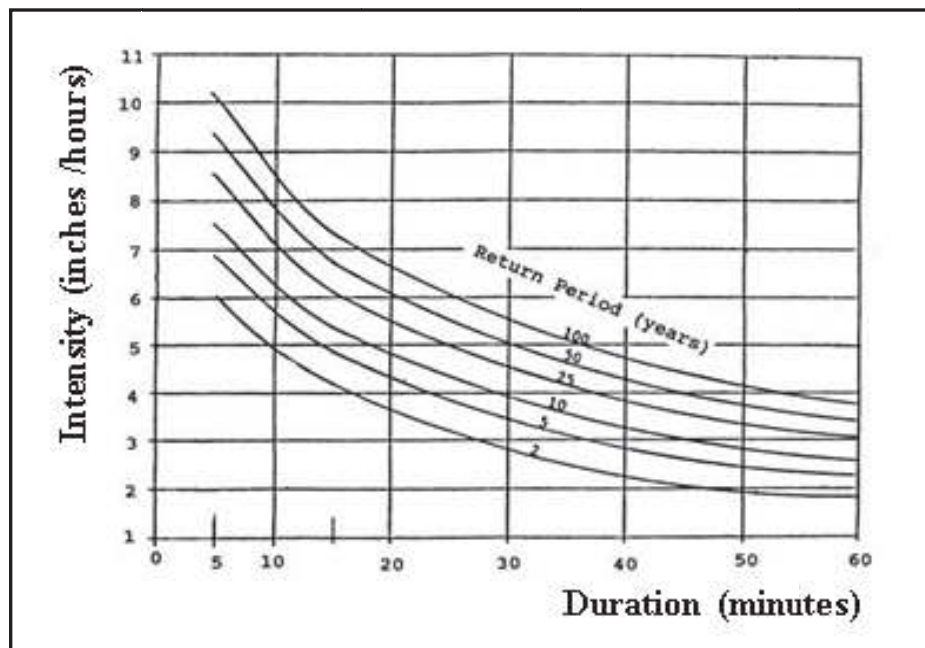


Fig. 2. Intensity – Duration - Frequency curve (Viessman et al. 1977)

Rys. 2. Krzywa Intensywność – Czas trwania – Częstość (Viessman et al. 1977)

To determine the maximum flow in Sebeş representative hydrographical basin, we used the multi-criteria overlay spatial analyses offered by ArcGIS, one implementation model in the rational formula according to Bilaşco, 2008.

According to this rational method, an important hydrological parameter in assessing the maximum flow of water in the basin is the runoff coefficient as rainfall-runoff integrator.

In order to compute the average runoff coefficient we used his function, which integrates the altitude, the slope, the land use, cover, the soil type (texture) and the rainfall intensity (Maftai et al. 2016) (Fig. 3).

The major factors affecting the rational method runoff coefficient value for a watershed are the land use, the soil type and the slope of the watershed. The physical interpretation of the runoff coefficient for a watershed is the fraction of rainfall on that watershed that becomes storm water runoff; the runoff coefficient must have a value between zero and one.

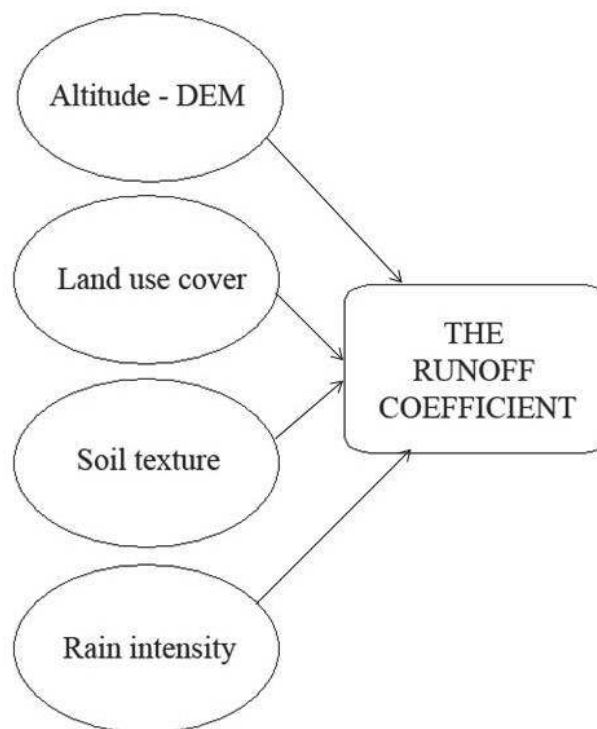


Fig. 3. The field-based spatial model used to calculate the runoff coefficient

Rys. 3. Przestrzenny model terenowy stosowany do obliczenia współczynnika odpływu

3. Results and discussion

The size of a hydrological basin, its form, and the morphometric features of the relief elements, have a particularly important role in producing hydrological phenomena, changing their variability in space and time.

The rational method lacks a physical loss model, yet initial abstraction exists and increases with watershed size (Asquith & Roussel 2007).

In the case of a hydrological basin reduced in size, such as Sebeș hydrological basin, the runoff trend closely follows the rainfall, the rain being felt immediately in the increase of the amount of water carried by that river, and a relatively short period of drought results in their depletion (Arba 2016).

The determination of the runoff in Sebeș hydrological basin, using ArcGIS software, could be performed by quantifying the computational elements (the delimitation of the hydrographical basin, the hydrographical river, the hypsometry, the slope etc.) (Fig. 4-5).



Fig. 4. Sebeș catchment – hydrographical network

Rys. 4. Zlewnia Sebeș – sieć hydrograficzna

The average altitude of a hydrographical basin has a great influence on the runoff. The hydrological basins located at high altitudes benefit from an increased amount of precipitation and a lower evaporation than the hydrological basins located at lower altitudes, therefore a hydrological basin located at high altitudes has a richer runoff than the one located at lower altitudes (Teodorescu 2003).

Another important element in the analysis of the runoff in Sebeș hydrographical basin is the slope influencing the water flow, both in

terms of speed and in terms of the accumulation time. The slope leads to a lower or higher speed of the water movement on its slopes and a weaker or a heavier erosion and transport of solid particles on slopes.

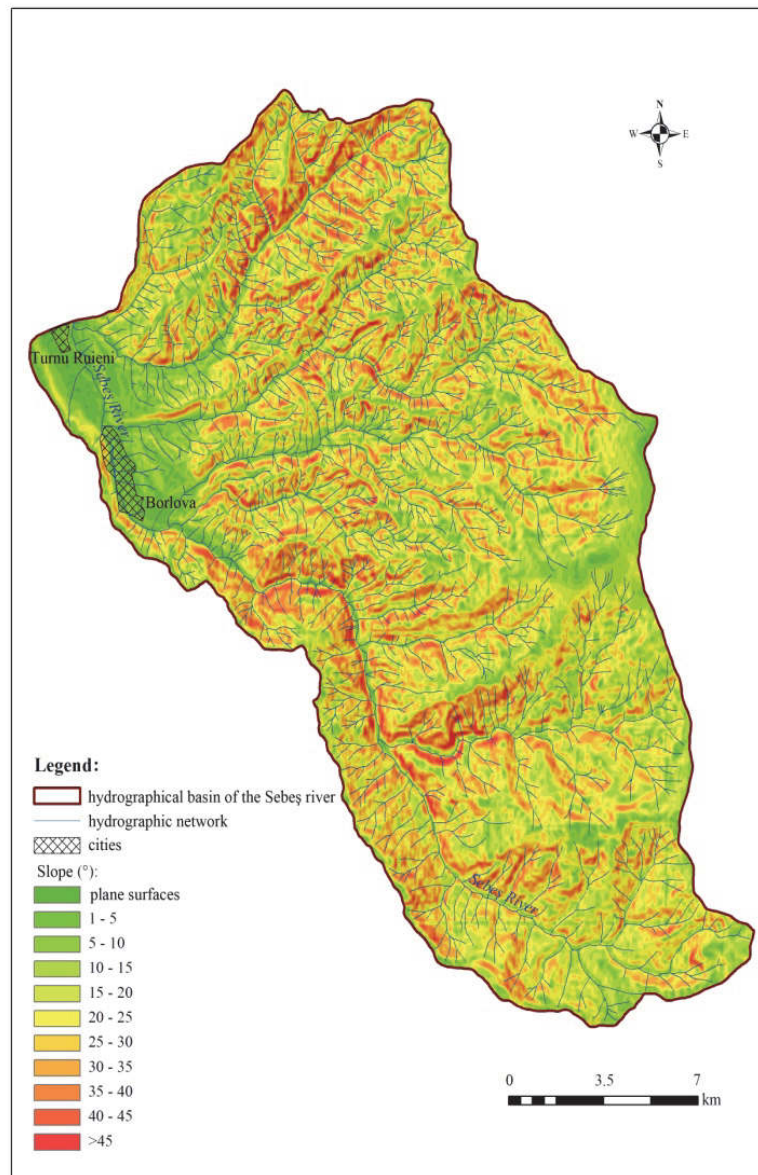


Fig. 5. Sebeș catchment – slope map

Rys. 5. Zlewnia Sebeș – mapa spadków

The physical and geographical features have a significant impact on the runoff, and cannot be neglected in the determination and the evaluation of the liquid flow. It is known that the surfaces of a hydrographical basin covered with forests contribute to the adjustment

of the maximum flow, the reduction of precipitations on the ground etc. (Fig. 6-7).

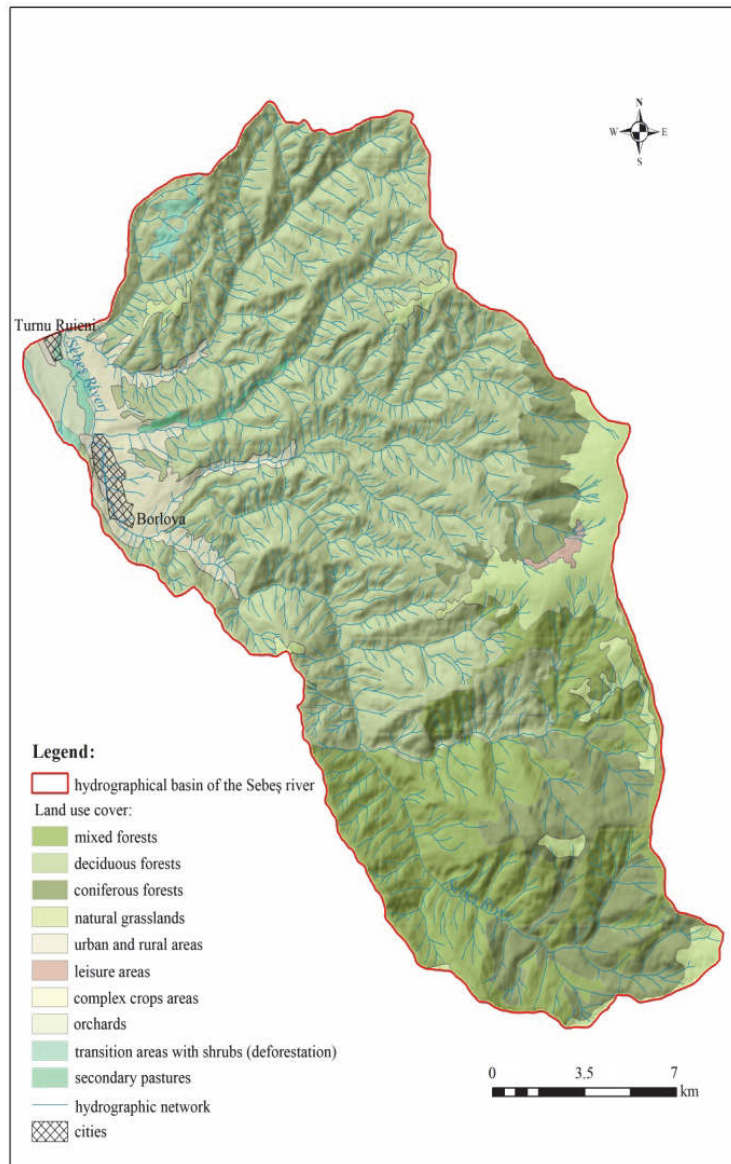


Fig. 6. Sebeș catchment – the land use cover

Rys. 6. Zlewnia Sebeș – zagospodarowanie terenu

The vegetation has a very important role in the formation of the runoff on Sebeș hydrographical basin, one the one hand, because it influences the formation of soil types, and, on the other hand, because it determines the size of water infiltration possibilities, the reduction of evaporation and the reduction of soil erosion.

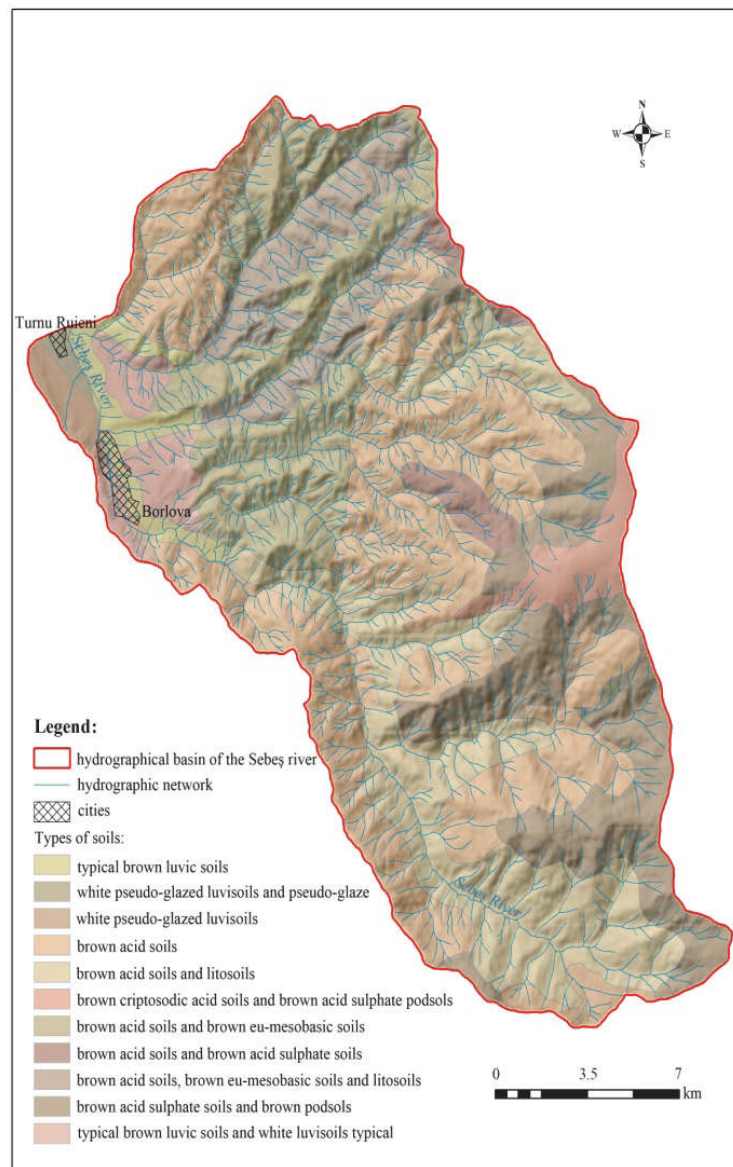


Fig. 7. Sebeș catchment – the soils type

Rys. 7. Zlewania Sebeș – rodzaje gleb

The influence of the vegetation on the runoff regime in the hydrological basin of Sebeș River occurs differently, according to the phytosociological groups and their extension.

The water coming from the precipitations is easily infiltrated in large quantities on the soil covered with vegetation, on extended basin surfaces, than on soils lacking vegetation, due to the fact that the vegetation-covered soil is loose and more structured, and the evaporation of the water from the soil is reduced.

For the hydrographical basin of Sebeş River, the runoff coefficient was determined based on the Frevert tables, integrating all the spatial values in a maximum flow model: topography altitude, slope, land use cover, soil features (class, type, texture) and rain intensity.

In this way we obtained the spatial distribution of runoff within the hydrographical basin of Sebeş River (Fig. 8).

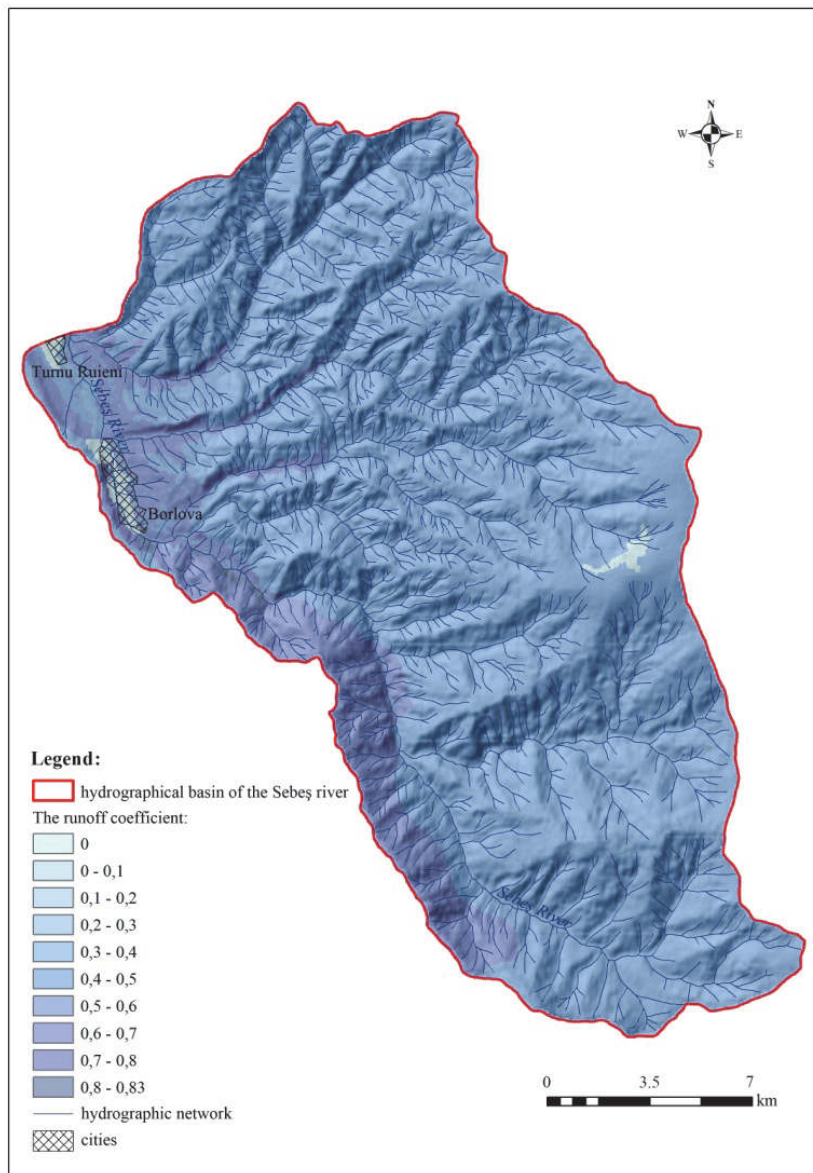


Fig. 8. Sebeş hydrographical basin – runoff obtained with the values of the runoff coefficient

Rys. 8. Dorzecze hydrograficzne Sebeş – odpływ otrzymany na podstawie współczynnika odpływu

Table 2. Runoff coefficient values and features of the Sebeş hydrological basin**Tabela 2.** Wartości współczynnika odpływu i cechy dorzecza hydrologicznego Sebeş

Runoff coefficient	Localization	H (m)	Slopes (°)	Classes and types of soils	Soil texture	Land use cover
0.3	Everywhere except: the western and eastern side	variables	variables	variables	variables	variables
0.4	East South North-East North-West	450-600 > 900	< 15	podsoils (brown acid sulphate soils and brown podsols); ambisoils (brown acid and brown criptosodic acid and brown acid sulphate podsols);	medium medium medium	natural grasslands
0.5	Everywhere except: the western and eastern side	< 1500	< 20	ambisoils (brown acid and brown criptosodic acid and brown acid sulphate podsols); Argiluisoils (typical brown luvic);	medium medium medium	all except urban, rural and leisure areas

Table 2. cont.

Tabela 2. cd.

Runoff coefficient	Localization	H (m)	Slopes (°)	Classes and types of soils	Soil texture	Land use cover
0.6	West	< 600 900-1050	variabile	ambisoils (brown acid); argiluisoils (white pseudo-glazed luvisoils); Undeveloped soils (alluvial protosoils); Argiluisoils (typical brown luvic);	hard medium medium medium	complex crops areas (crops and orchards), and deciduous and mixed forests
0.7	North-West	< 600	< 5	Undeveloped soils (alluvial protosoils); Cambisoils (brown acid); Argiluisoils (white pseudo-glazed luvisoils); Argiluisoils (typical brown luvic); Cambisoils (brown acid and brown eu-mesobasic);	medium medium medium medium	complex crop areas (crops and orchards) and secondary pastures
0.8	West	< 450	< 5 15-20	Cambisoils (brown acid);	hard	complex crop areas – agricultural crops

Analysing the spatial distribution map of the runoff along flow paths in Sebeș hydrographical basin, according to the runoff coefficient, we could distinguish many categories of surfaces, as shown in the Table 2.

The smallest values of the maximum runoff are recorded locally on the plan surfaces situated within Borlova and Turnu Ruieni localities and in the high area of Muntele Mic. These areas are the least vulnerable to high values of maximum runoff, so the risk of floods is low.

The runoff coefficient value of 0.3 resulted on surfaces that are situated everywhere within Sebeș hydrographical basin except: the western and eastern side and which have variable spatial values (altitudes, slopes, soils and land use cover).

The runoff coefficient of 0.4 was obtained in several areas located at high altitude (> 1200 m) in the eastern, southern, north-eastern and north-western part of the basin, with low slopes ($< 15^\circ$), covered with natural grasslands and several types of soils with medium texture, within the category of spodosoils and cambisoils.

The runoff coefficient value of 0.5 resulted on surfaces that are situated everywhere within Sebeș hydrographical basin except: the western and eastern side. These surfaces have specific parameters as follows: high altitude (< 1500 m), high slope ($< 20^\circ$), various land use cover (all except urban, rural and leisure areas), medium texture of soils and some characteristics classes and types of soil (cambisoils and argiluisoils).

The runoff coefficient value of 0.6 was obtained in several areas with low and medium altitudes (< 600 m and 900-1050 m), located in the western part of the basin, with variable slopes, covered with complex crops (crops and orchards) and deciduous and mixed forests, with soils that have a heavy and medium texture belonging to the classes of: cambisoils, argiluisoils and undeveloped truncated or rutted soils.

The runoff coefficient value of 0.7 resulted on surfaces situated in north-western part of the Sebeș hydrographical basin with low altitude (< 600 m), with low slopes ($< 5^\circ$), covered with complex crops (crops and orchards) and secondary pastures and with medium texture of soils, which are part of the following classes: undeveloped, cambisoils and argiluisoils.

The runoff coefficient of 0.8 was obtained in several areas located at low altitude (< 450 m), in the western part of the Sebeș hydrographical basin, with low slopes ($< 20^\circ$), covered with complex crops (agricultural crops) and heavy textured soils from the cambisoil class.

The highest values of the maximum runoff occur in the western part of the basin, especially on both sides of Sebeş River, where is situated the two localities from the basin (Borlova and Turnu Ruieni). These surfaces are the most vulnerable to such a type of runoff, which is responsible for producing hydrological risk phenomena such as floods.

4. Conclusion

This article focuses on the determination of the maximum runoff within the representative and experimental hydrographical basin of Sebeş River, which is a small basin but responsible for producing hydrological risk phenomena like floods.

The maximum runoff occurring in this representative and experimental hydrographical basin was calculated based on the input data processed in GIS and then the model obtained was calibrated based on the scheme that includes optimisation of multiple objectives that measure different meteorological and hydrological aspects. Direct methods are based on the field-observed data from gauging stations, which are then evaluated by various statistical methods.

Especially, the role of digital elevation model (DEM) is important since its accuracy can significantly affect the resulting quality of runoff maps. The role of DEM and its quality is crucial for the results of surface runoff modelling.

The calculation equation for determining the maximum runoff of this small hydrographical basin used the physical and geographical features of the basin, namely: the relief altitude, the slope, the land use cover, the soil types, the rain intensity and their features.

From the analysis of the runoff spatial distribution within Sebeş hydrological basin, we may notice that various geomorphometric components have a higher or lower share in determining the runoff coefficient.

Runoff data are often matched to statistical distributions with known forms. Extrapolation can be made relatively simple where a good adherence to a statistical distribution can be found, but hydrological data may not conform, or different distributions may be more suitable in different geographical regions.

The smallest values of the maximum runoff are recorded locally on the plan surfaces situated within Borlova and Turnu Ruieni localities and in the high area of Muntele Mic. These areas are the least vulnerable to high values of maximum runoff, so the risk of floods is low.

The highest values of the maximum runoff occur in the western part of the basin, especially on both sides of Sebeș River, where is situated the two localities from the basin (Borlova and Turnu Ruieni). These surfaces are the most vulnerable to such a type of runoff, which is responsible for producing hydrological risk phenomena such as floods.

The ArcGIS software, used in this study to calculate the runoff coefficient, allows the spatial analysis of the maximum flow in a small hydrographical basin with a quite high accuracy.

The Rational Method which estimates peak flows is a simplified representation of the complicated process whereby rainfall amount and intensity, catchment conditions and size as well as human activity, determine runoff amount, but it is suitable where the consequences of the failure of structures are limited. The method is usually restricted to small watersheds and is based on the rainfall/runoff assumptions of the hydrograph below.

The main importance of the paper can be seen in the method used which can be replicable in other similar small catchments.

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Wyznaczenie maksymalnego odpływu w reprezentatywnym i doświadczalnym dorzeczu hydrograficznym rzeki Sebeș (Banat, Rumunia)

Streszczenie

W kontekście zmian klimatycznych coraz poważniejsze stają się kwestie bardziej racjonalnego wykorzystywania zasobów wodnych i ekstremalnych zdarzeń hydrologicznych, takich jak powodzie, powodujące liczne negatywne skutki każdego roku. W małych dorzeczach hydrograficznych, takich jak dorzecze rzeki Sebeș (Rumunia), powodzie i ich destrukcyjne skutki zostały wzmocnione przez masowe wylesianie i niewłaściwe zagospodarowanie terenu. Analiza fizycznych i geograficznych cech dorzecza Sebeș pozwala ustalić reżim odpływu, także dla okresów o wysokim stanie wody i powodzi. Maksymalny odpływ występujący w tym reprezentatywnym i eksperymentalnym dorzeczu hydrograficznym został obliczony na podstawie danych wejściowych przetworzonych w GIS. Równanie obliczeniowe maksymalnego odpływu z badanego małego dorzecza wykorzystuje fizyczne i geograficzne cechy dorzecza, a mianowicie: wysokość wypiętrzenia, nachylenie, pokrycie terenu, typ gleby, intensywność opadów i ich cechy. Na podstawie analizy rozkładu przestrzennego odpływu w obrębie dorzecza Sebeș można zauważyć, że różne składniki geomorfometryczne mają większy lub mniejszy udział w określaniu współczynnika spływu.

Abstract

In the context of climate change, issues on more rational use of water resources and hydrological extreme events, such as floods, causing numerous negative effects every year, are becoming more acute. In small hydrographical basins, like the hydrographical basin of the Sebeș River (Romania), floods and their destructive effects have been and are amplified by the massive deforestation and the improper exploitation of surfaces. The analysis of the physical and geographical features of Sebeș hydrographical basin enables us to establish the runoff regime, including for the periods with high waters and floods. The maximum runoff occurring in this representative and experimental hydrographical basin was calculated based on the input data processed in GIS. The calculation equation to determine the maximum runoff of this small hydrographical basin used the physical and geographical features of the basin, namely: the relief altitude, the slope, the land use cover, the soil types, the rain intensity and their features. From the analysis of the runoff spatial distribution within Sebeș hydrological basin, we may notice that various geomorphometric components have a higher or lower share in determining the runoff coefficient.

Słowa kluczowe:

rzeka Sebeș, dorzecze hydrograficzne, odpływ, zagospodarowanie terenu, rodzaje gleb, współczynnik odpływu, GIS

Keywords:

Sebeș River, hydrographical basin, runoff, land use cover, soil type, runoff coefficient, GIS



Ecological and Economic Savings of Fly Ash Using as Geopolymer

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1. Introduction

Geopolymer are rather new and not so known alternative materials. Number of geopolymer is replacing naturally appearing materials due to their unique characteristics. Therefore society should to give attention to by-products or waste, such as geopolymer from fly ash that could be contribution from ecological, as well as from economic aspect. Every year European Union produces several hundred millions of fly ash as a waste from heat and energy production. There are different types of industrial wastes such as biomass ash, red mud, recycled glass and heavy metals waste, in their application for geopolymer production (Toniolo & Boccaccini 2017).

Fly ash belongs to the group of by-product from coal burning, stocking to the pond, where its specific physical and chemical characteristics are degraded. According researches fly ash could be full valued raw material, replacing some naturally appearing materials, or in dependence of qualitative characteristics of the coal it could be more convenient than naturally appearing materials. Common use of fly ash using is filling of not used mining spaces, application to the soil, in which fly ash improves significantly its physical, chemical and mechanical characteristics.

Number of professional, scientific research papers published on geopolymer was close to zero in 1991, it rose to over 400 per year in 2013 (Geiger 2011). Abroad, fly ash as a raw material is used for decades, since it presents cheap raw material, often with sufficient functional characteristics, usually without harmful effects on humans or the envi-

ronment (Rosik-Dulewska & Karwaczyńska 2008, Davidovits 2011). But not many laics have idea about their existence and possibilities for using in the industry and living environment protection. Geopolymer had become common idea mostly in USA, in France and India, where there is given great attention during whole decades (Vilamová & Piecha 2016). In addition to various technical and technological aspects of fly ash using, which favorably affects the characteristics of the materials, their use also has substantial economic and environmental benefits (Ahmaruzzan 2010). Fly ash with a high content of residual coal can also serve to remove various inorganic substances (Iyer & Scott 2001). Moreover, recent studies have shown that geopolymer concrete based on fly ash does not require such heat treatment, when there is not added a small volume of the ingredient, which is a carrier of calcium, for example a slag (Yao 2015). The experimental investigations on the compressive strength and permeation properties of geopolymer concrete prepared with low calcium fly ash (Jindal et al. 2017).

Using of geopolymer in agriculture had been studied by (Suksiripattanapong et al. 2017) that investigated the strength and microstructure properties of spent coffee grounds (CG) stabilized with rice husk ash (RHA) and slag geopolymers to produce a green construction subgrade material (Suksiripattanapong et al. 2018). The outcome of this research will enable CG, furnace slag and RHA waste products to be used as sustainable materials in pavement applications. The amount of sludge wastes produced from mining, domestic agriculture and industrial activities are about 60200 tons per year. The waste increase will have a significant impact on the energy conservation and also on the environment. Geopolymer has an ability to encapsulate heavy metals. In this sense Abdullah et al. (2016) studied the potential of sludge waste to be utilized as construction materials, finding its effective using in the area (Abdullah et al. 2016). Other possible geopolymer using can be as boiler ash waste from waste of palm oil industry, which provide area of potential use as raw material for geopolymer production (Yahya et al. 2013).

As a result of across the world, water is contaminated with nutrients and pesticides which threaten riverine environments, wetlands, urban drinking water supplies and also marine assets. Much can be done and sustainable management practices (SMP) can be put into place to reduce water impacts from agriculture. Required investment levels are

insignificant compared to the economic advantages to be gained from adopting appropriate SMP across global agribusiness. SMP technologies need to be targeted at specific pesticides (eg. atrazine, simazine, diruron, ametryn, hexazinone, tebuthiuron, dieldrin, metalochlor, 2,4 D, triclopyr, picloram and bromacil). Research, development and testing of appropriate non-leaking/reactive spillways and subsurface of geo structures need to take place across the various agricultural industries. The challenge for engineers is to come up with geo structural designs which are efficient, cost effective and which will be taken up and embraced by Australian and world agribusiness (Craig et al. 2015).

The other research of fly ash using in concrete production studied the interface between fly ash concrete and steel rebar (Liang et al. 2017). The results showed that the general shape of the bond-slip curve between fly ash concrete and steel rebar was similar to that for the normal concrete and steel rebar.

2. Experimental

The main target of the research was to compare economic and environmental contribution of fly ash. Comparison had been done in case of concrete production with and without fly ash using.

Object of searching is fly ash, rising during coal burning in heat and electric energy production, which is possible without further elaboration to use as an input raw material in the industry, especially during concrete prefabricates production:

- a) as a full replacement or
- b) as partial replacement of cement in final concrete mixture for prefabricates production.

The process of searching for fly ash using and its contributions was according calculation of costs for production of concrete with and without fly ash using. Data had been obtained from price list of individual materials for concrete production as follows:

1. Data collection: type of materials used, unit prices per materials.
2. Calculation of assumed consumption of individual types of material.
3. Total costs calculation for individual types of concrete.
4. Comparing of costs effectiveness with determination of benefit of fly ash using.

5. Determination of resulting values of alternatives (with or without fly ash).
6. Decision, which alternative is convenient.

The cost calculation for the concrete production with using of geopolymer is based on the properties of individual types of concrete, which provide technical standards, as well as the requirements of the individual components. Concretes are divided into 16 basic strength classes under current Slovak technical standard norm EN 206-1. National Annex to this standard provides requirements and specifications for all types of concrete, as well as the conditions, under which the concrete can be used. All mentioned characteristics are included in calculation according Table 1.

Table 1. The cost calculation for the concrete production with using of geopolymer

Tabela 1. Kalkulacja kosztów produkcji betonu z użyciem geopolimerów

	Total price [€]	Volume of concrete prefabricate [m ³]	Price of concrete prefabricate [€]	Possible fly ash consumption [t]	Possible price savings [€]
1 st section					
2 nd section					
.....					
n - section					
total					

Cement is the most active part of the concrete and it is usually the most expensive. Its selection and proper using is essential to achieve economic balance between the desired properties of the prepared concrete mix and the cost of its production. We calculated with cement category I and II, since it is the most popular among manufacturers of concrete, ensuring an adequate level of strength and durability.

3. Results and discussion

Geopolymer as a new material is used for surface treatment and bonding, binders for fiber composites, encapsulation of waste as well as cement for concrete production. Using of geopolymer is searched in number of scientific and industrial sectors: modern inorganics chemistry, physical chemistry, colloidal chemistry, mineralogy, geology and all types of technological processes. Broad scale of potential application includes: resistant materials, decorative artefacts from stone, heat isolation, technologically not demanded construction materials, energetically not demanded ceramic pavement, fireproof elements, biotechnology (material for medicine using), foundry industry, cement and concrete, elements for infrastructural repairs and reinforcement, technological elements for aerial and automotive industry, resinous systems, packages for radioactive and toxic waste, arts and decoration, archeology, etc. (Davidovits 2011). Main using in the individual sectors is given by Table 2.

Table 2. Possibilities for fly ash using as raw material in various sectors

Tabela 2. Możliwość wykorzystania popiołów lotnych jako surowca w różnych sektorach

Sector	Possibilities for using
Metallurgy	Steel production, preparation of heating layers, preparation of backfills, forming mass during casting steel
Mining	Establishment of mined mining spaces
Agriculture	Treatment of heavy soils, preparation of bio organic material fertilizers, seed dressing as a source of micro and macro elements
Construction	Production of artificial stones and concrete, production of ceramics and bricks, road construction

The fly ash contains significant amounts of SiO_2 , Al_2O_3 , CaO and Fe_2O_3 , which are considered low-cost materials for the ceramics industry. In addition, the powdery consistency makes the ash a suitable material that can be mixed into ceramics adhesives and adhesives without any treatment. As for the using of kaolin clay and fly ash in the manufacture of ceramic tiles and floor tiles for interiors and exteriors, the results of research have been so good that they have achieved the quality of commercial ceramic materials. In addition, glass ceramic and ceramic materi-

als from fly ash without further additives have achieved better physical, chemical and mechanical properties (Yao 2015).

Metals and metal oxides are often used as catalysts in various industrial applications. Fly ash is composed of various oxides of metals with high ferric oxide content and achieves high thermal stability. Chakraborty and his team prepared CaO catalyzed with fly ash support for transesterification of soybean oil and showed a high catalytic efficiency in converting soybean oil to biodiesel with a high fatty acid content of up to 96.97% (Yao 2015).

3.1. Fly ash as a waste

Coal using is inseparable part of human activity. In past time coal played very important role and it is still remaining, either for electric energy production, or steel production, or as a source of heat. Only in EU countries consumption in 2012 was 837 million tons of coal, in the world it presented 6,6 billion tons of coal (see Table 3) (International... 2017).

Table 3. Annual coal consumption in tones

Tabela 3. Roczne zużycie węgla w tonach

	2009	2010	2011	2012	Average / year
Slovakia	8 567 164	8 415 045	8 288 279	7 691 523	8 240 503
EU-27	776 680 000	786 142 000	812 833 000	837 620 000	803 318 750
Europe	959 656 000	966 325 000	1 003 697 000	1 026 713 000	989 095 250
World	7 471 823 000	7 750 518 000	8 123 601 000	8 449 496 000	7 948 859 500
Growth (t)		278 695 000	373 083 000	325 895 000	
Growth (%)		3,73	4,81	4,01	

According statistics coal consumption in the world is increasing more than 4% per year, as well as volume of fly ash. Whole world annual increase is 550 million tons of fly ash and only 30% of total volume is produced in Europe and it is used as secondary raw material. 70% presents not used waste (Špak et al. 2012). Also improper treatment with fly

ash became environmental problem. In present time there is pressure to the research in area of fly ash recycling. Important task in consequent treatment with fly ash or its using plays physical, chemical and mineral characteristics of individual fly ashes. Specific characteristics depend on coal type, conditions of burning, setting the collection device.

3.2. Influence of Portland concrete production to the living environment

Broad using of fly ash is production of Portland concrete, but during its production there is greenhouse gas emission to the atmosphere. During clinker production there is produced 0,55 tons of chemical CO₂ and its production demands burning of carbon fuels, which increases the number by other 0,44 tons. Exception is mixed concretes with fly ash, due to which CO₂ emission is decreased by 10-15% (Antošová et al. 2013). Mentioned is illustrated in Table 4, 5.

Table 4. Comparing of emission during production of Portland and geopolymer concrete

Tabela 4. Porównanie emisji w trakcie produkcji cementu portlandzkiego i geopolimerowego

CO ₂ emission (t)	Burning	Crushing	Solvents	Total	Reduction
Portland Concrete	1,000	0,020	0	1,020	0
Geopolymer Concrete	0,140	0,018	0,050	0,208	80%

Table 5. Comparing of energy consumption during production of Portland and Geopolymer Concrete

Tabela 5. Porównanie zużycia energii do produkcji cementu portlandzkiego i geopolimerowego

Energy consumption (MJ/t)	Burning	Crushing	Solvents	Total	Reduction
Portland Concrete	4 270	430	0	4 700	0
Geopolymer Concrete	1 200	390	375	1 965	59%

3.3. Fly ash as a secondary raw material using

In present time almost everybody perceives necessity to use secondary raw materials. This trend is obvious in the industry, where using of secondary raw materials can increase economic effectiveness of the production. Considerable is also contribution of secondary raw materials using in area of living environment protection, since it backwardly uses wastes from industrial activity (Sisol et al. 2014). Comparing of production and using of secondary products from coal burning in USA and EU is given by Table 6 and 7.

Table 6. Production and using of secondary products from coal burning in USA in 2013

Tabela 6. Produkcja i zużycie odpadów ze spalania węgla w USA w roku 2013

	Fly ash	Ash	Slag
Produced volume	53 400 000	14 450 000	1 355 939
Consumed volume (t)	23 321 230	5 640 693	897 185
Consumed volume (%)	43,67	39,02	66,16
Concrete /concrete products	12 356 726	497 074	0
Mixed concrete / clinker additive	2 286 144	1 324 131	0
Construction fillings	3 141 454	2 140 800	0
Agriculture / soil treatment	284 106	457 287	1 000
Using during snowing	0	421 087	11 797
Using in mining	1 843 292	250 113	0
Waste stabilization	2 034 182	59 751	727
Services for oil fields	313 373	73 883	0
Others	1 061 953	319 567	895 542

Table 7. Production and using of secondary products from coal burning in EU 15 in 2010**Tabela 7.** Produkcja i zużycie odpadów ze spalania węgla w 15 krajach Unii w roku 2010

	Fly ash	Ash	Slag
Produced volume	31 616 000	4 052 000	1 000 000
Consumed volume (t)	13 785 000	1 890 000	1 000 000
Consumed volume (%)	43,6	46,64	100,00
Concrete production	2 152 000	178 000	0
Mixed concrete	1 947 000	1 000	0
Concrete additives	4 947 000	62 000	3 000
Concrete blocks	760 000	798 000	0
Ceramics / bricks	83 000	16 000	0
Fillings	3 174 000	513 000	0
Soil treatment	115 000	0	0
Temporary storages	201 000	87 000	0
Storage at landfill	2 260 000	87 000	0
Others	607 000	322 000	997 000

3.4. Economic aspects of fly ash using

Using of geopolymer in the industry offers some economic benefit, since costs for fly ash are negligible. Producers of heat and electric energy treat fly ash as a waste, which presents for them a problem. Waste stocking has its limitation, legislative as well as its localization and capacity (Okoro et al. 2017).

For example in Slovakia according Statistical Office in 2013 there was produced 286 863 663 kg of concrete prefabricates, which presents 120 000 m³ concrete, necessary for its production. In case producers would replace Portland concrete with concrete, mixed with fly ash, 9 360 tons of fly ash could be consumed (Khouri et al. 2016).

Economic contribution of fly ash using will be illustrated by case of National Highway Society, Joint Stock Company, supplying concrete prefabricates in volume 14 678 m³. During production of such prefabricates part of concrete could be replaced with fly ash, which could mean economic evaluation by almost 1 150 tons of fly ash and saving more than half a million euro. Table 8 concludes all possible economic savings.

Table 8. Possible fly ash using and savings for highway construction

Tabela 8. Możliwości wykorzystania popiołów lotnych przy budowie autostrad i uzyskiwane oszczędności

	Total price [€]	Volume of concrete prefabricate [m ³]	Price of concrete prefabricate [€]	Possible fly ash consumption [t]	Possible price savings [€]
D1 Trnava – crossing Lúka	9 399 451	7 501	1 289 546	586	232 118
D1 Ivachnová – Važec	32 628 700	5 288	1 262 959	413	227 332
D1 Prešov – Budimír	14 998 877	1 889	306 332	148	55 139
Total	57 027 028	14 678	2 858 837	1 145	514 589

In case Slovak Republic would install condition for fly ash using as partial replacement of cement for concrete prefabricates, used during highway construction, till 2020 volume of fly ash could decrease by more than 11 000 tons. Savings in individual years are calculated according Table 9.

Table 9. Plan of highway construction in Slovakia during 2015-2020

Tabela 9. Plany budowy autostrad w Słowacji w latach 2015-2020

Year	Planned road construction [m]	Assumed volume of necessary prefabricates [m ³]	Estimated volume of fly ash, necessary for prefabricates production [t]
2015	71 274 m	9 266 m ³	723 t
2016	175 240	22 782	1 777 t
2017	148 580	19 316	1 507 t
2018	45 510	5 917	462 t
2019	60 850	7 911	618 t
2020	606 400	78 832	6 149 t
Total	1 107 854	144 024	11 236 t

According available literature there was no suggested such structure of concrete mixture, which could content higher rate of fly ash, achieving at least 50 MPa resistances. While using of concrete with 30 MPa resistances in concrete prefabricates, it could mean replacing yet 30% cement with fly ash and in this case resulting price would be lower, since volume of cement, necessary for production would decrease and at the same time waste material would be consumed.

4. Conclusions

Although fly ash cannot be put into practice economically, the CO₂ production of Portland cement remains an open problem as well as the way the fly ash treatment. It is only a matter of time when it will be necessary to take much stricter measures to reduce emissions so that global warming and the associated global dimming are at least slowed down as it is not possible to stop it completely. It is undeniable that the industry will still need concrete, so the demand for Portland cement will not fall naturally.

Concrete with fly ash is an alternative that would replace Portland cement, but only if the cost of water glass is reduced to a level comparable to the price for Portland cement, and if it is questionable whether construction engineers are going after a not yet well-known alternative, or if they even at the cost of higher costs continue to prefer a traditional, verified option.

One of the possibilities that could help to solve problem with high CO₂ production, which is costly affordable, is the use of biomass in cement production, with aim to at least partially reduce emissions that are released into the atmosphere. Another possibility is the recycling of old concrete, which by its properties can replace part of aggregate in new concrete, or it can be used as a foundation for road construction. Similarly fly ash could be used as a mixture to concrete.

In spite of mentioned aspects fly ashes produced in eastern Slovakia, having a high content of unburned coal residues (more than 10% LOI), cannot be utilized as a secondary raw material for building materials. Currently, one possibility for the utilization of high-LOI (Loss On Ignition) fly ashes is in the synthesis of geopolymers (Geopolymer... 2015). Also there is necessary to deal with ash, since due to industrializa-

tion, several countries have attained sustainable development with some degree of environmental degradation. These activities influence the environment; however tend to produce pollutants (gases, acids, oils, cooling water, ash and so on) (Okoro et al. 2017). Re-use of fly ash presents system approach as a potential tool to support further regional development, but only during accepting of valid legal regulations of the country, as well as the principles of sustainable environmental development (Khouri et al. 2016).

Awareness of the society has so far insufficiently focused on the possibilities offered; recycling is a business issue for PR, which is presented to the public. According to the European Commission's statistical indicators, only one-third of the produced construction waste is reused, and the reason for such a small amount is not technical problems, but the traditionally used methods in the industry. Netherlands presents a leader in recycling of waste, which yet 95% waste, rising in the industry, is reused. Average of EU member states is against Netherland only 30-60%. It can be not easily predicted, if society will still slather rare sources and alternatively, similar qualitative materials stock at the dump as a waste (Geopolymer... 2015).

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Ekologiczne i ekonomiczne oszczędności wynikające z zastosowania popiołów lotnych jako geopolimeru

Streszczenie

Głównym celem badań było porównanie wpływu popiołów lotnych na gospodarkę i środowisko. Porównanie przeprowadzono dla produkcji betonu z użyciem popiołu lotnego i bez niego. Wyniki pokazują, że popioły lotne mają w wpływ na ochronę środowiska i oszczędności podczas produkcji betonu.

Geopolimery to raczej nowe i mało znane materiały alternatywne. Liczne geopolimery zastępują materiały naturalne ze względu na ich unikalne cechy. Dlatego społeczeństwo powinno zwracać uwagę na produkty uboczne lub odpady, takie jak geopolimer z popiołów lotnych, które mogą mieć pozytywny wpływ na środowisko jak i ekonomię. Każdego roku Unia Europejska produkuje kilkaset milionów popiołów lotnych jako odpad z produkcji ciepła i energii. Popiół lotny powstaje podczas spalania węgla i jest składowany na hałdach, gdzie jego szczególne właściwości fizyczne i chemiczne ulegają degradacji. Zgodnie z badaniami popiół lotny mógłby być pełnowartościowym surowcem, zastępując niektóre naturalnie występujące materiały, lub w zależności od cech jakościowych węgla może być wygodniejszy niż materiały naturalne. Powszechne stosowanie popiołów lotnych polega na wypełnianiu wyrobisk górniczych, aplikacji do gleby, w której popiół lotny znacznie poprawia jej właściwości fizyczne, chemiczne i mechaniczne.

Chociaż zastosowanie popiołów lotnych, z punktu widzenia ekonomii, jest niemożliwe, emisja CO₂ z produkcji cementu portlandzkiego pozostaje problemem otwartym, podobnie jak sposób przetwarzania popiołów lotnych. Jest kwestią czasu, kiedy konieczne będzie podjęcie znacznie ostrzejszych środków w celu zmniejszenia emisji, tak aby globalne ocieplenie i związane z nim globalne zaciemnianie uległy przynajmniej spowolnieniu, ponieważ nie można go całkowicie zatrzymać. Nie można zaprzeczyć, że przemysł nadal będzie potrzebował betonu, więc popyt na cement portlandzki nie spadnie naturalnie.

Beton z popiołem lotnym to alternatywa, która zastąpiłaby cement portlandzki, ale tylko wtedy, gdy koszt szkła wodnego obniży się do poziomu porównywalnego z ceną cementu portlandzkiego, a jest wątpliwe, czy inżynierowie budowlani będą stosowali nie do końca jeszcze dobrze znaną alternatywę, nawet pomimo wyższych kosztów niż tradycyjną, zweryfikowaną opcję.

Jedną z możliwości, które mogą pomóc rozwiązać problem związany z wysoką produkcją CO₂, która jest dostępna finansowo, jest wykorzystanie biomasy do produkcji cementu, w celu przynajmniej częściowego zmniejszenia emisji do atmosfery. Inną możliwością jest recykling starego betonu, który dzięki swoim właściwościom, może zastąpić część kruszywa w nowym betonie lub może być wykorzystany jako fundament do budowy dróg. Podobnie popioły lotne mogą być użyte jako składnik betonu.

Abstract

The main target of the research was to compare economic and environmental contribution of fly ash. Comparison had been done in case of concrete production with and without fly ash using. Results speak about contribution of fly ash using in area of living environment protection and costs savings during concrete production.

Geopolymers are rather new and not so known alternative materials. Number of geopolymer is replacing naturally appearing materials due to their unique characteristics. Therefore society should to give attention to by-products or waste, such as geopolymer from fly ash that could be contribution from ecological, as well as from economic aspect. Every year European Union produces several hundred millions of fly ash as a waste from heat and energy production. Fly ash belongs to the group of by-product from coal burning, stocking to the pond, where its specific physical and chemical characteristics are degraded. According researches fly ash could be full valued raw material, replacing some naturally appearing materials, or in dependence of qualitative characteristics of the coal it could be more convenient than naturally appearing materials. Common use of fly ash using is filling of not used mining spaces, application to the

soil, in which fly ash improves significantly its physical, chemical and mechanical characteristics.

Although fly ash cannot be put into practice economically, the CO₂ production of Portland cement remains an open problem as well as the way the fly ash treatment. It is only a matter of time when it will be necessary to take much stricter measures to reduce emissions so that global warming and the associated global dimming are at least slowed down as it is not possible to stop it completely. It is undeniable that the industry will still need concrete, so the demand for Portland cement will not fall naturally.

Concrete with fly ash is an alternative that would replace Portland cement, but only if the cost of water glass is reduced to a level comparable to the price for Portland cement, and if it is questionable whether construction engineers are going after a not yet well-known alternative, or if they even at the cost of higher costs continue to prefer a traditional, verified option.

One of the possibilities that could help to solve problem with high CO₂ production, which is costly affordable, is the use of biomass in cement production, with aim to at least partially reduce emissions that are released into the atmosphere. Another possibility is the recycling of old concrete, which by its properties can replace part of aggregate in new concrete, or it can be used as a foundation for road construction. Similarly fly ash could be used as a mixture to concrete.

Słowa kluczowe:

popioły lotne, geopolimer, ochrona środowiska, oszczędności ekonomiczne, Słowacja

Keywords:

fly ash, geopolymer, environment protection, economic savings, Slovakia



Measurement of Ambient Air Pollution with SO₂ Applying Lichens and Passive Samplers

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1. Introduction

Ambient air pollution is a complex mixture composed of both solid particles and gaseous pollutants (Kan et al. 2012). Air pollution has many negative effects on the natural environment, from changes in plant growth patterns to loss of ecosystem function (Chaiazzo et al. 2013). In support of this observation, the World Health Organization estimates that the every year, 2.4 million people die because of the effects of air pollution on health (Sierra-Vargas et al. 2012). About 400 000 premature adult deaths attributable to air pollution occur each year in Europe (Amato et al. 2014). Monitoring air quality by using living organisms as biomonitors has received increasing attention in recent years (Gerdol et al. 2014). It is hard to establish a region-wide monitoring system to reveal environmental risk assessment levels. Increasing awareness of the potential hazards of large-scale contamination of ecosystems by pollutants has highlighted the need for continuous monitoring of the levels of contaminants in the environment (Giordani et al. 2002).

Lichens are used in environmental monitoring of industrial pollution (Oksanon 2006). Changes in lichen diversity are used as indicators of environmental conditions and have been widely applied in air quality assessments and monitoring programs around the world (Landis et al. 2012).

The bio monitoring of pollution by the atmospheric aerosol most commonly utilizes lichens and mosses, which have no root parts and collect nutrients and pollutants through the entire body surface. Analysis of trace elements accumulated in lichens and mosses provides much informa-

tion on the emission of pollutants into the environment, enables the assessment of a changing quality of the environment, and allows the determination of directions in which the pollutants propagate (Kłos et al. 2011).

Lichens in particular have been widely used as trace element atmospheric bio-monitors as they are widespread and capable of absorbing elements directly from the atmosphere and accumulating them in their tissues. Lichen bio-monitoring is often used as receptor based method in air quality studies. It can be useful in risk assessment for human health.

There are not enough scientific data about comparison of two different methods for air quality evaluation – application of passive sampling method and bio indication method with lichens. The idea was to apply two different methods for air pollution with SO₂ evaluation – passive samplers and bioindication (with lichens) and this idea was realised in the chemical laboratory of Environmental protection department at Vilnius Gediminas Technical University.

In terrestrial environments, probably epiphytic lichens are the most widely used biomonitors, which can detect and monitor numerous pollutants such as SO₂, HF, various metals, nitrogen deposits and radionuclides. They can be used as bio indicators, bio accumulators and ecological indicators, where the approaches vary in terms of biological organization from individual species-to-species associations and lichen communities (Attanayaka et al. 2013). The major effects of pollutants on lichens (especially SO₂) are summarized as follows (Pescott et al. 2015): reproductive potential, changes in morphology, changes in ultrastructure, membrane integrity, photosynthesis and respiration, loss of biodiversity and changes in lichen communities and other effects (inhibition of nitrogen fixation in lichens).

SO₂-levels greater than 40 µg/m³ determine the disappearance of sensitive lichen species. Mean sulphur dioxide levels higher than 150 µg/m³ cause lichen deserts. Lichen zones correspond to certain SO₂ concentrations in the exploratory ambient air. Zoning of lichens in the cities has been known long, it is based on the resistance degree of different groups and species of lichens to harmful substances (toxic tolerance) (Stravinskienė 2009). This principle was applied in article.

The passive sampler method is widely used in order to quantify ambient gaseous air pollutant concentrations (Pekey and Yılmaz 2011, López-Aparicio and Hak 2013, Caballero et al. 2012, Hien et al. 2014, Zielinska et al. 2014, Šerevičienė et al. 2014, Król et al. 2012, Adema et al. 2012, Byanju et al. 2012, Estellano et al. 2012, Fridh et al. 2014, Přibyllová et al. 2012). Passive diffusion samplers provide a cost-effective way to monitor air-pollutant species at both local and regional scales. Compared with conventional methods, they can be deployed unattended for extended periods and do not require power supply (Adema et al. 2012).

Applying lichens average concentration of ambient air pollution during long period (growing of lichens on tree surface) can be found. Applying passive sampler's concentration of ambient air pollution during short period (typically 2-4 weeks) can be found. Hypothesis – approximate evaluation of ambient air pollution with sulphur dioxide can be found applying lichens. This hypothesis was tested applying certificated method – passive samplers.

Aim of research – comparison of two different methods for air quality (air pollution with SO₂) evaluation in Raseiniai district (Lithuania) – applying passive sampling method and bioindication method with lichens.

2. Materials and methods

2.1. Study area

Using lichens as bio-indicators, air pollution studies were carried out in Raseiniai town and its surroundings (Fig. 1). Raseiniai district municipality is located in the western part of Lithuania, 76 km north-west of Kaunas city. Raseiniai district area covers 157.3 thousand ha, of which 113.206 thousand hectares are agricultural areas, 23% – forests, 4.3% – towns and settlements, 2.8% – industrial enterprises and roads, 3.8 thousand ha – water, 13.4 thousand ha – areas intended for other purposes (Raseinių rajono... 2008). Raseiniai district includes twelve elderships (Figure 1), its population is 33 520 (at the beginning of 2017), two towns (Raseiniai – population is 10 256, Ariogala – population is 3208). There are seven small towns, three railway stations, 597 villages (Raseinių seniūnijos... 2009).

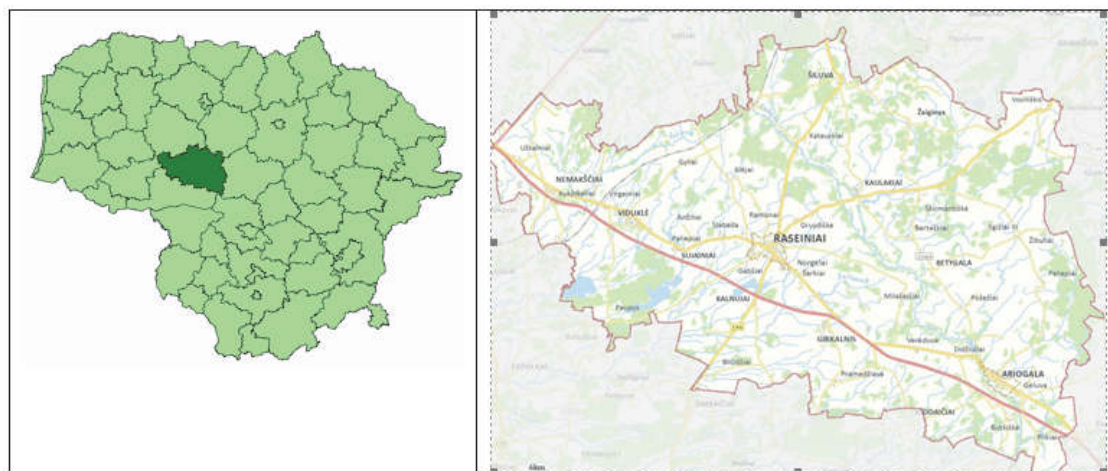


Fig. 1. Location of the study area

Rys. 1. Lokalizacja badanego obszaru

In the Raseiniai district municipality, pollutants to the ambient air come from stationary sources of pollution (energy, industrial and economic objects, as well as individual residential buildings) and from mobile sources of pollution (road transport). Many pollutants come from the large boiler-houses located in Raseiniai, Ariogala and Viduklė, and individual homes. The amount of the main air pollutants (SO_2 and other pollutants) emitted into the atmosphere from the stationary sources in Raseiniai district municipality, are presented in Figure 2.

The emissions of sulphur dioxide in the Raseiniai district municipality, as compared to previous years, have significantly decreased, as energy companies use clean fuel – biofuel instead of sulphury heavy fuel oil from approximately 2011 year. After installing of biofuel boilers, the emission of sulphur dioxide into the atmosphere remained almost unchanged.

Emissions from individual housing especially increase during the cold season, when boilers are being heated intensively, and weather conditions for the pollution dispersion are adverse; in addition to this, the increase in pollution also depends on the type of fuel used, its quality, and sometimes on the waste fired.

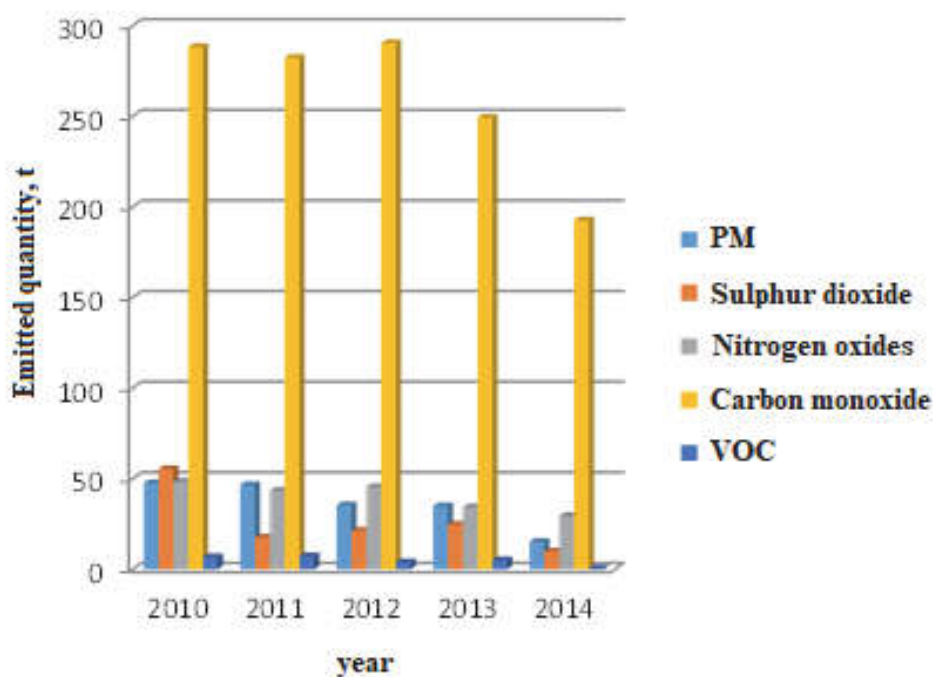


Fig. 2. Quantity of particulate matter, sulphur dioxide, nitrogen oxides, carbon monoxide and volatile organic compounds (t/y) emitted into the atmosphere from stationary sources in Raseiniai district municipality (Data from the Lithuanian Department of Statistics)

Rys. 2. Emisja cząstek stałych, dwutlenku siarki, tlenków azotu, tlenku węgla i lotnych związków organicznych (t/rok) do atmosfery ze źródeł stacjonarnych w gminie powiatowej Raseiniai (Dane z litewskiego departamentu statystyki)

2.2. Methodology of lichen sampling

During the cartography, whole Raseiniai city and its surroundings on the map were divided into separate 500 m x 500 m areas. A particular study area network was formed. With the assistance of the simulation software SelmaGIS, coordinates for mid-points of each square were determined. These coordinates were entered in the GPS device. Thus the particular location marked was known. According to LCS (Lithuanian coordinates system) coordinates, we went to each location. Using GPS technology, exact location of exploratory trees was recorded in each study area. The location of exploratory trees was indicated on the area plan (Figure 3). During the study, dominant tree species were determined and all the species of lichen on the tree trunks and branches were examined. 86 trees in 9 out of 12 Raseiniai elderships were examined in total.

In urban areas sometimes mosses and lichens are found in not sufficient quantities. In such cases, transplant techniques have been used to monitor air pollution. One of these techniques consists in exposing bags containing lichen or moss in the studied area to measure concentrations of contaminants affecting the samples (Salo et al. 2012). Tree age can be estimated by counting tree-rings in each individual tree without any additional correction (Madrigal-Gonzalez et al. 2014). Stem diameter at breast height and tree height are used also for measures of tree growth (Sumida et al. 2013). Selection of trees for research in Raseiniai district municipality were carried out after consulting with foresters, which according to archival data, selected trees of the similar age. The old trees could have lichens extant there from the times when there was no pollution in this area (Gries 2003).

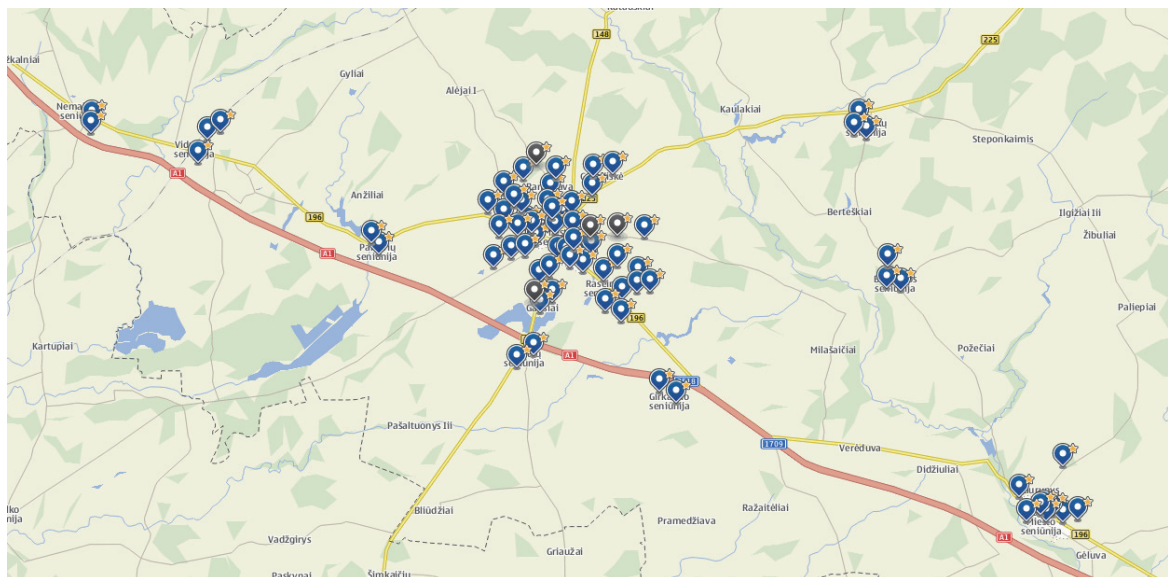


Fig. 3. Topographic map of the study area

Rys. 3. Mapa topograficzna badanego obszaru

Composition of lichen species was determined on each tree of selected species dominant in that area, and coverage in percent was studied using a grid (Figure 4). To this end, a frame in the height of 130-150 cm was placed from the northern side (it was determined using a compass built in the GPS device), and the percentage of area which covered the trunk with lichens was calculated. In order to get accurate results, the same trunk test was repeated 3-4 times and the average was calculated. The study was carried out covering not only Raseiniai and Ariogala

elderships and their surroundings, where main industry of Raseiniai district is situated, but also adjacent elderships: Nemaškiai, Viduklė, Paliepiei, Kalnujai, Girkalnis, Betygala and Pagojukai. Assuming that the concentration of pollutants in the ambient air starts to decrease when receding from the pollution sources, to confirm this hypothesis only a few points for the study were selected in the elderships distant from Raseiniai town. Coverage with lichens on the species of trees such as birch, oak, aspen, linden, maples and alders was measured during the study. Since the study methodology requires examination of the same species of trees, most frequently encountered species of trees – maples (*Acer platanoides*) birches (*Betula pendula*) and lindens (*Tilia cordata*) were chosen. The choice was influenced by the possibilities of comparison of results.

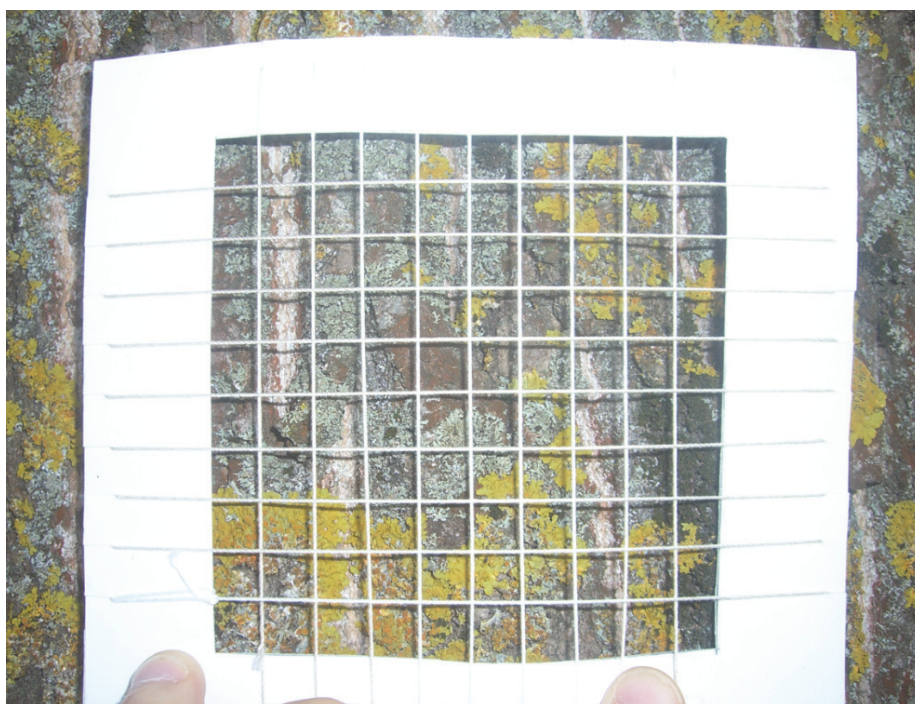


Fig. 4. Example of the sampling grid on a chestnut tree

Rys. 4. Przykład siatki do pobierania próbek na drzewie kasztanowca

According to studies, the area has been divided into zones, as it is required by the methodology (Table 1) (Stravinskienė 2010).

Table 1. Lichen distribution in zones according to their prevalence (Stravinskienė 2010)

Tabela 1. Rozkład porostów w strefach w zależności od ich występowania (Stravinskienė 2010)

Zone number	Zone description	Lichens coverage,%	Number of species in the sample
I	<i>Normal zone:</i> Various fruticose lichens, foliose lichens and crustose lichens can be found in this zone.	70-100%	10
II	<i>External resistance zone:</i> Lower number of fruticose lichens and foliose lichens. Crustose lichens are dominating.	50-70%	5-10
III	<i>Internal resistance zone:</i> Crustose lichens are dominating. Few foliose lichens might be found.	50%	No more than 5
IV	<i>Desert zone:</i> No lichens or few crustose lichens might be found in this zone. Desert zone is usually in large industrial areas.	0-20%	0.3

According to the experience of Lithuanian (Motiejūnaitė 2007) scientists and researchers from other countries, to describe the borderline of lichen areas not only the coverage rate of tree trunk was chosen, but also such indicators as: life-zones of lichens, number of species, frequency of different species.

2.3. Methodology of evaluation of SO₂ concentration

Distribution of lichens depends on the SO₂ concentration in ambient air. Lichen zones (Table 1) correspond to certain SO₂ concentrations in the exploratory ambient air (Table 2). Zoning of lichens in the cities has been known long, it is based on the resistance degree of different groups and species of lichens to harmful substances (toxic tolerance) (Stravinskienė 2009).

Coverage rate of lichens is obtained directly through the measurements with the grid (Fig. 4). When interpolating the range of SO₂ concentration (µg/m³) given in Table 2 according to the distribution of lichens (%), exact concentration of SO₂ in the range of each zone is calculated. The following calculations are carried out for each study area of Raseiniai district.

Table 2. Dependence of SO₂ concentration in ambient air on lichens coverage (Stravinskienė 2005)

Tabela 2. Zależność stężenia SO₂ w powietrzu od występowania porostów (Stravinskienė 2005)

Zone	Lichens coverage,%	Number of species in the sample	Concentration of SO ₂ , µg/m ³
I	70-100%	10	0-30
II	50-70%	5-10	30-40
III	50%	No more than 5	40-45
IV	0-20%	0.3	45-65

The concentration of SO₂ was analysed also by diffusive sampling method. In order to reduce uncertainty and the risk of data loss, three samplers were exposed in parallel at each of the sampling locations for a period of 2 weeks (August 10, 2016-August 23, 2016). A total numbers of 39 samples for SO₂ were collected. Passive samplers were exposed at 3-4 m height. The exposure time of each cartridge was 2 weeks. All samplers were placed in the special shelters to protect them from the rain and minimize the wind influence during the exposure. The places of passive samplers were selected according the principle - distance must be till 10 m from investigated trees (with lichens). The area of the samplers' exposure was open, free from buildings, trees and other objects, at least 1 m from any structures that could disrupt the airflow. During the transportation and forwarding for analysis, the passive samplers were sealed. After exposure, the diffusion samplers were analyzed in laboratory and the quantity of SO₂ was determined. According to air quality directive (2008/50/EC), the results of indicative measurements shall be taken into account for the assessment of air quality with respect to the limit values.

Statistical analysis

Descriptive statistical analysis was used (mean, standard deviations, confidence interval and Pearson coefficients). 95% confidence level was used. Data were analysed with Excel 2013.

3. Results

3.1. Lichen flora and coverage of lichens

86 trees have been studied in whole Raseiniai district. 9 different species of lichens were found on them, 20% of which were crustose (paint-like, flat), 45% foliose (leafy) and 35% fruticose (branched). The resulting percentage of distribution of lichens is given in Figure 5.

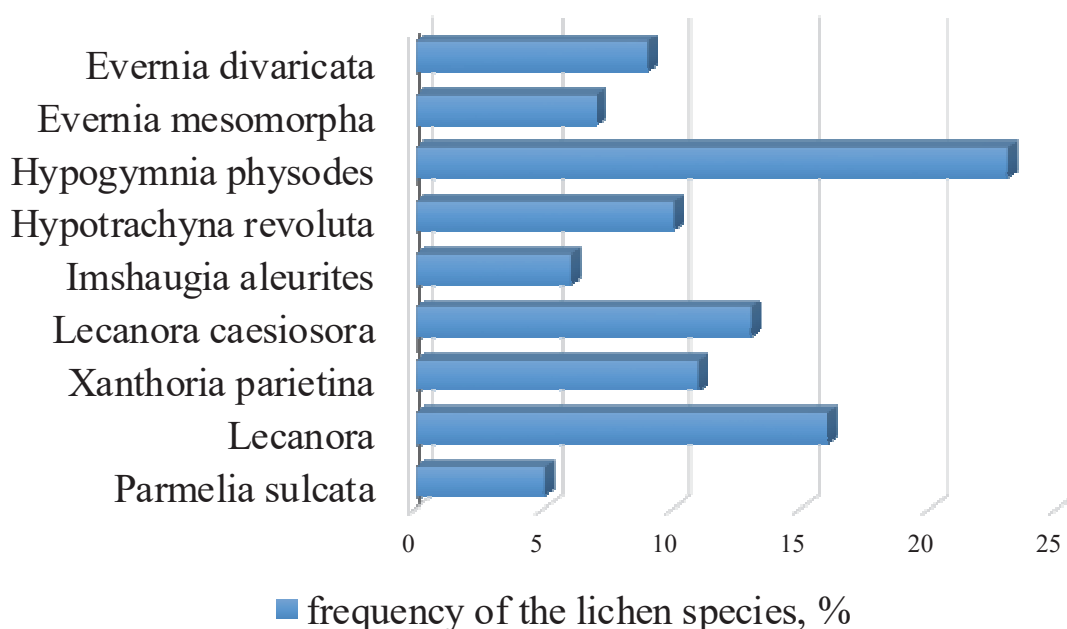


Fig. 5. List of the lichen species found on the study area

Rys. 5. Lista gatunków porostów znalezionych na badanym obszarze

Most of the trees studied were covered with lichens of type *Hypogymniarevoluta* (L.) (as much as 23%) and *Lecanora* (L.), (16%). Somewhat less *Xanthoria parietina* (L.) and *Lecanoracaesiosora* (L.) species of lichens were found on trees, respectively, they made 11% and 16% of the total amount of lichens found. Minimal amount of *Parmeliasulcata* (L.) (5%) and *Imshaugiaaleurites* (L.) (6%) species of lichens was found (Fig. 4).

Coverage of lichens (%) on the trunks of maple, birch and linden trees is shown in Figure 6. According to the average coverage area of lichens (Table 1), it was determined (Figure 6) that Raseiniai town and its surroundings (Gabšių and Andriušaičių villages) are attributed to zone III, i. e. moderate fighting zone, where the coverage rate of lichens is up to 50%, and the amount of species in each sample does not exceed 5. Ariogala and Paliepių elderships (Figure 6) are assigned to the same zone. Kalnujų, Pajokukų elderships and surroundings of Raseiniai town – Ramanava and Gruzdiškės – are attributed to zone II area, which is External (resistance) fighting zone. Percentage of fruticose (branched) lichens is decreased here, crustose (paint-like, flat) lichens begin to dominate, and amount of foliose (leafy) lichens decreases. Coverage rate of lichens on tree trunks ranges between 50-70%, and the number of species detected increases from 2-3 to 5-7. The remaining Nemakščiai, Betygala, Girkalnis and Viduklė elderships are attributed to zone I. This is a Normal zone. Various fruticose (branched), foliose (leafy) and crustose (paint-like, flat) lichens grow here. Coverage rate is up to 70-100%. Specific composition of lichens found here is the highest.

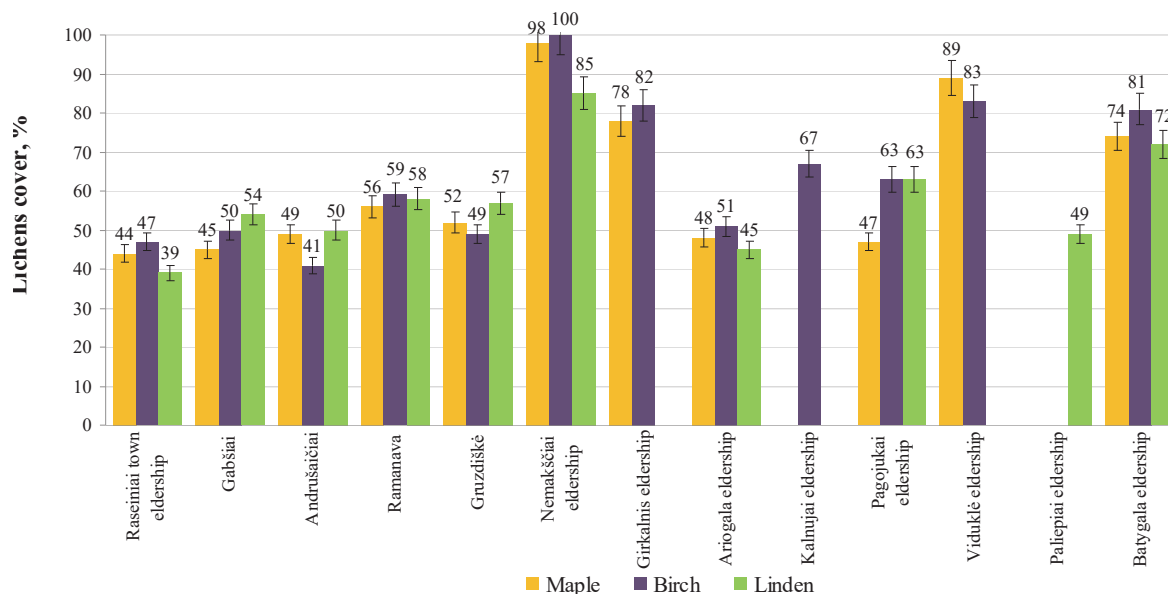


Fig. 6. Lichen ground-cover on tree stems in different investigation areas

Rys. 6. Stopień pokrycia pni drzew porostami w różnych obszarach badawczych

Amount of lichen species found on each tree trunk varies from 5 to 8. Measurement error is $\pm 5\%$.

3.2. Concentration of SO₂ according to lichens coverage

SO₂ concentration in Raseiniai district municipality

SO₂ is a respiratory irritant and bronchoconstrictor that has been associated with cardiovascular abnormalities including decrease in heart rate variability (Chen et al. 2012). Therefore, ambient SO₂ concentration must be controlled. Concentration of SO₂ according to the lichens is carried out according to the procedure described (Section 2.3). Values obtained are given in Figure 7.



Fig. 7. Concentration of SO₂ (µg/m³) in ambient air in Raseiniai district
Rys. 7. Stężenie SO₂ (µg/m³) w powietrzu w rejonie Raseiniai

Figure 7 shows that SO₂ concentration in Raseiniai town and its surroundings (Gabšiai, Andrušaičiai, Gruzdiškės) is the highest compared with other study areas, and ranges from 39 ± 2 µg/m³ to 41 ± 2 µg/m³. The same SO₂ concentration is attributed to Ariogala and Paliepiei elderships. Increase in concentration can be influenced by the main industry of Raseiniai district rallied in these places. The survey also found that the concentration of SO₂ in the ambient air decreases when receding from the pollution sources (major industrial enterprises of Raseiniai district). This is affected by the distribution of pollutants in space. Lower concentration of SO₂ was determined in Kalnujū, Pagojukū elderships and the settle-

ment Ramanava of Raseiniai town. Concentration in these areas varies between 31 ± 2 and 36 ± 2 $\mu\text{g}/\text{m}^3$. The lowest concentration of SO₂ is attributed to Nemaškiai and Viduklė elderships, where, respectively, SO₂ concentration is up to 4 ± 2 and 16 ± 2 $\mu\text{g}/\text{m}^3$. Calculation error is ± 2 $\mu\text{g}/\text{m}^3$. The lowest concentration in the whole Raseiniai district is influenced by the fact that most of these elderships are distant from the major industrial enterprises most.

The studies have shown that sulphur dioxide concentrations in Raseiniai district do not exceed the limitary values for pollution. Calculations of ground-level concentration of the ambient air pollutant were compared with the limitary value of pollution, approved by the Order No 591/640 of 11 December 2001 by the Ministers of Health and Environment of the Republic of Lithuania “Relating to the determination of standards for the ambient air pollution” (Official Gazette, 2001, No. 106-3827; 2010, No 2-87), where the maximum daily limitary value of SO₂ can be up to 125 $\mu\text{g}/\text{m}^3$.

SO₂ concentrations determined in Raseiniai district applying passive samplers varied from 2.0 ± 0.18 to 5.1 ± 0.50 $\mu\text{g}/\text{m}^3$ with average value of 3.5 $\mu\text{g}/\text{m}^3$.

The biggest SO₂ concentrations in ambient air were recorded in Raseiniai town (5.1 ± 0.50 $\mu\text{g}/\text{m}^3$) and the smallest concentrations – in Nemaškiai eldership (2.0 ± 0.18 $\mu\text{g}/\text{m}^3$). In other measurement points SO₂ concentrations were within 2.7 ± 0.26 - 4.5 ± 0.41 $\mu\text{g}/\text{m}^3$.

Evaluation of ambient air quality was carried out in 2010-2011 in Lithuania and concentration of sulphur dioxide, nitrogen dioxide and benzene were measured with passive samplers in 375 places. According to data of this measurements the biggest ambient air pollution with SO₂ was measured in Stonų street 4, Raseiniai, because in this place the biggest quantity of private houses. In other places of Raseiniai district municipality average SO₂ concentration was until approximately 1 $\mu\text{g}/\text{m}^3$ (Raseiniai... 2015). The average concentration of SO₂ applying passive samplers during different seasons in the Raseiniai district municipality in 2015-2016 year was set: 0.6 $\mu\text{g}/\text{m}^3$ in winter, 1.0 $\mu\text{g}/\text{m}^3$ in spring, 0.5 $\mu\text{g}/\text{m}^3$ in summer, 0.8 $\mu\text{g}/\text{m}^3$ in autumn. The increase in SO₂ concentrations during the spring season could be caused by heating of individual homes in the cold season. Pollution from individual residential houses may depend on the type of fuel used and its quality, as well as on the distribution of pollutants under adverse meteorological conditions.

The decreasing of SO₂ concentration in the summer season can be explained by decreasing of car traffic intensity.

Similar concentrations of sulphur dioxide were measured in other urban areas of Lithuania with medium and low population applying passive samplers. The measured concentration of sulphur dioxide with passive samplers in Visaginas municipality ambient air were in range from 0.3 to 4.0 µg/m³ in period from 2013 to 2017 year. Visaginas has 18 541 inhabitants in 2018 (Visaginas... 2017).

The concentration of sulphur dioxide measured with passive samplers in Anykščiai municipality ambient air (2017-2018) was in range from below 0.6 to 6.8 µg/m³. Anykščiai has 8848 inhabitants in 2018 year). (Research... 2018).

Table 3. SO₂ concentration measured with passive samplers

Tabela 3. Stężenie SO₂ zmierzone za pomocą próbników pasywnych

Place	SO ₂ , µg/m ³
Raseiniai town	5.1±0.50
Gabšiai	4.0±0.39
Andrušaičiai	4.3±0.41
Ramanava	4.0±0.44
Gruzdiškė	3.5±0.32
Nemakščiai	2.0±0.18
Girkalnis	2.7±0.25
Ariogala	4.5±0.41
Kalnujai	3.3±0.30
Pagojukai	3.0±0.28
Viduklė	2.7±0.26
Paliepiei	3.5±0.33
Batygala	2.9±0.27

Correlation between concentrations of SO₂ measured with lichens and passive samplers. There were significant statistical relationships between measured SO₂ concentrations with both methods when Pearson's correlation matrix was applied to the variables at a 95% confidence interval. A strong positive correlation ($r = 0.84$) between concentrations of SO₂ measured with lichens and passive samplers indicates

that lichens can be applied for approximate evaluation of SO₂ concentrations in ambient air.

4. Conclusions

1. The comparison of two different methods for air quality evaluation – application of passive sampling method and bio indication method with lichens was done. There were significant statistical relationships between measured SO₂ concentrations with both methods when Pearson's correlation matrix was applied to the variables at a 95% confidence interval. A strong positive correlation ($r = 0.84$) between concentrations of SO₂ measured with lichens and passive samplers suggests the application of lichens as a primary tool in determining the spatial distribution of airborne pollutant, e.g. SO₂.
2. Lichens are well suited for biomonitoring studies, since they effectively accumulate the atmospheric pollution and they can be applied to monitor temporal and spatial distribution of air pollution effects.
3. The study results show that the highest concentration of SO₂ in the ambient air determined applying bio indication method was found in Raseiniai district ($41 \pm 2 \mu\text{g}/\text{m}^3$) and its surroundings (Gabšiai ($40 \pm 2 \mu\text{g}/\text{m}^3$), Andrušaičiai ($41 \pm 2 \mu\text{g}/\text{m}^3$) and Gruzdiškės ($39 \pm 2 \mu\text{g}/\text{m}^3$). The highest concentration of SO₂ in the ambient air determined applying passive samplers was in Raseiniai district ($5.1 \pm 0.50 \mu\text{g}/\text{m}^3$) and its surroundings (Gabšiai ($4.0 \pm 0.39 \mu\text{g}/\text{m}^3$), Andrušaičiai ($4.3 \pm 0.41 \mu\text{g}/\text{m}^3$) and Gruzdiškės ($3.5 \pm 0.32 \mu\text{g}/\text{m}^3$).
4. The lowest concentration of SO₂ was determined in the Nemaškiai and Viduklė elderships where, respectively, the concentration of SO₂ was 4 ± 2 and $16 \pm 2 \mu\text{g}/\text{m}^3$ determined applying lichens and 2.0 ± 0.18 and $2.7 \pm 0.26 \mu\text{g}/\text{m}^3$ applying passive samplers. The lowest concentrations in investigated elderships are influenced by the fact that they are distant from the major industrial enterprises.
5. Applying of lichens and passive samplers indicated that road traffic and industrial activities are significant emission sources of SO₂ in region of Raseiniai district municipality, Lithuania. Study showed that concentration of SO₂ as strictly regulated air pollutant by EU Directives 2008/50/EC and 2000/69/EC did not exceed set threshold $125 \mu\text{g}/\text{m}^3$ in the Raseiniai district municipality during the study period in August 2016. It can be assumed that air quality in the considered area is high.

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Pomiar zanieczyszczenia powietrza atmosferycznego SO₂ z zastosowaniem porostów i próbników pasywnych

Streszczenie

Możliwe jest przeanalizowanie negatywnego wpływu na jakość powietrza w środowisku poprzez zastosowanie bio-indykatywnej reakcji żywych organizmów na zanieczyszczenia. Porosty (*Lichenes* L.) są bardzo wrażliwe na zanieczyszczenia gazowe, więc można je wykorzystać do oceny zanieczyszczenia powietrza. Trzyście punktów w okręgu Raseiniai zostało wybranych do pomiarów stężenia dwutlenku siarki w powietrzu z użyciem porostów i próbników pasywnych dla porównania. Zmierzone wartości stężeń SO₂ porównano z wartościami granicznymi ustalonymi dla tego zanieczyszczenia w powietrzu zgodnie w dyrektywach 2008/50/WE i 2000/69/WE. Stężenia SO₂ określone za pomocą porostów były wyższe niż uzyskane za pomocą próbników pasywnych, ale w obu przypadkach były one niskie i nie osiągały wartości granicznych w powietrzu. Im dalej od górnych źródeł zanieczyszczeń (główne przedsiębiorstwa przemysłowe w okręgu Raseiniai) tym wartości stężenia SO₂ w powietrzu spadały. Średnie stężenia SO₂ w powietrzu w rejonie Raseiniai nie osiągnęły dopuszczalnych wartości granicznych dla powietrza atmosferycznego (125 µg/m³) w okresie badania (w sierpniu 2016 r.). Wyniki badań wskazują, że najwyższe stężenie SO₂ w powietrzu określone z użyciem porostów były w rejonie Raseiniai (41±2,0 µg/m³) i jego otoczeniu (Gabsiai (40±2,0 µg/m³), Andrušaičiai (41±2,0 µg/m³) i Gruzdiškės (39±2,0 µg/m³). Najwyższe stężenie SO₂ w powietrzu zmierzone próbnikami pasywnymi było w rejonie Raseiniai (5,1±0,50 µg/m³) i jego otoczeniu (Gabsiai (4,0±0,39 µg/m³), Andrušaičiai (4,3±0,41 µg/m³) i Gruzdiškės (3,5 µg/m³). Najniższe stężenie SO₂ zmierzono z zastosowaniem porostów w Nemakščiai i Viduklė (4±2,0 µg/m³ i 16±2,0 µg/m³) i 2,0±0,18 µg/m³ oraz 2,7±0,26 µg/m³ z zastosowaniem próbników pasywnych. Stwierdzono istotne zależności statystyczne między zmierzonymi stężeniami SO₂ stosując obie metody. Zastosowano macierz korelacji Pearsona dla zmiennych w przy 95% przedziale ufności. Silna dodatnia korelacja (r = 0,84) między stężeniami SO₂ mierzonymi za pomocą porostów i próbników pasywnych wskazuje, że porosty można stosować do oceny stężeń SO₂ w powietrzu. Najniższe stężenia w badanych starostwach spowodowane są ich odległością od głównych zakładów przemysłowych i obiektów energetycznych.

Abstract

It is possible to analyse a negative impact on environmental air quality by using living organism's bio indicative reaction to pollutants. Lichens (*Lichenes* L.) are very sensitive to gaseous pollutants so may be used to evaluate air pollution. Thirteen points in Raseiniai district were selected for measurements of sulphur dioxide concentrations in ambient air using lichens and passive samplers for comparing. Measured values of SO₂ concentrations were compared with limit values set for this pollutant in ambient air according to 2008/50/EC and 2000/69/EC directives. SO₂ concentrations determined with lichens was bigger than determined with passive samplers, but in both cases, they were low and did not reach permissible limitary values in ambient air. Further from, the main pollution sources (main industrial enterprises in Raseiniai district) values of SO₂ concentration in the ambient air gradually decreased. Average SO₂ concentrations in ambient air of Raseiniai district did not reach permissible limitary values set for ambient air (125 µg/m³) during the study period in August 2016. The study results show that the highest concentration of SO₂ in the ambient air determined applying lichens was in Raseiniai district (41±2.0 µg/m³) and its surroundings (Gabšiai (40±2.0 µg/m³), Andrušaičiai (41±2.0 µg/m³) and Gruzdiškės (39±2.0 µg/m³)). The study results show that the highest concentration of SO₂ in the ambient air determined applying passive samplers was in Raseiniai district (5.1±0.50 µg/m³) and its surroundings (Gabšiai (4.0±0.39 µg/m³), Andrušaičiai (4.3±0.41 µg/m³) and Gruzdiškės (3.5 µg/m³)). The lowest concentration of SO₂ was determined in the Nemakščiai and Viduklė elderships where, respectively, the concentration of SO₂ was 4±2.0 µg/m³ and 16±2.0 µg/m³ determined applying lichens and 2.0±0.18 µg/m³ and 2.7±0.26 µg/m³ applying passive samplers. There were significant statistical relationships between measured SO₂ concentrations with both methods when Pearson's correlation matrix was applied to the variables at a 95% confidence interval. A strong positive correlation (r = 0.84) between concentrations of SO₂ measured with lichens and passive samplers indicates that lichens can be applied for approximation evaluation of SO₂ concentrations in ambient air. The lowest concentrations in investigated elderships are influenced by the fact that they are distant from the major industrial enterprises and energetic objects.

Słowa kluczowe:

zanieczyszczenie powietrza, porosty (*Lichenes* L.), SO₂, wskaźniki biologiczne, próbniki pasywne, powiat Raseiniai

Keywords:

air pollution, lichens (*Lichenes* L.), SO₂, bio-indicators, passive samplers, Raseiniai district



CFD Model of SNCR with Shifting Effect of CO

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1. Introduction

The retrofitting of large coal fired boilers with NO_x control systems has been concluded in Western Europe many years ago. Since the selective catalytic reduction process (SCR) was considered as the best available technology (BAT) in the eighties and nineties, most of the boilers are equipped with SCR now (Dąbrowski at al. 2013).

The SNCR process has been considerably improved during the last years for small and medium sized boilers burning municipal and industrial waste, biomass, sludge, etc. These types of boilers are generally designed in such a way that the first flue gas pass is free of heat exchangers so that the injection and distribution of the reagent into the optimum temperature window can easily be realized. Since, for these applications, NO_x limits of 100 mg/Nm³ and lower can now be achieved and maintained at all operating conditions, the SNCR process represents today the 'Best Available Technology' (BAT). Therefore more and more owners of waste-to-energy plants replace their existing SCR NO_x control system by SNCR technology because of the low operating costs at comparable performance.

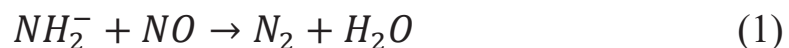
The kinetic behavior of the deNO_x process is very complex and there are not many studies providing experimental information from laboratory-scale combustors operating with this process. Tayyeb et al. presented an experimental investigation concerned with an assessment of additives such as CO and H₂ on urea deNO_x over a temperature range of 850–1200°C. They observed that both of the additives have significant influence on the process performance with H₂ being observed to be more profound on the NO_x reduction performance. A shift of 215°C was observed in peak reduction temperature with the addition of CO in flue gas up to 1000 ppm, whereas the kinetic modeling suggested 150°C. The discrepancy was due to the plateau of about 100°C noticed during the experimental observations without injection of any additive. The addition of H₂ had a significant influence on the process performance and a downward shift of 275°C in the peak reduction temperature was observed although with an impaired efficiency (Tayyeb et al. 2008). Zhou et al. confirmed that CO can lower the SNCR reaction temperature, narrow the temperature region and reduce the maximum NO_x removal efficiency. The higher the CO volume fraction is, the more obvious changes will be (Zhou et al. 2015).

Since emission limits and operating costs are still increasing, it is necessary to use modern methods, such as CFD simulation, to help efficiently manage the deNO_x process. At present, there are SNCR models, but they are so simplified that they do not affect a range of influences, such as the temperature window shifts depending on the CO concentration at the injection area. By including these phenomena, and by expanding the CFD simulation of these effects, far more accurate simulations can be achieved. This is necessary to estimate the efficiency of SNCR technology and the subsequent design of the injection nozzles and their location. During last years CFD models of SNCR have been improved and modified with respect to current computer performance. Nowadays, researchers focus on extending the original 9-step kinetics mechanism of SNCR (Modliński 2015, Musa et al. 2013).

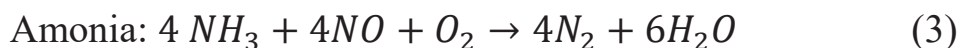
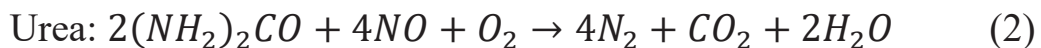
The main objective of this paper is the modification of original 9-step kinetics mechanism of SNCR in such a way that it is able to predict the effect of CO and modification of the kinetics mechanism of SNCR model for practical application in CFD codes.

2. Elementary Chemistry of SNCR Technology

Selective Non-Catalytic Reduction (SNCR) technology is based on injection of reductant in aqueous solution (Urea solution, Ammonia water) or in gaseous form (Ammonia) into hot flue gas downstream of main combustion zone where nitrogen oxides NO_x are reduced by amine radical NH_2^- to molecular nitrogen N_2 and water vapour H_2O . A dominant chemical reaction is very simple and defined by the following chemical formula (Kohl et al. 1997, Von der Heide 2008):



Basically, both urea solution and ammonia water are usually used for the NO_x reduction in combustion plants at the present. The SNCR process can be described by the following chemical net reaction (Kohl et al. 1997, Von der Heide 2008):



Depending on the application both reductants have specific advantages and disadvantages. For an optimum NO_x reduction with a minimum NH_3 slip it is “only” necessary to evenly distribute and thoroughly mix the reductant in the flue gases within the appropriate temperature window in which a NO_x reduction is possible. The optimum temperature range to achieve a high NO_x reduction together with a minimum consumption of reductant and a low ammonia slip is rather narrow and mainly depends on the flue gas composition.

The main problem of SNCR method is a relatively narrow temperature window (870-1050°C). For coal-fired boilers the optimum temperature lies between ca 960 and 1020°C, which is so called “temperature window”, what is presented in Fig. 1.

Above this temperature range ammonia is oxidised to an increasing extent and, e.g. nitrogen oxides are formed. At lower temperatures the reaction rate is slowed down, causing an ammonia slip, which may result in the formation of ammonia salts like ammonium sulphate and ammonium bisulphate and may lead to secondary problems, downstream the flue gas path. Therefore, the ammonia slip should be kept at a minimum. The objective of all NO_x control technologies is to reach

a high NO_x reduction with a minimum consumption of reagent while the ammonia slip must be kept low at the same time. This only can be achieved with an even distribution of the reagents in the flue gas at the right temperature. In the following part of this article we will focus on effect of CO and exact specification of shift of the temperature window.

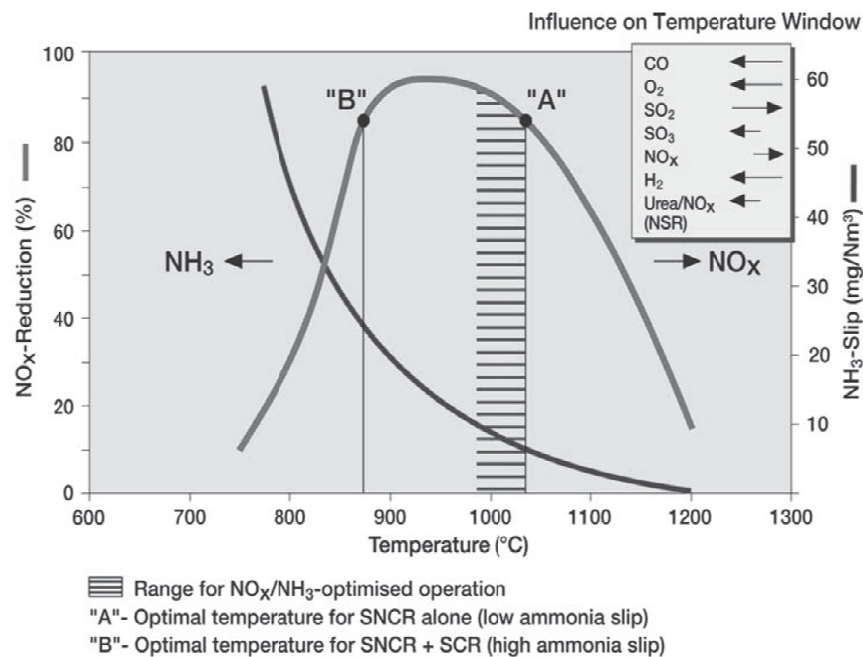
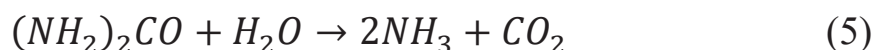


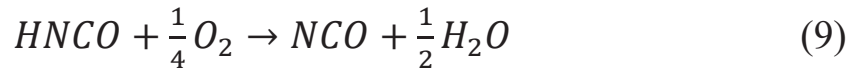
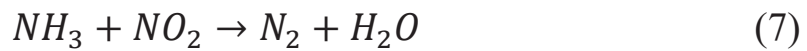
Fig. 1. NO_x reduction as a function of temperature and composition of flue gas (Von der Heide 2008)

Rys. 1. Redukcja NO_x w funkcji temperatury i składu spalin (Von der Heide 2008)

3. SNCR Chemical Kinetics Model

Proposed model of SNCR technology with urea solution, as a reagent, is based on nine-step kinetic mechanism proposed by Brouwer (Brouwer et al. 1996). The origin nine-step mechanism was modified to exclude the radical NH_2^- due to removal of problematic non-stable transitional material. This model also includes two-way mechanism for breakdown of urea into ammonia NH_3 and radical HNCO .





Chemical reactions included in CFD algorithm are usually based on the Arrhenius equation, which describes the reaction rate:

$$k = A \cdot e^{\frac{-E}{R \cdot T}} \cdot T^\beta \left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right] \quad (13)$$

where:

k – reaction rate, A – pre-exponential factor, E – activation energy, R – universal gas constant, T – temperature, β – temperature exponent, n – the sum of the number of reaction orders. The Table 1 lists the kinetic parameters of the individual equations.

Table 1. Kinetic parameters of SNCR model

Tabela 1. Parametry kinetyczne modelu SNCR

Reaction	A $\left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right]$	β [1]	E $\left[\frac{J}{mol} \right]$	n [1]
(4)	1.27E+04	0	65048	1; [(NH ₂) ₂ CO] ¹
(5)	6.13E+04	0	87819	2; [(NH ₂) ₂ CO] ¹ ; [H ₂ O] ¹
(6)	4.20 E+02	5,3	315937	2; [NH ₃] ¹ ; [NO] ¹
(7)	4.20E+02	5.3	349937	2; [NH ₃] ¹ ; [NO ₂] ¹
(8)	3.50E-03	7.65	544487	2; [NH ₃] ¹ ; [O ₂] ¹

Table 1. cont.

Tabela 1. cd.

Reaction	A $\left[\left(\frac{\text{mol}}{\text{m}^3}\right)^{1-n} \cdot \frac{\text{K}^{-\beta}}{\text{s}}\right]$	β [1]	E $\left[\frac{\text{J}}{\text{mol}}\right]$	n [1]
(9)	6.24E+09	0.85	284637	1.25; [HNCO] ¹ ; [O ₂] ¹
(10)	1.00E+07	0	-1632	2; [NCO] ¹ ; [NO] ¹
(11)	6.90E+12	-2.5	151075	1; [N ₂ O] ¹
(12)	1.26E+06	0	167742	1.75; [CO] ¹ ; [O ₂] ^{0.25} ; [H ₂ O] ^{0.5}

4. Influence of CO – Temperature Shift

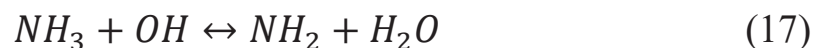
The influence of CO on the SNCR process indicates that the presence of CO shifts the selectivity, by increasing the rate of NH₂[·] formation and the rate of NH₃ oxidation, to NO. Higher CO level shifts the optimal temperature for NO reduction to lower temperatures due to enhanced chemical rates in presence of CO. The shift in the selectivity is accomplished by two mechanisms:

- increasing local temperature,
- increasing net production of OH radical.

The first effect is due to exothermicity of the main CO burnout reaction (14), while the second effects is due to chain branching that results from the H produced in this reaction (Kohl at al. 1997):



Presence of CO in injection area products radical OH[·], which leads to high concentration of NH₂[·] radical (see eq. 17-18).



Higher concentration of CO in injection zone leads to shift the temperature window towards lower temperatures (Fig. 2) and/or increase the efficiency of NO_x reduction.

The contribution of CO oxidation to the local temperature is accounted for in the model. Empirical adjustment to the rates is used to account for the effect of CO without including details radical chemistry. The empirical adjustment is applied in the form of shift in effective temperature to account for the radical chemistry effects of CO as follows.

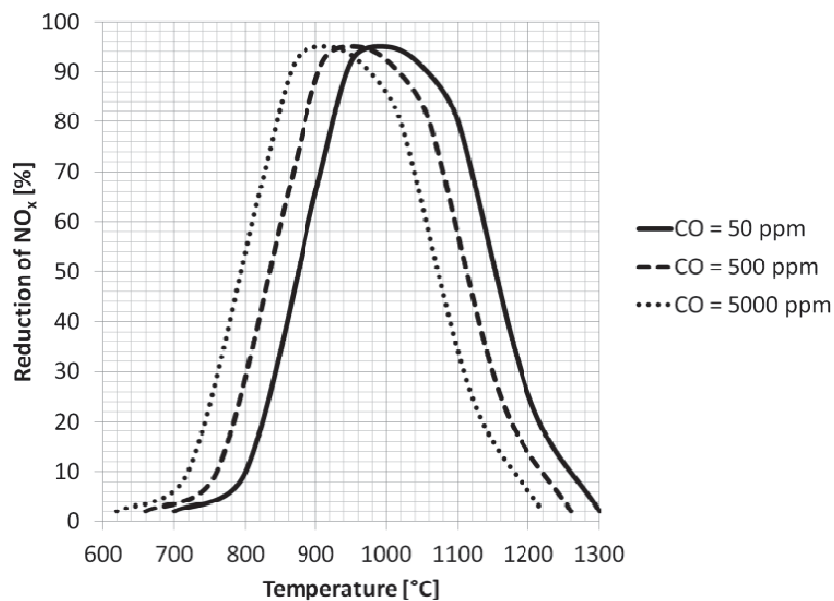


Fig. 2. Temperature shift as a function of CO concentration

Rys. 2. Przesunięcia temperatury w funkcji stężenia CO

Brouwer proposed a modification of reactions rate for reactions (6-9) as follows (Brouwer et al. 1996):

$$k = A \cdot e^{\frac{-E}{R(T+S_{CO})}} \cdot (T + S_{CO})^{\beta} \quad (19)$$

S_{CO} is the shift in the temperature required to achieve the same NO reduction and reagent decomposition compared to the case without CO.

$$S_{CO} = 17.5 \ln(X_{CO}) + 173 \quad (20)$$

where:

X_{CO} – volume fraction of CO.

Application of modified rate of reaction is not possible to set in CFD code ANSYS CFX. Analysis of equations (19) and (20) shows that the equation (19) can be simplified as follows and term X_{CO}^γ describes CO shift in simplified form.

$$k = A \cdot X_{CO}^\gamma \cdot e^{\frac{-E}{R \cdot T}} \cdot T^\beta \left[\left(\frac{\text{mol}}{\text{m}^3} \right)^{1-n} \cdot \frac{\text{K}^{-\beta}}{\text{s}} \right] \quad (21)$$

Kinetic parameters of SNCR model with CO shift are presented in table 2.

Table 2. Kinetics parameters of SNCR model with CO shift

Tabela 2. Parametry kinetyczne modelu SNCR z przesunięciem CO

Reaction	A $\left[\left(\frac{\text{mol}}{\text{m}^3} \right)^{1-n} \cdot \frac{\text{K}^{-\beta}}{\text{s}} \right]$	β [1]	γ [1]	E $\left[\frac{\text{J}}{\text{mol}} \right]$	n [1]
(6)	8.63E+04	5.27	0.58	311822	2; [NH ₃] ¹ ; [NO] ¹
(7)	1.39E+05	5.27	0.63	345403	2; [NH ₃] ¹ ; [NO ₂] ¹
(8)	2.63E+01	7.61	0.97	537456	2; [NH ₃] ¹ ; [O ₂] ¹
(9)	3.88E+11	0.84	0.46	281090	1.25; [HNCO] ¹ ; [O ₂] ¹

5. CFD Model of SNCR Technology

Proposed kinetics model of SNCR was checked by the comparison with several experimental data, which are available in studies. Reduction of NO_x depending on temperature of flue gas and reduction of NO_x depending on stoichiometric ratio β was confronted with experimental results, which are generally validated.

The constant improvement of computer resources is providing a continuous increase of the use of computational fluids dynamics in various branches of engineering. Nowadays they are supplied not only to optimise aerodynamic equipment, but also to simulate typical industrial processes, such as SNCR. The main advantage of CFD codes is their capability to describe complex processes in detail (detail simulation of reagent injection in combustion chamber), thus avoiding the simplifying assumption required to solve the lumped-parameters model.

The simplified kinetics model was tested by means of CFD simulation of simply real-size reactor, showed in Fig. 3, in typical industrial condition, such as real composition of flue gas, spraying of reagent etc.

The simulation of SNCR process was realized as solution with constant residence time. Residence time specifies the time of all chemical compounds interaction. A lot of conditions of simulation and experimental research data were the same. The mathematical background of multi-phase flow with chemical reaction is discussed in several books, which basically deal with numerical simulation of the turbulent fluid flow.

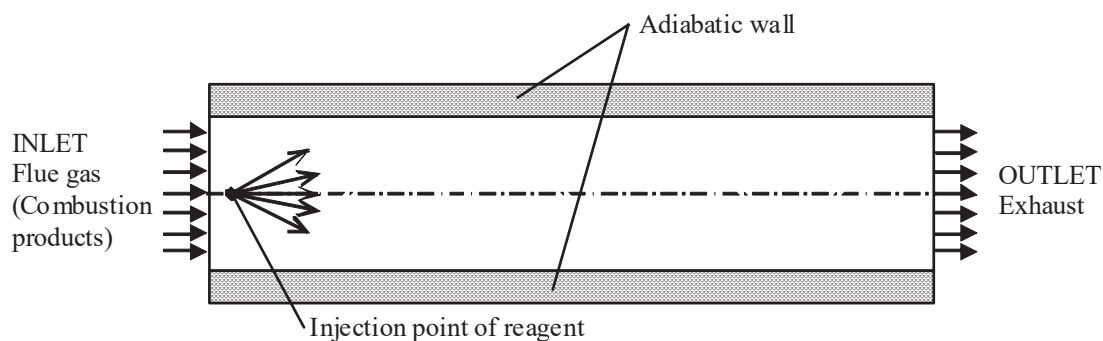


Fig. 3. Basic design of test reactor

Rys. 3. Schemat reaktora badawczego

At first there was investigated the influence of coupling the CFD with the simplified kinetics model previously discussed. The effect of turbulence was modelled using standard $k-\varepsilon$ approaches. The classical approach to model of turbulent flows is based on single point averages of the Navier-Stokes equations. These are commonly called Reynolds Averaged Navier-Stokes Equations (RANS). The most simple model for turbulent flow is $k-\varepsilon$ one. Even though it certainly is the best compromise for engineering design using RANS approach.

6. Results of CFD simulation

The results obtained with the simplified kinetics model of test reactor CFD simulation are presented in Fig. 4.

Analyzing the figure one can see that, in spite of the severe limitations of this kinetics model, it is able to reproduce the main trends evidenced experimentally. In particular, it is worthwhile to mention that in the low temperature range the prediction of the CFD model is equal to the experimental data. Moreover, one can see that in the high temperature

region the CFD model predicts lower NO reduction in good agreement with experimental measurements. This is an important point since it means that the CFD model is able to identify correctly the transition from the region where chemical kinetics reaction controls from the one where mixing become controlling.

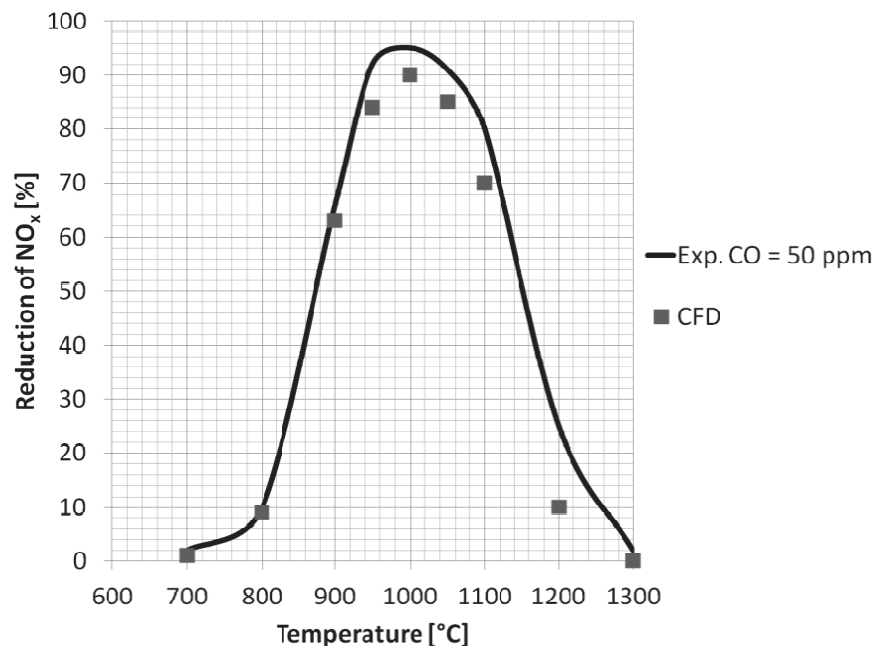


Fig. 4. Comparison of NO_x reduction - temperature window given by experimental data and simplified kinetics CFD model with concentration of CO = 50 ppm

Rys.4. Redukcja NO_x w funkcji temperatury. Wyniki eksperymentalne i z modelu kinetycznego CFD dla stężenia CO = 50 ppm

However, this also means on one side that reduced kinetics model provide roughly the same characteristics time for reaction, and on the other side that the influence of mixing has to be mainly ascribed to macroscopic phenomena. In spite of some quantitative discrepancies among the model predictions are evident, it is also evident that the main quantitative features (maximal reduction of NO located around 970-1020°C) are well reproduced by the simplified kinetics model.

Next, CFD simulations for a modified model, involving the influence of CO, were calculated. CO shift was simulated for lower and higher concentration of CO = 20 and 200 ppm respectively. Figures 5 and 6 illustrate the CO temperature shift.

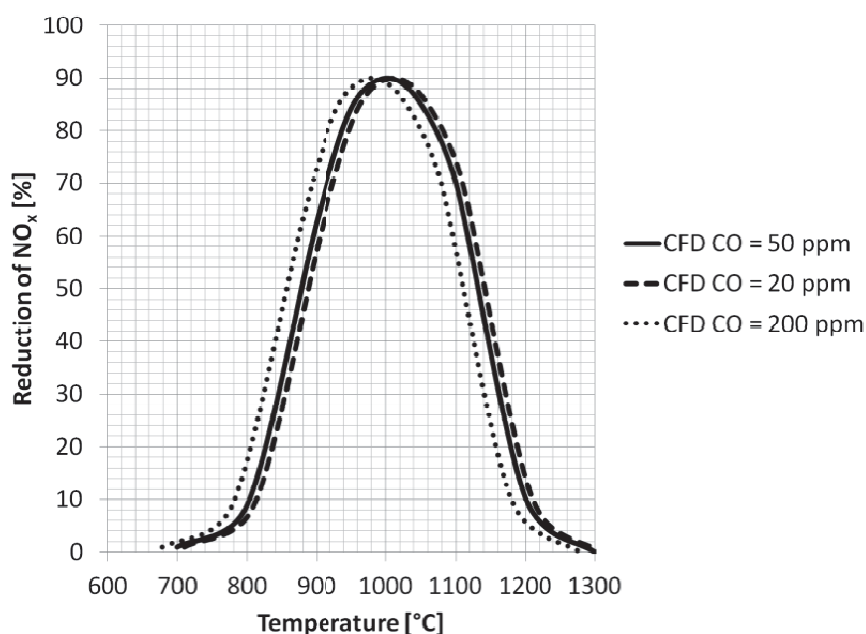


Fig. 5. CO temperature shift calculated by CFD simulation with modified mechanism

Rys. 5. Przesunięcie temperaturowe dla różnych stężeń CO obliczone za pomocą symulacji CFD ze zmodyfikowanym mechanizmem

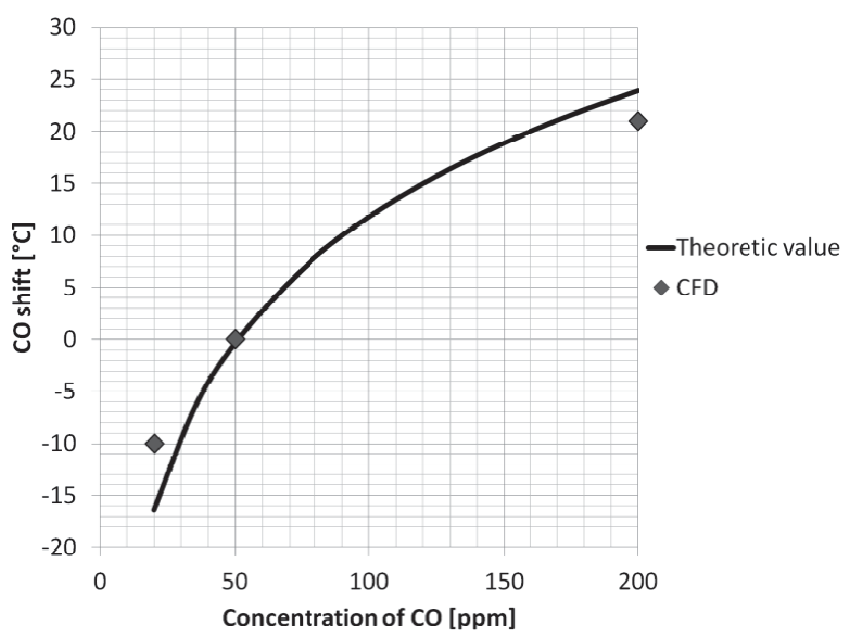


Fig. 6. Comparison of CO temperature shift calculated with empirical adjustment (19), (20) and CFD model with modified mechanism

Rys. 6. Przesunięcie temperaturowe CO obliczone na podstawie założeń empirycznych (19), (20) i modelu CFD ze zmodyfikowanym mechanizmem

7. Conclusions

Over many years of experiences in continuous operation in various combustion plants, the SNCR process has proven to be a reliable and economical solution for NO_x reduction fulfilling the required NO_x limits. In the discussed power plants all guarantees were satisfied and in many cases exceeded by far. From the process point of view, it is practically of no relevance whether urea solution, ammonia water or a mixture of both is used as reagent. If a plant is engineered, installed and operated appropriately, neither media is expected to have an impact on the availability of the overall plant.

Furthermore, all technological measures like optimizing the combustion and flue gas recirculation should be taken if they are technically feasible as well as commercially justified. New boilers could be designed in such a way that they meet the requirement of SNCR, which is basically an extension of the space in the area of the injection levels. The invest cost would be negligible in comparison to the cost of the whole boiler. The application of the SNCR technology for large power boilers still leaves open questions and not all problems are solved yet. However, the situation was not much different five years ago for waste incinerators. Today NO_x levels $< 100 \text{ mg/Nm}^3$ are state of the art.

Still increasing pressure to reduce NO_x and increase the efficiency of the SNCR method (small ammonia slip) cause intensive optimization of SNCR technology, which cannot be done without modern methods such as CFD simulations. The proposed CFD model of SNCR technology with CO temperature shift could be used for optimisation of SNCR technology at the stage of the basic and detailed design.

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Modelowanie procesów SNCR uwzględnieniem efektu przesunięcia w zakresie CO

Streszczenie

Artykuł przedstawia wyniki symulacji procesów SNCR z wykorzystaniem obliczeń CFD z uwzględnieniem przesunięcia temperaturowego związanego z obecnością CO oraz parametrów kinetycznych przedstawionych w tekście reakcji chemicznych. Wpływ CO na proces SNCR opisuje empiryczna korekta parametrów kinetyki reakcji chemicznych. Wyniki symulacji CFD porównano z wynikami pomiarów eksperymentalnych. Chociaż proponowany kinetyczny model technologii SNCR jest uproszczony, to jest w stanie opisać redukcję NO_x, z uwzględnieniem wielu parametrów technologii SNCR, z dobrą precyzją. Opisany model może być wykorzystany na etapie projektowania instalacji SNCR uwzględniając m.in. miejsca iniekcji i układ lanc.

Abstract

The paper deals with CFD simulation of SNCR technology with implemented CO temperature shift. The influence of CO on the SNCR process is described by empirical adjustment of kinetics parameters of chemical reactions. Results of CFD simulation were compared with results of experimental measurements. Although the proposed kinetics model of SNCR technology is simplified, it is able to describe reduction of NO_x and other phenomena of SNCR with good precision. The model can be used to verify of injection levels and injection lances arrangement at design phase.

Słowa kluczowe:

technologia SNCR, roztwór mocznika, tlenki azotu NO_x, usuwanie NO_x

Keywords:

SNCR technology, Urea solution, NO_x nitrogen oxides, NO_x removal



Characteristics of Bottom Ash from Municipal Solid Waste Incineration

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1. Introduction

Increasing population, rapid urbanization and developing living standards generates large amounts of municipal waste (Jin et al. 2012, Arena & Di Gregorio 2014, Lin et al. 2015, Adamcová et al. 2016). Therefore, collection, recycling, treatment and disposal of increasing quantities of solid waste are a big challenge for municipalities, and therefore waste management is one of the main priorities of environmental protection (Turskis et al. 2012, Pinto et al. 2014, Tan et al. 2014). The Integrated Solid Waste Management (ISWM) includes several solutions to reduce negative impact on the environment and mankind. This alternative combines the reduction of waste generation, the materials recovery, the recycling, the energy recovery and waste landfilling (Leme et al. 2014).

In many countries, after recovery of recyclable materials, a large part of municipal solid waste (MSW) is disposed in landfills (Ferraris et al. 2009, Ghinea & Gavrilesco 2016). In recent years biofuel production from agricultural waste and biomass as well as waste-to-energy (WTE) technologies from MSW have been actively investigated (Ng et al. 2014). WTE is widely used in many countries around the world, and one such technology is MSW incineration (Rocca et al. 2012, Zhou et al. 2015).

Using municipal solid waste incineration (MSWI) can help recover energy (heat and electricity) and reduce the waste volume by 90% (the waste mass by 70%) (Veli et al. 2008, Santos et al. 2013, Zhou et al.

2014, Rentizelas et al. 2014). During the incineration process, different gaseous emission and solid residues are generated. Two main types of by-products are fly ash (FA) and bottom ash (BA), the latter accounting for 80-85% of all the residues (Cornelis et al. 2012, Allegrini et al. 2014, Lin et al. 2015, Tang et al. 2015, Di Gianfilippo et al. 2016, Holm & Simon 2017). BA contains inorganic matter (stone, ceramic, glass), ferrous and non-ferrous metals and small quantities of unburned organic matter (plastic, fibre, wood etc.) (Tang et al. 2015, Allegrini et al. 2016, Chang et al. 2015). Unlike FA, BA is classified as non-hazardous waste by the European Waste Catalogue. MSWI bottom ash is composed mainly of silica, alumina, calcium and iron oxide, which are natural aggregate compounds (Del Valle-Zermeño et al. 2015, Su et al. 2013, Del Valle-Zermeño et al. 2016, Xia et al. 2017,). BA properties differ from plant to plant and from country to country (Zekkos et al. 2013). Table 1 presents the chemical compositions of BA that was generated in MSWI plants in various European countries.

Also, without these oxides in BA were found soluble salts, such as chlorides, sulphates, fluorides, bromides, and many heavy metals, such as copper, zinc, lead, chrome, nickel and cadmium. Research on BA composition carried out in various countries showed the presence of high amounts of chlorides (up to 5,900 mg kg⁻¹), sulphates (up to 7,000 mg kg⁻¹) (Santos et al., 2013, Lin et al., 2015, Tang et al., 2015) and heavy metals, such as zinc (903-7,732 mg kg⁻¹), lead (1,022-4,552 mg kg⁻¹), copper (1,041-7,743 mg kg⁻¹) and barium (1,300-3,920 mg kg⁻¹). In addition, chromium, nickel and arsenic were found (Rambaldi et al. 2010, Bayuseno & Schmahl 2010, Su et al. 2013, Tang et al. 2016).

Landfilling and using in civil engineering are the most commonly used BA management technologies in the world (Ore et al. 2007, Haiying et al. 2011, Torlando et al. 2013, Gori et al. 2013, Del Valle-Zermeño et al. 2014b). Owing to atmospheric precipitation and various chemical reactions in landfills, leachate is formed. It contains various heavy metals and salts. A leachate can cause harmful effects in soil and underground water if it gets into the environment (Yao et al. 2014, Mucsi et al. 2016).

Table 1. Chemical composition of major oxides in MSWI bottom ash in various European countries

Tabela 1. Skład chemiczny podstawowych tlenków w popiele dennym ze spalania stałych odpadów komunalnych (SOK) w różnych krajach europejskich

Oxide	Amount, % wt						
	Netherlands (Tang et al. 2015)	Spain (Del Valle-Zermeño et al. 2014a)	Italy (Rambaldi et al. 2010)	Germany (Müller & Rübner, 2006)	Slovenia (Jurič et al. 2006)	Sweden (Lidelöv & Lagerkvist 2007)	France (Rednek et al. 2007)
SiO ₂	54.23	43.3	33.70	55.70	24.00	37.00	47.82
CaO	13.45	16.9	35.00	11.9	39.00	15.00	15.99
Fe ₂ O ₃	13.83	14.1	5.37	8.80	2.70	15.00	6.23
Na ₂ O	2.81	7.58	2.27	1.40	0.90	0.28	6.34
Al ₂ O ₃	7.86	5.80	13.31	14.1	14.8	13.00	8.63
MgO	1.81	2.22	4.62	2.70	1.70	0.25	2.38
K ₂ O	0.88	1.11	1.66	1.2	0.20	0.14	n. d.

Note: n. d. – no data

The aim of this study is to determine the chemical composition of the BA, and eluate parameters such as quantities of heavy metals, chlorides and sulphates, and pH. In this study, the bottom ashes were provided by the waste-to-energy plant, which is located in Klaipėda, in Lithuania. The incineration plant in Klaipėda became operational in 2013. Combustion chamber capacity is 255,000 tonnes of solid fuel per year. The feed stream is commonly composed of household waste, commercial waste in lower proportions and solid biofuel (wood processing waste). In the various regions of Lithuania household waste that is collected first goes through a separation line to extract the recyclable materials (metals, plastics, paper and glass), before being incinerated.

2. Materials and methods

The representative six BA samples (30 kg each) were collected from the different spots of the large BA piles once a week (in February-April 2016) and sealed in plastic buckets before testing.

The moisture content was determined using the oven-drying method: a test portion (2 kg) after homogenization and weighting was dried in the oven at 105°C until a constant mass. Moisture content in BA was determined according to the formula (Willits 1951):

$$w_w = (m_a/m_b) \cdot 100 \quad (1)$$

where:

w_w – the moisture content (%),

m_a – the mass of the dried sample (g),

m_b – the mass of sample (g)

The chemical composition of the major and minor elements in MSWI bottom ash was determined in duplicate by X-ray Fluorescence Spectroscopy (XRF) using an Axios mAX X-ray spectrophotometer.

The compliance leaching test was performed according to the Standard LST EN 12457-2:2003. The samples, which originally and after pretreatment were below 4 mm in size, were put in contact with distilled water in capped bottles. The solid to liquid ratio was 1/10 (90 g dry BA and 900 mL distilled water), and the suspension was agitated for 24 h at room temperature (20±5°C). Solid residue was separated by filtration.

Eluate pH (Metler Toledo) and conductivity (WTW Terminal 740) were determined. Furthermore, after acidification (pH 2 using HNO₃), 18 metals content was analysed by AAS according to ISO 15586:2003.

Soluble salts (chlorides, sulphates, bromides and fluorides) concentration in eluate was determined by liquid chromatography of ions, according to LST EN ISO 10304-1:2009. Further, total organic carbon (TOC) and dissolved organic carbon (DOC) were determined according to LST EN 13137:2002 and ISO 8245:2003 standards.

The amount of total dissolved solids (TDS) was determined by the evaporation procedure: 50 mL of eluate is placed in the weighed porcelain dish, to which is added 0.5 mL of concentrated hydrochloric acid. The sample is placed on a hotplate until completely evaporated. After

evaporation the porcelain plates are once again weighed. The amount of TDS calculated according to (2) the formula:

$$TDS = [(m_e - m_d) \cdot 1000] / v \quad (2)$$

where:

TDS – concentration of total dissolved solids (mg/L),

m_d – mass of empty porcelain dish (mg),

m_e – mass of porcelain dish after evaporation (mg),

v – volume of eluate (mL).

The results of eluate parameters were compared with the limit leaching values for inert and non-hazardous waste, according to the 2003/33/EC.

3. Results and discussion

3.1. Water content in BA

After drying six samples to constant weight the amount of water was prescribed by Eq. (1). The results are shown in Figure 1.

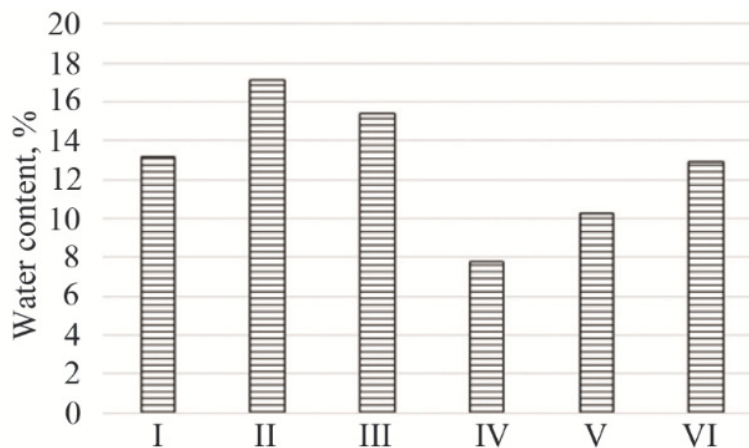


Fig. 1. Moisture content in MSWI bottom Ash

Rys. 1. Zawartość wilgoci w popielie dennym ze spalania SOK

The results (Fig. 1) reveal that fresh (not aged) BA water content varies from 7.80 to 17.16%. Water content values are not stable because BA in the waste incineration plant is cooled by water. One part of the cooling water evaporates immediately, while the other part is absorbed by BA.

3.2. Chemical composition of BA

The six samples' BA chemical composition determination research showed that the main components ($>10\%$) were silicon and calcium. Also found were (1-8%) aluminum, magnesium, sodium, potassium and iron. The aforementioned elements were found in the form of oxides. Review of scientific literature shows that silicon, a part of silicon dioxide (SiO_2), is the main element of the composition of BA (Jurič et al. 2006, Müller et al. 2006, Lidelöw & Lagerkvist 2007, Rednek et al. 2007, Rambaldi et al. 2010, Cheng 2012, Li et al. 2012, Abbà et al. 2014, Del Valle-Zermeño et al. 2014a, Del Valle-Zermeño et al. 2015, Tang et al. 2015). The researches show (Figure 2) that this oxide constitutes more than half ($57\pm 2\%$) of the total weight of BA. In its composition also is $16\pm 2.5\%$ CaO, $8\pm 3.2\%$ Fe_2O_3 , $5\pm 1\%$ Na_2O and $5\pm 0.5\%$ Al_2O_3 .

Comparing of the study results with bottom ash composition in other countries (Table 1), we see that the BA composition are most similar to BA which formed in Spanish and French incineration plants.

Silicon oxide content in BA from Italian (Rambaldi et al. 2010), Slovenian (Jurič et al. 2006) and Swedish (Lidelöw & Lagerkvist 2007) incineration plants is 1.54-1.69 times lower than in BA from Lithuania (56.94%). Amount of SiO_2 are almost the same in BA of Lithuania plant and in BA which are generated in German plant (Müller & Rübner 2006). After sorting, the remaining waste contains a significant proportion of inert waste (such as glass, construction and demolition waste, ceramics, etc.), and therefore BA contains a high amount of SiO_2 .

Amount of calcium oxide in different countries MSWI BA is 11.9-39.0% (Table 1), in Lithuanian BA – 16.12%. Similar CaO content as determined in the Spanish, Swedish and French bottom ashes. Amount of CaO in the BA is mostly dependent on a variety of paper waste in incinerated waste stream.

Content of iron oxide in different countries BA varies highly (2.70-14.10%), this study showed that the BA from Lithuania plant average contains of 7.82% Fe_2O_3 . The separation of ferrous metals from BA, using magnetic separation method, leads the relatively small amount of Fe_2O_3 .

Comparing other countries (Table 1) and the results of Lithuania, the content of aluminum in Lithuanian BA is lowest (approximately 4.88%). Literature analysis showed that the highest amount of Al_2O_3 (14.1-14.8%) are found in BA from Germany and Slovenia plants (Jurič

et al., 2006, Müller and Rübner, 2006). It can be assumed that in incinerated waste stream enters a small amount of aluminum waste (foil, drinks cans, etc.) in Lithuania. Operating a deposit system for drinks cans can lead a small amount of aluminum waste in the stream.

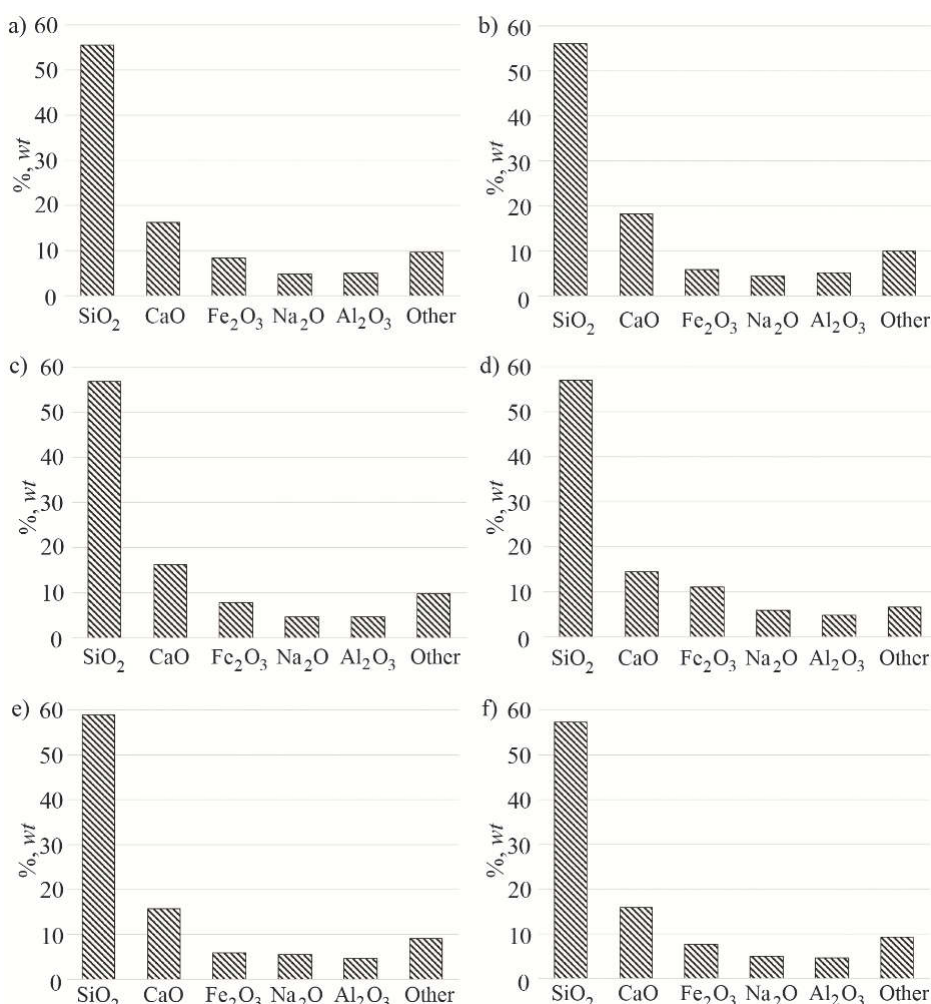


Fig. 2. Concentrations of major oxides MSWI bottom ash, sample number: a) I; b) II; c) III; d) IV; e) V; f) VI

Rys. 2. Zawartość podstawowych tlenków w popiele dennym ze spalania SOK, numer próbek: a) I; b) II; c) III; d) IV; e) V; f) VI

Concentrations of heavy metals (Ba, Mn, Cu, Pb, Sr, Cr, Sn, Ni) in BA were relatively low (<1%). The highest amounts were of barium (2,780-4,190 mg kg⁻¹), manganese (700-1,160 mg kg⁻¹), lead (670-1,760 mg kg⁻¹) and zinc (1,330-2,010 mg kg⁻¹). The amounts of minor elements in the six samples of MSWI bottom ash are shown in Figure 3.

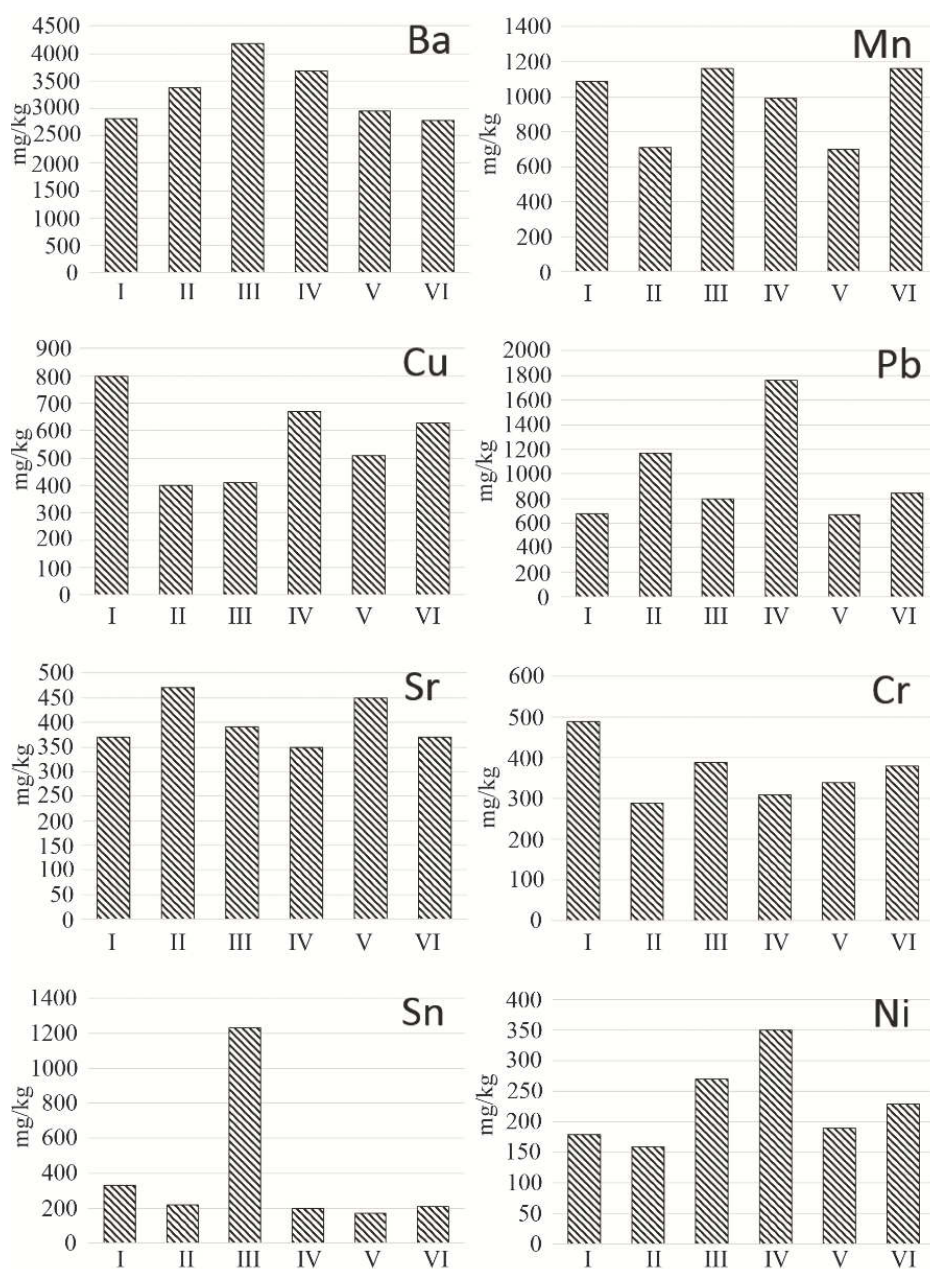


Fig. 3. Concentrations of minor elements (heavy metals) in MSWI bottom ash
Rys. 3. Zawartość drugorzędnych pierwiastków (metali ciężkich) w popiele dennym ze spalania SOK

The chemical composition of BA depends mainly on the initial composition of the incinerated waste and BA pretreatment technology. It can be concluded that the main elements (SiO_2 , CaO_2) are almost constant in time but that concentrations of heavy metals vary.

3.3. Leaching Results

The results of the natural pH batch leaching tests on the collected materials are shown in Table 2 and Table 3. The leaching data are compared with the European Commission decision 2003/33/EC regulatory limit values for waste removal in inert and non-hazardous waste landfills.

Table 2. Heavy metals concentrations in MSWI BA eluate (mg kg⁻¹)

Tabela 2. Stężenie metali ciężkich (mg kg⁻¹) w popiele dennym ze spalania SOK

Element, parameter	I sample	II sample	III sample	IV sample	V sample	VI sample	2003/33/EC	
							Inert waste	Non-hazardous waste
Arsenic (As)	0.01	0.01	0.01	0.01	0.01	<0.01	0.5	2
Barium (Ba)	3	5	5	3	4	5	20	100
Cadmium (Cd)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.04	1
Chrome (Cr)	0.2	0.3	0.2	0.1	0.3	0.2	0.5	10
Copper (Cu)	2	1	2	1	0.1	0.1	2	50
Mercury (Hg)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.01	0.2
Molydenum (Mo)	0.9	1.0	1.8	1.8	0.5	0.8	0.5	10
Nickel (Ni)	<0.02	<0.02	<0.02	<0.02	0.03	0.08	0.4	10
Lead (Pb)	2.3	2.4	2.5	0.3	0.1	0.2	0.5	10
Antimony (Sb)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.7
Selenium (Se)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.1	0.5
Zinc (Zn)	5	2	2	0.4	1	1	4	50

Table 3. MSWI bottom ash eluate characteristics**Tabela 3.** Charakterystyka eluatu z popiołu dennego ze spalania SOK

Element, parameter	I sample	II sample	III sample	IV sample	V sample	VI sample	2003/33/EC	
							Inert waste	Non-hazardous waste
Chlorides (Cl), mg kg ⁻¹	2,259	2,441	3,046	2,006	1,869	2,330	800	15,000
Fluorides (F), mg kg ⁻¹	2	3	2	3	2	2	10	150
Bromides (B), mg kg ⁻¹	8	7	13	5	8	1	N*	N*
Sulphates (SO ₄), mg kg ⁻¹	6,687	7,120	10,012	4,273	3,566	2,816	1,000	20,000
Total dissolved solids (TDS), mg kg ⁻¹	32,917	32,000	40,443	22,998	21,663	28,575	4,000	60,000
Dissolved organic carbon (DOC), mg kg ⁻¹	139	123	171	82	71	55	500	800
Total organic carbon (TOC), mg kg ⁻¹	2,380	1,550	2,150	2,760	2,710	1,880	30,000	5%
pH	12.7	12.6	12.6	12.5	12.4	12.6	N*	>6
Acid neutralization capacity (ANC), mol kg ⁻¹	1.78	2.76	2.53	1.64	2.33	2.76	N*	Must be evaluated
Electrical conductivity (EC), μS cm ⁻¹	8,900	8,750	9,530	6,260	5,820	8,240	N*	

Note: *Not regulated

Concentrations of five metals (As, Cd, Hg, Sb, Se) were $<0.01 \text{ mg kg}^{-1}$. Mo, Pb, Zn concentrations in eluate were $0.5\text{-}1.8 \text{ mg kg}^{-1}$, $0.1\text{-}2.5 \text{ mg kg}^{-1}$ and $0.4\text{-}5.0 \text{ mg kg}^{-1}$, respectively. The concentration of molybdenum in five eluate samples was higher than the permissible concentration of inert waste eluates, namely 0.5 mg kg^{-1} , lead three times (0.5 mg kg^{-1}) and zinc (4 mg kg^{-1}) one time. It can be assumed that the high concentrations of metals in eluate were for incomplete separation of metals from BA.

Also determined were the concentrations of sulphate, chloride, bromide and phosphate in eluates, as well as parameters such as electrical conductivity, pH, quantities of dissolved and total carbon, and acid neutralization capacity. The results are given in Table 3.

When the BA affects the fluid (in this case distilled water, and deposited BA in landfills – precipitation), the salts (chlorides and sulphates) that are contained in BA melt and pass into the solution. Table 3 data show that the concentrations of sulphates ($4,273\text{-}10,012 \text{ mg kg}^{-1}$), chlorides ($1,869\text{-}3,046 \text{ mg kg}^{-1}$) and TDS ($21,663\text{-}40,443 \text{ mg kg}^{-1}$) are high. Concentration of chlorides 2.3/3.8 times, sulphates 2.8/10.0 times and TDS 5.4/10.1 times were higher than the permissible concentrations for inert waste eluates.

It was established that there is a strong correlation between total dissolved solids and electrical conductivity ($R^2 = 0.9031$) (Fig. 4).

The researchers have carried out various analysis to find out the mathematical correlation between TDS and EC values, therefore TDS concentration can be estimated from EC value. However, relations between TDS and EC is not directly linear, because ionic species conductivity of mobility is variable. (Brown et al. 1960, Walton 1989, Patil et al. 2012, Marandi et al. 2013). The correlation between TDS and EC calculated according to (3) the formula:

$$\text{TDS} = k \cdot \text{EC} \quad (3)$$

where:

TDS – concentration of total dissolved solids (mg/L),

k – value, which depends on the concentration of ions in eluate (k will increase along with the increase of ions in liquid),

EC – electrical conductivity ($\mu\text{S cm}^{-1}$).

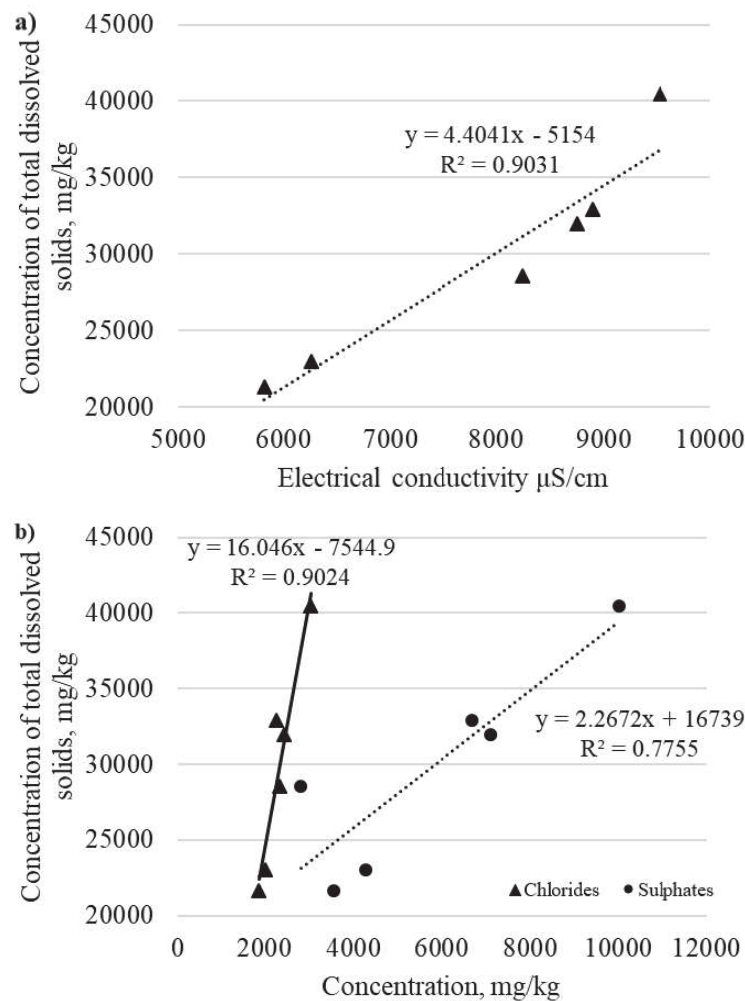


Fig. 4. Correlation relations in MSWI bottom ash eluate: a) correlation between total dissolved solids and electrical conductivity; b) correlation between total dissolved solids, chlorides and sulphates concentration

Rys. 4. Relacje korelacyjne w eluacie z popiołu dennego ze spalania SOK:
a) korelacja między przewodnictwem i stężeniem substancji rozpuszczonych;
b) korelacja między stężeniem substancji rozpuszczonych i stężeniem chlorków oraz siarczanów

This expression is approximate, because nonionic species does not affect EC values and ionic species have unequal weights. The actual multiplier (k) depends on individual mobility of dissolved ions and the average mobility of all ions, which in turn depends on the temperature of the liquid, the relative amount of different ions and the total concentration of soluble solids (Thirumalini & Joseph 2009). Based on formula 3 and the results of the TDS and EC values determination, was found that k values are 3.47-4.24. Then in natural water, than $EC = 500\text{-}3000 \mu\text{S cm}^{-1}$, k value

ranges from 0.55 to 0.75). (Brown 1960, Thirumalini & Joseph 2009, Rusydi 2018).

Figure 4 b shows strong relations between TDS and chlorides ($R^2 = 0.9024$) and sulphates ($R^2 = 0.7755$). Bearing in mind that the TDS consists of various inorganic anions (carbonates, chlorides, sulfates and nitrates) and inorganic cations (sodium, potassium, calcium and magnesium), these correlations is quite predictable. Thirumalini1 & Joseph (2009) claims that linear coefficient of correlation (r) among the TDS and clorides in fresh water can be 0.95, and respectively between TDS and suphates 0.82.

Concentrations of fluorides and bromides were quite low (2-3 mg kg⁻¹ and 1-13 mg kg⁻¹ respectively). Also, total (TOC) and dissolved organic carbon (DOC) quantities in MSWI bottom ash eluate were determined to be 1,550-2,760 mg kg⁻¹ and 55-171 mg kg⁻¹. Figure 5 shows the correlation of copper, lead and DOC concentrations in eluate.

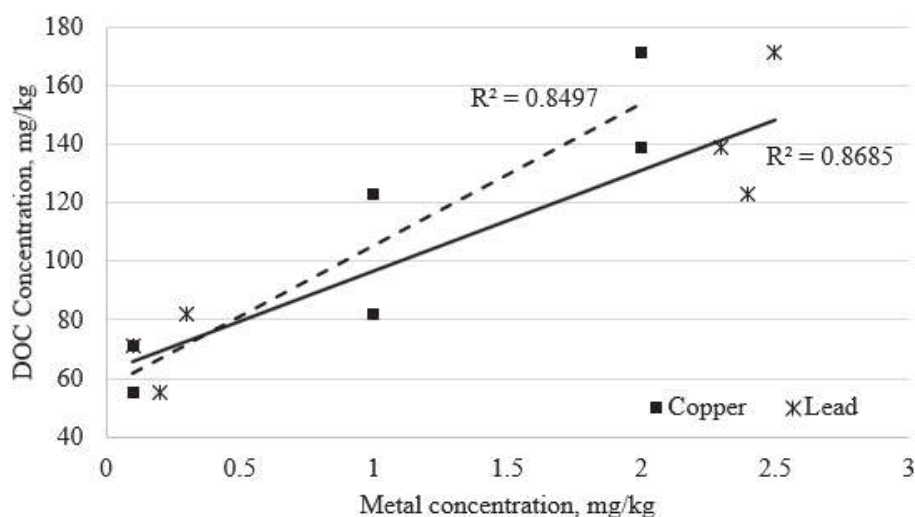


Fig. 5. Correlation of copper, lead and DOC in eluate from MSWI bottom ash

Rys. 5. Korelacja między zawartością miedzi, ołowiu oraz rozpuszczonego węgla organicznego w eluacie z popiołu dennego ze spalania SOK

The graphs in Fig. 5 show that copper and lead concentrations in the eluate have a strong dependence on DOC. It was found that copper and DOC correlation coefficient $R^2 = 0.8497$, lead and DOC – $R^2 = 0.8685$.

Van der Sloot et al. (2000) and Robinson et al. (2004) contend that organic complexation has a significant influence over Cu leaching from BA.

The eluate at all times was alkaline ($\text{pH} = 12.5 \pm 0.2$), electrical conductivity – $5,820\text{--}9,530 \mu\text{S cm}^{-1}$ and acid neutralization capacity – $2.2 \pm 0.56 \text{ mol kg}^{-1}$. According to the obtained values (Table 3), neither parameter exceeded the limit values for waste removal in non-hazardous waste landfills.

As previously mentioned, one possible BA reuse option is production of road and construction structural elements of inert material, replacing part of the inert material in BA. Currently, this technology is only beginning to be used in Lithuania. This technology is widely used in Germany, Denmark, France, Italy and the Netherlands. Table 4 presents a comparison of the eluate parameters maximum values and leaching limit values of BA in Lithuania (D1-805) and in Germany (LAGA 20).

Table 4. Comparison of the eluate parameters maximum values and BA leaching limit values in Lithuania and Germany, mg kg^{-1}

Tabela 4. Porównanie wartości maksymalnych parametrów w eluacie oraz wartości granicznych ługowania popiołu dennego na Litwie i w Niemczech, mg kg^{-1}

Element, parameter	Sign	Units	This study	Lithuanian limit values (D1-805)	German limit values (LAGA 20)
Chlorides	Cl	mg kg^{-1}	3,046	1,000	2,500
Sulphates	SO_4	mg kg^{-1}	10,012	2,000	6,000
Lead	Pb	mg kg^{-1}	2.5	0.5	0.5
Cadmium	Cd	mg kg^{-1}	<0.003	0.03	0.05
Chrome	Cr	mg kg^{-1}	0.3	2	2
Copper	Cu	mg kg^{-1}	2	1.5	3
Mercury	Hg	mg kg^{-1}	<0.001	0.001	0.001
Nickel	Ni	mg kg^{-1}	0.08	0.4	0.4
Zinc	Zn	mg kg^{-1}	5	3	3

Table 4 data show that the maximum concentrations of the four parameters Cl, SO_4 , Pb and Zn, which are, respectively, $3,046 \text{ mg kg}^{-1}$, $10,012 \text{ mg kg}^{-1}$, 2.5 mg kg^{-1} and 5 mg kg^{-1} , are higher than the limit values of BA in Lithuania and Germany. One metal (copper) maximum concentration (2 mg kg^{-1}) is higher than permissible value in Lithuania, which are 1.5 mg kg^{-1} .

It can be concluded that the unprocessed BA generated in the MSWI plant in Klaipėda cannot be used in concrete and road construction elements. The document (D1-805) which describes possibilities for BA utilization in civil and construction engineering in Lithuania, states that BA must be exposed to natural aging (weathering) for at least three months first. It can be assumed that, after the natural aging process of BA from the Klaipėda MSWI plant, leaching values will be smaller than limit values.

4. Conclusions

The six samples of BA chemical (elemental and oxide) composition analysis show that the chemical composition of the time is variable. The main elements of the BA are silica ($57\pm 2\%$), calcium ($16\pm 2.5\%$), iron ($8\pm 3.2\%$), sodium 5 ($\pm 1\%$) and aluminum ($5\pm 0.5\%$) oxides. A wide range of heavy metals are also found in the BA. The highest concentrations are barium (2,780-4,190 mg kg⁻¹), manganese (700-1,160 mg kg⁻¹), lead (670.0-1,760 mg kg⁻¹) and zinc (1,330-2,010 mg kg⁻¹).

MSWI bottom ash does not meet the requirements for inert waste (2003/33/EC) because were too high concentrations of Mo (0.5-1.8 mg kg⁻¹), Pb (2.5-12.2 mg kg⁻¹), Zn (5 mg kg⁻¹), Cl (1,869-3,046 mg kg⁻¹), SO₄ (4,273-10,012 mg kg⁻¹) and TDS (21,663-40,443 mg kg⁻¹) in the eluate. But BA parameters meet the requirements for the waste removal in non-hazardous waste landfills.

The results of the study have shown that the concentration of TDS is directly dependent on the electrical conductivity ($R = 0.9031$) and quantity of chlorides ($R = 0.9024$) and sulphates ($R = 0.7755$) in BA eluate. Further, a correlation was found between the concentrations of copper, lead and dissolved organic carbon. The correlation coefficients are, respectively, 0.8497 and 0.8685. Heavy metal (Cu, Pb) concentrations correlation on the DOC can be explained by organic complexation processes.

Changing concentrations of the environmentally hazardous heavy metals (Zn) and soluble (Cl, SO₄) salts indicate that BA cannot be used in concrete and road construction elements. First necessary full separation of metals and BA aging, at least three months. After that continuous BA eluate test is important in order to assess the BA application possibilities in the civil and construction engineering fields.

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Charakterystyka popiołów dennych ze spalania stałych odpadów komunalnych

Streszczenie

Technologie produkcji energii z odpadów są szeroko stosowane w gospodarce odpadami komunalnymi. Spalanie stałych odpadów komunalnych zmniejsza ich objętość o 90%. W procesie spalania wytwarzane są dwa główne typy produktów ubocznych: popioły lotne (PL) i popioły denne (PD). W pracy omówiono właściwości chemiczne i środowiskowe PD pochodzących ze spalania stałych odpadów komunalnych (SOK). Określono skład chemiczny i wymywanie substancji z PD z litewskiej spalarni odpadów, której siedziba mieści się w Kłajpedzie. Wyniki pokazują, że skład chemiczny PD jest prawie stabilny w czasie, a podstawowe tlenki to dwutlenek krzemu ($57\pm 2\%$), tlenek wapnia $16\pm 2,5\%$ i tlenek żelaza $8\pm 3,2\%$.

Koncentracja różnych metali ciężkich w PD wynosi $< 1\%$. Badania wymywania wykazały, że z PD wymywano duże ilości rozpuszczalnych soli (siarczanów $2\ 816-10\ 012\ \text{mg kg}^{-1}$ i chlorków $1\ 869-3\ 046\ \text{mg kg}^{-1}$), a także niektórych metali ciężkich (Mo $0,5-1,8\ \text{mg kg}^{-1}$, Pb $0,1-2,5\ \text{mg kg}^{-1}$). Popiół denny ze spalania stałych odpadów komunalnych nie spełnia wymagań dotyczących odpadów obojętnych (2003/33/WE), ale spełnia wymagania dotyczące ich usuwania na składowiska odpadów innych niż niebezpieczne. Zmieniające się koncentracja niebezpiecznych dla środowiska metali ciężkich wskazuje na konieczność ciągłego badania eluatu z popiołów dennych.

Abstract

Waste-to-energy technologies are widely used for municipal solid waste management. Municipal solid waste incineration has reduced waste volume by 90%. The combustion process results in two types of waste: fly ash (FA) and bottom ash (BA). This study focuses on the chemical and environmental proper-

ties of municipal solid waste incineration (MSWI) bottom ash. The chemical composition and leaching properties of BA from Lithuania's waste-to-energy plant, located in Klaipėda, was determined. Results show that chemical BA composition is almost stable in time and that major elements are silicon dioxide ($57\pm 2\%$), calcium oxide $16\pm 2.5\%$ and iron oxide $8\pm 3.2\%$.

The concentration of various heavy metals in BA is $< 1\%$. Leaching tests showed that from BA leached large quantities of soluble salts (sulphates $2,816\text{--}10,012\text{ mg kg}^{-1}$ and chlorides $1,869\text{--}3,046\text{ mg kg}^{-1}$) and certain heavy metals (Mo $0.5\text{--}1.8\text{ mg kg}^{-1}$, Pb $0.1\text{--}2.5\text{ mg kg}^{-1}$). MSWI bottom ash does not meet the requirements for inert waste (2003/33/EC) but meets those for waste removal in non-hazardous waste landfills. The changing concentration of environmentally hazardous heavy metals indicates that the need for continuous BA eluate test is important.

Słowa kluczowe:

spalanie odpadów komunalnych stałych, popiół denny, metale ciężkie, sole rozpuszczalne

Keywords:

municipal solid waste incineration; bottom ash; heavy metals; soluble salts



Water Requirements of Bird Cherry (*Padus avium* Mill.)

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1. Introduction

In the aspect of human influence on the environment, we usually mean the negative impact of man activity on nature. Post-industrial areas that are heavily degraded particularly threaten people's health and life. Meanwhile, as a result of industrial activity, man unconsciously created new habitats, which often became an enclave for many plant and animal species that are interesting research objects. The side effects of minerals exploitation are heaps and landfills of industrial waste. These areas create the conditions for primary succession, where there is no soil layer rich in nutrients and groundwater, and rainwater quickly penetrates deep into the ground. Poor in minerals and quickly drying soil of dumps and landfills of industrial waste are not conducive to the spontaneous development of vegetation, especially since these areas are also devoid of a natural reser-

voir of seeds. Years ago, heaps and landfills of industrial waste were considered as a "biological deserts", where plants are unable to survive or their growth is very slow. However, it turned out that post-industrial areas, despite difficult conditions, are effectively colonized by plants. The long-term lack of vegetation management on the post-industrial areas favors the succession of plants, which usually after a few years leads to the formation of a strong plant cover.

One of the dominant plant species that spontaneously invades post-industrial areas is bird cherry (*Padus avium* Mill.). Bird cherry, also called hackberry, hagberry or Mayday tree, is a medicinal and ornamental plant. Its flowers, fruits and bark are used in herbal medicine (Podbielkowski 1989). The bird cherry trees are planted in parks and along roads, and also used in landscape or reclamation plantations. The first three years after planting determines the seedling survival rate of the introduced plants (Żakowicz 2010). However, the seedling survival rate during the first period of growth depends mainly on the suitable soil water conditions that should be controlled using a properly designed and operated irrigation system.

The aim of the present research was to assess the water requirements of bird cherry during the first three years after planting.

2. Material and Methods

In the present study, as a measure of the bird cherry (*Padus avium* Mill.) water needs, the potential evapotranspiration (Etp) of the plants was calculated. The formula of Blaney-Criddle, modified by Żakowicz (2010) for Polish conditions, by using the adjusted crop coefficients, was applied. The values of crop coefficients are similar in the first, second and third year after planting and range from 0.70 in April to 0.95 in October. It was assumed that the growing season of bird cherry starts on April 1 and ends on October 31.

The calculations were carried out for five agro-climatic regions of Poland in the years 1981-2010. The borders of studied regions and the corresponding representative meteorological stations were adapted according to Łabędzki et al. (2013) recommendation. The north-eastern region – with the station in Olsztyn – includes the following provinces: Podlaskie, Warmian-Masurian and Pomeranian. The central-north-western region – with the station in Bydgoszcz – includes the following

provinces: West Pomeranian, Kuyavian-Pomeranian, Łódź, Lubusz and Greater Poland. The central-eastern region – with the station in Warsaw – includes the following provinces: Masovian, Holy Cross and Lublin. The south-western region – with the station in Wrocław – includes the following provinces: Lower Silesian, Opole and Silesian. The south-eastern region – with the station in Kraków – includes the following provinces: Lesser Poland and Subcarpathian (Fig. 1). The rainfall deficiency (or excess) during the period from April to October was calculated based on the difference between the water needs of bird cherry (showed as potential evapotranspiration for this period) and the precipitation totals.

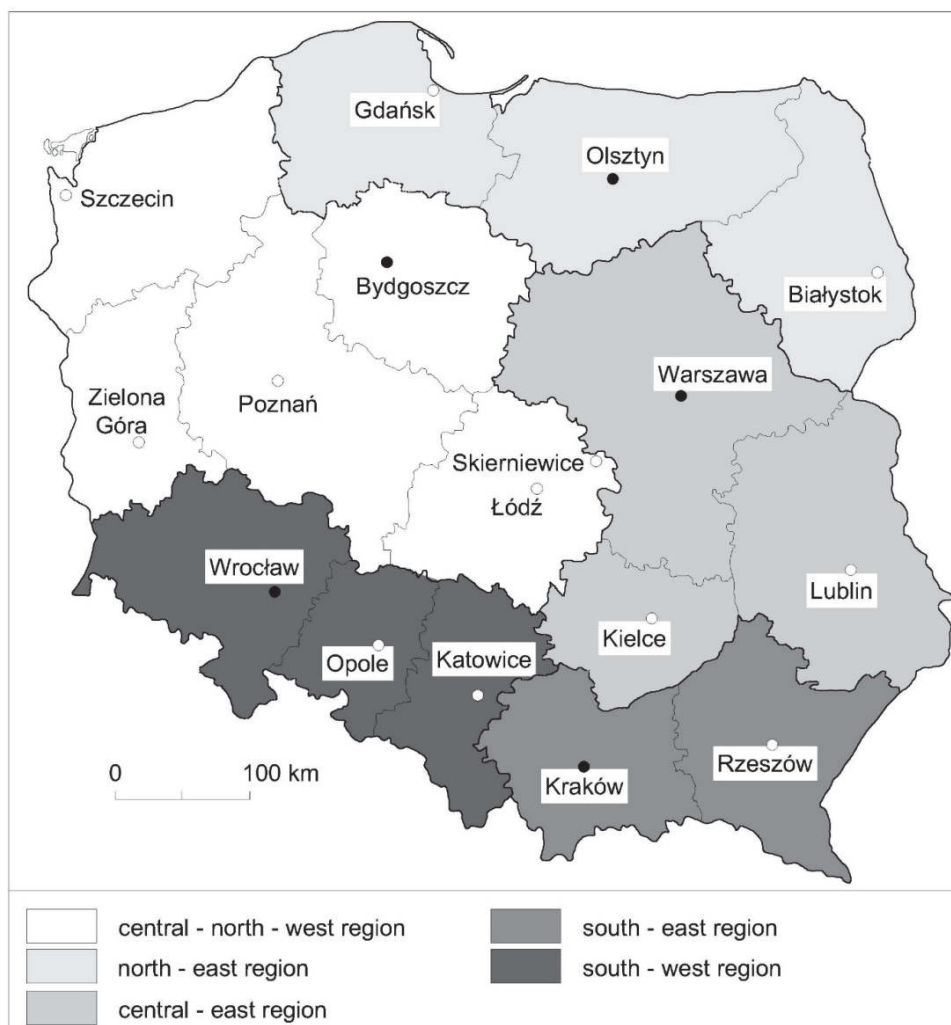


Fig. 1. Agro-climatic regions of Poland with the representative meteorological stations (according to Łabędzki et al. 2013)

Fig. 1. Regiony agro-klimatyczne w Polsce z reprezentatywnymi stacjami meteorologicznymi (według Łabędzki i in. 2013)

The water requirements variability of bird cherry during the first three years of growing in reclamation plantings during the growing period (April-October) was low, because the coefficient of variation ranged from 2.7 to 2.9%. The higher variability of water needs occurred in the period of the highest water requirements (July-August), when the coefficient of variation varied from 4.1 to 4.7% (Table 1).

Table 1. Bird cherry water requirements during the growing period

Tabela 1. Wymagania wodne czeremchy w czasie sezonu wegetacyjnego

Specification	Region of Poland	Water requirements (mm)	
		July-August	April-October
Mean	north-eastern	229	531
	central-north-western	242	566
	central-eastern	241	567
	south-western	230	549
	south-eastern	223	534
Minimum	north-eastern	211	495
	central-north-western	222	531
	central-eastern	223	531
	south-western	212	518
	south-eastern	205	508
Maximum	north-eastern	251	565
	central-north-western	261	599
	central-eastern	263	604
	south-western	251	582
	south-eastern	244	561
Median	north-eastern	231	534
	central-north-western	242	566
	central-eastern	241	566
	south-western	232	550
	south-eastern	225	537

Table 1. cont.

Tabela 1. cd.

Specification	Region of Poland	Water requirements (mm)	
		July-August	April-October
Standard deviation	north-eastern	10.7	15.1
	central-north-western	11.4	15.6
	central-eastern	10.5	15.8
	south-western	10.3	15.6
	south-eastern	9.3	15.4
Variability coefficient (%)	north-eastern	4.6	2.8
	central-north-western	4.7	2.7
	central-eastern	4.4	2.8
	south-western	4.5	2.8
	south-eastern	4.1	2.9

3. Results and Discussion

The water needs of bird cherry in the period July-August estimated as the long-term average from the years 1981-2010 for the five regions of Poland was 233 mm. The highest water requirements were calculated in the central-north-western (242 mm) and central-eastern (241 mm) regions. The lowest water needs were noted in the north-eastern (229 mm) and south-eastern (223 mm) regions (Fig. 2).

The average water requirements of bird cherry, calculated for the period July-August in the years 1981-2010, presented the increasing tendency in all studied regions of Poland; but the values of determination coefficients were low. Additionally, the temporal variability of water needs, with the exception of the central-north-western region, was significant for all considered regions. In each subsequent decade of the studied thirty years, the water requirements of bird cherry increased in the period from July 1 to August 31 in the range from 5.2 to 5.7 mm in the south-western and north-eastern regions, respectively. On average, in the years 1981-2010 in all investigated regions of Poland, the water needs of bird cherry increased in the period July-August by 5.1 mm per decade. In the central-north-western region the rising tendency of bird cherry water requirements was not significant and amounted 3.4 mm per decade (Fig. 3).

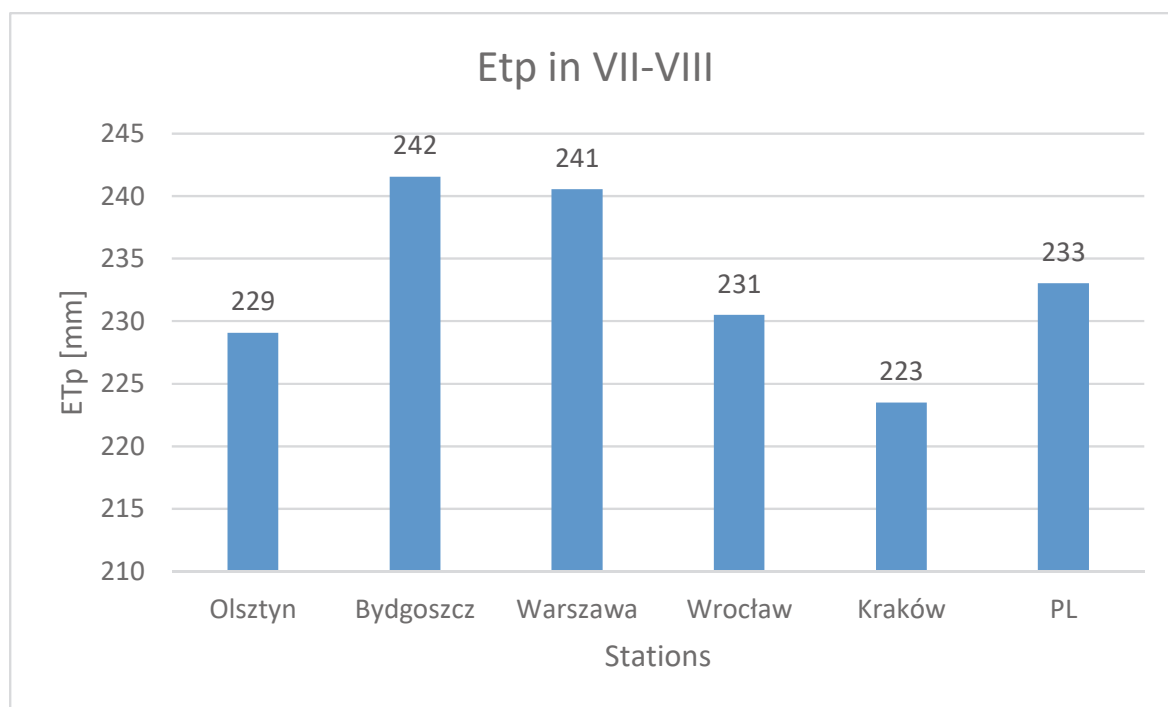


Fig. 2. Water needs (Etp) of bird cherry in the period of the highest water requirements (July-August) in the different regions of Poland

Fig. 2. Potrzeby wodne (Etp) czeremchy zwyczajnej w okresie największego zapotrzebowania na wodę (lipiec-sierpień) w różnych regionach Polski

The relationship between precipitation totals and rainfall deficiency (or excess) in the period July-August are presented in Figure 4. In the north-eastern and central-eastern regions, as well as, on average in Poland, during 29 out of 30 considered years, the precipitation deficit was observed. In the south-eastern region, the rainfall deficiency occurred during 25 years, in the south-western region during 27 years and in the central-north-western region during 28 years.

The long-term (1981-2010) average precipitation deficit for bird cherry in Poland during the period July-August amounted to 87 mm. The highest rainfall deficiency in this period occurred in the central-north-western (103 mm) and central-eastern (102 mm) regions. The lower precipitation deficit was observed in the north-eastern and south-western regions, 90 and 82 mm, respectively. Finally, the lowest rainfall deficiency (58 mm) in the south-eastern region was estimated (Fig. 5).



Fig. 3. Temporal variability of bird cherry water needs (Etp) in the period July-August in the different regions of Poland

Fig. 3. Trend czasowy potrzeb wodnych (Etp) czeremchy w lipcu i sierpniu w różnych regionach Polski

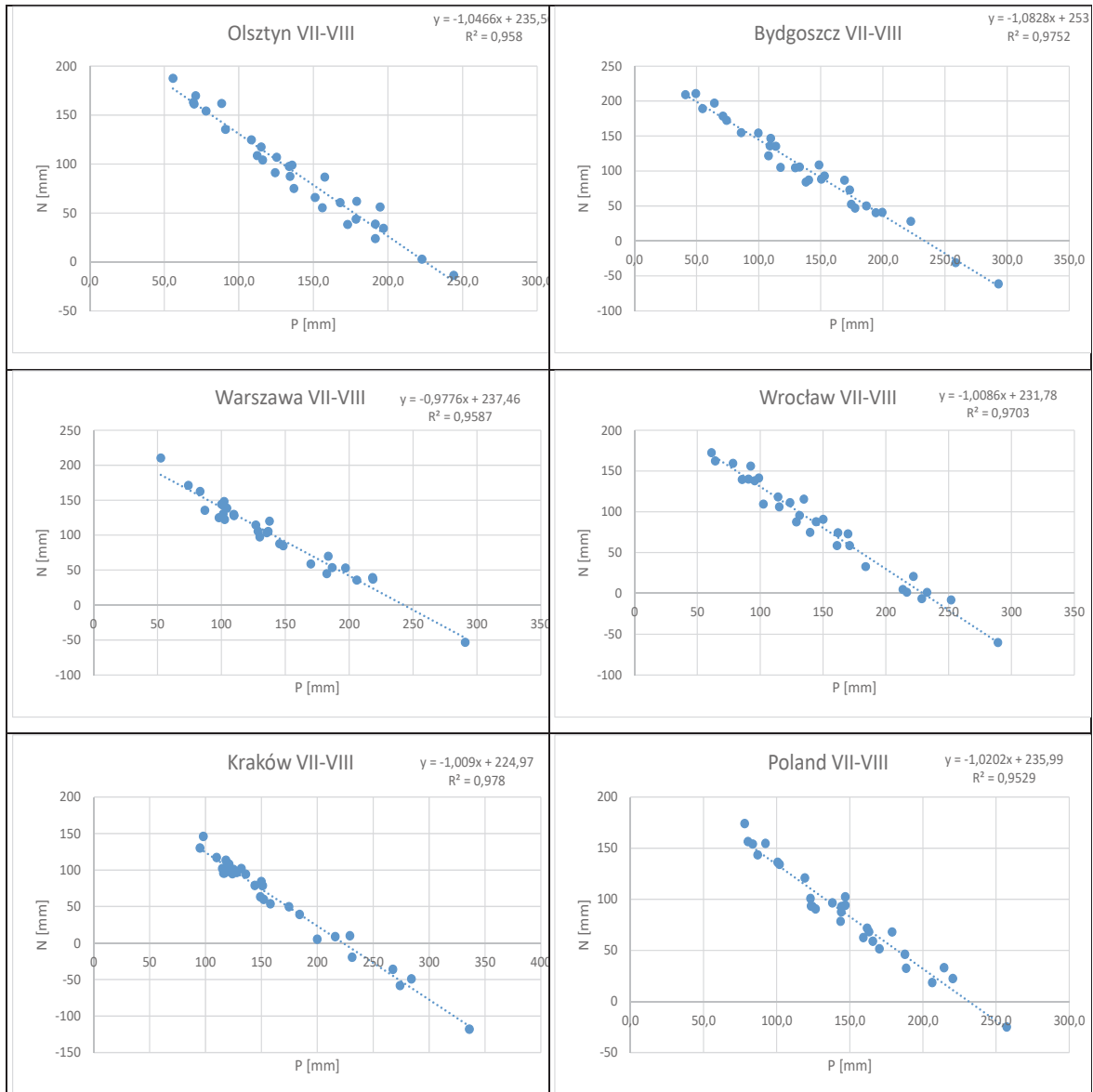


Fig. 4. Relationship between rainfall totals and rainfall deficiency (or excess) for bird cherry in the period July-August in the different regions of Poland
Fig. 4. Zależność pomiędzy sumami opadów a niedoborami (lub nadmiarami) opadów dla czeremchy w lipcu i w sierpniu w różnych regionach Polski

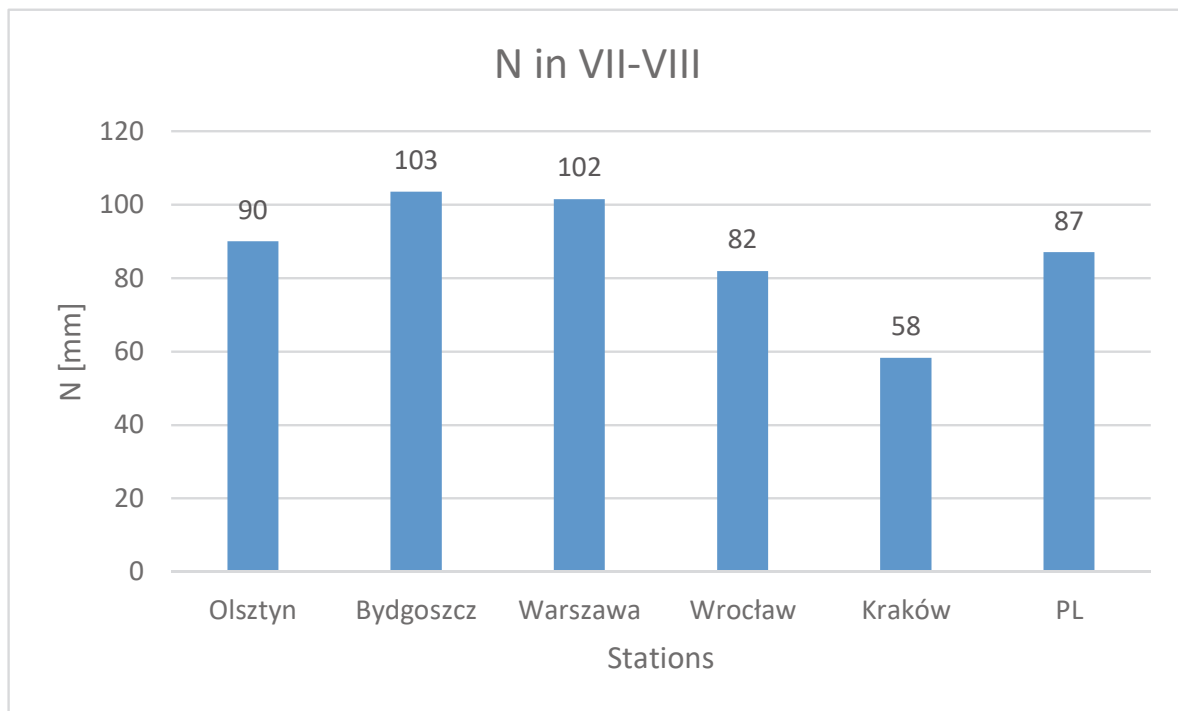


Fig. 5. Long-term (1981-2010) average rainfall deficiency (N) in the growing of bird cherry in the period July-August in the different regions of Poland

Fig. 5. Średnie z wielolecia (1981-2010) niedobory opadów (N) w uprawie czeremchy w okresie od lipca do sierpnia w różnych regionach Polski

In August, the water requirements of bird cherry increased in all studied regions of Poland. The temporal variability of water needs was significant in the north-eastern, south-western and south-eastern regions; however, the values of determination coefficients were low. Whereas in the central-north-western and central-eastern regions, non-significant dependencies were noted (Fig. 6).

On average, in the years 1981-2010, the highest water requirements in August (110 mm) were observed in the central-north-western and central-eastern regions. While the lowest water needs (102 mm) were found in the south-eastern region (Fig. 7).

Figure 8 presents the relationship between precipitation totals and rainfall deficiency (or excess) in August. In the central-north-western and central-eastern regions, precipitation deficit occurred in 93% of the studied years, in the north-eastern and south-western regions in 26 years (87%), whilst in the south-eastern region in 24 years (80%).

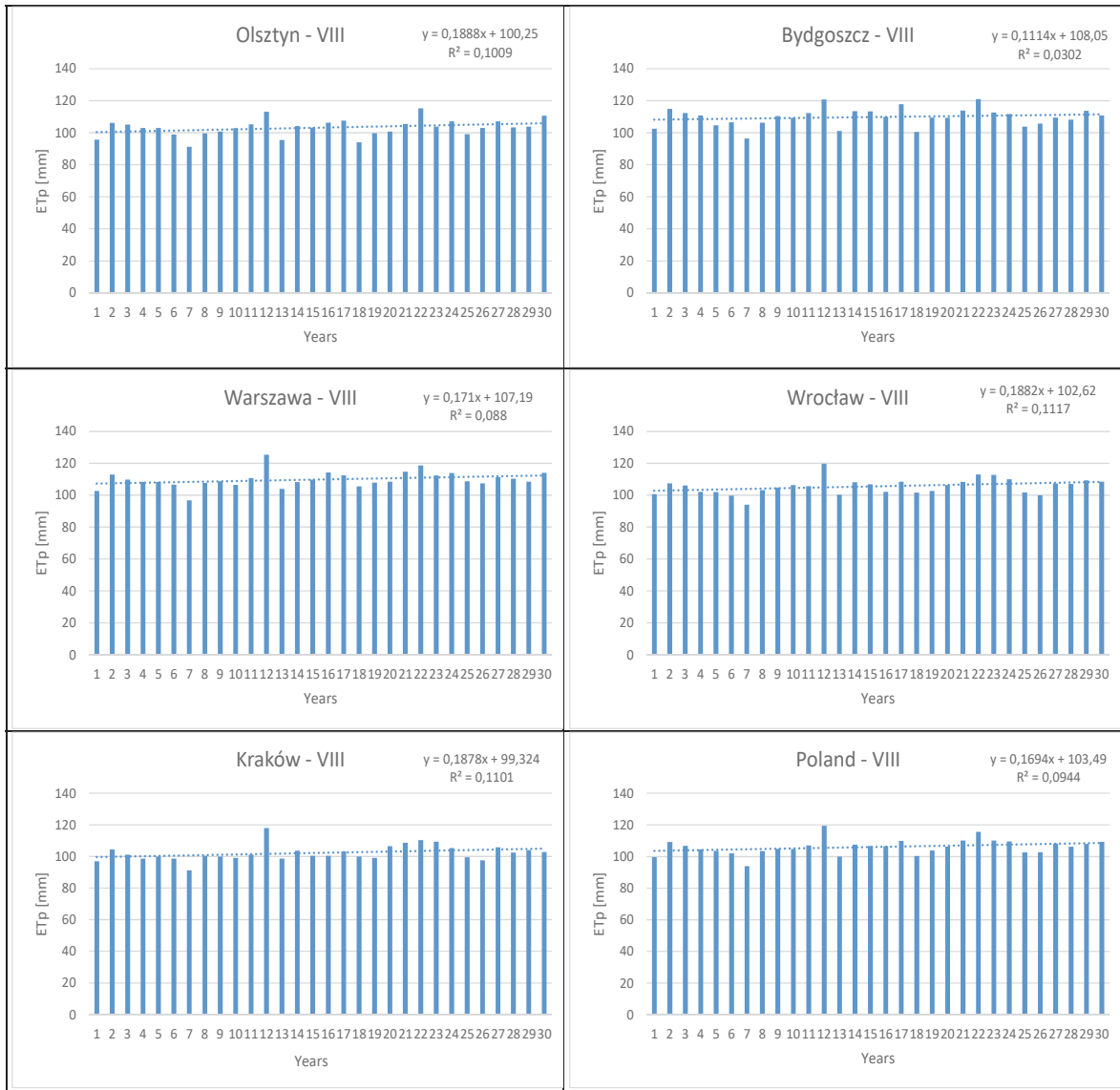


Fig. 6. Temporal variability of bird cherry water needs (Etp) in August in the different regions of Poland

Fig. 6. Trend czasowy potrzeb wodnych (Etp) czeremchy w sierpniu w różnych regionach Polski

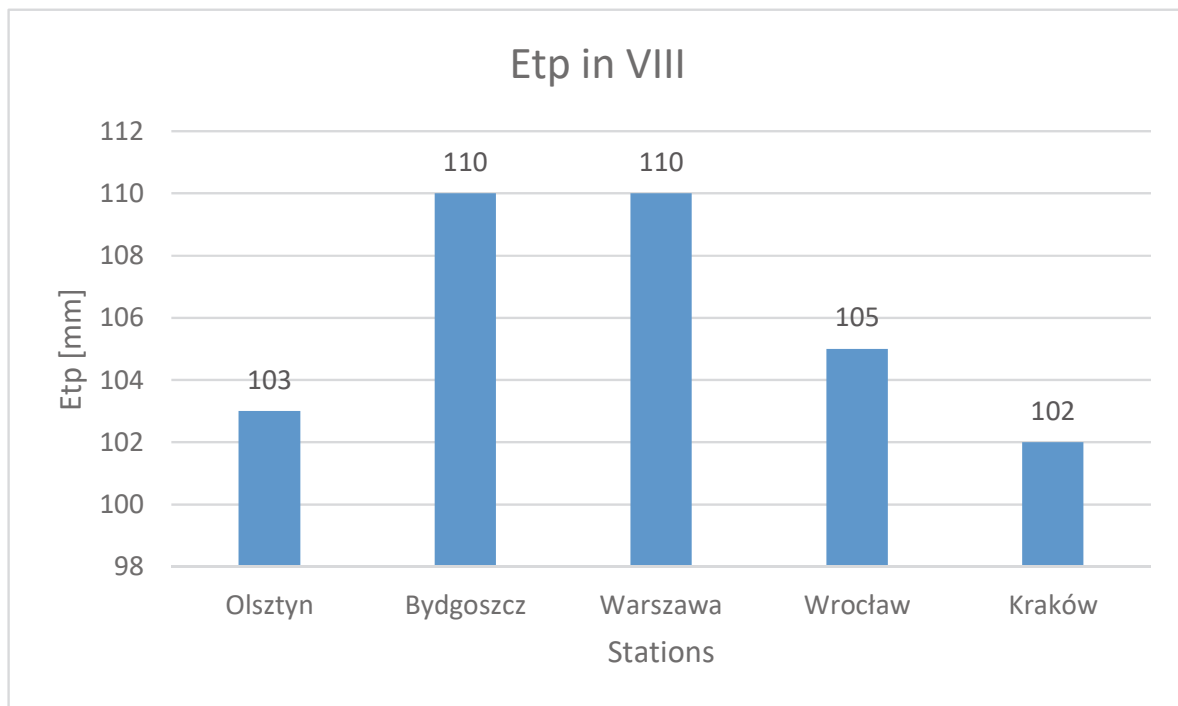


Fig. 7. Long-term (1981-2010) average water needs (Etp) of bird cherry in August in the different regions of Poland

Fig. 7. Średnie z wielolecia (1981-2010) potrzeby wodne czeremchy w sierpniu w poszczególnych regionach Polski

In August, the average rainfall deficiency in Poland during the years 1981-2010 amounted to 40 mm. The precipitation deficits, higher than the long-term average, were noted in the central-north-western (50 mm) and central-eastern (47 mm) regions. Comparing to the long-term average from the years 1981-2010, lower rainfall deficiency (25 mm) was found in the south-eastern region (Fig. 9).

The results of the present research confirm the reports published by Łabędzki (2009), Stachowski (2009), Stachowski & Markiewicz (2011), Źarski et al. (2013) and Rolbiecki et al. (2018), noted the highest irrigation requirements to supplement the precipitation deficit just in the central Poland, so in the region where the rainfall deficiency is the highest.

The presented observations may be useful in the irrigation arrangement of bird cherry during the first three years after planting. The plants introduction to on the reclamation area requires, on the one hand, the properly selected species; on the other hand, the adequate amount of water replenished by irrigation system. The effectiveness of the irrigation treatments during the introduction of bird cherry to on the reclamation areas has been reported by Źakowicz (2010) and Źakowicz & Hewelke (2012).

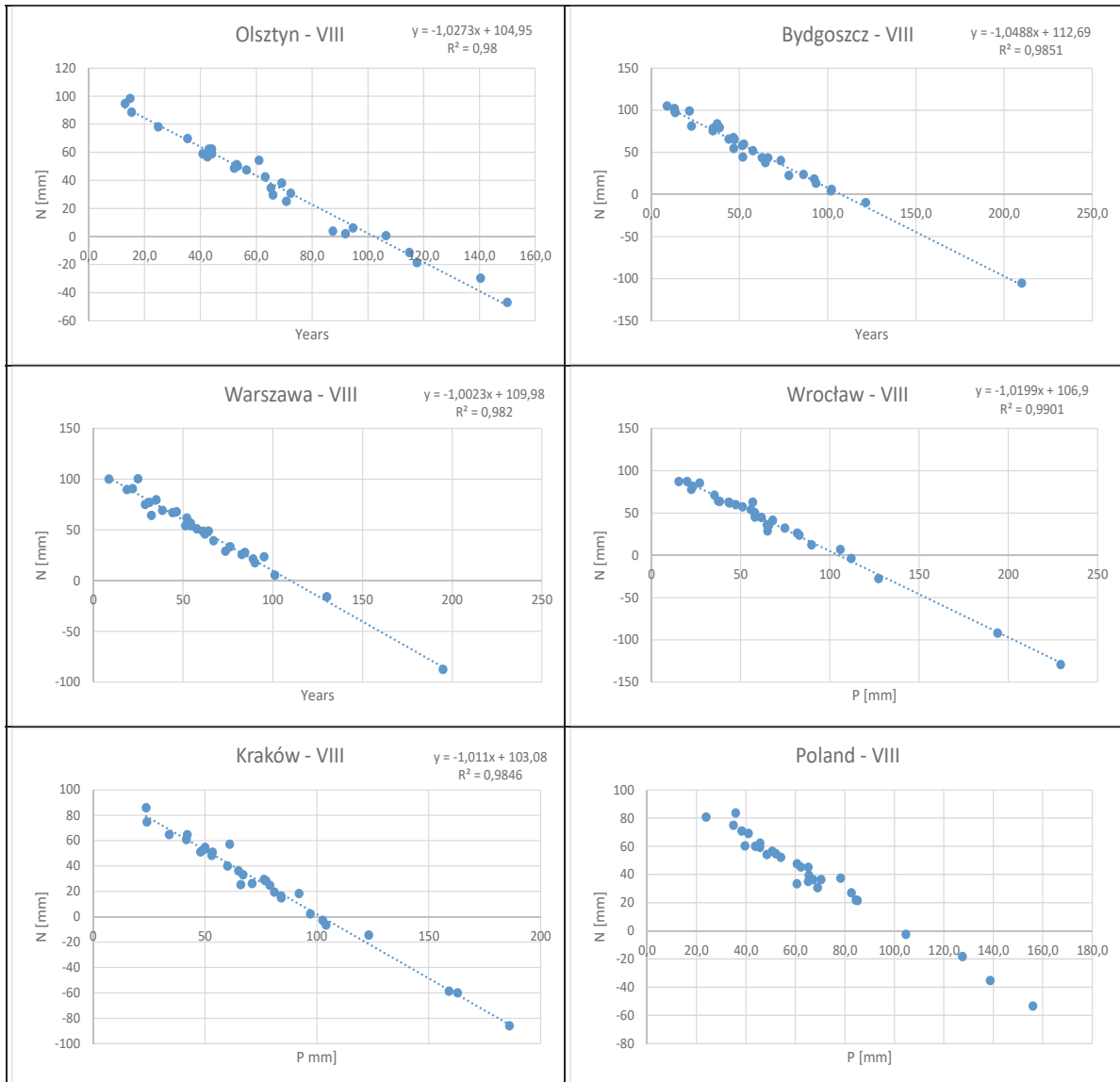


Fig. 8. Relationship between precipitation totals and rainfall deficiency (or excess) for bird cherry in August in the different regions of Poland
Fig. 8. Zależność pomiędzy sumami opadów a niedoborami (lub nadmiarami) opadów w sierpniu dla czeremchy w różnych regionach Polski

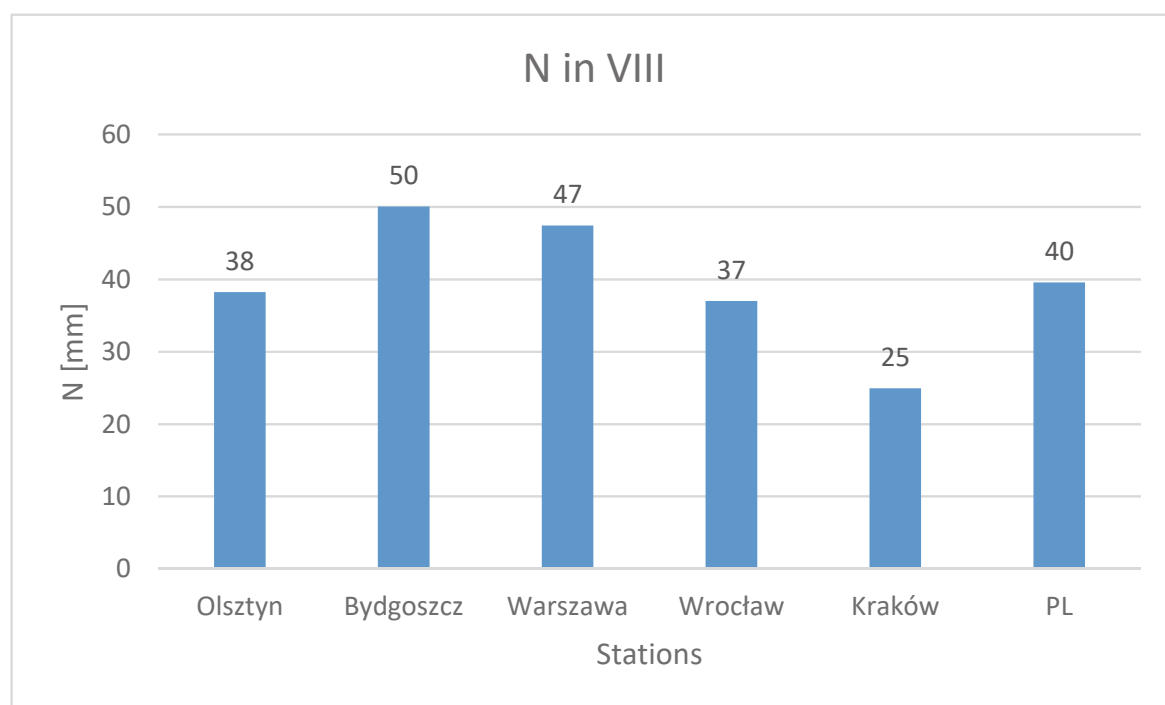


Fig. 9. Long-term (1981-2010) average rainfall deficiency (N) in the growing of bird cherry in August in the different regions of Poland

Fig. 9. Średnie z wielolecia (1981-2010) niedobory opadów (N) w uprawie czeremchy w sierpniu w różnych regionach Polski

The irrigation techniques are considered one of the most important melioration treatments that ensure the proper development and growth of trees and shrubs seedlings in the forest nurseries and other plantings (Rzekanowski & Pierzgałski 2006, Ptach et al. 2018). The results of the experiments performed in the region of Bydgoszcz, also confirmed a positive effect of micro-irrigation, as well other melioration revitalizing techniques, on the development of seedlings of many tree species, including Scots pine (Klimek et al. 2008), white birch (Klimek et al. 2009), European larch (Klimek et al. 2011) and littleleaf linden (Klimek et al. 2013).

Summarizing, the predicted climate changes indicate the increase of plant water requirements, including the reclamation plantings. Consequently, the adaptation activities will have to be undertaken; one of them is irrigation, the importance of which will gradually increase with the progress of climate changes (Kuchar & Iwanski 2011, Kuchar & Iwański 2013, Żarski et al. 2013, Kuchar et al. 2015, Kuchar et al. 2017, Łabędzki 2009).

4. Conclusions

1. The bird cherry water needs in the period of the highest water requirements (July-August) calculated as the long-term average from the years 1981-2010 for the five regions of Poland was 233 mm. The highest water needs (around 242 mm) in the period July-August occurred in the central-north-western and central-eastern regions. The lowest water requirements (227 mm) were noted in the north-eastern and south-eastern regions. In each subsequent decade of the studied long-term, a significant increasing tendency of the water needs in the period July-August by 5 mm was revealed.
2. The raise of the bird cherry water requirements in August was recorded in all studied regions of Poland. On average, in the studied long-term, the highest water requirements in August (110 mm) occurred in the central-north-western and central-eastern regions, while the lowest (102 mm) in the south-eastern region.
3. The highest rainfall deficiency in the period July-August was noted in the central-north-western (103 mm) and central-eastern (102 mm) regions, lower in the north-eastern (90 mm) and south-western (82 mm) regions, and the lowest (58 mm) in the south-eastern region.
4. During the studied long-term, the precipitation deficits in July-August were observed in 29 years in the north-eastern and central-eastern regions, in 28 years in the central-north-western region, in 27 years in the south-western region and in 25 years in the south-eastern region.
5. In August, the rainfall deficiency was noted in 93% of studied years in the central-north-western and central-eastern regions, in 87% of considered years in the north-eastern and south-western regions and in 80% of analyzed years in the south-eastern region.

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Potrzeby wodne czeremchy zwyczajnej (*Padus avium* Mill.)

Streszczenie

Czeremcha zwyczajna (*Padus avium* Mill.), nazywana również czeremchą pospolitą, jest rośliną leczniczą i ozdobną. Jej kwiaty, owoce i kora są wykorzystywane w ziołolecznictwie. Bywa sadzona w parkach i przy drogach, a także stosowana w zadrzewieniach krajobrazowych i rekultywacyjnych. Decydującym o wysokiej udatności nasadzeń jest zwłaszcza okres pierwszych trzech lat po nasadzeniu roślin wprowadzanych na dany teren. Wymaga to zapewnienia wystarczającej ilości wody poprzez dobrze zaprogramowane nawodnienia. Celem podjętych badań była próba oszacowania potrzeb wodnych czeremchy zwyczajnej w pierwszych trzech latach po nasadzeniu. Jako miarę zapotrzebowania wody przez rośliny przyjęto ewapotranspirację potencjalną. Wykorzystano do tego celu, zmodyfikowany dla warunków Polski przez Żakowicza (2010), wzór Blaney-Criddle'a, z użyciem dostosowanych do niego współczynników roślinnych. Przyjęto, że sezon wegetacyjny czeremchy zwyczajnej rozpoczyna się 1 kwietnia a kończy 31 października. Obliczenia przeprowadzono dla różnych regionów agro-klimatycznych Polski w latach 1981-2010. Niedobory (lub nadmiary) opadów w okresie kwiecień-październik obliczono z różnicy pomiędzy potrzebami wodnymi czeremchy, wyrażonymi, jako Etp dla tego okresu, a sumą opadów atmosferycznych. Potrzeby wodne czeremchy w okresie jej największego zapotrzebowania na wodę (lipiec-sierpień) w 5 regionach Polski wyniosły 233 mm. Największe potrzeby wodne w lipcu i w sierpniu, wystąpiły w dwóch regionach Polaki: środkowo-północno-zachodnim i środkowo-

wschodnim (około 242 mm). Najmniejsze potrzeby wodne (średnio 227 mm), stwierdzono w północno-wschodnim i południowo-wschodnim regionie Polski. W każdej dekadzie analizowanego wielolecia zaznaczyła się istotna tendencja wzrostu zapotrzebowania na wodę o 5 mm w okresie lipca i sierpnia. W badanym trzydziestoleciu, niedobory opadów w okresie lipiec-sierpień wystąpiły w 29 latach w regionach północno-wschodnim i środkowo-wschodnim, w regionie środkowo-północno-zachodnim w 28 latach, w południowo-zachodnim w 27 latach, a w południowo-wschodnim niedobory opadów wystąpiły w 25 latach. We wszystkich badanych regionach rozpatrywanego trzydziestolecia, zaznaczyła się tendencja do zwiększenia się potrzeb wodnych czeremchy w okresie wegetacji. Trend zmienności czasowej potrzeb wodnych był, z wyjątkiem regionu środkowo-północno-zachodniego, istotny w przypadku każdego regionu.

Abstract

Bird cherry (*Padus avium* Mill.) is a medicinal and ornamental plant. Its flowers, fruits and bark are used in herbal medicine. Bird cherry is planted in parks, along roads and also used in the landscape and reclamation plantations. The first three years after planting determines the seedling survival rate of introduced plants. During this period, the plants should have adequate soil moisture, which can be provided by the properly designed and operated irrigation system. The aim of the research was to assess the bird cherry water needs during the first three years after planting. As a measure of water requirements, the potential evapotranspiration (Etp) of the plants was applied. The modified for Polish conditions by Żakowicz (2010) Blaney-Criddle's formula using the adjusted crop coefficients was applied. It was assumed that the growing season of plants starts on April 1 and ends on October 31. The estimates were carried out for five agro-climatic regions of Poland during the years 1981-2010. The rainfall deficiency (or excess) in the period from April to October was calculated based on the difference between the plants water needs (showed as Etp) and the precipitation totals. The average water requirements of bird cherry in all studied regions during the period of the highest water needs (July-August) were 233 mm. The highest water requirements (around 242 mm) in the period July-August occurred in the central-north-western and central-eastern regions. The lowest water requirements (227 mm) were noted in the north-eastern and south-eastern regions. In each decade of the long-term, a significant rising tendency of water needs in the period July-August by 5 mm was noted. During the years 1981-2010, the rainfall deficiency in the period July-August occurred in 29 years in the north-eastern and central-eastern regions, in 28 years in the central-north-western region, in 27 years in the south-western region and in 25 years in

the south-eastern region. In all studied regions during the long-term, the increasing tendency of bird cherry water requirements during the growing season was noted. The temporal variability of bird cherry water needs, with the exception of the central-north-western region, was important for each region.

Słowa kluczowe:

hałdy, nawadnianie, przemysłowe tereny, rekultywacja, udatność nasadzeń

Keywords:

heaps, irrigation, post-industrial areas, reclamation, seedling survival rate



Operational Problems of Selected Elements of the Dobrzyca Barrage on the Głomia River

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1. Introduction

The construction of barrages leads to permanent environmental transformations and changes in the water flow regime in rivers (Kałuża et al. 2014). Therefore, a design process of hydro-technical objects shall consequently emphasize design calculations related to the stability and strength of such facilities as correct hydraulic dimensioning of water structures and their components (Tyimiński 2010). The application phase, however, is beset by a number of problems, which may hinder or prevent their proper use. Downstream erosion and upstream bedload accumulation are the most known and recognizable related phenomena. Additionally, badeffects of river structure localization can be observed: overgrowth of river beds (Tyiminski & Kałuża 2012, Walczak et al. 2018), improper operation of fish passes, and – in case of hydroelectric power plants – deposition of organic and inorganic material on bars.

In the paper by Wiatkowski (2015) there are presented selected problems of water management of Młyny reservoir located at 6+968 in the Julianpolka river, in the municipality of Rudniki, Opole Province. The dammed reservoir is faced with numerous difficulties. It does not have a fish pass, which is critical to migration and continuity of biological life in water. There is also no continuous monitoring of the reservoir, especially during the occurrence of extreme hydrological phenomena in the catchment area. Conducting a continuous hydrological monitoring

would enhance proper water management of the reservoir. Mioduszewski & Łoś (2002) and Wiatkowski & Rosik-Dulewska (2011) indicate as a significant impediment when using small retention reservoirs the fact that these facilities are often not provided with permanent maintenance by professional services that can properly handle movable discharge devices and they lack constant technical and maintenance control. Zawadzki et al. (2015) describing the Skórka barrage on the Głomia river state that one of the main operational concerns is the current of the river that is too weak to attract fish to the fish pass. Głowski & Parzonka (2007) analysing the operation of the barrage in Brzeg Dolny on the Oder river claim that upstream silting and bedload deposition have an impact on limiting the capacity of three gates of the weir. Siltation has also contributed to a reduction in the reservoir capacity. On the other hand local scours created in the area of damaged reinforcements in the downstream part of the weir pose a threat to the stability of the barrage. Pagliara et al. (2017) addresses the issue of creating local scours below the impoundment structure. Dysarz & Wicher-Dysarz (2013) present their studies related to the effect a two-stage retention tank has on depositing of material in the initial part. (The calculations show that the two-stage construction of the reservoir seems to perform well. Sediment particles are settled in the upper part of the reservoir as expected). Kasperek & Głowski (2016) claim that the construction of the barrage in Brzeg Dolny has caused changes in bedload transportation, and further erosion below the dam has resulted in creating shallow areas impeding navigation. Mazur et al. (2016) and Walczak et al. (2013) present another problem i.e. the transportation of plant debris in high water and the effect of vegetation in floodplains on water velocity distributions in the river. Laks et al. (2013) present issues related to modelling of flow rate distribution in the river network with hydro-technical development exemplified by Kaliski Węzeł Wodny (Kaliski Water Node).

The study of technical condition and capacity of the weir on the Uszwica river is conducted by Tarnawski & Michalec (2007). They claim that despite a good condition of the concrete weir, the technical assessment of the structure is low due to damage to the end sill and abutments. Furthermore, it lacks control and measurement equipment required by legal regulations. Additionally, the results of their study indicate that the

weir is characterised by too low capacity providing for not more than approx. 52% reliable flow rate required for this type of structures.

During many years of operation of the water reservoir in Gołuchów on the Ciemna river there were conducted research on the deformation of the dam body and changes in the level of the ground water table. The analysis of readings from benchmarks found on the structure and changes in piezometric water levels conducted by Kowalski et al. (2007) demonstrates a high degree of similarity, which evidences the stiffness and improvement in water-soil relations of the dam body.

The fact that authors of the paper have undertaken this research topic finds scientific justification in operational problems related to small retention reservoirs and barrages. On the one hand there is a large number of the aforementioned objects that serve to increase overall retention (Liberacki et al. 2016), on the other hand the literature lacks a proper in-depth evaluation of their operation and problems that may arise during their use. The paper analyses a technical condition and the operation of selected elements of the Dobrzyca barrage on the Głowia river. Location of the barrage, position of its structures in mutual relation and their operation have an effect on specific problems related to its functioning.

2. Methodology

The research facility is located in the north Wielkopolska, near Piła city. The barrage consists of a weir, a fish pass and a small hydro power plant (SHPP). Due to lack of design documentation, during field research there were conducted geometry measurements of the weir and the fish pass as well as hydrometric measurements in selected cross sections of the Głomia river.

The aim of the study was to technically assess a condition of particular elements of the barrage (Fig. 1 – weir, fish pass and power plant) and to analyse its operation under specific hydrological conditions. The main element of the Dobrzyca barrage is a three-gate movable weir. Figure 1 shows a schematic diagram of the structure.

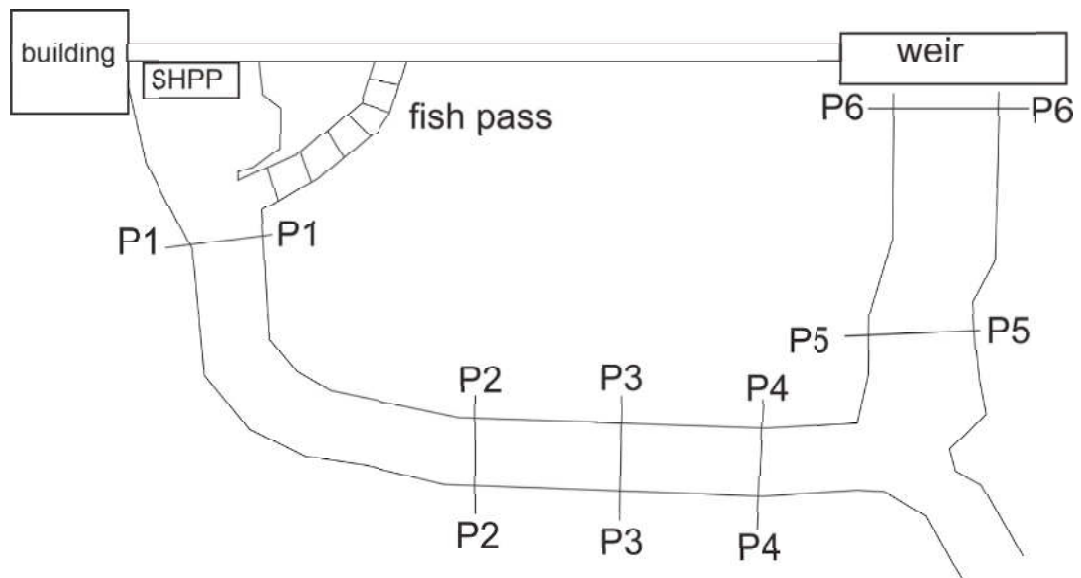


Fig. 1. Sketch of barrage elements with spacing cross section

Rys. 1. Szkic stopnia wodnego z zaznaczonym rozmieszczeniem przekrojów poprzecznych



Fig. 2. View on the weir in Dobrzyca on the Głomia river

Rys. 2. Widok jazu Dobrzyca na rzece Głomi

The weir on the Głomia river belongs to the group of movable weirs (Fig. 2 and 3). The structure has three gates of $b_1 = 1.7$ m, $b_2 = 2.75$ m, $b_3 = 2.45$ m respectively, and two piers of 0.57 m and 0.60 m. The weir is equipped with flat shutters – stop logs used for constant impoundment of water. There is an abutment of 0.55 m width located on the right side/bank of the weir at a distance of 0.7 m from the gate no 1. The standard impoundment level of the barrage is 64 m a.s.l.

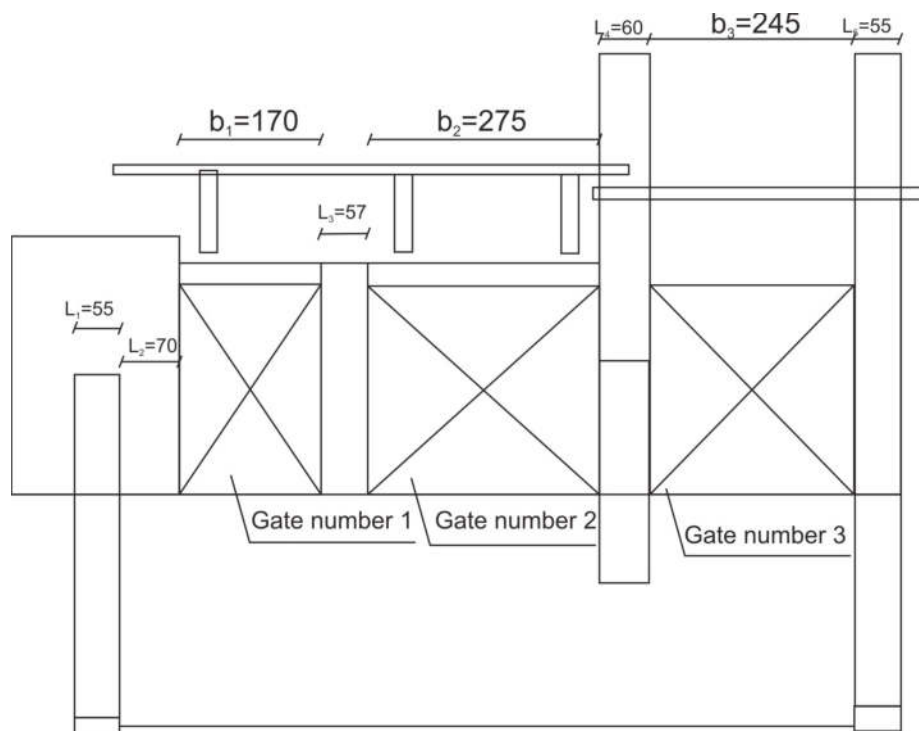


Fig 3. Weir draft, Dobrzyca barrage on the Głomia river (dimension in cm)

Rys. 3. Szkic jazu, stopnia Dobrzyca na rzece Głomi (wymiały w cm)

Small hydro power plant is equipped with two turbines: a tubular turbine and a Francis turbine, and is located in the derivational channel (Fig. 4). The advantage of this type of a channel is that it provides a greater fall than the impoundment on the weir and it shortens a natural course of the river. Comparing classic solutions, a leverage does not require maintenance services or shutters, thus it enables a significant reduction in investment outlay. Increase in the water level in the upstream part e.g. above the maximum level of impoundment causes flooding and sucking of the leverage, and consequently, water – which in the initial phase occupies only part of its cross section – fills it completely. This is the state of normal operation of the leverage.



Fig. 4. Downstream view of SHPP at the Dobrzyca barrage on the Głomia river

Rys. 4. Widok na dolną wodę MEW na stopniu Dobrzyca na rzece Głomi

An important element of the barrage is its pool fish pass, consisting of 9 pools of length from 1.2 m to 1.85 m and an average width of 1.0 m (Fig. 5). The fish pass is 0.15 m thick and its pools fish pass are approx. 0.4 m. deep. Measurements carried out during field tests have proven a poor technical condition of the fish pass and its overall malfunction.

Field research included a geodetic analysis of the studied areas.. Measurements were made using a classic geodetic survey method by means of Topcon leveller. The bottom of the river bed was subject to hydraulic measurements and geometry testing in six cross sections located on the drainage channel of hydroelectric power station and below the weir. Cross sections were made using a bottom probing technique. Measurements of velocity distributions below the weir and in the riverbed of Młynówka were conducted with the use of model 801 electromagnetic open channel flow meter manufactured by Valeport.



Fig. 5. Pool fish pass by Dobrzyca barrage on the Głomia river

Rys. 5. Przepławka komorowa stopnia Dobrzyca na rzece Głomi

The technical condition of the barrage was evaluated according to the methodology proposed by Zawadzki (2005). The choice of Zawacki's method for assessing the technical condition of hydrotechnical constructions results from the ease of the assessment, its precise weights and the clarity of the parameters. During fieldwork particular elements of the facility (fixed and movable components and control and measuring devices) were subject to technical inspection, determining their appearance and condition. Concrete elements were checked for the occurrence of cracks, defects, reinforcement exposures, infiltrations, soaks and discoloration, and fixed elements (body, abutments, reinforcement) for the appearance of lichen. The assessment of the condition of shutters and hoisting mechanisms includes the evaluation of their maintenance, the occurrence of corrosion and deformation of movable parts. According to the methodology proposed by Zawadzki (2005), the following are also to be included: equipping the facility with control and measuring devices, in particular, benchmarks, piezometers and stream gauges from the upstream and downstream side. All elements of the facility, i.e. fixed, mov-

able components, control and measurement devices, are rated on a scale from 0 to 5, taking into account the occurrence and intensity of unfavourable or harmful processes. According to the scale: 5 means very good condition (no unfavourable processes), 4 – good condition, 3 – satisfactory condition, 2 – unsatisfactory condition, 1 – bad condition (very bad unfavourable processes). In the absence of, for example, control equipment required for a given water facility, a rating of 0 should be adopted, indicating its unacceptable status. A final technical assessment is determined by the arithmetic mean of partial evaluations. This method was verified and applied among others by Michalec (2013), who drew attention to the subjectivity of technical condition assessment and the need to develop the competences of people performing it.

The technical assessment of the weir on the Głomia river and in Dobrzyca was carried out in two variants. Variant I (WI) involved an assessment compiled on the basis of a direct field inspection carried out by one of the "independent experts 1". Variant II (WII) provided for a technical assessment carried out by another "independent experts 2" based on detailed photographic documentation of the examined structure. Results obtained allow verifying technical assessment only on the basis of carefully taken photographic documentation.

Water distribution scenarios for particular elements of the barrage were based on the determination of the hydraulic head value, water discharge through the fish pass, weir and SHPP. Calculations of the discharge of water flowing of water from under shutters were the basis for designating water discharge for particular gates of the weir. There were assumed 6 operational variants of the weir (opening of particular shutters or simultaneous opening of two or three shutters). First three from six variants concern singly gates. Next in turn variants connected with combination of gates opening. Water distribution on SHPP was defined by the designed flow rate of particular turbines. The volume of water flowing through the fish pass was determined on the basis of measurements.

Hydraulic head curves included in scenarios show correlation between the hydraulic head value and flow rate, at the constant level of impoundment. Hydraulic head is a difference in the normal impoundment level (NI) and the downstream water level (DW). In the absence of systematic hydrometric measurements carried out in the downstream, on the basis of which the authors would be able to determine a flow rate curve,

the curve has been determined based on computer simulations. The measured of the water levels were used to identify the parameters of the mathematical model of HEC-RAS. Based on the known geometry of the cross-sections, flow rate, and the water elevations the manning coefficient was specified and it was equal $0.038 \text{ m}^{-1/3} \cdot \text{s}$.

Assuming steady motion conditions, the calculations have been based on the Bernoulli equation, which describes the energy balance between two cross sections of the river bed (Brunner 2010).

3. Results

3.1. Technical condition assessment of structures of the barrage

The results of the technical condition assessment of individual elements of the barrage are presented in Table 1. The condition of the weir is unsatisfactory. There are no hoisting devices that serve to operate shutters. Footbridges are equipped only with temporary wooden railings (the structure lacks railings from the upstream side). Additionally, there is no fixed footbridge for the gate no. 3. The ordinates of piers, abutments and footbridges do not meet safety recommendations for the existing impoundment on the weir. There are observed some damaged reinforcements in the downstream. Though, riprap near the end sill is visible only at a length of approx. 1m. The structure is subject to systematic maintenance work, however, some damage to the abutment (concrete defects) are found on the right bank, as well as there are some soaks on the impoundment wall and concrete cracks in the structure near the gate no. 3. The data collected both on the basis of direct observations (WI) – 2.13 as well as an analysis based on photographic documentation (WII) – 2.25 have given an overall unsatisfactory rating.

Due to the fact that the weir in Dobrzyca on the Głomia river is not equipped with hoisting devices for wooden shutters, the author have taken a rating of 0 for calculating an average assessment value. It indicates that movable elements are in an unacceptable condition. The low technical assessment of the weir is also resulted in the condition of its concrete structure.

Table 1. Assessment of the technical state of the weir, SHPP and fish pass
Tabela 1. Ocena stanu technicznego jazu, małej elektrowni wodnej oraz przepławki dla ryb

Technical state	Weir		SHPP		Fish pass	
	WI	WII	WI	WII	WI	WII
Solid elements:						
surface	2	3	3	3	3	3
cracks	2	2	4	3	4	4
decrements	2	2	4	3	4	4
uncover of reinforced rods	3	3	4	3	4	4
dripstones, leakages	2	2	4	4	4	4
tints		3	3	3	3	3
lichens	3	3	3	3	3	3
A. Movable elements:						
gate	2	2	3	3	2	2
drawing gears	0	0	3	2	2	2
deformations	1	1	2	2	2	2
corrosion	2	2	3	3		
conservation	3	3	4	4	3	3
B. Monitoring and measurement devices:						
bench-marks	2	2	2	0	2	0
piezometers	0	0	0	0	0	0
water-level Gauges	5	5	3	5	2	2
information boards	3	3	2	3	0	0
Mean	2.13	2.25	2.94	2.75	2.53	2.40

What is more, the power plant is also in an unsatisfactory technical condition. A provisional shed roofed with corrugated plate requires significant repair works. Reinforcements from the downstream side also require replenishment, especially on the right bank at the corner of the building. There is no possibility of manoeuvring with an idle discharge at the power plant – it has been permanently closed with stop logs. There is no water gauge in the downstream part. According to method WI, an average rating of 2.94 has been obtained, and according to WII – 2.75, indicating its unsatisfactory condition.

The fish pass has been rebuilt recently, however on the basis of Tymiński et al. 2017 and FAO/DVWK 2002 it was found that condition and potential for fish migration are still unsatisfactory. The entrance to the fish pass from the upstream side is very narrow. Currently, the fish pass has been remodelled as a pool fish pass (incl. chambers), except for there is no bottom opening in walls of pool fish pass overflows. Therefore, the fish pass operates as a cascade, with water flowing over upper openings (Fig. 5). In addition, the last pool fish pass is located approx. 10m from the end of the fish pass, and a difference in water levels between the last poolfish pass and the downstream is approx. 40 cm. From the downstream side the fish pass lacks several last pools fish pass (overflows). Its exit is incorrectly situated, since the last section is directed at the right angles to the outlet from the power plant. The system also does not provide reinforcements at the final section, the right bank of the fish pass. The fish pass entrance from the downstream side is very shallow approx. 20 cm. According to method WI the fish pass has been given an average rating of 2.53, whilst according to WII – 2.40, what indicates an unsatisfactory condition of the structure.

In general, the system lacks piezometers and benchmarks, as well as the basic recognition of hydraulic and hydrologic working conditions of the barrage (e.g. flow rate curves in the downstream part of the weir and SHPP). The technical condition of the Dobrzyca barrage on the Głomia river, determined on the basis of an inventory carried out as a one-step diagnostic (Zawadzki 2005), has been considered unsatisfactory. In consequence, it implies urgent and necessary repair and modernisation works. Similar values are reflected in the results of assessments obtained by methods WI and WII.

3.2. Hydraulic analysis of operation of the Dobrzyca Node

The curves for the operation of the node characterise the distribution of water into individual barrage elements. At the Dobrzyca barrage the distribution of water is divided into the fish pass, the weir and SHPP. On the basis of previously designated curves for opening of shutters, the height values of shutters' opening is taken in various combinations due to different widths of gates. Two cases are considered: the situation when SHPP does not work, and when the siphon turbine and Francis turbine included in the SHPP operate. Then, after summing up flow rates from

all elements of the barrage, based on previously designated hydraulic head curves, there are taken the hydraulic head value.

In order to develop different operational concepts of the barrage there were conducted simulations taking into account the operation of the power plant (first the systematic inclusion of the siphon turbine, and after reaching a certain level of flow rate - the inclusion of the Francis turbine) and manoeuvring with shutters of the weir gates. It has been assumed that with the activated power plant, the flow rate is increased until its maximum value is reached ($2,2 \text{ m}^3 \cdot \text{s}^{-1}$), which is the sum of the maximum flow rate for the siphon and Francis turbine. The downstream ordinate is read from the flow rate curve. The volume of water passed through the fish pass is constant for all analysed cases.

The distribution of water into particular elements of the Dobrzyca barrage is presented in Tables 2 and 3. Based on the compiled data, the authors have designated operational curves for the node considering opening of shutters 1, 2, 3 as well as 1+2, 2+3 and 1+2+3.

Table 2 presents the distribution of water into particular elements of the Dobrzyca barrage, on the assumption that SHPP is activated. It has been assumed that the flow rate through the fish pass is constant and equals $0.24 \text{ m}^3 \cdot \text{s}^{-1}$. At the beginning, the siphon turbine, which works until it achieves its maximum flow that is $1.00 \text{ m}^3 \cdot \text{s}^{-1}$, is activated, then additionally the Francis turbine with the maximum flow rate of $1.20 \text{ m}^3 \cdot \text{s}^{-1}$ is activated. SHPP operates until it reaches the maximum head value of 2m. The flow rate is then $7.21 \text{ m}^3 \cdot \text{s}^{-1}$. When the flow rate reaches $7.21 \text{ m}^3 \cdot \text{s}^{-1}$, SHPP is deactivated.

Figure 6 presents the operational scenario for the node assuming the operation of all openings of the weir. In the initial stage the fish pass and SHPP operate, following an increase in the flow rate all three shutters are being opened simultaneously. By opening up all gates, the impoundment structure significantly increases its capacity. Figure 7 shows how different water levels of the downstream affect the operational curve of the node for flow rates higher than $14 \text{ m}^3 \cdot \text{s}^{-1}$. Summing up the flow rate of the weir and the fish pass, the barrage can transfer $30.95 \text{ m}^3 \cdot \text{s}^{-1}$ of water. With regard to the design flow rate, that is $20 \text{ m}^3 \cdot \text{s}^{-1}$, the total capacity of the barrage is sufficient.

Table 2. Distribution water at particular elements of barrage with set working SHPP**Tabela 2.** Rozdział wody na poszczególne element stopnia wodnego przy pracującej MEW

Difference of levels	Fish pass	Weir	Lift of gate						SHPP		Sum of discharge
			1	2	3	1+2	2+3	1+2+3	Syphon turbine	Francis turbine	
[m]	[m ³ ·s ⁻¹]	[m ³ ·s ⁻¹]	[m]	[m]	[m]	[m]	[m]	[m]	[m ³ ·s ⁻¹]	[m ³ ·s ⁻¹]	[m ³ ·s ⁻¹]
2.89	0.24	0	0	0	0	0	0	0	0.2	0	0.44
2.83	0.24	0	0	0	0	0	0	0	0.6	0	0.84
2.76	0.24	0	0	0	0	0	0	0	1	0	1.24
2.70	0.24	0	0	0	0	0	0	0	1	0.4	1.64
2.64	0.24	0	0	0	0	0	0	0	1	0.8	2.04
2.58	0.24	0	0	0	0	0	0	0	1	1.2	2.44
2.38	0.24	0.7	0.11	0.07	0.07	0.04	0.04	0.02	1	1.2	3.14
2.34	0.24	1.20	0.18	0.11	0.12	0.07	0.06	0.04	1	1.2	3.64
2.28	0.24	1.89	0.28	0.17	0.19	0.10	0.09	0.07	1	1.2	4.33
2.22	0.24	2.49	0.38	0.22	0.25	0.14	0.12	0.09	1	1.2	4.93
2.16	0.24	3.08	0.47	0.27	0.31	0.17	0.14	0.11	1	1.2	5.52
2.13	0.24	3.65	0.57	0.33	0.37	0.20	0.17	0.13	1	1.2	6.09
2.08	0.24	4.22	0.66	0.38	0.43	0.23	0.20	0.15	1	1.2	6.66
2.04	0.24	4.77	0.76	0.43	0.48	0.26	0.22	0.17	1	1.2	7.21
2.00	0.24	5.27	0.85	0.48	0.54	0.29	0.25	0.19	1	1.2	7.71
1.98	0.24	7.71	1.31	0.71	0.81	0.43	0.36	0.27	0	0	7.95
1.95	0.24	8.21		0.76	0.87	0.46	0.39	0.29	0	0	8.45
1.87	0.24	9.21		0.87	0.99	0.52	0.44	0.33	0	0	9.45
1.795	0.24	10.21		0.97	1.11	0.58	0.49	0.37	0	0	10.45
1.73	0.24	11.21		1.08	1.23	0.64	0.54	0.40	0	0	11.45
1.66	0.24	12.21		1.19	1.36	0.70	0.59	0.44	0	0	12.45
1.59	0.24	13.21		1.30		0.76	0.64	0.48	0	0	13.45
1.57	0.24	13.71		1.36		0.80	0.67	0.50	0	0	13.95
1.54	0.24	14.21				0.83	0.69	0.54	0	0	14.45
1.48	0.24	15.21				0.89	0.75	0.61	0	0	15.45
1.42	0.24	16.21				0.96	0.80	0.68	0	0	16.45
1.36	0.24	17.21				1.02	0.85	0.75	0	0	17.45
1.31	0.24	18.21				1.09	0.91	0.81	0	0	18.45
1.26	0.24	19.21				1.16	0.96	0.87	0	0	19.45
1.21	0.24	20.21				1.23	1.02	0.92	0	0	20.45
1.17	0.24	21.21				1.30	1.08	0.98	0	0	21.45
1.13	0.24	22.21				1.37	1.13	1.03	0	0	22.45
1.10	0.24	22.71				1.40	1.16	1.05	0	0	22.95
1.09	0.24	23.21					1.19	1.07	0	0	23.45
1.05	0.24	24.21					1.25	1.12	0	0	24.45
1.01	0.24	25.21					1.31	1.16	0	0	25.45
0.98	0.24	26.21					1.37	1.21	0	0	26.45
0.97	0.24	26.71					1.40	1.23	0	0	26.95
0.95	0.24	27.21						1.25	0	0	27.45
0.92	0.24	28.21						1.29	0	0	28.45
0.90	0.24	29.21						1.33	0	0	29.45
0.87	0.24	30.21						1.36	0	0	30.45
0.86	0.24	30.71						1.38	0	0	30.95

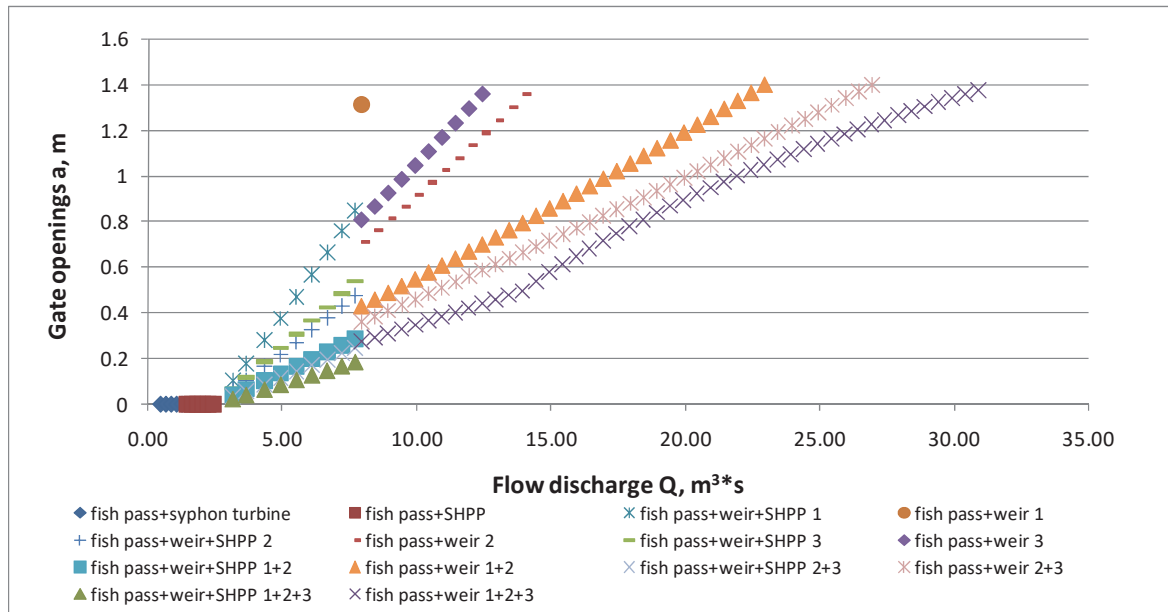


Fig. 6. Barrage operation curve with opening all gates and SHPP in Dobrzyca barrage on the Głomia river

Rys. 6. Krzywa pracy stopnia Dobrzyca na rzece Głomi dla pracujących wszystkich zamknięć i MEW

Table 3 presents the distribution of water into particular elements of the Dobrzyca barrage, on the assumption that SHPP is deactivated. It has been assumed that the flow rate through the weir depends on the hydraulic head value and the constant flow rate through the fish pass of $0.24 \text{ m}^3 \cdot \text{s}^{-1}$. The hydraulic head value is taken from previously designated hydraulic head curves.

The calculations have been made for each gate separately and for simultaneous opening of several shutters. Figure 9 presents the calculated operational curves of the node for the deactivated SHPP.

Table 3. Distribution water at particular elements of barrage with switched off SHPP

Tabela 3. Rozdział wody na poszczególne element stopnia wodnego przy wyłączonej MEW

Difference of levels [m]	Fish pass [m ³ ·s ⁻¹]	Weir [m ³ ·s ⁻¹]	Lift of gate						SHPP		Sum of discharge [m ³ ·s ⁻¹]
			1 [m]	2 [m]	3 [m]	1+2 [m]	2+3 [m]	1+2+3 [m]	Syphon turbine [m ³ ·s ⁻¹]	Francis turbine [m ³ ·s ⁻¹]	
2.58	0.24	0.64	0.10	0.06	0.07	0.04	0.03	0.02	0	0	0.88
2.50	0.24	1.50	0.22	0.13	0.15	0.08	0.07	0.05	0	0	1.74
2.41	0.24	2.50	0.38	0.22	0.25	0.14	0.12	0.09	0	0	2.74
2.33	0.24	3.50	0.54	0.31	0.35	0.19	0.16	0.12	0	0	3.74
2.24	0.24	4.50	0.71	0.40	0.46	0.25	0.21	0.16	0	0	4.74
2.16	0.24	5.50	0.89	0.50	0.56	0.30	0.26	0.19	0	0	5.74
2.08	0.24	6.50	1.08	0.59	0.67	0.36	0.31	0.23	0	0	6.74
2.00	0.24	7.50	1.27	0.69	0.79	0.41	0.35	0.27	0	0	7.74
1.92	0.24	8.50		0.79	0.90	0.47	0.40	0.30	0	0	8.74
1.85	0.24	9.50		0.90	1.02	0.53	0.45	0.34	0	0	9.74
1.78	0.24	10.50		1.00	1.14	0.59	0.50	0.38	0	0	10.74
1.71	0.24	11.50		1.11	1.27	0.65	0.55	0.41	0	0	11.74
1.64	0.24	12.50		1.22	1.39	0.71	0.60	0.45	0	0	12.74
1.58	0.24	13.50		1.33		0.77	0.66	0.49	0	0	13.74
1.52	0.24	14.50				0.84	0.71	0.56	0	0	14.74
1.46	0.24	15.50				0.90	0.76	0.64	0	0	15.74
1.40	0.24	16.50				0.96	0.82	0.70	0	0	16.74
1.35	0.24	17.50				1.03	0.87	0.77	0	0	17.74
1.30	0.24	18.50				1.10	0.92	0.83	0	0	18.74
1.25	0.24	19.50				1.16	0.98	0.89	0	0	19.74
1.20	0.24	20.50				1.23	1.04	0.94	0	0	20.74
1.16	0.24	21.50				1.30	1.09	0.99	0	0	21.74
1.12	0.24	22.50				1.37	1.15	1.04	0	0	22.74
1.08	0.24	23.50					1.21	1.09	0	0	23.74
1.04	0.24	24.50					1.27	1.13	0	0	24.74
1.00	0.24	25.50					1.33	1.18	0	0	25.74
0.97	0.24	26.50					1.39	1.22	0	0	26.74
0.94	0.24	27.50						1.26	0	0	27.74
0.91	0.24	28.50						1.30	0	0	28.74
0.89	0.24	29.50						1.34	0	0	29.74
0.87	0.24	30.50						1.37	0	0	30.74
0.86	0.24	30.71						1.38	0	0	30.95

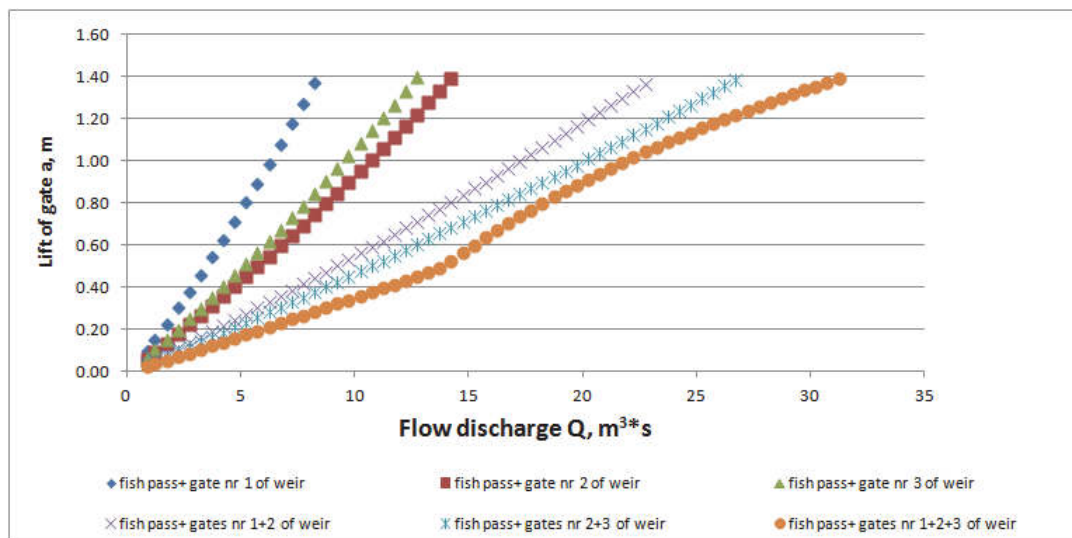


Fig. 7. Barrage operation curve at switch off SHPP

Rys. 7. Krzywa pracy stopnia wodnego przy wyłączonej MEW

Due to the high threshold of the weir, only when all shutters are simultaneously open, the downstream part of the weir is filled with water. It occurs when the opening is more than 0.5 m. By analysing Fig. 10 it can be stated that opening of the widest gate no. 2 enables the structure to transfer $13.5 \text{ m}^3 \cdot \text{s}^{-1}$, and opening of gates no. 1 and 2 increases the value to approx. $22.5 \text{ m}^3 \cdot \text{s}^{-1}$. The highest capacity is obtained when all shutters are open. The value is $30.71 \text{ m}^3 \cdot \text{s}^{-1}$.

4. Discussion

The paper analyses selected aspects of a technical condition assessment and operational issues of the Dobrzyca barrage on the Głomia river. The technical condition of the Dobrzyca weir was specified on the basis of an inventory carried out as one-step diagnostics. The unsatisfactory assessment of the structure results from i.e. condition of concrete elements of the barrage and lack of hoisting devices, both for shutters of the weir as well as the fish pass and SHPP. Furthermore, it lacks piezometers, benchmarks and a water gauge. Unfortunately, the state of this structure is not an exception. Practical experience shows many similarly neglected structures, although they do have a significant share in key and necessary development plans for small retention. Modification of Zawadzki's method (Zawadzki 2005) presented in the paper allowed for assessing the technical condition of the structure on the basis of detailed

photo documentation. The assessment basically coincides with the evaluation results obtained through a direct field inventory. In extreme cases, a method based on photographic analysis can complement and validate results obtained in a classical way.

On the basis of the data included in the article by Sterpejkowicz-Wersocki & Bolt (2002) it has been stated that backwater of the Koszyce barrage on the Gwda river does not affect the estuary table level of the Głomia river. Therefore, the operation of the node depends on local hydraulic and flow distribution conditions in the downstream part of the facility.

The majority of small water structures do not have a basic recognition of their hydraulic and hydrologic operating conditions (e.g. flow rate curves in the downstream part, systematic hydrological observation). It causes a serious concern for sustainable exploitation and rational water management of the aforementioned structures. Similar problems have been studied in the Skórka barrage on the Głomia river by Hämmerling et al. (2017).

5. Summary and conclusions

The authors analysed the capabilities of passing water through individual elements of the barrage. By analysing operating conditions of SHPP, it is stated that there is no danger of high water in its downstream due to too high volumes of water flowing through the weir. The power plant is activated until it reaches the maximum head value that is 2m. The flow rate is then $7.21 \text{ m}^3 \cdot \text{s}^{-1}$. When the flow rate value amounts to $7.21 \text{ m}^3 \cdot \text{s}^{-1}$, the power plant is deactivated. If the power plant operates, the weir is activated at the hydraulic head value of 2.38m, however, when the power plant does not operate, the weir starts its action at the hydraulic head value of 2.58m. The capacity of all elements of the barrage allows for safe flowing of the design water. The maximum capacity when all shutters are open is $30.71 \text{ m}^3 \cdot \text{s}^{-1}$. The lack of hoisting devices may significantly impede flow rate control, particularly in periods of high water. The flow rate value through the fish pass for the existing technical condition is $0.24 \text{ m}^3 \cdot \text{s}^{-1}$. Ineffectively, due to the technical condition of the fish pass, it cannot guarantee safe fish migration.

On the basis of earlier analysis of results can indicate the following conclusions:

- the Dobrzyca barrage on the Głomia river along with other impoundment structures (weirs in Krajenka and Skórka) can provide for an important element of the water management system in the catchment area of the Głomia river,
- this is crucial for both passing high waters as well as water retention during low seasons,
- the Dobrzyca barrage just like the other the majority of small water structures do not have a basic recognition of their hydraulic and hydrologic operating conditions,
- unfortunately, the current state of the facility raises legitimate concerns about the possibility of realizing its potential,
- Zawadzki's method can be successfully used to assess the technical condition of hydrotechnical constructions. This method allows even people without extensive experience to carry out research into the technical condition of the building.

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Problemy eksploatacyjne wybranych elementów stopnia wodnego Dobrzyca na rzece Głomii

Streszczenie

W skład stopnia wodnego wchodzi wiele różnych budowli, których poprawna eksploatacja umożliwi działanie całego stopnia zgodnie z instrukcją gospodarowania wodą. Analizowany w pracy stopień zlokalizowany jest na rzece Głomia w km 0+640. W jego skład wchodzi: mała elektrownia wodna, jaz trzy przęsłowy oraz przepławka techniczna (komorowa). Lokalizacja stopnia, wzajemne usytuowanie obiektów i ich eksploatacja wpływają na określone problemy funkcjonowania stopnia wodnego Dobrzyca. Należą do nich, między innymi kłopoty z zamulaniem dna zbiornika, odkładaniem się na kratkach rumożu roślinnego, a także zarastaniem koryta. W pracy przedstawiono ocenę stanu technicznego budowli oraz przeanalizowano warunki przepływu wody przez stopień wodny. Wykorzystując program komputerowy HEC – RAS przebadano wpływ zmian układu zwierciadła wody w korycie rzeki na pracę elektrowni wodnej. Przeanalizowano różne możliwe warianty pracy jazu i elektrowni wodnej. Wskazano możliwe zagrożenia i niebezpieczeństwa związane z pracą stopnia wodnego.

Abstract

A barrage is a type of diversion dam consisting of numerous different structures, demanding high level of maintenance which allow for operating in accordance to water management instructions. The barrage analysed in the present paper is located at 0+640 km of the Głomia river. It includes: a small hydropower plant, a three-gate weir and a technical fish pass (pool fish pass). Location of the barrage, position of its structures in mutual relation, as well as their operation have a practical effect on its specific operational problems. These include i.e.: silting of the reservoir bottom, depositing of plant debris on the weir bars, overgrowing of the river bed. The paper presents a technical condition assessment of these structures and analyses flow rate characteristics of the barrage. With the use of HEC-RAS software the authors tested the effect the topological changes in the water table of the river on the operation of the hydroelectric power station. Besides different possible operational variants of the weir and the power station studied, potential hazards and threats associated with the operation of the barrage are indicated in the paper.

Słowa kluczowe:

stopień wodny Dobrzyca, problemy eksploatacji, budowla piętrząca, przepławka komorowa, ocena konstrukcji hydrotechnicznych

Keywords:

the Dobrzyca barrage, operational problems, impoundment structure, pool fish pass, hydrotechnical structure assessment



Analysis of Water Quality of the Stobrawa River at the Location of the Walce Small Retention Reservoir

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1. Introduction

Small water reservoirs have several economic, hydropower, natural and recreational functions, and improve the water balance. Most of them are constructed for the purpose of storing water in periods of its excess and discharging it during droughts (Grzywna et al. 2016, Jurik et al. 2015, Wiatkowski et al. 2010). In addition, they help to reduce the risk of flooding. As in the upper and central river Odra within the territory of Poland the possibility of construction of large retention reservoirs is limited due to location conditions and costs, building small retention reservoirs appears to be a viable solution (Wiatkowski 2009, Wiatkowski et al. 2010). When planning the construction of a retention reservoir, one should consider not only the amount of water that will be retained in it, but also its quality (Cymes & Glińska-Lewczuk 2016, Mosiej & Bus 2015, Kanownik et al. 2013, Przybyła et al. 2015, Slaughter & Mantel 2018, Wiatkowski et al. 2015, 2018, Yunussova & Mosiej 2016). Frequently, the use of a reservoir and even its very existence is threatened by the inflowing contaminants (Bartoszek et al. 2017, Pütz & Benndorf 1998, Wiatkowski & Paul 2009). In many cases the water retained in a reservoir undergoes degradation, loses its utility values, and blooms appear frequently. The quality of water supplying a reservoir depends

mainly on the methods of water and sewage management within the catchment. Here, the phosphorus and nitrogen compounds have a significant impact on water quality in a reservoir (Dąbrowska et al. 2016, Koszelnik 2014, Pütz & Benndorf 1998, Wiatkowski & Paul 2009). For this reason, it is important to monitor the catchment areas of rivers on which the construction of water reservoirs is planned. As follows from the Development Strategy for the Opolskie Province until 2020, the irregularly distributed hydrographic network of the Province and its insufficient retention capacities (also for the needs of agriculture), require a series of intervention activities, including an extension of natural and artificial retention capacities (Strategy 2012).

The purpose of this study is to analyze the water quality of the Stobrawa river and to determine the possibility of its retention in the planned Walce reservoir. For the purpose of the study, an analysis of the quality of water in the Stobrawa river was conducted in the area of the future reservoir's basin. The quality of water of the Stobrawa river was evaluated in terms of physicochemical indicators. The paper presents a preliminary evaluation of the quality of water and an estimate of eutrophication of the waters being analyzed. An analysis of the catchment area of the Walce reservoir in the aspect of matter supply to the reservoir was also performed.

2. Material and method

Characterization of the Walce reservoir and its catchment area

The Walce reservoir will be located at kilometer 82.683 of the Stobrawa river (a right-hand tributary of the Odra river). It will be situated administratively in the Opolskie Province (South of Poland), in the Oleski District (Fig. 1). The reservoir will be situated in the upper, spring part of the Stobrawa river catchment, upstream from the town of Olesno. The average annual precipitation for Olesno, from the multi-year period of 1971-2000, is 650 mm, and the mean air temperature is about 8°C.

The primary role of the Walce reservoir will be water storage for agricultural purposes. The waters from the reservoir can be effectively used for irrigation (Assessment 1997). The stored water can also be used for various other purposes, e.g.: recreation, leisure, firefighting, angling, etc., hence the importance of the quality of water in the reservoir. No flood reserve capacity is planned.

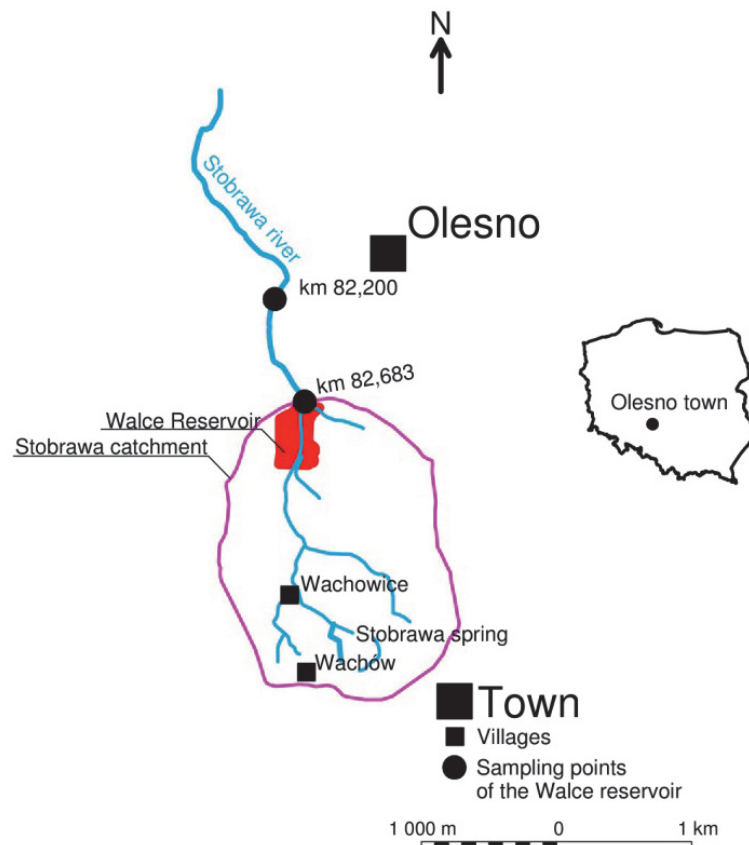


Fig. 1. Location of the planned Walce reservoir with a dam on the Stobrawa river and the sampling points for hydrochemical measurements

Rys. 1. Lokalizacja projektowanego zbiornika Walce wraz zaporą na rzece Stobrawie oraz z punktami do pomiarów hydrochemicznych

The main elements of the Walce reservoir are the dam and the weir structure. The catchment surface area at the profile of the reservoir dam is 5.6 km^2 and the longitudinal slope of the catchment area is about 17.1%. The catchment area of the Walce reservoir is under agricultural use. Arable lands and forests account for 81.9% and 10.4% of its area, respectively. Urbanized areas constitute about 6%. The Normal Pool Level in the reservoir is 243 m a.s.l. The capacity of the reservoir is 0.215 million m^3 and its surface area is 9.5 ha. The average flow rate SSQ in the Stobrawa at the dam section is $0.032 \text{ m}^3 \cdot \text{s}^{-1}$. The damming height will be 6.7 m and the average depth of the reservoir will be about 2.2 m. In terms of topography, the area in which the reservoir will be constructed is diversified. Narrow valleys of water courses are surrounded with hilly areas. The basin of the reservoir is characterized by large

lateral slopes. Land elevation differences approach 20 m. Sand formations cover the entire area. The area of the projected dam of the reservoir and its vicinity is covered with alluvial sand formations. Those are mainly sands (particle size distribution from silt sands to fine and medium sands). The ground water table is situated at the depth of about 3.5 m and deeper on the slopes. The topographic, geological-water and natural conditions in the planned location of the reservoir are good (Assessment 1997). Most of the area to be covered by the reservoir is occupied by agricultural lands under extensive use – with a large number of trees and bushes. The adaptation work will require the trees and bushes to be rooted up. The planned location of the reservoir is outside of any nature protection areas. Prior to the construction of the reservoir, the drainage and sewage system in the catchment of the reservoir will have to be improved, including in the village Wachowice situated upstream from the reservoir. The Province Inspectorate for Environmental Protection in Opole deals with the monitoring of the quality of surface waters in the Opolskie Province. The last study of the quality of the Stobrawa river (at the Stare Olesno profile, km 74,000) was carried out in 2004 as part of the regional monitoring. At present, in the Olesno commune, the quality of surface waters is not being monitored. According to the classification of the uniform parts of surface waters (UPSW), the analyzed profile of the river should be classified as "Stobrawa from sources to Kluczbork Stream" with the European code PLRW60001713231. It has the status of a heavily changed water body with ecological potential good and below good, but with poor assessment of status (National Water and Environmental Program 2010, Ordinance of the Council 2016). The nearest measuring point of the mentioned UPSW is located only at the Czapple Stare profile, km 45.000 of the Stobrawa river (Results of the surface water analysis from 2015).

The analysis of water quality of the Stobrawa river in the vicinity of the basin of the planned reservoir was conducted in two measurement periods. The first period lasted from November 2006 to October 2007 (water was sampled at kilometer 82.200, once a month), and the second from April 2011 to February 2012 (water was sampled at kilometer 82.683, once every two months). The following physicochemical indicators were analyzed: PO_4^{3-} (orthophosphates), P_{tot} , NO_3^- , NO_2^- , NH_4^+ , BOD_5 , dissolved oxygen, water temperature, reaction and electrolytic

conductivity. The temperature was investigated in situ and the remaining water quality indicators were tested in the laboratory of the Department of Land Surface Protection at the University of Opole in accordance with Polish standards. Water samples were collected from the stream of the Stobrawa river, from the subsurface layer. Estimation of eutrophication of the analyzed water was made on the basis of the Ordinance of the Minister of the Environment (2002), using the Vollenweider criterion (1976). Evaluation of the catchment of the Walce reservoir with regard to matter supply to the reservoir was conducted on the basis of the Bajkiewicz-Grabowska criterion (2002).

3. Results

Water quality

Table 1 presents the water quality characteristics of the Stobrawa river in the profile of the planned Walce reservoir in two measurement periods. Fig. 2 presents the changes in the content of phosphates and total phosphorus. Fig. 3 presents the changes in the content of nitrates, nitrites and ammonia over the study period.

The comparison of the Stobrawa river water quality testing results from the second measurement period (2011-2012) with those from the first measurement period presented in (Wiatkowski et al. 2012) reveals an improvement in water quality. An analysis of the results shows that the highest mean value corresponds to higher values of spread and deviation from the mean, which indicates a greater variation of results (Tab. 1).

In the case of phosphates (Fig. 2), the analysis of the two measurement periods showed that the lowest concentrations of these compounds occurred in November 2006 ($0.17 \text{ mg PO}_4^{3-} \cdot \text{dm}^{-3}$) and in April 2011 ($0.08 \text{ mg PO}_4^{3-} \cdot \text{dm}^{-3}$), while the highest were recorded in September 2007 ($2.22 \text{ mg PO}_4^{3-} \cdot \text{dm}^{-3}$) and in August 2011 ($0.14 \text{ mg PO}_4^{3-} \cdot \text{dm}^{-3}$).

The concentration of total phosphorus in the waters of the Stobrawa river in the first measurement period varied from 0.06 (November 2006) to $9.76 \text{ mg P} \cdot \text{dm}^{-3}$ (June 2007), and in the second period - from 0.12 (December 2011) to $0.35 \text{ mg P} \cdot \text{dm}^{-3}$ (April 2011) (Tab. 1, Fig. 2).

Tabela 1. Water quality indicators of the Stobrawa river in the profile of the planned Walce reservoir in two measurement periods

Tabela 1. Wskaźniki jakości wody rzeki Stobrawy w przekroju planowanego zbiornika Walce w dwóch okresach badawczych

Parameter	First measurement period Sept. 2006 – Oct. 2007	Second measurement period June 2011 – Feb. 2012
	<u>minimum – mean – maximum</u> standard deviation	<u>minimum – mean – maximum</u> standard deviation
Phosphates [mg PO ₄ ³⁻ ·dm ⁻³]	<u>0.17 – 0.91 – 2.22</u> 0.57	<u>0.08 – 0.10 – 0.14</u> 0.02
Phosphorus [mg P·dm ⁻³]	<u>0.06 – 1.93 – 9.76</u> 2.60	<u>0.12 – 0.18 – 0.35</u> 0.09
Nitrates [mg NO ₃ ⁻ ·dm ⁻³]	<u>0.35 – 8.45 – 26</u> 7.88	<u>1.67 – 2.06 – 2.23</u> 0.21
Nitrites [mg NO ₂ ⁻ ·dm ⁻³]	<u>0.04 – 0.10 – 0.23</u> 0.06	<u>0.05 – 0.08 – 0.11</u> 0.02
Ammonia [mg NH ₄ ⁺ ·dm ⁻³]	<u>0.27 – 2.14 – 3.2</u> 0.83	<u>0.0 – 0.40 – 0.73</u> 0.28
BOD ₅ [mg O ₂ ·dm ⁻³]	<u>1.20 – 6.19 – 24.0</u> 6.05	<u>0.2 – 2.33 – 4.46</u> 1.54
DO [mg O ₂ ·dm ⁻³]	<u>0.0 – 5.79 – 10.1</u> 3.76	<u>6.88 – 9.28 – 11.54</u> 1.85
Temperature [°C]	<u>0.6 – 8.7 – 15.3</u> 4.75	<u>1.9 – 9.63 – 16.5</u> 5.86
Reaction [pH]	<u>6.7 – 7.14 – 7.80</u> 0.30	<u>6.96 – 7.78 – 8.8</u> 0.88
Electrolytic conductivity [μs·cm ⁻¹]	<u>331 – 462 – 805</u> 133	<u>250 – 295 – 353</u> 41

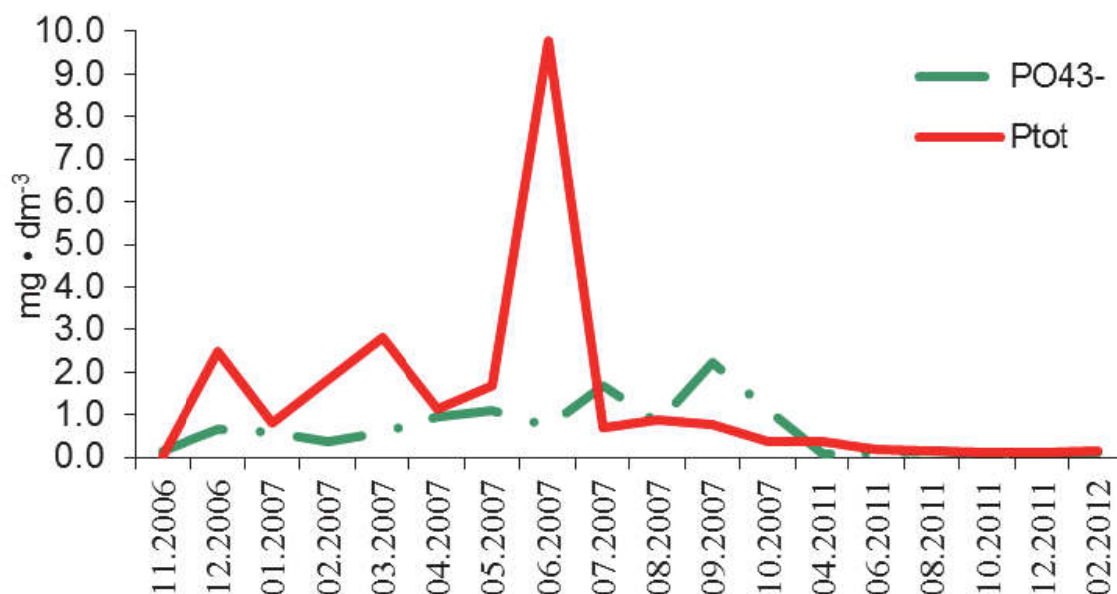


Fig. 2. Changes in the content of total phosphorus and phosphates in the Stobrawa river over the period from November 2006 to October 2007 and from April 2011 to February 2012

Rys. 2. Zmiany zawartości fosforu ogólnego i fosforanów w wodach rzeki Stobrawy w okresie od listopada 2006 do listopada 2007 i od kwietnia 2011 do lutego 2012

During the period of the study, the concentration of nitrates varied considerably (Fig. 3). The highest levels of this indicator were observed in winter periods (October 2007 – 26 mg NO₃⁻ · dm⁻³ and October 2011 – 2.23 mg NO₃⁻ · dm⁻³). The high levels of this indicator in winter were most likely caused by the surface runoff. The lowest nitrate concentrations were recorded in summer periods (August 2007 – 0.35 mg NO₃⁻ · dm⁻³ and August 2011 – 1,67 mg NO₃⁻ · dm⁻³), when the levels of nitrogen were regulated by plant vegetation.

The highest concentrations of nitrites were recorded in winter periods (Fig. 3). The highest content of nitrites was observed in January 2007 (0.23 mg NO₂⁻ · dm⁻³) and in December 2012 (0.11 mg NO₂⁻ · dm⁻³). The appearance of that form of nitrogen in water indicates an influx of household contaminants from localities situated in the catchment area of the Stobrawa river.

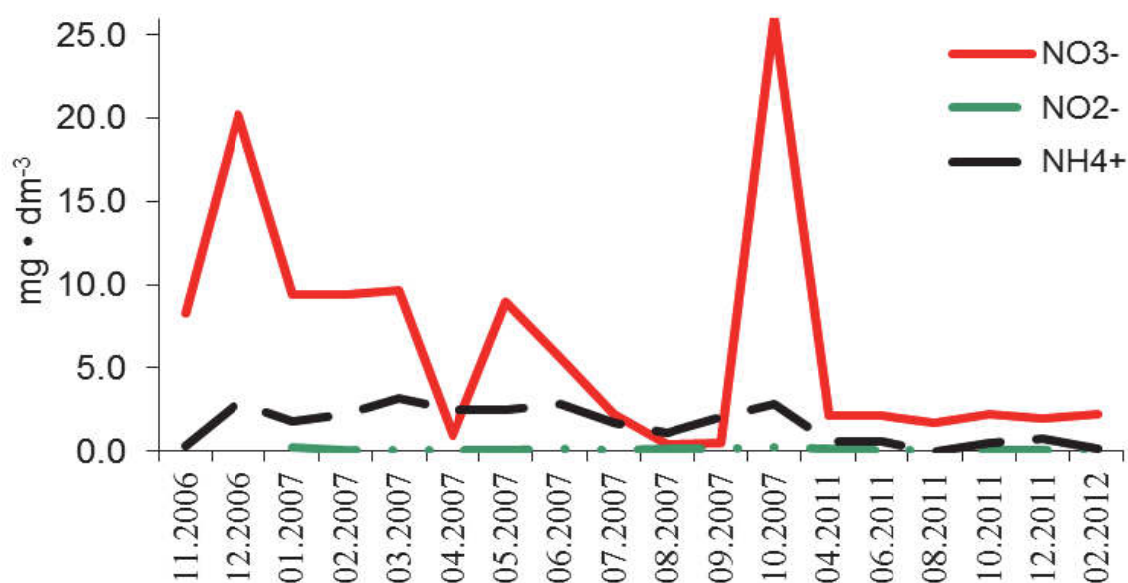


Fig. 3. Changes in the content of nitrates, nitrites and ammonia in the Stobrawa river over the period from November 2006 to October 2007 and from April 2011 to February 2012

Rys. 3. Zmiany zawartości azotanów, azotynów i amoniaku w wodach rzeki Stobrawy w okresie od listopada 2006 do października 2007 i od kwietnia 2011 do lutego 2012

The concentration of ammonia in the waters of the Stobrawa river in the first measurement period varied from 0.27 to 3.20 mg NH₄⁺ · dm⁻³, and in the second period – from 0 to 0.73 mg NH₄⁺ · dm⁻³ (Tab. 1).

As in the case of nitrite concentration, an analysis of the results of ammonia content determinations revealed that the mean levels of this element in winter periods were higher than in summer periods. Ammonia content in water is an important indicator of contamination with protein substances which, as a rule, occur at rather high concentrations in sewage. The high levels could be due to the runoff over the frozen ground cover and from household sewage. Another cause of increased levels of those compounds is the ageing and decay of macrophytes that absorb nitrogen and phosphorus compounds only in the spring and summer. Biogens are nutrients for macrophytes (Kajak 2001).

The level of BOD₅ in the waters of the Stobrawa in the first measurement period varied from 1.20 to 24 mg O₂ · dm⁻³ (Tab. 1), and in the second period – from 0.20 to 4.46 mg O₂ · dm⁻³. Higher values of BOD₅ were recorded in winter periods (the highest value was recorded in October

2007 and in December 2012). The higher the level of water contamination with easily degradable organic matter, the higher the values of BOD₅.

Oxygen content in the waters of the Stobrawa in the period of 2006-2007 varied from 0 to 10.1 mg O₂·dm⁻³, and in the period of 2011-2012 from 6.9 to 11.5 mg O₂·dm⁻³ (Tab. 1). Higher levels of oxygen were observed in the months with lower temperatures (January 2007, December 2012) than in summer and autumn.

Moreover, the study showed that the water temperature in the Stobrawa varied from 0.6°C to 15.3°C, from 1.9 to 16.5°C during the measurement period of 2006-2007 and 2011-2012, respectively (Tab. 1).

In the period of 2006-2007 the reaction of the waters of the Stobrawa river varied from pH 6.7 to 7.8, and in the period of 2011-2012 – from pH 6.9 to 8.8. The lowest pH values were observed in September 2007 and in December 2011, and the highest in October 2007 and in June 2011 (Tab. 1).

The electrolytic conductivity of water depends on the amount of ions dissolved in water, and also on the water temperature. The electrolytic conductivity of water of the Stobrawa ranged from 331 to 805 μS·cm⁻¹, and from 250 to 353 μS·cm⁻¹ in the period of 2006-2007 and 2011-2012, respectively – (Tab. 1).

Water management in the catchment area of retention reservoirs is of particular importance for their functioning, as being situated at the lowest point of their catchment such reservoirs are the recipients of the contaminants from the entire catchment area (Pütz & Benndorf 1998, Wiatkowski et al. 2010). The process of eutrophication constitutes a considerable threat to dam reservoirs. The possibility of use of water retained in a reservoir often depends on its quality, which results, from the kind of water-sewage management in place within the catchment of the reservoir (Wiatkowski & Paul 2009). Unfortunately no permanent monitoring of water quality is conducted in the catchment of the planned Walce reservoir.

Preliminary estimation of water quality of the Walce reservoir

All of the 10 water quality indicators analyzed for the Stobrawa river, are taken into account in the Polish classification of water quality status (Ordinance of the Minister of the Environment 2016). Analysis of the results of water quality of the Stobrawa revealed that the values of water temperature, electrolytic conductivity, pH, and the content of NO₃⁻

(in the two measurement periods), dissolved oxygen, BOD₅, phosphates and total phosphorus (only in the second period) did not exceed the limit values pertaining to water class I. As follows from the analysis of the data, the concentrations of ammonia and nitrites (the second period) exceeded the limit values for class I, but did not exceed those for water class II. However, the concentrations of dissolved oxygen, ammonia, nitrites, BOD₅, phosphates and total phosphorus (the first measurement period) did exceed the limit values of water quality indicators pertaining to uniform areas of surface waters in natural water courses such as a river, relevant for water class II.

In order to determine to what degree the Walce reservoir will be threatened by eutrophication, preliminary calculations were performed for the two measurement periods. By analyzing the concentration of total phosphorus from the two measurement periods and the limit value of this concentration ($> 0.25 \text{ mg P} \cdot \text{dm}^{-3}$) given in the Ordinance of the Minister of the Environment (2002) it was found that the waters of the Stobrawa river should be considered eutrophic during the first period of study. The average annual concentration of total phosphorus ($2.60 \text{ mg P} \cdot \text{dm}^{-3}$) exceeded the limit given in the Ordinance (2002). The calculations carried out based on the Vollenweider criterion allowed more parameters of the designed reservoir. Based on this criterion and taking into account that in the first period of research the concentration of total phosphorus in the profile of the future reservoir was $1.93 \text{ mg P} \cdot \text{dm}^{-3}$ (Tab. 1), with average flow rate of $0.032 \text{ m}^3 \cdot \text{s}^{-1}$, it was calculated that the load of phosphorus would be $1.95 \text{ mg P} \cdot \text{year}^{-1}$. The amount of phosphorus per 1 m^2 of the reservoir would be $20.5 \text{ g P} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$ with the ratio of the mean depth of the reservoir – 2.2 m to the time of retention – 0.213 year. For the total phosphorus concentration recorded in the second measurement period ($0.18 \text{ mg P} \cdot \text{dm}^{-3}$), it was found that the load of phosphorus per 1 m^2 of the reservoir would amount to $1.9 \text{ g P} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$. Thus, given the phosphorus load for both measurement periods, and the parameters of the Walce reservoir, eutrophication will take place. According to the Vollenweider classification (Kajak 2001), the planned Walce reservoir was classified as eutrophic. According to Kajak (2001), actual loads are often several times higher than the threshold or danger levels, and may attain a dozen and more grams of phosphorus and nearly 200 g of nitrogen per 1 m^2 of the reservoir surface area. This is several hundreds times more than the permissible levels (with the mean depth of up to 5 m the

allowable load for N and P should be up to 1.0 and 0.07 g·m⁻²·year, respectively, while the danger level for N and P should be up to 2.0 and 0.13 g·m⁻²·year, respectively).

The prevailing opinion on the quality of waters and the effect of their retention in small reservoirs is that when the waters supplying the reservoir are strongly contaminated they deteriorate the quality of water in the reservoir, and the smaller the reservoir the greater the load per unit surface area (Wiatkowski 2009, Wiatkowski and Paul 2009).

4. Evaluation of the Stobrawa catchment in terms aspect of the matter supplied to the Walce reservoir

Water reservoirs have the ability of intercepting matter migrating from their catchment areas (Wiatkowski et al. 2015). Water quality in reservoirs is largely determined by external inflows. The rate of natural eutrophication of a reservoir depends on the physical and geographical structure of the catchment that functions as a permanent supplier of various forms of matter to the reservoir (including nutrients), and on the morphometric parameters of the reservoir and its hydrological status (Pütz & Benndorf 1998, Paul & Pütz 2008, Koszelnik 2014, Wiatkowski & Paul 2009, Wiatkowski et al. 2010). The susceptibility of a reservoir to eutrophication can be estimated on the basis of the system proposed by Bajkiewicz-Grabowska (2002), that is used successfully by researchers (Wiatkowski et al. 2012). The natural physical and geographical features of the catchment allow the immediate catchment area of the reservoir to accelerate or inhibit the supply of matter (including nutrients) to the reservoir.

The effect of the catchment area on the rate of matter supply to a reservoir is estimated using assessment of each of the above characteristics in a scale from 0 to 3 points, where 0 means very weak effect on matter supply and no possibility of its reaching the reservoir, and 3 – a strong effect and rapid supply of matter to the reservoir (Bajkiewicz-Grabowska 2002). The characteristics describing the degree of catchment effect on the reservoir include e.g. the Ohle lake index and the balance type of reservoir. The strength of the impact in the immediate catchment is defined by the endorheic character of terrain, average slope of catchment, density of river network, surface formations and method of land use. Table 2 presents the evaluation of the Stobrawa catchment as a matter supplier to the Walce reservoir.

Table 2. Evaluation of the Stobrawa river catchment– source of supply of matter to the Walce reservoir

Tabela 2. Ocena zlewni rzeki Stobrawy – dostawcy materii do zbiornika Walce

Characteristics of the catchment area of the Walce reservoir		Bajkiewicz-Grabowska criterion (2002)	Number of points
Lake (Ohle) index – quotient of A of basin (5.3 km ²) and F of reservoir (9.5 ha at Normal Pool Level))	51	40-150	2
Type of reservoir	Throughflow	Throughflow	3
Morphometry			
- river network density [km · km ²]	1.0	0.5-1.0	1
- average slope	17.1	10-20	2
- endorheic areas (%)	0.2	<20	3
Geological structure	Quaternary formations, Mainly sands and gravels	Loamy-sandy	2
Type of land use	Forests 10.4%, agricultural lands 83.4%, built-up area 6.1%, water reservoirs 0,1%	Forest-agricultural with buildings, Pasture-agricultural with buildings, Agricultural with buildings	3
Mean			2.3

Source: Bajkiewicz-Grabowska E., 2002, own work

The final rating – arithmetic mean of points awarded to the individual features – is 2.3 and qualifies the Stobrawa catchment area, from the springs to the profile of the Walce reservoir, as a catchment area with a high capacity for supplying matter to the reservoir (susceptibility group 4).

With regard to the Walce reservoir, the estimation of environmental impact (Assessment 1997) recommend that, for the safe of protection of water quality in the reservoir, actions should be taken to reduce the uncontrolled inflow of sewage from settlement units and of area contaminants. Also the study (Wiatkowski et al. 2012) presents results indicating that the waters of the Stobrawa river, in the profile of the planned Walce reservoir, are characterized by considerable contamination.

At present, it is important to analyze the quality of waters in the catchment areas of planned water reservoirs, as the supply of nutrients from point and area sources (including agricultural ones) results in anthropogenic eutrophication of waters and is the primary threat to the achievement of good status of stagnant waters in Poland and in other countries of the European Community. Therefore, some actions should be taken, e.g. a reducing the concentration of nutrients in water inflowing to a reservoir, improve in the water-sewage management, performing suitable treatments in the land use in catchment area, creating protective zones in the buffer belt around the reservoir, the so-called ecotones, and using pre-reservoirs (Jurik et al. 2015, Mosiej & Bus 2015, Paul & Pütz 2008, Pütz & Benndorf 1998, Skonieczek et al. 2013, Wiatkowski & Paul 2009, Wiatkowski et al. 2010). In addition, each time, when a decision is to be taken concerning the construction of a reservoir, a water gauge section should be created for hydrological and water quality analyses at the inflow to the reservoir (Ignatius & Rasmussen 2016).

5. Conclusions

When making the decision to construct a water reservoir one should consider the quality of water which will flow into and be retained in the reservoir. Therefore, it is extremely important to conduct monitoring studies and analyses of water quality in the catchment basins of rivers on which water reservoirs are planned.

The analysis of water of the Stobrawa river, in two measurement periods, has revealed that the values of water temperature, electrolytic conductivity, reaction, and NO_3^- (in two measurement periods), dissolved oxygen, BOD_5 , phosphates and total phosphorus (the second measurement period) did not exceed the limit values for water class I. However, the concentrations of DO, NH_4^+ , NO_2^- , BOD_5 , PO_4^{3-} and P_{tot} (the first measurement period) did exceeded the limit values of water quality indicators pertaining to uniform areas of surface waters in natural water courses such as a river, relevant for water class II.

It was found that the quality of water in the Stobrawa river in the second research period (2011-2012) was characterized by lower pollution values compared to the first period (2006-2007).

Based on the limit value of the total phosphorus concentration given in the Ordinance (2002), the waters of the Stobrawa river, in the first measurement period, were classified as eutrophic.

On the basis of the Vollenweider criterion, it was found that, in terms of eutrophication, the hydrochemical conditions in the Stobrawa river catchment for the construction of the Walce reservoir are unfavorable. Analyses for both the first and the second measurement period demonstrated that the level of contamination of water inflowing to the Walce reservoir is high, and that the inflowing water can deteriorate the quality of water retained in the reservoir. Base on the acquired data (phosphorus load), the planned Walce reservoir was classified as eutrophic.

The evaluation of the Stobrawa river catchment as a supplier of matter to the Walce reservoir showed that the catchment is prone to supplying matter to the reservoir. Therefore, by proper water management in the reservoir catchment one should be aim to reduce the concentration of nutrients in the water inflowing to the reservoir and to create protective zones in the belt around the reservoir, that would allow the land use to be limited; moreover, the creation of sections for hydrochemical tests at the inflow to the reservoir should be considered.

The study conducted in the area of the catchment of the Walce reservoir provided important information on the status of purity of the waters supplying the planned reservoir.

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Analiza jakości wód rzeki Stobrawa dla lokalizacji małego zbiornika retencyjnego Walce

Streszczenie

Małe zbiorniki wodne spełniają funkcje gospodarcze, energetyczne, przyrodnicze, rekreacyjne i poprawiają bilans wodny. Budując zbiornik wodny, oprócz zagadnień ilościowych wody, należy także wziąć pod uwagę jakość wody, która będzie retencjonowana w zbiorniku. Często wykorzystaniu zbiornika, jak i jego istnieniu, mogą zagrozić zanieczyszczenia dopływające do niego głównie z wodą i rumowiskiem. Ważne są badania monitoringowe w zlewniach rzek na których zamierza się budować małe zbiorniki wodne, ponieważ w tych zlewniach najczęściej nie prowadzi się badań jakości wody. Bardzo ważnym problemem jest więc zanieczyszczenie zbiorników planowanych. Celem pracy

jest analiza jakości wód rzeki Stobrawy dla określenia możliwości jej retencjonowania w planowanym, w programie małej retencji dla województwa opolskiego, małym zbiorniku wodnym o nazwie Walce. W pracy przeprowadzono analizę jakości wód rzeki Stobrawy w pobliżu czaszy przyszłego zbiornika, w dwóch okresach pomiarowych (od listopada 2006 r. do października 2007 r. oraz od kwietnia 2011 r. do lutego 2012 r.). Jakość wód rzeki Stobrawy oceniono pod względem wskaźników fizyczno-chemicznych: NO_3^- , NO_2^- , NH_4^+ , Pog., PO_4^{3-} , BZT₅, tlenu rozpuszczonego, temperatury wody, odczynu i przewodności elektrolitycznej. Podstawową funkcją zbiornika ma być magazynowanie wody do celów rolniczych, przeciwpożarowych oraz rekreacji, wypoczynku i wędkarstwa, dlatego ważnym zagadnieniem jest jakość wód zbiornika. Przeprowadzone badania wykazały, że zanieczyszczenie wody rzeki Stobrawy w przekroju planowanego zbiornika Walce jest znaczne. Na podstawie uzyskanych danych zakwalifikowano projektowany zbiornik Walce do zbiorników eutroficzných. Przeprowadzona ocena zlewni rzeki Stobrawy jako dostawcy materii do zbiornika Walce wykazała, że zlewnia odznacza się dużą możliwością dostarczania materii do zbiornika.

Abstract

Small water reservoirs have economic, hydropower, natural and recreational functions, and improve the water balance. When building a water reservoir, one should consider not only the amount of water that will be retained in it, but also its quality. Frequently, the use of a reservoir and its existence can be threatened by contaminants brought into it with water and rubble. It is important to conduct monitoring in the catchment areas of rivers on which small water reservoirs are to be built, as most often no water quality analyses are conducted in such catchments. Therefore, contamination of planned water reservoirs is a very important problem. The objective of the study was to analyze the quality of water of the Stobrawa river to determine the possibility of its retention in the planned small water reservoir Walce, included in the small retention program for the Opolskie Province. For the purpose of the study, an analysis of water quality of the Stobrawa river was conducted in the vicinity of the basin of the future reservoir, in two measurement periods (from November 2006 to October 2007, and from April 2011 to February 2012). The quality of water of the Stobrawa river was evaluated in terms of the physicochemical indicators NO_3^- , NO_2^- , NH_4^+ , P tot., PO_4^{3-} , BOD₅, dissolved oxygen, water temperature, reaction and electrolytic conductivity. The primary function of the reservoir is to be a water storage for agriculture, fire-fighting, as well as recreation, leisure and angling, hence the importance of water quality. The study demonstrated that the contamination of water of the Stobrawa river in the profile of the planned Walce

reservoir is considerable. Based on the data obtained from the study, the planned Walce reservoir was classified as an eutrophic. The analysis of the Stobrawa river catchment, as a supplier of matter to the Walce reservoir, revealed that the catchment is characterized by a high capacity for the supply of matter to the reservoir.

Słowa kluczowe:

małe zbiorniki wodne, jakość wody, rzeka Stobrawa, zbiorniki projektowane

Keywords:

small waters reservoir, water quality, Stobrawa river, planned water reservoirs



Analysis of the Vegetation Process in a Two-stage Reservoir on the Basis of Satellite Imagery – a Case Study: Radzyny Reservoir on the Sama River

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1. Introduction

One of the most serious problems related to the functioning of reservoirs is the vegetation process. Reservoirs are more sensitive to degradation than other water bodies (Oszczapińska & Szczykowska 2016). It is related to their morphometric parameters, especially smaller depth and volume and a larger elongation ratio (Dąbrowska et al. 2016, Staniszewski & Szoszkiewicz 2010). Additionally, reservoirs receive biogenic compounds from a larger basin area, including anthropogenic and natural factors (Borek 2017, Kowalik et al. 2014, Nicula et al. 2017, Sojka & Murat-Błażejewska 2009, Sojka et al. 2016). One of the most interesting and promising approaches related to protection of water resource quality is construction of two-stage reservoirs (Bartoszek & Koszelnik 2016, Dysarz & Wicher-Dysarz 2013, Paul & Pütz 2008, Sojka et al. 2017). In such construction, the reservoir is split into two parts – the main and the pre-dam zone. The pre-dam zone is a smaller reservoir located upstream of the main reservoir. The main role of the pre-dam reservoir is to store sediments and water pollutants. Over recent years, such constructions have been increasingly used in Poland (Stare Miasto on the Powa river, Jezioro Kowalskie on the Główna river and Mściwojów on the Wierzbak river). The effectiveness of the pre-dam zone has been confirmed in many studies (Dysarz & Wicher-Dysarz 2011, Dysarz & Wicher-Dysarz 2013, Pikul & Mokwa 2008).

Eutrophication of reservoirs significantly contributes to depletion of flora and restriction of available water resources. Degradation of global water resources forced EU Members to protect them by adopting the Water Framework Directive (WFD 2000). Monitoring of the aquatic environment is an integral part of the water management strategy to meet the objectives of the WFD. Recently, remote sensing and GIS techniques present the most effective solutions for mapping aquatic environments (Luo et al., 2017, Palmer et al., 2015, Walczak et al. 2013, Walczak et al. 2016, Wang et al., 2012). Satellite imagery data enable detection of temporal and spatial changes in water bodies by repeat coverage of satellite instruments and multispectral characteristics of provided data. Multispectral characteristic is defined as a number of wavelength intervals in the electromagnetic spectrum which a satellite records. Additionally, remote sensing techniques have an economic advantage – imagery is provided by non-cost access. In recent years, remote sensing data from environmental satellites such as Sentinel-2, Landsat-7, Landsat-8, MERIS/OLCI and MODIS have been widely used for agricultural, forestry and aquatic applications (Agutu et al. 2017, Brown 2015, Chormański et al. 2011, Gökkaya et al. 2017). Results obtained on the basis of satellite data have been validated by field and laboratory measurements in many studies (Dörnhöfer et al. 2018, Kiefer et al. 2015, Yadav et al. 2017). Remote sensing techniques in aquatic monitoring are mainly used to assess algal blooms (Clark et al. 2017, Nazeer et al. 2017) and water transparency (Lee et al. 2016).

Aquatic environment monitoring is based on spectral indices, which are a combination of selected bands, mainly representing red and blue wavelengths. One of the most popular and widely used vegetation indices is the normalized difference vegetation index (NDVI), first proposed by Rouse et al. (1974). Many researchers have used the NDVI to detect vegetation for environmental purposes (Dlamini et al. 2016, Gao et al. 2012, Zhengjun et al. 2008). The values of the NDVI vary from -1 to +1, depending on land cover. Low values (minus or approaching zero) represent water and soil areas, while higher values represent vegetation – in an aquatic environment there are seasonal algal blooms, and emergent and floating plants.

The main purpose of the study was to assess the dynamics of the vegetation process in a two-stage reservoir on the basis of satellite data. The analysis is based on Sentinel-2 satellite data from the period 2015-2017. The NDVI was selected to detect the vegetation process in the Radzyny reservoir located on the Sama river.

2. Materials and Methods

The Sentinel-2 is part of the Copernicus Earth Observation mission, previously known as Global Monitoring for Environment and Security (GMES) program. The Sentinel-2 is a constellation of two satellites. The launch of the first satellite (Sentinel-2A) occurred on June 23, 2015, while the second (Sentinel-2B) was on March 7, 2017. The main instrument of the satellite, Multi-Spectral Imager (MSI), provides systematic data with a 5-day repeat cycle (Xue & Su 2017). The MSI sensor features 13 spectral bands for visible, near-infrared (VNIR) and short-wave infrared (SWIR) radiation in 10, 20 and 60 m spatial resolution.

The remote sensing data were acquired from the Sentinel Hub website (<https://sentinel-hub.com/>). Satellite imagery was selected for the vegetation months (May, June, July, August and September) in the period 2015-2017. Finally, thirteen Sentinel-2 images were selected for the analysis, three for 2015, and five each for 2016 and 2017. Analysis was carried out for pixels more than 50% of whose area consisted of reservoir. In the first step of data processing the NDVI was calculated for each satellite image. According to Xue and Su (2017), NDVI is very sensitive to the effects of atmosphere, cloud, and cloud shadow, and requires remote sensing calibration. The equation of the NDVI for Sentinel-2 data is based on a combination of NIR (ρ_{NIR}) and red (ρ_R) bands:

$$NDVI = \frac{\rho_{NIR} - \rho_R}{\rho_{NIR} + \rho_R}$$

Finally, to assess spatial and temporal dynamics of the vegetation process, values of NDVI for each satellite image were extract to point data. In this study, the degradation process was analyzed for the main and pre-dam reservoir. To specify areas mainly covered by vegetation, the reservoir was split into 10 parts, depending on the distance from the in-

flow of the Sama river (distance between profiles splitting polygons equals 500 m). All calculations were performed with Quantum GIS 2.18 and ArcGIS 10.5 software, and statistical analysis was conducted using Statistica 13 software. The statistical analysis was aimed at comparing the NDVI values in the pre-dam and main reservoir and additional between 10 parts of the reservoir designated for analysis. The assessment was based on the non-parametric Kruskal–Wallis (KW) test. One-way analysis of variance for Kruskal–Wallis ranks was employed for the verification of the hypothesis of significance of differences between medians value of NDVI (Ptak et al. 2018). Statistical analysis was made in Statistica 13 software.

3. Study area

The Radzyny reservoir was built in 2001 on the Sama river located in the Warta basin. The object has a two-stage construction. The main dam is located at 20.76 km, while the pre-dam is at 23.54 km of the Sama river. The total inundation area of the reservoir is 109.44 ha, while the capacity is 2.88 million m³. The area of the main reservoir equals 80.31 ha and its capacity is 2.48 million m³. The mean depth of the main reservoir is 3.10 m, while in the pre-dam reservoir it is 1.40 m. In the period from November to March, the water levels are 69 m a.s.l. and 71 m a.s.l. in the pre-dam and main dam reservoir respectively. However, in the period from March to November, the water levels in the reservoirs are set to 72 m a.s.l. and 72.5 m a.s.l. The Radzyny reservoir is a multi-purpose reservoir. The main functioning purposes include water supply capacity, flood protection, stability of environmental flows for biological life in the Sama river, tourism and recreation. The total catchment area of the reservoir is 239.90 km², and it is mainly covered by agriculture lands. The mean flow from the years 1982-2012 in the main dam profile was 0.64 m³·s⁻¹. However, extreme flows range from 0.016 to 12.38 m³·s⁻¹.

The main problem related to the management of the Radzyny reservoir is water quality. According to the report “Water management and water quality assessment of the Radzyny reservoir with operational guidelines for water quality improvement” developed by the Institute of Meteorology and Water Management – National Research Institute (IMGW-PIB), the vegetation process in the pre-dam reservoir may be

caused by high concentrations especially of phosphorus compounds. The results of water quality monitoring are presented in Table 1.

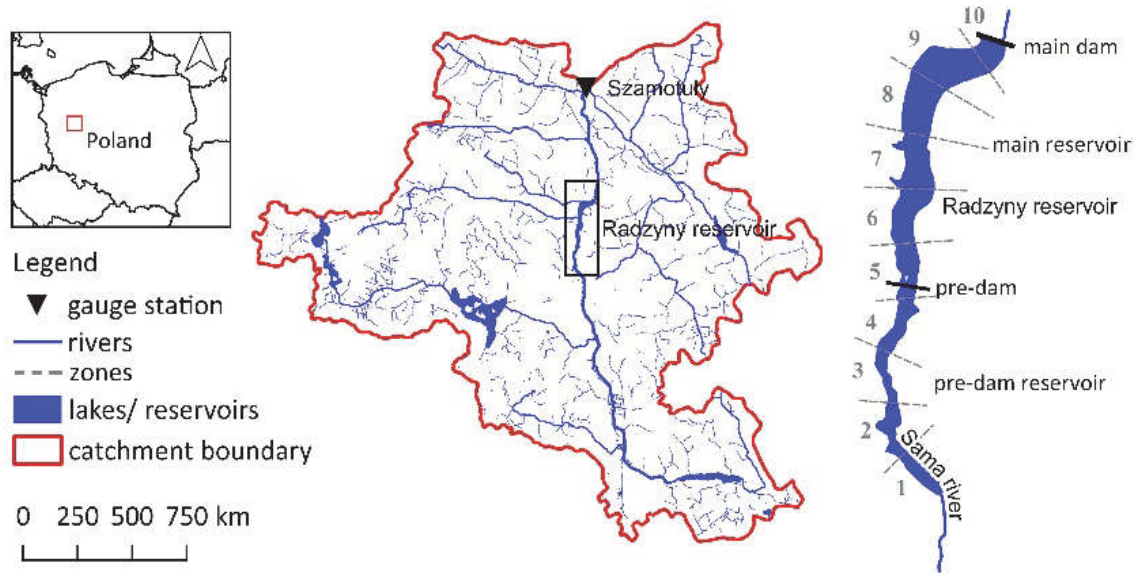


Fig. 1. Study site location

Rys. 1. Lokalizacja obszaru badań

Table 1. Mean values of water quality parameters in the Radzyny reservoir in the vegetation period in the years 2015-2017

Tabela 1. Średnie wartości parametrów jakości wody w zbiorniku Radzyny w miesiącach wegetacyjnych w latach 2015-2017

Parameters	Pre-dam reservoir	Main reservoir
Water temperature [°C]	22.90	23.15
Dissolved oxygen [mg O ₂ /dm ³]	9.85	8.15
Electrical conductivity [mS/cm]	936	973
Secchi depth [m]	0.48	0.68
Phosphates [mg P/dm ³]	0.65	0.24
Total phosphorus [mg P/dm ³]	0.85	0.43
Ammonia nitrogen [mg N/dm ³]	0.25	0.14
Total nitrogen [mg N/dm ³]	2.52	1.73

4. Results

Spatiotemporal changes of the NDVI value in the Radzyny reservoir are presented in Figure 2. During analyzed months in the period 2015-2017, the NDVI values varied from -0.528 to 0.917.

The NDVI in the Radzyny reservoir during July 2015 varied from -0.47 to 0.92. The difference between mean values in the main and pre-dam reservoir is 0.46 (Table 2). The highest value in August 2015 was 0.89 and was observed in the pre-dam reservoir. The difference between mean values depending on parts of the reservoir is 0.42. During September 2015, the difference between the two parts started to equalize, and was 0.22.

In May 2016, the difference between mean values in the pre-dam and main reservoir was 0.31. The lowest NDVI was observed in the main part. The highest values were comparable between parts of the Radzyny reservoir. During June 2016, the difference between NDVI mean values depending on parts of the reservoir was 0.21. The results obtained for July and August were in a similar range. Similarly to previous months, the mean values of the NDVI were higher in the pre-dam part, respectively 0.18 and 0.21.

During May 2017, the difference between NDVI mean values in the main and pre-dam reservoir was 0.23. The highest value in June 2017 was observed in the pre-dam reservoir, while the lowest value was observed in both parts. Similarly, to previous years, the mean values of the NDVI in July, August and September 2017 were higher in the pre-dam part. During September 2017 values of NDVI were in range of -0.53 to 0.88. The difference between parts was 0.47.

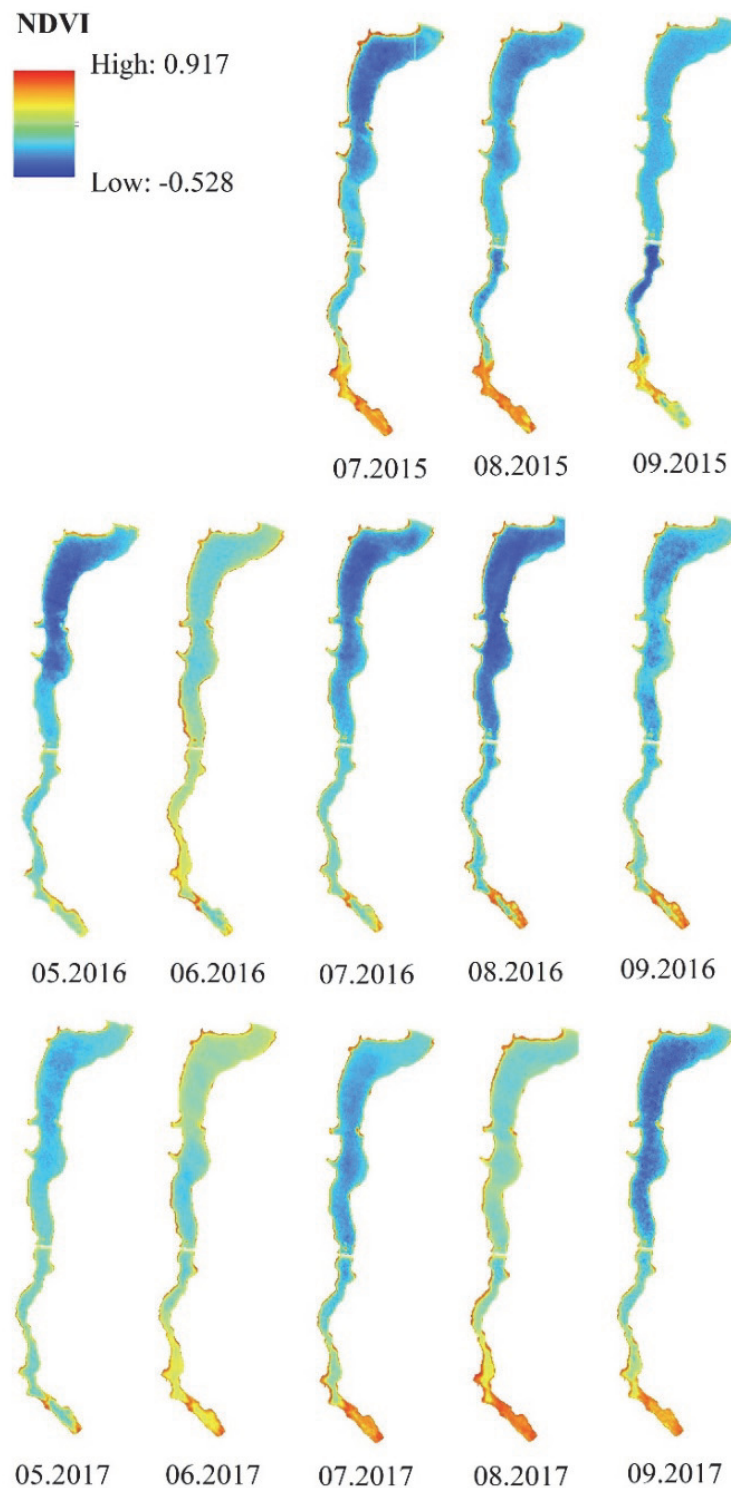


Fig. 2. Spatio-temporal changes of vegetation process for vegetation months in the period 2015-2017

Rys. 2. Przestrzenno-czasowa zmienność procesu wegetacji w miesiącach wegetacyjnych w latach 2015-2017

Table 2. Characteristics of NDVI in the Radzyny reservoir for vegetation months in the period 2015-2017 (minimum, maximum, mean and median)

Tabela 2. Wartości charakterystyczne NDVI w zbiorniku Radzyny w miesiącach wegetacyjnych w latach 2015-2017 (minimum, maksimum, średnia i mediana)

Date	Overall	The main part	The pre-dam part
07.2015	$\frac{-0.47}{0.01} / \frac{0.92}{-0.13}$	$\frac{-0.47}{-0.10} / \frac{0.89}{0.20}$	$\frac{-0.24}{0.36} / \frac{0.92}{0.49}$
08.2015	$\frac{-0.39}{0.02} / \frac{0.89}{-0.15}$	$\frac{-0.39}{-0.09} / \frac{0.84}{0.17}$	$\frac{-0.38}{0.33} / \frac{0.89}{0.51}$
09.2015	$\frac{-0.52}{-0.02} / \frac{0.83}{-0.14}$	$\frac{-0.27}{-0.08} / \frac{0.81}{0.15}$	$\frac{-0.52}{0.14} / \frac{0.83}{0.18}$
05.2016	$\frac{-0.47}{-0.08} / \frac{0.86}{-0.14}$	$\frac{-0.47}{-0.16} / \frac{0.86}{0.22}$	$\frac{-0.21}{0.15} / \frac{0.86}{0.08}$
06.2016	$\frac{-0.17}{0.18} / \frac{0.91}{0.11}$	$\frac{-0.17}{0.12} / \frac{0.89}{-0.05}$	$\frac{-0.11}{0.33} / \frac{0.91}{0.29}$
07.2016	$\frac{-0.47}{-0.05} / \frac{0.85}{-0.15}$	$\frac{-0.47}{-0.13} / \frac{0.84}{0.22}$	$\frac{-0.17}{0.18} / \frac{0.85}{0.07}$
08.2016	$\frac{-0.48}{-0.08} / \frac{0.88}{-0.24}$	$\frac{-0.48}{-0.19} / \frac{0.84}{0.30}$	$\frac{-0.35}{0.21} / \frac{0.88}{0.07}$
09.2016	$\frac{-0.39}{0.01} / \frac{0.87}{-0.09}$	$\frac{-0.39}{-0.05} / \frac{0.81}{0.14}$	$\frac{-0.28}{0.24} / \frac{0.87}{0.11}$
05.2017	$\frac{-0.30}{0.03} / \frac{0.87}{-0.04}$	$\frac{-0.30}{-0.03} / \frac{0.84}{0.08}$	$\frac{-0.18}{0.20} / \frac{0.87}{0.10}$
06.2017	$\frac{-0.18}{0.21} / \frac{0.88}{0.15}$	$\frac{-0.18}{0.15} / \frac{0.86}{0.12}$	$\frac{-0.18}{0.36} / \frac{0.88}{0.37}$
07.2017	$\frac{-0.35}{0.04} / \frac{0.87}{-0.09}$	$\frac{-0.35}{-0.06} / \frac{0.85}{0.14}$	$\frac{-0.29}{0.32} / \frac{0.87}{0.23}$
08.2017	$\frac{-0.18}{0.21} / \frac{0.91}{0.09}$	$\frac{-0.09}{0.13} / \frac{0.85}{-0.06}$	$\frac{-0.18}{0.46} / \frac{0.91}{0.48}$
09.2017	$\frac{-0.53}{-0.01} / \frac{0.88}{-0.15}$	$\frac{-0.53}{-0.13} / \frac{0.80}{0.23}$	$\frac{-0.27}{0.34} / \frac{0.88}{0.33}$

The analysis showed that the NDVI values in the period from May to September in the pre-dam reservoir were higher than those recorded in the main reservoir (Fig. 3a). Also, in the pre-dam reservoir the variation of NDVI was over 2.5 higher than in the main reservoir. The highest variation of NDVI within the pre-dam reservoir was observed in August and the lowest in May. In the main reservoir, NDVI values were characterized by similar variability for all of the analyzed months.

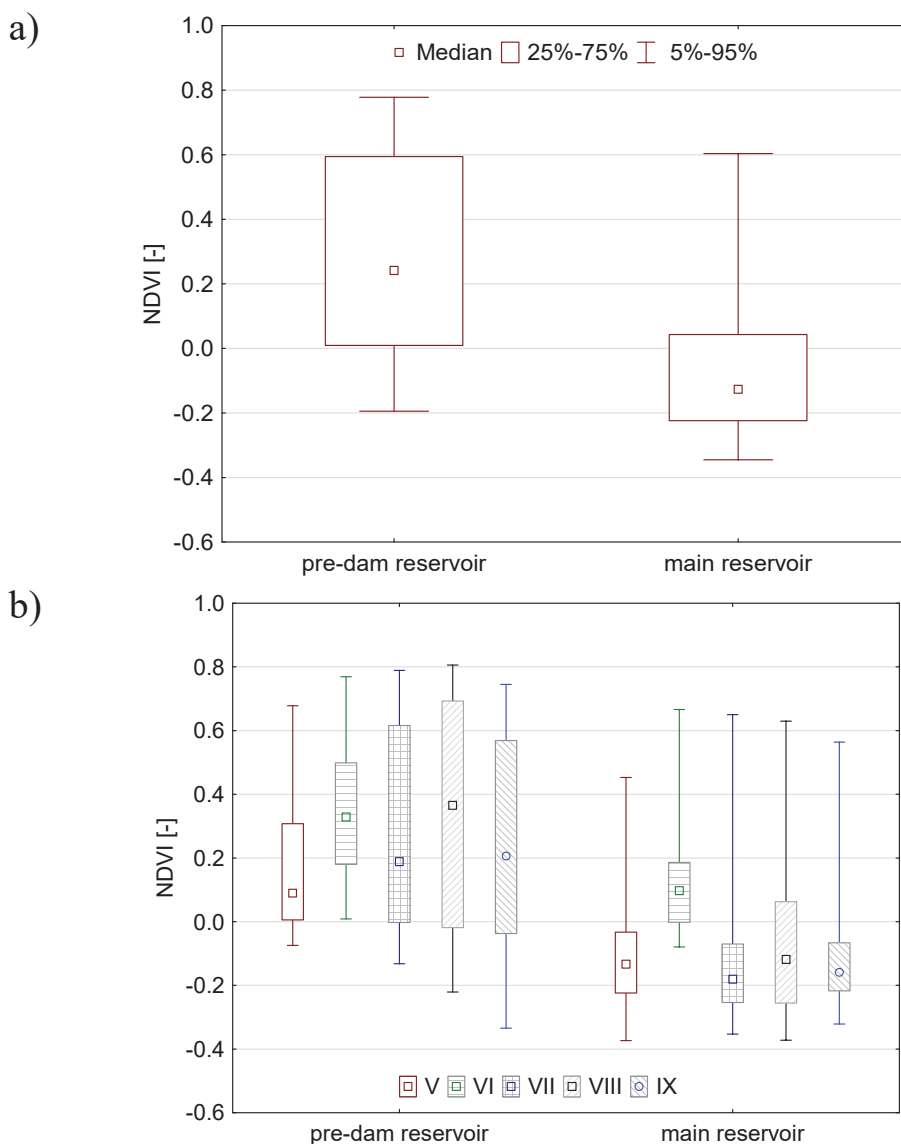


Fig. 3. Changes in NDVI values in pre-dam and main reservoir from July 2015 to September 2017 (a) and individual months (b)

Rys. 3. Zmienność wartości NDVI w części wstępnej i głównej zbiornika od lipca 2015 do września 2017 (a) i poszczególnych miesięcy (b)

NDVI median values in the main reservoir in May, July, August and September were at a similar level; the highest value was recorded in June (Fig. 3b). The NDVI values in the pre-dam reservoir were higher than in the main reservoir. These differences were statistically significant at the level of $\alpha = 0.05$.

The analysis of the vegetation process along the reservoirs showed that in the pre-dam reservoir in zones 1-4 there was a marked decrease in the NDVI value (Fig. 4a). The differences in NDVI values for zones 1 and 2, 2 and 3 and 3 and 4 were statistically significant at the level of $\alpha = 0.05$. The highest NDVI values occurred at the inlet to the pre-dam reservoir (zone 1) while the lowest occurred near the pre-dam (zone 4). In the inlet part of the pre-dam reservoir there are the lowest depths, which favors the development of vegetation. The highest variability of NDVI within the pre-dam reservoir occurred in the middle part (zones 2 and 3). In the main reservoir the NDVI values in each zone were at a similar level. Slightly higher values were recorded in the upper and lower parts of the main reservoir (zones 5 and 10) and the lowest in the middle part (zone 8). In the main reservoir, differences in NDVI values only for zones 5 and 6, and 9 and 10 were statistically significant at the level of $\alpha = 0.05$. The variation of NDVI values in zones from 5 to 10 was similar. The NDVI values within the pre-dam reservoir confirm the intensive process of overgrowth and degradation, which is particularly visible in zones 1 to 3. In the lower part of the pre-dam reservoir, the values are slightly higher than those recorded in the main reservoir. This confirms the effectiveness of this type of solution in the protection of the main reservoir against degradation. The analysis of changes in NDVI values along the pre-dam reservoir in the months from May to September showed that the greatest dynamics of changes in zone 1 occurred in May and June (Fig. 4b), whereas in zones 2 and 3 they occurred in July and August. In the main reservoir, the largest changes of NDVI were in August and the lowest in June. In June NDVI values in the main reservoir were the highest, and in July and September, generally at the lowest level.

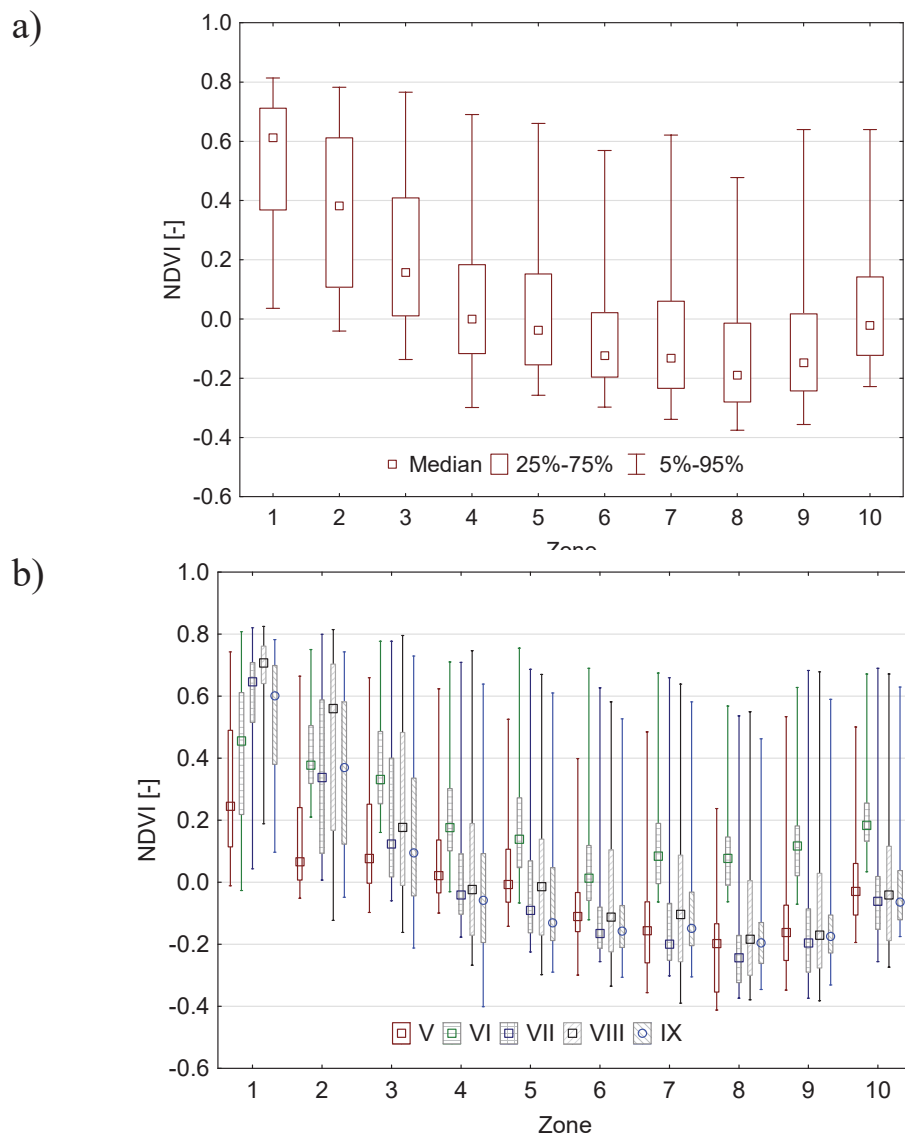


Fig. 4. Changes in NDVI values along pre-dam (zones 1 to 4) and main reservoir (zones 5 to 10) from July 2015 to September 2017 (a) and individual months (b)

Rys. 4. Zmiany wartości NDVI wzdłuż części wstępnej (strefy od 1 do 4) i głównego zbiornika (strefy od 5 do 10) od lipca 2015 do września 2017 (a) i poszczególnych miesięcy (b)

The analysis showed high variability of NDVI values in the corresponding months during the period 2015-2017. Also, the spatial changes of NDVI values were at a high level. The variability of the NDVI values show the dynamics of the vegetation process. This process in the analyzed period may result from thermal conditions and variability of inflows as well as the supply of biogenic compounds. These factors to-

gether determine the temporal and spatial direction of the vegetation process in the reservoir. The largest changes occurring in the preliminary reservoir indicate that the functions assumed at the design stage are implemented, i.e. protection of the main reservoir against sediment accumulation and water quality deterioration.

5. Discussion

Recently, open-access satellite data have enabled wider sources for aquatic monitoring than traditional in situ measurements, in which water bodies are represented by a single sampling point (Dlamini et al. 2016). Due to multispectral data, it is possible to detect areas of high vegetation abundance (Matthews et al. 2012). For aquatic monitoring there are in connection with the vegetation process seasonal algal blooms and the overgrowing process. The results obtained in this study confirm that remote sensing techniques have good potential for detecting the vegetation process in reservoirs in terms of spatial and temporal changes. Temporal changes could be detected especially by high temporal resolution of Sentinel-2, which provided data by a 5-day repeat cycle. In comparison to airborne imagery, satellite data have increasingly changed the possibility of using remote sensing data to monitoring of degradation phenomena of water bodies (Urquhart et al. 2017). Due to the spatial resolution of satellite imagery, the changes of the vegetation process are presented in resolution equal to 10 m. The analysis in this study was carried out on the basis of 10062 pixels, 7471 of them representing the main part and 2591 representing the pre-dam part of the reservoir. The obtained results show that spatial resolution of the Sentinel-2 allows detection of changes of the vegetation process in both parts of the reservoir.

6. Conclusion

On the basis of the obtained results, the following conclusions can be made:

1. SENTINEL-2 satellite imagery allows analysis of the vegetation process in retention reservoirs in terms of time and space.
2. Temporal changes of the vegetation process in the reservoirs are related to the thermal and hydrological conditions and the inflow of biogenic compounds.

3. The spatial changes of the vegetation process are the result of the reservoir morphometry and the dynamics of the water level in the reservoir.
4. In the Radzyny reservoir, large spatiotemporal changes in the NDVI value were observed.
5. Higher values and variability of NDVI in the pre-dam reservoir indicate its greater degradation in relation to the main reservoir.
6. The NDVI values in the pre-dam reservoir decrease from the inlet to the pre-dam, which indicates decreasing degradation of the reservoir along with the distance from the inlet.
7. The values of the NDVI index along the main reservoir were at a similar level and are characterized by similar variability, which indicates a similar course of the degradation process.
8. The lowest NDVI values in the pre-dam reservoir occur in May and the highest in August. In the main reservoir, the highest NDVI values occur in June and in the remaining months they are at a similar level.
9. The analyses carried out in this study confirm the effectiveness of the pre-dam part in protection of the main reservoir.

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Analiza procesu wegetacji w dwustopniowym zbiorniku retencyjnym na podstawie zdjęć satelitarnych – zbiornik Radzyny na rzece Sama

Streszczenie

Celem pracy była analiza procesu wegetacji w dwustopniowym zbiorniku retencyjnym na podstawie zdjęć satelitarnych. Do analizy wykorzystano zobrazowania z satelity Sentinel-2 z okresu 2015-2017. Ocenę procesu wegetacji w zbiorniku Radzyny na rzece Samie przeprowadzono na podstawie indeksu spektralnego - Normalized Vegetation Index (NDVI).

Analizowany zbiornik Radzyny ma dwustopniową konstrukcję. Wydzielono w nim część główną oraz wstępną. Do podstawowych zadań części wstępnej należy ochrona zbiornika głównego przed sedymentacją oraz dopływem związków biogennych. Jednym z podstawowych problemów związanych z funkcjonowaniem zbiornika Radzyny jest dopływ związków fosforu, który prowadzi do eutrofizacji wód gromadzonych w zbiorniku.

Proces wegetacji w zbiorniku Radzyny był analizowany dla części wstępnej oraz zbiornika głównego. W celu dokładnego określenia części zbiornika, które są najbardziej narażone na proces degradacji, podzielono zbiornik na 10 części, w zależności od odległości od wpływu rzeki Sama (dystans pomiędzy przekrojami ograniczającymi wydzielone strefy wynosił 500 m). Wszystkie analizy przestrzenne wykonane zostały w programie Quantum GIS 2.18 oraz ArcGIS 10.5. Analizy statystyczne zostały przeprowadzone w programie Statistica 13.

Przeprowadzone analizy wykazały, że wartości wskaźnika NDVI w okresie od maja do września były wyższe w zbiorniku wstępnym. Największą zmienność wskaźnika NDVI w części wstępnej zaobserwowano w sierpniu, natomiast najmniejszą w maju. Zbiornik główny w okresie 2015-2017 charakteryzował się niższymi wartościami i większą stabilnością wskaźnika NDVI. Analiza zmienności NDVI wykazała, że w części wstępnej (strefy 1-4) następuje spadek wartości na długości zbiornika. Najwyższe wartości wskaźnika występują w pobliżu wpływu rzeki do zbiornika (strefa 1), podczas gdy najniższe przy przegrodzie (strefa 4).

Na podstawie uzyskanych wyników, potwierdzono, że część wstępna pełni funkcję ochronną zbiornika głównego, m.in. ogranicza dopływ związków biogennych oraz skupia proces akumulacji osadów dennych. Uzyskane wyniki potwierdzają możliwość zastosowania danych satelitarnych Sentinel-2 do analizy procesu wegetacji w zbiornikach retencyjnych w ujęciu czasowym i przestrzennym. Stwierdzono, że analiza na podstawie zobrażeń satelitarnych charakteryzuje się większą efektywnością w monitoringu środowisk wodnych niż tradycyjne pomiary terenowe, w których wody powierzchniowe oceniane są na podstawie pojedynczych pomiarów.

Abstract

The main purpose of the study was to assess the dynamics of the vegetation process in a two-stage reservoir on the basis of satellite data. The analysis is based on Sentinel-2 satellite data from the period 2015-2017. The normalized difference vegetation index (NDVI) was selected to detect the vegetation process in the Radzyny reservoir located on the Sama river. The reservoir is split into two parts – the main and the pre-dam zone. The main role of the pre-dam reservoir is to store sediments and water pollutants. The main problem related to

the management of the Radzyny reservoir is water quality. Particularly high concentrations of phosphorus compounds may lead to reservoir vegetation.

The vegetation process was analyzed for the main and pre-dam reservoir. To specify areas mainly affected by vegetation, the reservoir was split into 10 parts, depending on the distance from the inflow of the Sama river (distance between profiles splitting polygons is 500 m). All calculations were performed using Quantum GIS 2.18 and ArcGIS 10.5 software, and statistical analysis was conducted with Statistica 13 software. The analysis showed that the NDVI values in the period from May to September in the pre-dam reservoir were higher than those recorded in the main reservoir. The greatest variation of the NDVI within the pre-dam reservoir was observed in August while the lowest was observed in May. In the main reservoir, NDVI values were characterized by similar variability. The analysis of the vegetation process along the reservoirs showed that in the pre-dam reservoir in zones 1-4 there was a marked decrease in the NDVI. The highest NDVI values occurred at the inlet to the pre-dam reservoir (zone 1) while the lowest values occurred near the pre-dam (zone 4).

The results indicate that the functions assumed at the design stage for the preliminary reservoir have been implemented, i.e. protection of the main reservoir against sediment accumulation and water quality degradation. SENTINEL-2 satellite imagery allows analysis of the vegetation process in retention reservoirs in terms of time and space. The study suggests that open-access satellite data are a more effective source for aquatic monitoring than traditional in situ measurements, in which water bodies are represented by a single sampling point.

Słowa kluczowe:

proces wegetacji, zbiornik dwustopniowy, zobrazenia satelitarne, NDVI, Sentinel-2

Keywords:

vegetation process, two-stage reservoir, satellite imagery, NDVI, Sentinel-2



Experimental Study of Air Lift Pump Delivery Rate

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1. Introduction

An air lift pump does not have any movable parts and it is used to lift liquids or liquid-solid mixes. The device is built of a vertical pipe, partly submerged in liquid, where air under pressure is introduced into its lower part. During introduction of air, a two-phase (liquid-air) or three-phase (liquid-air-solid) mix arises inside the vertical pipe, having lower density than the liquid. As the mix within the vertical pipe becomes lighter than the surrounding liquid, the mix is pushed up by the air.

Air lift pumps were usually used to transport liquid both in water supply and sewage systems. Nowadays in Poland, these devices are used to lift sewage and sewage sediments in small near-home container sewage-treatment plants and big group sewage-treatment plants (Sawicki 2004, Skoczko et al. 2016, Skoczko et al. 2017) as well as in high-rate filters with self-regenerating bed (Kalenik 2017) or for renovation of bored wells (Solecki 2010). However, in other countries, the air lift pumps have much wider application. They are used to aerate and mix water as well as to remove carbon dioxide from water in industrial fish farming (Barrut et al. 2012), to mix water in deep lakes and to aerate it by means of transport of water from the lake bed onto its surface (Fan et al. 2013). Due to the simple construction and high reliability of the air lift pumps, they are applied in various branches of industry, especially in the petrochemical industry to raise oil from dead wells (Hanafizadeh et al. 2011), in the chemical industry to transport corrosive, radioactive, arid or toxic fluids as well as to pump boiling fluids, where the change of liquid phase into gas phase occurs (Kassab et al. 2007). They are also used to

transport suspensions in mining industry and to lift manganese concretions from deep seabed up to ca. 4000-6000 m (Kassab et al. 2007).

A two-phase (liquid-gas) or three-phase (liquid-gas-solid) flow exists in the air lift pumps which is very difficult for mathematical modeling, for it depends on many factors and variables (Fujimoto et al. 2004, Kalenik 2017). The hydraulic operating conditions of two- and three-phase flow in the air lift pumps are very poorly identified. Some attempts are made to describe flow structures, occurring in various conditions of liquid-gas flow or liquid-gas-solid flow, and to work out so-called flow structure maps for them and mathematical models for simulation of flows occurring in the air lift pumps (Meng et al. 2013, Kim et al. 2014, Wahba et al. 2014).

Tests of air lift pumps built of rectangular (Esen 2010) and curved (Fujimoto et al. 2004) pipes were also carried out. The performed investigations of the air lift pumps with the curved pipes behind the air injector show that the pumping efficiency for solid bodies significantly falls in such air lift pumps. However, if only liquid is being pumped then the air lift pump pipe curvature does not affect its efficiency (Mahrous 2013). The performed investigations show that the air lift pumps are characterized by small working efficiency compared to conventional pumps (Tighzert et al. 2013, Kassab et al. 2009, Kalenik 2015, Kalenik & Malariski 2018).

There is no information in the technical and scientific literature on principles of calculations of flow rate of sand (Q_s) and water (Q_w) in air lift pumps used for lifting of filter bed (sand) in water conditioning filters with self-regenerating bed. Such types of air lift pumps are characterized by three-phase flow (water-sand-air). Moreover, there is no information how to design injectors to obtain the best operating parameters of the air lift pump. From the investigations to date it arises that the type of an injector and the diameter of a vertical pipe applied in the air lift pump affect its efficiency and hydraulic operating conditions (Fan et al. 2013, Kalenik 2017). The number, diameter and distribution of holes in the injector has very big influence on the types of structure of two-phase flow of air and liquid in air lift pumps. The types of the two-phase flow structures in the air lift pumps depend mainly on the air flow rate. Along with the rise in the air flow rate, the two-phase flow structures change in the air lift pumps. Other researchers also confirm that such dependences

occur in the air lift pumps (Hanafizadeh et al. 2011, Kalenik 2015). As the air flow rate grows in the air lift pumps, there become to occur: bubbly flow, slug flow, churn flow, annular flow. The researchers concluded that the slug flow is the most appropriate for air lift pumps for liquids (Hanafizadeh et al. 2011).

This paper presents the analysis of results of investigations of flow rate of an air lift pump which transports sand and water. The scope of the investigations encompassed the derivation of formulas for calculation of flow rate of sand (Q_s) and water (Q_w) in the PVC air lift pump with the internal diameter of the discharge pipe $d = 0.03$ m, by the fixed sand-water mix delivery head H : 0.40 m, 0.80 m, 1.20 m.

2. Methodology of derivation of the structural equation

Taking into consideration that the flow structures of air-water mix are so diverse and the work of air lift pumps is very dynamic and various (Kassab et al. 2009, Hanafizadeh et al. 2011, Kalenik 2015, Kalenik 2017), it must be stated that it is very hard to work out a classical mathematical model for derivation of a formula for calculation of a flow rate of sand and water in an air lift pump. Due to this, the dimensional analysis (Kokar 1979, Kalenik 2015, Kalenik 2017) was applied to determine the formula. Basing on the performed literature review and on the measurements made on the air lift pump test rig (Figure 1), an assumption was made that the air lift pump flow rate depends on the following dimensional variables: H – sand-water mix delivery head [m], Q_s – sand flow rate [$\text{m}^3 \cdot \text{s}^{-1}$], Q_w – water flow rate [$\text{m}^3 \cdot \text{s}^{-1}$], k – absolute roughness coefficient [m], p_b – barometric pressure [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$], p_a – air pressure [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$], d – discharge pipe diameter [m], Q_a – air flow rate [$\text{m}^3 \cdot \text{s}^{-1}$], ρ_w – water density [$\text{kg} \cdot \text{m}^{-3}$], ρ_a – air density [$\text{kg} \cdot \text{m}^{-3}$], ρ_s – wet sand density [$\text{kg} \cdot \text{m}^{-3}$], μ_w – water dynamic viscosity [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$], μ_a – air dynamic viscosity [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$], g – gravitational acceleration [$\text{m} \cdot \text{s}^{-2}$].

The absolute roughness coefficient k , which is equal 0.02 mm for PVC pipes, was also taken into consideration. However, the hydraulic resistance along the discharge pipe length was neglected because – as it results from the literature (Mahrous 2013, Tighzert et al. 2013, Wahba et al. 2014) – it is very low (unmeasurable), thus it must not be considered in calculations. In technical conditions, the vertical pipes in air lift pumps

are applied without thermal insulation, so the temperature of gas (air), liquid (water) and solids (sand) is close to the ambient temperature. Therefore it can be assumed that the temperature of gases, liquids and solids is constant along the vertical pipe and the flow of gases, liquids and solids is isothermal, thus $p_a/\rho_a = \text{const.}$, $p_w/\rho_w = \text{const.}$ and $p_s/\rho_s = \text{const.}$ Along with the rise in delivery head (H) the flow of sand (Q_s) and water (Q_w) diminishes. Taking the above assumptions into account, the dimensional equation which describes the phenomenon being considered can be written in a form:

$$f\left(\frac{Q_s}{Hk}, \frac{Q_w}{Hk}, p_b, \frac{p_a}{\rho_w}, \frac{p_a}{\rho_a}, \frac{p_a}{\rho_s}, \mu_w, \mu_a, d, Q_a, g\right) = 0 \quad (1)$$

There is $n = 11$ dimensional quantities in this equation and their dimensions contain $i = 3$ basic units: m, kg, s. According to the Buckingham's Π -theorem, this equation can be transformed to a dependence of $n - i = 8$ mutually independent dimensionless parameters π . Three quantities were chosen: μ_a , d , Q_a , which contain the aforementioned basic units; their dimensional independence was checked below:

$$\begin{aligned} [\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}]^{a_1} \cdot [\text{m}]^{a_2} \cdot [\text{m}^3 \cdot \text{s}^{-1}]^{a_3} &= \text{b}, \\ \text{kg}^{a_1} \cdot \text{m}^{-a_1} \cdot \text{s}^{-a_1} \cdot \text{m}^{a_2} \cdot \text{m}^{3a_3} \cdot \text{s}^{-a_3} &= \text{b}, \\ \text{m}^{-a_1+a_2+3a_3} \cdot \text{kg}^{a_1} \cdot \text{s}^{-a_1-a_3} &= [\text{m}]^0 \cdot [\text{kg}]^0 \cdot [\text{s}]^0, \\ -a_1+a_2+3a_3 &= 0 \Rightarrow a_2 = 0, \\ a_1 &= 0 \Rightarrow a_1 = 0, \\ -a_1-a_3 &= 0 \Rightarrow a_3 = 0, \end{aligned}$$

thus $a^1 = a^2 = a^3 = 0$, $b = 1$ (they are dimensionally independent).

The subsequent connection of the remaining five dimensional quantities with the product of the powers of the chosen dimensionally independent quantities allows to determine the dimensionless parameters π .

$$\pi_1 = \frac{Q_s}{Hk} \mu_a^{a_1} d^{a_2} Q_a^{a_3} \quad (2)$$

$$\pi_2 = \frac{Q_w}{Hk} \mu_a^{b_1} d^{b_2} Q_a^{b_3} \quad (3)$$

$$\pi_3 = p_b \mu_a^{c_1} d^{c_2} Q_a^{c_3} \quad (4)$$

$$\pi_4 = \frac{P_a}{\rho_w} \mu_a^{d1} d^{d2} Q_a^{d3} \quad (5)$$

$$\pi_5 = \frac{P_a}{\rho_a} \mu_a^{e1} d^{e2} Q_a^{e3} \quad (6)$$

$$\pi_6 = \frac{P_a}{\rho_s} \mu_a^{f1} d^{f2} Q_a^{f3} \quad (7)$$

$$\pi_7 = \mu_w \mu_a^{g1} d^{g2} Q_a^{g3} \quad (8)$$

$$\pi_8 = g \mu_a^{h1} d^{h2} Q_a^{h3} \quad (9)$$

The substitution of these individual quantities and comparison of the power exponents standing by the basic units of the both sides of the subsequent equations (analogically as during checking of the dimensional independence of the quantities) yields the values of these quantities:

$$\pi_1 = \frac{Q_s d^2}{Hk Q_a} \quad (10)$$

$$\pi_2 = \frac{Q_w d^2}{Hk Q_a} \quad (11)$$

$$\pi_3 = \frac{p_b d^3}{\mu_a Q_a} \quad (12)$$

$$\pi_4 = \frac{p_a d^4}{\rho_w Q_a^2} \quad (13)$$

$$\pi_5 = \frac{p_a d^4}{\rho_a Q_a^2} \quad (14)$$

$$\pi_6 = \frac{p_a d^4}{\rho_s Q_a^2} \quad (15)$$

$$\pi_7 = \frac{\mu_w}{\mu_a} \quad (16)$$

$$\pi_8 = \frac{g d^5}{Q_a^2} \quad (17)$$

According to the Buckingham's Π -theorem, the dimensional equation (1) can be written in a form of dimensionless dependence between the parameters π :

$$f(\pi_1, \pi_2, \pi_3, \pi_4, \pi_5, \pi_6, \pi_7, \pi_8) = 0 \quad (18)$$

hence for:

- sand flow rate:

$$\pi_1 = f(\pi_2, \pi_3, \pi_4, \pi_5, \pi_6, \pi_7, \pi_8) \quad (19)$$

- water flow rate:

$$\pi_2 = f(\pi_1, \pi_3, \pi_4, \pi_5, \pi_6, \pi_7, \pi_8) \quad (20)$$

Substitution of the terms (10)-(17) instead of π , after rearrangement, gives the structural equation for:

- sand flow rate:

$$Q_s = f\left(\frac{Q_w d^2}{Hk Q_a}, \frac{p_b d^3}{\mu_a Q_a}, \frac{p_a d^4}{\rho_w Q_a^2}, \frac{p_a d^4}{\rho_a Q_a^2}, \frac{p_a d^4}{\rho_s Q_a^2}, \frac{\mu_w}{\mu_a}, \frac{g d^5}{Q_a^2}\right) \frac{Hk Q_a}{d^2} \quad (21)$$

- water flow rate:

$$Q_w = f\left(\frac{Q_s d^2}{Hk Q_a}, \frac{p_b d^3}{\mu_a Q_a}, \frac{p_a d^4}{\rho_w Q_a^2}, \frac{p_a d^4}{\rho_a Q_a^2}, \frac{p_a d^4}{\rho_s Q_a^2}, \frac{\mu_w}{\mu_a}, \frac{g d^5}{Q_a^2}\right) \frac{Hk Q_a}{d^2} \quad (22)$$

As the structural equations had been derived, an experiment was carried out to determine their numerical coefficients.

In Eqs. (21), (22), the dimensional quantities:

- ρ_w, μ_w – describe physical features of water,
- ρ_a, μ_a – describe physical features of air,
- ρ_s – describes physical features of sand,
- d, k, H – characterize the research object, i.e. discharge pipe – they have constant values,
- p_a, Q_a – describe so-called input quantities being a result of intentional actions being applied on the object being examined – they are controlled and controllable quantities,
- Q_s, Q_w – describe so-called output quantities – they are a response of

the object being examined on the input quantities (actions).

On the other hand, the dimensionless quantity in Eqs. (21) and (22) describes:

- π_1 – ratio of forces evoked by the sand flow to friction forces,
- π_2 – ratio of forces evoked by the water flow to friction forces,
- π_3 – ratio of forces evoked by the barometric pressure to friction forces,
- π_4, π_5, π_6 – ratio of forces evoked by the air pressure to dynamic forces,
- π_7 – ratio of water viscosity (friction) forces to air viscosity (friction) forces,
- π_8 – ratio of gravity forces to dynamic forces evoked by the air flow.

3. Experimental procedures

3.1. Description of the air lift pump test rig

Figure 1 shows the construction and operating principle of a stand for investigations of hydraulic operating conditions of air lift pumps (air lift pump test rig). After the opening of a ball valve (2), a pipeline (1) delivered water to a tank (3), filled with sand. During the tests the tank (3) was permanently filled with water up to the height of 1.0 m. After the opening of another ball valve (9), the excess of the water being delivered to the tank (3) was carried by an overfall (8) to the sewerage through a floor inlet (13). A draining pipeline (16) served to empty the tank (3) from water after the ball valve (15) opening. Inside of the tank (3), at the height of 0.20 m upon its bottom, a PVC discharge pipe (5) with the internal diameter of 0.03 m was mounted. The measurements of the air lift pump delivery rate were carried out for the three sand-water mix delivery heads (H): 0.40 m, 0.80 m, 1.2 m, measured over the water level in the tank (3). In the discharge pipe (5), at the height of 0.30 m over its lower edge, an air injector (10) was mounted. To measure water temperature in the tank (3), an electronic resistance thermometer (19) was applied.

Figure 2 shows a constructive solution of the tested air injector which provided a one-point air supply to the air lift pump. The injector had a form of a steel, externally screwed tip (2) with the internal diameter of 0.01 m. The steel tip (2) had an elastic pipe (7, Figure 1) put on it, having the external diameter of 0.013 m and supplying air from a compressor

(25) to the injector (10). At the air supplying pipe (7) an electromagnetic air flow meter (20), piezoelectric pressure sensor (21), electronic resistance thermometer (22) to measure air temperature as well as a poppet valve (23) and ball cut-off valve (24) were mounted.

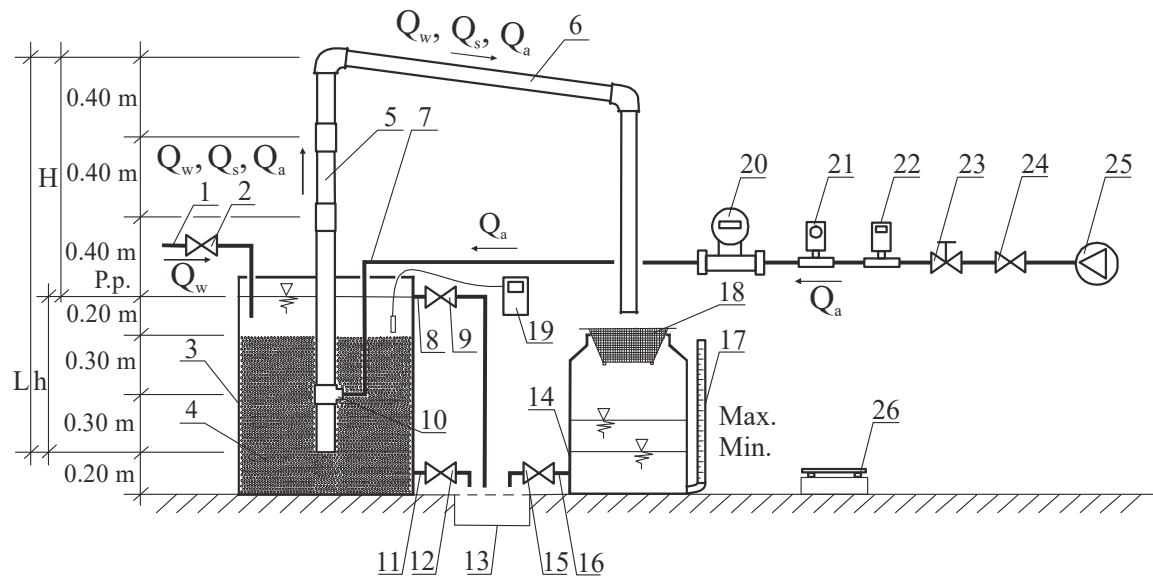


Fig. 1. Scheme of the air lift pump test rig: 1 – discharge pipe, 2, 9, 12, 15, 24 – ball cut-off valve, 3 – tank with water and sand, 4 – sand, 5 – discharge pipe $d = 0.03$ m, 6 – water, sand and air channeling pipe, 7 – air supplying pipe, 8 – overflow, 10 – air injector, 11, 16 – draining pipe, 13 – floor inlet, 14 – measuring container, 17 – scaled water level gauge, 18 – basket, 19, 22 – electronic resistance thermometer, 20 – electromagnetic air flow meter, 21 – piezoelectric pressure sensor, 23 – poppet valve, 25 – compressor, 26 – scales, h – discharge pipe submergence length, L – discharge pipe length-to-outlet, H – water-sand mix delivery head

Rys. 1. Schemat stanowiska do badania powietrznego podnośnika: 1 – rurociąg doprowadzający wodę, 2, 9, 12, 15, 24 – odcinający zawór kulowy, 3 – zbiornik z wodą i piaskiem, 4 – piasek, 5 – rurociąg tłoczny $d = 0,03$ m, 6 – rurociąg odprowadzający wodę, piasek i powietrze, 7 – rurociąg doprowadzający powietrze, 8 – przelew, 10 – mieszacz, 11, 16 – rurociąg spustowy, 13 – wpust podłogowy, 14 – zbiornik pomiarowy, 17 – wodowskaz ze skalą, 18 – koszyk, 19, 22 – elektroniczny termometr, 20 – elektroniczny przepływomierz powietrza, 21 – elektroniczny czujnik ciśnienia, 23 – zawór grzybkowy, 25 – sprężarka, 26 – waga, h – długość zanurzenia rurociągu tłoczego, L – długość rurociągu tłoczego do wylotu, H – wysokość podnoszenia mieszaniny piasku i wody

The investigations were performed with use of Endress & Hauser devices. The electromagnetic air flow meter (20) measuring range was 0.0 to 30.0 m³·h⁻¹ and the piezoelectric pressure sensor (20) measuring range – 0.0 to 400 kPa. According to the Endress & Hauser catalogue, the measuring error of the applied electromagnetic air flow meter and piezoelectric pressure sensor is lower than 1% and the output current signal falls into the range 4-20 mA. The measuring accuracy of the applied thermometer, however, was ±1°C and its measuring resolution 0.1°C.

The measurements concerned water and air temperature, air pressure, barometric pressure, air flow rate, water volume and air lift pump operating time. The scale (26) weighted the sand. The poppet valve (23) was used to regulate the air pressure.

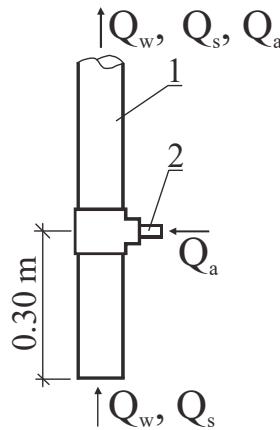


Fig. 2. Construction of the air injector: 1 – discharge pipe $d = 0.03$ m, 2 – steel tip to join an air supplying pipe

Rys. 2. Konstrukcja mieszacza: 1 – rurociąg tłoczny $d = 0,03$ m, 2 – stalowa końcówka do podłączenia rurociągu doprowadzającego powietrze

To measure the air lift pump delivery rate, the measuring vessel method was applied, i.e. there was used a plastic measuring container (14) which was scaled at each 1 dm³. The measuring container (14) capacity scale was put on the transparent water-level gauge (17), mounted at the side of the measuring container (14). Such solution allowed to read very precisely the volume of the water lifted by the air lift pump per time unit. For a fixed delivery head (H), the lifted water-sand mix flew down through the channeling pipe (6) with the internal diameter 0.03 m to a basket (18) placed in the inlet to the measuring container (14). During the measurements the sand was collected in the basket (18) and the water from the

basket (18) flew down into the measuring container (14). The wet sand collected in the basket was weighted. The sand applied in the tests had graining 0.8-2.0 mm and the density in wet condition $\rho_s = 1632.0 \text{ kg}\cdot\text{m}^{-3}$.

3.2. Methodology of investigations of the air lift pumps

Before each measuring series had begun on the air lift pump test rig (Figure 1), an actual barometric pressure (p_b) was measured using the piezoelectric pressure sensor (21). Then, on the water-level gauge (17) connected to the measuring container (14), it was marked the minimum level of a water free surface in the measuring container (14) by which the stop-watch was switched on as well as the maximum level of free surface of water by which the stop-watch was switched off. The level marked on the water-level gauge (17) scale referred to a certain water volume (V_w).

The measurement of the sand flow rate (Q_s) and water flow rate (Q_w) was started from the opening of the valves (2, 9), filling the tank (3) with sand (4) and water, turning on the compressor (25) and opening the valve (24) on the pipeline (7) supplying the air injector (10) with air. Then a demanded value of the air pressure (p_a) was fixed on the piezoelectric pressure sensor (21) using the poppet valve (23). As the determined air pressure had been fixed, some quantity of sand and water – depending on the air lift pump flow rate – flew out from the tank (3). To make the measurement reliable, the water level in the tank (3) had to be kept constant. Changes of the submergence of the air injector (10) or the water level changes in the tank (3) cause significant changes in the air lift pump flow rate. The constant water level in the tank (3) was kept using the valve (2) placed on the discharge pipe (1) supplying water to the tank (3). Each time the valve (2) was set in the position which balanced the water flux through the channeling pipe (6) for a given value of the air pressure. The observations and regulations of the water level in the tank (3) were performed relatively to the level in the overfall (8) which channeled the water excess. As these actions were completed and the working conditions of the air lift pump stabilized, the measurement started. At first, for a fixed value of the air pressure, the air flow rate (Q_a) was being read from the electromagnetic air flow meter (20) and the air and water temperatures – from the electronic resistance thermometers (19 – water, 22 – air). As the water-level gauge (17) showed that the water free surface in the measuring container (14) reached the marked minimum level,

then the stop-watch was switched on and the basket (18) was placed under the water, air and sand channeling pipe (6), in the inlet to the measuring container (14). The stop-watch measured a container (14) filling time (t) till the moment when the water free surface reached the marked maximum level – then the stop-watch was switched off and the poppet valve (23), cutting off the air to the air injector (10), was turned off. During the measurement the sand gathered in the basket (18) and the water from the basket flew down to the measuring container (14). As the measuring container (14) filling time t was read, the sand in the basket (18) was weighted with the scale (26) and then the sand was dropped into the basket again. Then the measuring container (14) was emptied, a next value of the air pressure was set on the piezoelectric pressure sensor (21) and a next measurement started. The measurements were carried out for the fixed air pressure (p_a) from 110 till 180 kPa with intervals 5 kPa. The water flow rate (Q_w) was calculated by dividing the volume (V_w) of water being in the measuring container (14) through the filling time (t) and the sand flow rate (Q_s) was calculated by dividing the weight (C_s) of the sand collected in the basket (18) through the filling time (t) and the density (ρ_s) of the wet sand. During the tests, five measuring series were carried out – each of them for a fixed value of the air pressure (p_a) and all three sand-water mix delivery heads (H): 0.40 m, 0.80 m, 1.20 m, measured relatively to the water free surface in the tank (3).

4. Results of the tests and their discussion

Figure 3 presents a dependence of the air flow rate (Q_a) in the air lift pump vs. the air pressure (p_a) and sand-water mix delivery head (H). Analysis of the obtained results allows to state that the air flow rate in the air lift pump rises along with the air pressure. On the other hand, the rise in the sand-water mix delivery head by the constant submergence of the air injector and big values of the air pressure slightly affected the fall of the air flow rate. Independently on the sand-water mix delivery head, the values of the air flow rate by a given air pressure were comparable, what resulted from big quantity of air.

Figures 4 and 5 present the results of measurements (solid lines) of sand flow rate (Q_s) and water flow rate (Q_w) depending on the air pressure (p_a) and water-sand mix delivery head (H) as well as the results of

calculations (broken lines) performed with use of the determined formulas (23, 24). In the tested air lift pump, for the given water-sand mix delivery heads, the values of water flow rate are higher than those of the sand flow rate. The values of water and sand flow rate fall along with the rise in the water-sand mix delivery head and initially grow with the rise of air pressure, achieve the maximum and then they fall.

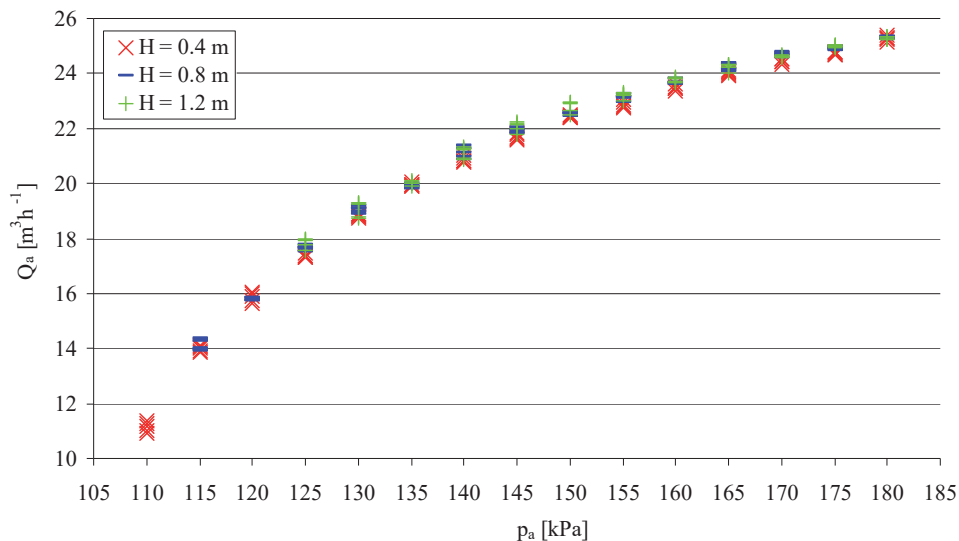


Fig. 3. Air flow rate (Q_a) in the air lift pump vs. air pressure (p_a) and sand-water mix delivery head (H)

Rys. 3. Zależność natężenia przepływu powietrza (Q_a) w podnośniku powietrznym od ciśnienia powietrza (p_a) i wysokości podnoszenia mieszaniny piasku i wody (H)

To enable the outflow of the sand of graining 0.8-2.0 mm from the air lift pump on a demanded delivery head, it must be provided an appropriate minimum air pressure which forces an appropriate air flow rate in the discharge pipe. Along with the rise in the water-sand mix delivery head the minimum demanded air pressure grew, thus so did the minimum air flow rate in the discharge pipe. In the tested air lift pump, for the water-sand mix delivery head 0.40 m, the demanded minimum air pressure was equal 110 kPa what corresponded to the average minimum air flow rate $11.6 \text{ m}^3 \cdot \text{h}^{-1}$. For the water-sand mix delivery heads equal 0.8 m and 1.2 m these values were equal 115 kPa and $14.10 \text{ m}^3 \cdot \text{h}^{-1}$ as well as 125 kPa and $17,85 \text{ m}^3 \cdot \text{h}^{-1}$, respectively.

For the given water-sand mix delivery heads, when the air pressure exceeded 150 kPa, what corresponds to the average air flow rate $22.59 \text{ m}^3 \cdot \text{h}^{-1}$, the values of sand and water flow rates did not grow further but started to reduce. This phenomenon is described in the literature (Hanafizadeh et al. 2011, Meng et al. 2013, Kalenik 2017, Kalenik & Malarski 2018). Due to this fact, the maximum demanded injector air pressure for the tested air lift pump with the applied (Figure 2) air injector should not exceed 150 kPa.

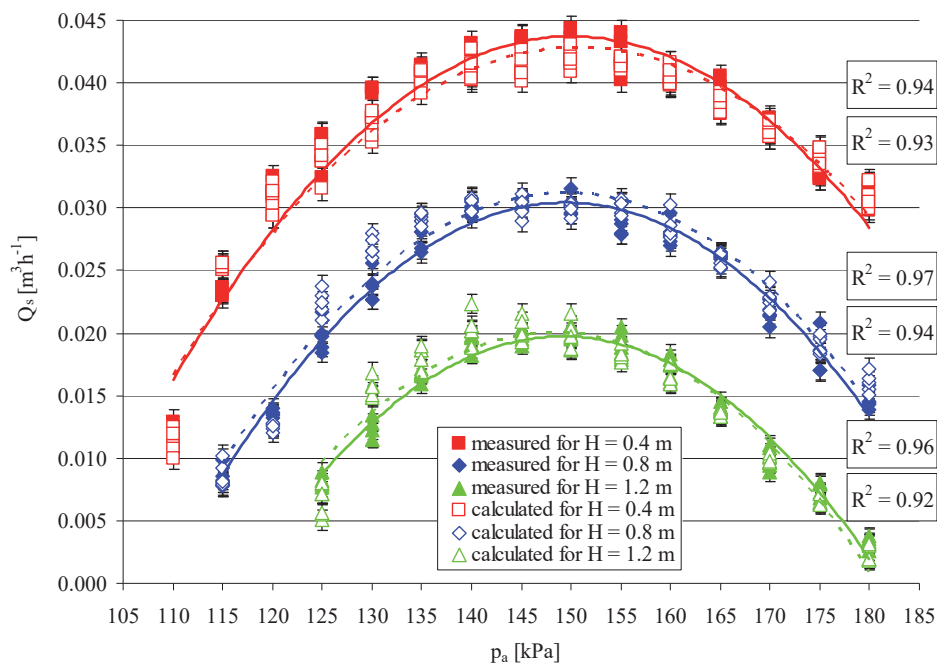


Fig. 4. Sand flow rate (Q_s) vs. air pressure (p_a) according to the measurements and calculations

Rys. 4. Zależność natężenia przepływu piasku (Q_s) od ciśnienia powietrza (p_a) według pomiarów i obliczeń

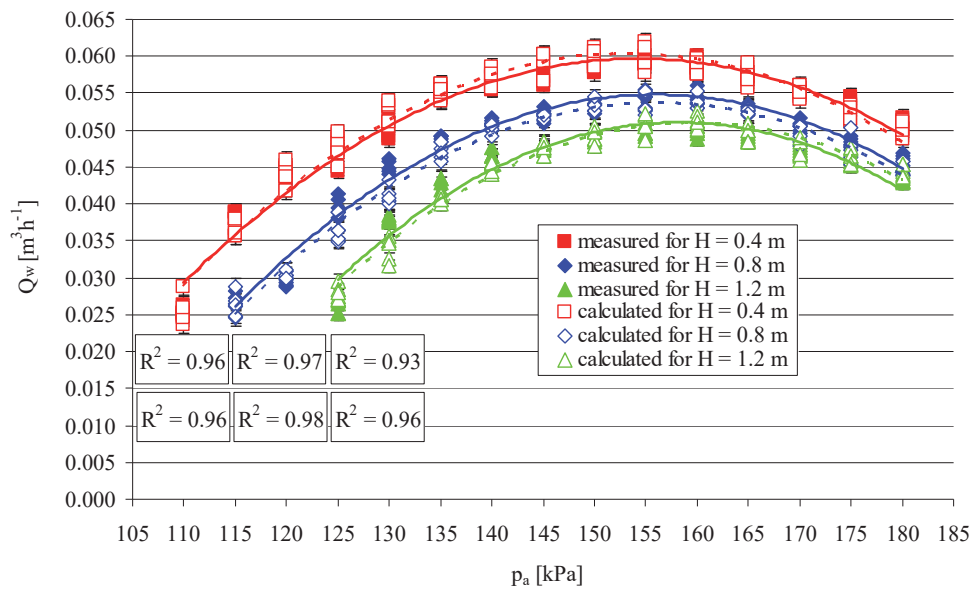


Fig. 5. Water flow rate (Q_w) vs. air pressure (p_a) according the measurements and calculations

Rys. 5. Zależność natężenia przepływu wody (Q_w) od ciśnienia powietrza (p_a) według pomiarów i obliczeń

To determine the flow capacity of the tested air lift pump, appropriate empirical formulas were derived. In this aim, using the measurements performed on the air lift pump test rig (Figures 1 and 2), the dimensionless parameters π_1 (10), π_2 (11), π_3 (12), π_4 (13), π_5 (14), π_6 (15), π_7 (16), π_8 (17) were calculated from the derived structural equations for Q_s (21) and Q_w (22). Basing on the measured temperatures of water and air, the following constants were calculated from the tables (Orzechowski et al. 2001): the density of water (ρ_w) and air (ρ_a), the dynamic viscosity of water (μ_w) and air (μ_a). Then appropriate data tables were built and – using the multiple regression method and the computer package STATISTICA – the numerical coefficients to the empirical formulas for calculation of Q_s and Q_w . Substitution of the determined numerical coefficients to the structural equations (21, 22) and reduction of significant digits in them for the sake of facilitation finally yields the following empirical formulas for calculation of sand and water flow rate in air lift pumps:

$$Q_s = \left(\begin{array}{l} -1.23 \cdot 10^{-1} + 8.36 \cdot 10^{-1} \frac{Q_w d^2}{Hk Q_a} + 5.39 \cdot 10^{-9} \frac{p_b d^3}{\mu_a Q_a} - 3.4 \cdot 10^{-2} \frac{p_a d^4}{\rho_w Q_a^2} \\ -1.236 \cdot 10^{-5} \frac{p_a d^4}{\rho_a Q_a^2} - 2.7 \cdot 10^{-2} \frac{p_a d^4}{\rho_s Q_a^2} + 1.17 \cdot 10^{-3} \frac{\mu_w}{\mu_a} + 9.29 \frac{g d^5}{Q_a^2} \end{array} \right) \frac{Hk Q_a}{d^2} \quad (23)$$

$$Q_w = \left(\begin{array}{l} 1.21 \cdot 10^{-1} + 1.19 \frac{Q_s d^2}{Hk Q_a} - 6.23 \cdot 10^{-9} \frac{p_b d^3}{\mu_a Q_a} + 3.95 \cdot 10^{-2} \frac{p_a d^4}{\rho_w Q_a^2} \\ + 2.04 \cdot 10^{-5} \frac{p_a d^4}{\rho_a Q_a^2} + 3.56 \cdot 10^{-2} \frac{p_a d^4}{\rho_s Q_a^2} - 1.07 \cdot 10^{-3} \frac{\mu_w}{\mu_a} - 13.32 \frac{g d^5}{Q_a^2} \end{array} \right) \frac{Hk Q_a}{d^2} \quad (24)$$

where:

- Q_s – sand flow rate [$\text{m}^3 \cdot \text{s}^{-1}$],
- Q_w – water flow rate [$\text{m}^3 \cdot \text{s}^{-1}$],
- p_b – barometric pressure [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$],
- Q_a – air flow rate [$\text{m}^3 \cdot \text{s}^{-1}$],
- H – sand-water mix delivery head [m],
- k – absolute roughness coefficient [m],
- p_a – air pressure [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$],
- d – discharge pipe diameter [m],
- ρ_w – water density [$\text{kg} \cdot \text{m}^{-3}$],
- ρ_a – air density [$\text{kg} \cdot \text{m}^{-3}$],
- ρ_s – wet sand density [$\text{kg} \cdot \text{m}^{-3}$],
- μ_w – water dynamic viscosity [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$],
- μ_a – air dynamic viscosity [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$],
- g – gravitational acceleration [$\text{m} \cdot \text{s}^{-2}$].

The functional dependence between the flow rates of sand (Figure 4) and water rate (Figure 5) on the one hand and the air pressure on the other hand presents a nonlinear trend in the whole range of the values of p_a – both for the values of Q_s and Q_w obtained from the measurements and from the formulas (23), (24). The deviations of Q_s and Q_w obtained from the calculations related to those obtained from the measurements were small for the water-sand mix delivery heads being tested. The trend (regression) was of second degree in the whole range of the values of the air pressure for the values of Q_s and Q_w obtained from the measurements and calculations. The trend lines for the values of Q_s and Q_w obtained from the calculations were slightly shifted in relation to the values of Q_s

and Q_w obtained from the measurements. Figures 4 and 5 show also the pairs of coefficients of determination (R^2) from the sample. In Figure 4, the higher values of R^2 concern the measured values of Q_s and the lower ones – the values calculated from (23); whereas in Figure 5, the lower values of R^2 concern the measured values of Q_w and the higher ones – the values calculated from (24). The values of R^2 were higher than 0.92 what indicates that the water and sand flow rate in the air lift pump at least in 92% depended on the air pressure, thus on the air flow rate and the water-sand mix delivery head and only in 8% on remaining factors like the density of water, air and sand or the gravitational acceleration.

To evaluate the accuracy of the formulas (23), (24), the calculated values of Q_s and Q_w were compared to those measured on the test rig. It has been stated that within the following ranges of the values of the presented parameters: $d = 0.03$ m, 110 kPa $\leq p_a \leq 180$ kPa, $2.15 \cdot 10^{-3}$ m³·h⁻¹ $\leq Q_s \leq 4.23 \cdot 10^{-2}$ m³·h⁻¹, $2.76 \cdot 10^{-3}$ m³·h⁻¹ $\leq Q_w \leq 6.27 \cdot 10^{-2}$ m³·h⁻¹, 10.93 m³·h⁻¹ $\leq Q_a \leq 25.39$ m³·h⁻¹, 1.3330 kg·m⁻³ $\leq \rho_a \leq 2.1836$ kg·m⁻³, 999.3336 kg·m⁻³ $\leq \rho_w \leq 999.6184$ kg·m⁻³, $\rho_s = 1632.0$ [kg·m⁻³], $1.1796 \cdot 10^{-3}$ kg·m⁻¹·s⁻¹ $\leq \mu_w \leq 1.2084 \cdot 10^{-3}$ kg·m⁻¹·s⁻¹, $1.7755 \cdot 10^{-5}$ kg·m⁻¹·s⁻¹ $\leq \mu_a \leq 1.7855 \cdot 10^{-5}$ kg·m⁻¹·s⁻¹, an average deviation of Q_s does not exceed 4% for the water-sand mix delivery head of $H = 0.40$ m, 6% for $H = 0.80$ m and 10% for $H = 1.20$ m; whereas an average deviation of Q_w does not exceed 3% for the water-sand mix delivery head of $H = 0.40$ m and $H = 0.80$ m, 4% for $H = 1.20$ m. The dimensional analysis of the formulas (23), (24) proved that the dimensions of their both sides are consistent.

Furthermore, Figures 4 and 5 contain standard error bars which are small for the measured and calculated values of Q_s and Q_w . The standard error for the measured values oscillated between 0.7% and 8.1% (average 2.6%), whereas for the calculated values – between 0.6% and 12.7% (average 2.9%). The standard error was calculated with use of the STATISTICA computer program.

5. Conclusions

For the tested air lift pump, the air flow rate (Q_a) increased along with the increase of the air pressure (p_a). The flow rate of water (Q_w) and sand (Q_s) also increased along with the rise in the air pressure, then reached a maximum and fell. Along with the increase of the water-sand

mix delivery head (H), the flow rate of water and sand decreased and the values of the water flow rate (Q_w) were higher than those of the sand flow rate (Q_s).

For the tested air lift pump with the internal diameter of the discharge pipe 0.03 m with the applied air injector, the water and sand flow rates increased along with the rise in the air pressure within the range 110-150 kPa whereas they decreased for higher values of the air pressure. Due to this, it is recommended that the maximum air pressure for such devices should be higher than 110 kPa and should not exceed 150 kPa.

The values of the sand and water flow rates calculated from the derived formulas (23), (24) very well coincided with those determined from the direct measurements. Due to this, these formulas can be used for design of air lift pumps with the air injector presented in Figure 2.

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Eksperymentalne badania wydajności powietrznego podnośnika

Streszczenie

W artykule przedstawiono analizę wyników badań natężenia przepływu piasku (Q_s) i wody (Q_w) w podnośniku powietrznym. Badania wykonywano na wybudowanym w laboratorium w skali 1:1 stanowisku do badania podnośnika

powietrznego. W artykule przedstawiono budowę i zasadę działania stanowiska badawczego oraz omówiono metodykę wyznaczenia empirycznych wzorów do obliczania natężenia przepływu piasku i wody. Przeprowadzono analizę porównawczą wartości natężenia przepływu piasku i wody wyznaczonych z bezpośrednich pomiarów z wartościami obliczonymi za pomocą wyznaczonych empirycznych wzorów. Zakres badań obejmował wyprowadzenie wzorów do obliczania natężenia przepływu piasku i wody w podnośniku powietrznym z tworzywa sztucznego PVC o średnicy wewnętrznej rurociągu tłoczego $d = 0,03$ m, przy zadanej wysokości podnoszenia mieszaniny piasku i wody H : 0,40 m, 0,80 m, 1,20 m. Do wyznaczenia empirycznych wzorów do obliczania natężenia przepływu piasku i wody zastosowano analizę wymiarową i metodę regresji wielokrotnej. W badanej konstrukcji podnośnika powietrznego wraz ze wzrostem wysokości podnoszenia mieszaniny piasku i wody, natężenie przepływu piasku i wody malało, a wartości natężenia przepływu wody były większe w stosunku do wartości natężenia przepływu piasku. W badanym urządzeniu ciśnienie powietrza nie może być mniejsze niż 110 kPa i nie powinno przekraczać 150 kPa, ponieważ przy wyższych ciśnieniach powietrza natężenie przepływu piasku i wody zaczynało spadać. Wartości natężenia przepływu piasku i wody obliczone za pomocą wyprowadzonych wzorów, bardzo dobrze pokrywały się z wartościami wyznaczonymi z bezpośrednich pomiarów.

Abstract

This paper presents analysis of results of investigations of flow rate of sand (Q_s) and water (Q_w) in an air lift pump. The investigations were performed on an air lift pump test rig, constructed in a laboratory on a scale of 1:1. The paper describes the construction and working principle of this air lift pump test rig and presents a methodology of derivation of empirical formulas for calculation of sand and water flow rate. A comparative analysis of the values of the sand and water flow rate obtained in direct measurements with analogical values of flow rate calculated with use of the derived empirical formulas was carried out. The research scope encompassed the derivation of the aforementioned empirical formulas in the PVC air lift pump with the internal diameter of the discharge pipe $d = 0.03$ m by the fixed sand-water mix delivery heads H : 0.40 m, 0.80 m, 1.20 m. To derive the empirical formulas for calculation of the sand and water flow rate, dimensional analysis and multiple regression was applied. In the air lift pump being tested, the water and sand flow rate fell along with the rise in the delivery head and the water flow rate was higher than the sand flow rate. Air pressure in such devices cannot be lower than 110 kPa and cannot exceed 150 kPa as for higher values of air pressure the sand and water flow rate starts to fall. The values of the sand and water flow rate calculated with use of

the derived formulas coincide very well with the values determined from the direct measurements.

Słowa kluczowe:

podnośnik powietrzny, mieszacz, przepływ trójfazowy, natężenie przepływu piasku, natężenie przepływu wody

Keywords:

air lift pump, air injector, three-phase flow, sand flow rate, water flow rate



Start-up of a One-stage Biofilm Reactor for the Removal of Nitrogen from Digester Supernatant in the Partial Nitrification-Anammox Process

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1. Introduction

The digester supernatant that comes from sludge handling facilities is one of a range of difficult-to-treat wastewaters with high nitrogen and low organics concentrations. It is difficult to remove nitrogen from this wastewater by sequential autotrophic nitrification and heterotrophic denitrification due to its low concentration of organic compounds. One promising alternative process is the co-operation of aerobic and anaerobic ammonium-oxidizing bacteria and heterotrophic denitrifying bacteria (Langone et al. 2014). This alternative is the most attractive when the treatment is performed in a single reactor in which partial nitrification followed by Anammox can successfully support heterotrophic denitrification for the removal of high nitrogen loads without external carbon sources. The advantages of this solution over conventional technologies for nitrogen removal include lower energy consumption, reduced need for additional carbon sources, minimal sludge production (Jetten et al. 2009) and lower emissions of the greenhouse gases NO and N₂O (Kampschreur et al. 2009).

In the Anammox reaction, performed under anaerobic conditions by autotrophic bacteria, ammonium and nitrite contribute in equimolar amounts to the formation of dinitrogen gas (Strous et al. 1999). It is possible to obtain simultaneous partial nitrification and Anammox in one-stage reactors with immobilized biomass (Dreissen & Reitsma 2011) but in such systems, nitrite limitation is a problem (van der Star et al. 2007). Dissolved oxygen, temperature, pH, free ammonia, and free nitrous acid are important factors for encouraging the growth of I-phase nitrifiers and inhibiting the growth of II-phase nitrifiers in the reactor (Volcke et al. 2006). Our experience has shown that partial nitrification, without external control of factors like pH or temperature, is possible in reactors with immobilized biomass. In these reactors, high concentrations of ammonium can be effectively oxidized to nitrite as a result of the accumulation of free ammonia at levels high enough to inhibit II-phase nitrifiers (Cyzdik-Kwiatkowska et al. 2014).

Although Anammox bacteria are able to remove nitrogen effectively, their growth rate is very low (generation time 10–12 days), their sludge yield is low, and they are vulnerable to changes in environmental conditions (Monballiu et al. 2013). For these reasons, the start-up periods of Anammox reactors are longer than those of other nitrogen removal technologies. Anammox biomass easily attaches to solid surfaces (Monballiu et al. 2013). Since the physical retention of slow-growing Anammox bacteria in the reactor is crucial, these have been retained in membranes (Tao et al. 2012), immobilized in PVA cryogel carriers (Magri et al. 2012) or in moving-bed biofilm reactors (Szatkowska et al. 2007). These practices have allowed nitrogen removal with over 93% efficiency due to the higher resistance of the immobilized bacteria to inhibition by nitrites. The start-up period can be shortened by using the biomass from existing Anammox reactors for inoculation (van der Star et al. 2007). Without large amounts of active biomass, this period is much longer, up to several months.

Until recently, Anammox bacteria were considered obligate autotrophs that are negatively affected by organic carbon. Ni et al. (2012) reported that the number of Anammox bacteria decreased and the number of denitrifiers increased when the influent contained 400 mg COD/L. Tang et al. (2013) compared two SBRs: one operated under inorganic conditions with efficient and stable Anammox performance and another

under organic conditions with up to 800 mg COD/L in the influent. The authors reported that there was a risk of elimination of Anammox bacteria from the SBRs due to preferential metabolism of nitrite by denitrification, which starved the Anammox bacteria. However, although organic load has an inhibitory effect on Anammox activity, Anammox bacteria have the capacity to oxidize volatile fatty acids with nitrate as an electron acceptor, while forming ammonium with nitrite as the intermediate (Güven et al. 2005, Kartal et al. 2008). Anammox bacteria do not incorporate fatty acids into biomass, but completely oxidize them to CO₂, thus maintaining low biomass yield (Kartal et al. 2007). Winkler et al. (2012) have suggested that Anammox bacteria use their organotrophic capability to successfully compete with heterotrophs for organic carbon, which reduces sludge production. Anammox bacteria can outcompete heterotrophic denitrifying bacteria at ambient temperatures when the ratio of C/N in the influent is less than 0.5 g COD/g N (Tang et al. 2010).

The present study investigated the possibility of initiating efficient nitrogen removal from digester supernatant in a one-stage biofilm reactor for nitrification-Anammox process. The biofilm reactor was seeded with aerobic granular sludge collected from full-scale reactors that were not operated with the Anammox process. Because inorganic carbon (IC) limitation may be the main reason for the decrease in growth and in the activity of nitrifying bacteria at acidic pH (Wett & Rauch 2003) and of the Anammox bacteria (Liao et al. 2008, Yang et al. 2010), IC concentration in the wastewater may be important for the enrichment of Anammox microorganisms and can influence the length of the period of the reactor start-up. Therefore, the goal of the study was to determine the effect of bicarbonate addition on overall reactor performance, species composition of biofilm and changes in nitrogen forms in the effluent during the transformation of non-Anammox biomass to nitrification/Anammox biomass when treating nitrogen-rich wastewater under low oxygen concentration.

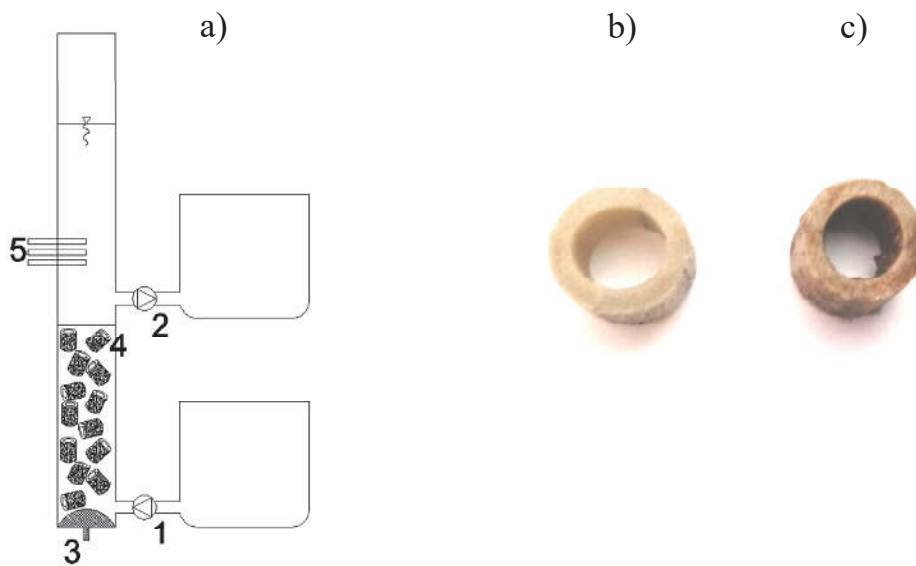
2. Materials and methods

In this study, a one-stage biofilm batch reactor with a working volume of 3 L treated digester supernatant from a sludge dewatering station in a full-scale municipal wastewater treatment plant (Fig. 1). In the supernatant, the average concentrations of pollutants were as follows:

320±52 mg COD/L, 413±78 mg TN/L, 328±46 mg NH₄-N/L and 97±19 mg TP/L, 7.5±0.1 pH, and alkalinity 31.0±2.5 mval/L. As inoculum (seed sludge, SS), aerobic granular sludge from a full-scale municipal wastewater treatment plant operated with simultaneous nitrification and denitrification was used. The experimental reactor was operated with a volumetric exchange rate of 50% and at a hydraulic retention time of 16 h. The operation of the reactor was automated to maintain the appropriate cycle length. The cycle length was 8 h, and it consisted of 5 min of filling, a 460 min reaction phase, 10 min of settling, and 5 min of decantation. Air was supplied continuously through a fine-bubble diffuser. To decrease the activity of nitrite-oxidizing bacteria (NOB) in the one-stage reactor, selection pressure was employed by maintaining a low dissolved oxygen (DO) concentration of about 0.5 mg/L at the end of the cycle, and a high temperature of about 35°C. After the filling stage in the reactor cycle, the DO concentration was almost zero, and it increased to 0.5 mg/L after 3 h of aeration, therefore, in fact, the reactor worked under intermittent anoxic/oxic conditions. The reactor was protected from sunlight, which negatively affects Anammox activity (Yang et al. 2010). To stimulate nitrification and Anammox, external doses of bicarbonate solution were added into the digester supernatant. The experiment was conducted in phases that differed in the bicarbonate/TN ratio in the influent: Phase 1 (ratio of 2.5), Phase 2 (ratio of 0), Phase 3 (ratio of 1.5), Phase 4 (ratio of 2.5), and Phase 5 (ratio of 3.5).

In the reactor, the biomass inhabited porous supports, which were cylinders with an external diameter of 15 mm, an internal diameter of 10 mm and a height of 10 mm. These supports were made of plasticized PVC modified with a blowing agent, which allows for a highly porous structure. The physical characteristics of the supports were as follows: density 892.73±3.43 kg/m³, porosity 39.66±1.59%, hardness 23.9±0.96 °Sh and tensile strength 138.97±2.41 N.

During the adaptation of the reactor to the treatment of digester supernatant, the influents and effluents were sampled to measure the concentrations of COD, total nitrogen (TN), ammonium, nitrites and nitrates, phosphate, pH and alkalinity (Hermanowicz 1999, HACH). DO was measured using an YSI ProODOTM probe.



Rys. 1. Schemat bioreaktora; (a): 1 – dopływ, 2 – odpływ, 3 – napowietrzanie, 4 – kształtki, 5 – pomiar tlenu, temperatury i pH, (b): fotografia kształtki, (c): fotografia kształtki z błoną biologiczną

Fig. 1. Scheme of the bioreactor; (a): 1 – influent, 2 – effluent, 3 – aeration, 4 – supports, 5 – control of DO, temperature and pH, (b): photo of the support (c): photo of the support with biofilm

To indicate changes in biofilm composition, fluorescence *in situ* hybridization (FISH) was used as an indicator of adaptation of the microorganisms to high influent nitrogen concentrations. A sample of inoculum and samples of biomass collected from the reactor at the end of each phase were fixed and microorganisms were identified as described by Nielsen (2009). The molecular probes used in this study are listed in Table 1; the conditions used for applying these probes can be found in ProbeBase (www.microbial-ecology.net/probebase). The probes were labeled with Cy3 or Fluos fluorochromes. Vectashield (Vector laboratories, USA) was used to mount the samples prior to visualization with a Nikon Eclipse (Nikon, Japan) epifluorescence microscope. The FISH-defined populations were quantified by image analysis using ImageJ software (<http://rsb.info.nih.gov/ij/>) and the ratio of the bio-area fraction of the targeted microbial population (stained by the specific probe) relative to that of the total microbial community (stained by the universal probe) was expressed as the percentage abundance. This analysis was

based on examination of at least 20 fields of view for each probe. For FISH quantification, three replicates per inoculum and each biomass sample were analyzed. The standard deviations of all values obtained with each probe were 15-20% of the mean value for that probe. Only means are shown in Figure 3.

Tabela 1. Sondy oligonukleotydowe 16S rRNA do identyfikacji AOB, NOB I bakterii Anammox (EUBmix była znakowana Fluos, pozostałe sondy – Cy3)
Table 1. 16S rRNA oligonucleotide probes for the identification of AOB, NOB and Anammox bacteria (EUBmix was labeled by Fluos, the rest probes – by Cy3)

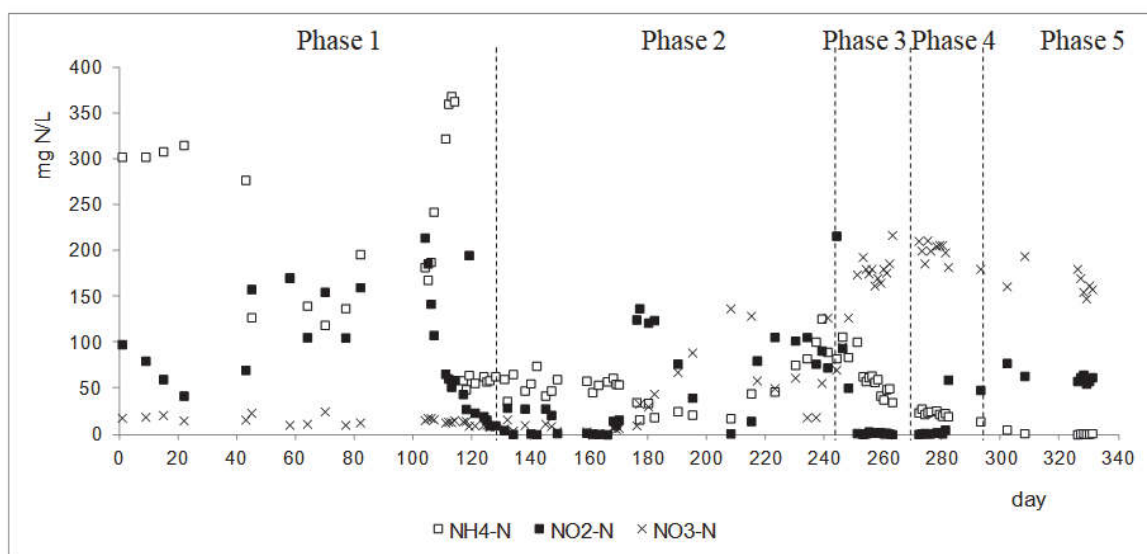
Probe	Sequence 5'-3'	Target	FA* (%)	Reference
EUBmix	EUB338-I (GCTGCCTCCCGTA-GGAGT), EUB338-II (GCA GCC ACC CGT AGG TGT), EUB338-III (GCT GCC ACC CGT AGG TGT)	Bacteria	20	Amann et al. (1990), Daims et al. (1999)
Nso190	CGATCCCCTGCTTTT CTCC	Betaproteobacterial ammonium- oxidizing bacteria	55	Mobarry et al. (1996)
NIT3	CCTGTGCTC- CATGCTCCG	<i>Nitrobacter</i> sp.	40	Wagner et al. (1996)
Ntspa662	GGAATTC- CGCGCTCCTCT	<i>Nitrospira</i> sp.	35	Daims et al. (2001)
Amx368	CCTTTCGGGCAT- TGCGAA	All Anammox microorganisms	15	Schmid et al. (2005)

*FA – formamide

3. Results and discussion

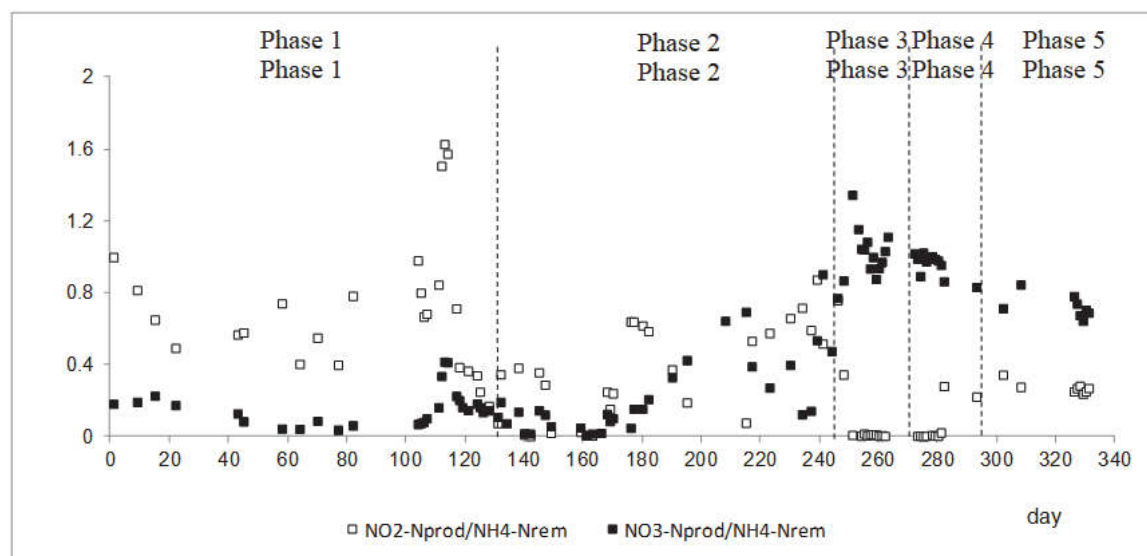
In this study, the adaptation of biomass, taken from the conventional municipal wastewater treatment plant with simultaneous nitrification and denitrification, to nitrogen-rich digester supernatant was investigated in terms of overall reactor performance, changes in nitrogen forms in the effluent and changes in microbial composition of the biofilm. During the whole period of the study, the suspended part of biomass was characterized by good settling abilities, with the sludge volume index of about 50 mL/g MLSS.

In the first period of biomass adaptation (Phase 1), ammonium was the main nitrogen form in the effluent (Fig. 2) and the average efficiency of ammonium removal was $44 \pm 19\%$. In this Phase 1, bicarbonates were added to obtain the bicarbonate/TN ratio in the influent of 2.5. The biomass yield was minimal in the reactor (yield coefficient below 0.2 g MLSS/g COD); therefore, the ammonium use for biomass synthesis can be neglected. In addition, loss of ammonium by stripping was not taken into account under all experimental conditions because a significant ammonium removal by stripping was observed at pH of 10.5 and 11 (Guštin & Marinšek-Logar 2011) and at pH of above 11.5 (Bonmati & Flotats 2003) that was not observed in the present experiment. Apart from the fact that it was a period of a start-up of the reactor, the reason for inefficient ammonium removal was the presence of free ammonia (FA). The FA inhibition threshold is $10\text{-}150 \text{ mg NH}_3\text{-N/L}$ and $0.1\text{-}4.0 \text{ mg NH}_3\text{-N/L}$ for nitrification and nitrification, respectively (Anthonishen et al. 1976, Bae et al. 2001). In the present experiment, FA concentration was $18 \text{ mg NH}_3\text{-N/L}$ at the beginning of the reactor cycle that could cause a low ammonium loss and, in addition, accumulation of nitrites. After about 10 days, ammonium concentration started to decrease to about $50 \text{ mg NH}_4\text{-N/L}$ and it corresponded to the increase in nitrite concentration. Excluding the initial period of nitrification inhibition, the effluent consisted of similar concentrations of ammonium and nitrites, whereas nitrate concentration was about $10\text{-}20 \text{ mg NO}_3\text{-N/L}$. In one-stage reactors, the main problem in cultivating Anammox bacteria is the maintenance of the most important parameter required for Anammox process, which is the nitrite/ammonium ratio that should be of about 1:1. The insufficient alkalinity of wastewater may limit nitrification. However, in this study, the addition of bicarbonate could have balanced the acidifying effect of nitrification (van Dongen et al. 2001). The alkalinity of the effluent was about 21 mval/L , and pH 8.3. The calculated ratio between nitrite produced ($\text{NO}_2\text{-N}_{\text{prod}}$) and ammonium removed ($\text{NH}_4\text{-N}_{\text{rem}}$) in the reactor cycle (Fig. 3) in Phase 1 was 0.66, which indicates that nitrite produced could have been removed either in the Anammox process or in denitrification.



Rys. 2. Stężenia związków azotu w ściekach oczyszczonych w fazach eksperymentalnych

Fig. 2. Concentrations of nitrogen compounds in the effluents in the experimental phases



Rys. 3. Stosunki powstałego azotu azotanowego(III) i usuniętego azotu amonowego oraz powstałego azotu azotanowego(V) i usuniętego azotu amonowego w fazach eksperymentalnych

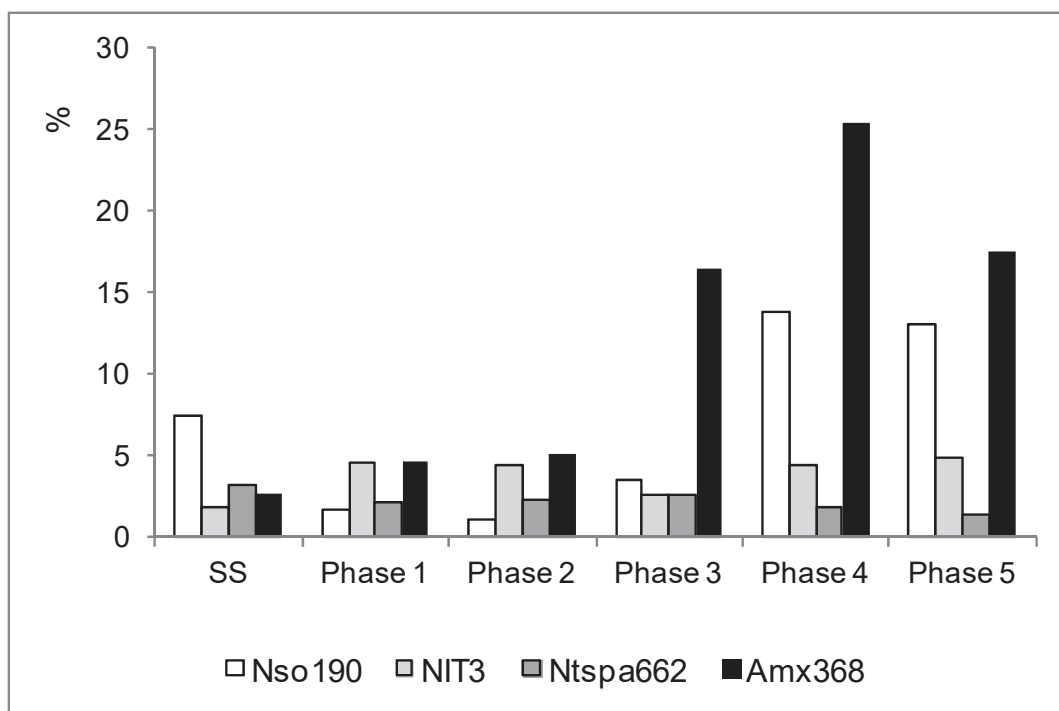
Fig. 3. The ratios between nitrite produced and ammonium removed and between nitrate produced and ammonium removed in the experimental phases

In Phase 2, nitrogen changes in the reactor were tested when there was no additional bicarbonate in the influent. The average ammonium loss was $64 \pm 15\%$. During the first half of this phase, the alkalinity in the bioreactor was quite high (10-15 mval/L, pH 8.0), as the effect of alkalinity that was present in raw digester supernatant. In this period, ammonium concentration in the effluent was about 50-60 mg $\text{NH}_4\text{-N/L}$ and nitrite and nitrate concentrations were low (Fig. 2). In the second half of Phase 2, the acidifying effect of nitrification started to be observed resulting in the alkalinity of the effluent of about 0.5-3.6 mval/L. As a result, ammonium concentration increased to about 100 mg $\text{NH}_4\text{-N/L}$ and simultaneously the nitrite concentration increased resulting in the ammonium/nitrite ratio of about 1. These could have created favorable conditions for the Anammox process or denitrification because the observed increase in nitrite concentration was not stoichiometric, which is indicated by the $\text{NO}_2\text{-Nprod}/\text{NH}_4\text{-Nrem}$ ratio of 0.36 (Fig. 3). At the second half of the Phase 2, the increase in the $\text{NO}_3\text{-Nprod}/\text{NH}_4\text{-Nrem}$ ratio was observed to about 0.4, indicating the nitrification.

In Phases 3, 4, and 5, the bicarbonate/TN ratio in the influent was increased to 1.5, 2.5 and 3.5, respectively. Bicarbonate addition increased the alkalinity of the effluent to above 7 mval/L, pH was 8.4. As a result, ammonium concentration in the effluents gradually decreased to achieve 0–10 mg $\text{NH}_4\text{-N/L}$ in the Phase 5 (Fig. 2). The efficiency of ammonium removal was $77 \pm 4\%$, $89 \pm 1\%$ and $98 \pm 2\%$ in Phase 3, 4 and 5, respectively. In Phases 3 and 4, nitrite concentration in the effluent did not exceed 5 mg/L. Efficient nitrite conversions are indicated by the $\text{NO}_2\text{-Nprod}/\text{NH}_4\text{-Nrem}$ ratio of 0.01-0.04 (Fig. 3). Nitrate concentrations of about 170-210 mg $\text{NO}_3\text{-N/L}$ indicated good activity of nitrite-oxidizing bacteria. It was also confirmed by high values of $\text{NO}_3\text{-Nprod}/\text{NH}_4\text{-Nrem}$ ratio of about 0.8. According to van der Star et al. (2007), nitrate production is an indicator of Anammox activity. In the Phase 5, in which the bicarbonate/TN ratio was 3.5, the nitrification was inhibited. This resulted in the accumulation of nitrite in the effluent to about 65-77 mg $\text{NO}_2\text{-N/L}$ and a decrease in the nitrate concentration to about 150-160 mg $\text{NO}_3\text{-N/L}$. The $\text{NO}_2\text{-Nprod}/\text{NH}_4\text{-Nrem}$ ratio increased to 0.27. The obtained results point out that the start-up of the reactor during the treatment of nitrogen-rich wastewater is difficult and time-consuming when the inoculum taken from Anammox reactors is not

available. As the main problems during start-up, apart from the limitation of nitrite as a substrate for the Anammox process, incidental nitrite toxicity is reported, which is caused by a too high loading rate (van der Star et al. 2007). The ranges of the nitrite concentrations that adversely affect the Anammox process are wide, from 100 mg NO₂-N/L (Strous et al. 1999) to 400 mg NO₂-N/L (Lotti et al. 2012).

According to van der Star et al. (2007), in initial phase of reactor operation, Anammox conversions could not be identified by traditional methods such as following the nitrogen profiles. As reliable indicators of the Anammox bacteria growth, molecular methods are reported. In the present experiment, in Phases 1, 2 and 3, the abundance of aerobic AOB in the biomass was lower than in the inoculum (1.1-3.5%) (Fig. 4).



Rys. 4. Udział w biomacie AOB (Nso190), NOB (NIT3 i Ntspa662) i bakterii Anammox (Amx368) w fazach eksperymentalnych

Fig. 4. The abundance of AOB (Nso190), NOB (NIT3 and Ntspa662) and Anammox bacteria (Amx368) in the biomass in the experimental phases

In Phases 4 and 5, AOB accounted for 13% of the biomass, which resulted in the ammonium concentration in the effluent lower than 28 NH₄-N/L. Regarding NOB, the abundance of *Nitrobacter* sp. was slightly

higher than in the inoculum and in all phases was about 4.2%. The *Nitrospira* sp. abundance in all phases was similar to that in the inoculum. *Nitrospira*-like bacteria are usually more numerous NOB in wastewater treatment systems than *Nitrobacter*-like bacteria (Daims et al. 2011), however our studies indicated higher abundance of *Nitrobacter* sp. than *Nitrospira* sp. Such a proportion between NOB is also reported as typical for the nitrification-Anammox biomass (Langone et al. 2014). Significant numbers of *Nitrobacter* sp. was reported to be an indicator for high-loaded wastewater treatment plants (Gieseke et al. 2003). In addition, *Nitrobacter* sp. is more resistant to free nitrous acid than *Nitrospira* sp. (Blackburne et al. 2007).

In this study, the presence of low abundance (2.7%) of Anammox bacteria was observed already in the inoculum (Fig. 4). In Phases 1 and 2, the abundance of Anammox bacteria was slightly higher than in the inoculum. Starting from Phase 3, their abundance highly increased to 25.4% in Phase 4. According to Duan et al. (2012), Anammox bacteria can account even for 50% of all the bacteria in the reactor in which Anammox process was started-up from conventional activated sludge with ammonium concentration in the effluent elevated from 50 to 270 mg NH₄-N/L. To conclude, in the final phases of the experiment, FISH tests confirmed high abundance of microorganisms responsible for ammonium removal: AOB and Anammox bacteria. This could have been the result of the nitrifier presence in the outer parts of the biomass particles and biofilm, which protected Anammox bacteria located in the internal zones from low oxygen concentration in the reactor.

4. Conclusions

In this study, the effect of bicarbonate addition on the nitrogen compound conversions during the start-up of the one-stage biofilm reactor treating digester supernatant was investigated with the bicarbonate/TN ratio in the influent from 0 to 3.5. Only with the highest ratio in the influent of about 3.5 the final ammonium concentration in the effluent was below 10 mg NH₄-N/L. Under these conditions, nitrates were the predominant form of nitrogen in the effluent. Aerobic AOB and Anammox bacteria were major components of the biomass (13.0% and 17.5%, respectively) that ensured efficient ammonium removal.

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Wpracowanie jednostopniowego reaktora z błoną biologiczną do usuwania azotu z wód nadosadowych w procesie częściowej nitryfikacji-Anammox

Streszczenie

Proces częściowej nitryfikacji-Anammox jest obiecującą alternatywą wobec konwencjonalnej nitryfikacji-denitryfikacji do usuwania azotu ze ścieków o wysokim stężeniu związków azotowych i niskim stosunku ChZT/N, skutkującą oszczędnością energii i dodatkowych źródeł węgla organicznego. W procesie Anammox, prowadzonym w warunkach anoksycznych przez bakterie autotroficzne, azot amonowy i azot azotanowy(III) uczestniczą w równoważnych ilościach w powstawaniu azotu cząsteczkowego.

Wpracowanie jednostopniowych reaktorów, w których planowane jest prowadzenie częściowej nitryfikacji i Anammox, jest trudne. Z uwagi na niską szybkość autotroficznego wzrostu (czas generacji 10-12 dni), biomasa bakterii Anammox charakteryzuje się niskim przyrostem. Ponadto, azot azotanowy(III) jest substratem do procesu Anammox, jednak w pewnych stężeniach inhibuje proces. Dodatkowo, niedostatek nieorganicznych związków węglowych jest czynnikiem limitującym wzrost tlenowych bakterii utleniających azot amonowy

oraz bakterii Anammox. Celem badań było określenie wpływu dozowania do reaktora jednostopniowego wodorowęglanów na występowanie poszczególnych form związków azotowych w ściekach oczyszczonych oraz skład biomasy podczas wpracowania reaktora do oczyszczania ścieków bogatych w azot z wykorzystaniem procesu Anammox.

W prezentowanych badaniach, jednostopniowy reaktor porcjowy z błoną biologiczną był wykorzystywany do oczyszczania wód nadosadowych pochodzących z oczyszczalni ścieków komunalnych pracującej w skali technicznej. Stężenia zanieczyszczeń w wodach nadosadowych były następujące: 320 ± 52 mg ChZT/dm³, 413 ± 78 mg N_{og}/dm³, 328 ± 46 mg NH₄-N/dm³ i 97 ± 19 mg P_{og}/dm³. Reaktor został zaszczipiony tlenowym osadem granulowanym z oczyszczalni ścieków komunalnych pracującej w skali technicznej eksploatowanej z jednoczesną nityfikacją i denityfikacją. Parametry eksploatacyjne reaktora badawczego były następujące: objętość robocza 3 dm³, długość cyklu 8 h, stopień wymiany objętościowej 50%. W reaktorach jednostopniowych bakterie utleniające azot azotanowy(III) muszą być poddawane selektywnej presji w celu ograniczenia ich aktywności. Z tego względu w reaktorze eksperymentalnym utrzymywano niskie stężenie tlenu (około 0,5 mg/dm³), pH około 8,0 i wysoką temperaturę (około 35°C). Wskaźnikiem adaptacji mikroorganizmów do wysokich stężeń azotu w ściekach dopływających były zmiany w profilu związków azotowych w odpływie oraz wyniki uzyskane techniką fluorescencyjnej hybrydyzacji *in situ*, pozwalającą na określanie liczebności poszczególnych grup mikroorganizmów w biomacie.

Stabilną pracę reaktora uzyskano przy stosunku wodorowęglanów do azotu ogólnego w dopływie równym około 3,5; stężenie azotu amonowego w ściekach oczyszczonych nie przekraczało 10 mg/dm³. Główną formą azotu w odpływie był azot azotanowy(V). W okresie wpracowania proporcje między liczebnością w biomacie tlenowych bakterii utleniających azot amonowy i azot azotanowy(III) oraz bakterii Anammox podlegały dynamicznym zmianom. Część biomasy pozostająca w zawieszeniu charakteryzowała się dobrymi właściwościami sedymentacyjnymi; indeks objętościowy osadu wynosił poniżej 50 cm³/g s.m.

Abstract

For nitrogen-rich wastewater with a low COD/N ratio, the partial nitrification-Anammox process is considered a promising alternative to conventional nitrification-denitrification, saving energy and additional carbon source. In the Anammox reaction, performed under anoxic conditions by autotrophic bacteria, ammonium and nitrite contribute in equimolar amounts to the formation of dinitrogen gas.

Anammox bacteria are characterized by low biomass yield because of their autotrophic growth mode and their high maintenance requirement due to their slow growth rate (doubling time of 10-12 days). In addition, nitrite is a substrate for Anammox on one hand and an inhibitor of Anammox microorganisms at some concentrations on the other hand. Next, inorganic carbon limitation is the limiting factor in the growth of nitrifiers and Anammox bacteria. These are the reasons that one-stage reactors are extremely difficult to start-up. The goal of this study was to determine the effect of bicarbonate addition on the changes in nitrogen forms in the one-stage reactor, biofilm composition and overall reactor performance during the adaptation of non-Anammox biomass to nitrogen-rich wastewater.

In this study, a one-stage biofilm batch reactor treated the digester supernatant from the full-scale municipal wastewater treatment plant. In the supernatant, the average concentrations of pollutants were as follows: 320 ± 52 mg COD/L, 413 ± 78 mg TN/L, 328 ± 46 mg $\text{NH}_4\text{-N}$ /L and 97 ± 19 mg TP/L. Aerobic granular sludge from the full-scale municipal wastewater treatment plant operated with simultaneous nitrification and denitrification was used as inoculum. The operational parameters of the reactor were: working volume 3 L, 8-hour cycle, volumetric exchange ratio 50%/cycle. In one-stage reactors, nitrite-oxidizing bacteria (NOB) must be selectively pressured to decrease their activity. Therefore, in this reactor, low dissolved oxygen, about 0.5 mg/L, a pH of about 8.0, and a high temperature, about 35°C, were maintained. Apart from determining changes in nitrogen profile, fluorescence *in situ* hybridization technique indicating the changes in the biofilm composition was used as an indicator of adaptation of the microorganisms to high influent nitrogen concentrations.

With the bicarbonate/TN ratio in the influent of about 3.5, stable reactor performance was obtained with the final ammonium concentration in the effluent below 10 mg N- NH_4 /L. Nitrate was the predominant form of nitrogen in the effluent. In this period, the abundance proportion between Anammox bacteria, ammonium-oxidizing bacteria (AOB) and NOB dynamically changed in the biomass. This part of biomass that was suspended in the reactor was characterized by good settling abilities, with the sludge volume index below 50 mL/g MLSS.

Słowa kluczowe:

Anammox, częściowa nitryfikacja, wody nadosadowe, bakterie utleniające azot amonowy, bakterie utleniające azot azotanowy(III)

Keywords:

Anammox, partial nitrification, digester supernatant, AOB, NOB



Environmental Aspects of Abrasive Water Jet Cutting

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1. Introduction

Among the methods of machining special attention they deserve environmentally friendly. This is mainly plastic processing (Kukielka 2003), (Kukielka & Kukielka 2006) and high pressure water jet technology. Use of conventional coolants in traditional machining and grinding is being looked upon critically from the point of view of its impact on environment.

In water jet machining is used pure (deionized) water with the addition of a small amount of abrasive (17-20% by mass).

Cutting by high-pressure water jet is one of advanced methods of materials machining. Treating materials using a high pressure abrasive water jet is more complex than conventional treatments. In addition, this advanced manufacturing technology replaces many operations traditionally carried out by cutting and does not cause structural changes in the machining material. Therefore, optimization of the machining is the subject of many studies (Hloch et al. 2007), (Perec 2016), (Valicek 2016). High pressure water is converted to a high speed jet inside a nozzle (Fig. 1a.) and flows out of the nozzle at a speed of several hundred meters per second, seizes abrasive particles and accelerates them to large kinetic energies.

Adding to the water jet the dry abrasive in a special mixer injector (Fig. 1b), causes increase cutting efficiency. As a result, it becomes possible to almost any material cutting with low roughness of cutting surface

(Perec et al. 2015). The most commonly used pressure in the system, called AWJ, ranges from 400 to 600 MPa and common abrasive is garnet (Perec 2011).

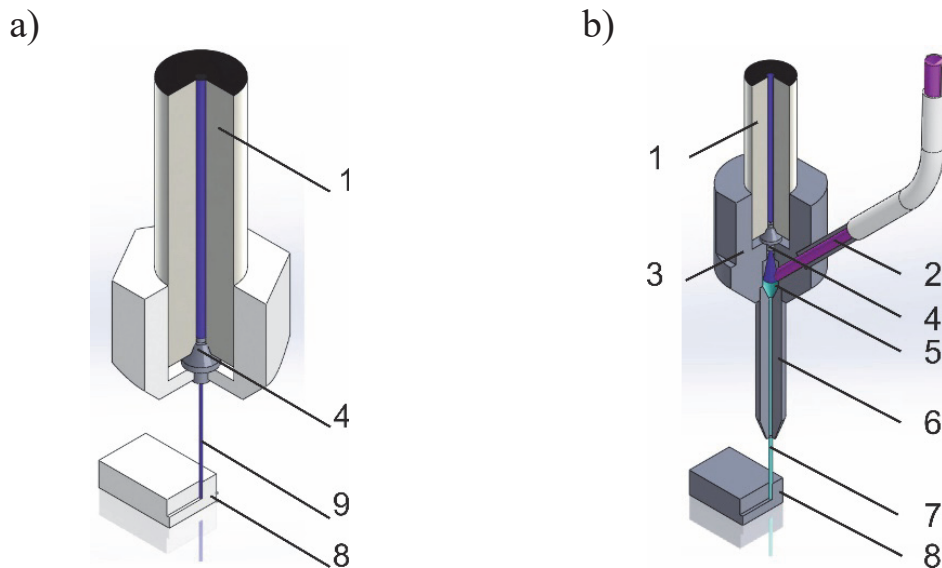


Fig. 1. Schematic diagram of Water Jet cutting (a) and Abrasive Water Jet cutting (b): 1. High pressure water inlet, 2. Abrasive inlet, 3. Cutting head body, 4. Water nozzle, 5. Mixing chamber, 6. Focussing tube, 7. High Pressure Abrasive Water Jet, 8. Machining sample, 9. High Pressure Water Jet

Rys. 1. Schemat cięcia strugą wody (a) oraz cięcia strugą wodno-ścierną (b):
 1. Dopływ wysokiego ciśnienia, 2. Dopływ ścierniwa, 3. Korpus głowicy tnącej,
 4. Dysza wodna, 5. Komora mieszania, 6. Dysza wodno-ścierna,
 7. Wysokociśnieniowa struga wodno-ścierna, 8. Przedmiot obrabiany,
 9. Wysokociśnieniowa struga wody

Its popularity in the processing jet as an abrasive garnet is caused by achieving high performance at relatively low wear focusing tube (Hreha et al. 2014). The cost of abrasive is the main cost of processing an abrasive water jet (Perec & Tavodova 2016), therefore purposeful work aimed towards the use of the cheapest abrasive materials and their recycling. The roughness of the cut surface is comparable with the surface of the rough grinding and reaches a value R_a equal $2 \mu\text{m}$ (Perec et al. 2016).

2. Research materials

2.1. Abrasive materials

Garnet

The study used GMA Garnet abrasives supplied by GMA Garnet Pty Ltd, Western Australia. Almandine is the iron aluminium garnet. Almandine, like other garnets, forms rounded crystals with 12 rhombic or 24 trapezoidal faces or combinations of these and some other forms. This crystal habit is classic for the garnet minerals. Almandine is the most common of the garnets but seldom occurs in specimens worthy of collections or fit for gems. Almandine is usually found either as rocks forming mineral in magmatic and metamorphic acid rocks (such as migmatites, garnet-biotite gneisses, granulites, micaschists, pegmatites, diorites, etc.) or as heavy mineral sand from weathered hard rocks, secondary concentrated in present-day and/or pre-existing streams and other alluvial deposits or in present-day and/or pre-existing beaches and other shore line marine deposits. Only selected few localities are mentioned. Industrial abrasive made from garnet almandine is prevalent abrasive used in AWJ cutting.

Degree of damage of big crystals of garnet almandine (porphyroblasts) in rocks (i.e. number of individual particles limited by cracks in one porphyroblast (crystal)) plays an important role in determination of suitability of the almandine for production of industrial abrasive concentrate for AWJ cutting (Martinec et al. 2002). The properties of abrasives and view of crystal shape are shown in Table 1.

Table 1. Garnet (almandine) properties (Martinec et al. 2002)

Tabela 1. Właściwości granatu (almandynu) (Martinec et al. 2002)

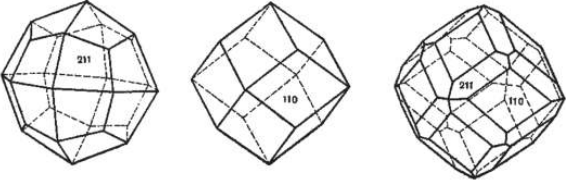
	
Crystal system	Cubic
Twinning	None
Unit cell	$a = 11.53 \text{ \AA}$

Table 1. cont.**Tabela 1.** cd.

Habit	Crystals usually dodecahedrons or trapezohedrons; also in combination or with hexocathedron; massive; granular
Cleavage	1; {110} parting sometimes distinct
Fracture	Conchoidal to uneven
Tenacity	Brittle
Color	Deep red to reddish-brown, sometimes with a violet or brown or brownish black hue
Hardness (Mohs)	6.5-7.5
Density	4.1-4.3

Ilmenite

The study used ilmenite abrasives supplied by GMA Garnet Pty Ltd, under New Steel trade name. Ilmenite is an economically important and interesting mineral for production of titanium white pigment and titanium. It is named for its place of discovery at Ilmen Lake in the Ilmen Mountains, Ilmenite forms as a primary mineral in mafic igneous rocks and is concentrated into layers by a process called “magmatic segregation”. It crystallizes out of a magma relatively early before most of the other minerals. As a result, the heavier crystals of ilmenite fall to the bottom of the magma chamber and collect in layers. It is these layers that constitute a rich ore body for titanium miners. Ilmenite also occurs in heavy sedimentary rocks (black fraction of sands). This mineral is very breakable and fragile (Martinec et al. 2002). The properties of abrasive and view of crystal shape are shown in Table 2.

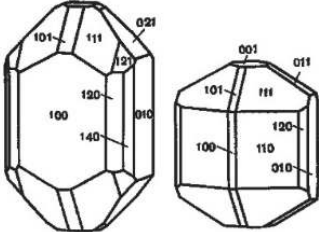
Table 2. Ilmenite properties (Martinec et al. 2002)**Tabela 2.** Właściwości ilmenitu (Martinec et al. 2002)

Crystal system	Hexagonal
Twinning	On {0001}, simple; on {10-11}, lamellar
Unit cell	$a = 5.09 \text{ \AA}$; $c = 14.09 \text{ \AA}$
Habit	Crystals thick tabular or acute rhombohedral; granular; massive, lamellar to compact
Cleavage	2; {0001} and {10-11} parting
Fracture	Conchoidal to uneven
Tenacity	Brittle
Color	Iron-black
Hardness (Mohs)	5-6
Density	4.5-5.0

Olivine

The study used olivine abrasives supplied by Sibelco Europe under *Green Lightning Olivine* trade name. Fayalite is one of two minerals that are simply known as olivine. It is found in ultramafic igneous rocks. Mafic is a word that is used to define igneous rocks with a high iron and magnesium content. The olivine minerals have a high melting point and are the first minerals to crystallize from a mafic magma. Forsterite crystallizes first with fayalite crystallizing last when other minerals such as the pyroxenes are just beginning to form. The early crystallization of olivine is the reason that molten lavas can contain already crystallized grains of olivine before they are ejected from volcanoes. Some ultramafic rocks can be composed of almost all olivine and these are called dunites or peridotites. Olivine is also present in marbles that formed from metamorphosed impure limestones (Martinec et al. 2002). The properties of abrasives and view of crystal shape are shown in Table 3.

Table 3. Olivine (Fayalite) properties (Martinec et al. 2002)**Tabela 3.** Właściwości oliwinu (fajalit) (Martinec et al. 2002)

	
Crystal system	Orthorhombic
Twinning	On {100}; on {031} as trillings
Unit cell	$a = 4.799 \text{ \AA}$; $b = 10.39 \text{ \AA}$; $c = 6.063 \text{ \AA}$
Habit	Crystals thick tabular, often with wedge-shaped terminations, small; massive, compact or granular
Cleavage	2; {010} and {100} imperfect
Fracture	Conchoidal
Tenacity	Brittle
Color	Greenish yellow, yellowish brown, brown
Hardness (Mohs)	7
Density	4.32

2.2. Focusing tubes

In research was used focusing tubes made from unique, patented materials that are literally changing the definition of wear resistance ROCTEC®100. The ROCTEC ®process enables the combination of these advanced ceramic materials without the need for a soft metal binder, as is the case with tungsten carbide/cobalt using traditional sintering technology. The ROCTEC process enables focusing tubes to be formed using very short consolidation cycles to minimize the natural tendency of ceramic particles to grow in size, when exposed to high heat for long periods. Eliminating a metallic binder and maintaining extra-fine grain size both contribute to optimum focusing tube performance. The result is an extremely durable material that fiercely resists abrasive and erosive wear.

3. Apparatus

The equipment used was a KMT Intensifier type I50, 2 axis CNC table type ILS55 by Techni Waterjet with computer control system (Fig. 3a). To capture abrasives after its exit from the focusing tube, a special receiver was used (Fig. 3b). The receiver was designed to collect the abrasives and to prevent any further particle disintegration after leaving the focusing tube. The bottom PVC receiver was covered by a steel plate to prevent perforation. No signs of wear were observed on the protective plate after conclusion of testing (Perec 2012). For establishing the particle size distribution of the abrasive, Retsch sieving equipment was used. The mass of abrasive remaining on the sieves was weighed on the digital lab scales. The statistical analysis of the abrasive materials grains distribution of was carried out using the Gradistat v.8.0 program (Blott & Pye 2001) based on the Folk & Ward method (Folk & Ward 1957). Microscopic photos of abrasive particles were taken on a microscope Olympus SZ-40.

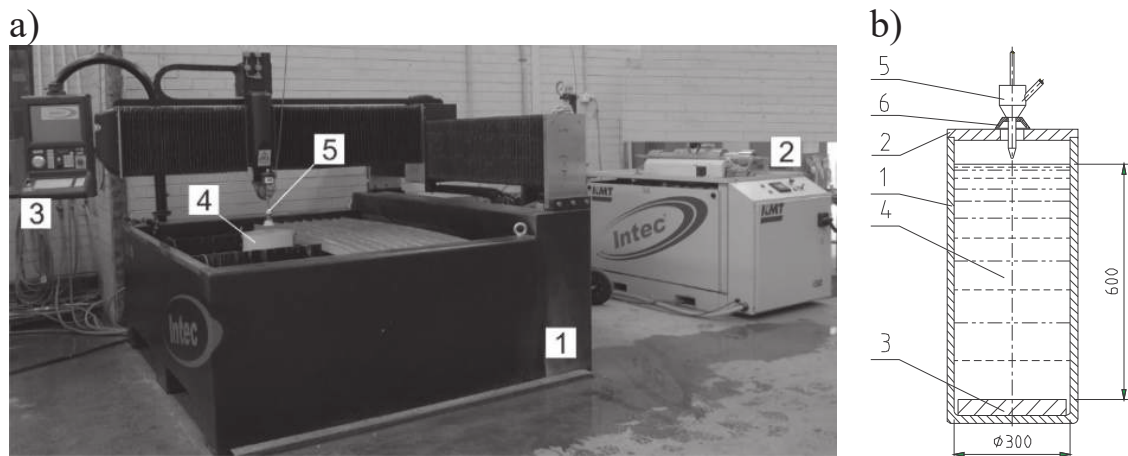


Fig. 2. Testing rig (a): 1) Cutting table, 2) Intensifier, 3) Control Unit, 4) Catcher, 5) Cutting Head, and catcher for abrasive jet (b): 1) Tank, 2) Tank Cap, 3) Mild Steel Shield, 4) Water, 5) Cutting Head, 6) Rubber Head Cap.

Rys. 2. Stanowisko badawcze (a): – 1) Stół roboczy, 2) Multiplikator ciśnienia, 3) Zespół sterujący, 4) Odbieralnik ścierniwa, 5) Głowica tnąca, oraz odbieralnik ścierniwa (b): 1) Zbiornik, 2) Pokrywa, 3) Osłona stalowa, 4) Woda, 5) Głowica tnąca, 6) Gumowa osłona głowicy.

3. Tests results

4.1. Abrasive grain disintegration

Garnet

The results of the study of GMA80 abrasive fractured during jet formation at a pressure of 390 MPa through a 0.25 mm orifice, 0.76 mm ID focusing tube and average of abrasive flow rate are shown in Fig. 3. The density function approximating the distribution before of the nozzle is symmetrical (Table 4) because skewness is near zero. Distribution is mesokurtic ($0.9 < K_G < 1.11$).

Table 4. GMA garnet particle distribution statistics

Tabela 4. Statystyczne parametry rozkładu ziaren granatu GMA

	GMA before	GMA after	GMA recycled
Skewness, Sk_G	0.039	0.248	-0.081
Kurtosis, K_G	0.920	0.651	0.908

Figure 4 shows sample abrasive grains before and after leaving the focusing tube. One can observe different size grains, mostly isometric in shape, but with sharp edges. Most grains are fine. Among them, you can see a few grains with larger dimensions.

After passing of garnet through the nozzle, density function of distribution change to asymmetric (fine skewed), with negative asymmetry and a predominance of the grains below 53 μm , which previously was not presented. Skewness equal -0.248. The volume of grains 425-250 μm decreased significantly. Distribution is very platykurtic, because kurtosis $K_G < 0.67$.

In the process of recycling grains smaller than the limit (for garnet # 80 it is 125 μm) they are removed as inefficient during the cutting process [Perec, 2018]. The very small positive asymmetry density function approximating the grain distribution is also visible. Skewness is equal 0.081. Distribution is mesokurtic ($0.9 < K_G < 1.11$).

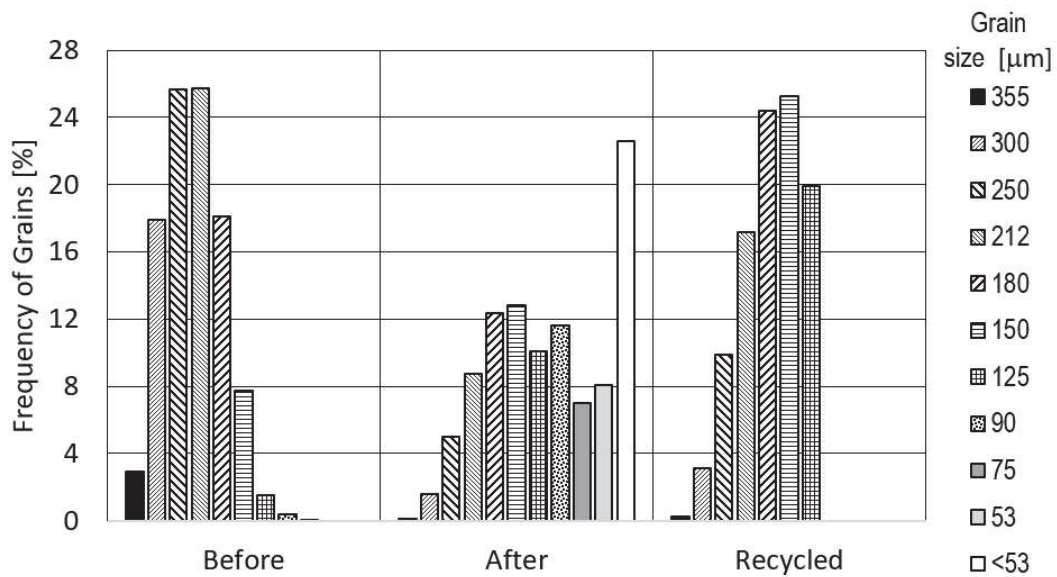


Fig. 3. Disintegration of garnet #80 after passing through cutting head with water nozzle ID 0.2 mm and focusing tube ID 0.76 mm. Pressure 390 MPa
Rys. 3. Rozdrobnienie granatu nr 80 po przejściu przez głowicę tnącą z dyszą wodną \varnothing 0.25 mm i dyszą wodno-ścierną \varnothing 0.76 mm. Ciśnienie 390 MPa

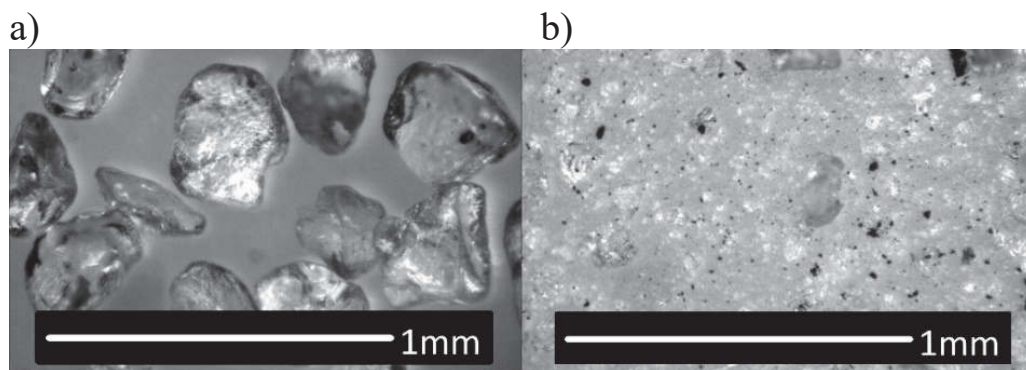


Fig. 4. Abrasive grains garnet 80 Mesh before (a) and after (b) forming in cutting head. Magnification 60 x

Rys. 4. Ziarna granatu nr 80 przed (a) i po (b) opuszczeniu głowicy tnącej. Powiększenie 60 x

Ilmenite

The study results of the Ilmenite abrasive fractured during formation of jets at a pressure of 390 MPa through a 0.25 mm dia orifice and 0.76 mm ID focusing tube are shown in Fig. 5. The density function approximating the distribution (Table 5) is coarse skewed ($0.1 < Sk_G < 0.3$). Distribution is leptokurtic ($1.11 < K_G < 1.50$).

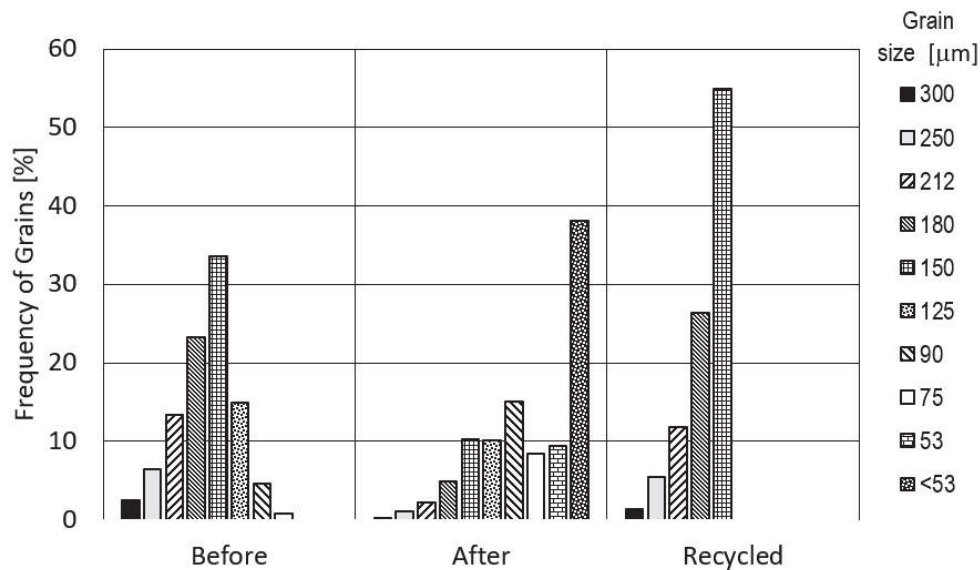


Fig. 5. Disintegration of Ilmenite #90 after passing through cutting head with water nozzle ID 0.25 mm and focusing tube ID 0.76 mm, Pressure 390 MPa.

Rys. 5. Rozdrobienie ilmenitu nr 90 po przejściu przez głowicę tnącą z dyszą wodną \varnothing 0.25 mm i dyszą wodno-ścierną \varnothing 0.76 mm. Ciśnienie 390 MPa.

After passing of the ilmenite through the nozzle density function of distribution leave strong asymmetric (coarse skewed), with negative asymmetry and the predominance of the share of grains below 53 μm , which previously was not presented. Skewness equal 0.142. The share of grains 250-125 μm decreased significantly and volume of grains 90 μm increased. Distribution is very platykurtic (kurtosis $K_G < 0.67$).

In the process of recycling grains smaller than the limit (for ilmenite #90 it is 90 μm) they are removed. The very coarse skewed density function approximating the grain distribution is also visible. Skewness is equal 0.39. Distribution is mesokurtic ($0.9 < K_G < 1.11$).

Table 5. Ilmenite particle distribution statistics

Tabela 5. Statystyczne parametry rozkładu ziaren ilmenitu

	Ilmenite before	Ilmenite after	Ilmenite recycled
Skewness, Sk_G	0.107	0.142	0.390
Kurtosis, K_G	1.134	0.632	1.017

Figure 6 shows sample abrasive particles of ilmenite before and after leaving the focusing tube. One can observe a very large number of very small grains and only few larger grains of ilmenite. This is confirmed by the distribution of abrasive particles as shown in Fig. 5.

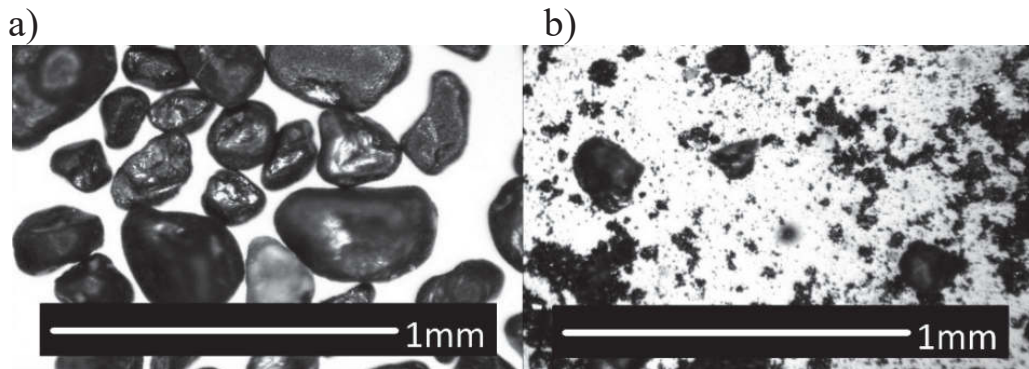


Fig. 6. Abrasive grains Ilmenite #90 before (a) and after (b) forming in cutting head. Magnification 60 x.

Rys. 6. Ziarna ilmenitu nr 90 przed (a) i po opuszczeniu (b) głowicy tnącej. Powiększenie 60 x.

Olivine

The study results of the olivine abrasive, disintegrated during jet formation at a pressure of 390 MPa through a 0.25 mm orifice, 0.76 mm ID focusing tube and average of abrasive flow rate are shown in Fig. 7. The density function approximating the distribution (Table 6) before the nozzle is fine skewed (skewness equal -0.139). Distribution is mesokurtic ($0.9 < K_G < 1.11$).

After passing through the nozzle persist fine skewed (skewness equal -0.139), with negative asymmetry and a predominance of the share of grains below 53 μm , which previously was not presented. Skewness equal 0.142. The volume of grains 300-180 μm decreased significantly. Distribution is very platykurtic (kurtosis $K_G < 0.67$).

Table 6. Olivine particle distribution statistics

Tabela 6. Statystyczne parametry rozkładu ziaren oliwinu

	Olivine before	Olivine after	Olivine recycled
Skewness, Sk_G	-0.139	-0.134	0.197
Kurtosis, K_G	1.009	0.615	0.926

In the process of recycling grains, smaller than the limit (for olivine #60 it is 125 μm) they are removed as inefficient during the cutting process. The asymmetry (coarse skewed) density function approximating the recycled grain distribution is also visible. Skewness is equal 0.197 and distribution is mesokurtic ($0.9 < K_G < 1.11$).

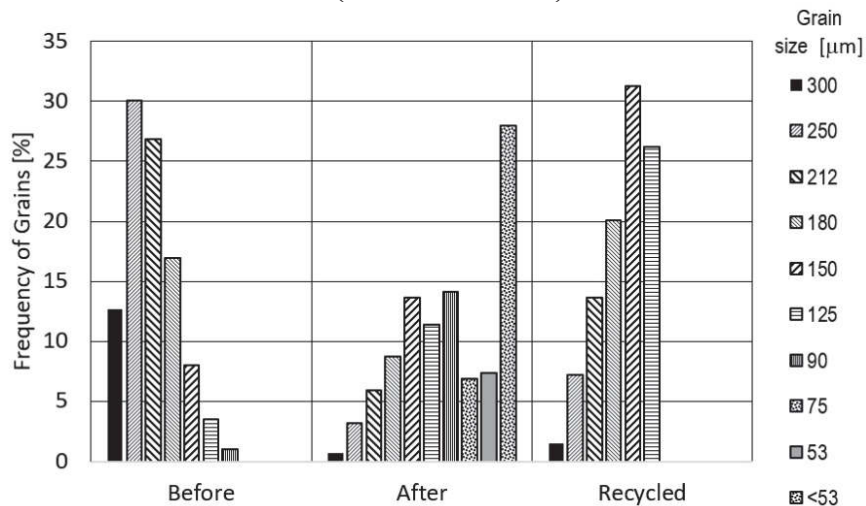


Fig. 7. Disintegration of olivine #60 after passing through cutting head with water nozzle ID 0.25 mm and focusing tube ID 0.76 mm, Pressure 390 MPa.

Rys. 7. Rozdrobnienie oliwinu nr 60 po przejściu przez głowicę tnącą z dyszą wodną \varnothing 0.25 mm i dyszą wodno-ścierną \varnothing 0.76 mm. Ciśnienie 390 MPa

Figure 8 shows abrasive particles before and after leaving the focusing tube. One can observe a large number of small grains and bigger grains of olivine. Lot of grains are fine.

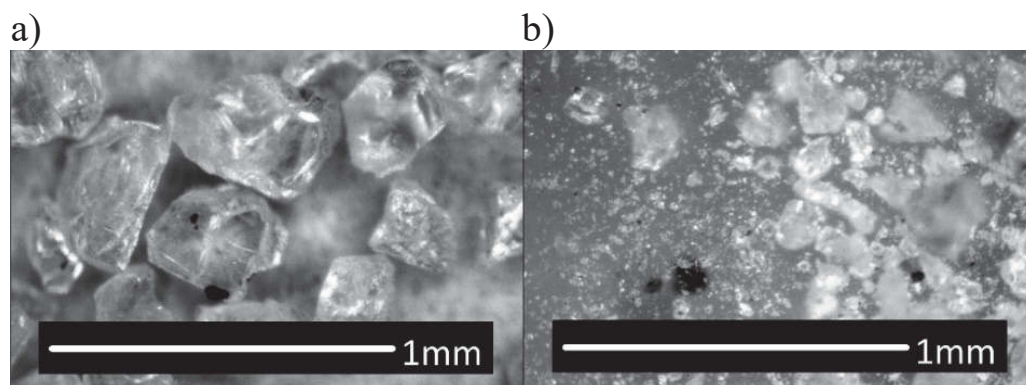


Fig. 8. Abrasive grains olivine #60: before (a) and after (b) forming in cutting head. Magnification 60 x

Rys. 8. Ziarna ilmenitu nr 60 przed (a) i po (b) opuszczeniu głowicy tnącej. Powiększenie 60 x

4.1. Recycling potential

After abrasive catching and drying sieve analysis was carried out and the analysis the amount of the individual fractions was determined. For test abrasive size #80 size range is from 300 to 125 μm . To determine what fraction of the original range found in the mass of particulate after treatment, all of the fractions smaller than the lower limit of the particle distribution, were rejected [Guo 1992]. It is illustrated in Fig. 3, 5, and 7.

The recycling rate was calculated on basis equation:

$$R_f = \frac{m_r}{m_t} \quad (2)$$

where:

R_r – abrasive recycling factor [g/g],

m_r – mass of recycled abrasive [g],

m_t – total mass of abrasive [g].

Specific results for tested abrasives are presented in Fig. 9. The biggest recycling factor, amounting to 0.51 was observed for the garnet. This means it can be expected that half of the spent abrasive is possible to re-use. The other abrasives was olivine, with the recycling factor equal to 0.32. This means that one third of the abrasive can be used again. The lowest potential recycling equal to 0.19, characterized ilmenite. In this only when not less than 1/5 could be used second time.

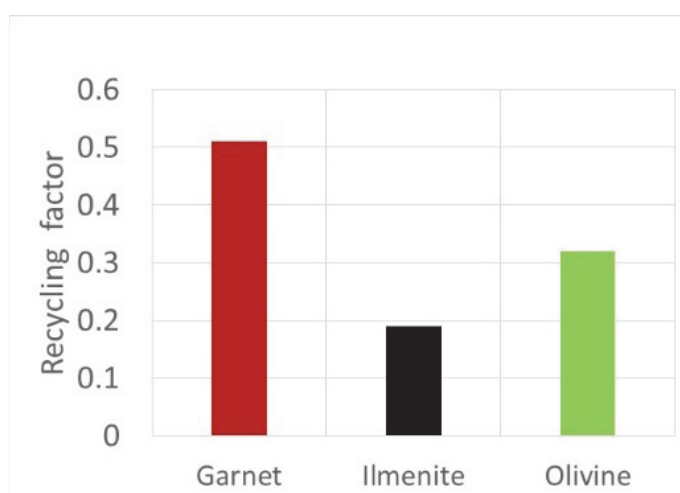


Fig. 9. Recycling rate for tested abrasives

Rys. 9. Wydajność recyklingu dla badanych ścierniw

4.3. Focusing tube wear

Erosive properties have an effect not only on the parameters of cut material but also on the durability of focusing tube (Barlić et al. 2008). On the studies basis, it's have identified the ability of erosion abrasive wear rates by calculating the focusing tube.

On Fig. 10 presented relation of focusing tube mass loss and abrasive flow for tested abrasive materials. The biggest focusing tube weight loss was observed for olivine. After the maximum test time, equal 7.2 min., the weight loss amounted to over 35 mg. The second in intensity order of focusing tube wear caused garnet type. After 7.2 min. loss in weight amounted 25 mg. Definitely the lowest focusing tube weight loss was observed for the ilmenite abrasive. After 7.2 min, wear was only 15 mg.

Focusing tube mass loss factor M_f is calculated based on the equation:

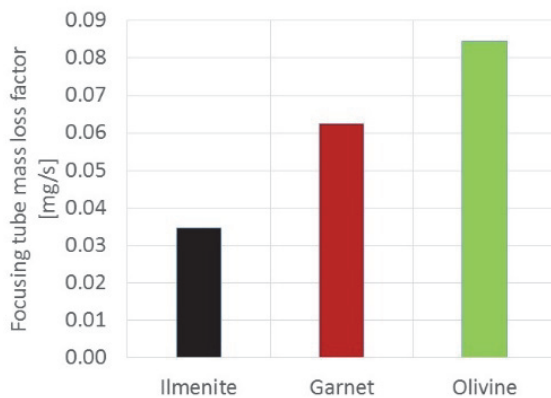
$$M_f(t) = \frac{\Delta m_t}{\Delta t} \quad (2)$$

where:

Δm_t – mass loss of focusing tube [g],

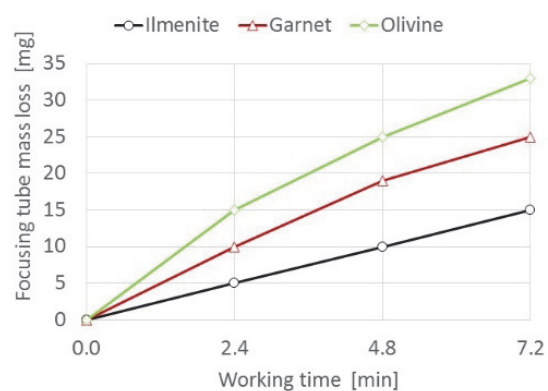
Δt – working time [s].

Illustrations of this equation for the tested abrasives shows Fig. 11.



Rys. 10. Współczynnik ubytku masy dyszy wodno-ściernej M_f dla badanych ścierniw

Fig. 10. Focusing tube mass loss factor M_f for tested abrasive



Rys. 11. Zależność ubytku masy dyszy wodno-ściernej od czasu pracy dla badanych ścierniw

Fig. 11. Relation of focusing tube mass loss and working time for tested abrasives

The highest focusing tube mass loss factor, equal to 0.084 is characterized by Olivine abrasive. For the garnet abrasive M_f factor is smaller and reaches value of 0.061. The smallest value of focusing tube mass loss factor, equal 0.035 gives ilmenite abrasive.

4. Conclusions

Based on the research following conclusions were drawn:

- the biggest recycling potential, over 50% characterized garnet,
- recycling potential of olivine is on 33% level, but abrasive wear of focusing tube is 20% bigger,
- recycling of ilmenite is not effective, despite the lowest focusing tube abrasive wear,
- further studies should test the cutting ability of recovered abrasive.

The possibility of again application of used abrasive materials as a full value in the process of water jet cutting on an industrial scale would largely resolve the problem of managing waste abrasives dumps. The recycling of abrasives makes the abrasive water jet machining greener, more sustainable, and more economical.

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Ekologiczne aspekty przecinania materiałów wysokociśnieniową strugą wodno-ścierną

Streszczenie

Tradycyjne metody produkcji mają negatywny wpływ na środowisko poprzez emisję produktów ubocznych procesu cięcia i erozji (wióry i mikrowióry), zużytej cieczy chłodząco-smarnej (oleje i emulsje, wzbogacone agresywnymi związkami chemicznymi) oraz wysokie zużycie energii. Nowoczesne systemy do obróbki mechanicznej powinny minimalizować ten wpływ. W artykule przedstawiono analizę zaawansowanej technologii produkcji – cięcia wysokociśnieniową strugą wodno-ścierną w aspekcie ochrony środowiska. W przeciwieństwie do tradycyjnej obróbki skrawaniem (szlifowanie, frezowanie) cięciu strumieniem wody nie towarzyszy emisja do środowiska pyłu i cząsteczek materiałów, które są szkodliwe. W artykule przedstawiono także analizę rozdrobnienia granatu – ścierniwa najczęściej stosowanego w tej technologii oraz ilmenitu i oliwinu oraz określono ich potencjał recyklingu.

Abstract

Traditional method of production has a negative impact on the environment by cutting and erosion products (chips and microchips), the used coolant (oils and emulsions, enriched aggressive chemicals) and high energy consumption. Modern systems for mechanical processing should be minimal this impact. This paper presented a study of advanced machining – Abrasive Water Jet (AWJ) technology in environmental aspects. Unlike traditional machining (grinding, milling) water jet cutting does not emit into the environment any dust or particles that are harmful if inhaled. Also presents an analysis of the fragmentation garnet – commonly used abrasive in this technology, ilmenite and olivine, and identified recycling potential of these abrasives.

Słowa kluczowe:

materiały ściernie, wysokociśnieniowa struga wody, aspekty ekologiczne, recycling, rozdrabnianie

Keywords:

abrasive, water jet, environmental aspects, recycling, disintegration



Accumulation of Cadmium, Chromium and Nickel in the Process of Stormwater Treatment

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1. Introduction

Among the most problematic pollutants of rainwater, acidifying compounds (Pokrývková et al. 2016) and suspension with other absorbed components (e.g. organic compounds, biogenes or heavy metals) are often mentioned (Wakida et al. 2014, Wojciechowska et al. 2017). According to Królikowski et al. (2006) rain runoffs from urbanized areas can contain $3,000 \text{ mg} \cdot \text{dm}^{-3}$ of suspensions on average, which gives 3 Mg of sediment per $1,000 \text{ m}^3$ of liquid. In turn, Dąbrowski (2001) reports that rainwater is able to collect up to 2.3 Mg of suspension from one hectare of the sealed area of the urban catchment. This amount of sediment sometimes complicates the operation and exploitation of rainwater management systems (sewage system, natural and artificial receivers). Reduction of the throughput or dropping of the active capacity of particular facilities may be mentioned (Sawicka-Siarkiewicz & Błaszczyk 2007, Zubala 2013). Another important issue is the strong affinity of suspensions and heavy metals. Metal compounds are characterised by very high durability and the ability to accumulate in the environment, even if they are introduced periodically in small doses. They easily go to trophic chains. Some heavy metals in trace amounts are vital to life, but their excessive concentration has negative effects on plant, animal and human health (Giri & Singh 2015, Kabata-Pendias & Mukherjee 2007). For this reason, particular attention should be paid to the process of capturing and the safe disposal of rainwater suspensions, and indirectly other pollutants.

Contemporary studies in the vast majority of cases concern sludge released in small rainwater management facilities, e.g. separators, settlers, infiltration wells, infiltration basins, retention and infiltration tanks (Tran & Kang 2013, Zubala & Patro 2015). They collect rain runoffs from small areas (small settlements, car parks, fuel stations, road sections) and are located in their immediate vicinity. Complex multi-hectare systems, serving much larger areas (large residential quarters, industrial areas) and performing multiple functions at the same time, are unfortunately rarely used. This stems from the significant implementation costs and spatial restrictions within the agglomeration. Their effectiveness, including the quantity and quality of retained sediments, is poorly recognised. Only a few research papers include the evaluations of technical and operational parameters and the reasonability of using such systems. Unfortunately, the lack of proper knowledge and legal regulations results in improper handling of rainwater sludge; for example, depositing them in random and unprotected places without qualitative analysis.

The aim of this article is to assess the degree of accumulation of cadmium (Cd), chromium (Cr) and nickel (Ni) in sludge of a municipal stormwater treatment plant and to identify possible dangers resulting from this fact. The research facility is located in Puławy (south-eastern Poland). It receives outflows from an area of about 500 hectares of the city and is characterised by high throughput, retention capacity and innovative implemented technology. Due to the nature of drained surfaces, the considerable size of the treatment plant, the location of the individual devices, the variable hydraulic load and periods of rainwater retention (sedimentation time), a diversified concentration of pollutants in sediments in the subsequent stages of purification should be expected.

2. Material and methods

2.1. The study area

Puławy is located on the right bank of the Vistula river in its middle course. This area is characterised by a large diversity of geomorphological and geological forms. There are both slopes and loess gorges, as well as sandy and clayey glacial moraines. Limestone outcrops or inland dunes are also visible (Kondracki 2000). In the study area there are 165 days with precipitation during the year. The average total annual

precipitation is about 570 mm. Their maximum heights are recorded in July. The average annual air temperature reaches 8°C. The time of snow cover does not exceed 60 days and the growing season lasts 220 days (Kaszewski 2008).

The municipality of Puławy covers an area of about 50 km² and has a population of nearly 50 thousand. The ring water supply system spans almost 98%, and the separate drainage system – 96% of the total population. Underground water intakes as well as a modern mechanical and biological wastewater treatment plant are utilised here. Around 330 business entities in the industrial sector and 460 in the construction sector are registered in the city. The chemical industry represented by Zakłady Azotowe S.A. (nitrogen plants) is growing rapidly. National road no. 12 and regional roads no. 801 and 824 run through Puławy (UMP 2004, US 2016).

In the 1990s, a stormwater treatment plant was built in the southwestern part of the city. The facility is located on the lower floodplain of the Vistula river (1 km from the river bed) in the immediate vicinity of its oxbow. The adjacent area is characterised by a large variety of land use forms. There are large areas of arable fields, a single-family housing estate, poorly developed lands with old buildings and a Roman Catholic cemetery.

2.2. Characteristic of stormwater treatment plant

The main elements of analysed technological line are screen chambers (2 pc.), grit chambers (2 pc.), a settler (1 pc.) and a retention pond (1 pc.) (Fig. 1). In the treatment plant there is only gravity flow - possible because of preserving the appropriate slopes and differences in bottom elevation of the individual devices. During the flow, physical, chemical and biological processes of self-cleaning occur - characteristic for aquatic and wetland ecosystems. Among them, straining, filtration, sedimentation, sorption, mixing, dilution, oxidation, reduction and biological decomposition can be mentioned (Braskerud 2001, Herrmann 2012). The receiver of treated sewage is the oxbow of the Vistula.

The municipal stormwater drainage system consists of two main interceptors of 1.4 and 1.6 m diameters and smaller side channels with necessary elements of utilities. Interceptor 2 drains nearly twice the area of interceptor 1. The drainage system spans most urbanized areas – among others, the main street of the city, residential districts with a predominance of multi-family buildings, and areas of services, education and sports.

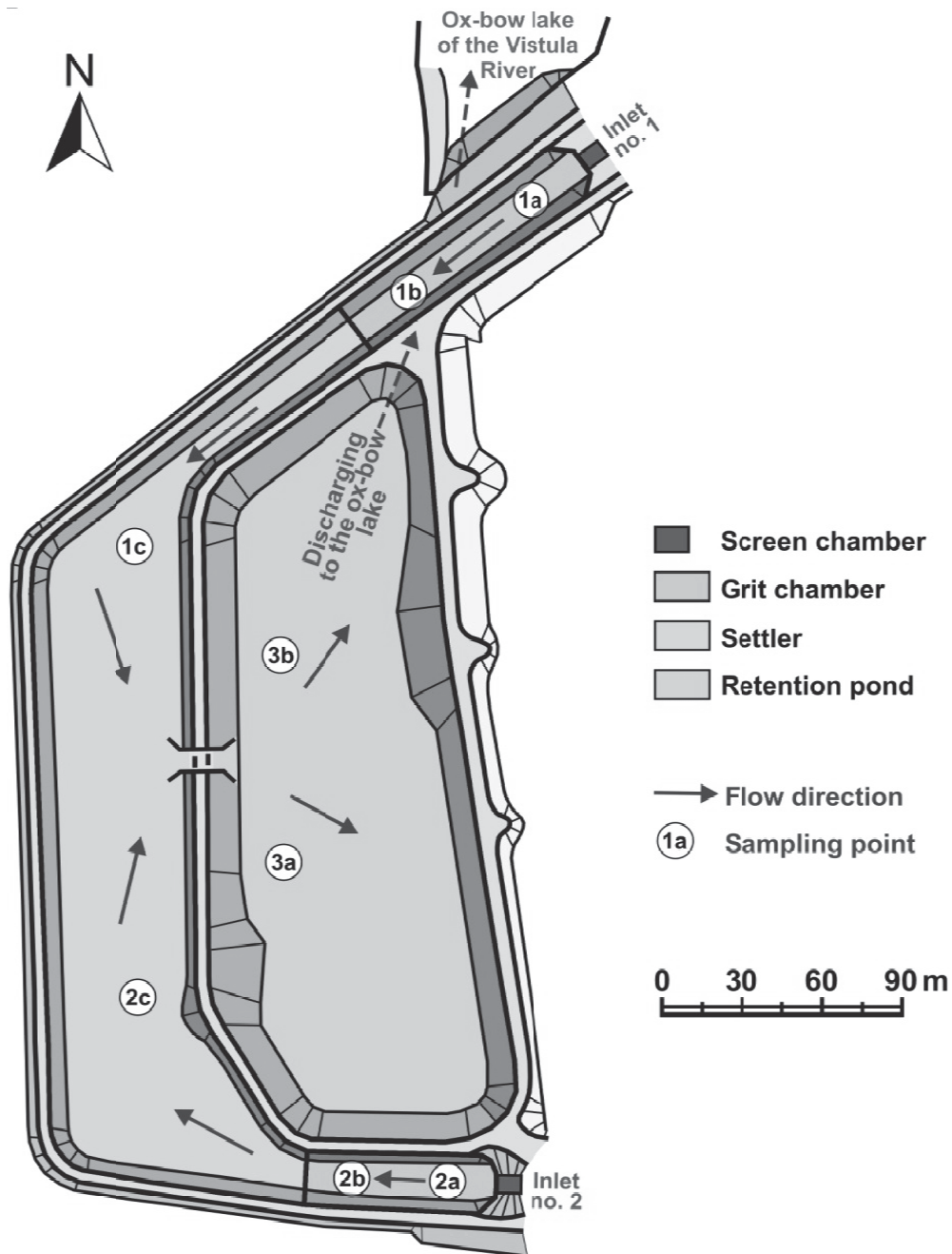


Fig. 1. Scheme of the stormwater treatment plant in Puławy

Rys. 1. Schemat oczyszczalni ścieków deszczowych w Puławach

Both main interceptors carry rainwater sewage to separate inlet chambers of the treatment plant. In each flat, screens with a clearness of 8 cm were installed (Fig. 2). The purpose of the screens is to stop larger solid effluents in the process of straining (e.g. municipal waste that accidentally gets into the drainage). The other elements of the treatment plant

are two parallel grit chambers, 100 and 70 m long. They have the same width (10 m) and active depth (1 m). Designed speeds of sewage flow are approximately $0.4 \text{ m}\cdot\text{s}^{-1}$ (grit chamber 1) and $0.2 \text{ m}\cdot\text{s}^{-1}$ (grit chamber 2). Hydraulic conditions allow for sedimentation of heavy suspensions - mainly mineral fraction. The grit chambers are separated from the settler by overflows equipped with weirs.

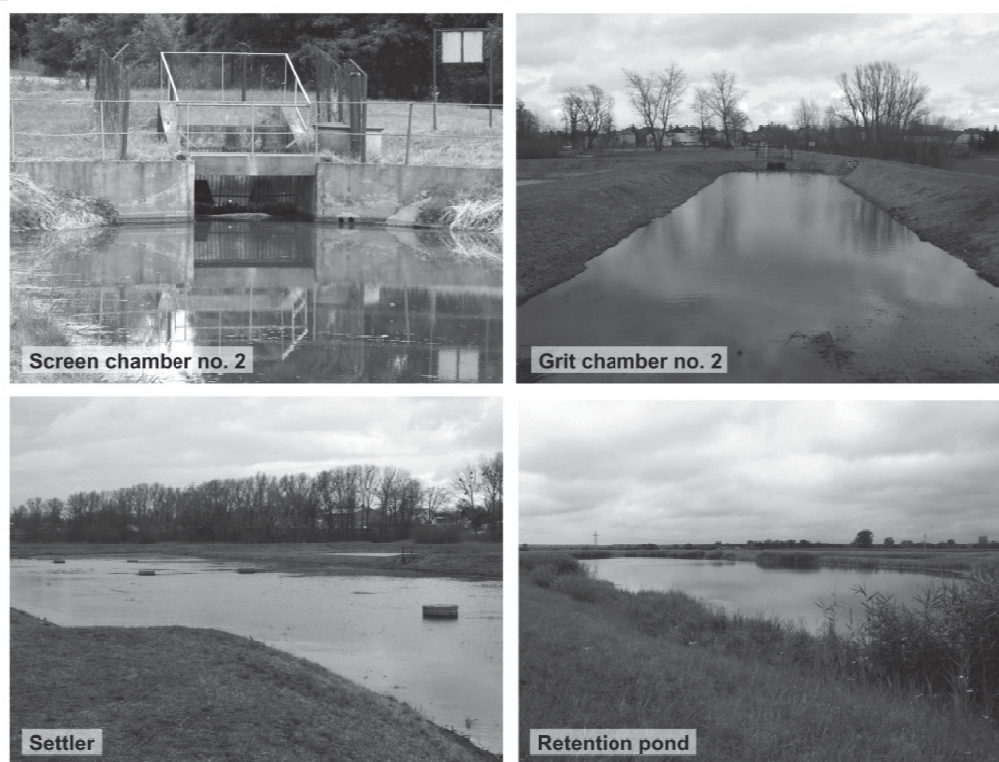


Fig. 2. Basic devices of the stormwater treatment plant

Rys. 2. Podstawowe urządzenia oczyszczalni ścieków deszczowych

In the settler, wastewater flowing from opposite directions mixes. The length of the main part of the settler is 190 m, and the width 46 m. The working depth does not exceed 1.2 m. The bottom of the settler is levelled, which guarantees slow flow and allows stopping light suspensions (mineral and organic fractions). The last facility of the treatment plant is the retention pond (Fig. 2), where sewage gets through the culvert with weirs. The surface of the reservoir is 1.5 ha, and the total capacity reaches $38,100 \text{ m}^3$. The lower layer is kept permanently, powered by groundwater. The upper retention layer is discharged to the oxbow lake

of the Vistula. For this purpose, the culverts with weirs and two channels under the bottom of grit chamber 1 are used.

The bottoms of both the grit chambers and the settler were reinforced with openwork concrete slabs. Underneath there is a drainage that intercepts potential percolation, which reduces the risk of contamination of groundwater. It also enables rapid drainage of the grit chambers and settler, and then cleaning from accumulated sludge. The retention pond is a typical earth structure formed by adapting the end part of the oxbow lake. Like other devices, it was not sealed. It does not have its own drainage and technical reinforcements. In order to protect the adjacent farmlands against flooding, a band-shaped trench was constructed around the treatment plant. In the settler and at the base of dikes of the grit chambers and the retention pond, water-loving vegetation appears spontaneously. It is periodically mowed and removed from the area of the stormwater treatment plant.

2.3. Sediments sampling

Sewage sludge was collected using a sediment core sampler, type Beeker, by Eijkelkamp in the autumn of 2007 and 2015. The material of intact structure was taken from the bottom of particular stormwater treatment facilities from the 0-10 cm layer. This took place the year after the removal of sludge from the grit chambers and the settler, as part of routine operational activities. Due to a small amount of suspensions accumulated in the retention pond its bottom was not cleaned during the study period.

The exact locations of points of sediments sampling are showed in Figure 1:

- grit chamber 1 – 15 m behind the screen chamber (sample 1a) and 3/4 of its length – 75 m (sample 1b),
- grit chamber 2 – 15 m behind the screen chamber (sample 2a) and 3/4 of its length – 55 m (sample 2b),
- settler – 100 m behind grit chambers – half the distance between baffles separating grit chambers from the settler and the culvert of retention reservoir (samples 1c and 2c),
- retention pond – 30 m from the culvert connecting the pond with the settler (samples 3a and 3b).

2.4. Methods of analysis

The analyses were carried out in the certified Central Laboratory of Agroecology of the University of Life Sciences in Lublin. During laboratory work, the sludge samples were homogenised and dried at 105°C. Then, 0.5 g samples were mineralised in a microwave digestion at 210°C (Mars Xpress). The ash was digested in 10 ml of concentrated nitric acid (V), and then distilled water was added to the solution to obtain a final volume of 50 cm³. The cadmium content (Cd) was determined in plasma using a quadrupole mass spectrometer and an ion detector (Varian 820-MS). Chromium (Cr) and nickel (Ni) contents were determined using the method of atomic absorption spectrometry in acetylene-air flame (Varian SpektrAA 280-FS). The analyses were repeated three times and the obtained data was averaged. The results were checked using the RTC reference material (Trace Metals – Wet Sewage Sludge CRM018-50G). The basic measurement conditions have also been determined. These include, among others: precision – 4% (Cd), 5% (Cr), 6% (Ni); recovery – 98% (Cd), 102% (Cr), 103% (Ni); expanded uncertainty – 9% (Cd), 11% (Cr), 14% (Ni).

To assess the degree of accumulation of heavy metals in sewage sludge, the characteristic and average values of analysed indicators were taken into account - both for each checkpoint and each device of the treatment plant. The percentage differences in pollutant concentrations between chosen positions were evaluated. The obtained data was compared with the data available in the scientific papers.

3. Research results and discussion

The contents of trace metals (Cd, Cr, Ni) in sludge of the stormwater treatment plant in Puławy are characterised by relatively large diversity. In the case of Cd and Cr the highest average concentrations were recorded in grit chamber 1 – successively 0.227 and 21.4 mg·kg⁻¹, and the lowest in the retention pond – respectively 0.005 and 4.5 mg·kg⁻¹. The highest average content of Ni was in sediments of the settler – 20.5 mg·kg⁻¹, and the lowest in grit chamber 2 – 14.3 mg·kg⁻¹. Sediments in grit chamber 1 were more polluted than in grit chamber 2, which specifically concerns Cd. Differences in average concentrations of metals between these devices ranged from 0.9% (Cr) to 93.1% (Cd). Comparing the quality of sludge near raw

sewage inlets (checkpoints 1a and 2a), similar regularity can be observed, but only in the case of Cd and Ni. In point 2a the average content of Cr was significantly higher than in point 1a (table 1).

Table 1. Percentage differences between average concentrations of trace metals in particular observation posts ("-" – decrease, "+" – increase)

Tabela 1. Różnice procentowe pomiędzy średnimi zawartościami metali śladowych na poszczególnych stanowiskach obserwacyjnych badanej oczyszczalni („-” – spadek; „+” – wzrost)

Variable	Sampling points (comparison)							
	1a-2a	1a-1b	1b-1c	2a-2b	2b-2c	grit chambers-settler	settler-pond	grit chambers-pond
Cd	-92.9	+33.2	+2.8	+23.5	+285.7	+37.2	-97.5	-96.6
Cr	+239.5	+328.4	-62.8	-45.8	-33.6	-46.5	-60.5	-78.9
Ni	-2.6	+32.2	+8.5	-6.8	+39.9	+28.1	-11.2	+13.8

High differences of metal concentrations were also found within the grit chambers. Analysing data in points a and b, an increase in the concentration of pollutants in sediments of grit chambers 1 with the distance from the inlet of the treatment plant can be seen. In point 1b the maximum concentrations of Cd ($0.461 \text{ mg}\cdot\text{kg}^{-1}$) and Cr ($62.1 \text{ mg}\cdot\text{kg}^{-1}$) were recorded. In sediments of grit chamber 2 similar trends were observed only in the case of Cd. The cause of these phenomena may be different hydraulic conditions prevailing in different zones of grit chambers, and in particular, the rates of sewage flow. They decrease with the distance from the inlets. As a result, there is an opportunity for sedimentation of increasingly lighter fractions of suspension. The smallest fraction is retained in the settler whose bottom is levelled and the speed of wastewater flow is the smallest. The average accumulations of Cd and Ni in sediments of the settler were 37.2% and 28.1% higher than the average values for the grit chambers. In turn, the content of Cr decreased by 46.5% when moving from the grit chambers to the settler. In checkpoint 1c of the settler, the maximum values of Cd ($0.461 \text{ mg}\cdot\text{kg}^{-1}$) and of Ni ($22.4 \text{ mg}\cdot\text{kg}^{-1}$) were recorded. The strong impact of sewage supply from the side of grit chamber 1 on the quality of sludge in the settler was no-

ticed. In point 1c, the average concentrations of Cd, Cr and Ni were higher by 75.2, 23.3 and 11.5% respectively than in point 2c, adjacent to grit chamber 2. More pollutant loads brought to the northern part of the treatment plant are probably related to the character of the drained area by interceptor 1. There are more pollutant sources than in the basin of interceptor 2. A significant share of roads (including the main street of the city), high intensity of road traffic, and high density of diverse technical infrastructure can be mentioned. Studies of other authors have shown that transport (including transport routes) is a supplier of large quantities of suspensions, as the result of corrosion, abrasion of vehicle components and road pavements (Hjortenkrans et al. 2006, Mangani et al. 2005). The existence of a correlation between the way of catchment management and the quality of outflowing rainwater is also indicated by Goonetilleke et al. (2005) and Zubala (2018).

During the study, a significant decrease of pollutant accumulation in sludge in the passage from the settler to the retention pond (the last facility of the treatment plant) was observed. In the case of particular metals it amounts to 97.5% (Cd), 60.5% (Cr) and 11.2% (Ni) on average (table 1). The relatively low content of metals in the pond may indicate that they are well bonded to suspension particles, which are largely retained in the grit chambers and the settler. The existence of relationships between the types (including particle size), the concentrations of suspensions and the level of trace metal pollution has been demonstrated. Gunawardana et al. (2014) and Zhu et al. (2008), examining suspensions deposited on roads, have shown that metals are most often transported with finer and slower sedimenting fractions. This could explain the increased concentrations of some metals in the settler of the treatment plant.

Taking into account the average contents of metals, it was noted that the studied sediments in 2007 were characterised, in the majority of cases, by a higher degree of pollution than in 2015. The exception is grit chamber 2, where a significant increase in the contents of Cr and small increase of Ni were recorded. This is probably due to major changes in the management of catchment 2, which have occurred for the last few years (technical infrastructure expansion) and the emergence of new sources of pollution.

In comparison with results obtained by other authors, the degree of accumulation of trace metals in the sludge of the treatment plant in

Puławy is not very high (table 2). Their presence in the research area is probably related to the functioning of road transport and burning of fuels for energy purposes. A certain pool of metals can be released from various components of the technical infrastructure (Petrucci et al. 2014, Wojciechowska et al. 2017). Due to the lack of data in specialist literature on complex urban systems (combination of technical and semi-natural elements), the degree of pollution of analysed sediments was compared with the accumulation of metals in the ponds and wetlands rainwater management systems.

Table 2. Comparison of average concentrations of metals in sludge of the treatment plant in Puławy (own studies) with average accumulation in other tank-type stormwater management systems (literature data)

Tabela 2. Porównanie średnich stężeń metali w osadach oczyszczalni w Puławach (badania własne) z przeciętną akumulacją w innych zbiornikowych systemach zagospodarowania wód deszczowych (dane literaturowe)

Variable ($\text{mg}\cdot\text{kg}^{-1}$)	Treatment plant in Puławy				Literature data			
	Grit chamber 1	Grit chamber 2	Settler	Retention pond	Wetlands, ponds ^a	Detention pond ^b	Drainage system ponds ^c	Wet detention ponds ^d
Cd	0.277	0.019	0.203	0.005	2.000	0.431	0.285	0.150
Cr	21.4	21.2	11.4	4.5	41.0	25.7	85.9	1.7
Ni	17.7	14.3	20.5	18.2	30.0	38.7	69.8	0.7

^a Allinson et al. (2015), ^b Färm (2002), ^c Heal et al. (2006), ^d Mallin et al. (2002)

Depending on the checkpoint, in the metal pool definitely dominate Cr and Ni (advantage of one or second element), while the percentage of Cd, considered as one of the most ecotoxic pollutions, is minor. Similar proportions in the contents of trace metals in rain sludge have been shown by authors of other articles (table 2). The highest pollution is observed in rainwater runoffs from large agglomerations, industrial areas or roads with greater traffic. For example, in the sludge of the rainwater management system of the metropolitan area of Melbourne (Australia) (Allinson et al. 2015), mean concentrations of Cd, Cr and Ni were higher than those of grit chambers in Puławy, respectively: 1,251.4, 92.5 and 87.5%. Most of the rainwater receivers presented in the literature also

show high variability of sediment quality.

The direct source of trace metals in rain runoffs from communication routes in the city are motor exhaust gases (Cd, Ni), products of abrasion of tyres and brake discs (Cd, Cr, Ni), products of attrition of pavements and construction materials (Cr, Ni). The analysed metals can also be released from painted and varnished surfaces (components of pigments), galvanic coatings, plastics, metal alloys and impregnated wood. A significant anthropogenic source of Cd, Cr and Ni in the environment is also the burning of fossil fuels and waste (Kabata-Pendias & Mukherjee 2007, Królikowski et al. 2006).

Although no disturbingly high levels of heavy metals were found in the sediments, their quality should be continuously monitored. The city is developing dynamically and it is not possible to exclude the emergence of further potential pollution sources (e.g. increase in sealed surfaces and intensity of road traffic, establishing new production plants and service). Trace metals are characterised by very high durability and an ability to accumulate in the environment. According to the literature data, excessive concentrations of Cd, Cr and Ni are very harmful to living organisms. Plants do not have any metabolic needs towards toxic Cd, but its relatively easy solubility and assimilability show the serious threat to particular links of the food chain (Jayarathne et al. 2017, Zhang et al. 2017). Phytotoxic concentrations of Ni and Cr are varied depending on the species or variety of the plant. Kabata-Pendias & Mukherjee (2007) report that the range of excessive or toxic amounts of Ni in most plant species fluctuates from 10 to 1,000 mg·kg⁻¹. According to Wilk & Gworek (2009), the harmful effects of Cr are found at concentrations of 2-20 mg·kg⁻¹ dry matter. Plants accumulate Cr in much smaller amounts than Cd and Ni, because its compounds are poorly soluble (Jayarathne et al. 2017).

In the case of plants, dwarfism and chlorosis are usually symptoms of toxic effects. Damage and disturbances in the growth of a root system and metabolic dysfunctions are noted (Wilk & Gworek 2009). Exposure of animals and people to high doses of Cd, Cr and Ni may result in kidney damage, liver failure, skeletal deformity, and tumour growth (kidney, liver, lungs). In some cases, arterial hypertension, anaemia, emphysema, allergy, asthma and reduction of reproductive potential occur (Eisler 1985, Klein 1996, Sunderman 2004).

4. Summary

One of the aspects of the functioning of the stormwater treatment plant is the formation and accumulation of sludge. Its periodic removal and disposal are among the core operational activities. They condition the maintenance of proper hydraulic parameters and should prevent the uncontrolled transfer of pollutants to the environment. The studies have shown that rainwater sludge can be a convenient place to accumulate heavy metals such as cadmium, chromium or nickel. Their concentration, however, is characterised by a considerable variability, evident in the case of comparing particular dates (time variability), as well as plant facilities or checkpoints in specific devices. This is probably due to the variable quality of inflowing stormwater sewage, conditioned by e.g. way and intensity of use of drained areas, transport of various fraction of sludge, weather phenomena, etc. The specific nature of the applied cleaning technology (non-uniform hydraulic loading and period of wastewater retention) and performed operational activities can also be of great importance.

The highest concentrations of studied heavy metals were observed in sediments collected in the northern part of the wastewater treatment plant – powered by rainwater from the main streets of the city. These roads are characterised by heavy traffic. In their neighbourhood, numerous shopping and service facilities with large parking spaces and roofs are located. The least polluted were sediments from the retention pond, from which purified sewage flows to the water receiver. The highest accumulation of metals concerns the points of the treatment plant in which the lightest fractions of suspension are sedimented. In the pool of studied pollutants retained in the grit chambers, Cr has the highest share and ranges from 54% (grit chamber 1) to 60% (grit chamber 2). In turn, in the settler and the retention pond Ni dominates - successively 64 and 80%. In all devices, Cd has the smallest share in the pool of analysed metals (0.02-0.7%).

The quality of the sludge in the stormwater treatment plant should be constantly monitored due to the dynamic development of the city (numerous investments, expansion of technical infrastructure) and the emergence of potential sources of pollution. In the case of increased concentrations of metals, an effective method of neutralization of sediments should be developed and implemented, e.g. using bioremediation processes.

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Akumulacja kadmu, chromu i niklu w procesie oczyszczania ścieków deszczowych

Streszczenie

W pracy dokonano oceny stopnia akumulacji kadmu, chromu i niklu w osadach dużej oczyszczalni ścieków deszczowych. Obiekt zbiera spływy z powierzchni około 500 ha miasta Puławy (południowo-wschodnia Polska) i pod względem innowacyjności, przepustowości oraz pojemności retencyjnej wyróżnia się wśród innych krajowych rozwiązań tego typu. Podstawowymi elementami analizowanego ciągu technologicznego są: kraty, piaskowniki, osadnik i staw retencyjny. W oczyszczalni odbywa się wyłącznie przepływ grawitacyjny – możliwy dzięki zachowaniu odpowiednich spadków i różnic rzędnych den poszczególnych urządzeń. W trakcie przepływu zachodzą fizyczne, chemiczne i biologiczne procesy samooczyszczania. Osady ściekowe pobierano za pomocą próbnika Beeker firmy Eijkelkamp. Materiał o nienaruszonej strukturze pozyskiwano z dna poszczególnych obiektów oczyszczalni z warstwy 0-10 cm. Zawartość kadmu oznaczano w plazmie za pomocą kwadropolowego selektora mas oraz detektora jonowego. Natomiast zawartość chromu i niklu oznaczano metodą spektrometrii absorpcji atomowej ze wzbudzeniem w pło-

mieniu acetylen-powietrze. Zawartości metali śladowych w osadach cechuje stosunkowo duże zróżnicowanie. Przyczyną mogą być odmienne warunki hydrauliczne panujące w poszczególnych urządzeniach – przede wszystkim prędkości przepływu cieczy. W efekcie następuje sekwencyjna sedymentacja różnych frakcji zawiesiny, a wraz z nią zaadsorbowanych metali. Duże znaczenie może mieć sposób użytkowania powierzchni odwadnianych. Największe stężenia badanych zanieczyszczeń obserwowano w części oczyszczalni zasilanej spływami z głównych ulic miasta. Najmniej zanieczyszczone były osady ze stawu retencyjnego, z którego ścieki oczyszczone odpływają do starorzecza Wisły. W piaskownikach, w puli analizowanych metali największy udział wykazuje Cr (54-60%). Natomiast w osadniku i stawie retencyjnym zdecydowanie dominuje Ni (kolejno 64 i 80%). Udział Cd mieści się w granicach 0,02-0,7%. W porównaniu z wynikami uzyskiwanymi przez innych autorów, stopień akumulacji metali śladowych w osadach nie jest wysoki. Ich obecność w obszarze badań prawdopodobnie wiąże się z funkcjonowaniem transportu drogowego oraz spalaniem paliw w celach energetycznych. Pewna pula metali może uwalniać się z różnych elementów, wchodzących w skład infrastruktury technicznej. Mimo, że nie stwierdzono w badanych osadach niepokojąco wysokich zawartości metali ciężkich, ich jakość powinna być stale monitorowana. Miasto rozwija się dynamicznie i nie można wykluczyć pojawiania się kolejnych potencjalnych źródeł zanieczyszczeń (m.in. wzrost powierzchni uszczelnionych i natężenia ruchu, tworzenie nowych zakładów produkcyjnych i usługowych). W przypadku wzrostu stężeń metali należy opracować i wdrożyć skuteczną metodę neutralizacji osadów, np. z wykorzystaniem procesów bioremediacji.

Abstract

The degree of accumulation of cadmium, chromium and nickel in sludge of a large rainwater treatment plant was assessed in the paper. The facility collects runoffs from an area of about 500 hectares of Puławy (a city in south-eastern Poland) and in terms of innovativeness, throughput and retention capacity stands out among other national solutions of this type. The main elements of analysed technological line are screen chambers, grit chambers, a settler and a retention pond. In the treatment plant there is only gravity flow - possible because of preserving the appropriate slopes and differences in bottom elevation of the individual devices. During the flow, physical, chemical and biological processes of self-cleaning occur. Sewage sludge was collected using a sediment core sampler, type Beeker, by Eijkelkamp. The material of intact structure was taken from the bottom of particular stormwater treatment facilities from the 0-10 cm layer. The cadmium content was determined in plasma using a quadrupole mass spectrometer and an ion detector. Chromium and nickel con-

tents were determined using the method of atomic absorption spectrometry in acetylene-air flame. The trace metal contents in sediments are characterised by relatively large diversity. Different hydraulic conditions prevailing in individual devices – especially speeds of liquid flow – may be the cause. As a result, sequential sedimentation of various fractions of suspension occurs, along with adsorbed metals. The use of drained surfaces may be of great importance. The highest concentrations of pollutants were observed in the part of the treatment plant supplied with runoffs from the main streets of the city. The least polluted was sludge from the retention pond, from which purified sewage flows to the oxbow of the Vistula river. In grit chambers, Cr (54-60%) has the highest share in the pool of analysed metals. In contrast, the settler and the retention pond are dominated by Ni (respectively 64 and 80%). The contribution of Cd is in the range of 0.02-0.7%. In comparison with results obtained by other authors, the degree of accumulation of trace metals in the sludge is not very high. Their presence in the research area is probably related to the functioning of road transport and burning of fuels for energy purposes. A certain pool of metals can be released from various components of the technical infrastructure. Although no disturbingly high levels of heavy metals were found in the sediments, their quality should be continuously monitored. The city is developing dynamically and it is not possible to exclude the emergence of further potential pollution sources (e.g. increase in sealed surfaces and intensity of road traffic, establishing new production plants and service). In the case of increased concentrations of metals, an effective method of neutralization of sediments should be developed and implemented, e.g. using bioremediation processes.

Słowa kluczowe:

woda deszczowa, osady, zanieczyszczenia, metale śladowe, oczyszczalnia

Keywords:

rainwater, sludge, pollutants, trace metals, treatment plant



The Application of Artificial Neural Networks in the Assessment of Pressure Losses in Water Pipes in the Design of Water Distribution Systems

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1. Introduction

The water distribution system is a complex, technical object, extremely expensive and difficult to modernise. Pipelines should fulfil their role for many years. In connection with the above, one very important task is the correct design and execution of hydraulic calculations. During the implementation of calculations, it is often necessary to correct data, in order to obtain a correct solution. Numerous parameters are evaluated in the calculation process, including flow velocity through water supply pipelines, flow rate, pressure loss and pressure in individual network nodes. An important parameter, often underestimated, is the level of pressure loss in the calculation of sections of water pipes. This paper proposes a method for the assessment of pressure loss and for the use of artificial neural networks. For this purpose, one class DH1, describing the correct conditions and four classes DH2-DH5, describing problems related to the amount of pressure losses in the water pipes, have been defined. Based on the parameters characterising the operation of the water pipe, the artificial neural network selects one of the classes and thus indicates the occurrence of a specific problem -or gives the 'all clear'.

2. Literature review of the use of artificial intelligence in the calculation of water distribution systems

Artificial neural networks are increasingly being used in relation to water supply issues. A review of artificial intelligence methods, including artificial neural networks in the design and operation of water distribution systems, is provided in article (Czapczuk et al. 2015).

In works (Piasecki et al. 2016, Cieżak 2005), artificial neural networks were used to predict water demand. In the calculation of hydraulic water distribution systems, artificial neural networks are used to support the taring of simulation models (Lingireddy et al. 1998, Saldarriaga et al. 2004). This article (Xu et al. 1997) proposes recursive neural networks for calculating flows and looped systems in water supply networks.

Linear pressure losses are calculated by, among other methods, the use of the Darcy-Weisbach Formula which requires calculations of the linear friction factor, using, in the main, the iterative method. There are many works in which artificial neural networks are proposed for calculating the linear friction factor (Brkić & Čojbašić 2016, Offor & Alabi 2016, Besarati et al. 2015, Shayya & Sablani 1998) which allows the calculation of time to be reduced. Proposals for a neural network in the calculation of direct linear pressure losses are provided in the article (Czapczuk et al. 2017).

Calculation modules, based on artificial neural networks, have also been introduced into the simulation methods used in the real-time control of water supply networks. The task of neural calculations is, in this case, to simplify the calculation model and speed up calculations (Damas et al. 2000, Yongchao & Wending 2003).

In the article (Kamiński et al. 2017), artificial neural networks were used to assess the technical condition of the water supply system.

The verification method for the results of hydraulic calculations, with the use of process diagnostics and artificial neural networks, is presented in the paper (Dawidowicz 2015). The method for estimating pressure levels and the pattern of pressure zones, using artificial neural networks, is described in the article (Dawidowicz 2017) and using the induction method of the decision tree at work (Dawidowicz 2012). The problem of the assessment of pressure loss, is discussed in papers (Biedugnis & Czapczuk 2018, Czapczuk 2013), in which different meth-

ods of artificial intelligence have been used, including expert systems and the method of k-nearest neighbours. In this work, artificial neural networks of the perceptron type have been used for the above purpose. The application of RBF neural networks for the assessment of the water flow rate in the pipework is presented in the paper (Czapczuk & Dawidowicz 2018). A method for estimating the diameter of water pipes using artificial neural networks of the multilayer perceptron type is presented in the paper (Dawidowicz 2018).

3. An introduction to artificial neural networks

In a multilayer perceptron, the number of neurons in the first layer, corresponds to the number of input variables. In the case of multi-criteria classifications, in the output layer, the number of neurons is equal to the number of classes. The number of K neurons in the hidden layer, should be determined in neural network training. Initially, the number of neurons based on Kolmogorov's Theory can be assumed (Bishop 1996, Konar 2005):

$$K = 2 \cdot N + 1 \quad (1)$$

where:

K – the initial number of neurons in the hidden layer,

N – number of variables in the input vector $X = [x_1, \dots, x_n]^T$.

Nonlinear neurons, with the logistic function, were used in the hidden layer:

$$y = \frac{1}{1 + e^{-\beta S}} \quad y \in (0 \dots + 1) \quad (2)$$

where:

β – is a numerical factor, usually with the value of 1,

S – the value of the post-synaptic potential function (PSP).

In the output layer of the network, the Softmax activation function was used, according to the formula:

$$y = \frac{e^S}{\sum_{m=1}^M e^{S_m}} \quad y = (0...+1) \quad (3)$$

where:

M – the number of neurons of the output layer,

S – the value of the post-synaptic potential function.

The Softmax type activation function is used in classifying tasks; this is an exponential function that assumes values to make the sum of the activation all M neurons in the network output layer, equal to 1. In addition to the fact that network signals are the basis for recognising the appropriate class, the output values, for individual neurons, can be interpreted as an estimation that they probably belong to a given class (Bridle 1990).

The set of all training examples has been divided into training, validation and testing subsets. The basis for selecting neural networks is the error obtained in the validation set. The backpropagation method was applied initially, followed by the Quasi-Newton Method. In the network training process, the Entropy Multiple Error Function was adopted (EME) where each class corresponds to one neuron in the output layer (M > 1) (Bishop 1996):

$$E_{EME} = - \sum_{t=1}^T \sum_{m=1}^M d_m^{(t)} \log y_m^{(t)} \quad (4)$$

where:

M – the number of neurons of the output layer.

T – the number of examples in the training subsystem,

t = 1, ..., T - the number of training examples,

d – the reference value (set) of the neural output signal,

y – the calculated value of the neuron in the output layer.

The artificial neural network was also evaluated on the basis of the accuracy of classification η , defined as:

$$\eta = \frac{n_{cor}}{n_{all}} \quad (5)$$

where:

n_{cor} – the number of correctly classified training examples.

n_{all} – the number of all training examples subjected to classification.

Detailed classification results for the training, validation and testing subsets are included in the confusion matrix. This is a square matrix in which information, regarding the individual classes that the examples actually belong to, is given in rows, while information, as to the classes into which they were classified, by the classifier, is given in columns. The diagonal contains examples that have been correctly categorised, while those located beyond the diagonal have been incorrectly classified. At the same time, examples beyond the diagonal, indicate the classes into which they were incorrectly classified.

4. Evaluation of design solutions for water distribution systems

At the design stage, for water distribution systems, it is necessary to evaluate the results of the calculation and design solutions, covering technical, economic and reliability issues. The basic technical parameters, determining the correct operation of a water supply network, are the flow velocity, through the pipelines and the pressure levels in the nodes. It is possible to indicate other issues that should be taken into account when assessing the design, as is shown in Fig. 1 (Czapczuk, 2013).

Currently, when choosing water pipe diameters, the basic parameter is flow velocity. It seems that such parameters as linear pressure losses, which largely determine the pressure level in the individual nodes of the network, are also of importance. In the final phase of the calculation, it should be checked as to whether the pressure loss is not too high, thus causing a rapid drop in the pressure line, or whether it is too low, which may be due to the over-sizing of the diameters of the pipework. Currently, this problem remains the designer's responsibility only, for it is he/she who assesses the values obtained, on the basis of his/her own experience and knowledge. The wide range of economic velocity levels, often makes it possible to adjust the diameter while maintaining a favourable flow rate, thus obtaining better network conditions from the point of view of losses to linear pressure.

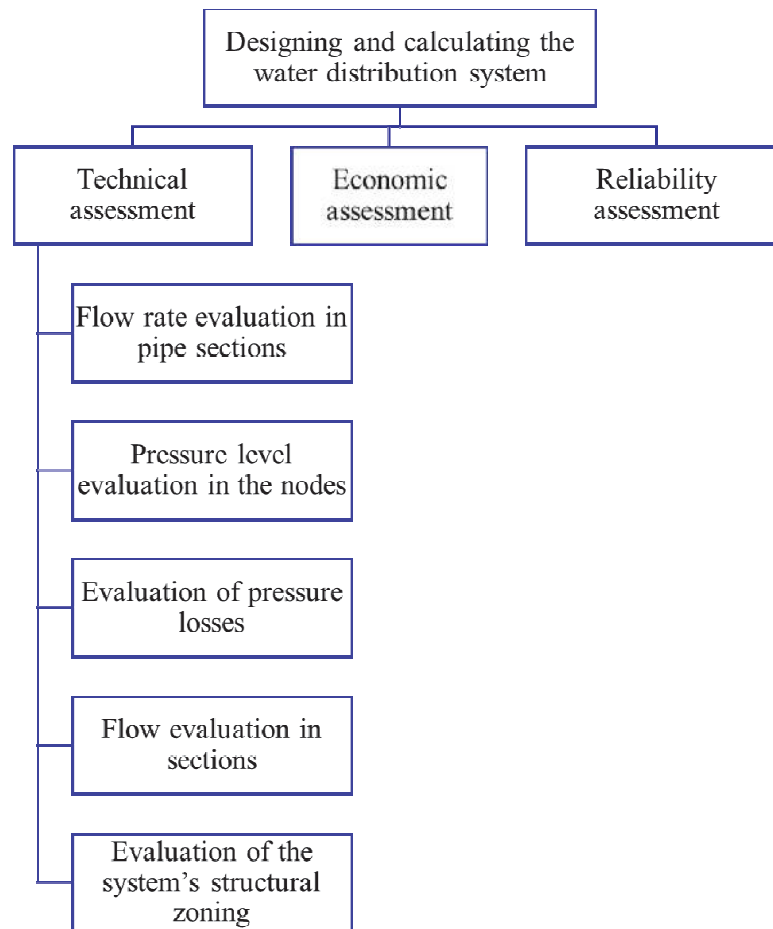


Fig. 1. Evaluation of the design solution and of the calculation results of the water distribution system (Czapczuk 2013)

Rys. 1. Ocena rozwiązania projektowego i wyników obliczeń systemu dystrybucji wody (Czapczuk 2013)

The pressure level in the nodes ensures that the supply of water is provided under the required pressure, however, at the same time, this pressure should be as low as possible. This is governed by a reduction in water loss and a reduction in pumping costs.

Factors determining levels of pressure loss are the diameter of the water pipe D_{in} , the length of the pipeline section L , the flow velocity V and, indirectly, the coefficient of absolute roughness k . Pressure losses in the pipeline, Δh_l are calculated on the basis of the Darcy-Weisbach Formula in the form (Knapik & Bajer 2010).

In the literature (Knapik & Bajer, 2010), the economic velocity levels, resulting from the economic and operational conditions of water supply networks. It should be emphasised that the given speed ranges are indicative and require correction, in many cases, due to the working conditions of the entire water distribution system.

When evaluating pressure losses, it is necessary, initially, to determine whether Δh_1 is correct for a given condition, that is, to determine whether it is too low or too high and what the reason might be for this situation. A review of the results for individual sections, especially in the case of large water distribution systems, can be tedious, time consuming, and confusing. For the purposes of this work, four classes, namely, DH2-DH5 have been defined, describing the reasons for the incorrect value of pressure losses Δh_1 – while one class, namely, DH1, corresponds to the range of appropriate values.

Class DH1 corresponds to the range of correct values of pressure losses in the section calculated, taking into account not only flow velocity and diameter, but also the length of the section and the absolute roughness coefficient k [mm]. It is assumed that the range of permissible pressure losses occurs when the following conditions are met (Czapczuk 2013):

- the flow rate is higher than 0.5 [m/s],
- the flow velocity for individual diameters does not exceed the recommended values for individual diameters,
- the coefficient of absolute roughness does not exceed $k = 1.5$ [mm],
- pressure losses resulting from the length of the calculation, at section L will not cause a pressure line drop below 25.5 [m], assuming that the losses resulting from the absolute roughness coefficient k are normal. The initial value of the pressure level is assumed to be 40 [m], hence pressure losses resulting from this, cannot exceed 14.5 [m].

The DH2 class describes a case, where small pressure losses are caused by too large a diameter in the water pipe, or a small flow at the end of the water supply network. Flow rate is less than 0.5 m/s.

The DH3 class characterises a variant in which pressure losses are due to too small a diameter in the water pipe. The value of the absolute roughness coefficient is below the upper limit where $k = 1.5$ [mm].

The DH4 class describes the conditions in which pressure losses, resulting from the high value of the absolute roughness coefficient k , are above the k limit of 1.5 [mm].

The DH5 class describes a case where the reduction in pressure is below the required pressure loss value, associated with the length of the calculation section of the pipeline. This variant indicates the need for zoning, throughout the system. This length, depending on diameter, flow rate and roughness, is different each time.

The above classes will be assigned to individual calculation sections of the water distribution system, using an artificial neural network. Training examples, in the form of calculation results for sections of the water distribution system have been prepared, using EPANET software and the Excel spreadsheet.

This step was introduced since variability, throughout the whole range of possible attributes, must be taken into account in the examples. Some of the hydraulic calculations were deliberately incorrect, but these examples were described in the appropriate DH classes, so that the expert system could identify the cause of the incorrect losses in pressure.

SDR17 series, PE100 polyethylene plastic pipelines, based on the standard EN 12201-2:2011 were assumed for the calculations.

Hydraulic calculations were made using the following assumptions:

- internal diameters of the pipelines, D_{in} [mm] were taken for the calculations,
- the minimum pipeline diameter DN110 [mm],
- the maximum pipeline diameter DN630 [mm],
- the following absolute roughness coefficients were assumed:
 $k = 0.01; 0.1; 0.5; 1.0; 1.5; 2.0$ [mm],
- the maximum length of the calculation sections – 3000 [m].

The training examples relate to the individual sections of the water supply network and were developed in such a way that they can be used to assess pressure loss according to the DH1-DH5 classes. In order to generate a decision tree, the problem domain was defined according to the following attributes:

- the length of the computational line L [m],
- calculation flow in the Q_m section [l/s],
- the absolute roughness coefficient of the pipeline, in a given section k [mm],
- linear pressure losses on the computational section Δh_l [m].

All training examples were described using the DH1-DH5 label, indicating that they belong to a specific classification, characterising pressure losses. A collection of 17018 training examples, representing all of the DH1-DH5 classes described above, was obtained.

5. The application of artificial neural networks in assessing pressure losses

The search for the proper structure of the neural network, with one hidden layer, began with 9 neurons in the hidden layer. A larger network was constructed where the neural network had not undergone any improvement or only an insignificant improvement, after long training cycles. This suggested that an insufficient number of neurons, processing layers, or learning algorithms had become stuck in the local minimum. Networks with the same structure were trained several times to prevent them from becoming stuck in the local minimum (Hornik 1991).

A list of multi-layer perceptrons with one hidden layer for the assessment of pressure losses, is given in Table 1. The neural network with one hidden layer, is placed in pos. 5.

The above neural network has the lowest number of the Entropy Multiple Error Function E_{EME} for validation subset and a very high accuracy of classification.

Table 1. Artificial neural networks for the assessment of pressure losses in water supply pipelines

Tabela 1. Sztuczne sieci neuronowe do oceny strat ciśnienia w przewodach sieci wodociągowej

No.	K	$E_{EME}(L)$	$E_{EME}(V)$	$E_{EME}(T)$	$\eta(L)$	$\eta(V)$	$\eta(T)$
1	9	0.435014	0.616146	0.484385	0.778587	0.777908	0.772033
2	18	0.312509	0.373041	0.488254	0.842167	0.837368	0.838073
3	27	0.304561	0.368381	0.763289	0.860266	0.853584	0.857109
4	36	0.279509	0.598582	0.808997	0.899283	0.882726	0.884371
5	45	0.275838	0.362148	0.660753	0.934893	0.928555	0.932785
6	54	0.436712	0.503457	0.700952	0.57022	0.557697	0.560517

where:

K – the number of neurons in the inner layer of the multi-layered perceptron [-],

$E_{EME}(L)$ – the error for the training subset [-],

$E_{EME}(V)$ – the error for the validation subset [-],

$E_{EME}(T)$ – the error for the test subset [-],

$\eta(L)$ – the relevance of the classification of the training subset [-],

$\eta(V)$ – the relevance of the classification of the validation subset [-],

$\eta(T)$ – the relevance of the classification of the testing subset [-].

The neural network adopted, consists of the following elements:

- an input layer with neurons for 4 input variables: L , Q_m , k , Δh_l ,
- one hidden layer, constructed of 45 neurons with a logistic activation function (2),
- an output layer, composed of 5 neurons, with the Softmax activation function (3), corresponding to DH1-DH5 classes.

Figure 2 shows the network diagram for the assessment of pressure losses by means of a classification in which activation of the neuron, in the output layer, is visible, indicating the selection of the class DH3 assigned to it.

Tables 2 to 4 show the results of the classification in the form of an error matrix for the neural network, from Tab. 3, pos. 5 for the training, validation and testing subsets.

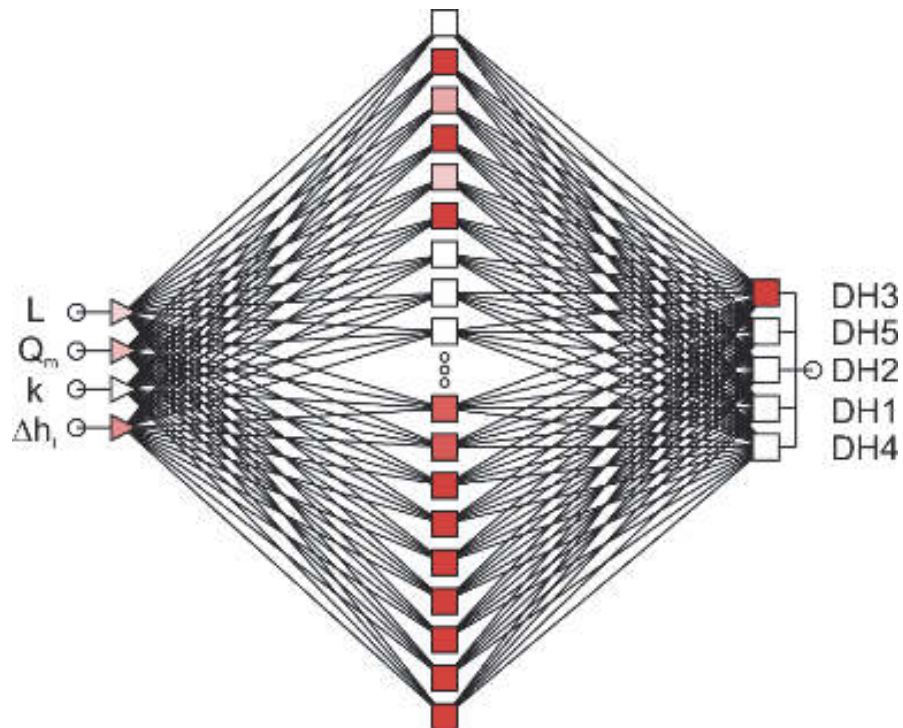


Fig. 2. A schematic diagram of a neural network for calculating pressure losses in water pipes

Rys. 2. Schemat sieci neuronowej do oceny strat ciśnienia w przewodach wodociągowych

Table 2. Results for the classification of pipeline diameters for the training subset

Tabela 2. Wyniki klasyfikacji średnic rurociągów dla podzbioru uczącego

	DH3	DH5	DH2	DH1	DH4
Total	2081	372	1945	2876	1235
Correct	1985	338	1865	2574	1193
Incorrect	4	1	13	7	2
Undetermined	92	33	67	295	40
DH3	1985	0	0	4	0
DH5	3	338	0	3	2
DH2	0	0	1865	0	0
DH1	1	1	13	2574	0
DH4	0	0	0	0	1193

Table 3. Results for the classification of diameters for the validation subset**Tabela 3.** Wyniki klasyfikacji średnic rurociągów dla podzbioru walidacyjnego

	DH3	DH5	DH2	DH1	DH4
Total	1066	163	1014	1388	624
Correct	1006	151	955	1237	602
Incorrect	1	3	9	3	0
Undetermined	59	9	50	148	22
DH3	1006	2	0	1	0
DH5	1	151	0	2	0
DH2	0	0	955	0	0
DH1	0	1	9	1237	0
DH4	0	0	0	0	602

Table 4. Results for the classification of pipeline diameters for the testing subset**Tabela 4.** Wyniki klasyfikacji średnic rurociągów dla podzbioru testowego

	DH3	DH5	DH2	DH1	DH4
Total	979	184	1014	1450	628
Correct	935	171	967	1280	616
Incorrect	2	3	6	6	0
Undetermined	42	10	41	164	12
DH3	935	2	0	4	0
DH5	1	171	0	2	0
DH2	0	0	967	0	0
DH1	1	1	6	1280	0
DH4	0	0	0	0	616

Determining the affiliation to one of the classes consists in selecting the neuron of the output layer, in which a value, close to 1, appears; with other neurons, the values should be close to 0, however this is practically impossible to obtain. For this reason, two threshold values are introduced, *viz.*, the acceptance threshold and the rejection threshold, to which the activation level of the neurons of the output layer, is compared. The activation level above the acceptance threshold results in the object being accepted into the class, while the activation value below the reject threshold indicates that the object is not affiliated to any class. In this

task, the acceptance threshold is set at 0.95, while the rejection threshold is at 0.05. If this condition is not met, the case is described as indefinite, meaning that the network is unable to classify the object, at all. Table 5 presents the activation values of neurons with the Softmax (3) function of the neural network output layer, for one of the training examples in which the DH3 class was selected.

Table 5. Activation values of neurons of the neural network output layer, in the assessment of pressure losses in water Pipes

Tabela 5. Wartości aktywacji neuronów warstwy wyjściowej sieci neuronowej do oceny strat ciśnienia w przewodach wodociągowych

Pipeline diameter, assigned to the output layer neuron	Activation of the output layer neuron
DH3	0.999999900
DH5	5.33E-12
DH2	1.33E-21
DH1	5.81E-08
DH4	1.75E-22
Activation sum:	1.000000000

6. Summary and conclusions

The process of creating a set of training data and searching for the appropriate structure of an artificial neural network is complicated and time-consuming. Training artificial neural networks should be carried out repeatedly, in order to avoid the local minimum of the error function. The artificial neural network was developed for computer programmes, in order to calculate hydraulic water distribution systems, in which it acts as an additional module, in the assessment of the results obtained. After completing the calculations, additional DH1-DH5 classes will be assigned to each calculation section. The proposed solution is to indicate the pipelines where it would be possible, or recommended, to adjust the diameter, in order to ensure adequate linear pressure losses and therefore more favourable operating conditions, from the point of view of the network pressure level. The neural network obtained is highly accurate at classifying. Using the previously prepared neural network should not cause users much trouble, as it is intended to be part of a computer programme.

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Zastosowanie sztucznych sieci neuronowych do oceny strat ciśnienia w przewodach wodociągowych

Streszczenie

System dystrybucji wody stanowi jeden z najważniejszych elementów wodociągu, którego budowa pochłania największą część kosztów, a jednocześnie w głównej mierze decyduje o możliwościach dostawy wody. Rurociągi wodociągowe powinny spełniać swoją rolę przez wiele lat. W związku z powyższym bardzo ważnym zadaniem jest poprawne zaprojektowanie i wykonanie obliczeń hydraulicznych. Podczas realizacji obliczeń najczęściej konieczne jest wielokrotne korygowanie danych w celu uzyskania poprawnego rozwiązania. W procesie obliczeń ocenie podlega wiele parametrów, w tym prędkość przepływu przez rurociągi wodociągowe, natężenie przepływu, wysokość strat ciśnienia oraz ciśnienie w poszczególnych węzłach sieci. Istotnym parametrem, często niedocenianym, jest wysokość strat ciśnienia na odcinkach obliczeniowych przewodów wodociągowych. W niniejszej pracy zaproponowano metodę oceny strat ciśnienia a pomocą sztucznych sieci neuronowych. W tym celu zdefiniowano jedną klasę DH1 opisującą poprawne warunki oraz cztery DH2-DH5, charakteryzujące problemy związane z wysokością strat ciśnienia w przewodach wodociągowych. Sztuczna sieć neuronowa na podstawie parametrów charakteryzujących pracę przewodu wodociągowego dokonuje wyboru jednej z klas, wskazując w ten sposób na występowanie określonego problemu lub jego brak.

Abstract

The water distribution system is one of the most important elements of the water supply system, the construction of which accounts for the largest part of the costs involved, while at the same time, being the determining factor in the supply of water. Pipelines should be equipped to continue fulfilling their role for many years. In connection with the above, a very important task is the correct design and execution of hydraulic calculations. During the implementation of calculations, it is often necessary to correct data frequently, in order to obtain the correct solution. Numerous parameters are evaluated in the calculation process, including flow velocity through water supply pipelines, flow rate, pressure loss and pressure in individual, network nodes. An important parameter, often underestimated, is the level of pressure loss in the calculation sections of water pipes. This paper proposes a method for the assessment of pressure loss and for the use of artificial neural networks. For this purpose, one DH1 class, describing the correct conditions and four DH2-DH5 classes, characterising problems related to the amount of pressure losses in the water pipes, have been determined. Based on the parameters characterising the operation of the water pipe, the artificial neural network, selects one of the classes and thus indicates the occurrence of a specific problem, or gives the 'all clear'.

Słowa kluczowe:

system dystrybucji wody, obliczenia hydrauliczne, liniowe straty ciśnienia, sztuczne sieci neuronowe

Keywords:

water distribution system, hydraulic calculations, pressure losses, artificial neural networks



Occurrence and Survivability of *Escherichia coli* and Enterococci in Waters Used as Bathing Areas

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1. Introduction

Waters used as bathing areas are an important element of summer recreation. During the holiday season, they attract tourists for recreation purposes. However, these waters may become contaminated, and therefore pose a serious health risk to people who use them. They are also one of the most dynamically changing natural environments, due to the physical and biological factors affecting them (Kubera & Małecka-Adamowicz 2017). The source of microorganisms in recreational waters are improperly processed sewage, agricultural run-off, rainwater, human and animal excrements (Byappanahalli et al. 2003, Imamura et al. 2011) as well as boats, plant residues, contaminated groundwater, soil and sand from the beach (Sercu et al. 2009, Whitman & Nevers 2003). According to many authors, rainfall, storms and wind on land may cause a drastic increase in the concentration of microorganisms in the water (Olivieri et al. 2007, Reeves et al. 2004, Byappanahalli & Fujioka 2004, Mote et al. 2012, Crowther et al. 2001). The bacterial population in the aquatic environment is significantly influenced by conditions prevailing in particular months of the year (Frączek et al. 2015). Direct assessment of all pathogenic microorganisms occurring in water is very complicated and time-consuming, which caused the appointment of indicator bacteria. In Poland and in most countries, *Escherichia coli* and enterococci were used for the assessment of the microbiological contamination of waters used as bathing areas (Olańczuk-Neyman 2003). The occurrence of these

bioindicators in the water, indicates the recent contamination of the reservoir with fecal microorganisms and hence, the possibility of other pathogenic bacteria, also of intestinal origin. (Walters et al. 2011), as well as numerous viruses (Soller et al. 2010), parasites and other pathogens. The study results of Viau et al. (2011) confirm the correlation between the occurrence of enterococci and pathogenic bacteria of the *Campylobacter* and *Salmonella* genus. Additionally, there was an explicit relation between the presence of streptococci in water and the number of cases of people using bathing areas, which in the summer season is definitely increasing. It may create a real epidemiological threat, therefore it is necessary to conduct systematic monitoring of microbiological status of waters used for bathing purposes (Attoui et al. 2016, Berninger et al. 2012, Zimoch & Paciej 2013).

The aim of the study was to assess the purity of water used for bathing purposes and to determine the survival time of *Escherichia coli* and *Enterococcus faecalis* bacteria in the water.

2. Material and methods

2.1. Subject, place and time of study

Samples of water for the study were taken from the Koronowo Reservoir located in the lower part of the Brda river, which is located within Kujawsko-Pomorskie Province. The reservoir has an extended shape with an area of approximately 1600 ha, a capacity of approx. 81 million m³ and the maximum depth exceeds 20 m. Reservoir has a varied coastline, which has a total length of 100 m. The waters of the reservoir are used with high frequency, they also constitute an interesting recreational offer. Over the years, taking into account the state of cleanliness of the waters, the Koronowo Reservoir obtained the third class of purity. Due to heavy rainfall, which contributes to the increase of water levels in rivers, it is often possible to observe a significant increase in transport of humic compounds along with waters of Brda river which are responsible for giving the waters of the Koronowo Reservoir a brown color and contribute to the eutrophication process. Water samples of 2000 ml were taken from three bathing areas: Samociążek (bathing area I), Pieczyska (bathing area II), Kręgiel (bathing area III) three times in the months of July, August and September. The choice of sampling time was dependent

on the use of recreational beach resorts. Samples were collected 30 cm under the surface of water into sterile, glass bottles and then transported to the laboratory where microbiological analyzes were performed in accordance with the Polish Standard PN-EN ISO 9308-1 and PN-EN ISO 7899-2. The number of indicator bacteria *Escherichia coli* and enterococci was determined in the water samples. Additionally, each time the samples were taken, the water temperature and the number of bathers were measured.

2.2. Procedures of microbiological tests

2.2.1. Methods for determination of the number of indicator bacteria

The determination of the number of *Escherichia coli* and enterococci bacteria in the tested water samples was performed by membrane filtration with usage of filtration apparatus and membrane filters of cellulose esters with a size of 47 mm and a pore size of 0.45 μm . Due to the significant microbiological contamination of the tested samples, a series of decimal dilutions in the range from 10^{-1} to 10^{-3} were made. After filtering 100 ml of water, the filter was transferred to a Petri dish with Lactose TTC Agar with TergitolTM-7 substrate and incubated for 24 hours at 37°C. After the incubation, all characteristic colonies of lactose-positive bacteria with yellow-orange approbate were counted, which caused yellow color on the substrate with the filter. All characteristic colonies were transplanted into Trypton Soy Agar (TSA) and tryptophan broth. TSA agar with inoculated bacteria was incubated for 24 hours at temperature of 37°C. After incubation, a cytochrome oxidase occurrence and indole production tests were performed. All colonies which exhibited a negative reaction to cytochrome oxidase and were producing indole, were counted as *E. coli* bacteria. In order to determine the number of enterococci, after filtering 100 ml of the water from sample tested, filter with microorganisms detained on it was transferred to a Petri dish with Slanetz and Bartley medium and incubated for 48 hours at temperature of 37°C. After incubation, convex colonies, either whole red or only in the middle, pink or maroon color, were considered to be typical *Enterococcus* bacteria. In the next stage, in order to confirm the results, the membrane filter was transferred together with the grown colonies on agar with kanamycin, esculin and azide and then incubated for 2 hours at temperature of 44°C. As a result of bacterial growth, occurs decomposition of esculin into glu-

cose and escullet, which reacts with the iron ions present in the medium, creating a dark brown or black complex, which is visible in the form of a characteristic darkening of the substrate (black sediment around grown colonies). Colonies of light brown to black color, clearly diffusing into the interior of the substrate were considered typical.

2.2.2. Survivability studies of *Escherichia coli* and *Enterococcus faecalis*

Water for testing of the survivability of indicator organisms was taken from the bathing areas of the Koronowo Reservoir. *Escherichia coli* ATCC 25922 and *Enterococcus faecalis* ATCC 19433 were used as indicator bacteria. By usage of System Vitex 1550 densitometer, a suspension was prepared with the above mentioned strains with a turbidity of 10^8 cells/ml. The result of the suspension was introduced into the test water in an amount of 5 ml per 5000 ml of water and left at room temperature for 1 hour and then the number of indicator bacteria in the inoculated water sample was determined. Samples of inoculated water were placed at temperature of 4°C and 20°C, and then the number of *Escherichia coli* and *Enterococcus faecalis* was determined at the specified intervals by usage of MPN method (most probable number of bacteria). In order to determine the number of *E. coli*, a lactose broth with bromocresol purple (incubation at temperature of 44°C/24-48h) was used in the preliminary tests. Positive and doubtful results were confirmed using Tryptone Bile Glucuronic Agar (TBX). The final confirmation consisted in usage of the API 20E microtest. For the determination of *Enterococcus faecalis*, broth with glucose and azide (incubation at temperature of 37°C/24h) was used in the first stage. The results were confirmed by usage of agar with kanamycin, esculin and azide, while the final identification was performed with API 20 Strep.

2.3. Statistical analysis of results

The Microsoft Excel 2010 and Statistica 2013.1 programs were used to calculations and to execute the charts. The results of the survivability studies of *Escherichia coli* and *Enterococcus faecalis* in water used for bathing purposes were digested and then subjected to statistical analysis based on changes in the number of bacteria tested at the time in accordance to formula 1:

$$y = ax + b \quad (1)$$

while:

y – logarithm of the number of indicator bacteria, elimination of bacteria in one day, a – the directional coefficient corresponding to the average change in the number of bacteria in the form of log per one, b – day the number of bacteria in the zero phase, x – time counted in days.

3. Results and discussion

The results of the studies on the presence of indicator bacteria *Escherichia coli* and enterococci in water samples taken from three bathing areas are presented in Figures 1-2. The analyzes indicated that the tested water was characterized by significant microbiological contamination, because in the July the occurrence of *E.coli* bacteria was recorded at an average of 3697 cfu/100 ml (bathing area I) to 4539 cfu/100 ml (bathing area II). Additionally, in the samples of water taken from the bathing area III, the number of these bacteria was also high and amounted to 3836 cfu/100 ml (Fig. 1).

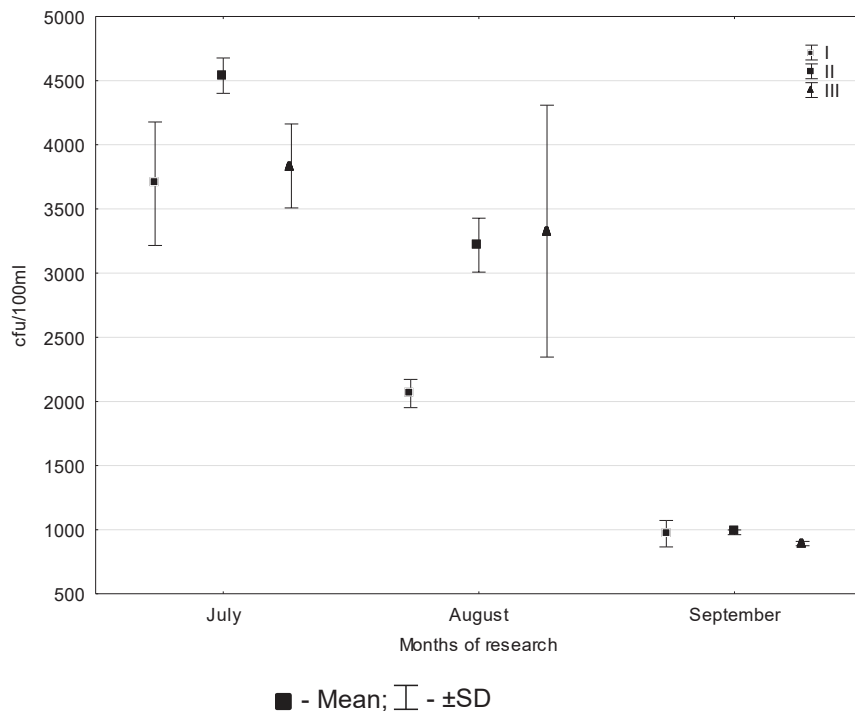


Fig. 1. Average number of *E. coli* in water from individual bathing areas
Rys. 1. Średnia liczba *E. coli* w wodzie z poszczególnych kąpielisk

However, in August, the number of these bacteria decreased and ranged from 2062 cfu/100 ml (bathing area I) to 3327 cfu/100 ml (bathing area III). Similar relations were noted by An et al. (2002), stating that the highest number of *E. coli* bacteria and coliform bacteria occurred in water samples from the lake during the summer. Own study indicated that the least number of *E. coli* was isolated from water samples taken in September, where the number of these bacteria was at a similar level in all bathing areas (892-980 cfu/100 ml). Analyzing the occurrence of enterococci, it was found that the majority of these microorganisms were isolated from water samples taken from bathing area I in July when their number was 412 cfu/100 ml and from bathing area III in August - 404 cfu/100 ml (Fig.2). In the rest of the samples of the analyzed water, the number of enterococci didn't exceed the normative value of 400 cfu/100 ml.

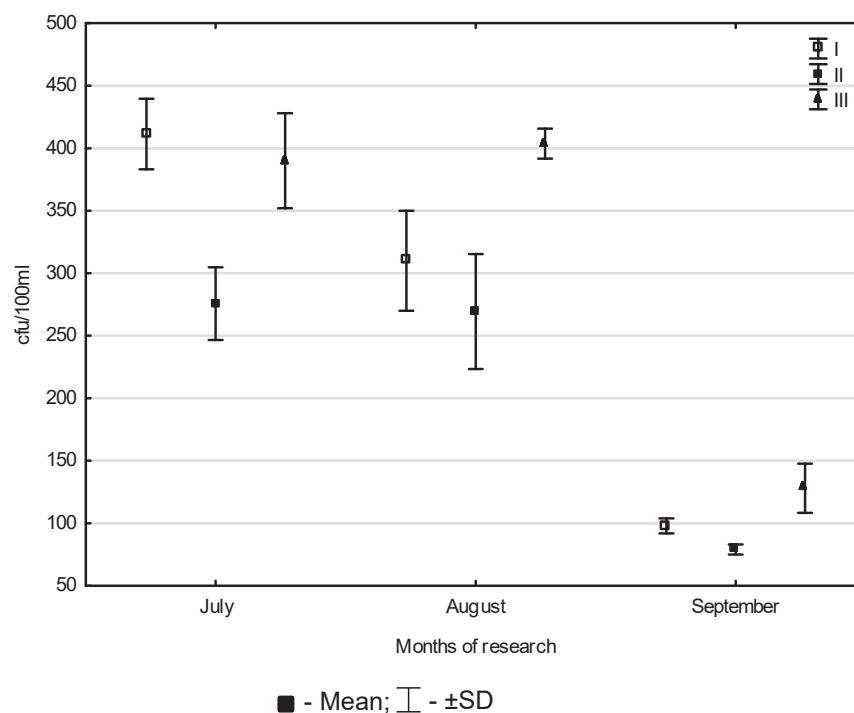


Fig. 2. Average number of enterococci in water from individual beach resorts
Rys. 2. Średnia liczba enterokoków w wodzie z poszczególnych kąpielisk

It was also indicated that in every water sample from bathing areas, regardless of the month of research, *E. coli* bacteria were significantly more numerous than enterococci. Similar conclusions were obtained by Alm et al. (2003) who noticed over four times higher number of *E. coli*

bacteria in water used for bathing purposes than enterococci. Considering sanitary indicators in own study, it should be noted that only in September the analyzed water samples met the microbiological requirements for the assessment of the current quality of bathing water and the place used for bathing specified in the Regulation of the Minister of Health of 8 April 2011 on the supervision of the quality of bathing water and the place used for bathing (Dz.U. 2011 no 86 item 478; Dz.U. 2015 item 1510). Higher results were obtained by Kostecki et al. (2000), who studied the number of streptococci in the Dzierżno Duże reservoir. The highest values were noted at the river inflow, where they amounted to 1000 cfu/100 ml. According to the authors, the number of bacteria in water is always higher in the coastal zone of the lake than in the middle part. Niewolak & Gotkowska-Płachta (1999) after analyzing 20 samples of water taken from Hańcza Lake, found that the average number of streptococci in the summer was the highest in the July and was 43 cfu/100 ml for coastal waters, while the average number of streptococci from 80 samples taken from the deepest point of the lake reached its highest value in August: 14 cfu/100 ml. Own study indicated that there is a noticeable relationship between water contamination and the number of people taking baths, because in July the number of people using the water reservoir was the largest and ranged from 35 to 68 people (Table 1).

Table 1. Water temperature and the number of bathers

Tabela 1. Temperatura wody i liczba kąpiących się osób

Place of study	Temperature of water (°C)			Number of bathers		
	Months of study			Months of study		
	VII	VIII	IX	VII	VIII	IX
Bathing area I	25	21	18	35	30	3
Bathing area II	26	21	19	68	45	12
Bathing area III	24	20	18	36	26	9

Additionally, the highest number of *Escherichia coli* and enterococci in the tested water was also recorded this month. In August, the water temperature was lower than in month July by an average of 4-5°C,

while the number of bathers at the time of sampling was also lower than in the previous month. In August, the number of people taking baths ranged from 26 to 45 people. At the same time, the number of indicator bacteria in water samples decreased during this period. The number of people using bathing areas for recreational purposes had the greatest impact on the microbiological contamination of the reservoir. The argument confirming this fact was the last month of research (September), because microbiological indicators in samples of water were much below the acceptable standards. The relation between the number of bathers and the contamination of water and sand on the beach with *E. coli* bacteria was also found by Whitman & Nevers (2003).

Table 2. The survivability of *E. coli* and *Enterococcus faecalis* bacteria at temperature of 4 and 20°C

Tabela 2. Przeżywalność bakterii *E. coli* i *Enterococcus faecalis* w temperaturze 4 i 20°C

Day of study	Temperature of 4°C		Temperature of 20°C	
	Number of bacteria [cfu/ml]			
	<i>Escherichia coli</i>	<i>Enterococcus faecalis</i>	<i>Escherichia coli</i>	<i>Enterococcus faecalis</i>
1	$4.5 \cdot 10^7$	$2.5 \cdot 10^7$	$4.5 \cdot 10^7$	$2.5 \cdot 10^7$
3	$2.5 \cdot 10^6$	$2.5 \cdot 10^6$	$3.0 \cdot 10^6$	$2.5 \cdot 10^6$
7	$1.5 \cdot 10^6$	$1.5 \cdot 10^6$	$4.5 \cdot 10^2$	$4.5 \cdot 10^5$
10	$1.5 \cdot 10^5$	$1.5 \cdot 10^5$	$4.5 \cdot 10^1$	$1.5 \cdot 10^3$
15	$1.5 \cdot 10^4$	$1.5 \cdot 10^5$	$4.5 \cdot 10^1$	$4.5 \cdot 10^2$
20	$4.5 \cdot 10^3$	$1.5 \cdot 10^4$	0	$1.5 \cdot 10^2$
25	$2.5 \cdot 10^3$	$1.5 \cdot 10^4$		0
30	$4.5 \cdot 10^1$	$1.5 \cdot 10^3$		
35	$4.5 \cdot 10^1$	$4.5 \cdot 10^2$		
40	$1.0 \cdot 10^1$	$2.5 \cdot 10^1$		
45	0	0		

Due to the long survivability of pathogenic microorganisms in the aquatic environment, studies have been undertaken to determine the survival time of *E. coli* and *Enterococcus faecalis* in water used for bathing purposes. The obtained results are presented in Table 2 and Figures 3-6.

At the beginning of the study the number of *E. coli* bacteria in the initial sample was $4.5 \cdot 10^7$ cfu/ml for water stored at temperature of 4°C and also 20°C . A significant decrease in the number of these bacteria at temperature of 4°C by more than 3 logarithmic units was recorded after 15 days of the study. In the next days of the study, successive decreases in the *E. coli* number were registered, while in the 45th day of the study, the presence of these microorganisms wasn't found in the water samples. A definitely faster elimination of these bacteria was found in water at temperature of 20°C and after 15 days of study the number of *E. coli* decreased to the level of $4.5 \cdot 10^1$ cfu/ml (Table 2).

The equation of regression indicated that the daily rate of elimination of these bacteria in water was 0.16 log cfu at temperature of 4°C (Fig. 3) and 0.45 log cfu at temperature of 20°C (Fig. 4). The prognostic calculations indicated that these indicator bacteria survived 45 days at temperature of 4°C , while at temperature of 20°C they survived for 29 days shorter. Wcisło & Chróst (2000) determined that *E. coli* bacteria can survive in an aqueous environment for 30 days. The reason for this phenomenon is probably the ability to adapt these bacteria to adverse conditions. At low temperature, the volume of microorganisms decreases a few times, and vital functions are slowed down, which makes their survival time additionally longer even up to several months (Stojek 2010).

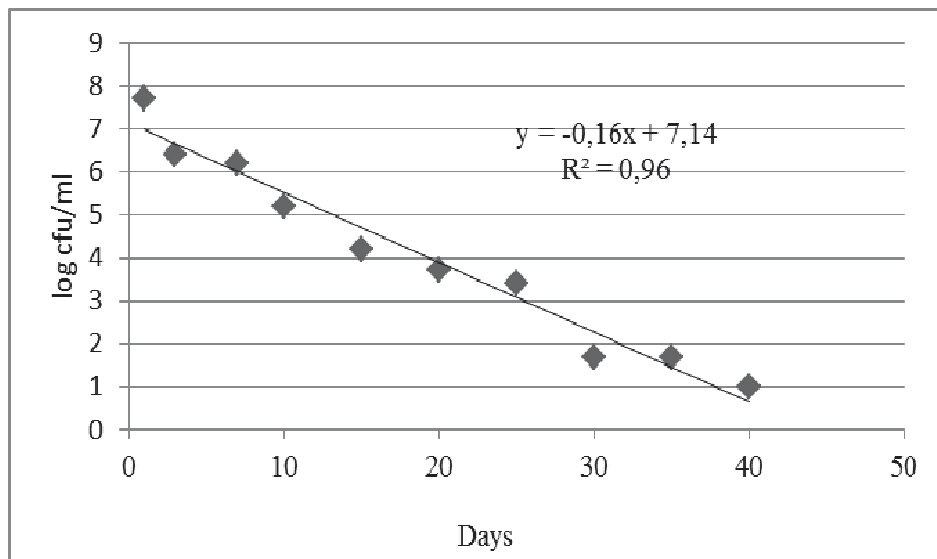


Fig. 3. The survivability of *E. coli* at temperature of 4°C

Rys. 3. Przeżywalność *E. coli* w temperaturze 4°C

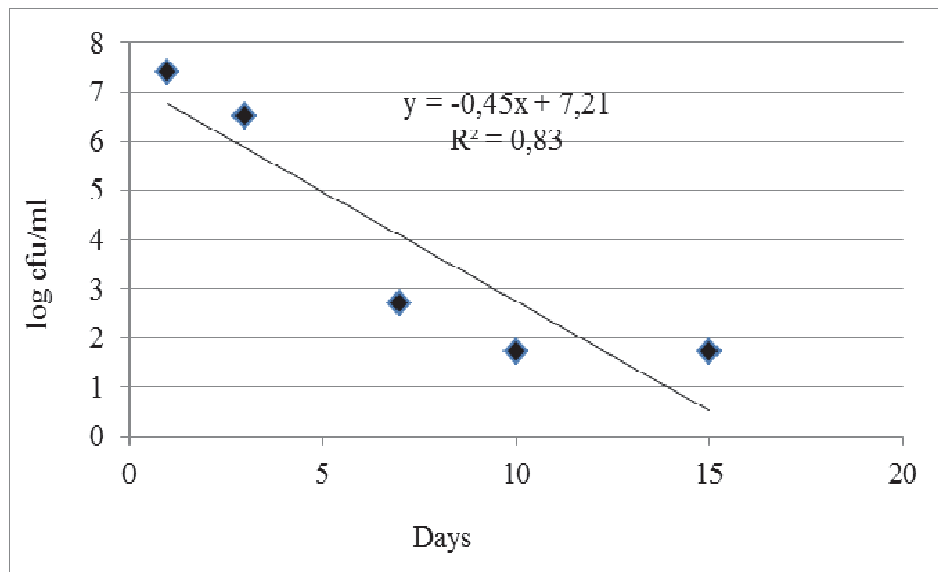


Fig. 4. The survivability of *E. coli* at temperature of 20°C

Rys. 4. Przeżywalność *E. coli* w temperaturze 20°C

Enterococci are used as indicators of fecal contamination of recreational waters around the world (Boehm & Sassoubre 2014). In the own study on the survivability of *Enterococcus faecalis*, it was indicated that these bacteria were also inactivated in the test water. At the beginning of the study, the number of streptococci was at the rate of $2.5 \cdot 10^7$ log cfu/ml at temperature of 4°C and 20°C. In the first days of the study, a slight decrease in the number of these bacteria at temperature of 4°C was observed, while a significant elimination of *Enterococcus faecalis* to the rate of $1.0 \cdot 10^1$ cfu/ml was recorded on the 40th day of the study. In water at temperature of 20°C, a rapid decrease in the number of these bacteria was found on the 20th day of the study, since these bacteria were isolated from the water in the number of $1.5 \cdot 10^2$ cfu/ml (Table 2). With usage o equation of regression, it was calculated that the maximum survival time of *Enterococcus faecalis* in water at temperature of 4°C was 52 days, while at temperature of 20°C it was 26 days (Fig. 5-6). The obtained results proved that the daily rate of elimination of these bacteria in water at both temperatures was slower as compared to *E. coli* and amounted to 0.14 log (4°C) and 0.28 log (20°C).

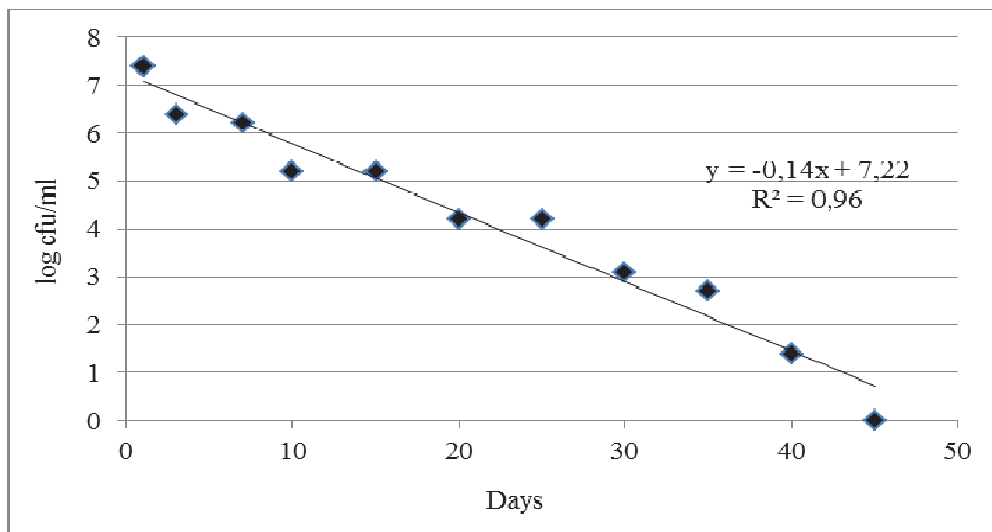


Fig. 5. The survivability of *Enterococcus faecalis* at temperature of 4°C
Rys. 5. Przeżywalność *Enterococcus faecalis* w temperaturze 4°C

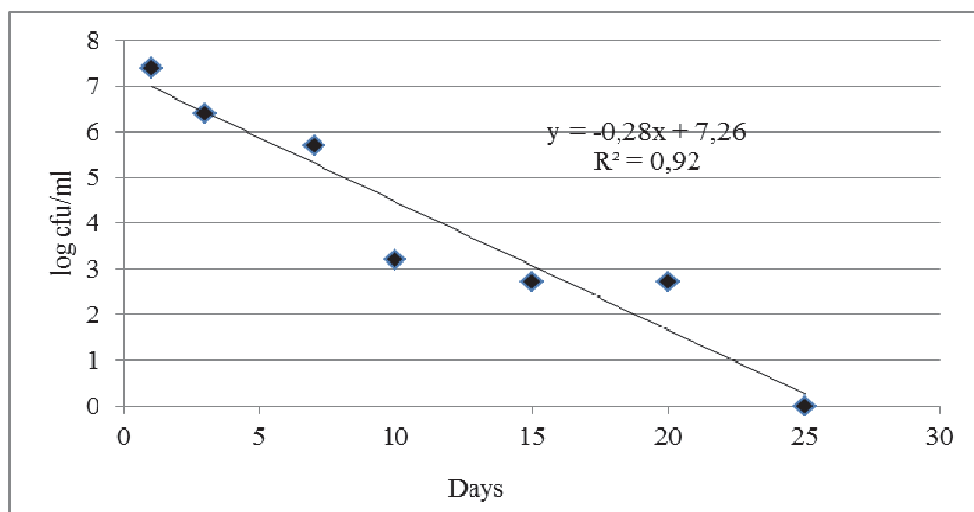


Fig. 6. The survivability of *Enterococcus faecalis* at temperature of 20°C
Rys. 6. Przeżywalność *Enterococcus faecalis* w temperaturze 20°C

As reported by many authors, enterococci are characterized by longer survivability in water than other bacteria, including *Escherichia coli* (Boehm & Sassoubre 2014, Craig et al. 2004, Byappanahalli et al. 2003). Lleò et al. (2005) explain the cause of this phenomenon by the ability of enterococci to transition into VBNC state (Viable But Not Culturable) and resuscitation capacity. The authors state that this strategy of survival of enterococci should be taken into account when assessing the microbiological quality of water, especially when these bacteria act as

sanitary indicators. Researchers found that the number of enterococci found in recreational waters was strongly correlated with the number of people suffering from gastrointestinal diseases. The presence of pathogenic bacteria in surface waters used for recreational purposes is particularly dangerous due to epidemiological reasons. Many people have access to infected water during the holiday season, which poses a very high risk for them due to the rapid spread of pathogenic microorganisms (Boehm & Soller 2011).

4. Conclusions

1. Performed study has indicated that there are numerous *Escherichia coli* bacteria in water from three bathing areas, especially in the months of July and August, where the number of these bacteria has exceeded the normative values several times.
2. It was found that the number of enterococci in the water from bathing areas was definitely lower compared to the *E. coli* bacteria. In the samples of water coming from two bathing areas in the months of July and August, the number of these bacteria was noted at the level slightly exceeding the sanitary requirements.
3. It was indicated that in September, the water from all the examined bathing areas met the microbiological requirements specified in the applicable legal acts.
4. The obtained results proved that the number of indicator bacteria was determined by the temperature of water and the number of bathers. Prognostic studies indicated that *Escherichia coli* and *Enterococcus faecalis* lasted longer in water at temperature of 4°C, respectively: 45 and 52 days, while at temperature of 20°C their survival time was shorter by 29 and 26 days.
5. The study indicated the necessity to perform permanent sanitary control of water used for bathing purposes in the aspect of epidemiological threats.

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Występowanie i przeżywalność *Escherichia coli* i enterokoków w wodach wykorzystywanych jako kąpieliska

Streszczenie

Wody kąpieliskowe w sezonie wakacyjnym wykorzystywane są z dużą częstotliwością w celach rekreacyjnych. Należy podkreślić, że ulegają one zanieczyszczeniu mikrobiologicznemu, w związku z czym stanowią poważne zagrożenie zdrowotne dla korzystających z nich osób. W związku z powyższym podjęto badania, których celem była ocena stanu czystości wody wykorzystywanej w celach kąpieliskowych oraz ustalenie w badanej wodzie czasu przeżywalności bakterii *Escherichia coli* i *Enterococcus faecalis*. Próbkę wody pobierano z trzech kąpielisk Zalewu Koronowskiego: Samociążek (kąpielisko I), Pieczyńska (kąpielisko II), Kręgiel (kąpielisko III) trzykrotnie w miesiącach lipcu, sierpniu oraz we wrześniu. W próbkach wody oznaczono liczbę bakterii wskaźnikowych *Escherichia coli* i enterokoków. Dodatkowo przy każdym poborze próbek dokonywano pomiaru temperatury wody oraz liczbę kąpiących się osób. Oznaczenie liczby bakterii *Escherichia coli* oraz enterokoków w badanych próbkach wody przeprowadzono metodą filtracji membranowej. W bada-

niach dotyczących ustalenia czasu przeżywalności wykorzystano dwa szczepy *Escherichia coli* ATCC 25922 oraz *Enterococcus faecalis* ATCC 19433. Zmiany liczebności bakterii wskaźnikowych oznaczono metodą NPL (najbardziej prawdopodobna liczba bakterii). Przeprowadzone analizy wykazały, że badana woda charakteryzowała się znacznym zanieczyszczeniem mikrobiologicznym, ponieważ w miesiącu lipcu odnotowano występowanie bakterii *E. coli* średnio na poziomie od 3697 cfu/100 ml (kąpielisko I) do 4539 cfu/100 ml (kąpielisko II). Ponadto w próbkach wody pobranych z kąpieliska III liczba tych bakterii była wysoka i wynosiła 3836 cfu/100 ml. Z kolei w sierpniu liczba tych bakterii zmniejszyła się i kształtowała się w zakresie od 2062 cfu/100 ml (kąpielisko I) do 3327 cfu/100 ml (kąpielisko III). W przypadku enterokoków stwierdzono, że najwięcej tych drobnoustrojów wyizolowano z próbek wody z kąpieliska I w lipcu, liczba ich wynosiła 412 cfu/100 ml oraz z III kąpieliska w miesiącu sierpniu – 404 cfu/100 ml. W pozostałych próbkach analizowanej wody liczba enterokoków nie przekroczyła wartości normatywnej 400 cfu/100 ml. Wykazano, że w miesiącu wrześniu woda ze wszystkich badanych kąpielisk spełniała wymagania mikrobiologiczne określone w obowiązujących aktach prawnych. Uzyskane wyniki dowiodły, że liczba bakterii wskaźnikowych determinowana była temperaturą wody i liczbą kąpielących się osób. Na podstawie równań regresji ustalono że bakterie *Escherichia coli* i *Enterococcus faecalis* dłużej przeżywały w wodzie o temperaturze 4°C odpowiednio: 45 i 52 dni, natomiast w temperaturze 20°C czas ich przetrwania wynosił 52 i 26 dni. Przeprowadzone badania wskazują na konieczność ciągłego monitoringu wody wykorzystywanej w celach kąpieliskowych w aspekcie zagrożeń epidemiologicznych.

Abstract

Bathing waters during the holiday season are used with great frequency for recreational purposes. It should be noted that they are subject to microbiological contamination, and therefore pose a serious health risk to the people using them. In accordance with the above, study which was undertaken aimed at assessing the purity status of water used for bathing purposes and determining the survival time of *Escherichia coli* and *Enterococcus faecalis* bacteria in the test water. Water samples were taken from three bathing areas of the Koronowo Reservoir: Samociążek (bathing area I), Pieczyska (bathing area II), Kręgiel (bathing area III) three times in the months of July, August and September. The number of indicator bacteria *Escherichia coli* and enterococci was determined in the water samples. Additionally, each time the samples were taken, the water temperature and the number of bathers were measured. The determination of the number of *Escherichia coli* and enterococci bacteria in the tested water samples was performed by membrane filtration. Two strains of *Escherichia coli* ATCC

25922 and *Enterococcus faecalis* ATCC 19433 were used in studies to determine the survival time. Changes in the number of indicator bacteria were determined by usage of MPN method (most probable number of bacteria). The analyzes indicated that the water tested was characterized by significant microbiological contamination, because in July the occurrence of *E.coli* bacteria was recorded at an average of 3697 cfu/100 ml (bathing area I) to 4539 cfu/100 ml (bathing area II). Additionally, in the samples of water taken from the bathing area III, the number of these bacteria was high and amounted to 3836 cfu/100 ml. However, in August the number of these bacteria decreased and ranged from 2062 cfu/100 ml (bathing area I) to 3327 cfu/100 ml (bathing area III). In the case of enterococci, it was found that the majority of these microorganisms were isolated from water from bathing area I in July and their number was 412 cfu/100 ml and from the bathing area III in August – 404 cfu/100 ml. In the remaining samples of the analyzed water, the number of enterococci didn't exceed the normative value of 400 cfu/100 ml. It was indicated that in September the water from all the examined bathing areas met the microbiological requirements specified in the applicable legal acts. The obtained results proved that the number of indicator bacteria was determined by the temperature of water and the number of bathers. In accordance to regression equations, it was found that *Escherichia coli* and *Enterococcus faecalis* lasted longer in water at temperature of 4°C respectively: 45 and 52 days, while at temperature of 20°C their survival time was 52 and 26 days. The study indicated the necessity to perform permanent sanitary control of water used for bathing purposes in the aspect of epidemiological threats.

Słowa kluczowe:

woda kąpieliskowa, bakterie wskaźnikowe, przeżywalność, *Escherichia coli*, *Enterococcus faecalis*

Keywords:

bathing water, indicator bacteria, survivability, *Escherichia coli*, *Enterococcus faecalis*



The Possibility of Using UV Absorbance Measurements to Interpret the Results of Organic Matter Removal in the Biofiltration Process

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1. Introduction

Organic substances present in all natural waters are most often referred to as natural organic matter (NOM). NOM is a heterogeneous mixture of compounds, still largely unexplored from a chemical point of view. Due to its heterogeneity, it is not possible to characterise NOM according to individual components. The standard water quality indicators, such as chemical oxygen demand (COD), dissolved organic carbon (DOC), UV_{254} , pH and other do not offer information on the nature of NOM, such as molar mass or hydrophobicity (Matilainen et al. 2010, Gibert et al. 2013). This complex mixture is often characterised according to chemical groups with similar properties which are identified on the basis of concentration and fractionation data (Huber et al. 2011, Pruss 2015). The methods, however, require considerable effort, as well as pre-treatment of samples which may affect the form of the compounds. In the pursuit of NOM characterisation, analytical techniques which require minimum preparation of samples are gaining popularity, including the high-performance size exclusion chromatography (HPSEC) and the fluorescence excitation-emission matrix (F-EEM) spectroscopy (Baghoth 2011) which allow for the determination of the molecular mass distribution and the hydrophilic or hydrophobic nature of the organic compounds (Matilainen et al. 2010, Huber et al. 2011).

Removal of organic micropollutants from water requires the use of advanced methods of water treatment, including sorption and biological processes which take place in biological activated carbon filters (BAF) (Pruss 2009, Holc et al. 2016a, b, Pruss et al. 2018, Mądrecka et al. 2018). The activity of BAF is based on the combination of two processes: biodegradation and adsorption. In the initial stage of BAF operation, the predominant process is sorption. When an adequate amount of pollutants is absorbed and biological film develops, biodegradation becomes predominant. Activated carbon is an adsorbent with a very high porosity and specific surface area (600-1000 m²/g). During the operation of the filter bed, the bacteria naturally occurring in water begin to settle on the porous surface of the grain. They are mainly heterotrophic bacteria for which the environmental conditions in the bed are suitable. After about 2-3 months, biofilm forms on the grain surface (Simpson 2008, Mądrecka et al. 2018).

The degradation of pollutants due to the activity of microorganisms is a very effective process. Microorganisms are useful in the biodegradation of substances which are difficult to eliminate using traditional methods (Simpson 2008, Olesiak & Stępniaak 2014, Holc et al. 2016b). Thanks to high efficiency of dissolved organic matter removal by biological activated carbon filters, the demand for disinfectants from the treated water is much lower (Kołaski et al. 2017). In the case of such water, there is a lower probability of the development of undesirable by-products and of secondary bacterial load growth in the water supply network that could cause degradation of water quality supplied to the consumers (Wolska 2014, Gibert et al. 2015, Szuster-Janiaczyk 2016, Włodyka-Bergier et al. 2016).

An indirect method for determining biological activity in BAF is the Eberhardt, Madsen and Sontheimer (EMS) test. It is based on the determination of the coefficient *S*, which is calculated as the quotient $\Delta[\text{COD}]$ by $\Delta[\text{O}_2]$, where $\Delta[\text{COD}]$ denotes the reduction of the chemical oxygen demand of water and $\Delta[\text{O}_2]$ is the loss of dissolved oxygen in water. The test is helpful in determining the relationship between the adsorption and the biodegradation process on the BAF bed, assuming that organic compounds are removed both by way of sorption and biodegradation, and oxygen is consumed by aerobic microorganisms to oxidize carbon. If $S = 1$, both adsorption and biodegradation proceed with the

same intensity in the filter bed. If $S > 1$, adsorption predominates, and if $S < 1$, biodegradation is predominant. When S and $\Delta[\text{COD}]$ equal 0, the sorption and biodegradation processes are stopped. If $\Delta[\text{COD}] > 0$ and $\Delta[\text{O}_2] = 0$, sorption is present and biodegradation does not occur. In turn, when both $\Delta[\text{COD}]$ and $\Delta[\text{O}_2]$ are equal 0, neither of the processes takes place (Wolborska et al. 2003, Papciak et al. 2016, Mądrecka et al. 2018).

UV absorption is a popular and relatively simple indicator used to determine the content of organic pollutants in water. The functional groups of organic compounds which absorb UV and VIS radiation are chromophores. Most chromophore groups are found in humic acid particles. Water which contains organic compounds with chromophores demonstrates absorbance within the range of 200 to 350 nm. To track UV absorption changes, the 254 nm wavelength was considered most suitable and is widely used in drinking water analysis. Based on absorbance, it is possible to determine the total dissolved organic carbon fraction and organic compounds with a high content of aromatic rings which are precursors of disinfection or oxidation by-products. Its value is often interpreted as an indicator of the degree of aromatic rings activation which serves as the basis for predicting the reactivity of aromatic components during chlorination (Mołczan et al. 2006, Nowacka et al. 2012, Szerzyna et al. 2017). The different wavelengths are believed to identify different chromophores: absorbance at 220 nm is associated with both the carboxylic and aromatic chromophores, whereas absorbance at 254 nm is typical for aromatic groups with varying degrees of activation (Korshin et al. 2009). The correlation of the UV absorbance in the range 251-256 nm to values in the range 202-205 nm is used as an indicator of the relative proportion of aromatic to aliphatic groups present in NOM. UV_{254} has been identified as a potential surrogate measure for DOC despite its tendency to represent only the aromatic character. The absorbance at 436 nm represents functional groups contributing to the color of water, from yellow to brown. Ratios between two different wavelengths, such as 254 nm/204 nm, 254 nm/436 nm or 250 nm/365 nm have also been reported to aid NOM characterization (Hur et al. 2006, Valencia et al. 2012). For example, the ratio of 253 nm/203 nm correlates with the formation of disinfection by-products (DBPs). The value of the 254 nm/436 nm correlation is higher, when the functional groups causing color of water are removed from the water (Kim & Yu 2007, Valencia et al. 2012).

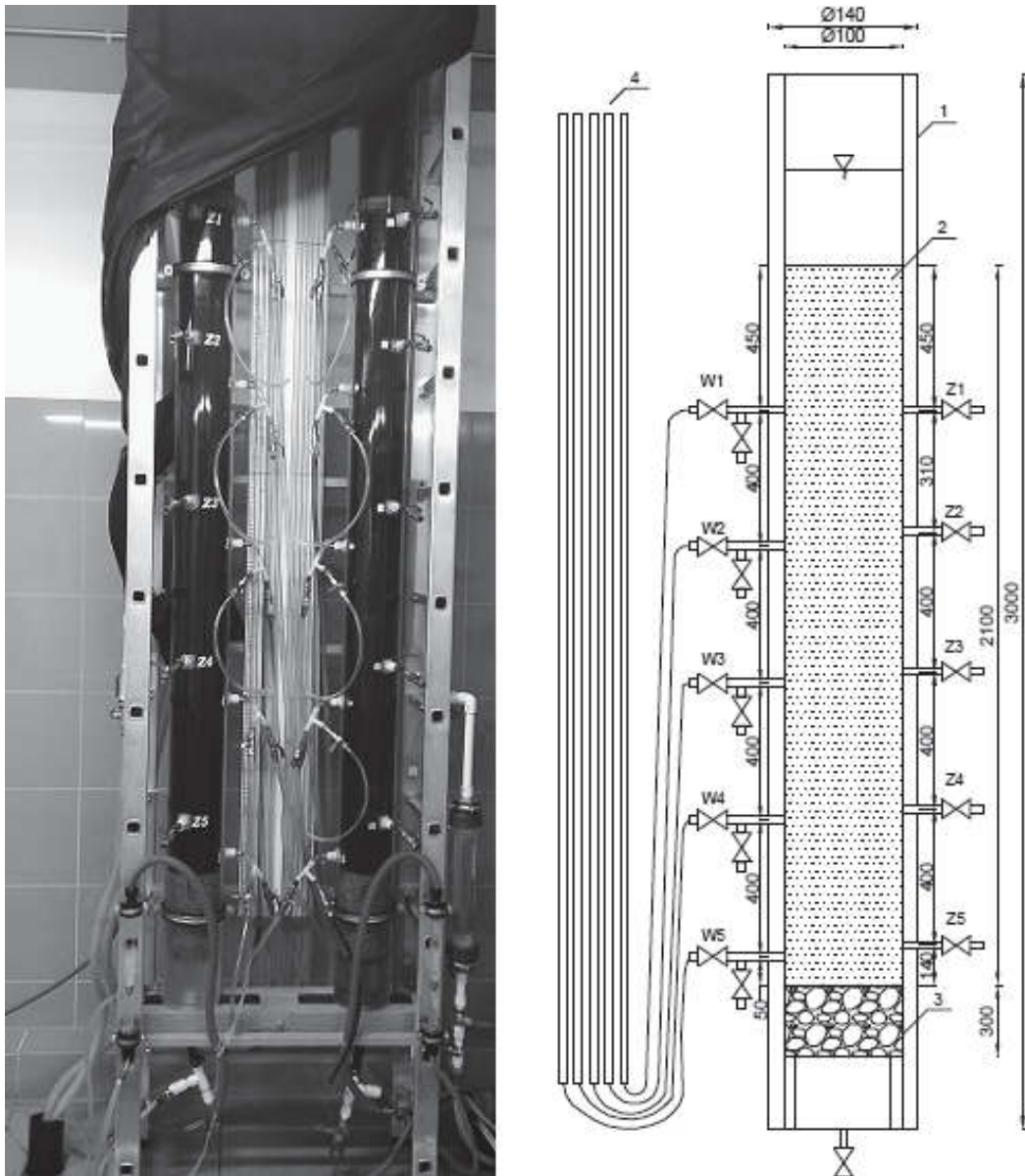
This article, present the results of research on the use of different wavelengths UV absorbance and their rations to interpret the transformations of organic compounds in biologically active filters. The analysis of these results is a supplement to the information published in 2016 (Holc et al. 2016a, b).

2. Methods

The technological investigation was conducted on a pilot scale. The experimental stand consisted of two filtration columns with the diameter of 100 mm and the height of 300 cm (Fig. 1). The columns were filled with WG-12 granulated activated carbon with parameters: iodine number 1100 mg/g, methylene blue adsorption 30 g/100 g, total surface area B.E.T 1100 m²/g, particle size 0.75-1.5 mm. Stable temperature was maintained across the entire filter bed height thanks to a water jacket – a pipe with the inner diameter of 140 mm filled with water. The water flowing through the pipe had a temperature equal to the filtered water temperature. In order to prevent the growth of algae, the filters were covered with black geotextile. The water supplied to the filters was dechlorinated tap water. The filtration rate was 2.5 m/h and the contact time was 50 minutes, respectively. Across the entire filter height, stub pipes were located for the sampling of water and the filter bed. Samples were taken at the beginning of filters exploitation in April 2015. The system is still operated.

The filtration columns differed with regard to the method of the filter bed activation (Holc et al. 2016a) and the microorganisms found there (Holc et al. 2016b). In the first filtration column (F1), the microorganisms residing in the filter bed came from the water passing through the filter i.e. from the network water. The filter bed of the other filtration column (F2) was inoculated with the wastewater from the backwashing of carbon filters operated in a selected water treatment plant. Detailed information about this water treatment plant technology and technical BAF exploitation are presented in other publication (Kołaski et al. 2017, 2018).

The samples of water for analysis were collected on the supply line from the filtration columns and from the filter bed cross-section, at the depth of 45 cm, 85 cm, 125 cm, 165 cm and 205 cm. BAF were backwashed with a one-day shift according to a predetermined schedule. A detailed method of BAF backwashing was presented in another publication (Komorowska-Kaufman et al. 2018).



1 – filtration column, 2 – WG-12 activated carbon filter bed, 3 – gravel support layer, 4 – piezometers W1-W5 – water sampling points, Z1-Z5 – filter bed sampling points

Fig. 1. The experimental station consisting of two identical filtration columns
Rys. 1. Model badawczy złożony z dwóch identycznych kolumn filtracyjnych

The effectiveness of organic substances elimination from water was assessed using the following parameters: chemical oxygen demand (COD KMnO_4), dissolved oxygen (DO) concentration, total organic carbon (TOC), pH, alkalinity and UV absorbance for the following wavelengths: 204 nm, 254 nm, 365 nm and 436 nm.

Absorbance measurements were made using a Merck Spectroquant Pharo 300 spectrophotometer. Water samples before the measurement were not filtered.

3. Results and discussion

The analysis of the EMS value shows that biodegradation processes took place ($\text{EMS} < 1$) from the twenty third day of Filter 1 operation and essentially throughout the entire period of Filter 2 operation. The reduction of COD (KMnO_4), TOC and UV_{254} absorbance proceeded with a very high efficiency in both analysed filters, although higher effectiveness in terms of the change in COD (KMnO_4) (by 74% on average), TOC (by 80% on average) and UV_{254} absorbance (by 81% on average) was observed in the case of Filter 2 inoculated with filter backwashings. Detailed results were presented in the publications of 2016 (Holc et al. 2016a, b).

The research results presented herein are complementary to the ones already published and pertain to the possibility of using the measurements of UV absorbance at the wavelengths of 204 nm, 254 nm, 365 nm and 436 nm, respectively, for the purpose of interpretation of the transformations of organic compounds in biological activated carbon filter beds.

The quality of water at entry to the physical filter model is presented in Table 1.

Figure 2 show the changes in the UV_{254} absorbance value in water across the F1 and F2 filter beds. The UV_{254} absorbance value at entry differed significantly and ranged from 0.001 cm^{-1} to 0.0194 cm^{-1} . The average value of UV_{254} absorbance in water supplied to the filter was 0.0051 cm^{-1} . As a result of the filtration of water through the biologically active filter bed, the absorbance value went down even to 0.0000 cm^{-1} , which is an evidence of very high effectiveness of organic pollutants removal. The difference in the UV_{254} absorbance value in water occurring

between the inflow and the outflow is the smallest at day 23 of filter operation. On this day, based on the EMS value, for the first time the biodegradation processes prevailed in the filter bed. Since then, the change of absorbance value UV_{254} , in inflow and outflow, is systematically increasing. This indicates that organic compounds containing an aromatic ring in their molecule are removed in the biodegradation process.

Table 1. Quality parameters and concentrations found in the water supplied to BAF columns

Tabela 1. Parametry jakościowe i stężenia w wodzie dopływającej do kolumn BAF

Parameter	Unit	Range	Average value	Standard deviation
Temperature	°C	16.2-21.8	18.5	1.5
pH	–	7.23-7.35	7.3	0.05
DO	mg O ₂ /dm ³	6.85-8.90	8.2	0.6
Alkalinity	mg CaCO ₃ /dm ³	147-230	169	24
COD (KMnO ₄)	mg O ₂ /dm ³	2.65-4.88	3.6	0.7
TOC	mg C/dm ³	4.4-5.5	4.8	0.6
UV ₂₅₄	cm ⁻¹	0.001-0.0194	0.0067	0.0051

The different values of the UV_{254} absorbance within the filtration bed reflect the varying effectiveness of the elimination of organic compounds determined on the basis of UV_{254} absorbance in both filters. Most likely, the differences can be attributed to the methods of the filter bed activation and different microorganisms found in the two beds which played a role in the biodegradation process (Holc et al. 2016a, b).

In the analysis of the results, attention was paid to the interdependencies of the absorbance ratios measured at different wavelengths. Such a correlation offers indirect information about organic substances contained in the analysed water and the transformations they undergo. The evaluated ratios included UV_{254}/UV_{204} , UV_{254}/UV_{436} and UV_{254}/UV_{365} and the results are presented in Figures 3-5.

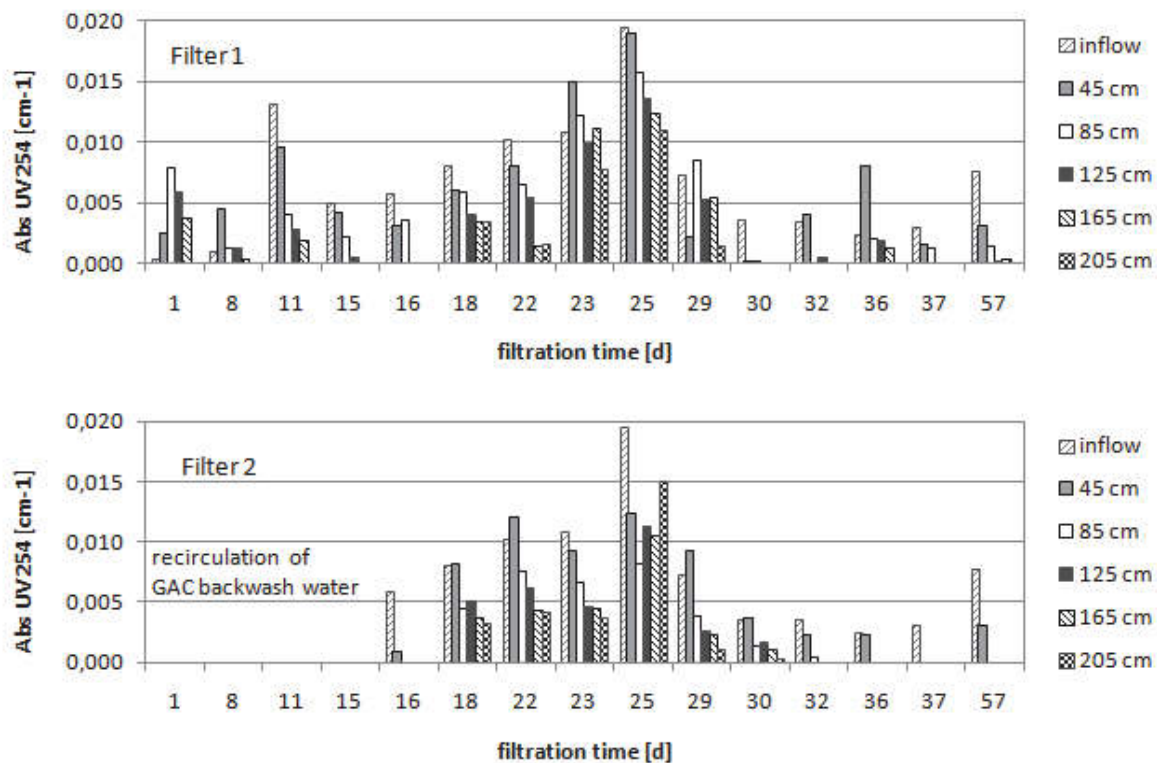


Fig. 2. Changes in the UV_{254} absorbance ratio in filter F1 and F2

Rys. 2. Zmiany wartości absorbancji UV_{254} w filtrze F1 i F2

The values of UV_{254}/UV_{204} and UV_{254}/UV_{436} ratios in both F1 and F2 filter showed minor changes in the initial period of the system operation. From the 30th day of continuous operation, a clear drop in the values of the abovementioned absorbance ratios was observed. The values recorded at the time were very low which evidences high effectiveness of aromatic organic compounds removal by way of biodegradation and that water potential for the formation of disinfection by-products is very low. Analyzing the obtained values in the vertical cross-section of filters, from the 30th day, it should be noted that for the correlation UV_{254}/UV_{204} the highest values were obtained in samples taken from the upper filter layers that indicate the most intense development of microorganisms capable of biodegradation in that part of the filter. This phenomenon is known and often described in many literature items (Simpson 2008, Pruss et al. 2009).

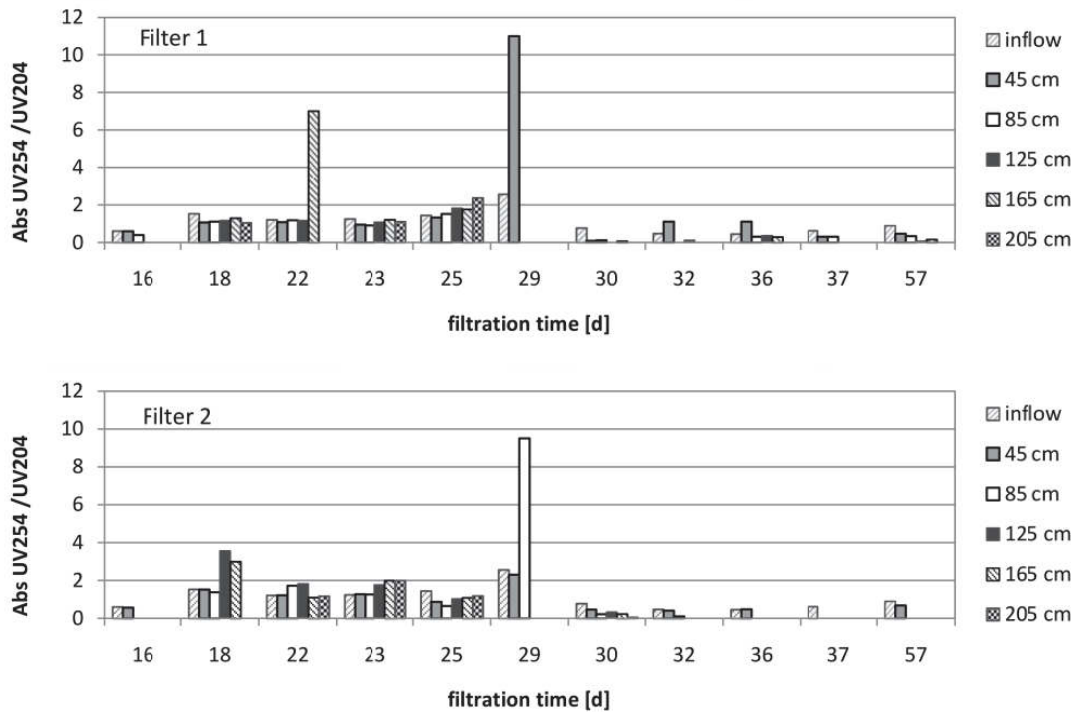


Fig. 3. Changes in the UV_{254}/UV_{204} absorbance ratio in filter F1 and F2
Rys. 3. Zmiany wartości absorbancji UV_{254}/UV_{204} w filtrze F1 i F2

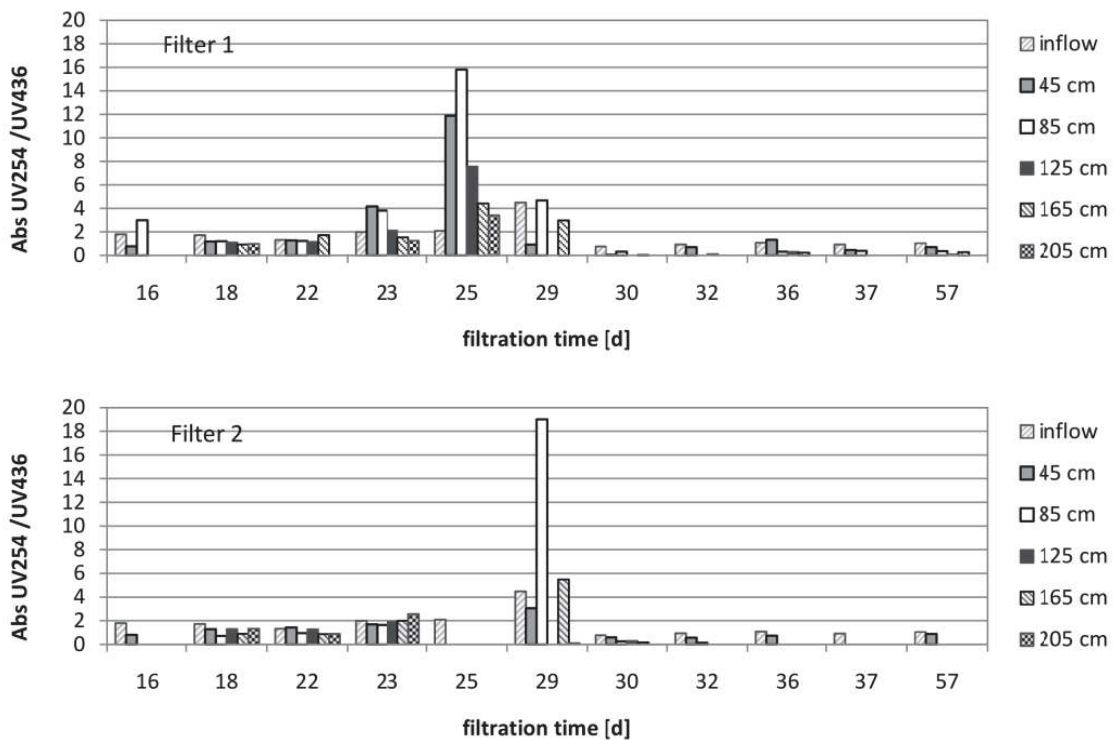


Fig. 4. Changes in the UV_{254}/UV_{436} absorbance ratio in filter F1 and F2
Rys. 4. Zmiany wartości absorbancji UV_{254}/UV_{436} w filtrze F1 i F2

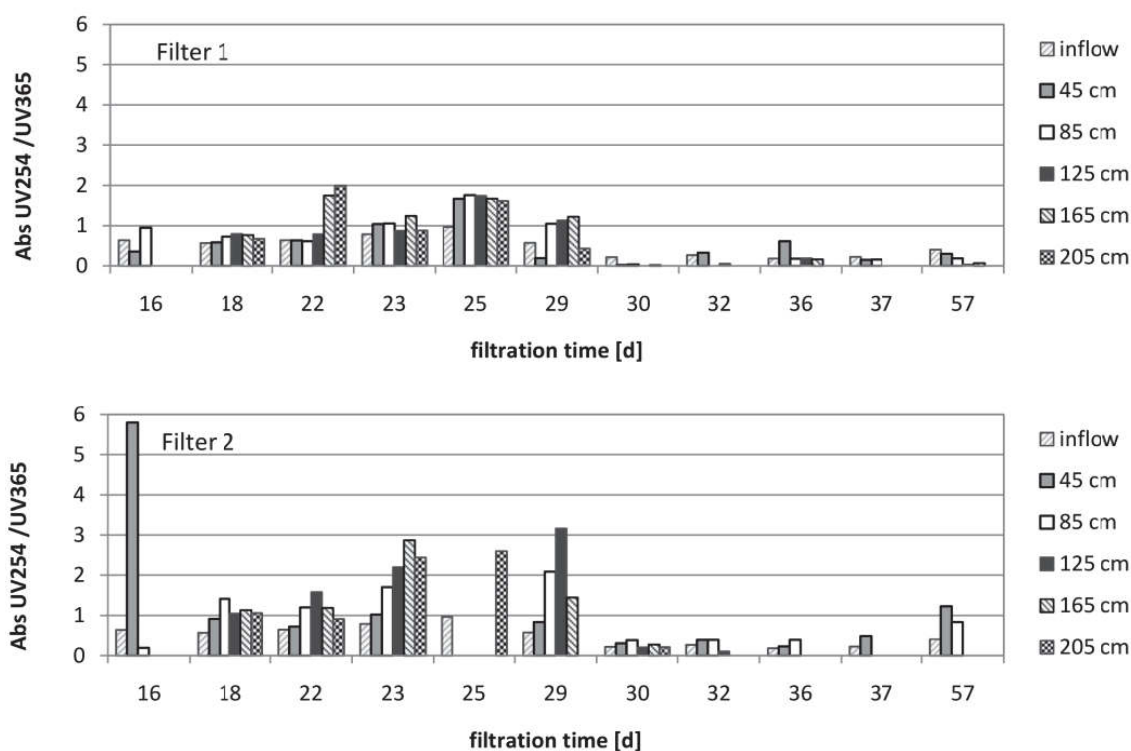


Fig. 5. Changes in the UV_{254}/UV_{365} absorbance ratio in filter F1 and F2

Rys. 5. Zmiany wartości absorbancji UV_{254}/UV_{365} w filtrze F1 i F2

The UV_{254}/UV_{365} relationship allows for the tracking of changes in the size of particles of the dissolved organic matter. Throughout the entire period under review, the value of UV_{254}/UV_{365} ratio remained low in both analysed filters. As of the 30th day of operation a clear decrease in its value was observed. Low values of the UV_{254}/UV_{365} ratio are often recorded in the presence of aromatic functional groups (Yan et al. 2012).

4. Conclusion

The filtration of water using biological activated carbon filters is a process which ensures effective removal of organic substances from water. Due to the significant role of microorganisms found in biological activated carbon filters in the elimination of biodegradable organic matter, the proper operation of the filters is very important.

The use of UV radiation may greatly improve the monitoring of the filter performance. The investigations have proven that it is possible to use the measurements of UV absorbance at the wavelengths of 204 nm, 254 nm, 365 nm and 436 nm, respectively, for the interpretation

of the transformations of organic compounds in biological activated carbon filters. It is worth emphasising that absorbance measurements are quick and can significantly facilitate the work of water technology engineers in charge of the treatment processes, especially in that Water Treatment Plants which use biological activated carbon filters and are equipped with UV absorbance analyzers operating in an online mode.

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Możliwość wykorzystania pomiarów absorbancji UV do interpretacji wyników usuwania materii organicznej w procesie biofiltracji

Streszczenie

Naturalna materia organiczna (NOM), czyli substancje organiczne występujące w wodach naturalnych, to heterogeniczna mieszanina związków, wciąż nieodkryta z chemicznego punktu widzenia. Standardowe wskaźniki jakości wody, takie jak chemiczne zapotrzebowanie na tlen (ChZT), rozpuszczony węgiel organiczny, absorbancja UV₂₅₄, pH i inne, nie dostarczają wystarczających informacji o charakterze NOM, takich jak masa molowa, czy hydrofobowość. Do scharakteryzowania NOM coraz bardziej przydatna okazuje się absorbancja UV dla różnych długości fal.

Absorpcja UV jest popularnym i względnie prostym wskaźnikiem określającym zawartość zanieczyszczeń organicznych w wodzie. Grupy funkcyjne związków organicznych pochłaniają promieniowanie UV i VIS to chromofory. Uważa się, że różne chromofory są identyfikowane przez różne długości fal. Absorbancja UV przy długości 220 nm jest związana zarówno z chromoforami karboksylowymi jak i aromatycznymi, podczas gdy absorpcja UV przy długości 254 nm jest typowa dla grup aromatycznych o różnych stopniach aktywności. Na podstawie wartości absorbancji można określić całkowitą zawar-

tość rozpuszczonego węgla organicznego i związków organicznych o wysokiej zawartości pierścieni aromatycznych, które uważa się za prekursory ubocznych produktów dezynfekcji lub utleniania. Zauważono także, że zależności występujące między dwoma różnymi długościami fal, jak na przykład: 254 nm/204 nm, 254 nm/436 nm, czy 250 nm/365 nm, pomagają w charakteryzowaniu NOM.

W artykule przedstawiono wyniki badań nad wykorzystaniem absorpcji UV o różnych długościach fal do interpretacji przekształceń związków organicznych w biologicznie aktywnych filtrach węglowych (BAF). Analiza tych wyników stanowi uzupełnienie informacji opublikowanych w 2016 roku (Holc i in. 2016a, b).

Badania nad efektywnością usuwania związków organicznych w procesie biofiltracji prowadzono w skali pilotowej. Stanowisko badawcze stanowiły dwie kolumny filtracyjne o średnicy 100 mm oraz wysokości 3,0 m, wypełnione granulowanym węglem aktywnym WG-12. Filtry zasilano dechlorowaną wodą wodociągową. Kolumny filtracyjne różniły się między sobą sposobem aktywacji złoża filtracyjnego. Skuteczność eliminacji substancji organicznych z wody oceniano za pomocą następujących parametrów: pH, tlen rozpuszczony, zasadowość, utlenialność, OWO, absorpcję UV dla kilku długości fal: 204 nm, 254 nm, 365 nm i 436 nm.

W trakcie prowadzonych badań zauważono, że w wyniku filtracji wody przez złożę BAF, wartość absorpcji UV_{254} obniżyła się nawet do 0 cm^{-1} , co świadczy o bardzo wysokiej efektywności usuwania zanieczyszczeń organicznych. W trakcie przeprowadzonych badań zaobserwowano także korelację między wartościami absorpcji mierzonymi dla różnych długości fal. W obu kolumnach filtracyjnych odnotowano bardzo niskie wartości stosunku absorpcji: UV_{254}/UV_{204} i UV_{254}/UV_{436} , co wskazuje na skuteczne usuwanie aromatycznych związków organicznych z wody poprzez biodegradację.

Abstract

Natural organic matter (NOM) found in natural waters, is a heterogeneous mixture of compounds, still undiscovered from a chemical point of view. Standard water quality indicators, such as chemical oxygen demand (COD), dissolved organic carbon (DOC), UV_{254} , pH and others, do not provide information about the nature of NOM, such as molar mass or hydrophobicity. UV absorbance at different wavelengths is becoming more and more useful for characterizing NOM.

UV absorption is a popular and relatively simple indicator determining the content of organic pollutants in water. The functional groups of organic compounds absorbing UV and VIS radiation are chromophores. It is believed that different chromophores are identified by different wavelengths. The UV

absorbance at 220 nm is associated with both carboxylic and aromatic chromophores, while UV absorption at 254 nm is typical of aromatic groups with different degrees of activity. From the absorbance it is possible to determine the total content of dissolved organic carbon and organic compounds with a high content of aromatic rings that are precursors of by-products of disinfection or oxidation. It was also noticed that the relationships between two different wavelengths, such as: 254 nm/204 nm, 254 nm/436 nm, or 250 nm/365 nm, can characterize NOM.

This article, presents the results of research on the use of UV absorbance at different wavelengths to interpret transformations of organic compounds in biologically active carbon filters (BAF). The analysis of these results complements the information published in 2016 (Holc et al 2016a, b).

Research on the effectiveness of organic compounds removal in the biofiltration process was carried out on a pilot scale. The test stand consisted of two filtration columns with a diameter of 100 mm and a height of 3.0 m, filled with granulated activated carbon WG-12. The filters were fed with dechlorinated tap water. The filter columns differed from each other in the manner of activation of the filter bed. The effectiveness of organic substances elimination from water was assessed using the following parameters: pH, dissolved oxygen (DO) concentration, alkalinity, chemical oxygen demand (COD KMnO_4), total organic carbon (TOC) and UV absorbance for the following wavelengths: 204 nm, 254 nm, 365 nm and 436 nm.

In the research, it was noticed that as a result of filtration of water through the BAF bed, the absorbance value of UV_{254} decreased even to 0 cm^{-1} , which indicates very high efficiency of removing organic pollutants. During the research, was observed the correlation between the absorbance value measured at different wavelengths. There were very low values of the absorbance ratio: $\text{UV}_{254}/\text{UV}_{204}$ and $\text{UV}_{254}/\text{UV}_{436}$ in both filter columns, which indicates effective removal of aromatic organic compounds from water through biodegradation.

Słowa kluczowe:

biofiltracja, filtry biologicznie aktywne, związki organiczne, badania technologiczne w skali pilotowej, absorbancja UV

Keywords:

biofiltration, biologically active filter (BAF), organic compounds, pilot scale technological investigation, UV absorbance



Thermal-flow Study of Closed Cooling System with Cooling Towers

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1. Introduction

Although power plants are mainly seen as producers of electricity and heat, they are also significant customers of fresh water which is widely used in many technological processes including e.g.: water-steam cycle in power boiler, cooling systems cooperating with condensers or cooling installations of boiler's auxiliary equipment. The daily consumption of fresh water by large power units is usually accounted, at least, at the level of a several thousand m³.

Large demand of fresh water by power energy sector is always connected with the issues of its proper management due to the unquestionable interference of the industry with local water ecosystems. It is worth mentioning that the water demands of power plant cooling systems may strain natural water reservoirs and make power production vulnerable, as well as natural environment, to water scarcity (Loew 2016). Moreover, meaningful increase of production of wastewater and its influence on environment, recently reported by e.g. Blog (Blog 2016), indicates on the need for new restrictive regulations for water environment protection like e.g. EU directive on industrial emissions from 2010. The attempts to the modelling of changes in chemical compounds in wastewater are presented in (Skoczko 2017, Regucki 2017).

Beside environmental aspects, proper management of fresh water in cooling systems has also significant influence on the overall efficiency of electricity and heat production in coal-fired power plants, which is gradual decrease with ages (Campbell 2013). Over the years, the working

parameters of cooling installations are subjected to the changes due to e.g. reconstruction of these systems, unfavorable deterioration of the circulating pumps characteristics or deposition of mineral deposits on heat-exchange surfaces or pipelines. In order to improve the overall efficiency of currently in use power units, Ryabchikov suggested a number of specific actions, among which the retrofit of cooling water installations is one of the most important (Ryabchikov 2012). Nichols estimated that the modernization of cooling system performance in American power plants could lead to improving the overall efficiency of the unit by about 0.2-1.0% (Nichols 2008). Similar estimations, made for APEC countries, indicate that the improvement of feed water heaters and condensers could update the overall power unit efficiency by a value of approximately 0.8% (Boncimino 2005).

Taking into account the abovementioned facts, closed cooling systems cooperated with cooling towers have become, in natural way, the object of research and analysis of many scientists. The interests split into two main parts focusing on the numerical modeling of the cooling systems and research of influence of ambient conditions on working parameters of cooling towers. An example of numerical investigation of the cooling system as a whole is presented by Wróblewski in (Wróblewski 2013) where the comparison of two different variants of cooling system for 900 MW ultra-supercritical power unit is done. His analysis focuses on the impact of the thermal-flow properties of the cooling system on the lowest possible pressure achieved inside the condensers. Numerical modeling of the thermal-flow conditions inside the cooling towers is presented in (Blain 2016, Opris 2017). Blain in (Blain 2016) presents the results of CFD modeling of cooling tower basing on the Poppe and Merkel equations and splitting the interior of the cooling tower into three parts: fill, spray and rain zones. The model was validated on the small scale fill (7mx7m counter-flow section) and next on the real object achieving good agreement with measurements. Opris in (Opris 2017) presents other methodology of design the cooling towers using block-modules which takes into account division of the cooling tower into three main parts: spray and fill zone, rain zone and natural draft zone.

Another approach focuses on the influence of the ambient conditions, strength and direction of wind or air-water flow ratio on heat and mass processes inside the cooling towers. Li in (Li 2018) shows that cold

inflow at the top of the cooling tower could have unfavorable influence on the natural draft blocking heat rejection. Her experiments, done on 20 m test cooling tower, indicate that the undesired turbulence inside the cooling tower could cause the increase of outlet cooling water temperature even up to 3°C. Similar consideration presents Weiliang in (Weiliang 2016) analyzing the influence of wind on the operational conditions of cooling tower. The vortices, created by the wind in outer and inner space of cooling tower, affect air flow decreasing the efficiency of heat and mass processes. He considers the implementation of windbreaks to prevent the deterioration of the cooling performance inside the natural draft dry cooling tower. The influence of air water flow ratio on the operating performance is studied by Liu in (Liu 2017). She shows that various meteorological parameters have a significant impact on the large variation of air water flow ratio what causes unstable operation of cooling tower. Martín in (Martín 2017) evaluates the influence of weather conditions and cooling tower localization on its operation parameters. He shows that weather conditions have an significant influence on non steady production of energy by power units. Among others, he confirms that the extreme temperatures in summer time reduce the electricity production capacity due to limitations in the heat transfer capacity inside the cooling tower.

The paper presents the thermal-flow study of a closed cooling system with special emphasis on the operating parameters of the cooling tower. The uniqueness of the analysis lays in measurements done inside the working cooling tower to identify the heat and mass transfer processes across its radius. Next, the analysis of a cooling water temperature drop, in the cooling system cooperated with a set of cooling towers, is considered. As an example of these studies there are calculated the optimal cooling water flow rates through the cooling towers to achieve the highest possible cooling water temperature drop in the installation.

2. Study of thermal-flow processes inside cooling tower

Cooling systems are very important parts of the power units and, as it was mentioned previously, they have a significant influence on the overall efficiency of electricity and heat production. The scheme of a closed cooling water system cooperated with natural draft cooling tower is presented in Fig. 1.

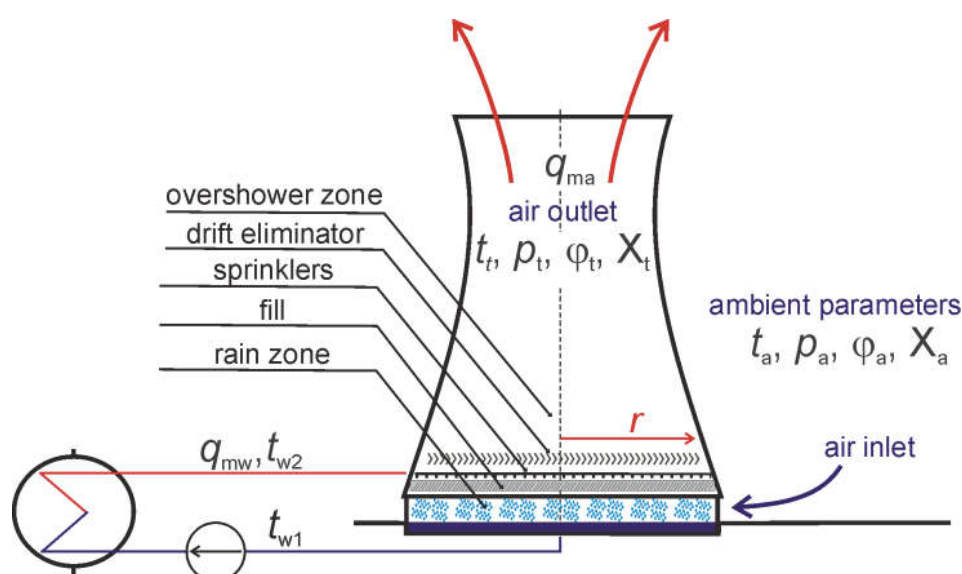


Fig. 1. Scheme of closed cooling water system with natural draft cooling tower. The symbols used in the drawing: t_a, t_t – temperature of the air; p_a, p_t – pressure of the air; φ_a, φ_t – relative humidity of the air; X_a, X_t – absolute humidity of the air at inlet and outlet respectively; q_{ma}, q_{mw} – mass flow rate of air and cooling water respectively; t_{w2}, t_{w1} – temperature of cooling water at inlet and outlet respectively

Rys. 1. Schemat zamkniętego układu chłodzenia z chłodnią kominową.

Oznaczenia przedstawione na rysunku: t_a, t_t – temperatura powietrza;

p_a, p_t – ciśnienie powietrza; φ_a, φ_t – wilgotność względna powietrza;

X_a, X_t – wilgotność bezwzględna powietrza odpowiednio na wlocie i wylocie

z chłodni; q_{ma}, q_{mw} – strumień masy powietrza i wody chłodzącej;

t_{w2}, t_{w1} – temperatura wody chłodzącej na wlocie i wylocie z chłodni kominowej

Circulating water is heated in a condenser by condensing steam from the low pressure turbine, and it is then cooled down in a cooling tower. The main mechanism of water temperature decrease inside the cooling tower is by its partial evaporation in contact with counter flowing air (Berman 1961). This phenomenon causes a continuous decrease in the mass of the circulating water in the installation which is replenished from natural resources. In the natural draft cooling tower the heat and mass transfer processes take place in two ways (notations according to Fig. 1):

- an increase in the temperature of the flowing air $\Delta t_t = t_t - t_a$
- an increase of the humidification of the flowing air $\Delta X = X_t - X_a$ (what results in changes of relative humidity of the air $\Delta \varphi_t = \varphi_t - \varphi_a$),

where:

t_a, t_t – air temperature,

X_a, X_t – absolute humidity of air,

φ_a, φ_t – relative humidity of air at inlet and outlet of the cooling tower, respectively.

The analysis shows that the highest temperatures of the returning cooling water t_{w1} are in summer time when the ambient air temperature t_a is high (in Poland ambient temperatures varies then between 20-30°C). Worse heat exchange conditions in the closed cooling system causes seasonal deterioration of the overall power unit efficiency (due to the fact of higher achievable pressure inside steam condensers), what leads to the increase of fossil combustion and, therefore, higher emission of GHG and other pollutants (Martín 2017, Campbell 2013). Table 1 presents an example of measurements done in June inside the natural draft cooling tower along the radius r (where $r = 0$ is at the center line of cooling tower – see Fig. 1). The investigated cooling tower has a height of 105 m and is made in the form of a hyperboloid reinforced concrete structure with natural draft. Its hydraulic load varies in the range of $q_{vw} = 20000-35000$ m³/h and thermal output is up to 300 MW. It is worth mentioning that the data presented in Table 1 for each position (r) are calculated from hundred of measurements collected in 30-minute time interval.

The measurement was done in the overshower zone above drift eliminators, where the radius of the cooling tower is $R = 35$ m. Pressure inside the cooling tower was uniformly distributed along the radius and equal $p_t = 977.7$ hPa, when the ambient pressure was $p_a = 980.0$ hPa. Additionally the profile of air velocity was measured using Testo 416 anemometer and the mean velocity u_t inside the cooling tower was 1.06 m/s.

Table 1. An example of measurements done inside the natural draft cooling tower along the radius r ($r = 0$ is at the center line of cooling tower – Fig. 1)

Tabela 1. Przykład pomiarów wykonanych wewnątrz chłodni kominowej wzdłuż jej promienia r ($r = 0$ jest na osi symetrii chłodni – rysunek 1)

Time, June hh:mm	radius r , m	air, ambient parameters		cooling tower, air at outlet		cooling tower, parameters of cooling water		
		t_a , °C	φ_a , %	t_t , °C	φ_t , %	t_{w2} , °C	t_{w1} , °C	q_{vw} , m ³ /h
15:55	2	26.4	59.0	35.3	99.5	38.5	30.7	34988
15:25	14	26.5	55.0	35.5	98.3	38.5	30.8	35585
14:55	20	27.4	53.0	35.4	97.6	38.5	30.7	34541
14:25	26	27.7	53.0	34.3	99.1	38.4	30.8	34435
13:55	29	27.9	52.0	36.0	97.3	38.4	30.8	34493
13:20	32	27.4	52.0	35.6	99.5	37.9	30.4	34628
mean value ± standard dev.		27.2±0.6	54.0±2.7	35.4±0.6	98.6±1.0	38.4±0.2	30.7±0.1	34778±441

The presented measurement data are the starting point for the analysis of mass and heat exchange processes inside a cooling tower. The authors' intention is to quantitatively analyze the data and to assess which processes play a leading role in obtaining the lowest possible outlet temperature of cooling water (especially in the summer, when the efficiency of blocks is the lowest one).

2.1. Heat and mass transfer processes inside a cooling tower

Collected data allows precisely to follow the heat exchange processes inside the cooling tower if one assumes steady thermal-flow conditions (Baker 1961):

$$c_w \cdot \rho_w \cdot q_{vw} \cdot (t_{w2} - t_{w1}) = q_{ma} \cdot (h_2(t_t, \varphi_t) - h_1(t_a, \varphi_a)) \quad (1)$$

where:

$c_w = 4189.9$ J/kgK – specific heat of water,

$\rho_w = 994.23$ kg/m³ – density of water at mean temperature equals 34.5°C,

q_{vw} – volumetric flow rate of circulating water,

q_{ma} – mass flow rate of air flowing inside the cooling tower,

t_{w2}, t_{w1} – inlet and outlet temperature of circulating water, respectively,

h_2, h_1 – enthalpy of moist air leaving and entering cooling tower, respectively.

Basing on values from Table 1, left hand side of (1) gives the heat flux released into the flowing air by cooling water (if one neglects the loss of water mass due to its partial evaporation process) $Q_w = 308.5$ MW. On the other side, the value of heat flux taken by the air is equal $Q_a = 315.4$ MW, where q_{ma} is calculated for air parameters inside the cooling tower: $u_t = 1.06$ m/s and $\rho_t(t_t, \varphi_t, p_t) = 1.08$ kg/m³.

The discrepancy between obtained values of heat fluxes $e = (Q_w - Q_a)/Q_w$ is at the level of 2.2% what is a very good result. This difference could be corrected if one takes into account a correction connected with the loss of circulating water Δq_{vw} due to its partial evaporation:

$$Q_w = c_w \cdot \rho_w \cdot (q_{vw} \cdot t_{w2} - (q_{vw} - \Delta q_{vw}) \cdot t_{w1}) \quad (2)$$

Amount of evaporated water is calculated from the difference of absolute humidity of air entering and leaving the cooling tower X_a and X_t respectively:

$$\Delta q_{mw} = q_{ma} \cdot (X_t(t_t, \varphi_t) - X_a(t_a, \varphi_a)) \quad (3)$$

For analyzed data, this value is $\Delta q_{mw} = 394.0 \text{ m}^3/\text{h}$. This is approximately 1% of total mass flow rate of circulating water and is in very good agreement with literature (Berman 1961). Correction of heat flux released by cooling water due to its partial evaporation is $\Delta Q_w = 14.0 \text{ MW}$. Finally, corrected value of total heat flux transferred from the cooling water is now equal $Q_w = (308.5 + 14.0) \text{ MW} = 322.5 \text{ MW}$ but the discrepancy e is still at the level of 2%. On the other hand, the calculation of relative humidity φ_t inside the cooling tower bases on the measurement of dry- and wet-bulb temperatures of flowing air (using two A class Pt100 thermometers). If one assumes that the leaving air has $\varphi_t = 100\%$ then the total heat flux transferred to the air will be $Q_a = 321.6 \text{ MW}$ and final discrepancy between corrected heat fluxes Q_w and Q_a is less than 1%.

Summarizing the above calculations, it seems that to balance correctly heat and mass transfer processes inside the cooling tower it is necessary to take into account the loss of circulating water as well as to assume that the air above the overshower zone is fully saturated and is at its dewpoint (what means that the relative humidity of leaving air φ_t equals 100%). It is worth mentioning that the source of potential discrepancies in analyzed results may be, on the one hand, the accuracy of the measurements made, and on the other, the use of an 0-dimensional heat and mass exchange model.

It is interesting how the total heat flux Q_a is divided between increase of temperature Δt_t and changes of humidification (expressed by changes of relative humidity $\Delta \varphi_t$) of the flowing air:

$$Q_a = Q_{a\Delta t} + Q_{a\Delta \varphi}, \quad (4a)$$

$$Q_{a\Delta t} = q_{ma} \cdot (h(t_t, X_a) - h_1(t_a, X_a)) \quad (4b)$$

$$Q_{a\Delta \varphi} = q_{ma} \cdot (h_2(t_t, X_t) - h(t_t, X_a)) \quad (4c)$$

For analyzed data, $Q_{a\Delta t} = 37.9 \text{ MW}$ and $Q_{a\Delta \varphi} = 277.5 \text{ MW}$ (for the case of $\varphi_t = 100\%$: $Q_{a\Delta t} = 37.9 \text{ MW}$ and $Q_{a\Delta \varphi} = 283.7 \text{ MW}$, respectively). It means that the main heat exchange process between the cooling water and

air is through partial evaporation of circulating water (approximately 88%) and only 12% of total heat flux Q_a is utilized to warm up the flowing air.

Above results show how significant are ambient conditions for the proper working parameters of the cooling system. This observation is especially important because power unit operation is characterized by non-steady production of energy that strongly depends on current weather conditions.

2.2. Thermal–flow characteristic of cooling tower

The heat flux balance (1) is a starting point to much more detailed analysis of the heat and mass transfer processes inside the cooling tower which bases on enthalpy potential as the driving force (Baker 1961). The heat transfers to air from a thin film of cooling water flowing down along the fill is considered in control volume dV :

$$dQ = \alpha(t_w - t)dV + h'dG_{mw} \quad (5)$$

where: α – volume heat transfer coefficient; t_w , t – local cooling water and air temperature, respectively; h' – enthalpy of water evaporation at local bulk water temperature; dG_{mw} – mass flow rate of evaporated water, in the control volume dV . Amount of evaporated water depends on the mass transfer coefficient between the water film and air β and difference of local absolute humidities on the interface water-air in control volume dV :

$$dG_{mw} = \beta(X'_w - X'_a)dV \quad (6)$$

The equations (5) and (6) describe the amount of heat transferred from the cooling water to the counter-flowing air in control volume dV of the fill. In this approach dV is equal $S \cdot dx$ where S is a surface of the cross-section of the cooling tower (perpendicular to the direction of air flow) and dx is a small section of the height of the fill. Due to the complexity of the arrangement of the fill inside the cooling tower there is impossible to consider the heat and mass transfer processes separately for individual components of the fill but rather simplified approach is applied. This is the reason why heat and mass balance equations (5) and (6) base on overall heat and mass transfer: α , β respectively.

Basing on (5), (6) and (1), Berman in (Berman 1961) shows that the total heat transferred to the flowing air is described by equation:

$$Q = \beta \cdot \Delta h_m \cdot V = G_{ma} \cdot (h_t - h_a) \quad (7)$$

where: V – is volume of fill; G_{ma} – mass of flowing air; Δh_m – mean enthalpy increase of flowing air expressed by formula:

$$\Delta h_m = \frac{(t_{w2} - t_{w1})}{\int_{t_{w1}}^{t_{w2}} \frac{dt}{(h' - h)}} \quad (8)$$

where: h' is enthalpy of water evaporation at local bulk water temperature and h – local enthalpy of moist air flowing through the fill (Baker 1961).

On the other side, the heat released from water is calculated from (2):

$$Q = \frac{1}{K} \cdot c_w \cdot G_{mw} (t_{w2} - t_{w1}) \quad (9)$$

where: K – correction factor due to partial evaporation of cooling water, ($K \cong 0.947$). Combining together (7) and (9) one can obtain the formula for the temperature of cooling water at outlet of cooling tower, t_{w1} (Berman 1961):

$$t_{w1} = t_{w2} - \frac{K \cdot V \cdot \beta \cdot \Delta h_m}{c_w \cdot G_{mw}} \quad (10)$$

Equation (10) is a non-linear one, because value of Δh_m depends, among other, on t_{w1} . Values of V and β are calculated individually for particular cooling tower because they depend on its geometry and current ratio of air and water mass flow rates q_{ma}/q_{mw} .

Basing on the measurement data from Table 1, there was possible to calculate the characteristic of the cooling tower showed at Fig. 2.

Presented curve depends on the current inlet parameters of air (t_a , p_a , ϕ_a) and cooling water (t_{w2} , q_{mw}). It is worth noting that value of $\Delta t_w = (t_{w2} - t_{w1})$ increases (what means that t_{w1} decreases) if the volumetric flow rate of cooling water decreases. The difference between the highest and lowest value of Δt_w is about 3.3°C and shows that the proper selection of the hydraulic load of cooling tower could increase its cooling properties.

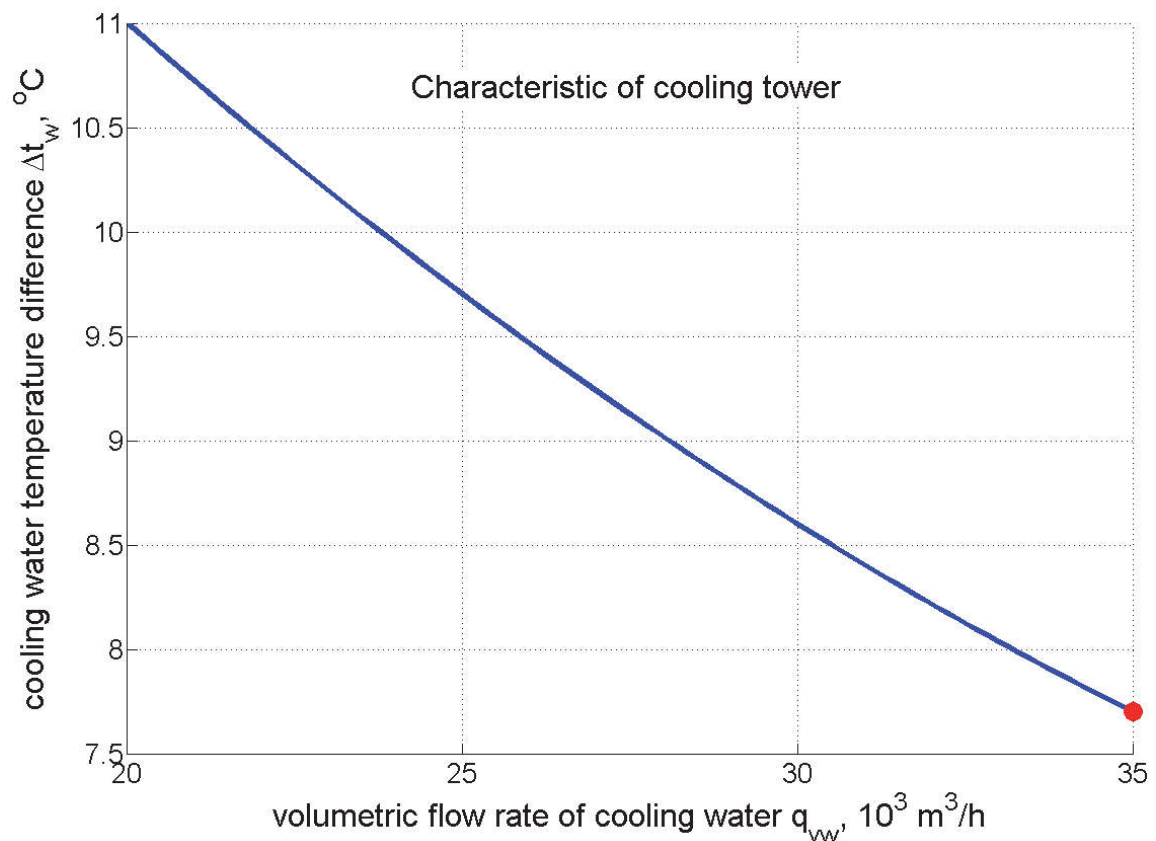


Fig. 2. Characteristic of natural draft cooling tower obtained for measurement data from Table 1. Red circle indicates actual working point of cooling tower

Rys. 2. Charakterystyka chłodni kominowej otrzymana dla danych pomiarowych z Tabeli 1. Czerwonym kołem oznaczono aktualny punkt pracy chłodni kominowej

3. Optimization of cooling process in closed cooling system

The idea of closed cooling system bases on the cooling towers, which are usually arranged in a group of few units and cooperate with several condensers of power units by common hydraulic installation. Such arrangement allows to model the flow rates to individual cooling towers in order to optimize the cooling process (Regucki 2018).

As an example of such approach one can consider the situation when two cooling towers, with different thermal characteristics show at Fig. 3, have to cool down fixed volumetric flow rate of water q_{vt} .

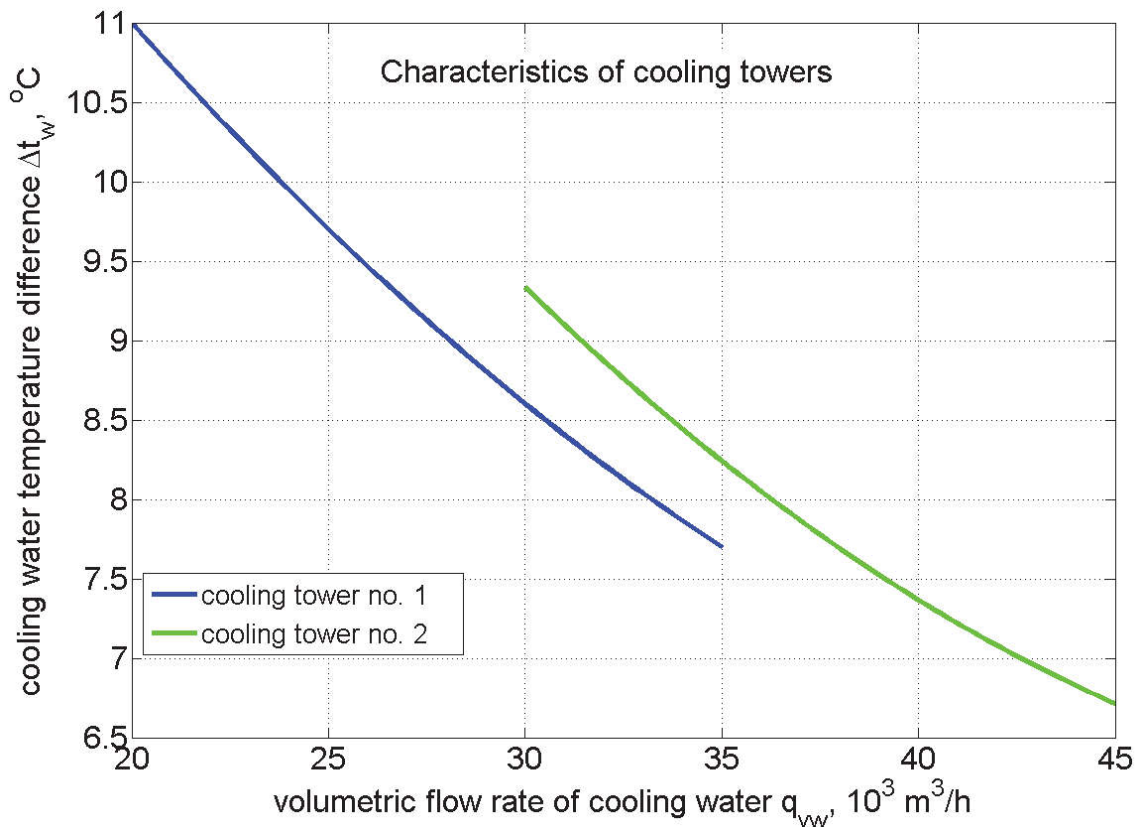


Fig. 3. Example of characteristics of two natural draft cooling towers

Rys. 3. Przykładowe charakterystyki dwóch chłodni kominowych

The total hydraulic load of these two cooling towers is between 50 and 80 thousand m^3/h . Let assume that one would like to cool down fixed flow rate of water $q_{vt} = 60,000 \text{ m}^3/\text{h}$. The optimal distribution of water between these two cooling towers could be achieved finding the maximum possible total cooling water temperature drop Δt_w :

$$\Delta t_w = (\Delta t_{w1}(q_{vw1}) \cdot q_{vw1} + \Delta t_{w2}(q_{vw2}) \cdot q_{vw2}) / q_{vt} \quad (11)$$

with constraint: $q_{vt} = q_{vw1} + q_{vw2} = 60,000$; where q_{vw1} , q_{vw2} – volumetric flow rates through first and second cooling tower, respectively. Solution of this non-linear problem is showed at Fig. 4.

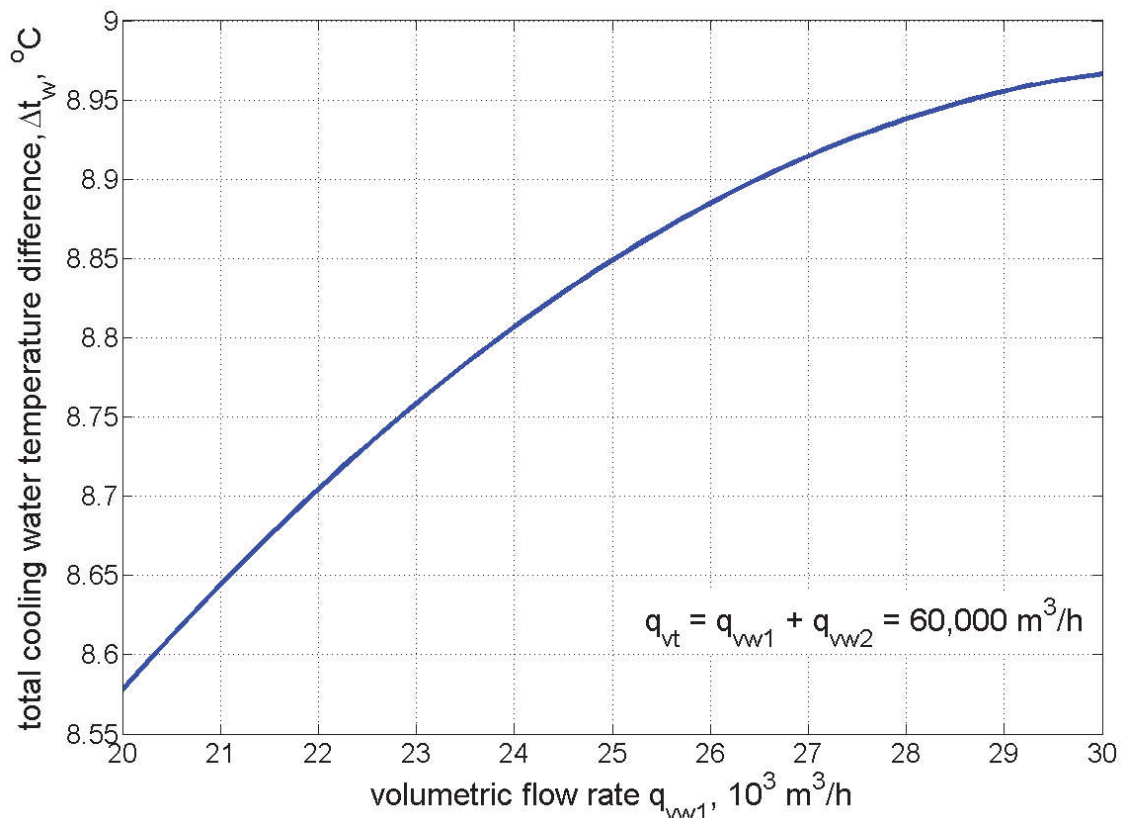


Fig. 4. Total cooling water temperature difference Δt_w calculated from (11) for characteristics presented at Fig. 3

Rys. 4. Całkowity spadek temperatury wody Δt_w obliczony z formuły (11) dla charakterystyk przedstawionych na rysunku 3

The value of Δt_w changes between 8.58 and 8.97°C. Presented calculations show that its maximum value is achieved for q_{vw1} equals 30000 m³/h (and $q_{vw2} = 30000$ m³/h). It is worth mentioning that this division of flow rates is valid for analyzed cooling water and weather (air) conditions. If the ambient temperature and relative humidity change then the characteristics will change as well and the optimal total cooling water temperature drop Δt_w could appear for other values of q_{vw1} and q_{vw2} . The problem of optimizing cooling water redistribution in a closed cooling system is a problem that should be referred to the currently analyzed installation. The example presented above was supposed to draw attention to the fact that the proper water redistribution in the cooling system has a direct impact on the obtained mean cooling water temperature in the installation t_{w1} . The presented optimization method can be applied to a system consisting of a larger number of cooling towers, if only their characteristics can be determined.

4. Conclusions

The efficient optimization process always bases on the scientific background involving mathematical modeling and numerical approach which are more and more widely used in power engineering. Due to the huge daily amount of utilized fresh water, closed cooling systems are an important part of power plants and its proper operation could significantly reduce the usage cost as well as increase the overall efficiency of power unit. Presented calculations show that, despite the simple construction, cooling towers are still subjected to research and modeling. Thermal-flow measurements across radius of cooling tower allows to identify the heat and mass exchange mechanisms between cooling water and counter flowing air. After analyzing the data, it was indicated that the measurement of relative humidity inside the cooling tower is not necessary. The calculations show that the relative humidity the inside the cooling tower can be assumed to be 100%. In addition, the presented analysis shows that the decisive parameter affecting the process of water cooling is the relative humidity of the air sucked into the tower. These observations can be used as a starting point for attempts to modernize cooling towers. Data analysis can be used to indicate representative places of measurement of thermodynamic parameters inside a cooling tower in order to evaluate its operating parameters. The presented optimization shows that the proper regulation of the flow rates between two cooling towers can increase the total cooling water temperature difference about 0.4°C. It is very important result if one pays attention to the fact that improvement of Δt_w by 1°C has a direct impact on the increase of overall efficiency of power unit by approximately 0.5%.

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Badania cieplno-przepływowe zamkniętego układu chłodzenia z chłodniami kominowymi

Streszczenie

W pracy przedstawiono cieplno-przepływowe badania zamkniętego układu chłodzenia ze szczególnym uwzględnieniem parametrów pracy chłodni kominowych. Unikalność analizy polega na pomiarze wykonanym wewnątrz pracującej chłodni kominowej w celu identyfikacji procesów wymiany ciepła i masy wzdłuż jej promienia. Następnie przeanalizowano stopień schłodzenia wody cyrkulującej w układzie chłodzenia współpracującym z zespołem chłodni kominowych. Jako przykładowy wynik tych badań zaproponowano dobór optymalnych strumieni przepływu wody chłodzącej w układzie dwóch chłodni kominowych, pozwalający uzyskać możliwie najwyższy spadek temperatury (stopień schłodzenia) cyrkulującej wody.

Abstract

The paper presents the thermal-flow study of closed cooling system with special emphasis on the working parameters of the cooling tower. The uniqueness of the analysis lays in measurement done inside the working cooling tower to identify thermal-flow processes across its radius. Next, the analysis of a cooling water temperature drop, in the cooling system cooperated with a set of cooling towers, is considered. As an example of these studies there are proposed the optimal cooling water flow rates between two cooling towers to achieve the highest possible water temperature difference in cooling system.

Słowa kluczowe:

elektrownia, zamknięty układ chłodzenia,
przeciwprądowa mokra chłodnia kominowa

Keywords:

power plant, closed cooling system, counter flow wet cooling tower



Vermicomposting of Post-harvest Maize Waste

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1. Introduction

Irrational soil use and other anthropogenic factors contribute to adverse changes in soil environment. The principal causes of soil degradation are, among others, deforestation, excessive grazing, wrong agricultural economy, industrialization and urbanization as well as biomass combustion. Nowadays, one of the most important challenges is also a problem of proper management of organic waste; if not properly used, it may contribute to environmental degradation (The EU Strategy for Soil Protection (IP/06/1241 of 22 September 2006)). Waste segregation and proper management are an important organizational issue. After the amendment of law in the system of municipal waste management in 2012-2016, an increase in the amount of selectively collected waste was noted, but ecological awareness of the society concerning waste management has been increasing slowly (Kostecka et al. 2016, Krempa et al. 2018). Still too high volume of waste is being landfilled on landfills or illegal rubbish dumps (Municipal infrastructure... 2016).

Post-harvest maize waste cultivated for seeds is a by-product remaining after plant production in agricultural farms. The waste consists of stems with leaves, cob covering leaves, cob cores, uncollected and damaged cobs as well as grain. The average crop of maize cultivated for grain was determined at the level of 14.9 Mg ha⁻¹ (Results of plant production of

2016...). In recent years, an increase in farmers' interest in sweet corn cultivation for consumption purposes has been observed. According to Niedziółka and Szymanek (2005), the residues constitute from 72 to 74.8% (depending on a cultivar and the depth of corn kernel cutting) of the total plant mass of sweet corn. In opinion of the same authors, waste parts amount to even from 24 to 31 Mg·ha⁻¹ calculated per unit area. Thus, the problem of post-harvest residues management grows together with increasing crop acreage, consumption and especially sweet corn processing. Waste remaining after corn harvest (corn straw) can be used as animal feed in agricultural farms or may be applied for field fertilization, but it is better to compost these residues and other types of organic waste (Szempliński 2012). This results from the fact that without composting, the ploughed corn residues stay in soil for years and are decomposed mainly in anaerobic conditions. The processes of decay that occur there, favour diseases and inhibit normal plant growth (Dubas & Michalski 2005). Moreover, agricultural waste including corn waste is often burnt. Instead of this, in the face of a need for constant supplementation of nutrients and organic matter in soils, the waste should be treated as a raw material for fertilizer production. Restoration of more available nutrients to soils can be also achieved using the vermicomposting process (Kostecka 2000, Villar et al. 2017, Suleiman et al. 2017, Sharma & Garg 2018).

In the present study, possibilities of using vermiculture for processing of corn straw remained after harvesting maize (*Zea mays* sp.) grown for grain were assessed. Vermicomposting of pure maize waste and waste of maize with addition of cellulose and horse manure was investigated. *E. fetida* and *D. veneta* earthworms were used for waste processing.

2. Material and methods

Experiments on vermicomposting waste mass composed of maize *Zea mays* ssp. *indurata* stems were conducted in the laboratory of the Department of Natural Theories of Agriculture and Environmental Education, University of Rzeszów. The study material consisted of maize *Zea mays* ssp. *indurata* stems that had been obtained from a field localised in Iwierzycy, in Ropczyce-Sędziszów county located 24 km from Rzeszów. The stems were mechanically ground to particles of 15-20 mm in diameter.

The second factor of the experiment were mature earthworms of species *Eisenia fetida* (Sav.) and *Dendrobaena veneta* (Rosa) with well-developed *clitellum* (Fig. 1). They were adapted to the conditions of climatic chamber for 2 weeks. Afterwards they were introduced to the respective study containers.



Eisenia fetida Sav.



Dendrobaena veneta Rosa

Fig. 1. Earthworm species used in vermicomposting of maize waste

Rys. 1. Gatunki dżdżownic wykorzystywanych do wermikompostowania odpadów kukurydzy

Studies were conducted in three experimental variants. The experiments were carried out in the climatic chamber at temperature of $20 \pm 0.5^\circ$ in containers of size 21 x 15 x 10 cm (Fig. 2, Table 1). In all the study variants the containers were filled with garden soil and in variant I – with fragmented maize stem residues, in variant II – with this organic waste added with cellulose (in the ratio of 2:1). Variant III included vermicomposting of the same maize waste with addition of horse manure (2:1). The waste (always at the amount of 300 g each) was introduced to the containers in a nylon large-mesh net and placed next to a stratification layer that was composed of garden soil. All was covered with a layer of the same soil, cardboard and nylon material, that reduced water evaporation and prevented from earthworm migrations (Fig. 2 a,b, Table 1). The experiments were run for 5 months.

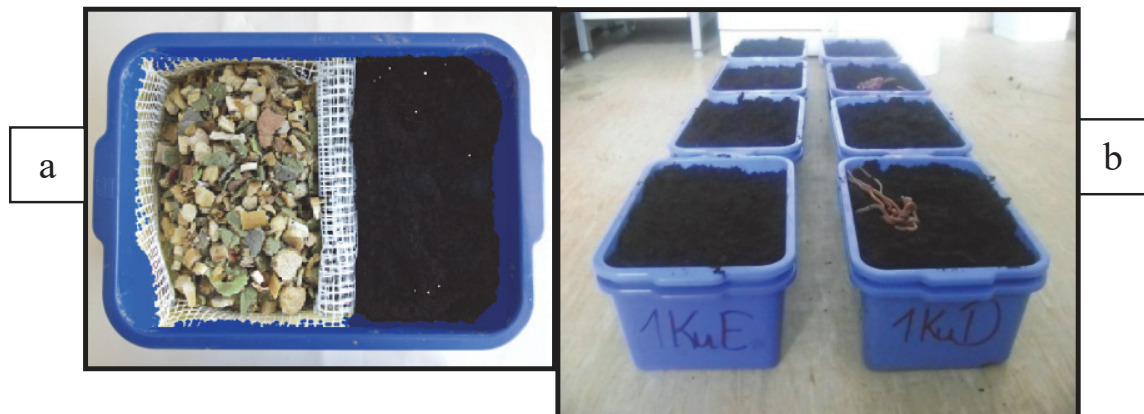


Fig. 2. Containers used in the experiment

Rys. 2. Pojemniki wykorzystywane w doświadczeniu

a – single container filled with maize residues and the stratification layer,

b – experimental series

a – pojedynczy pojemnik wypełniony resztami kukurydzy

i warstwą stratyfikacyjną, b – seria doświadczalna

Content of all the containers was regularly sprinkled (once a week) with tap water with the above characteristics. Acting in accordance with the standard (PN-ISO 2001), a constant humidity – of approximately 70% was maintained inside them.

The condition of earthworm populations in the neutralized waste was checked by the method of manual segregation of the entire volume of beddings. Biomass of the found specimens and the number of cocoons laid by them were assessed.

Maize waste and vermicompost were subjected to chemical analysis. The following were determined: C/N ratio (organic carbon using Turin's method; N- by Kjeldahl's method PN-Z (2001), pH in H₂O – by potentiometric method ISO (2005), salinity – by conductometric method, nitrate nitrogen content – using ionometer and ion-selective electrode, available phosphorus – by vanadium-molybdenum method PN-Z (2001), available potassium and calcium – using flame photometer, magnesium – on atomic absorption spectrophotometer.

Table 1. Schematic diagram of the experiment**Tabela 1.** Schemat prowadzonego doświadczenia

Study containers	Bedding – stratification layer	Earthworms	Balanced biomass of the introduced specimens	Organic waste
Experiment I – post-harvest maize residues				
1-4	garden soil (2dm ³)*	<i>E. fetida</i>	14.316±0.187 g (31±1 specimens)	300 g of fragmented maize stems
5-8		<i>D. veneta</i>	14.534±0.146 g (12±1 specimens)	
Experiment II – post-harvest maize residues with cellulose (2:1)				
1-4	garden soil (2dm ³)*	<i>E. fetida</i>	14.573±0.464 g (31±1 specimens)	200 g of fragmented maize stems + 100 g of cellulose
5-8		<i>D. veneta</i>	14.537±0.085 g (11±1 specimens)	
Experiment III – post-harvest maize residues with horse manure (2:1)				
1-4	garden soil (2dm ³)*	<i>E. fetida</i>	15.053±0.241 g (29±2 specimens)	200 g of fragmented maize stems + 100 g of horse manure
5-8		<i>D. veneta</i>	15.158±0.131 g (12±1 specimens)	
tap water**				

*universal substrate for decorative plants Fluro – hum with pH 5.5-6.5.

Composition: high-moor peat, low-moor peat, perlite, sand, microelements, NPK mineral fertilizer.

** tap water: pH 7.5 (min: 6.5; max: 9.5), nitrates 7.0 mg/l, nitrites 0.01 mg/l, total organic carbon 2.31 mg/l).

*uniwersalne podłoże do roślin ozdobnych Fluro – hum o pH 5,5-6,5.

Skład: torf wysoki, torf niski, perlit, piasek, mikroelementy, nawóz mineralny NPK.

** woda wodociągowa: pH 7,5 (min: 6,5; Max: 9,5), azotany V 7,0 mg/l, azotany III 0,01 mg/l, ogólny węgiel organiczny 2,31 mg/l).

The obtained results were presented as arithmetic means (\bar{X}) and standard deviations (SD). STATISTICA software v. 13.1 (*StatSoft*) was used for statistical calculations. Normal distribution was checked using *Shapiro-Wilk W test* and *Brown-Forsythe test* was used to confirm the homogeneity of variance. Statistically significant differences were assessed by *Student's t-test* and by variance method, using Tukey's test on Statistica PL software (Łomnicki 2014). Differences at the significance level $\alpha = 0.05$ were considered statistically significant.

3. Results and discussion

Maize waste is the type of waste that can be used for biogas production (Wiater & Horysz 2017). According to the data by Fugol and Szlachta (2010) biogas with average methane content of approximately 50-55% can be obtained from maize silage. However, aiming at such way of maize waste treatment is not entirely correct. Biomass processing for energetic purposes is not only associated with many risks (Gołofit-Szymczak et al. 2016), but also causes loss of potentially useful nutrients, including nitrogen, sulphur and carbon. Therefore, using this waste for vermicomposting is an alternative. Post-harvest maize waste is a valuable material that is a source of carbon (Table 2).

Table 2. Chemical analysis of maize stem (according to Arvanitoyannis and Tserkezou 2008) (%)

Tabela 2. Analiza chemiczna łodygi kukurydzy (za Arvanitoyannis i Tserkezou 2008) (%)

Feature	Carbon	Hydrogen	Oxygen	Nitrogen	Cellulose	Lignin	Ash	C/N
maize stem	43.6 ± 0.5	5.4 ± 0.2	42.3 ± 0.9	0.6 ± 0.1	50.4 ± 7.0	13.7 ± 1.1	0.9 ± 0.1	40-60

In the conducted experiment, a possibility of vermicomposting maize stems was demonstrated (Fig. 3). Valuable organic fertilizers were produced in all the variants of the experiment (Table 3).



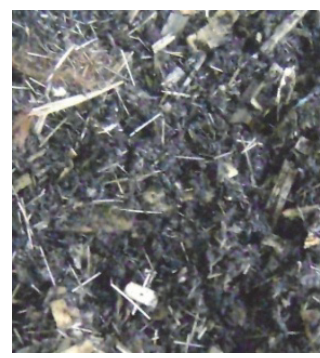
(post-harvest maize residues)

(resztki poźniwne kukurydzy)



(after 3 months of vermicomposting)

(po 3 miesiącach wermikompostowania)



(after 5 months of vermicomposting)

(po 5 miesiącach wermikompostowania)

Fig. 3. Gradual changes in the structure of bedding during vermicomposting of pure maize stems

Rys. 3. Stopniowe zmiany w strukturze podłoża podczas wermikompostowania czystych łodyg kukurydzy

Table 3. Features of vermicomposts obtained during the experiments

Tabela 3. Cechy wermikompostów uzyskanych w trakcie prowadzenia badań

Variants	<i>Eisenia fetida</i>			<i>Dendrobena veneta</i>			Optimal level for plants*
	Waste composed of			Waste composed of			
	maize stems	maize stems with cellulose	maize stems with horse manure	maize stems	maize stems with cellulose	maize stems with horse manure	
Features	min-max	min-max	min-max	min-max	min-max	min-max	min-max
pH in H ₂ O	5.8-6.1	5.9-6.1	5.8-6.1	5.6-5.9	5.9-6.1	5.8-6.1	6.0-7.5
(NaCl g·dm ⁻³)	0.5-1	1-1.5	1-1.5	0.5-1	1-1.5	1-1.5	about 1.0
NO ₃	70-72	74-88	76-97	66-68	74-79	69-88	50-120
P	67-77	79-91	89-102	66-74	81-88	91-98	40-80
K	239-252	258-268	272-289	232-247	237-255	247-263	125-250
Ca	679-704	675-726	757-780	659-688	677-707	690-730	1,000-2,000
Mg	96-122	119-146	131-156	88-118	98-127	117-136	60-120
C/N (%)	19-23	18-21	19-21	18-23	17-22	19-21	20

* according to Kończak-Konarkowska 2009

Vermicomposting of post-harvest maize stem residues in all the variants of the experiment resulted in their odourless transformation. During vermicomposting, earthworms permanently loosen organic waste. Organic and mineral aggregates of lumpy structure and increased water resistance are formed in their digestive tracts. Thus, the obtained fertilizers were characterised by lumpy structure and were rich in plant nutrients.

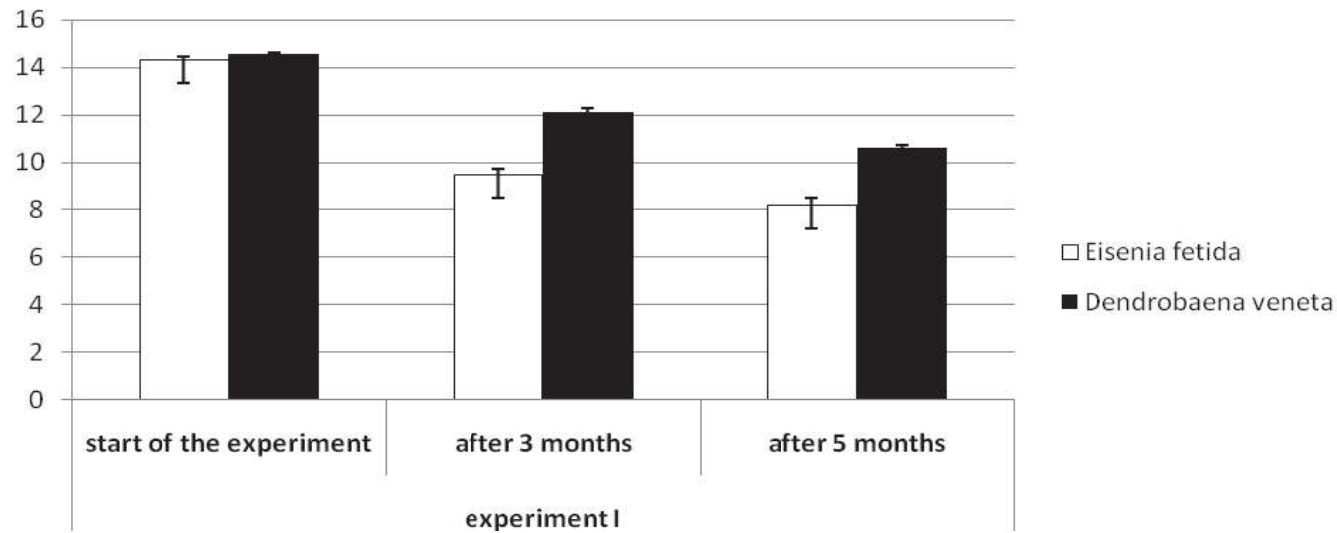
C:N ratio indicates the quality and maturity of vermicompost, so it is commonly used for the assessment of its quality. In vermicomposting process, C:N ratio can be regulated, for example, by increasing carbon content adding cardboard or straw. Therefore, variant II – post-harvest maize residues with cellulose was analysed in the present experiment. Kostecka (2000) proved that the addition of cellulose to the vermicomposted waste accelerates its processing. A decrease in C:N ratio below 20 indicates an advanced degree of organic matter stabilization (Lim et al. 2011) and expresses a satisfactory degree of organic waste maturity (Sharma & Garg 2018). On the other hand, nitrogen substances in vermicomposting process accelerate microbiological and enzymatic activity in earthworm gut, that has the effect on quicker rate of bedding mineralisation (Alidadi et al. 2016). A decrease in C:N ratio is also observed in the increased rate of humification of organic matter (Parthasarathi et al. 2016). Vermicomposts described by Sharm and Garg (2018), produced from a mixture of cattle manure, rice straw and paper, were characterised by C:N ratio fluctuating from 12.23% to 38.85%. These authors observed that when vermicomposting the above-mentioned mixtures, they obtained fertilizers characterised by various degrees of maturity: (12.23% C:N– mixture of 3:1:1) < (14.20% C:N – mixture of 9:0:1) < (14.53% C:N – waste mixture of 8:1:1). C:N ratio in maize vermicomposts amounted to 17-23%, that indicates a very high degree of maturity and stabilization of the produced fertilizer.

The obtained vermicomposts were characterised by similar features ($p > 0.05$). They did not differ in pH in water (min 5.6; max 6.1). This pH reaction was close to the neutral one, but lower compared to pH in kitchen waste vermicomposts observed by Kostecka (2000), where it amounted to between 6.5 and 7.5. Salinity in the produced fertilizer was close to the optimal level for plants (min 0.5; max 1.0). Meanwhile, Kostecka (2000) described that salinity of vermicomposts produced by

earthworms from kitchen organic waste rapidly increased throughout the year from $3.9 \text{ g NaCl}\cdot\text{dm}^{-3}$ to $12.6 \text{ g NaCl}\cdot\text{dm}^{-3}$.

Vermicomposts produced in all three variants using maize stem residues did not differ in the content of nitrate nitrogen (min 66; max 88 $\text{mg}\cdot\text{kg}^{-1}$), available phosphorus (min 66; max 102 $\text{mg}\cdot\text{kg}^{-1}$), potassium (min 232; max 289 $\text{mg}\cdot\text{kg}^{-1}$), calcium (min 675; max 780 $\text{mg}\cdot\text{kg}^{-1}$) and magnesium (min 88; max 156 $\text{mg}\cdot\text{kg}^{-1}$) ($p > 0.05$). The obtained fertilizers are a source of available nutrients for plants (table 3).

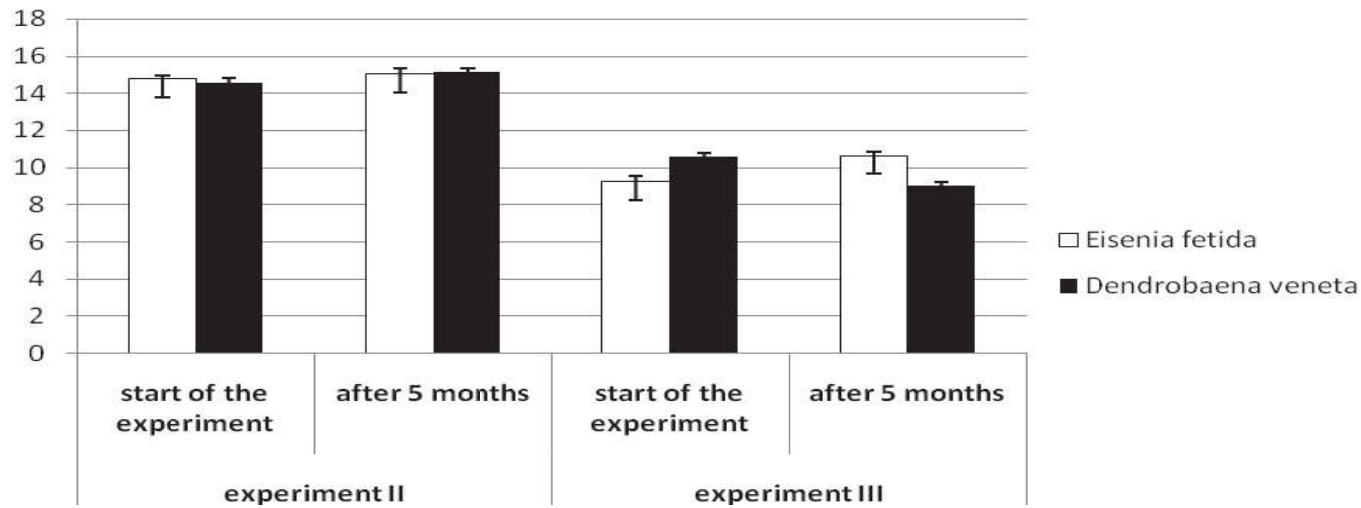
After 3 or 5 months of vermicomposting of the given waste mass, the mean earthworm biomass in all the variants of bedding was decreasing (in case of *E. fetida* in variant I it decreased by 50%, in variant II – by 30% and in variant III – by 25% ($p > 0.05$)); in case of *D. veneta* in variant I it decreased by 40%, in variant II – by 28% and in variant III – by 49% ($p > 0.05$)). The above-mentioned decreases were not statistically significant. Fig. 4 and 5 show that at the end of all the experiments the mean biomass of *E. fetida* earthworms is lower than the biomass of *D. veneta* on pure maize stem bedding, whereas the situation is opposite in case of maize stems mixed with horse manure. On maize stem bedding with cellulose, the mean biomass of both species was similar. Although the described differences between the studied species were not statistically confirmed ($p > 0.05$), they can indicate different food adaptations of the studied species. It seems that variant I of bedding – maize waste was preferred by *D. veneta* (according to Chachina et al. (2015) occurring in forests), whereas the variant with maize waste + horse manure was better for *E. fetida* species that naturally occurs in manure heap (Neuhauser 1980, Guandi et al. 2003).



(start of the experiment – mature specimens; after 3 months – mature and immature specimens;
 after 5 months of the experiment – mature and immature specimens)
 (początek doświadczenia – osobniki dojrzałe; po 3 miesiącach – osobniki dojrzałe i niedojrzałe;
 po 5 miesiącach doświadczenia – osobniki dojrzałe i niedojrzałe)

Fig. 4. Changes in the biomass of *E. fetida* and *D. veneta* earthworm populations in variant I of the experiment on pure maize stem bedding [g · container⁻¹]

Rys. 4. Zmiany biomasy populacji dżdżownic *E. fetida* i *D. veneta* w doświadczeniu I na podłożu z czystych łodyg kukurydzy [g · pojemnik⁻¹]



(start of the experiment – mature specimens; after 5 months of the experiment – mature and immature specimens)
 (początek doświadczenia – osobniki dojrzałe; po 5 miesiącach doświadczenia – osobniki dojrzałe i niedojrzałe)

Fig. 5. Changes in the biomass of *E. fetida* and *D. veneta* earthworm populations in variant II (maize stems + cellulose) and variant III (maize stems + horse manure) of the experiment [g · container⁻¹]

Rys. 5. Zmiany biomasy populacji dżdżownic *E. fetida* i *D. veneta* w doświadczeniu II (łodygi kukurydzy + celuloza) i III (łodygi kukurydzy + obornik koński) [g · pojemnik⁻¹]

Most probably, a decrease in biomass of the mean earthworm populations was a result of depletion of nutrients in the beddings, whereas a decrease in body weight of the mature specimens could be additionally conditioned by cocoon production (Kostecka 2000) (Fig. 6 a, b).

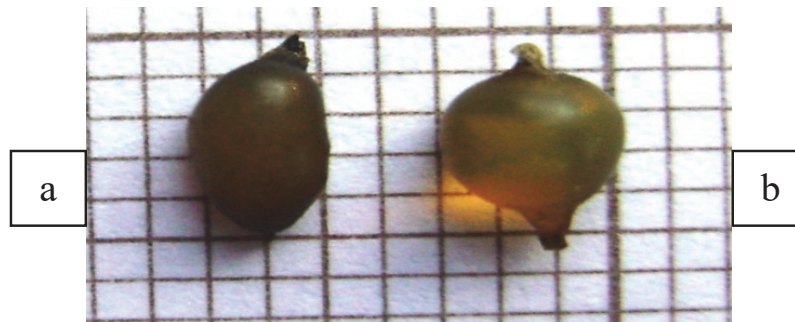


Fig. 6. Cocoons laid by *E. fetida* (a) and *D. veneta* (b) earthworms in the experiment III

Rys. 6. Kokony złożone przez dżdżownice *E. fetida* (a) i *D. veneta* (b) w doświadczeniu III

The mean count of cocoons produced by *D. veneta* was lower compared to the cocoons of *E. fetida* earthworms in all the experimental variants (Table 4). The addition of cellulose and horse manure to post-harvest maize residues had a positive effect on reproduction of *E. fetida* earthworms ($p < 0.05$) compared to the variant with maize stems only. As it was demonstrated in the studies by other authors, cocoon production in earthworms depends on many biotic (e.g. crowding in the population) and abiotic (temperature, humidity, type of food) factors (Dominguez & Edwards 2004, Monroy et al. 2006).

Table 4. The mean count of cocoons laid by one mature specimen depending on the species and variant of vermicomposted beddings

Tabela 4. Średnia liczebność kokonów złożonych przez jednego dojrzałego osobnika w zależności od gatunku i wariantu wermikompostowanych podłoży

Variant of the experiment	Mean number of cocoons / per one mature specimen	
	<i>E. fetida</i>	<i>D. veneta</i>
I – (maize)	1.60±0.01 ^a	1.08±0.00 ^a
II – (maize + cellulose)	3.87±0.01 ^b	2.30±0.001 ^a
III – (maize + horse manure)	4.30±0.001 ^b	2.70±0.003 ^a

ab – statistically significant differences, aa – no statistically significant differences

ab – różnice istotne statystycznie, aa – brak różnic istotnych statystycznie

A positive effect of cellulose on earthworm biomass growth and their reproduction was demonstrated by Kostecka & Surmiak (1999) and Kostecka (2004) as well as Kostecka and co-authors (2010). Guandi et al. (2003), analysing the changes in *E. fetida* population and the advancement of the degree of vermicomposting of cattle and pig manure, observed that the higher the growth in count and reproduction of compost earthworms, the lower the C:N ratio. In contrast, Ndegawa and Thompson (2000) noticed that during vermicomposting of paper waste mixed with oak bark, the slower the development of earthworm populations, the higher the C:N ratio.

4. Conclusions

1. Vermicomposting of maize residues is effective and the produced compost has valuable parameters. The conducted studies demonstrated that maize stems (*Zea mays*) can be processed by both *E. fetida* and *D. veneta* earthworms. Vermicomposting of this type of waste enable to provide plants with valuable nutrients in the available form.
2. The addition of cellulose and horse manure to maize stem waste did not significantly differentiate the content of principal nutrients ($p > 0.05$) in the produced vermicomposts.
3. Differences in biomass growth of both earthworm species in the studied waste and the number of cocoons laid by them indicate that *E. fetida* preferred the most maize waste with horse manure. *D. veneta* preferred pure maize waste.
4. Differences in the composition of waste vermicomposted by earthworms had a significant effect on the number of cocoons laid by *E. fetida* species.

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Wermikompostowanie odpadów poźniwnych kukurydzy

Streszczenie

W artykule przedstawiono wyniki badań nad wykorzystaniem zagęszczonych populacji dżdżownic z gatunku *Eisenia fetida* (Sav. 1826) i *Dendrobena veneta* (Rosa 1893), do unieszkodliwiania resztek poźniwnych kukurydzy zwyczajnej (*Zea mays ssp. indurata*). Doświadczenie prowadzono w warunkach komory klimatyzacyjnej w różnych wariantach (podłoże I – łodygi kukurydzy, podłoże II – łodygi kukurydzy z dodatkiem celulozy (2:1), podłoże III – łodygi kukurydzy z dodatkiem obornika końskiego (2:1)). W chowie dżdżownic na wskazanych podłożach analizowano zmiany w ich populacjach, określając biomasę oraz liczbę składanych kokonów. Otrzymane nawozy organiczne poddano analizie chemicznej. Wykazano, że odpady były utylizowane przez oba gatunki dżdżownic, a otrzymane wermikomposty posiadały korzystne właściwości jako podłoża do uprawy roślin.

Abstract

The article presents results of studies on using dense populations of *Eisenia fetida* (Sav. 1826) and *Dendrobena veneta* (Rosa 1893) earthworms for neutralization of post-harvest maize (*Zea mays ssp. Indurata*) waste. The experiment was conducted in climatic chamber conditions in various variants (bedding I – maize stems, bedding II – maize stems with cellulose (2:1), bedding III – maize stems with horse manure (2:1)). In earthworm cultures on the above-mentioned beddings, changes in their populations were analysed, assessing biomass and the number of laid cocoons. The obtained organic fertilizers were subjected to chemical analysis. It has been demonstrated that waste was neutralized by both earthworm species and the obtained vermicomposts had beneficial properties as beddings for plant cultivation.

Słowa kluczowe:

wermikultura, *Eisenia fetida* (Sav. 1826), *Dendrobena veneta* (Rosa 1893), odpady poźniwne kukurydzy

Keywords:

vermiculture, *Eisenia fetida* (Sav. 1826), *Dendrobena veneta* (Rosa 1893), post-harvest maize waste



Evaluation of Germination of Soybeans Treated with Natural Environment-Friendly Extracts Depending on the Method of their Application

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1. Introduction

The growing interest in the production of legumes, including soybean, is partly caused by integrated crop protection principles introduced into Polish agriculture, an important element of which is the rational succession of cultivated species, limiting the occurrence of harmful organisms (Ehler 2006). Legumes plants are considered a valuable link in crop rotation, not only because of nitrogen enrichment (Bagayoko 2000) but also their structure- building effect. Some varieties of legumes, including soybean, can be included in crop rotation to suppress pathogens, e.g. pathogenic root nematodes (Rodríguez-Kábana et al. 1988). The promotion of non-chemical methods in plant protection has led to the search for new, environmentally safe natural substances, referred to as biopesticides or biopreparations (Chandler et al. 2011, Kocira et al. 2017a-b, Procházka et al. 2017, Kocira et al. 2018a-b, Czerwińska & Szparaga 2015). Some of them can also be used in organic farming. One of the most important problems of organic farming is the shortage of natural seed treatments that are permissible for practical application (Rochalska et al. 2010). Lack of sufficient protection of seeds in the initial stages of development results in an incidence increase of seedlings for soil diseases. This leads to the weakening of seed sowing value and yield reduction (Shafique et al. 2016). Insufficient quality and organic seed salubrity encourages to search for alternative and natural substances used as seed treatments (Orzeszko- Rywka et

al. 2011). The aim of the conducted research was to show the influence of natural water extracts prepared on the basis of *Aesculus hippocastanum* L. on the shooting and germination of three varieties of soybean depending on the method of their application.

2. Material and methods

2.2. The greenhouse experiment

The seeds of three varieties of soybean (*Glycine max* L.) were used in the experiment: Abelina, Augusta and Merlin. The seeds were treated with aqueous extracts prepared from flowers *Aesculus hippocastanum* L. in dried form. Three types of aqueous herbal extracts were prepared: macerate, infusion, decoction, according to the procedure used by Sas-Piotrowska et al. (2005), Sas-Piotrowska and Piotrowski (2011). Decoction – 7 g of each dried plant was weighted and poured with 750 ml of distilled water. The suspension was thoroughly stirred and left for 24 hours and then boiled for 15 minutes. Macerate – 17,5 g of dried plant were poured with 350 ml of cold water and left for 24 h in temperature of 20°C, and afterwards were filtered. Infusion – 7 g of plant were weighed and poured with 350 ml of boiling water and left under cover for 30 minutes, when cold filtered. The three- factorial experiment was carried out in summer, in a greenhouse (dimensions: 6.0 m x 2.8 x 2.5 m – at the highest roof point) belonging to the Experimental Station of Varieties Testing in Karzniczka ($\varphi = 54^{\circ}29'$, $\lambda = 17^{\circ}14'$, H = 80 m above sea level). The soil used in the experiment came from a farm following the principles of organic farming. It was taken for experiment in July from the arable layer (0-20 cm) from the oat stand. Soil represented a granulometric group- sand, a subgroup - loose sand with an acidic value (pH in KCl = 5.3) and low content of bioavailable components. The soil was dried, sieved through 4 and 2 mm mesh and then mixed with peat (pH 6.5) in a 1:2 ratio (peat: ecological soil). The soil mixture with peat was wetted, mixed and then dried again.

The seeds were sown into plastic tray-fillers with 110 holes (depth 5.5 cm, width 4 cm). 50 seeds were used as a single experimental combination. Due to the requirements of statistical inference, the greenhouse experiment, carried out only in one environment, was planned in a completely random arrangement. A single series of experiments was

adopted in triplicates (Mađry 2007). Tray-fillers with seeds were placed in a greenhouse in a complete randomization system. Before starting the experiment, 400 ml of water was applied to each pot. To compare the effectiveness of water extracts on soybean germination, depending on the method of their application, two combinations of seed treatment were used: a) 24. hour soaking of seeds in extracts, drying in room conditions and then seeding into the soil to a 3 cm depth were performed. The aqueous extracts were prepared according to the procedure used in the 1st stage of testing. b) 24 hour soaking of seeds in distilled water, drying in room conditions, and then seeding into tray-fillers with spot application of the soil extracts (about 3 ml per hole) using a pipette at a depth of 3 cm were performed. Control samples were untreated seeds soaked for 24 hours in distilled water before sowing. Throughout the test, the plants were watered with tap water once a day.

In order to determine the course and pace of soybean growth, for 15 days (assuming the first day after sowing as the first), germinating seedlings were counted. During the experiment, microclimate conditions were controlled. The air temperature in the greenhouse fluctuated between 20°C (night) – 26°C (day), the temperature of the soil was about 22°C and the air humidity was approx. 50%. On the basis of the measurements carried out in the greenhouse test, the indicators indicating the vigor and the seed seeding quality were calculated: Pieper (1) and Maguire (2). Pieper's index (Jakubowski 2015) is defined as the average number of days required to germinate one seed, the Maguire's index determines the relative germination rate (Maguiere 1962):

Pieper's index (W_{Pi}) =

$$\frac{(x_1*s_1 + x_2*s_2 + \dots + x_n*s_n)}{s_1 + s_2 + \dots + s_n} \quad (1)$$

Maguire's index (W_{Magu}) =

$$\frac{s_1}{x_1} + \frac{s_2}{x_2} + \dots + \frac{s_n}{x_n} \quad (2)$$

where:

x – subsequent germination days,

s – number of seeds that normally germinated on a given day,

n – last day of the experiment.

2.2. Statistical analysis

Corrected means of the replicates of the examined plant characteristics were calculated based on data from a single series of two-factor experiments carried out in triplicate (for each variety separately, the factors tested are the form of the preparation and the method of application). Means comparisons were performed on two-way ANOVA for each variety separately and multiple comparisons (Tukey test) based on NIR (LSD). For all analyzes, the level of significance was set at $P \leq 0,05$. The analyzes were carried out using the Statistica 13 program.

3. Results and discussion

During the experiment, microclimate conditions were being monitored. These were optimal conditions for soybean germination (Tyagi & Tripathi 1983). Analysis of variance showed a significant impact of the method of application of aqueous extracts on the number of emerged plants of all soybean varieties (Table 1). Seed sowing with simultaneous dosing of preparations had a positive effect on germination and emergence, whereas the reaction of the Merlin cultivar for the technique of application was the largest (average number of plants raised 17.1- "per seeds"; 44.1 – "per soil". The results of tests carried out by other authors confirm the results from the discussed experiment. The germination rate of beet seeds (Czerwińska et al. 2016a) yellow lupine and pea (Czerwińska et al. 2016b) is better when applying extracts- infusions directly to soils than soaking in these preparations prior to seed. The beneficial effect of soil application is due to the fact that active substances contained in extracts may act, among others, as natural biopesticides and show efficacy against pathogens transmitted by seeds and soil (Perello 2013, Sengupta et al. 2008). Vegetable oils are known to be used in biological soil fumigation (Dhingra et al. 2013).

Table 1. Average values of the variety-dependent variables (average number of emergent plants, Pieper's and Maguire's index) tested, the form of the water extract and the method of its application, in relation to the control object (%)

Tabela 1. Średnie wartości testowanych zmiennych zależnych (średnie liczby wzeszłych roślin, współczynnik Piepera i Maguiera) od odmiany, formy ekstraktu wodnego oraz sposobu jego aplikacji z uwzględnieniem relacji wobec obiektu kontrolnego (%)

	Abelina			Augusta			Merlin		
application:	per seeds	per soil	average	per seeds	per soil	average	per seeds	per soil	average
Average number of emerged plants									
1 m	24,66 a	36 b	30,33 A	21,67 ac	32,33 ab	27 A	32,3 c	42,33 ac	37,33 B
2 d	33 ab	38 b	33,17 AB	16,33 c	33 ab	24,66 A	9,33 b	45,67 a	27,5 A
3 i	26,7 a	39,67 b	35,5 B	23,33 abc	37,3 b	30,3 A	9,67 b	44,33 a	27 A
\bar{X}	28,11 A	37,88 B		20,44 A	34,22 B		17,1 A	44,1 B	
Average number of emerged plants (% relative to control)									
1 m	-11,93	28,57	100	-32,29	1,04	100	-26,52	-3,79	100
2 d	17,86	35,71		-48,96	3,13		-78,79	3,79	
3 i	-4,76	41,67		-27,08	16,67		-78,03	0,76	

Table 1. cont.

Tabela 1. cd.

	Abelina			Augusta			Merlin		
application:	per seeds	per soil	average	per seeds	per soil	average	per seeds	per soil	average
Maguire's index									
1 m	2,2 a	4,52 c	3,35 B	3,29 cd	4,79 ad	4,04 A	2,85 c	6,21 b	4,63 A
2 d	3,03 a	6,01 b	4,51 A	2,57 bc	5,31a	3,94 A	0,75 a	6,56 b	3,66 B
3 i	2,03 a	5,85 b	3,94 B	1,54 b	5,92a	3,74 A	0,78 a	8,26 d	4,52 A
\bar{X}	2,42 A	5,46 B		2,47 A	5,34 B		1,53 A	7,01 B	
Maguire's index (% relative to control)									
1 m	-16,7	71,35	100	7,93	57,07	100	-40,61	29,3	100
2 d	15,02	127,6		-15,57	74,27		-84,33	36,76	
3 i	-22,8	121,9		-49,36	94,23		-83,68	72,04	

Table 1. cont.

Tabela 1. cd.

	Abelina			Augusta			Merlin		
application:	per seeds	per soil	average	per seeds	per soil	average	per seeds	per soil	average
Pieper's index									
1 m	11,7 b	8,49 a	10,1 AB	11,4 b	7,99 a	9,69 A	11,72 b	7,63 a	9,67 A
2 d	11,21 b	7,55 a	9,37 A	11,17 b	7,34 a	9,25 A	13,09 b	7,6 a	9,69 A
3 i	13,37 c	7,68 a	10,52 B	12,19 b	6,95 a	9,57 A	12,98 b	6,4 a	10,34 A
\bar{X}	12,08 B	7,9 A		11,58 B	7,42 A		12,6 B	7,20 A	
Pieper's index (% relative to control)									
1 m	6,26	-22,65	100	5,95	-25,6	100	23,67	-19,49	100
2 d	2,07	-31,26		3,87	-31,7		38,13	-19,83	
3 i	21,79	-30,02		13,44	-35,4		37,02	-32,42	

Comment: First column: 1 m – macerate, 2 d – decoction, 3 i – infusion. Average values within the same variety followed by the same letter do not differ significantly ($P \leq 0,05$). Lowercase letters are used to compare averages for combinations: form of the preparation x method of application.

The use of aqueous extracts in a "per seed" combination, i.e. with 24 hour wetting of seeds, generally limited the germination and emergence of all soybean cultivars. Only Abelina variety soaked for 24 hours in the decoction, an improvement in germination and emergence compared to the control was observed. Phytotoxic effect of natural substances may occur due to their high concentration in the prepared extracts. In the studies of Orzeszko-Rywka and Rochalska (2007) the suitability of natural preparations for the seed treatment of sugar beets was tested. It has been shown that soaking seeds in undiluted thyme oil worsens the field's ability to germinate. Undiluted oil of *Zhumeria majdae* leaves - Iranian aromatic and medicinal plant, inhibit germination of seeds and emergence of tomato and wheat seedlings (Soltanipoor et al. 2006). Treatment of seeds of other cultivated varieties, eg: *Allium cepa*, *Lactuca sativa* with an aqueous extract from *Zhumeria majdae* inhibited germination of the tested plants (Soltanipoor et al. 2007). The water extract of *Brassica nigra* leaves inhibits germination and emergency of lentil (Munir et al. 2002), wild oats (Turk & Tawaha 2002) and wild barley (Tawaha & Turk 2003) and the inhibitory effect increases with extract concentration.

The greenhouse test also showed a significant impact of the preparation form on the number of emerged plants of all varieties, however, different forms of preparations improved the value of the discussed variable. Irrespective of the treatment technique, the best results were obtained using infusions – an average of 35.5 plants of the Abelina variety, and macerate – an average of 37.3 plants of the Merlin variety. In contrast, the Augusta variety in which the seed treatment was present was average not statistically significant. However, the interaction of factors was statistically significant. Comparing the experimental results to control group, the greatest improvement in soybean germination was observed using the following forms in soil: macerate (+28.57%), decoction (+35.71), infusion (+41.67) as a seed treatment of Abelina cultivar, infusion (+16,67%) in combination with the Augusta variety, decoction (+ 3.79%) for Merlin variety. Soaking seeds of the Merlin variety in the decoction (-78.79%) and infusion (-78.03%) from *A. hypocastanum* inhibited the germination and emergence of plants to the greatest extent.

The values of germination and emergence indicators, i.e. Maguire and Pieper (Table 1) of all varieties were significantly dependent on the method of application of plant extracts. For the Merlin variety, the form

of the extract used had a significant effect on the relative germination rate. The values of the above indicators determined for the Abelina variety were also significantly dependent on the type of extract used as a treatment. The interaction of factors was also statistically significant. The soil application of extracts based on chestnut flowers improved the dynamics of soybean emergence, i.e. the acceleration of emergence by shortening the average germination time of a single seed was observed. The soil application method improved the vigor of seeds and seedlings. Prolonged and most unbalanced germination and emergence (low Maguire's index, high Pieper's index) was observed in the Merlin cultivar after 24 hours in the soaking of seeds in decoctions and infusions. Abelina and Augusta also germinated slower, but the values of the calculated coefficients were not so unfavorable. The method of application of natural plant preparations can influence the speed and uniformity of the emergence of different species belonging to the same botanical family and varieties. In research by Czerwińska et al. (2016 b) daily treatment of seeds with infusions of *Allium sativum* increased the germination rate and emergence of yellow lupine. For pea seeds, the reverse effect was obtained, similar to the observed in the independent experiment, i.e. the application of the extract from *Verbascum thapsiforme* (flowers) during seeding in the ecological soil determined the higher speed and shortening the time of emergence. The synergism in the action of the active substances contained in the various preparations used together means that the emergence of plants can proceed much faster than for each component separately. Powdered mixture of garlic and basil used for seed treatment by Rochalska & Orzeszko-Rywka (2009) significantly accelerated the field emergence of parsley. It was noted that sugar beet seeds, dinkel wheat, radishes, carrots and parsley reacted differently to active ingredients contained in all applications, but their utilization did not delay field emergence.

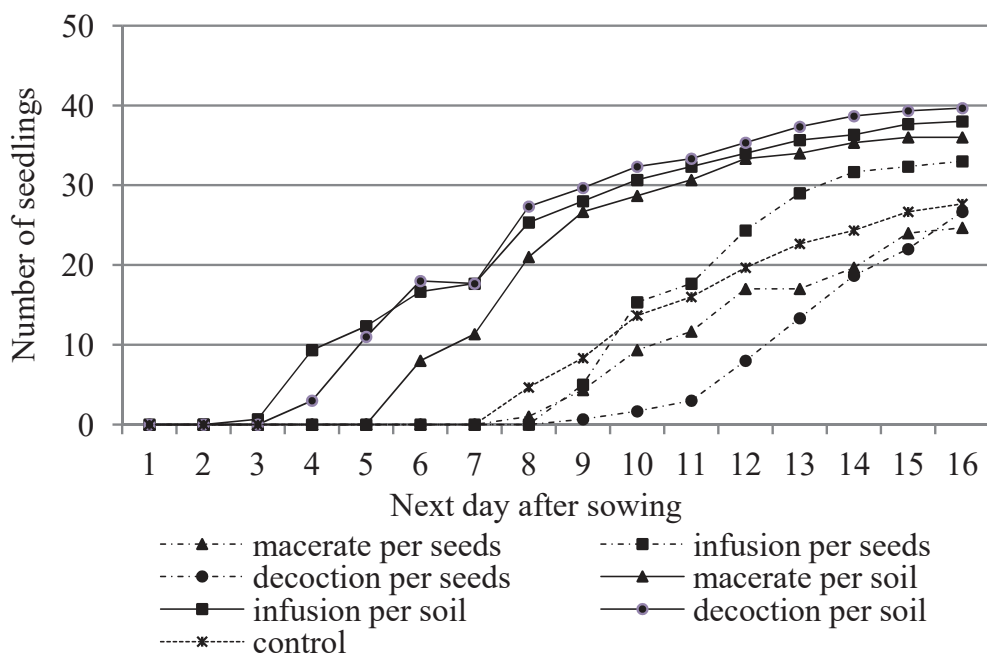


Fig. 1. Number of seeds of the Abelina, which germinated in the following days from sowing

Rys. 1. Liczba nasion odmiany Abelina, które skiełkowały w kolejnych dniach od siewu

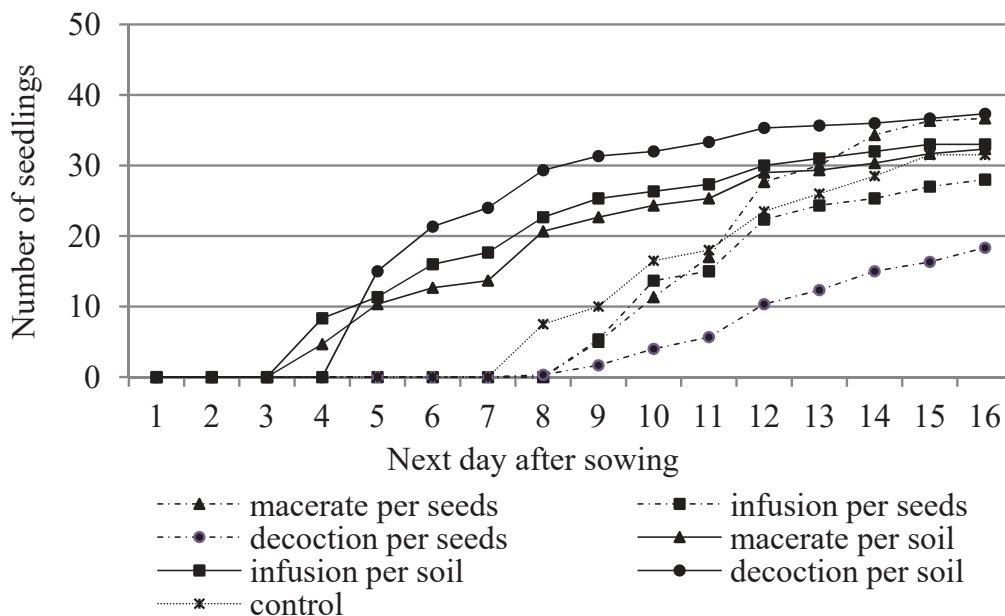


Fig. 2. Number of seeds of the Augusta, which germinated in the following days from sowing

Rys. 2. Liczba nasion odmiany Augusta, które skiełkowały w kolejnych dniach od siewu

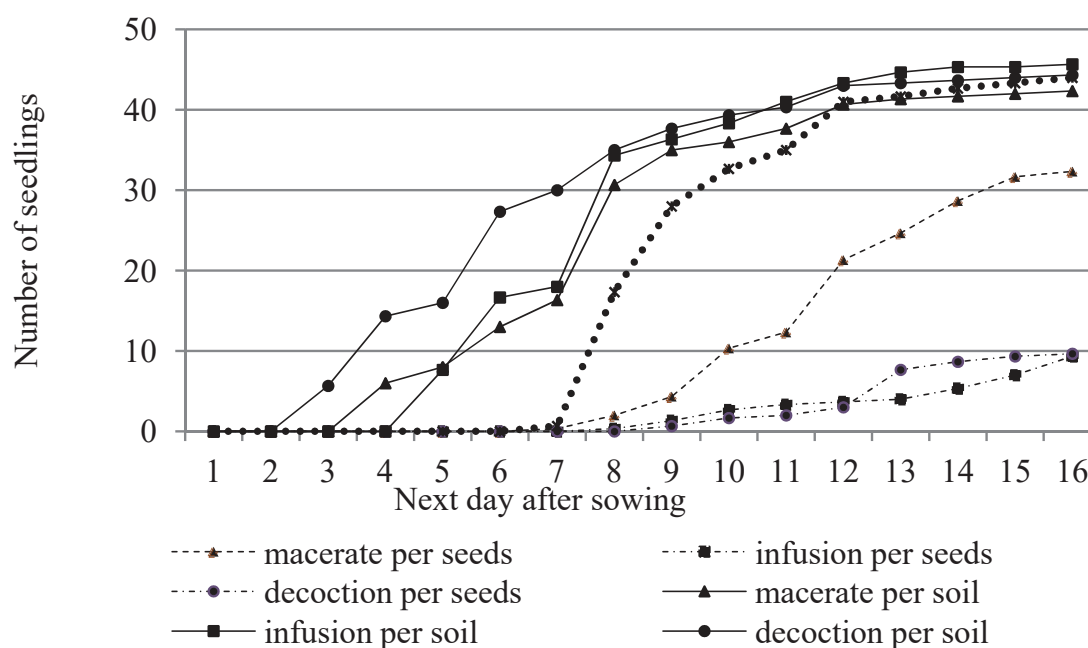


Fig. 3. Number of seeds of the Merlin, which germinated in the following days from sowing

Rys. 3. Liczba nasion odmiany Merlin, które skiełkowały w kolejnych dniach od siewu

Seeds of all varieties of soybean treated during seeding, germinated on the 3rd day of study (Figure 1-3). The first seedlings of control combinations appeared much later – one week after sowing. The seeds soaked in the extracts delayed soybean rising by 1-2 days compared to the control. Seedlings appeared very late and the emergence was the most monotonous. Extending the pre-sowing time of seed soaking in treatment solutions may lead to the weakening of their vigor. In a study conducted by Kaniewska et al. (2012) it was experimentally confirmed that with increasing concentration and prolongation of time of radish seeds storage in aqueous solutions of acetic acid, the vitality of seeds deteriorated significantly. The emerging seedlings were characterized by abnormal growth and their germination energy was low. Seeds soaked for a long time can undergo quicker damage and putrefaction.

The rapid increase in the number of emerging seedlings took place from 4 to 7 (soil application) and from 9 to 11 day of the experiment (seed soaking) (Figure 1-3). The reaction of the Augusta cultivar on seed soaking in macerate was quite unusual. For a long time after sowing, the seeds did not germinate, but after a week the seedlings began to

penetrate intensely through the soil layer. The worst emergence was observed in the Merlin variety after soaking of seeds in infusion and decoction. The emerging seedlings were low and weak.

4. Conclusions

1. Soil application of water extracts improved the germination effectiveness, quality and vigor of seeds and soybean seedlings. This is evidenced by the favorable development of the calculated coefficients: Pieper and Maguire's.
2. 24 h soaking of seeds in prepared extracts limited germination and soybean emergence. The exception was the Abelina variety, for which the seeds treated with decoction had a positive effect on the number of emerged seedlings and the speed of their emergence.
3. The form of water extract in which the seed treatment is put may have a significant effect on germination and soybean emergence, however, this relationship was not confirmed in all tested varieties.
4. The application of extracts directly to the soil may increase the effectiveness of treatment as a result of decontamination of not only the surface of the seed, but also its surroundings.

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treatment technology in the experiment.*

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Ocena kiełkowania nasion soi potraktowanych naturalnymi ekstraktami wodnymi w zależności od metody ich stosowania

Streszczenie

Soja (*Glycine max* L.) jest ważnym surowcem do produkcji pasz przemysłowych zarówno w Polsce, jak i w całej Unii Europejskiej. Niestety warunki klimatyczne, dostępne odmiany soi oraz mała podaż preparatów zarejestrowanych w tej uprawie to główna przyczyna niewielkiej produkcji w krajach UE. Przedmiotem niniejszych badań była reakcja trzech odmian soi (*Glycine max* L.): Abelina, Augusta, Merlin na naturalne, wodne zaprawy nasienne sporządzone w formie maceratu, wywaru i naparu na bazie suszu z kwiatów kasztanowca zwyczajnego (*Aesculus hippocastanum* L.). Doświadczenie zostało założone latem w obiekcie szklarniowym należącym do Centralnego Ośrodka Badań Odmian Roślin Uprawnych, Stacji Doświadczalnej Oceny Odmian w Karzniczce ($\varphi = 54^{\circ}29'$, $\lambda = 17^{\circ}14'$, H = 80 m n.p.m), zlokalizowanej w województwie pomorskim. W teście szklarniowym przez 16 dni określono średnią liczbę wzeszłych roślin po użyciu wyciągów wodnych. Na podstawie uzyskanych wyników obliczono dwa współczynniki: Piepera i Maguiera. Zastosowano dwie kombinacje aplikacji ekstraktów: dobowe zaprawianie w maceratach, wywarach i naparach, a następnie wysiew do gleby oraz wysiew moczonych w wodzie destylowanej ale niezaprawionych nasion przy jednoczesnym, ręcznym dozowaniu ziołowego wyciągu. Kombinację kontrolną stanowiły nasiona

nie traktowane preparatami, moczone przed dobę w wodzie destylowanej. Wykorzystaną w eksperymencie glebę pobrano w czerwcu z warstwy ornej (0-20 cm) spod uprawy owsa ekologicznego. Przedplonem dla owsa był ekologiczny łubin wąskolistny. Podczas 16 dni eksperymentu kontrolowano warunki temperatury i wilgotności. Wyniki eksperymentu szklarniowego wykazały, że nasiona wybranych odmian soi kiełkowały lepiej i szybciej, gdy zaprawiano je bezpośrednio podczas siewu (aplikacja doglebowa). Stosowanie ekstraktów „na nasiona” ograniczyło kiełkowanie i wschody soi. Dla dwóch testowanych odmian- Abeliny i Merlina, wykazano także istotny wpływ formy zaprawy na uzyskane wyniki w doświadczeniu. Najlepsze wschody zaobserwowano u odmiany Merlin, gdy jej nasiona moczo w wodzie destylowanej a ekstrakty aplikowano punktowo do gleby. Hamowanie kiełkowania i wschodów soi zaobserwowano po dobowym moczeniu nasion w ekstraktach w większości kombinacji doświadczalnych. Konieczne są dalsze badania w celu zidentyfikowania związków bioaktywnych zawartych w wodnych ekstraktach i ocena skuteczności aplikacji doglebowej preparatów w warunkach polowych. Przedstawione badania są niezwykle ważne z punktu widzenia praktyki rolniczej i ochrony środowiska. Poszukiwanie naturalnych metod zaprawiania nasion jest doskonałą okazją dla rolnictwa ekologicznego, gdzie nie dopuszcza się do stosowania zapraw syntetycznych.

Abstract

Soybean (*Glycine max* L.) is one of the most popular crop species in the world, which supplies raw material for the production of commercial fodder in Poland, as well as throughout the European Union. Unfortunately, climatic conditions and available varieties of soybeans and few preparations registered in plant protection are the main reason for low production in EU countries. The subject of the following study is examining the reaction of three varieties of soybeans (*Glycine max* L.): Abelina, Augusta, Merlin on natural seed treatments in the form of macerates, decoctions and infusions of *Aesculus hippocastanum* L. flowers. The experiment was carried out in a greenhouse facility belonging to Research Centre for Cultivar Testing, Experimental Station of Varieties Testing in Karzniczka ($\varphi = 54^{\circ}29'$, $\lambda = 17^{\circ}14'$, H = 80 m above sea level) in Pomeranian voivodship. In the greenhouse test, lasting 16 days the average number of sprouted plants were determined after applying water extracts and coefficients: Pieper and Maguire's. Two combinations of extracts were used: 24 h treatment in macerates, decoctions and infusions, followed by soil seeding and distilled water seeding using untreated seeds, while simultaneously dispensing herbal extracts. The control combination were seeds untreated with preparations. The soil used in the experiment was collected in June from the arable layer (0-20 cm) of organic oat field. The

forecrop was organic narrow-leafed lupine. During the 16 days of the experiment, the temperature and humidity conditions were controlled. The results of the greenhouse experiment showed that the seeds of selected soybean varieties sprouted better and faster when treated directly during seeding (soil application). The use of extracts "per seeds" limited emergence of soybean. For the two tested varieties- Abelina and Merlin, a significant effect of the seed treatment form on the obtained results in the experiment was also demonstrated. The best emergence was observed in the Merlin variety, when its seeds soaked in distilled water and the extracts were applied directly to the soil. Further research is needed to identify the bioactive compounds contained in the aqueous extracts and assess the effectiveness of the soil application of the extracts under field conditions. The conducted research is extremely important from the point of view of agricultural practice and environmental protection.

Słowa kluczowe:

Aesculus hippocastanum L., ekstrakty wodne, kiełkowanie, wschody, soja

Keywords:

Aesculus hippocastanum L., natural plant extracts, germination, emergence, soybean



Preliminary Study for Water Quality Improving in Storage Reservoir by Introducing of Artificial Phytolittoral

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1. Introduction

Eutrophication of waters is one of the main problems threatening its quality all over the world (Ilnicki 2002, Gałczyński 2008). Dam reservoirs are particularly vulnerable to eutrophication and require maintenance throughout their life-cycle for appropriate function and control (Prochal 1978, Ciepielowski 1999).

As the key building blocks of photoplankton cell walls, nitrogen and phosphorus compounds play major roles in the eutrophication process and the overabundance of phytoplankton in some lakes (Jachniak 2011). The pace of eutrophication depends primarily on the morphometric conditions of the aquatic ecosystem. The large surface area, low depth and an unfavorable shore structure increase lake susceptibility to eutrophication. Frequent mixing of lake waters further supplies phosphate from the bottom sediment. The location of the reservoir and the quality of river's water supplying the reservoir can also accelerate its degradation. On large loads of biogenes are the most exposed reservoirs located in urbanized and agricultural catchments (Koc et al. 2008, Kasza 2009, Pärn et al. 2012). Hydrological regimes in reservoirs, especially the time of water retention and fluctuations, greatly influence nutrient cycles (Soszka et al. 2012).

Zemborzycki reservoir is a small retention and recreation reservoir built on the Bystrzyca River within the borders of Lublin city and was put into use in 1974. It now protects the inhabitants of Lublin from floods and its associated hydropower plant generates energy for the surrounding areas. Since the 1990s, the reservoir has undergone unfavorable transformations from both natural and anthropogenic causes that hinder its recreational use. Anthropogenic factors including concrete banks, a lack of a littoral zone, adjacent farmland, and single family housing, as well as natural factors including small size and shallowness contributive to reservoir degradation (Sender 2007).

Littoral zones are often the richest areas of biodiversity within lake and are shaped by a variety of physical, morphological, chemical, and environmental factors (Penning et al. 2008, Khadija et al. 2015, Bolpagni & Piotti 2015). The littoral zone is also the only place where macrophytes occur.

Macrophytes are a morphologically diverse group of plants (Cook 1985, Wołek 1996). These include all national stonewort (*Charophyta*) species, some bryophytes (*Bryophyta*), a few pteridophytes (*Pteridophyta*) and a small group of seed plants (*Spermatophyta*) (Szmeja 2006). Most aquatic plant classification systems were established on the basis of growth criteria and can easily be categorized by growth form: submerged, emergent and floating-leaved.

The area of the littoral zone colonized by macrophytes in lakes is called the phytolittoral. This zone contributes greatly to the functioning of the entire reservoir. The influence this zone has on lake functioning is directly related to its diversity and size (Ozimek 1991, Thiebaut et al. 2002, Dhote & Dixit 2007, Pełechaty & Poronin 2015). Lake trophy within reservoirs greatly influences the species composition, the colonization depth and the biomass of macrophytes (Sender 2009a). The composition of aquatic plant communities is variable in time and space, mainly due to the instability of such factors as: light, temperature, quantity and availability of nutrients, sediment type, substrate angle, hydrodynamic phenomena, human pressure (Szmeja 2006, Bucak et al. 2012).

The Zemborzycki reservoir has undergone a successive eutrophication since its creation resulting in blooms of cyanobacteria that prevent recreational use. Several factors have contributed to this degradation and have adversely effected its functioning. Its 12 km of shoreline are con-

crete or surrounded by steep banks fortified with stones which prevent the development of rushes. The average depth of reservoir does not exceed 1.5 m. The large surface of the reservoir (about 280 ha), predominant western winds and a lack of well-developed rushes zone lead to significant wave action. In addition, a large portion of the shoreline is surrounded by compact buildings and farmlands. The major contaminant sources of Zemborzycki reservoir are direct discharges of wastewater to the Bystrzyca River and its tributaries from six municipal wastewater treatment facilities. The Bystrzyca river catchment area above the Zemborzycki reservoir is under severe pressure from agricultural land, which creates diffuse sources of pollution (Smal et al. 2015).

In 2010, experimental lagoons, or artificial land surfaces we introduced throughout the reservoir. Various native species were transplanted on these lagoons to enrich biodiversity within the reservoir and to reduce phosphorus supply through the plant barrier. We postulated that should be distinct, within the Zemborzycki reservoir, natural and recreation zone. Our works on the experimental creation of lagoons were carried out in the so-called natural part of reservoir. The zone in which the lagoons were located was characterized by the impact of many factors (agriculture, buildings, regulated and transformed shoreline, lack of rushes belt, strong winds). The logistic aspect was also taken into account. The first experimental construction work began in 2010, and the first plantings of native species from previously prepared seedlings in spring 2011 (Sender 2013). In the same year, in the autumn, the construction of another fragment of lagoon was started and planted the following spring in 2012. Two of the these lagoon structures were connected to the edge the reservoir. The third lagoon, which was built in autumn 2012, was constructed approximately 15m from the shore. The substrate of each lagoon was sand and gravel. Plantings were dominated by emergent macrophytes: *Typha angustifolia* L., *T. latifolia* L., *Phragmites australis* (Cav.) Trin. ex Steud., *Glyceria maxima* (Hartm.) Holmb. By 2015, these species fully occupied two of the three lagoons. At the third lagoon, which was far from the shore, waves and insulation likely contributed to failed establishment (Sender 2013).

The purpose of this study was to determine the role of these artificially constructed lagoons and their associated vegetation on phosphorus reduction throughout the reservoir. To this end, the phosphorus load from

surface flow, sources within the lake, the river flowing into the reservoir, and additional sources directly flowing into the reservoir was determined. In addition, phosphorus concentrations were measured from waters within naturally occurring vegetated areas and our artificially vegetated lagoons. The qualitative and quantitative structure of macrophytes within the reservoir was also measured prior to and post lagoon construction. In order to determine the influence of the lagoons and macrophytes on phosphorus within the reservoir data from before construction and post construction was compared. We wanted to find permanent and esthetical solution for water quality improving in storage reservoirs.

2. Study area and methods

The Zemborzycki dam reservoir (N 51°10' 45.05", E 22°31' 41.95) is located in the south-eastern part of the city of Lublin. It was created due to the dividing of the Bystrzyca River valley with a dam about 573m length. Its primary purpose is water regulation and retention but the reservoir is also utilized for recreational purposes. The south-eastern shore is comprised of mixed forests. The West bank is adjacent to agricultural fields and infrastructure of the Zemborzyce district. At the reservoir there are three resorts, including rope parks and playgrounds. There are harbors, sailing tracks and bike trails. The surface of the reservoir under normal damming is 278 ha, while at high water damming is 282 ha. The capacity under normal damming is 6.3 million m³. The length of the reservoir is 3 km and the average width is 0.8 km.

Studies were conducted in the spring, summer, and fall of 2010, 2012 and 2015. Study sites were selected: on the Bystryca River, before reaching the reservoir; at the mouth of the river; in lagoons 1 and 2 at two points -along the shore and in a more near the centre, within the recreational zone; and at the river outlet (below the reservoir) (Fig. 1). At each study site, the biomass, density, as well as the species composition of macrophytes were monitored (Sender 2009b). The syntaxsonomic system was adopted according to Matuszkiewicz (2008). Macrophytes were measured along horizontal transects. The density of emergent macrophytes was estimated at five randomly chosen sites, then to determine their biomass from the area of 0.25 m², limited by floristic fork, counting the hit ground part of shoots (only in summer). The biomass of submerged macrophytes and pleustonic was estimated using Bernatowicz

sampler of the area 0.16 m^2 and calculated per m^2 of bottom surface (Sender 2010). The visibility of the water was measured using Secchi disc. Phosphorus compounds were estimated using spectrophotometric method with ammonium heptamolybdate (PN-EN 1189) after samples were filtered three times. The reservoir trophic status was calculated using the Carlson formula (1977, behind Cooke et al. 2016).

Five piezometers from which groundwater was collected were also installed around the reservoir to assess P compounds flowing into the reservoir from ground water. The piezometers were placed at several sites: the edge of farmland (A), among the buildings (B), in the forest with buildings (D), and in the forest (E). Water was also sampled from the settler, in which ground water and rainfall collect and then enter the reservoir (C) (Fig. 1). Loading of TP and P-PO₄ were estimated using Vollenveider (1976) criteria, including concentration of total phosphorus and dissolved orthophosphates in reservoir, mean water current and mean residence time.

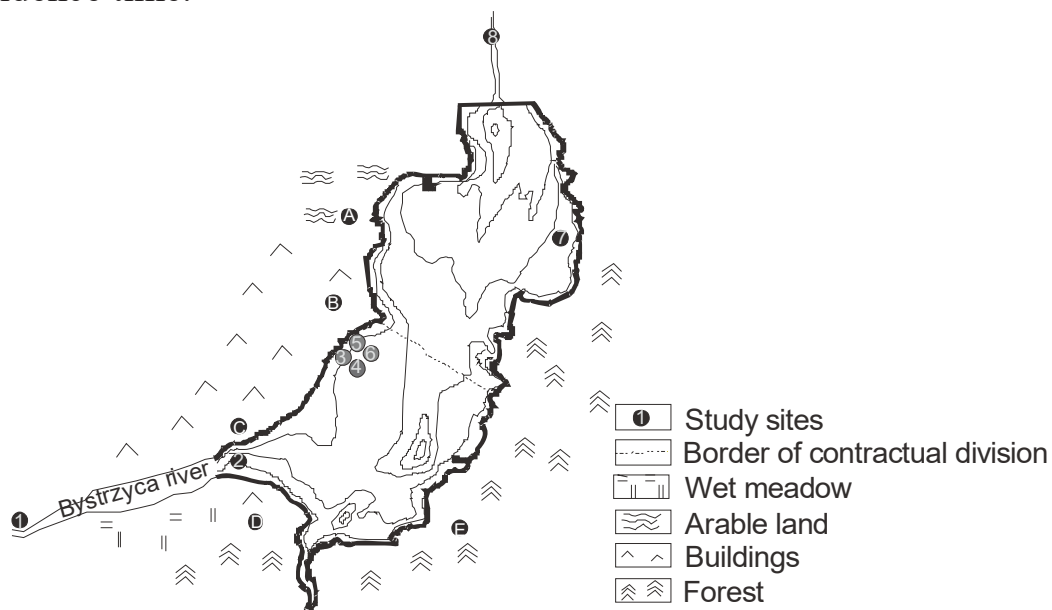


Fig. 1. Localization of study sites in investigated area: (1) the Bystrzyca River, before reaching the reservoir; (2) at the mouth of the river; (3, 4) in lagoons 1 and (5,6) in lagoons 2; (7) in a center zone of reservoir; (8) below the reservoir; and piezometers: (A) cultivated field, (B) compact development, (C) the settler, (D) in the forest with buildings, (E) in the forest.

Rys. 1. Lokalizacja stanowisk badań: (1) rzeka Bystrzyca przed wpłynięciem do zbiornika; (2) ujście rzeki; (3,4) laguna nr 1; (5,6) laguna nr 2; (7) środek

zbiornika; (8) poniżej zbiornika; piezometry: (A) pola uprawne, (B) zabudowa zwarta, (C) osadnik, (D) las z zabudową, (E) las

The influence of the water of Bystrzyca river on biomass and density of macrophytes was analysed by means of two-way ANOVA. For dam reservoir Pearson's correlation coefficients between biomass of macrophytes and P concentration was calculated. We tested P-values were considered statistically significant at the 0.01 and 0.05 level. All analysis were performed by STATISTICA program (ver.10, Statsoft). The correspondence analysis was complete in the Biodiversity Professional Version 2.

3. Results

3.1. Phosphorus concentration

The highest concentrations of total phosphorus (TP) and orthophosphates (P-PO₄) were found in the Bystrzyca River above Zemborzycki reservoir (point 1) but both declined from 2010 to 2015 from 0.8 mg dm⁻³ to 0.36 mg dm⁻³ and 0.59 mg dm⁻³ to 0.34 mg dm⁻³, respectively. In the area of inflow the Bystrzyca river, TP and P-PO₄ concentration decreased significantly and ranged from 0.45 mg·dm⁻³ TP in 2010 to 0.26 mg·dm⁻³ TP in 2015. As macrophytes developed through time, phosphorus concentration within the lagoons shows a clear reduction, decreasing from 2010 to 2012 and from 2012 to 2015.

In the littoral zone naturally formed in the reservoir, the concentration of TP ranged from 0.08 mg dm⁻³ in 2012 to 0.215 mg·dm⁻³ in 2015. The lowest values both total TP and P-PO₄ concentrations were found in the Bystrzyca river below the reservoir and ranged from 0.05 mg·dm⁻³ P-PO₄ in 2010 to 0.14 mg·dm⁻³ P-PO₄ in 2015 and 0.06 mg dm⁻³ TP in 2010 to 0.1 mg·dm⁻³ TP in 2015 (Fig.2). Most of studied parameters showed significant variability among study sites and study years (Table. 1).

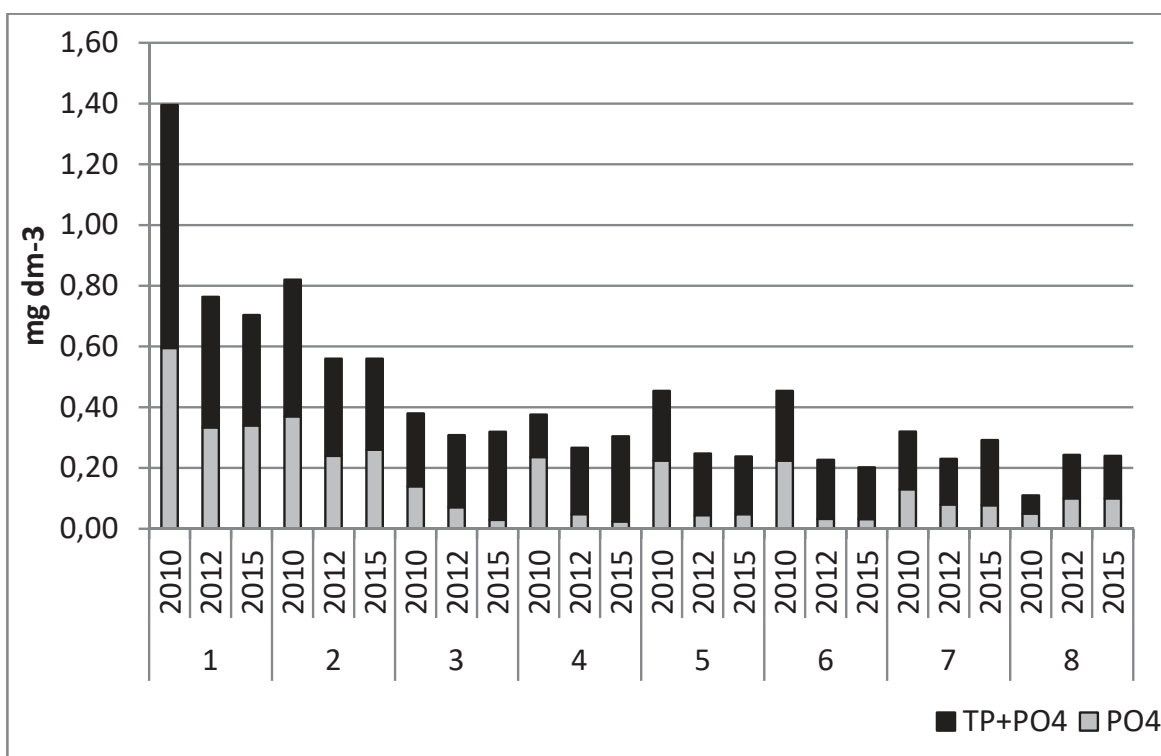


Fig. 2. Concentration of total phosphorous and dissolved orthophosphates in studied sites in particular years

Rys. 2. Stężenie fosforu całkowitego i rozpuszczonych ortofosforanów w badanych miejscach w poszczególnych latach

Table 1. Results of two-way ANOVA (site, year) for selected phosphorus concentration and macrophytes in Zemborzycki reservoir (n = 72; ns-not significant)

Tabela 1. Wyniki dwuczynnikowej analizy ANOVA (stanowiska, lata) dla wybranych, analizowanych cech makrofitów i koncentracji fosforu (n = 72; ns-nieistotne statystycznie)

	Site by site	site by year
TP	F = 3.42; p = 0.001	F = 8.98; p < 0.001
P-PO ₄	F = 17.07; p < 0.001	ns
Secchi disc (SD)	F = 11.3; p = 0.001	ns
Biomass of emergent	F = 5.62; p < 0.001	F = 6.87; p < 0.001
Biomass all macrophytes	F = 2.58; p < 0.001	F = 4.35; p = 0.001
Number of species	F = 2.86; p = 0.01	F = 6.16; p = 0.001
Emergent density	F = 25.8; p = 0.016	F = 0.59; p < 0.001

3.2. Phosphorus loadings

Loadings of TP and P-PO₄ introduced to Zemborzycki reservoir with the Bystrzyca River showed variability (Fig. 3). With the Bystrzyca River into the reservoir 4.29 g m⁻² P-PO₄ and 5.77 g m⁻² TP in 2010 was introduced. In all studied years there was a reduction in reservoir P loadings. The highest retention, 66% of P-PO₄ was noted in 2010, but in 2015 only 2%. Reduction of TP loadings was differentiated. In 2010 the highest reduction, 70% was observed and in 2012 only 25%.

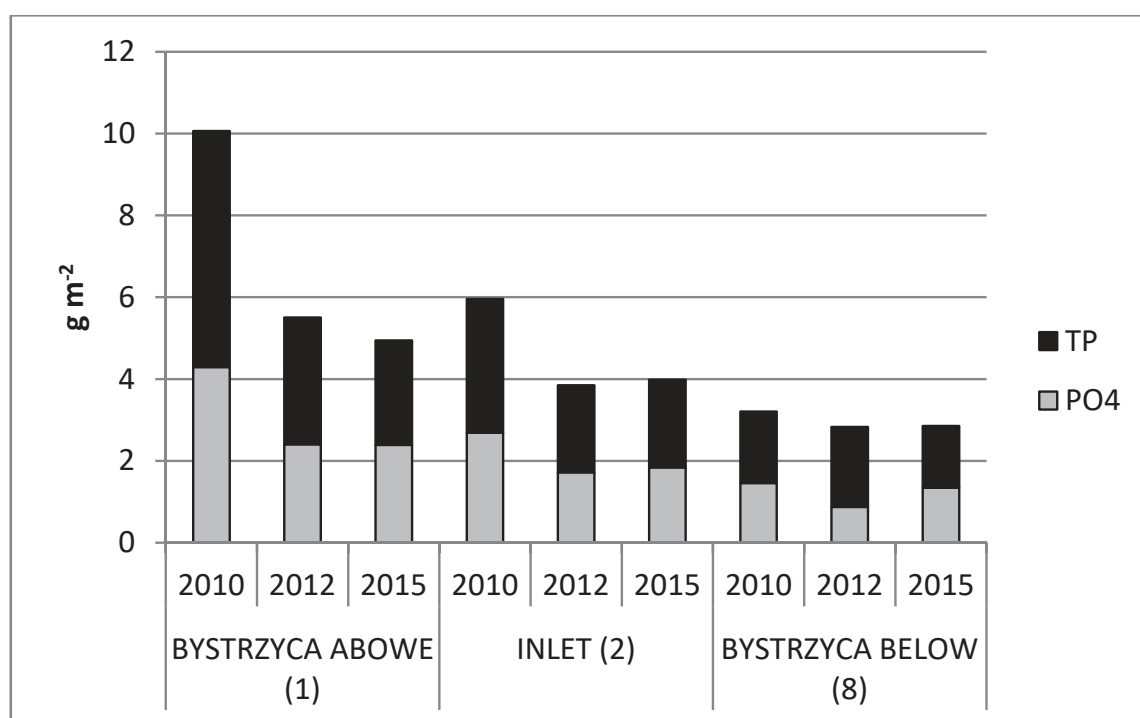


Fig. 3. Loadings of total phosphorus (TP) and dissolved orthophosphates (P-PO₄) in inflow (1, 2) and outflow (8) of Bystrzyca river to Zemborzycki reservoir during the years 2010, 2012, 2015

Rys. 3. Ładunek fosforu całkowitego (TP) oraz ortofosforanów (P-PO₄) na dopływie rzeki Bystrzycy do zbiornika Zemborzyckiego (1,2) oraz odpływie (8), poniżej zbiornika, w latach 2010, 2012, 2015

3.3. Phosphorus load of the reservoir from external sources

The highest concentrations of total phosphorus and orthophosphates were found in groundwater from arable land (A from Fig. 1, Table 2) and remained high throughout study years: 5.1 mg dm⁻³ P-PO₄ and 5.3 mg dm⁻³ TP in 2010 to 4.8 mg dm⁻³ P-PO₄ and 4.9 mg dm⁻³ TP in

2015. Within the points sampled around the reservoir, relatively high concentrations of phosphorus were also found in groundwater from the buffer zone with infrastructure development (B from Fig. 1, Table 2). The lowest concentrations of both forms of phosphorus were found in groundwaters from a forest-covered buffer zone (E from Fig. 1, Table 2). Waters that were collected from the girdling ditch within the settler, were characterized by very high values of both phosphorus concentrations (Table 2). The ditch flowed in the immediate vicinity of the buildings, and then the water flowed into the Zemborzycki reservoir.

Table 2. Phosphorus concentrations in ground waters of the buffer zone of the Zemborzycki reservoir

Tabela 2. Stężenia fosforu w wodach gruntowych strefy buforowej Zalewu Zemborzyckiego

Sampling Point	P-PO ₄ mg dm ⁻³			TP mg dm ⁻³		
	2010	2012	2015	2010	2012	2015
Piezometer – Arable land (A)	5.120	4.964	4.880	5.330	5.227	4.950
Piezometer – Infrastructure (B)	3.689	2.996	3.850	4.410	5.581	3.252
Piezometer – Settler (C)	3.668	3.224	2.992	3.470	3.648	3.874
Piezometer – Forest (E)	0.145	0.106	0.132	0.990	0.547	0.214
Piezometer – Infrastructure in forest (D)	3.953	3.823	2.897	3.510	2.859	2.114

3.4. Buffer zone utilization

Forests dominated in the buffer zone of the Zemborzycki reservoir, covering over 40% of surrounding areas. More than 24% of this area was covered by compact development. The smallest area was occupied by cultivated fields and meadows, covering about 11% of the buffer zone (Fig. 4).

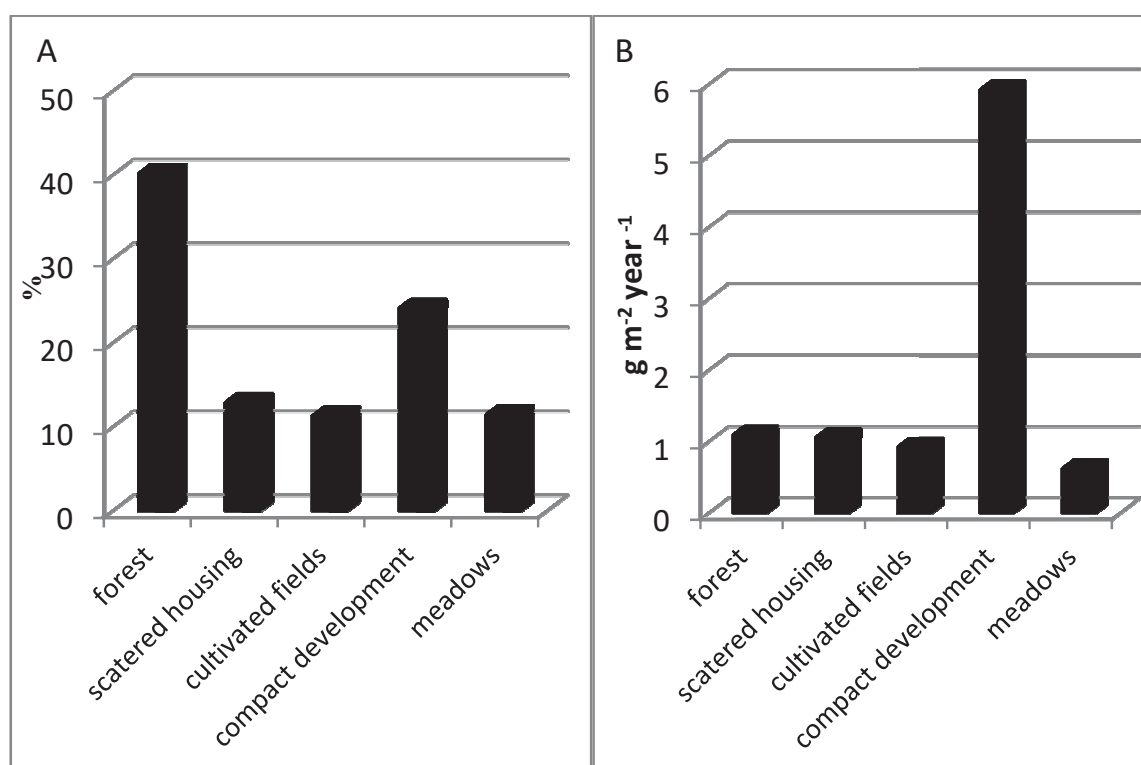


Fig. 4. A) Use of buffer zone; B) phosphorus load supplied from different type of a buffer zone

Rys. 4. A) użytkowanie strefy buforowej; B) ładunek fosforu dostarczany z poszczególnych form użytkowania strefy buforowej

The total supply of phosphorus from the buffer zone was $96.62 \text{ kg ha}^{-1}\text{year}^{-1}$. The largest supply of phosphorus comes from the area covered by buildings and amounted to $5.92 \text{ g m}^{-2} \text{ year}^{-1}$. The lowest concentrations of phosphorus flowed from the meadow area, about $0.62 \text{ g m}^{-2} \text{ year}^{-1}$ (Fig. 4).

3.5. Macrophytes structure

In 2015 macrophytes occupied 70 hectares in the Zemborzycki reservoir, which constituted 25.1% based on aerial photographs. Emergent macrophytes covered 43 ha and submerged covered 27 ha. When measured with cover grids at the reservoir, the average cover of the reservoir bottom with submerged macrophytes was low and amounted to 50%. The area occupied by macrophytes on lagoons was about 85 m^2 in 2015, 47% of total lagoon area.

3.6. Species diversity

The richest study sites in terms of number of species of macrophytes was the Bystrzyca River above the reservoir. In this area 13 to 20 plant species were present. Slightly fewer species were also found in the estuary of the river to the reservoir. The smallest number of species was found in the littoral zone of the reservoir within the recreational areas and where only two or three species were found (Table 3).

Species numbers were low in constructed lagoon areas prior to plantings in 2010 with only 1-5 species present. After planting in 2015, this number increased up to 15 species (Table 2).

3.7. Species biomass

Increases in macrophyte species richness did not necessarily correlate with increases in macrophyte biomass. The highest biomass values of macrophytes occurred in the estuary zone and ranged from 553 g_{DW} m⁻² in 2010 to 1330 g_{DW} m⁻² in 2015. The lower biomass values in this zone in 2012 were caused by construction work related to the shaping of the bicycle path. This project resulted in the destruction of the shoreline and macrophytes occurring there. High biomass values were also found in the lagoon zone during the last year of the study (from 1200 g m⁻² to 1500 g m⁻²). The lowest values of biomass occurred in the residual but typical for the Zemborzycki reservoir phytolittoral (from 102 g m⁻² to 239.1 g m⁻²) (Fig. 5).

There was a high positive correlation between increasing biomass of macrophytes and decreasing concentration of total phosphorus and orthophosphates ($r = 0.72$, $p < 0.05$).

Table 3. cont.

Tabela 3. cd.

study site	1			2			3,4			5,6			7			8			
	2010	2012	2015	2010	2012	2015	2010	2012	2015	2010	2012	2015	2010	2012	2015	2010	2012	2015	
<i>Salix pentandra</i> L.			+		+	+													
<i>Alnus glutinosa</i> (L.) Gaertn.	+	+	+		+	+													
<i>Salix viminalis</i> L.	+	+	+																
<i>Impatiens noli-tangere</i> L.			+																
<i>Ranunculus repens</i> L.	+	+	+																
<i>Elodea canadensis</i> Michx.		+	+	+	+														
<i>Veronica beccabunga</i> L.	+	+	+	+	+														
<i>Epilobium hirsutum</i> L.	+	+	+						+								+	+	+
<i>Iris pseudacorus</i> L.	+	+	+	+			+		+			+							
<i>Typha angustifolia</i> , L.																			
<i>Rumex hydrolapathum</i> Huds.				+		+													
<i>Mentha aquatica</i> L.		+	+	+					+										
<i>Carex pseudocyperus</i> L.																			
<i>Scirpus sylvaticus</i> L.	+	+	+	++	+	++			+			+			+		+	+	
<i>Myriophyllum spicatum</i> L.					+	+													
<i>Potamogeton acutifolius</i> Link ex Roem. & Schult.				+									+						
	13	18	20	18	13	16	5	5	15	1	5	12	3	2	3	4	11	10	

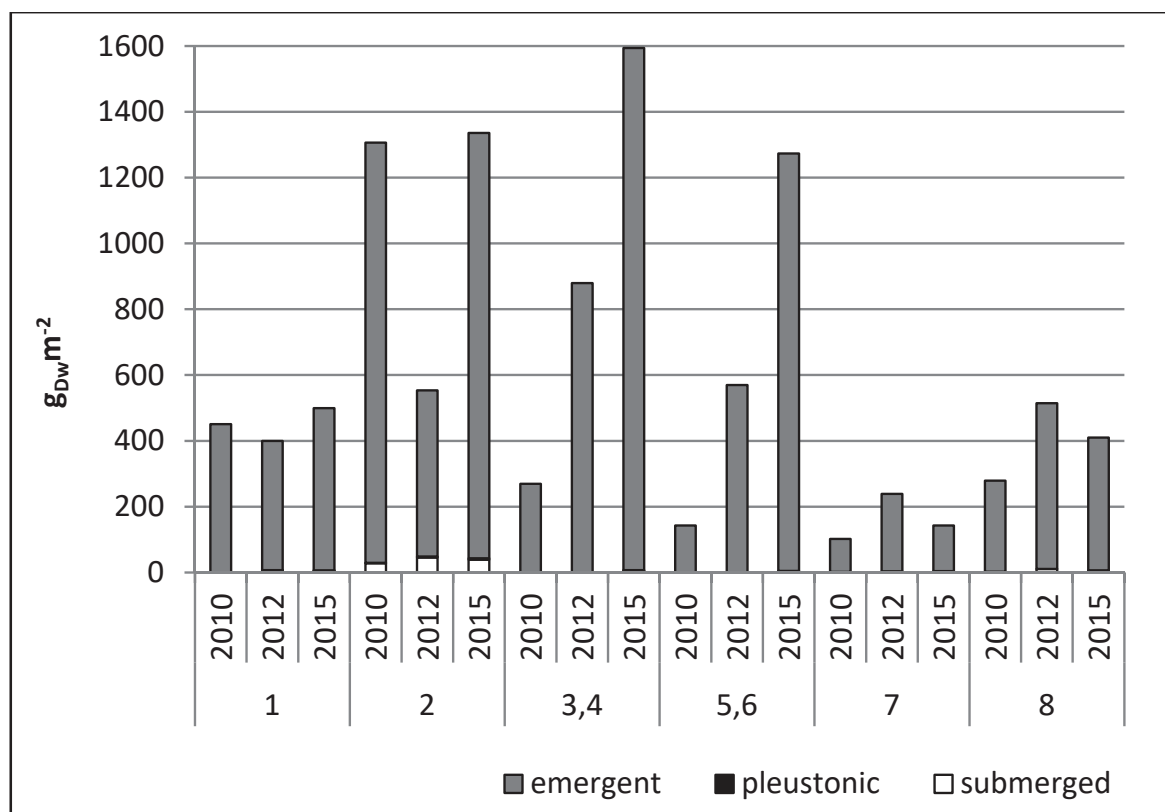


Fig. 5. Biomass of macrophytes at individual study sites in subsequent years of research

Rys. 5. Biomasa makrofitów na poszczególnych stanowiskach w kolejnych latach badań

Among the emergent macrophytes, the species that reached the highest values of biomass was *Glyceria maxima* (Hartm.) Holmb. *Sparganium erectum* L. em. Rchb.s.s. and *Phalaris arundinacea* L. also had a high biomass in the Bystrzyca river above the reservoir and in the estuary zone. Since 2012 the lagoons were also dominated by *Phragmites australis* (Cav.) Trin. ex Steud. Below the reservoir, *Sparganium erectum* L. em. Rchb.s.s., had the highest values of biomass (Fig. 6).

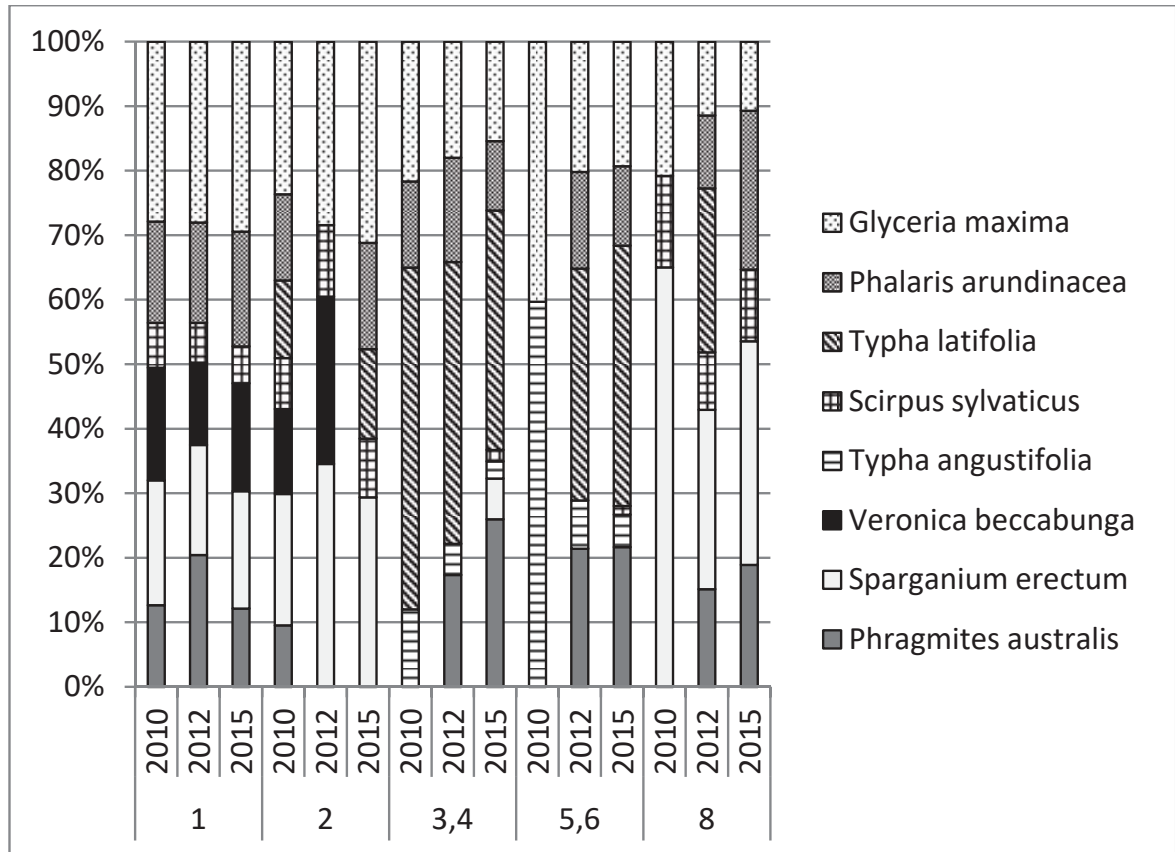


Fig. 6. Share of individual species of emergent macrophytes in biomass

Rys. 6. Udział procentowy poszczególnych gatunków makrofitów wynurzonych w ich biomase

In spite of their large share in the surface of the Zemborzycki reservoir, submerged macrophytes achieved significantly lower biomass values. The highest were in the estuary zone and amounted to only 43 g_{Dw} m² in 2015. *Elodea canadensis* Michx. contributed the most to submerged macrophytes biomass above the reservoir, and *Potamogeton praelongus* Wulfen predominated in the reservoir and below it (Fig. 7).

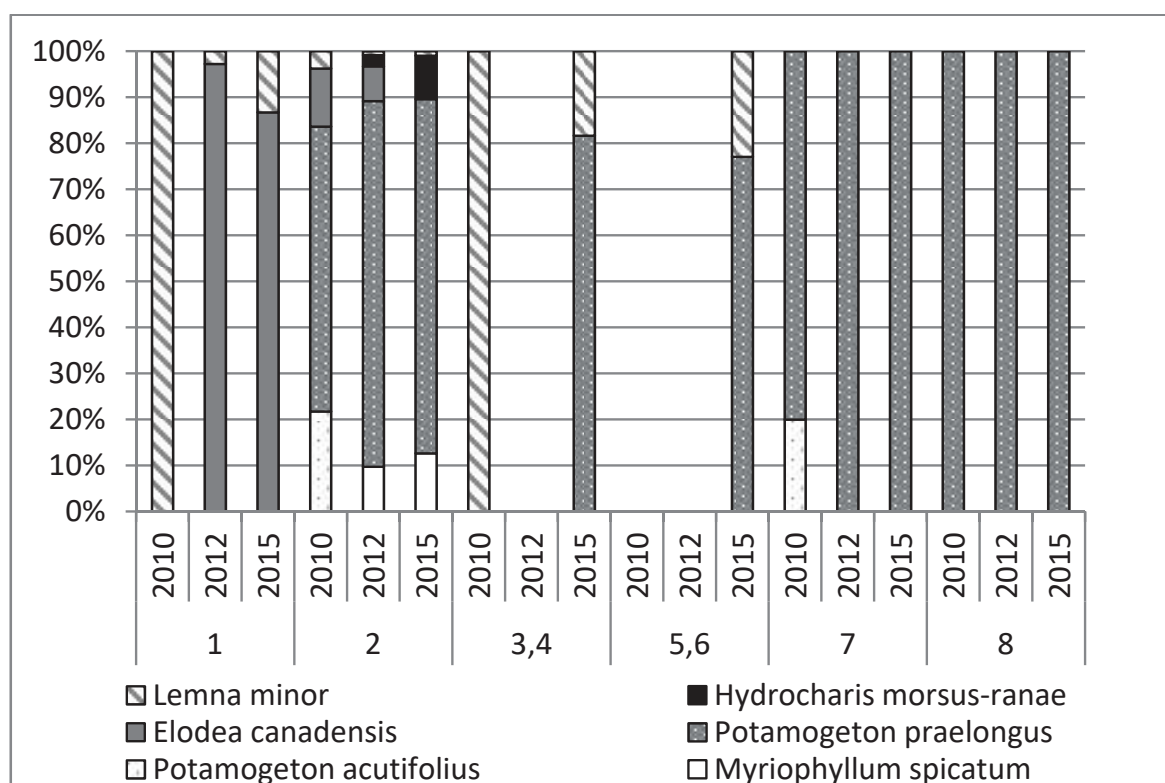


Fig. 7. Participation of individual species of submerged macrophytes in biomass
Rys. 7. Udział procentowy poszczególnych gatunków makrofitów zanurzonych w ich biomase

Within the artificially created lagoons, submerged macrophytes established only in 2015 and *Potamogeton praelongus* Wulfen dominated in biomass (Fig. 7).

Total inertia is 0.487. Two dimensions explain 64% of the total inertia (axis 1 – 42% eigenvalue 0.188, Axis 2 – 22%, the eigenvalue 0.124). Analyzing the distribution of points it can be concluded that emergent macrophyte biomass (EB), pleustonic biomass (PB), submerged biomass (SB) were the most correlated with the concentration of phosphorus (TP and P-PO₄). Independent of the concentration of phosphorus in water were number of species (SN) and the density of emergent macrophytes (ED). Visibility had a relatively small effect on the variation in variable distributions (Fig. 8).

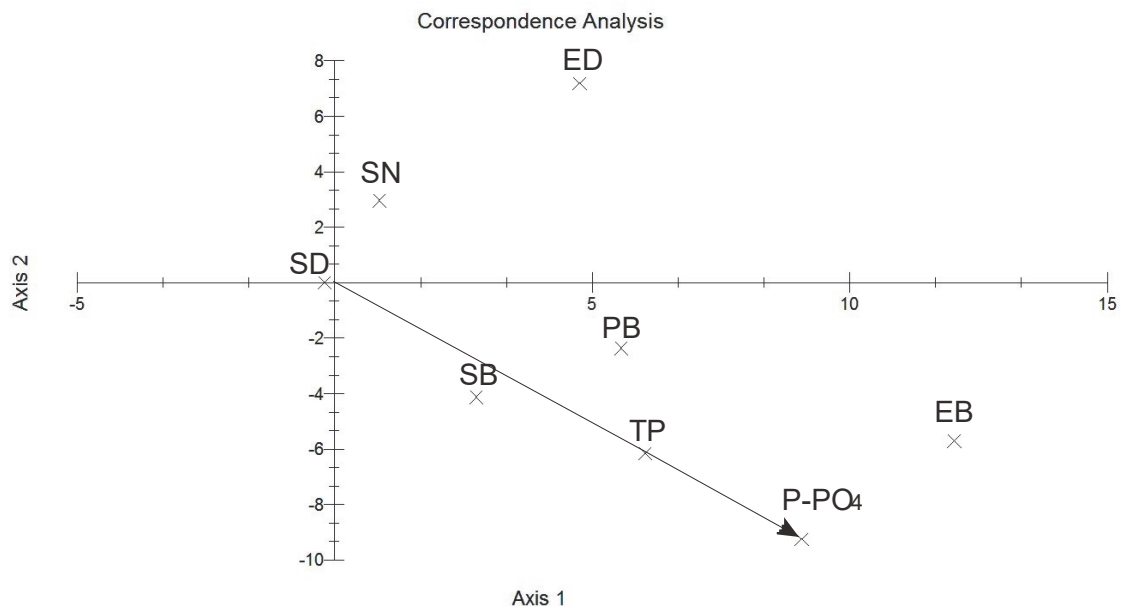


Fig. 8. Correspondence analysis SD – Secchi disc visibility, SN – Species number, ED emergent macrophytes density, PB – pleustonic biomass, EB – emergent macrophyte biomass; SB – submerged biomass; TP – total phosphorus; P-PO₄ - orthophosphates

Rys. 8. Analiza korespondencji, SD – widzialność krążka Secchiego, SN – liczba gatunków, ED – zagęszczenie makrofitów wynurzonych, PB – biomasa roślin pleustonowych, EB – biomasa roślin wynurzonych, SB – biomasa roślin zanurzonych, TP – fosfor całkowity, P-PO₄ – ortofosforany

4. Discussion

All water reservoirs are located in depressions and are a natural receiver of substances flowing from catchments. Still, the greatest threat to aquatic ecosystems are runoff from agricultural and urbanized areas in catchments (Kajak 2001). The natural cycling of nutrients in retention reservoirs is slower than in natural lakes (Kasza 2009). This process involves the conversion of compounds from organic into inorganic through microbial processes under aerobic conditions (Tranvik 1998) and the interception and capturing of nutrients by water plants (Chudyba & Kalwasiński 1998). With its low floristic diversity and biomass, the Zemborzycki reservoir is limited in its ability to cycle nutrients. Overall vegetation and diversity of species decreased in the last decade (Sender 2007). There are many causes of this phenomenon, among others, mechanical damage of macrophytes with large waves, large fluctuations in water

level, restoration work of the shore and frontal dam, very low visibility associated with the progressive eutrophication of the reservoir (Bucak et al. 2012, Stefanidis & Papastergidou 2013).

Zemborzycki reservoir is affected by water rich in phosphorus. Up to $4.29 \text{ g} \cdot \text{m}^{-2}$ P-PO₄ and $77 \text{ g} \text{ m}^{-2}$ TP are charged. In the estuary zone which hosts a developed phytolittoral zone with macrophytes phosphorus load is significantly reduced. In the lagoon area there was also a marked reduction in phosphorus concentration in study years, along with the progressive colonization of plants. In the littoral zone of Zemborzycki reservoir, with very low plant density, the concentration of phosphorus was much higher than in the lagoon zones. The lowest values were in the water of the Bystrzyca River below the reservoir. This means that a large proportion of phosphorus is deposited in the reservoir, mainly in bottom sediments. However, because of the unfavourable morphometry of this reservoir nutrients are re-suspended and waters undergo further eutrophication. Another negative factor is the supply of nutrients from external sources to the reservoir. It turns out that most of the phosphorus flows into the reservoir from the development area even though only 24% of surrounding areas are utilized for development.

The Zemborzycki reservoir along the almost entire shoreline is completely devoid of a natural buffer zone (except for the eastern part, covered with forest), as well as rushes. The presence of a natural buffer zone would allow for bioaccumulation in riparian plant, preventing the flow of phosphorus rich waters into the reservoir. The edges of the reservoir should be properly managed, to create well functioning buffer zones. Well developed and functioning vegetation zones occurring between terrestrial and aquatic ecosystems and display a gradient of biophysical conditions, ecological processes and a rich composition and diversity of organisms (Izydorczyk et al. 2013, Ryszkowski 1992, Correll 1997). Their most significant function is the buffering and filtering of pollutants between land and water ecosystems (Izydorczyk et al. 2015). If a buffer zone is lacking, rushes become the primary filters of nutrients (Sender & Grabowski 2016). Currently, in the Zemborzycki reservoir rushes are limited. The significant reduction of phosphorus compounds in the artificial phytolittoral zone confirms the necessity of such zones.

Macrophytes and associated periphyton are competing for phytoplankton, which is frequently represented in the waters of the Zemborzycki reservoir (Pawlik-Skowrońska & Toporowska 2011), in the uptake of

nutrients. Moreover macrophytes strengthen bottom sediments, reduce the re-suspension of nutrients, and discharge metabolites which have the ability to inhibit the growth of phytoplankton, especially among *Chara* meadows (Gross 2003).

Currently emergent macrophytes are the dominant group of plants in the reservoir. This group also serves an important roles including: the stabilization of the lake bottom; reduction of wave undulation; oxygenation of sediments and the associated inactivation of phosphorus compounds; and they create the base for other living organisms (Cazzanelli et al. 2008, Thomaz & Cunha 2010, Ławniczak 2010).

The worsening ecological status of the reservoir and the disappearance of macrophytes, especially submerged macrophytes, indicate the need for corrective action. The life-cycle of dam reservoirs is closely related to the preservation of a specific capacity but as a result of reservoir silting up this, decreases with age. In the case of small water bodies it ranges from 10 to a maximum 50 years (Bąk et al. 2011, Michalec 2012). The capacity of the small reservoir does not exceed 5 million m³ and the area 10 ha (Michalec 2012). The capacity of the Zemborzycki reservoir was 6.3 million m³, with an area of over 280 ha. In the current form the Zemborzycki reservoir will not be able to function as a reservoir for recreational purposes. Hence, it becomes reasonable to divide it into a recreational area and a natural area which could also act as initial reservoir. Initial reservoirs allow the elimination of phosphates loads (as a limiting factor for primary production (Koc & Skwierawski 2004, Bechmann et al. 2005, Jarzabek 1998). They will also significantly reduce the muddying of the whole reservoir (Bąk et al. 2011). Removal of bottom sediments should be considered as a last resort, because removing bottom sediments does not always bring expected results (Gołdyn et al. 2003).

Storage reservoirs are artificially created and in order to function properly, require constant human interference. As they are extremely valuable the natural and economic role of retention reservoirs (Czamara 2001) requires constant attention to maintaining them in a sustainable way. Management should primarily involve activities such as biomanipulation, development of buffer zones and artificial phytolittoral zones, and well managed catchment areas. If these activities fail then more invasive methods should be considered. Abandoning any action will lead to ecosystem degradation and loss of its basic functions.

5. Conclusions

With limited possibilities of forming a buffer zone, special care should be taken to develop artificial phytolittoral to create artificial substrates, allowing them to develop in regulated shorelines to reduce the phosphorus compounds in the water. At present, the negative ecological potential of the Zemborzycki reservoir and its declining natural and recreational values, it seems justified to separate the so-called natural zone in a reservoir that would serve as a natural biofilter. However, the most important action is to regulate incoming wastewater in the catchment area of the Bystrzyca river and the reservoir as phosphorus loads entering the reservoir are highest from area with buildings and infrastructures.

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Wstępne badania nad poprawą jakości wody zbiornika zaporowego poprzez wprowadzenie sztucznego fitolitoralu

Streszczenie

Zbiorniki retencyjne, utworzone przez człowieka, dla prawidłowego funkcjonowania wymagają ciągłej jego ingerencji. Zbiornik Zemborzycki ulega sukcesywnej eutrofizacji. W roku 2010 zapoczątkowane zostało tworzenie na obszarze zbiornika sztucznych powierzchni roślinnych dla wzbogacania bioróżnorodności. Ich powstanie miało także na celu wyhamowanie wody wpływającej do zbiornika i przez ich przepływ przez powierzchnię roślinną ograniczenie dostaw fosforu.

Celem badań było określenie roli sztucznie ukształtowanego fitolitoralu w redukcji fosforu. W tym celu określono ładunek fosforu dopływający do zbiornika ze źródeł powierzchniowych, z wodami rzeczными oraz ze źródeł zewnętrznych. Do zbiornika wpływa woda bogata w fosfor. W strefie ujściowej rzeki Bystrzycy, w której znajduje się rozwinięta strefa naturalnego fitolitoralu, ładunek fosforu jest znacznie zmniejszony. W strefie lagun odnotowano również znaczne zmniejszenie stężenia fosforu w kolejnych latach badań, wraz z postępującą kolonizacją ich przez rośliny. Znacząca redukcja związków fosforu w sztucznej strefie fitolitoralu potwierdza konieczność ich istnienia.

Przy obecnym, złym potencjale ekologicznym zbiornika Zemborzyckiego i obniżających się walorach przyrodniczych oraz możliwościach jego rekreacyjnego wykorzystania, uzasadnione wydaje się wydzielenie tzw. strefy przyrodniczej w zbiorniku, która pełniłaby rolę naturalnego biofiltra. Jednak najważniejszą jest uregulowana gospodarka ściekowa w zlewni rzeki Bystrzycy i zbiornika. Badane sztuczne podłoża dla roślin, chociaż wolno, ale sukcesywnie zasiedlane są przez rośliny, mogą stanowić narzędzie wspomagające oczyszczanie wód zbiorników zaporowych. Są jednocześnie trwałe i mogą być dowolnie kształtowane, co może stanowić dodatkowy atut – estetyczny.

Abstract

Storage reservoirs are artificially created and in order to function properly, require constant human interference. Zemborzycki reservoir has undergone a successive eutrophication. In 2010, an experimental artificial land surfaces were developed throughout the reservoir. Various native species were transplanted on these lagoons to enrich biodiversity within the reservoir and to reduce phosphorus supply through the plant barrier. The aim of this study was to determine the role of these artificially constructed lagoons and their associated vegetation on phosphorus reduction throughout the reservoir. The reservoir is affected by water rich in phosphorus. In the estuary zone which hosts a developed phytolittoral zone with macrophytes phosphorus load is significantly reduced. In the lagoon area there was also a marked reduction in phosphorus concentration in study years, along with the progressive colonization of plants. The significant reduction of phosphorus compounds in the artificial phytolittoral zone confirms the necessity of such zones. At present, the negative ecological potential of the reservoir and its declining natural and recreational values, it seems justified to separate the so-called natural zone in a reservoir that would serve as a natural biofilter. However, the most important action is to regulate incoming wastewater in the catchment area of the Bystrzyca River.

Studied artificial substrates for plants (sand and gravel), although slowly, but gradually settled by water plants, can be a tool supporting the purification of dam reservoir waters. They are also durable and can be shaped in any way, which can be an additional asset – aesthetic.

Słowa kluczowe:

zbiornik zaporowy, eutrofizacja, makrofity, związki fosforu, sztuczny fitolitoral

Keywords:

storage reservoir, eutrophication, macrophytes, phosphorus compounds, artificial phytolittoral



The Application of Microbial Additive in Poultry Production as a Way to Reduce Emission of Harmful Gases into the Environment

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1. Introduction

A breakthrough in the structure and demand for poultry meat constantly intensifies poultry production (Kozioł & Krzywoń 2014). Agriculture with industrial animal production, including poultry, is one of the main sources of environmental pollution.

During production of the poultry, volatile substances, such as ammonia (NH₃), hydrogen sulfide (H₂S) and carbon dioxide (CO₂) are emitted to the atmospheric air (Mituniewicz 2013). These gases have the ability to move in the atmosphere, undergoing chemical changes under the influence of sun-radiation, mutual interactions and lightning discharge. The gases released into the atmosphere lead to the cyclic exchange and self-cleaning of the atmospheric air. Unfortunately, the excessive amount of impurities causes that the biosphere loses its ability to regenerate, leading to the contamination of air, soil, water and the loss of biological biodiversity, reducing the quality of life of people and animals (Makles & Domański 2008).

Agricultural environment emits 80-95% of the total ammonia, of which 80% are derivatives of animal production. Ammonia emission is one of the perpetrators of ecosystem eutrophication, acidification of soils and damage to the ozone layer (Kołaczkowski & Dobrzański 2006). The regions with the increased ammonia emission are associated with intensive live-

stock production. It is in these areas where ammonium forms are recorded in the rainwater (Communication from the Commission to the Council and the European Parliament 2005). In addition, ammonia has a sharp pungent scent, which not only irritates the mucous membranes of the respiratory system, but together with other odour-creative substances becomes the source of many complaints regarding air quality.

Hydrogen sulfide (sulphan), which is created during production of the poultry, is a gas affecting the humans and the environment. This gas is toxic. At low concentrations it gives unpleasant scent resembling the smell of rotten eggs. Released to the environment it is involved in the formation of sulfur anions and acid rain.

The production of animals is also responsible for the emission of greenhouse gases, including CO₂. The share of farm and food sector related to the production of livestock accounts for 9% of carbon-dioxide exudation in anthropogenic emission of the main greenhouse gases (Steinfeld 2006).

The Food and Agriculture Organization of the United Nations (FAO) believes that "the livestock sector" has such profound and varied impacts that should be one of the leading areas of interest in environmental policy (Steinfeld 2006). By 2050, the FAO predicts a doubling of meat consumption. This situation will not have a beneficial effect on food production and the environment. Climate change, which is promoted by gases emitted during the production of animals, can cause more frequent droughts, hurricanes, floods and crop failures (report by Compassion in World Farming 2008).

Previous actions for limiting the effects of climate-related emission of harmful gases at the source focused on maintaining high welfare in the livestock room. Production of the poultry must therefore adapt to the general principles of the Common Agricultural Policy imposed by the European Union by observing the principle of cross-compliance (EMEP/CORINAIR 2007).

Table 1. Acceptable levels and concentrations of gases [ppm] in the livestock room (EMEP/CORINAIR 2007)

Tabela 1. Dopuszczalne stężenia i koncentracja gazów [ppm] w pomieszczeniu inwentarskim (EMEP/CORINAIR 2007)

Category of animals	Carbon dioxide concentration CO ₂ [ppm]	Hydrogen sulphide concentration H ₂ S [ppm]	Ammonia concentration NH ₃ [ppm]
Calves	3000	5	20
Pigs	3000	5	20
Broilers	3000	X	20

Ammonia (NH₃) and hydrogen sulphide (H₂S) together with other organic compounds can additionally become offensive odours, causing unpleasant scent spreading over large distances. These substances can be felt even at low concentrations (Kołodziejczyk et al. 2011) They are caused by the process of enzymatic-microbiological mineralization of organic bird droppings. These compounds pollute the atmospheric air with volatile odours that may not only affect the environment, but can also cause various diseases in people subjected to such exposure (Kończak & Dobrzański 2006).

Table 2. Characteristics of selected odour-creative compounds [ppm]

Tabela 2. Charakterystyka wybranych związków odorotwórczych [ppm] Own elaboration based on: „Lentech” – www.lenntech.com/table.html

The name of the compound	Chemical formula	Scent	Threshold value [ppm]
Ammonia	NH ₃	Sharp, acrid	0,037
Hydrogen sulfide	H ₂ S	Rotten eggs	0,00047

2. Methodology and scope of the study

The research was conducted in the years 2013-2015 on a poultry farm located in the Opole province in Poland in the temperate climate with four seasons. Researchers measured the concentrations of the following harmful gases: ammonia (NH₃), hydrogen sulfide (H₂S) and carbon dioxide (CO₂). The study was performed during eight production cycles of the ROSS 308 broiler and under different temperature conditions.

The farm, where the study was conducted, consisted of two production halls with the same dimensions 450 m² and the forced mechanical ventilation system. One of the halls, where production of the poultry was traditional was the control object, while in the other, parallel, the microbial additive was applied.

The application of microbial additive was based on the introduction of the solution containing probiotic bacteria to the litter. Prior to the insertion of chickens, it was 25% aqueous solution, next 10% aqueous solution in a seven-day cycle. It was applied by the E-turbo Mgła sprayer, intended for the use in Polish agricultural farms, with a liquid tank capacity of 10 litres and the droplet size and up to 50 micrometers.

The measurements of the test gases were performed in seven-day cycles using the multi-gas Mulitgas III.4 meter. The concentrations of gases were measured in 9 uniformly tagged measurement points on three different heights.

The applied formulation contained the starting materials, such as lactic acid bacteria, photosynthetic bacteria, fermenting fungi, yeast, organic molasses from sugar cane, revitalized water, salt and mineral complex. The maternal culture included the following bacteria: Bifidobacterium Animals, Bifidobacterium bifidum, Bifidobacterium longum, Lactobacillus acidophilus, Lactobacillus bulgaricus, Lactobacillus casei, Lactobacillus delbrueckii, Lactobacillus plantarum, Lactococcus diacetylactis, Lactococcus lactis, Streptococcus thermophilus, Bacillus subtilis var. natto., Saccharomyces cerevisiae, Rhodospseudomonas palustris.



Fig. 1. View of one of the production halls on the poultry farm where the study was conducted

Rys. 1. Widok jednej z hal produkcyjnych na fermie drobiu, w której prowadzono badania

3. Study results

The study results were used to compare the mean concentration of gases CO_2 , NH_3 , H_2S obtained during eight production series in the control hall with the results achieved in the hall where the microbial additive was used. Production cycles had different atmospheric conditions; there were slight differences in the amount of broilers inserted and the duration of the cycle associated with the market price of the livestock. The detailed data is presented in Table 3.

Table 3. Particulars of eight test series (C – control hall, EM – hall where the microbial additive was used)

Tabela 3. Dane szczegółowe dotyczące przeprowadzonych ośmiu serii badań
(C – hala kontrolna, EM – hala, w której stosowano dodatek mikrobiologiczny)

Series of tests	Start of test	End of test	Days	Weeks	Halls	Population	The mean outdoor temperature [°C]
I	2013-12-07	2015-01-23	56	8	C	16 160	4,10
					EM		
II	2014-02-17	2014-04-13	56	8	C	15 840	15,13
					EM		
III	2014-05-06	2014-06-30	56	8	C	17 010	21,25
					EM		
IV	2014-07-05	2014-08-29	56	8	C	16 400	25,63
					EM		
V	2014-09-09	2014-11-03	56	8	C	16 560	17,25
					EM		
VI	2014-11-23	2015-01-17	56	8	C	16 500	6,88
					EM		
VII	2015-01-23	2015-03-12	49	7	C	16 380	5,60
					EM		
VIII	2015-03-27	2015-05-14	49	7	C	16 430	14,00
					EM		

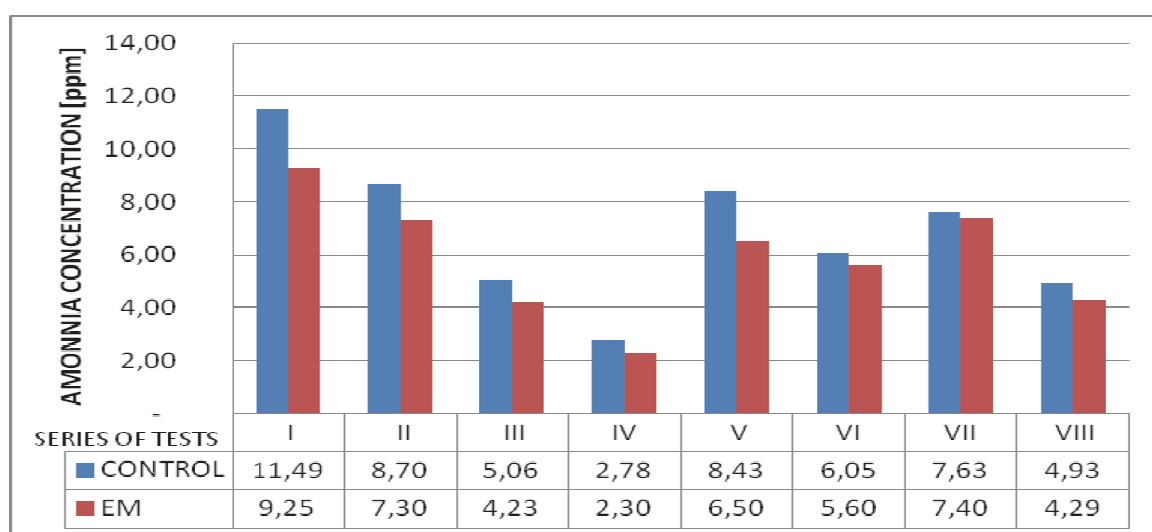


Fig. 2. Mean concentration of ammonia (NH_3) obtained in eight series of tests conducted in the control hall and the hall where the microbial additive was used
Rys. 2. Średnia zawartość amoniaku (NH_3) uzyskana w trakcie ośmiu serii badań w hali kontrolnej oraz w hali, w której stosowano dodatek mikrobiologiczny

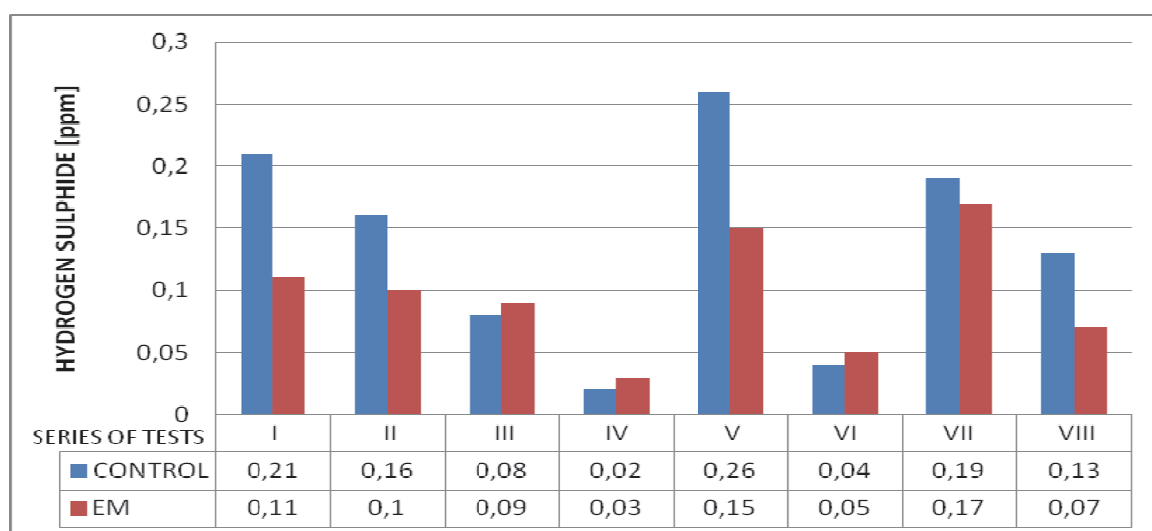


Fig. 3. Mean concentration of hydrogen sulphide (H_2S) obtained in eight series of tests conducted in the control hall and the hall where the microbial additive was used
Rys. 3. Średnia zawartość siarkowodoru (H_2S) uzyskana w trakcie ośmiu serii badań w hali kontrolnej oraz w hali, w której stosowano dodatek mikrobiologiczny

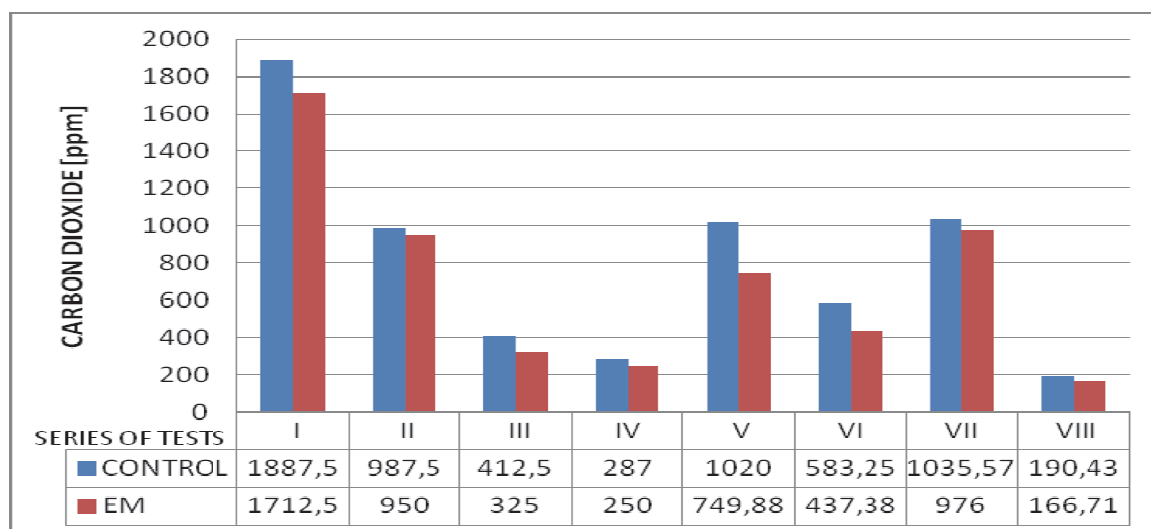


Fig. 4. Mean concentration of carbon dioxide (CO_2) obtained in eight series of tests conducted in the control hall and the hall where the microbial additive was used

Rys. 4. Średnia zawartość dwutlenku węgla (CO_2) uzyskana w trakcie ośmiu serii badań w hali kontrolnej oraz w hali, w której stosowano dodatek mikrobiologiczny

Table 4. A mean decrease in the concentration of CO_2 , NH_3 and H_2S [%], in each research series, in the control hall and the hall where the microbial additive with beneficial micro-organisms was used.

Tabela 4. Średni spadek stężenia CO_2 , NH_3 , H_2S [%], przypadający na poszczególne serie badawcze w hali, w której stosowano preparat zawierający pożyteczne mikroorganizmy w porównaniu z halą kontrolną

Series of test	The concentration difference NH_3 [%]	The concentration difference H_2S [%]	The concentration difference CO_2 [%]
I	19,50	47,62	9,27
II	16,09	37,50	3,80
III	16,40	-12,50	21,21
IV	17,27	-50,00	13,04
V	22,89	42,31	26,54
VI	13,85	-25,00	25,01
VII	3,01	10,53	5,75
VIII	12,98	46,15	12,46

4. Discussion

The analysis of the mean concentration of ammonia (NH_3) and carbon dioxide (CO_2) conducted for both halls showed the reduced mean concentration of these gases in all tested production cycles (Fig. 2), (Fig. 4). The greatest difference in the concentration (NH_3) and (CO_2) was reported in series V, where the mean outdoor temperature in this cycle was $17,25^\circ\text{C}$. The mean concentration of hydrogen sulphide (H_2S) during eight series of tests varied. In series III, IV and VI, the concentrations recorded in the hall, where the microbial additive was used, were higher. In these cases, the difference was between 0.01 and 0.02 ppm was within the normal range (EMEP/CORINAIR 2007). Hydrogen sulphide emission is not primarily associated with avian fauna. Its higher concentration is recorded and controlled in particular in calf and pig husbandry (EMEP/CORINAIR 2007). The differences obtained in the measurement results are related to atmospheric conditions prevailing outside the building affecting the intensification of mechanical ventilation work. Maintaining an appropriate temperature adapted to the age of birds guarantees safe and effective production. During summer heat, it is recommended to increase ventilation velocity up to (1 m/s) (Jankowski 2012). Therefore, during the tests performed, the air temperature and humidity in both halls were in accordance with zoo hygienic requirements (Kořacz & Dobrzański 2006). However, changes in the intensification of work of mechanical ventilation contributed to the effectiveness of the microbiological additive. When analysing results, the changes can be observed in the concentrations of the tested gases, depending on the season in which the tests were performed and the temperatures characteristic for it. The highest results were obtained in the autumn period, in the series V, where the average temperature for the particular weeks of breeding was within the range of $11\text{-}24^\circ\text{C}$. During this period, the hall using the microbiological additive reduced the ammonia (NH_3) content by 22.89% compared to the control hall. However, the highest average percentage difference in the content of carbon dioxide (CO_2) was 26.54% and hydrogen sulphide (H_2S) 42.31%.

5. Summary

The use of a microbiological additive can reduce the concentration of harmful gases at source during broiler production and their reduced emission to the environment.

The effectiveness of the additive depends on the temperature prevailing outside the production building and the related intensification of the mechanical ventilation work. The best results of using the selected microbiological additive are obtained during moderate temperatures of 11-24°C.

Summing up the all results of mean concentrations of gases tested in eight cycles, in the two 2 halls, under the same conditions, we can conclude that in the hall where the microbial additive was used, 73.53 ppm less ammonia, about 6604.9 ppm less carbon dioxide and 0.26 ppm less hydrogen sulfide penetrated to the natural environment than in the control hall.

Referring to odour nuisance and air pollution with offensive odours and taking into account the thresholds at which test compounds, such as ammonia (NH₃) and hydrogen sulphide (H₂S) can cause unpleasant scents (ammonia 0.037 [ppm], hydrogen sulphide 0.00047 [ppm]), it can be stated that the reduction of these gases could limit odour nuisance in the environment.

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Stosowanie dodatku mikrobiologicznego w produkcji drobiarskiej jako metody ograniczenia emisji szkodliwych gazów do środowiska

Streszczenie

Emisja szkodliwych gazów z produkcji zwierzęcej, w tym drobiarskiej, wzrasta ze względu na zwielokrotnienie spożycia mięsa drobiowego na świecie. Proces ten wiąże się nieodłącznie z niekorzystnym oddziaływaniem gazów na środowisko. Usuwanie mikrozanieczyszczeń staje się więc wiodącym zadaniem dla inżynierii środowiska.

Biorąc pod uwagę emisję szkodliwych gazów, w artykule tym przeprowadzono analizę stężeń gazów w trakcie produkcji drobiu. Przedstawiono stężenia amoniaku (NH_3), siarkowodoru (H_2S) i dwutlenku węgla (CO_2) oraz pokazano ich wpływ na środowisko oraz jakość życia człowieka. Zwrócono uwagę na narastający problem i poszukiwanie nowych rozwiązań, których wdrożenie mogłoby zapobiec procesom degradacji środowiska naturalnego, do którego przyczyniają się przede wszystkim gazy wytwarzane przez środowisko rolnicze i produkcję zwierzęcą (80%).

Aktualne działania redukcji gazów powstałych u źródła w trakcie produkcji zwierzęcej amoniaku (NH_3), siarkowodoru (H_2S), dwutlenku węgla (CO_2) skupiają się na utrzymaniu dobrostanu w pomieszczeniu inwentarskim. W związku z tym w artykule tym przedstawiono metodę, w której użyto dodatków mikrobiologicznych w celu minimalizacji stężeń szkodliwych gazów i ich emisji do środowiska naturalnego.

Badania, w których zastosowano nową metodę, przeprowadzono podczas ośmiu serii produkcyjnych na fermie drobiu znajdującej się na terenie województwa Opolskiego. Ferma ta składała się z dwóch hal o takiej samej powierzchni i takim samym systemie wentylacji mechanicznej wymuszonej.

W artykule szczegółowo przedstawiono charakterystykę badanych cykli produkcyjnych, w których panowały różne warunki atmosferyczne (uwzględniono średnią dobową temperaturę zewnętrzną). W poszczególnych cyklach wystąpiły również nieznaczne różnice w ilości wstawianych brojlerów. W długości trwania cykli również odnotowano nie wielkie różnice.

Oszacowano średnie stężenia amoniaku (NH_3), siarkowodoru (H_2S), dwutlenku węgla (CO_2), które uzyskano w poszczególnym cyklach produkcyjnych. Oszacowano również różnice badanych gazów [ppm] przypadające na poszczególne serie badawcze w hali, w której stosowano preparat zawierający pożyteczne mikroorganizmy i porównano z wynikami uzyskanymi w hali kontrolnej. W pracy zmierzono także ogólny spadek stężeń badanych gazów w [ppm] z ośmiu serii produkcyjnych, których emisja okazała się niższa od emisji uzyskanej w hali kontrolnej. Zwrócono uwagę na zanieczyszczenia powietrza atmosferycznego fetorami oraz na równoległą możliwość redukcji nieprzyjemnych doznań zapachowych przez zastosowanie nowej metody z wykorzystaniem dodatku mikrobiologicznego.

Przedstawione w artykule zagadnienia stanowią podstawę do dalszych wnikliwych badań, które pomogą przybliżyć skuteczność dodatku mikrobiologicznego, stosowanego przy produkcji drobiarskiej oraz w innych produkcjach związanych z chowem inwentarza żywego, w celu ograniczenia emisji szkodliwych gazów do środowiska.

Abstract

The emission of harmful gases from livestock production, including poultry, is growing due to the increasing consumption of poultry meat in the world. This process is inherent to the adverse effects of gases on the environment. Thus, the removal of micro-pollutants becomes a leading task for environmental engineering.

Taking into account the problem of harmful gases emission, the article focused on the analysis of gas concentrations in production of the poultry. The concentrations of ammonia (NH_3), hydrogen sulfide (H_2S) and carbon dioxide (CO_2) were shown together with their impact on the environment and the quality of human life. The attention was directed to this growing problem and the search for new solutions the implementation of which could prevent environmental degradation. This disadvantageous phenomenon is mainly due to the impact of gases produced by the agricultural industry and animal production (80%).

Current activities, which are aimed at reducing greenhouse gases generated at source during the production of animals, such as ammonia (NH_3), hydrogen sulfide (H_2S) and carbon dioxide (CO_2), are focused on maintaining high welfare in the livestock room. Therefore, this article presented a method in

which the microbial additive was used to minimize the concentration of harmful gases and emission to the natural environment.

The study, which used a new method, was carried out during eight series of production on the poultry farm located in the Opole province. The battery farm consisted of two halls of the same area and with the same forced mechanical ventilation system.

The article presents detail characteristics of the tested production cycles conducted under different atmospheric conditions (taking into account mean daily outdoor temperature). Individual cycles also slightly differed in terms of the number of inserted broilers. Small differences also related to the duration of cycles.

The study estimated the mean concentration of ammonia (NH₃), hydrogen sulfide (H₂S) and carbon dioxide (CO₂) obtained in each production cycle. The test gases were also assessed in terms of differences [ppm] per individual test series conducted in the control hall and the hall where the formulation containing beneficial micro-organisms was used. The study also measured the overall decline in the concentrations of the tested gases [ppm] in eight production series. Their emission turned out to be lower than the amounts generated in the control hall. The attention was directed to air pollution with offensive odours and the parallel possibility of reducing unpleasant scents by applying the new method using the microbial additive.

Słowa kluczowe:

dodatek mikrobiologiczny, produkcja drobiarska,
szkodliwe gazy – (NH₃), (H₂S), (CO₂)

Keywords:

microbial additive, poultry production, harmful gases – (NH₃), (H₂S), (CO₂)



The Impact of Urban Pollution on Soils and Plants of Homestead Gardens in Gorzów Wielkopolski (Poland)

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1. Introduction

Homestead gardens satisfy recreational needs of local communities and are used for amateur growing of vegetables and fruit. Being green areas, improving ecological standards of a given location, they are protected by legal regulations included in the Act on the Protection of Arable and Forest Land as well as the regulations concerning nature and environment protection (2013). In Poland, in 2011 there were 4941 homestead gardens, covering the total area of 43427 ha (GUS 2012). Generally, they are situated on the outskirts of urban-industrial agglomerations. Urban development brings about the intensification of factors limiting their functions e.g. by worsening soil conditions.

Many authors indicate that dust pollution emitted by local industrial plants, power plants and increased car traffic result in excessive accumulation of heavy metals in the soil of allotment gardens (Hjortenkrans et al. 2006, Kabała et al. 2009, Morton-Bermea et al. 2009, Ordóñez et al. 2003, Sindern 2007, Wei & Yang 2010).

Homestead gardens are frequently located close to main transport routes characterised by a great intensity of traffic. The highest accumulation of heavy metals has been observed in the topsoil adjacent to roads (Antisari et al. 2015, Bretzel & Calderisi 2006, Charlesworth et al. 2010, Forman & Alexander, 1998, Meinhardt et al. 2011, Säumel et al. 2012).

Therefore, it is indispensable to determine the amount of heavy metals in vegetables from these gardens. Numerous scientific papers reveal excessive accumulation of certain heavy metals in surface soil layer and the increase in their concentration in different vegetables (Antisari et al. 2015, Bretzel et al. 2016, Chaney et al. 1984, Gontarz & Dmowski 2004, Kachenko & Singh 2006, Staniak 2014, Sterrett et al. 1996, Rogóż 2003). Some authors suggest a weak accumulation of heavy metals in vegetables despite of soil contamination (Chodak et al. 1995, Sipter et al. 2008). By consuming contaminated vegetables, heavy metals may be included into a trophic chain (Kachenko & Singh 2006, Pruvot et al. 2006).

The area Gorzów is of about 86 km² and has 124.5 thousand residents. There are a well-developed chemical, electronic, energy, pharmaceutical, machine, metal, automotive, food and textile industries in the city. Many companies operate within the Gorzów Subzone of the Kostrzyn-Słubice Economic Zone. There is also an important transport hub connecting Western and Eastern Europe as well as southern and northern Europe. Reports on the state of the environment in the Lubuskie voivodship for the years 2009-2012 (WIOŚ in Zielona Góra 2011, 2013) indicate that the main source of pollution in Gorzów Wlkp. is the surface emission of dust associated with individual heating of housing in the municipal sector as well as the emission from transportation. Comparing Gorzów Wlkp. to other cities of the Lubuskie Voivodship, one can state that it shows the highest over-average of annual and daily average quantities of particulate matter (WIOŚ in Zielona Góra 2011, 2013). Heavy metals enter the environment together with dust and atmospheric precipitation.

On the pollution of urban soils with heavy metals of some squares, Gorzowa Wlkp. is indicated by the report on the state of the environment in Gorzów Wielkopolski in the years 2000-2001 (WIOŚ in Zielona Góra 2002). According to the report on the state of the environment in Gorzów Wlkp. in the years 2000-2001 (WIOŚ in Zielona Góra 2002), the cause of lead pollution of some urban soils is a faulty communication system of the city, which is a big problem with the growing number of motor vehicles.

The distribution of pollutants in the Gorzów Wlkp. environment is related to the strength and prevailing north-west and west wind directions. The main industrial facilities of Gorzów Wlkp. are located in the north-western and western parts of it. In contrast, the allotment gardens

studied are located in the southern part of Gorzów exposed to the imission of air pollutants.

The report on the state of the environment in Gorzów Wielkopolski in the years 2000-2001 (WIOŚ in Zielona Góra 2002) indicates on the pollution of urban soils of some squares with heavy metals. According to this report the main cause of lead pollution of some urban soils is a faulty communication system of the city, which became a big problem due to the growing number of motor vehicles.

The distribution of pollutants in the Gorzów Wlkp. environment is related to the strength of the wind as well as its prevailing north-western and west directions. The main industrial facilities of Gorzów Wlkp. are located in the north-western and western parts of it. In contrast, the studied allotment gardens are located in the southern part of Gorzów Wlkp., which is exposed to the imissions of air pollutants.

The main aim of the conducted research was to determine the content of heavy metals in soils and selected vegetables and indicator plants of family allotment in Gorzów Wlkp.

2. Materials and methods

The studies were carried out at the end of vegetation season (20-30 August 2011) in Gorzów Wlkp. within the Homestead Gardens along Kasprzaka street.

Three transects were designated on its area along which four research areas were designated: at the roadway, approx. 20, 50 and 100 meters from the roadway – a total of 12 research areas (Figure 1).

From each of the research areas the collective samples (representing the research area) of parsley leaves, carrot roots, leaves and roots of red beets, plantain leaves, dandelion leaves were collected in four replications. In addition, within the each research area under five examined plants: parsley, carrot, red beet, plantain and dandelion, were collected soil composite samples (a total of 20 individual samples) from the humus level.

Altogether 12 soil samples and 60 plant samples (parsley leaves, carrot roots, red beet leaves and roots, leaves of common plantain, leaves of common dandelion) were taken for laboratory analysis.



Fig. 1. An overview map of research area locations within the Family Garden Garden (ROD) in Gorzów Wielkopolski (I, II and III – transects with research surfaces: at the roadway, about 20, 50 and 100 meters from the road)

Rys. 1. Poglądowa mapa lokalizacji powierzchni badawczych w obrębie Rodzinnego Ogrodu Działkowego (ROD) w Gorzowie Wielkopolskim (I, II i III – transekty z powierzchniami badawczymi)

In the soil material the following determinations were made: granulometric composition by the Casagrande areometric method modified by Prószyński, granulometric groups according to the classification of Polish Soil Society (PTG 2008); $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} – potentiometrically; hydrolytic acidity (Hh), total bases (S) – by the Kappen method, on the basis of which adsorbing capacity (T) and base saturation (V) were calculated; the content of total carbon by means of elementary analyser (CHNS-O, Costech Italy); the content of available phosphorus and potassium by the method of Egner-Riehm; the content of available magnesium in mineral soils by the method of Schachtschabel; the content of the so-called total forms of macroelements – K, Mg, Ca, Na and heavy metals – Cd, Co, Cu, Zn, Ni, Pb, Mn, Fe (soluble in concentrated $\text{HNO}_3 + \text{HClO}_4$, at the ratio 1:1) – by means of atomic absorption spectrophotometer Unicam Solaar 929, whereas P – colorimetrically.

The plant material for the experiment consisted of the most common cultivated root vegetables i.e. carrot, parsley and red beet; and indicator plants – common plantain and common dandelion. Collected plants were thoroughly washed under running water and cut. After air-drying vegetables were ground in a high-speed mill. In plant samples the total content of heavy metals – Cd, Co, Cu, Zn, Ni, Pb, Mn, Fe (soluble in concentrated acids $\text{HNO}_3+\text{HClO}_4$, 1:1) was determined using atomic absorption spectrophotometer Unicam Solaar 929.

In order to assess heavy metals contamination of soil under study, permissible limits given in the Polish Regulation of Minister of Environment on soil and land quality standards (2002) and the criteria developed by Polish Institute of Soil Science and Plant Cultivation (IUNG 1993), based on elaborate, long-term investigations which allowed to determine borderline heavy metals levels in soil used for agriculture, were used.

The chemical composition of soil and plants between the study sites (located at the road, about 20, 50 and 100 meters from the road in three replications) were compared.

The obtained results were verified statistically by means of Anova for single-factor experiments and the Tukey test. Normal distribution of variables was checked by the Shapiro-Wilk test and homogeneity of variances by the Brown-Forsythe test. The programme *Statistica 10.0 PL* was used for statistical analysis.

3. Results and discussion

The soils of analyzed homestead gardens are characterized by a relatively little diversified granulometric composition. They are mostly slightly loamy sands, sandy loams and loose sands in the direct vicinity of roads (Table 1).

Soil reaction on which ion balance depends is an important and a decisive parameter for the solubility of heavy metals in soil, is. The solubility of heavy metals is usually low at neutral and alkaline reaction and is growing with decreasing pH values (Kabata-Pendias & Pendias 1999).

Table 1. Mean content of size fractions in the soil adjacent to road and soil of allotment gardens**Tabela 1.** Średnia zawartość frakcji granulometrycznych w glebie przyległej do jezdni i glebach ogródków działkowych

Distance from road (m)	Sand (2.0-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Soil textural group
	%			
0	93	4	3	loose sand
20	76	18	6	slightly sandy loam
50	84	10	6	slightly loamy sand
100	77	15	8	sandy loam

The reaction of examined soils ranged from neutral to alkaline. The highest values were recorded in the direct vicinity of roads $\text{pH}_{\text{H}_2\text{O}}$ and pH_{KCl} . With the distance from the road pH value was decreasing and statistically significant lower pH was detected on the study areas located 100 m away from the road. Similar regularity was found by Filipek & Badora (1992). The alkalinity of Lublin soils, analysed by these authors, was the higher the closer to the road they were situated, which was the result of chemicals alkalinising the soil, used in winter to fight ice and snow on roads.

Sorption capacity is an important parameter for estimating soil quality since it conditions the nutrient retention ability including immobilisation of potentially toxic elements. In the analysed soil material sorption capacity values were similar, only in the case of hydrolytic acidity a statistically significant increase was observed at a greater distance from the road (Table 2). The obtained sorption capacity values are lower than those recorded by Świerszcz & Sykała (2009) in the topsoil of Kielce allotment gardens (310.0 to 601.0 $\text{mmol}(+)\cdot\text{kg}^{-1}$).

Base saturation (V) of examined soils ranged from 92.8 to 98.4%, the highest values were found in the soils adjacent to the road. Both high sorption capacity and the highest saturation of soils adjacent to the road, may contribute to heavy metals retrogradation and therefore, as it had been emphasised by Kabata-Pendias & Pendias (1999), are vital factors preventing negative effects of soil contamination.

Total carbon content was in the range 13.54 to 21.36 $\text{g}\cdot\text{kg}^{-1}$ (Table 2), which in Gałka's opinion (2011) is typical of allotment gardens.

The highest level of organic carbon was obtained in the samples from the area 100 m from the road and the lowest from the site lying near the road.

The resources of available macroelements varied in the examined soil (Table 2). The soils bordering the road contained a low content of available phosphorus and magnesium whereas in the other soil samples it was within the values considered as very high by the Institute of Soil Science and Plant Cultivation (IUNG 1990). The concentration of these elements, found on the surface of study areas lying 20, 50 and 100 meters from the road, was significantly higher in comparison with the values obtained from the soil neighbouring the road. In the case of potassium the content of its available forms was low according to the criteria of IUNG (1990), in all analysed samples irrespective of localisation.

Table 2. Chosen soil properties of allotment gardens in Gorzow Wielkopolski
Tabela 2. Wybrane właściwości chemiczne gleb ogrodów działkowych Gorzowa Wielkopolskiego

Specification		Distance from road (m)				LSD _{0,05}
		0	20	50	100	
pH _{H2O}		7.47 a*	7.43 a	7.26 ab	7.05 b	0.32
pH _{KCl}		7.41 a	7.36 a	7.19 ab	6.97 b	0.27
Hh	mmol(+).kg ⁻¹	6.5 a	9.0 ab	13.5 ab	17.0 b	0.86
S		417.0 a	249.0 a	202.0 a	252.0 a	249.0
T		423.5 a	258.0 a	215.5 a	269.0 a	244.0
V	%	98.4 a	95.6 a	93.8 a	92.8 a	6.0
Available	P	54.6 a	272.2 b	281.6 b	250.5 b	128,5
	Mg	14.4 a	89.7 b	106.0 b	143.4 b	57,2
	K	31.6 a	78.9 a	112.3 a	147.3 a	127,3

Table 2. cont.

Tabela 2. cd.

Specification			Distance from road (m)				LSD _{0,05}
			0	20	50	100	
Total	C	g·kg ⁻¹ DM.	13.54 a	14.95 ab	18.85 ab	21.36 b	7.78
	Ca		3.07 a	1.89 ab	0.43 b	0.83 ab	2.32
	Na		0.34 a	0.09 b	0.10 b	0.10 b	0.17
	K		0.73 a	1.29 ab	1.39 b	1.69 b	0.63
	Mg		0.93 a	0.58 a	0.39 a	0.47 a	0.71
	Co	mg·kg ⁻¹ DM.	2.31 a	0.33 b	0.21 b	0.40 b	1.19
	Cd		0.31 a	0.05 b	0.01 b	0.04 b	0.22
	Ni		4.23 ab	5.37 a	5.00 a	1.77 b	2.58
	Cu		19.70 a	6.93 b	8.03 b	9.50 b	7.83
	Pb		15.13 a	7.23 a	10.13 a	13.07 a	9.30
	Zn		72.9 a	40.8 b	41.7 b	56.2 ab	29.9
	Mn		162.3 a	397.0 b	400.3 b	278.4 ab	153.8
	Fe		6471 a	8961 a	10784 a	9126 a	6406

*- homogeneous groups

The soil of allotment gardens under study, were characterised by differentiated resources of macroelement total forms (Table 2). The richest resources of total forms Ca, Na and Mg were detected in the soil next to the road but there were the lowest concentrations of potassium and carbon. As Gałka (2011) suggests, a great diversity in the content of total

forms of macroelements, in the soil of particular allotment gardens, may be the effect of different agricultural practices and fertilisation.

According to the Polish Regulation of Minister of Environment (2002) and (IUNG 1993), the discussed soils of Gorzow Wielkopolski should be regarded as unpolluted. However, elevated concentration of zinc was only recorded in the soil adjacent to the road.

Due to the report on the state of the environment in the Lubuskie Voivodeship in the years 2000 - 2001 (WIOS in Zielona Góra 2002), the state of the soils of the municipal gardens in Gorzów is good. There are a few places, which are polluted by lead from the public transport.

Our findings are in line with the investigations of Bielicka et al. (2009) on the soils and vegetables in allotment gardens of Gdańsk and its surroundings in which there was no breaking of legal norms concerning the soil heavy metals content. The lack of contamination of urban soils with lead is also indicated by Bielińska (2006), Bretzel et al. (2016), Sterrett et al. (1996). In turn, indicated that the soils of allotment gardens in Upper Silesia are strongly contaminated with zinc, lead and cadmium. Similar conclusions were drawn by Baran et al. (2007), Kabała et al. (2009), Wójcikowska-Kapusta (2007), who examined the soils of home-stead gardens in Silesia, Biała Podlaska and Lublin. Piotrowska and Koper (2007) in the studies conducted in Inowrocław found out that among 11 allotment garden samples, contamination with zinc, lead and cadmium was only in three of them. In addition, the studies of Antisari et al. (2015), Chaney et al. (1984), Charlesworth et al. (2010), Hough et al. (2004) and Mitchell et al. (2014) show also the heavy metals pollution of household gardens in urban agglomerations.

Although the permissible limits have not been exceeded in the analysed soils, there is no doubt that in the case of Co, Cd, Cu, Zn and Mn, their level is affected by the vicinity of the road. There is a statistically significant higher concentration of the above mentioned heavy metals in the soils adjacent to the road in comparison with the soils lying further away from the road (Table 2). Similar relationship was observed by Antisari et al. (2015), Baran et al. (2007), Czarnkowska (1995), Gherardi et al. (2009) and Säumel et al. (2012) in whose opinion the risk of soil and vegetation contamination with heavy metals mainly depends on the intensity of traffic and the distance from emission sources.

Other studies indicate that in urban agglomerations, despite the lack of soil contamination with heavy metals, vegetation is contaminated. It is related to the physiological predispositions of some plant species for accumulation in various parts (roots, shoots, fruits, seeds) of heavy metals from the soil and dust settling on plants (Murray et al. 2009, Kabata-Pendias & Pendias 1999, Peris et al. 2007).

Among field crops, vegetables are the most capable of storing metals, both by their uptake from soil and precipitation, via their above-ground parts (Hough et al. 2004, Staniak 2014).

From the surface of vegetables for consumption, the majority of metals may be removed by thorough washing but those absorbed by roots are built into the plant tissues and pose a threat to humans (Bielicka et al. 2009, Hough et al. (2004), Kabata-Pendias & Pendias 1999, Staniak 2014).

The content of particular heavy metals in plants depends on many factors including reaction and base saturation of a soil (V). High concentration of salts may reduce water uptake and thus ions, by increasing osmotic potential of soil solution. High pH immobilises metals in soils by the formation of carbonates and phosphates (Islam et al. 2007, Ross 1994).

In our studies, the content of heavy metals in vegetables varied, depending on plant species (Table 3).

Similar differences were found by Antisari et al. (2015), Finster et al. (2004), Säumel et al. (2012). No negative influence of the vicinity of the communication route and urban agglomeration on the content of heavy metals in the analyzed vegetables was found. However, research provided by Antisari et al. (2015), Säumel et al. (2012), Staniak (2014) show the impact of the communication route on the heavy metals content in vegetables. Hough et al. (2004) indicates that vegetables from urban agglomerations can be dangerous to human health. Cadmium and lead are particularly dangerous for human health. In the studied soils, the content of lead and cadmium was below the detectable level of the applied method ($<0.01 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$).

Table 3. Content of heavy metals in vegetables from allotment gardens in Gorzow Wielkopolski**Tabela 3.** Zawartość metali ciężkich w warzywach pochodzących z ogrodów działkowych Gorzowach Wielkopolskiego

Specification		Distance from road			LSD _{0,05}
		20	50	100	
Parsley aboveground parts	Mn	40.70 a	21.08 b	19.98 b	10.53
	Zn	36.17 a	26.79 a	33.77 a	13.30
	Co	1.33 a	3.22 b	4.90 b	11.74
	Ni	6.40 a	6.73 a	7.19 a	2.50
	Cu	9.34 a	8.43 ab	7.17 b	2.10
	Fe	470.1 ab	580.1 a	258.7 b	228.3
Carrot root	Mn	17.57 a	12.97 a	14.00 a	4.95
	Zn	31.47 a	22.76 b	24.30 ab	8.35
	Co	1.48 a	3.08 a	3.09 a	3.71
	Ni	14.27 a	5.93 b	5.75 b	4.89
	Cu	11.46 a	12.89 a	10.81 a	6.97
	Fe	256.6 a	188.8 a	299.2 a	317.3

Table 3. cont.

Tabela 3. cd.

Specification		Distance from road			LSD _{0,05}
		20	50	100	
Red Beet aboveground parts	Mn	43.37 a	69.09 b	40.30 a	24.68
	Zn	30.57 a	42.57 a	89.20 a	117.6
	Co	0.89 a	2.13 b	3.68 c	0.93
	Ni	6.23 a	13.81 b	6.00 a	6.41
	Cu	9.69 a	9.53 a	8.80 a	3.08
	Fe	469.3 a	660.7 a	866.0 a	545.1
Red Beet root	Mn	24.01 a	32.06 a	26.85 a	24.2
	Zn	27.05 a	34.07 a	50.23 b	15.23
	Co	5.39 a	6.05 ab	6.45 b	0.78
	Ni	6.14 a	7.65 b	6.72 ab	1.09
	Cu	12.44 a	13.20 a	15.56 a	5.70
	Fe	134.6 a	206.5 a	142.0 a	147.0

* – homogeneous groups

The contents of Mn, Zn and Fe in the examined plant material was lower compared to the data presented by Ostrowska & Porębska (2002). In the aboveground parts of parsley they found Mn – 77; Zn – 170; Fe – 984 mg·kg⁻¹ DM. However, the content of copper was almost 6-fold higher (mean 9.64 mg·kg⁻¹ DM on the study areas lying 20 m from road) than the results of the above mentioned authors (1.5 mg Cu·kg⁻¹ DM).

Moreover, in carrot roots ca. 2-fold higher than natural, amount of copper, was obtained in comparison with the data given by Ostrowska & Porębska (2002).

Kabata-Pendias & Pendias (1992) consider that the natural content of copper in plants to be less than $20 \text{ mg} \cdot \text{kg}^{-1} \text{ dm}$.

In the case of red beet, heavy metals values were closer to the amounts commonly regarded as natural (Ostrowska & Porębska 2002). Comparison of heavy metals level in red beet leaves and roots showed quantitative variations in their chemical composition. In aboveground parts there was higher concentration of manganese, zinc and iron than in roots, whereas the roots contained more cobalt and copper than the aboveground parts.

To assess the degree of environmental pollution, the so-called bioindicators of pollution (plants with high tolerance to pollution and commonly occurring in various environments) as dandelion and plantain can be used (Kabata-Pendias & Dudka 1991, Keane et al. 2001, Ligocki et al. 2011, Marr et al. 1997, Stolarska et al. 2004). At the same time Stolarska et al. (2004) points that the plantain is a better bioindicator than the dandelion. Marr et al. (1997) found that the dandelion did not show elevated concentrations of heavy metals according to their increase in soils.

Analysis of chemical composition of common dandelion did not indicate, except zinc, a negative impact of the road (Table 4). Bomze et al. (2007) and Dzierżanowski & Gawroński (2011) indicate the plain impact of communication routes on the heavy metal pollution of dandelion plants.

The increased contents of some heavy metals, however, indicate their anthropogenic origin (dust and gas pollution of the air). The obtained values in the aboveground parts are similar to those given by Dąbkowska-Naskręt et al. (2000), Kabata-Pendias & Krakowiak (1998), Ligocki et al. (2011), Marr et al. (1997), Niedźwiecki et al. (2004).

The carried out research have shown that under the same environmental conditions within studied plants the dandelion accumulates nickel in the highest values. These quantities are much higher than those found in urban agglomerations by Keane et al. (2001), Ligocki et al. (2011) and Stolarska et al. (2004). According to Kabata-Pendias & Pendias (1992), the values of 0.1-5 are natural and 10-100 $\text{mg} \cdot \text{kg}^{-1} \text{ s.m}$. excessive or toxic. Nickel is an element easily absorbed from the soil but

also by aerial parts of plants (it is bound by a cuticle in the leaves of plants Kabata-Pendias & Pendias 1999). The so-called hyper-accumulators, can uptake this element up to about 0.5% dm (Kabata-Pendias & Pendias 1992). According to values given by Kabata-Pendias & Pendias (1992) the content of cobalt in dandelion leaves can be described as high, more than normative.

Table 4. Content of heavy metals in selected indicator plants

Tabela 4. Zawartość metali ciężkich w wybranych roślinach wskaźnikowe

	Specification		Distance from road (m)				LSD _{0,05}
			0	20	50	100	
Common dandelion <i>Taraxacum officinale</i>	Mn	mg·kg ⁻¹ DM	50.31 a*	139.2 b	65.76 a	49.90 a	45.13
			70.43 a	61.22 b	55.02 b	62.03 b	7.56
			3.19 a	4.48 a	4.09 a	4.68 a	2.08
			22.15 a	50.21 b	47.07 b	14.18 a	21.31
			16.86 a	16.23 a	12.96 a	16.52 a	6.59
			1365.8 a	4227.0 a	1602.0 a	1395.8 a	4008.9
Common plantain <i>Plantago maior</i>	Mn	mg·kg ⁻¹ DM	94.43 a	110.96 a	63.69 ab	35.66 b	56.31
			54.68 a	50.46 a	45.70 a	68.00 a	28.11
			3.15 a	3.67 a	7.18 b	3.18 a	0.81
			20.49 a	11.75 a	8.93 a	6.48 a	14.27
			17.29 a	32.22 a	36.88 a	22.79 a	25.31
			2536.3 a	2536.0 a	976.6 a	904.1 a	16.64

* – homogeneous groups

The vicinity of road had no statistically significant negative effect on the chemical composition of common plantain (Table 4). The obtained heavy metal contents were similar irrespective of localization, only in the case of manganese and nickel they were higher closer to the road.

The amounts of heavy metals found in leaves of plantain do not exceed natural values in plant tissues given by Kabata-Pendias & Pendias (1992). Only the nickel and cobalt content, regardless of the distance from the road, is unnaturally high (Kabata-Pendias & Pendias 1992). Similar exceedance of natural content of nickel in common plantain in Szczecin agglomeration were also reported by Stolarska et al. (2004).

4. Conclusions

The following conclusions can be attained:

1. On the basis of heavy metal content, the soils of homestead gardens in Gorzów Wielkopolski may be regarded as the soils with their natural level. Neutral or alkaline soil reaction reduce heavy metal availability to plants.
2. No apparent negative impact of the vicinity of road on heavy metal concentration in parsley leaves, carrot roots and red beets. The obtained heavy metal values were generally lower or close to those commonly considered to be natural. Only the nickel and cobalt content was high.
3. The distance between homestead gardens and roads has no effect on the content of heavy metals in common dandelion (*Taraxacum officinale*) and common plantain (*Plantago maior*).

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Wpływ zanieczyszczeń miejskich na glebę i rośliny ogródków działkowych w Gorzowie Wielkopolskim (Polska)

Streszczenie

Ogrody przydomowe są często zlokalizowane w pobliżu głównych szlaków komunikacyjnych, charakteryzujących się dużym natężeniem ruchu. Najwyższe nagromadzenie metali ciężkich zaobserwowano w wierzchniej warstwie gleb przylegającej do dróg. Celem przeprowadzonych badań było określenie: wpływu zanieczyszczeń miejskich na właściwości chemiczne gleby i skład chemiczny wybranych warzyw i roślin wskaźnikowych w glebie rodzinnych ogródków działkowych w Gorzowie Wielkopolskim. Stwierdzono statystycznie istotne wyższe stężenie metali ciężkich w glebach przylegających do drogi w porównaniu z glebą leżącą 20, 50 i 100 m od drogi. Uzyskane wartości metali ciężkich były na ogół niższe lub zbliżone do tych powszechnie uznawanych za naturalne w glebach, warzywach i roślinach wskaźnikowych. Tylko zawartości niklu i kobaltu były wysokie.

Abstract

Homestead Gardens are frequently located close to main transport routes characterized by a great intensity of traffic. The highest accumulation of heavy metals has been observed in the topsoil adjacent to roads. The aim of conducted studies was to determine: the effects of urban pollution on soil chemical properties and chemical composition of selected vegetables and indicator plants, in the soil of family allotment gardens in Gorzów Wielkopolski. There is a statistically significant higher concentration of the heavy metals in the soils adjacent to the road in comparison with the soils lying ca. 20, 50 and 100 m from the road, respectively. The obtained values of heavy metals were generally lower or close to those commonly considered natural in soils, vegetables and indicator plants. Only the nickel and cobalt content was high.

Słowa kluczowe:

metale ciężkie, zanieczyszczenia miejskie, gleba, warzywa, rośliny wskaźnikowe

Keywords:

heavy metals, urban pollution, soil, vegetables, indicator plants



Environmental Aspects of Sorption Process

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1. Introduction

The perpetual progress of civilization associated with constant industry development especially in the field of transportation, chemical industry or refinery (Al-Majed et al. 2012, Piecuch and Piecuch 2013). brings the threat of uncontrolled release of hazardous substances into the environment (de Cassia et al. 2014, Polanczyk et al. 2013). Leakages of petroleum or other dangerous substances adversely affect the atmosphere, water or soil environment (Wu et al. 2014).

The substances classified as dangerous such as gasoline or petroleum, are exploited daily by most population. Therefore, the risk of environment contamination is extremely high. In case of emergency situation, e.g. a car accident where spillage of exploitation liquids appears, the Fire Department has to take actions to prevent chemical and ecological pollution (Lee and Jung 2013, Papadonikolaki et al. 2014, Zuo-fu and Jia-lin 2016). Therefore, substances with sorption properties, so-called sorbents, available in many forms, are able to collect not only petroleum substances but also other dangerous liquids, such as acids and alkalis (Demirel Bayik and Altin 2017, Dong et al. 2016, Thinakaran et al. 2008). The proper sorbent choice should include the location of the accident and the type and quantity of spilled petroleum substance (Półka et al. 2015). The ideal sorbent for cleaning oil spills should have the following features: good mutual solubility, high surface area (and/or high surface to thickness ratio), porous structure, high swelling, low degree of cross linking

(Wu et al. 2012). In potentially hazardous situation such as car accidents, the preventive activities are dedicated to stop spreading of the dangerous substances and to bring the road surface to its pre-event state (Ting Dong et al. 2015). In such situations the choice of sorbent type is directed into sand as it is “on hand” virtually everywhere and it prevents further soil contamination. However, in the case of large-scale leakages selection of the proper type of sorbent is necessary as application of the material with the best sorption properties may limit the costs of cleaning operation (Eakalak et al. 2004). Therefore, the aim of the study was to simulate and compare sorption process of petroleum products with the use of two types of sorbents.

2. Materials and methods

In this study the impact of sorption process of two sorbents (dry sand and compact) in contact with different petroleum substances (diesel and gasoline) was analyzed.

A dedicated set-up was applied for the analysis of sorption process in a laboratory scale. In the real conditions, excessive amount of sorbent is used to cover spilled sorbate (Fig. 1A). However, in the laboratory scale we used weighed sorbent that was packed in a dedicated syringe and immersed in a Petri dish filled with certain volume of sorbate (Fig. 1B).

To replicate the leakage of operating fluids from a car engine chamber to the ground, a Petri dish filled with certain volume of analyzed sorbate was used. Each time a longitudinal, transparent, cylindrical container made of polypropylene (Fig. 1Bb) was filled with 50 cm³ of analyzed sorbent (Fig. 1Be). A porous wall was located in the bottom of the longitudinal container to supports the contact between the sorbent and sorbate (Fig. 1Cg). The longitudinal container was hanged on the telescope joined with the electronic weight (Fig. 1Ba) placed on the anti-vibration table (Fig. 1Bc).. Each time the longitudinal container was immersed in 100cm³ volume of sorbate (Fig. 1Bf), placed in the Petri dish (Fig. 1Bd). The weight gain of the sorbate which penetrated the sorbent placed in a longitudinal container (Fig. 1Bb) was measured constantly with an electronic scale (mean error of the scale was equal to 2 mg). Data were recorded every 10 s, until the same value repeated three times at the scale monitor.

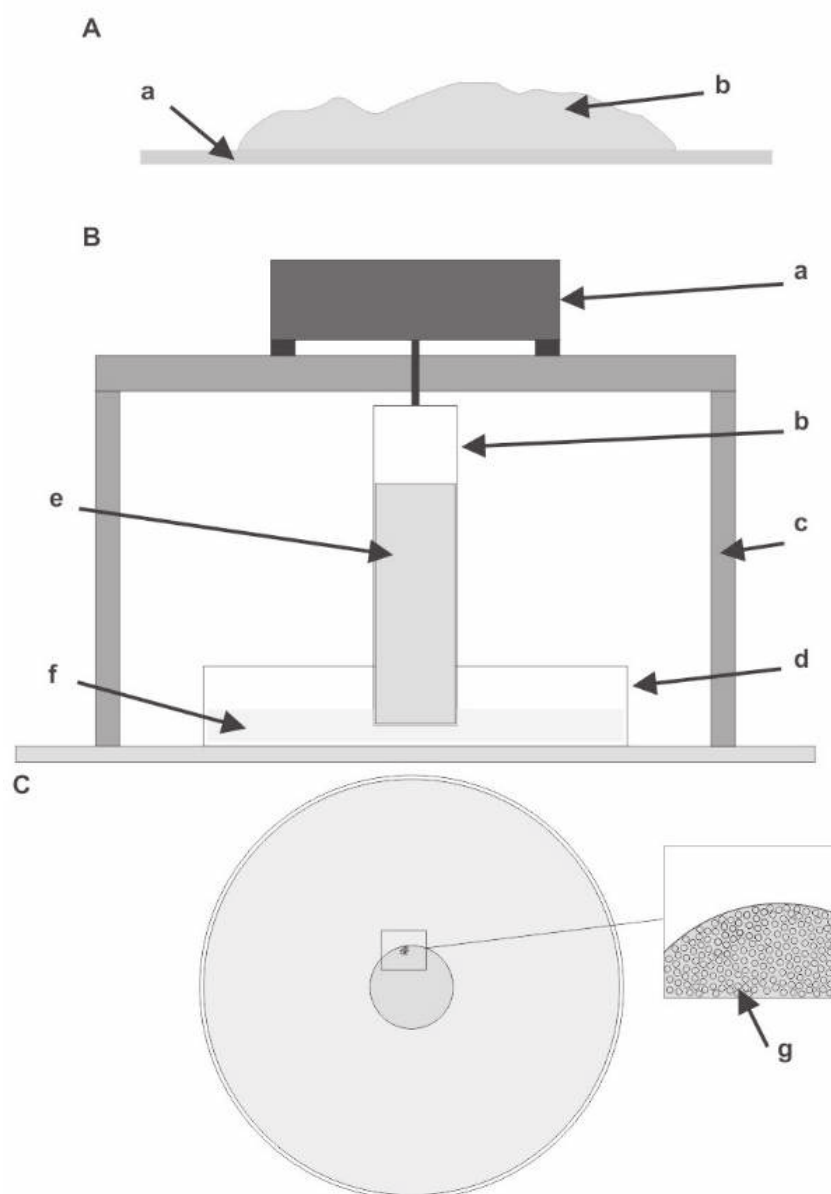


Fig. 1. A scheme of analyzed sorption process and experimental set-up, composed of: Part A real conditions – a) sorbate, b) sorbent; Part B (side view): a) an electronic weight, b) a cylindrical container for analyzed sorbent, c) an anti-vibration table, d) a Petri dish e) sorbent, f) sorbate; Part C (top view): g) porous bottom of a cylindrical container for analyzed sorbent

Rys. 1. Schemat procesu sorpcji i eksperymentalnego układu, składający się z: Część A rzeczywiste warunki – a) sorbent, b) sorbat; Część B (widok z boku): a) elektroniczna waga, b) cylindryczny pojemnik na analizowany sorbent, c) stół antywibracyjny, d) płytka Petriego, e) sorbent, f) sorbat; Część C (widok z góry): g) porowate dno cylindrycznego pojemnika na analizowany sorbent

Two operating fluids, diesel and gasoline (Table 1), in the final volume of 100cm³ were analyzed in different proportions (100% of gasoline or 100% of diesel; 50% of gasoline and 50% of diesel; 25% of gasoline and 75% of diesel; 75% of gasoline and 25% of diesel) and were exposed to two different types of sorbents, dry sand and compact (Table 1). Each time the sorption process was performed until no change in sorbate mass, recorded by scale, was detected. Also, reference sorption processes for 100% of gasoline and diesel were included. This approach allowed to compare the influence of volume proportion of both sorbates on the sorption process.

The analyses were performed for the following conditions: room temperature (20°C) and air relative humidity approximately 60%. The set-up was placed under a laboratory hood to avoid the influence of uncontrolled wind flow.

Table 1. Properties of analyzed sorbents and sorbates

Tabela 1. Właściwości analizowanych sorbentów i sorbatów

Properties	Dry sand	Compact	Diesel	Gasoline
Density (g/cm ³)	2.62	0.52	0.70	0.82
Size of grain (mm)	0.05-2.0	0.30	–	–
Viscosity (Pas)	–	–	0.83	0.80
Surface tension (mN/m)	–	–	28.40	24.65
Specific surface area (m ² /g)	–	–	0.1	18.00

Measurements were done in triplicates and presented as mean±standard deviation (SD).

3. Results

In this study we investigated the influence of applied sorbent and sorbate on the intensity of sorption process. At first 100% of each sorbate (gasoline and diesel) was investigated for both sorbents: compact and dry sand (Fig. 2a-b and Fig. 3a-b). Sorption for dry sand was equal to 0.12 ± 0.010 g/g and 0.14 ± 0.004 g/g for gasoline and diesel, respectively. While, for compact sorbent sorption was equal to 0.64 ± 0.003 g/g and 0.66 ± 0.038 g/g for gasoline and diesel, respectively. Similar trend, however with an increase in sorption intensity, was observed for both sorbents which contacted with the mixture of sorbates where: 50% was gasoline and 50% was diesel (Fig. 2c and Fig. 3c). Here the sorption process was equal to 0.14 ± 0.013 g/g and 0.71 ± 0.093 g/g for dry sand and compact sorbent, respectively. Moreover, further increase of the gasoline percentage in analyzed sorbate mixture (75% of gasoline and 25% of diesel) decreased sorption for dry sand to 0.12 ± 0.011 g/g. This value was equal to sorption of pure gasoline. Similar analysis made for compact indicated that sorption was equal to 0.65 ± 0.018 g/g, which was between the values received for pure gasoline and pure diesel. Finally, with the decrease of gasoline percentage in the analyzed sorbate mixture (25% of gasoline and 75% of diesel) sorption for dry sand was equal to 0.14 ± 0.012 g/g, which was comparable to 100% of diesel (Fig. 2e and Fig. 3e).

Moreover, the time of sorption was analyzed. The sorption time for concentrated diesel was 697 ± 94.5 s and 2180 ± 52.9 s for dry sand and compact, respectively. Interestingly, the sorption time of pure gasoline was 533 ± 20.8 s and 2325 ± 21.2 s for dry sand and compact, respectively. Therefore, sorption time for pure gasoline was longer compared to the diesel for both tested sorbents. Additionally, an increase in sorption process time was observed for increased concentration of diesel in sorbate mixture. For a mixture of 25% of gasoline and 75% of diesel sorption was equal to 845 ± 21.2 s and 2660 ± 102 s for dry sand and compact, respectively. When concentration of diesel was lower compared to gasoline (75% of gasoline and 25% of diesel) additional changes of sorption time were observed (860 ± 42.4 s and 2510 ± 240.4 s for dry sand and compact, respectively). Furthermore, an increase of sorption time was noticed for 50% of gasoline and 50% of diesel compared to concentrated sorbate (740 ± 10.0 s and 2675 ± 106.1 s for dry sand and compact, respectively).

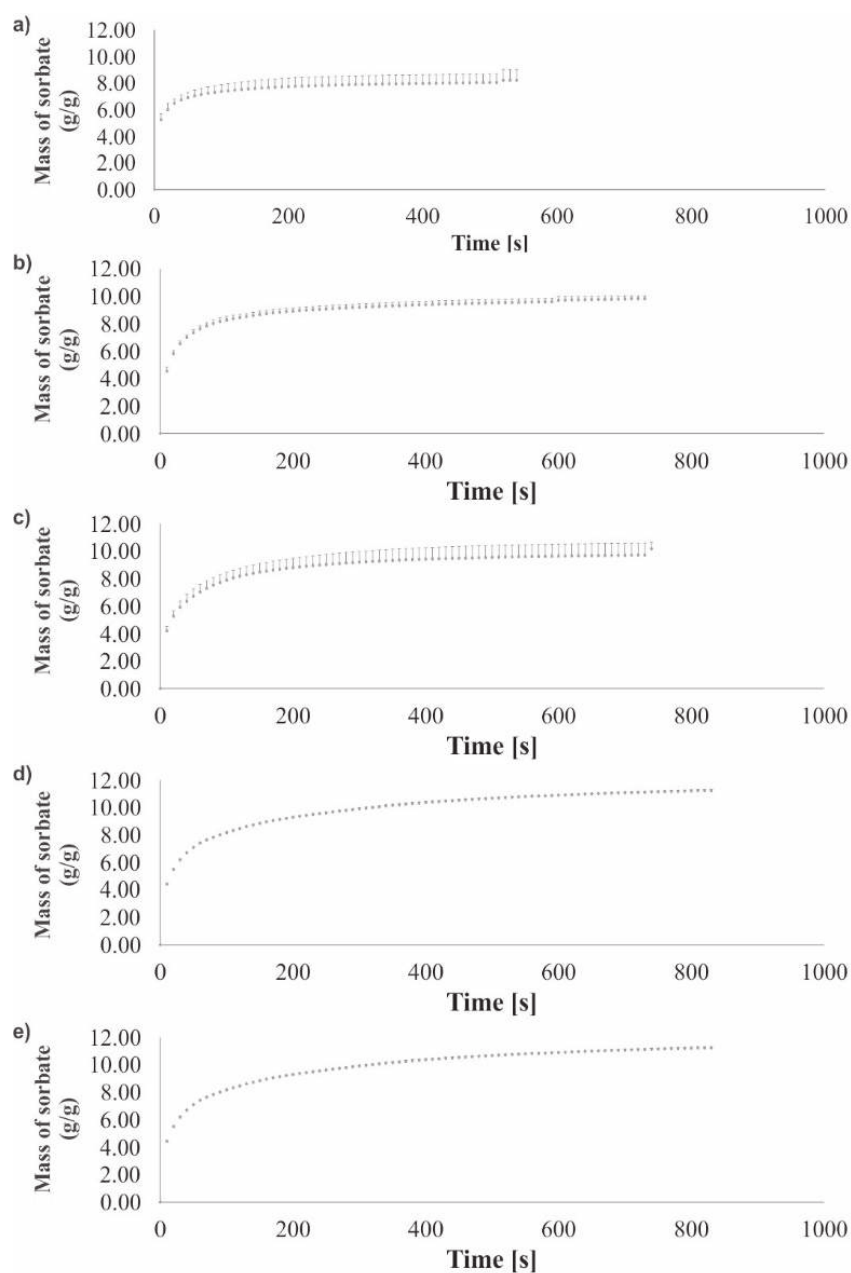


Fig. 2. Sorption process for dry sand in function of time for: a) 100% gasoline; b) 100% diesel; c) 50% gasoline 50% diesel; d) 75% gasoline 25% diesel; e) 25% gasoline 75% diesel. Results are presented as mean \pm SD

Rys. 2. Proces sorpcji dla suchego piasku w funkcji czasu dla: 100% benzyny; b) 100% diesla; c) 50% benzyny i 50% diesla; d) 75% benzyny i 25% diesla; e) 25% benzyny i 75% diesla. Wyniki sa przedstawione jako srednia \pm odchylenie standardowe (SD)

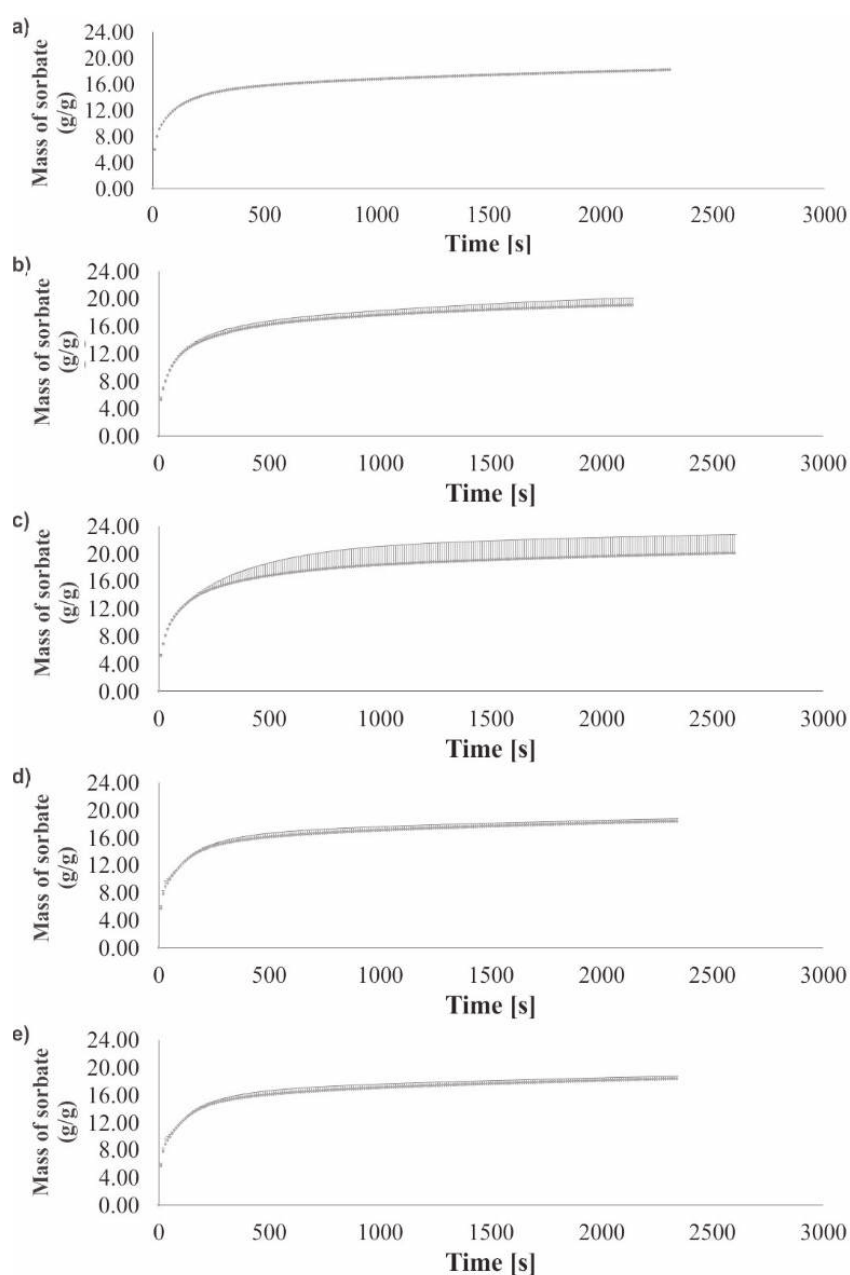


Fig. 3. Sorption process for compact sorbent in function of time for: a) 100% gasoline; b) 100% diesel; c) 50% gasoline 50% diesel; d) 75% gasoline 25% diesel; e) 25% gasoline 75% diesel. Results are presented as mean \pm SD

Rys. 3. Proces sorpcji dla sorbentu compact w funkcji czasu dla: 100% benzyny; b) 100% diesla; c) 50% benzyny i 50% diesel; d) 75% benzyny i 25% diesel; e) 25% benzyny i 75% diesel. Wyniki sa przedstawione jako $\text{średnia} \pm \text{odchylenie standardowe (SD)}$

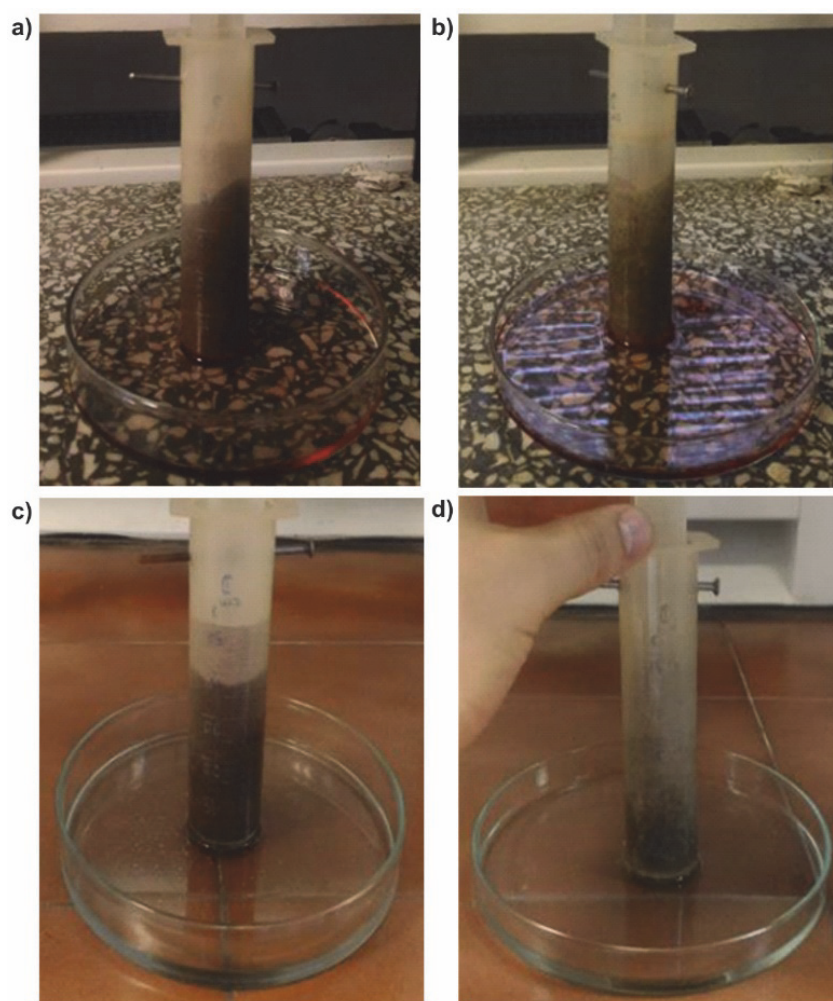


Fig. 4. An example of sorbate profiles for: a) compact for 50% of gasoline and 50% of diesel; b) dry sand for 50% of gasoline and 50% of diesel; c) compact for 100% of gasoline; d) dry sand for 100% of gasoline

Rys. 4. Przykład profilu sorbatu dla: a) sorbent compact dla 50% benzyny i 50% diesel; b) suchy piasek dla 50% benzyny i 50% diesel; c) sorbent compact dla 100% benzyny; d) suchy piasek dla 100% benzyny

Finally, a profile of sorbate in a dedicated container filled with dry sand or compact was analyzed. Each time the profile of sorbate (gasoline as well as diesel) for compact had a regular shape (Fig. 4b and Fig. 4d), while for the dry sand sorbate profile was irregular (Fig. 4a and Fig. 4c).

4. Discussion

This paper presents the results of sorption process of two petroleum products, gasoline and diesel, with the use of two types of sorbents, dry sand and compact. Gathered data showed that the effectiveness of sorption process is higher, and the sorption process is longer for compact sorbent compared to dry sand. These results were in line with Patrushev et al. who analyzed the properties of capillary columns with synthetic sorbents (Patrushev et al. 2015). Also, Choi et al. investigated biodegradable waste as sorbent material for oil spill cleanup (Idris et al. 2014), and Bandura et al. applied similar procedure to determine sorption of clinoptilolite towards diesel and biodiesel oils (Bandura et al. 2015).

In our paper sorption for dry sand was equal to 0.12 g/g and 0.14 g/g for gasoline and diesel, respectively. Similarly other authors examined sand in contact with diesel, however in glass column and smaller amount (Michel 2005). Michel noticed that sorption for sand and diesel was in range of 0.03-0.05 g/g (Michel 2005). While, Zadaka et al. received sorption equal to 0.17 g/g after connection of sand and diesel (Zadaka-Amir et al. 2013). Those results were close to Carmody et al. who received sorption in range 0.2-0.3 g/g (Carmody et al. 2007). Therefore, our results are in line with data received by other authors.

This study has the following limitations: the area of sorbent activity was restricted to cylindrical container's wall, while in real conditions sorbent is freely spilled. Moreover, we did not include stirring of sorbent and sorbate which could increase the intensity of sorption process.

5. Conclusions

To sum up, comparison of compact sorbent and dry sand indicated that the effectiveness of sorption process is 6-times higher for compact sorbent compared to dry sand. Additionally, the time of sorption process was 4-times longer for compact sorbent in comparison to dry sand which correlated with higher volume of absorbed liquid. Therefore, the results indicated that a compact sorbent in contact with petroleum substances i.e. gasoline or diesel is a better solution compared to dry sand. Moreover, compact sorbent is non-flammable substance, hence it does not pose an additional threat, even if rescuers do not have full knowledge about the collected medium. However, the dry sand is a suit-

able material for limiting of the area covered with potentially danger liquids especially in places where commercial sorbents are unavailable, and the area is covered with potentially dangerous liquids.

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Środowiskowe aspekty procesu sorpcji

Streszczenie

Substancje sklasyfikowane jako niebezpieczne, tj. benzyna czy ropa naftowa, są codziennie wykorzystywane przez ludzi. Ich stosowanie związane jest bezpośrednio z wysokim ryzykiem zanieczyszczenia środowiska np. w wyniku wypadku samochodowego. W przypadku wycieku stosuje się substancje umożliwiające zabezpieczenie miejsca zdarzenia, tj. sorbenty. Z tego też względu celem badania była analiza w jakim stopniu proces sorpcji zależy od rodzaju zastosowanego sorbentu, sorbatu, a także ich proporcji. Eksperymenty prowadzono w skali laboratoryjnej, w której dwa płyny eksploatacyjne, tj. olej napędowy i benzyna, były mieszane na płytce Petriego w różnych proporcjach w łącznej objętości 100 cm³. Analizowane płyny eksploatacyjne wystawiano na działanie dwóch różnych typów sorbentów: komercyjny sorbent „compact”

i suchy piasek. Waga sorbatu penetrującego sorbent była odczytywana co 10 s przy pomocy elektronicznej wagi. W celu odwzorowania rzeczywistych warunków, w których płyny eksploatacyjne po wycieku mieszają się, sorбаты były analizowane jako mieszaniny w następujących proporcjach: 100% do 0%, 0% do 100%, 50% do 50%, 25% do 75% i 75% do 25% (odpowiednio dla oleju napędowego i benzyny). Co więcej, w celu wyznaczenia referencyjnych punktów badania wykonano również dla czystych sorbatów. Na podstawie otrzymanych wyników opracowano wykresy procesu sorpcji dla dwóch sorbentów i dwóch sorbatów w funkcji czasu. Proces sorpcji dla suchego piasku wynosił odpowiednio $0,12 \pm 0,010$ g/g i $0,14 \pm 0,004$ g/g dla benzyny i oleju napędowego (100% udział analizowanych sorbatów). Podczas gdy dla komercyjnego sorbentu „compact” sorpcja wynosiła odpowiednio $0,64 \pm 0,003$ g/g i $0,66 \pm 0,038$ g/g dla benzyny i oleju napędowego (100% udział analizowanych sorbatów). Podobny trend procesu sorpcji zaobserwowano w przypadku kontaktu komercyjnego sorbentu „compact” z mieszaniną sorbatów (50% benzyny i 50% oleju napędowego udziału analizowanych sorbatów). Wówczas proces sorpcji wynosił odpowiednio $0,14 \pm 0,013$ g/g i $0,71 \pm 0,093$ g/g dla suchego piasku i komercyjnego sorbentu „compact”. Co więcej, przeanalizowano, który sorbat wywiera większy wpływ na proces sorpcji. W tym celu analizowano mieszaninę sorbatów w następujących udziałach: 75% do 25% i 25% do 75% dla benzyny i oleju napędowego. Uzyskane wyniki wskazują, iż dla benzyny i oleju napędowego (25% do 75%) proces sorpcji wynosił $0,14 \pm 0,012$ g/g dla suchego piasku. Natomiast dla komercyjnego „compactu” sorpcja wynosiła $0,65 \pm 0,018$ g/g. Również w badaniach analizowano czas procesu sorpcji. Otrzymane wyniki wskazują, iż czas procesu sorpcji dla suchego piasku w połączeniu z olejem napędowym i benzyną był około 4 razy krótszy w porównaniu do komercyjnego sorbentu „compact”. Podsumowując należy uznać, iż komercyjny sorbent „compact” bez względu czy jest stosowany do czystych płynów eksploatacyjnych czy też do mieszanin jest wydajniejszy w porównaniu do suchego piasku.

Abstract

Substances classified as dangerous such as gasoline and petroleum, are used daily by most of population. Therefore, they pose a potential threat of environment contamination for example in case of emergency, e.g. car accidents. This study aimed to simulate and compare sorption process of petroleum products with the use of two types of sorbents.. To replicate the leakage of operating fluids from a car engine chamber to the ground, a Petri dish filled with 100 cm³ volume of analyzed sorbate was used. Fluids were exposed to two different types of sorbents such as compact and dry sand. The weight gain of the sorbate which penetrated the sorbent was measured every 10 s with an electronic scale.

Analyzed sorbents, diesel and gasoline, were tested in the following proportions: 100% to 0%, 0% to 100%, 50% to 50%, 25% to 75% and 75% to 25% (diesel to gasoline, respectively). The figures of sorption processes for different types of sorbents and sorbates in function of time were prepared. Sorption process for dry sand was equal to 0.12 ± 0.010 g/g and 0.14 ± 0.004 g/g for concentrated gasoline and diesel, respectively. While, for compact it was 0.64 ± 0.003 g/g and 0.66 ± 0.038 g/g for gasoline and diesel, respectively. Similar trend, however with an increase in sorption intensity, was observed for both sorbents contacted with equal mixture of sorbates (50% of gasoline and 50% of diesel). Here, sorption process was equal to 0.14 ± 0.013 g/g and 0.71 ± 0.093 g/g for dry sand and compact, respectively. Moreover, further increase of the gasoline percentage in analyzed sorbate mixture (75% of gasoline and 25% of diesel) decreased sorption for dry sand to 0.12 ± 0.011 g/g. Moreover, sorption time for pure gasoline was 4-times longer for compact sorbent in comparison to dry sand which corresponds with higher volume of absorbed liquid. Also, sorption process was 6-times higher for compact sorbent compared to dry sand. Therefore, the results indicated that a compact sorbent in contact with petroleum substances i.e. gasoline or diesel is a better solution compared to dry sand. However, the dry sand is a suitable material for limiting of the area covered with potentially dangerous liquids especially in places where commercial sorbents are unavailable, and the area is covered with potentially dangerous liquids.

Słowa kluczowe:

sorpcja benzyny, sorpcja diesla, sorpcja paliwa, piasek sorbent compact

Keywords:

gasoline sorption, diesel sorption, petroleum sorption, sand sorbent compact



Investigation of a Slotted Separator for Hydromechanical Installation of Sludge Removal from a Water Reservoir

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1. Introduction

The gradual silting of reservoirs, causing their capacity reduction, is a crucial factor limiting their proper operation. In the summary of the KLIMAT project (Kloze & Sieinski 2012), it was assessed that the large retention reservoirs existing in Poland lost over 200 million m³ of their original capacity. It was found that in Poland there is no full, reliable information about the current capacity of dam reservoirs. This was supported by the analysis of data from 51 reservoirs, of which only on one measurement were carried out every 6 years, on 21 bathymetric measurement reservoirs were never performed, and on the other controls were carried out every 5-10 years or with breaks from 23 to 45 years. There are no systematic studies of smaller reservoirs that are more sensitive to capacity loss. The silting intensity of reservoirs, expressed in terms of the average annual reduction in their initial capacity, is for large reservoirs around 0.25%, for mediums around 0.5%, and for small ones even up to 3% (Madeyski et al. 2008). Michalec (2012) on the basis of research suggests that the function of small water reservoirs is limited already by reducing the volume from 40 to 60% and therefore the service life of these reservoirs should be determined for silting of 50% of primary capacity.

The operating costs associated with the removal of sludge usually exceed the investment costs for the construction of a new reservoir.

However, the possibility of locating and building large capacity reservoirs in Poland are significantly limited and therefore the degradation of existing reservoirs cannot be allowed (Kloze & Sieinski 2012).

Despite the recommendations of the EU Water Framework Directive (2000), to achieve good state and ecological potential of surface water by the end of 2015, more than half of these waters (including 90% of lakes) have not achieved this goal. One of the most important reasons for this ecological state of Polish waters is the accumulation of organic fractions of bottom sediments, which, by fermenting, emit soluble phosphorus compounds to the water body and extract oxygen. This leads to eutrophication and algal blooms that dies and fall massively to the bottom of the reservoirs.

The construction of a dam on the river interrupts the continuity of the flow of river sediment. Conditions are created for the development of undesirable processes: accumulation of sediment, decrease of useful capacity of the reservoir, rising of the bottom and level of water in the backwater of the reservoir, and erosion of the bottom and banks below.

One of many methods of revitalizing small water bodies is the removal of bottom sediments accumulated over the years, for example by leaching or periodically dredging sediments (Bartoszek et al. 2017). These works require the use of pumps with combustion engines, although the energy of accumulated water can be used to rinse the sediments from the reservoir (Zawadzki et al. 2017).

2. Installation of hydromechanical sludge removal

Morris & Fan (1997) proposed that in order to reduce the volume of accumulated sediment and leaching accumulated deposits, use the ducts laid on the bottom or floating on the surface and carried through the dam as a siphon or antisiphon. The technique has been successfully implemented and described by Liu et al. (2002) and Carone et al. (2006). The material transported in this way can flow directly to the river or fields. The debris entering the reservoir can be continuously or periodically transported from the inlet, upper part of the reservoir to the lower station by means of ducts arranged on the bottom (Morris & Fan 1997).

Zawadzki & Błażejowski (2017) developed a prototype installation that would allow sorting of transported sediments, of which thicker

mineral debris is directed to the river, below the strengthening of the bottom and minor mineral and organic fractions, after dewatering could be used for agricultural purposes. The installation guarantees continuous flow of water and sediment, and the use of only the difference between the upper and lower water levels. This installation has been described in the patent application and then covered by patent protection (decision of November 2017).

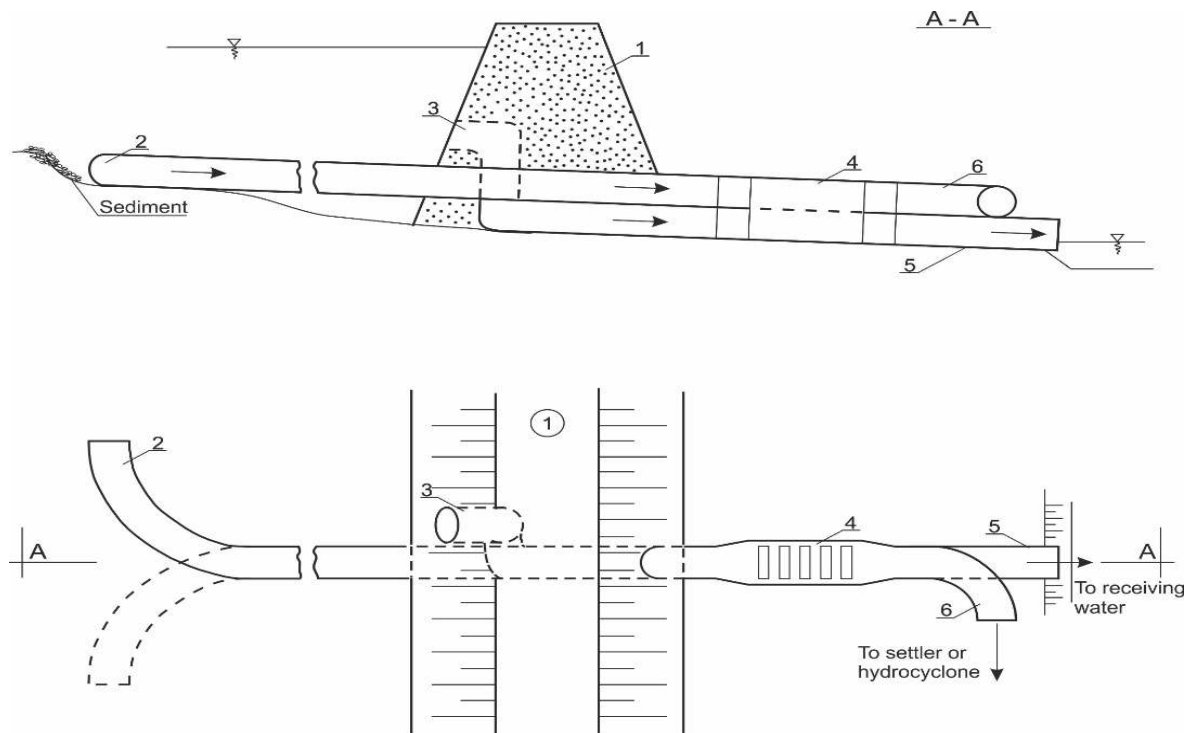


Fig. 1. Scheme of installation for hydromechanical sorting and removal of sediments (Zawadzki & Błażejowski 2017)

Rys. 1. Schemat instalacji hydromechanicznego sortowania i usuwania osadów dennych (Zawadzki i Błażejowski 2017)

The installation consists of two pipes, connected partly on a short section by a slot separator (4). The inlet to the pipe to which the sludge is sucked together with the water (2) is located in the reservoir upstream the dam (1). The second pipe (3) is used to extract pure water. In the separator (4), the thicker mineral material falls through the slots into the lower duct (5), which along with the clean water is transported directly to channel downstream of weir. Water carrying organic and fine mineral material, flowing above the slots, is guided by a pipe (6) to the hydrocyclone.

3. Slotted separator

The most important element of the hydromechanic installation for removing and purifying the bottom sediments is the slit separator, which is to separate the sediment collected from the bottom of the reservoir into two fractions. The operation of the separator is modeled on the work of a slotted sandbox, which is a horizontal flow device with a separate sand storage chamber outside the flow channel (Mołoniewicz et al. 1979, Cywiński et al. 1972). This sand is removed periodically mechanically or hydraulically. In the separator, continuous flow of water or water with sediments in the line below the slots is to ensure the transport of solid particles. The construction and operation of the separator should be carried out in such a way as to create working conditions in which:

- at least 75% of the mineral parts with a diameter of more than 0,2 mm are retained,
- organic particles more than 10% of the total amount of transported sediment should not be retained (Mołoniewicz et al. 1979).

The principle of operation of this type of separators is that as a result of the flow velocity reduction, a thicker fraction (sand) is released from the transported mixture, which is dragged through the bottom into the slots. According to Hazen's theory, the time t of a solid particle falling with the velocity $w \approx w_{ss}$ at the depth h is equal to the time of its horizontal transport to the distance $l = t \cdot v$. The velocity of the water flow in the separator v should depend on the settling velocity of the solid particle, the removal of which is desirable. The calculation parameters of horizontal channel separators are: flow velocity, flow time and hydraulic load on the surface of the grit chamber.

For the proper operation of the separator, it is necessary to create heterogeneous flow conditions or, possibly, a flow with a movable bottom (the highest concentration of solid particles is at the bottom of the duct). Assuming that in the water supply line with sediments to the slotted separator, the flow will be in a homo- or heterogeneous regime, at the beginning of the separator a velocity should be reduced to approx. $0.4 \text{ m}\cdot\text{s}^{-1}$ or $0.7 \text{ m}\cdot\text{s}^{-1}$ (Mołoniewicz et al. 1979). These velocities allow to stop sand with a diameter of 0.2 mm or 1.0 mm.

When separating mixtures of fine and very fine grains, the classification process (separation) is often carried out in a water or air medium, and different forces act on the grain of the classified material (centrifugal, jet or center resistance, gravity, buoyancy, etc.). It is not perfect and part of the grain goes to the wrong product.

Theoretically, a perfectly working slotted separator should allow the separation of two fractions: thicker (cleaned), after passing through the slots flowing down the lower duct, from finer (polluting), discharged with the upper duct. An undesirable effect would be the mutual contamination of the fraction after passing through the separator slots. In our research, it was proposed that the efficiency of the dispersive suspension separator should be calculated according to the formula:

$$\eta = \beta_p \cdot (1 - \beta_n) \quad (1)$$

where:

β_p – degree of sorting desired grains,

β_n – degree of sorting unwanted grains.

The definition of degree of sorting β was adopted after Kowalski (2004), which, with the degree of sedimentation (or degree of deposition) of the i -th grain class, determines the ratio of the mass stream of particles in the nozzle to the associated stream in the suspension introduced into the plant (in the feed). The degree of sorting informs what part of the grains of the i -th fraction transported by the upper duct flows along with the water through the fissures to the lower duct. It is expected that in a well-functioning separator the degree of sorting of the thicker fractions will be as high as possible ($\beta_p \rightarrow 1$), while for the fine and organic fractions, the smallest ($\beta_n \rightarrow 0$).

4. Laboratory tests

In order to determine the hydraulic conditions for the flow and sorting of the mixture of water and sand through a slotted separator, laboratory tests were carried out. The research installation was made at the water laboratory of the Department of Hydraulic and Sanitary Engineering, Poznań University of Life Sciences. The laboratory installation consisted of a supply pipeline, a sediment feeder, a slotted separator and two

discharge pipes with valves (Fig. 2). The installation allow to measure and regulate flows in the upper and lower separator ducts.

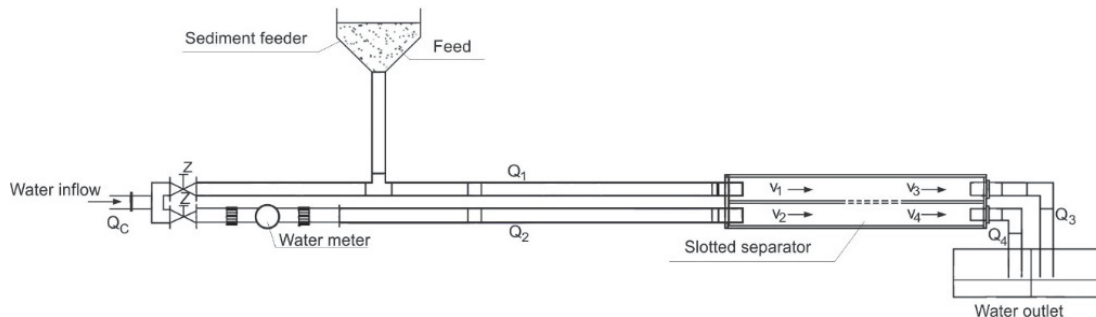


Fig. 2. Scheme of laboratory installation (own work)

Rys. 2. Schemat instalacji badawczej (opracowanie własne)

The slotted separator was made as a rectangular box with external dimensions: length 1020 mm, height 210 mm and width 100 mm. In the middle of the rectangular height, guides were made to install a baffle plate dividing the separator into working chambers with square cross-sections and dimensions of 80 x 80 mm. The cuboid was closed with front and back panels, in which two 50 mm diameter holes were made, allowing for supply and drainage of the water jet from the upper and lower separator wire. To enable observation of the processes taking place in the separator, all of its elements are made of transparent polymer plastic with a thickness of 10 mm. This resulted in a rigid and airtight installation, not subject to deformation under the influence of water pressure and the weight of the mixtures.

The tests on the physical model were conducted under steady state conditions, with total flows (flow fed to the research installation $Q_c = Q_1 + Q_2$) taken from the range of $3.50 \text{ dm}^3 \cdot \text{s}^{-1} < Q_c < 12.50 \text{ dm}^3 \cdot \text{s}^{-1}$. The assumed flow rates allowed to obtain the average water flow rates at which hydraulic separation of solid particles was possible.

In the separator, 3 slots with a width of 20 mm were chosen every 20 mm (spacing between the axis of the slots - 40 mm). A larger number (14 or 9) of slots meant that most of the mineral material fed to the separator through the upper duct, flows through the slots and flows out through the bottom duct of the separator. It was assumed that the first slot

should not be less than 0.5 m (half the length of the separator) and that this length allows the thicker mineral fractions to sink to the bottom of the sandbox and transport the particles in the bedloaded regime.

In the first stage of the research, as a mineral material, simulating the transported sludge, three mineral fractions with grains were used: from 0.125 mm to 0.5 mm, from 1.0 mm to 2.0 mm and from 4 mm to 20 mm. The fractions were obtained after sieving a sand. However, the results of the tests were not entirely satisfactory. During the tests, hydraulic conditions were created at which sorting of transported fractions took place and relatively high efficiency of the separator was achieved (maximum $\eta = 51\%$, average efficiency of the separator ranged from 32% to 0.35%). Higher efficiency of the separator was obtained for similar velocities in the upper and lower ducts ($v_1 \approx v_2$). The other velocity ratio on the inflow ($v_1 \ll v_2$ or $v_1 \gg v_2$) caused unfavorable hydraulic conditions for grain sorting.

Observation of transported mineral particles of different density and shape (which could have a significant influence on the transport of individual grains, Bridge & Bennett 1992, Hämmerling et al. 2014), does not allow assuming in the analysis the assumption that all fraction grains have equal density ($\rho_s = 2650 \text{ kg} \cdot \text{m}^{-3}$), a spherical shape described by d_s diameter as well as described by one value of the settling velocity w_{ss} of a single grain.

Therefore, in main studies, spherical particles of different density were used as the simulation material for the removed sediment. The balls were used - ASG ammunition (Air Soft Gun) for pneumatic guns, which manufacturers guarantee high accuracy (diameter $6.0 \pm 0.05 \text{ mm}$), and which is made of plastics of various density and different color (Fig. 3). Particles with specific gravity $\rho_s = 1061, 1768$ and $2653 \text{ kg} \cdot \text{m}^{-3}$ were used. Their detailed characteristics are presented in Table 1.

Two series of experiments were performed: **A** with spherical particles K^I and K^{III} and **B** with K^{II} and K^{III} . In experiment **A**, particles with a large difference in density were deliberately selected so that favorable hydraulic sorting conditions and high efficiency of the separator η (eq. 1) were obtained. In all experiments, the equal velocity at which water was supplied to the separator by the upper and lower lines $v_1 = v_2$ was assumed. In subsequent repetitions, the flow rate was increased so that the velocity v_1 were equal $0.4 \text{ m} \cdot \text{s}^{-1}$, $0.45 \text{ m} \cdot \text{s}^{-1}$, $0.5 \text{ m} \cdot \text{s}^{-1}$ and $0.55 \text{ m} \cdot \text{s}^{-1}$ on

the inflow. Dosing of solid particles was started after the water flow conditions were established. The experiments at four different velocities v_1 were carried out with a total mass of dosed particulates (feed) equal to: 400 g, 600 g and 1000 g (Tab. 2). Each experiment at a given average velocity and feed was repeated three times, performing a total of 36 experiments in each series. The results of experiments in series **A** and **B** of the studies are shown in Figures 4-6.



Fig. 3. The material used in the research. Spherical particles with diameter $d = 6.0 \pm 0.05$ mm and specific density $\rho_s = 1061, 1768$ and 2653 $\text{kg}\cdot\text{m}^{-3}$

Rys. 3. Materiał użyty w badaniach. Cząstki kuliste o średnicy $d = 6,0 \pm 0,05$ mm i gęstości właściwej $\rho_s = 1061, 1768$ i 2653 $\text{kg}\cdot\text{m}^{-3}$

Table 1. Hydraulic characteristics of spherical particles

Tabela 1. Charakterystyka hydrauliczna cząstek kulistych

Symbol	Specific density ρ_s	Mass	Drag coefficient C_D	Reynolds number for grain Re_s	Settling velocity w_{ss}
	$\text{kg}\cdot\text{m}^{-3}$	g	–	–	$\text{m}\cdot\text{s}^{-1}$
K^I	1061	0,12	0,571	545	0,092
K^{II}	1768	0,20	0,415	2273	0,381
K^{III}	2653	0,30	0,388	3447	0,578

Fig. 4 shows the degree of sorting and separator efficiency in subsequent **A**-series experiments. In these experiments the separation of particles of different density was relatively easy and effective. At the bottom of the separator from the separator, almost only K^{III} particles and few K^I were observed. This is confirmed by degree of sorting β (eq.1): very high 0.75-0.95 for K^{III} particles falling through the slots and very low 0.0-0.15 for K^I particles.

Table 2. The volume flow of solid particles Q_s during emptying of the feeder
Tabela 2. Objętościowe natężenie cząstek stałych Q_s przy wypływie z dozownika

Mixture	Feed mass	Volume of solid particles V_s	Average dispensing time \bar{t}_s	Volume flow of solid particles ¹ Q_s
	g	dm ³	s	dm ³ ·s ⁻¹
$K^I + K^{III}$	200+200	0,264	7,3	0,036
	300+300	0,396	10,9	0,036
	500+500	0,660	18,6	0,035
$K^{II} + K^{III}$	200+200	0,189	5,5	0,034
	300+300	0,283	7,8	0,036
	500+500	0,471	13,8	0,034

¹ volume flow of solid particles determined on the basis of $Q_s = \frac{V_s}{\bar{t}_s}$

In the **B** series experiments, the efficiency of the separator varied from 0.1 to 0.4 (Fig. 5) and was significantly lower than in the **A** series experiments. Although the degree of K^{III} particle sorting remained very high ($\beta_p = 0.78-0.91$) but at the same time too many K^{II} particles were flowing through the slots ($\beta_n = 0.53-0.85$). If for Mołoniewicz et al. (1979) criteria for evaluating the correct operation of the separator will be adopted (no less than 75% of the initial mass of the coarse fraction is retained, and the admixture of fine fraction – undesirable – does not exceed 10%). The expected efficiency should not be less than: $\eta = 0.75 \cdot (1-0.1) \cdot 100\% = 67.5\%$. In the **A** series experiments, higher efficiency of the separator was obtained.

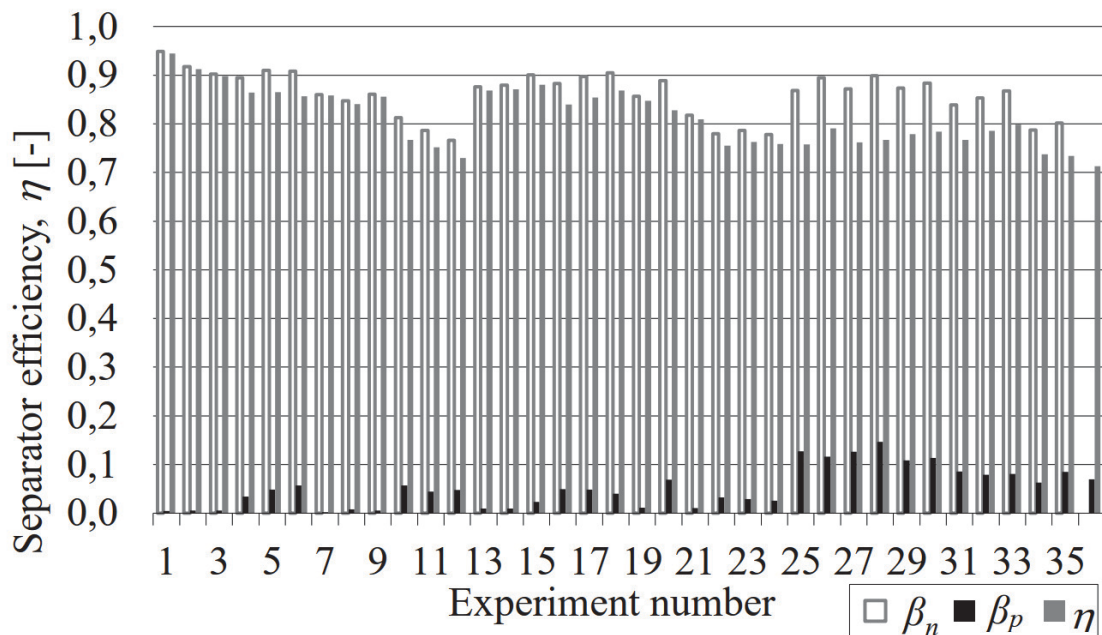


Fig. 4. Variations in degree of sorting and efficiency in subsequent experiments in series A

Rys. 4. Zmiany stopnia wysortowania i sprawności w kolejnych doświadczeniach serii A

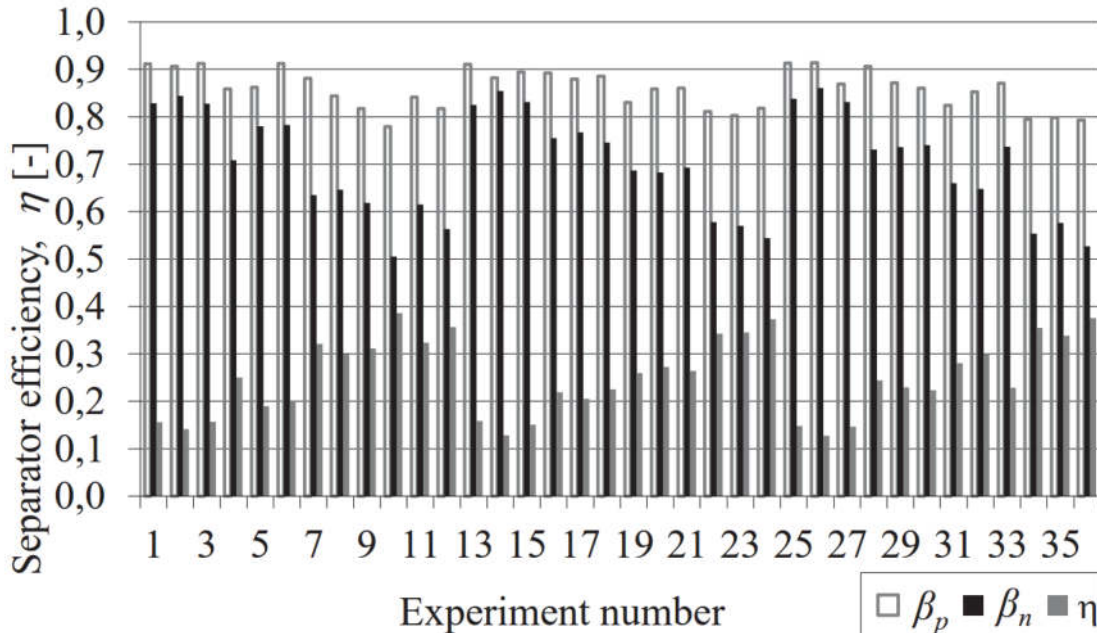


Fig. 5. Variations in degree of sorting and efficiency in subsequent experiments in series B

Rys. 5. Zmiany stopni wysortowania i sprawności w kolejnych doświadczeniach serii B

In experimental **A** the efficiency of the separator was not less than 70%, the highest was obtained with the velocity $v_1 = 0.4 \text{ m}\cdot\text{s}^{-1}$ and the feed 400 g $\eta = 0.9\text{-}0.95$, the smallest at $v_1 = 0.55 \text{ m}\cdot\text{s}^{-1}$ and feed 1000 g $\eta = 0.7\text{-}0.75$. It can be noticed that the efficiency of the separator decreased not only with the increase in the weight of the feed, but also with the increase in velocity v_1 (Fig. 6).

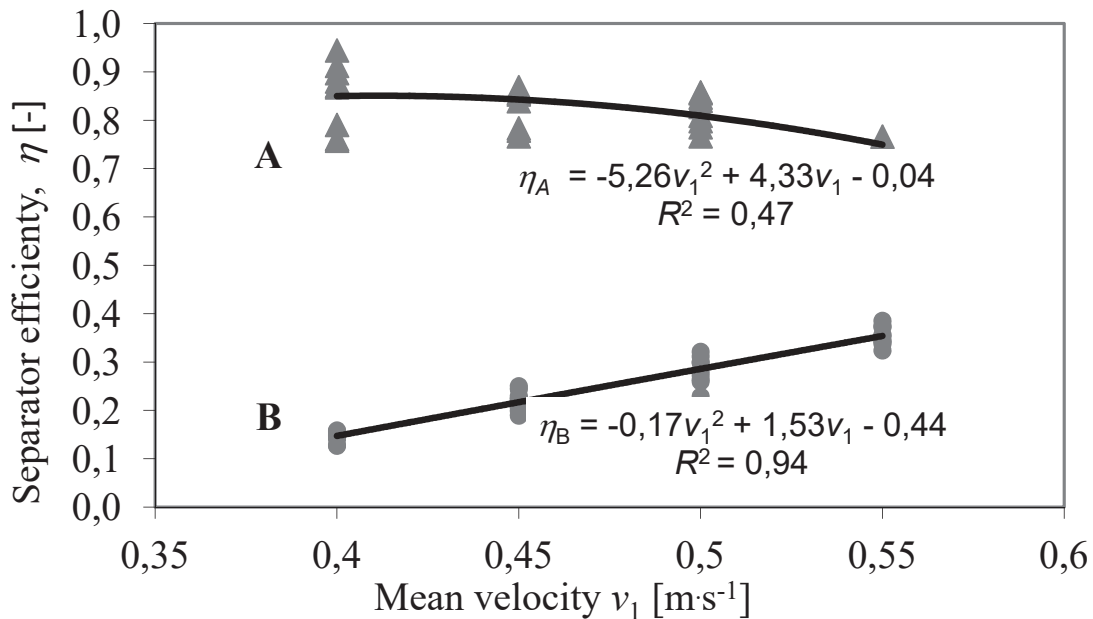


Fig. 6. Relationship between average approach velocity v_1 and separator efficiency in experiment of series **A** and **B**

Rys. 6. Zależność między prędkością średnią v_1 , stopniem wysortowania i sprawnością separatora w doświadczeniach serii **A** i **B**

Efficiency η significantly improved with the increase of the flow rate of the mixtures the upper separator line above the slots (Fig. 6). The value of the determination coefficient $R^2 = 0.94$ indicates a very strong relationship ($R^2 > 0.9$) between these values. The increase in velocity v_1 caused that a larger number of K^{II} particles did not roll over the bottom, but was carried over the slots and the sorting was more effective.

The increase in velocity in the upper duct above the v_1 slots in the **A** series experiments caused a slight decrease, and in the **B** series experiments a significant increase in the efficiency of the separator. Hydraulic conditions have an effect on the sludge flow regime, in this case in par-

ticular on lighter K^I or K^{II} particles. Fig. 7 shows the dependence of the sorting degree β and the velocity ratio in the upper conduit above the slots v_1 to the hydraulic feature of the w_{ss} particle. The value of the coefficient of determination shows a very strong relationship between these values. Variability of the degree of sorting in almost 90% is caused by changes in the relation of the average velocity and hydraulic characteristics of the grain (settling velocity). At velocities $v_1 \gg w_{ss}$, the particles are transferred above the slots.

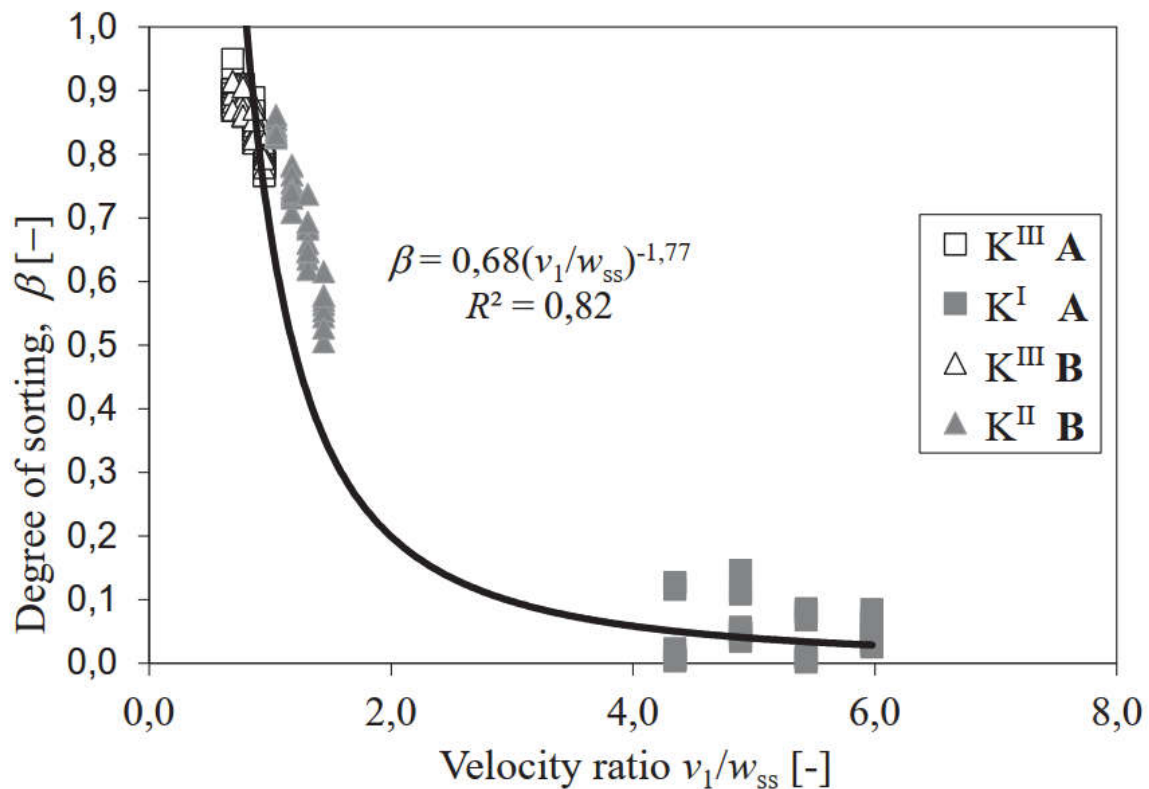


Fig. 7. Relationship between v_1/w_{ss} and degree of sorting β

Rys. 7. Zależność między v_1/w_{ss} i stopniem wysortowania β

The second parameter that can affect the efficiency of the separator is the area of the working chamber, determined to the edge of the last slot. As mentioned earlier, the work of a slotted separator is similar to the operation of a settling tank with continuous removal of deposits. According to Hazen's law, the efficiency of sedimentation of a free falling particle depends only on the surface of the settler, and the depth of the settler has not influence (Cywiński et al. 1972). Unfortunately, in the described

tests, an attempt to change the position configuration, spacing and the number of slots was unsuccessful. Although in the initial phase of the research (with mineral particles) the position and number of slots were changed, but after a series of experiments with 3 slots with 2 cm intervals, it was not possible to change the configuration of the slots.

The values determining the efficiency of the slotted separator can be taken into account by assuming the dimensionless Hazen number expressed in the formula for analysis

$$Ha = \frac{Q}{A_o \cdot w_{ss}} = \frac{v_1 \cdot A}{A_o \cdot w_{ss}} = \frac{v_1}{w_{ss}} \cdot \frac{A}{A_o} \quad (2)$$

where:

Q – volumetric flow rate, $\text{m}^3 \cdot \text{s}^{-1}$,

A_o – surface area of the horizontal projection of the settling chamber, m^2 ,

w_{ss} – settling velocity of single particle, $\text{m} \cdot \text{s}^{-1}$,

v_1 – average velocity, $\text{m} \cdot \text{s}^{-1}$,

A – cross-sectional area of the working chamber, m^2 .

Fenner & Tyack (1997) and Gulliver et al. (2009) as the similarity criteria for hydrodynamic separators, they propose Hazen number:

$$Ha = idem \quad (3)$$

Accepting the Hazen number as a similarity criterion allows for planning subsequent laboratory tests, designing an installation for drowning water reservoirs in a technical scale or forecasting the efficiency of geometrically similar slot separators. Considering the Hazen number, when modeling geometrically similar separators and using the same size particles $(w_{ss})_M = (w_{ss})_{M\alpha}$ we calculate the volumetric flow rate of water according to the dependence

$$\frac{Q_{M\alpha}}{Q_M} = \frac{(w_{ss} \cdot A_o)_{M\alpha}}{(w_{ss} \cdot A_o)_M} = 1 \cdot \alpha^2 = \alpha^2 \quad (4)$$

where:

α – scale ratio.

The fulfillment of this condition causes that on geometrically similar separators, its dimensions can be changed: width, number and spacing of slots, assuming the average flow velocity and the ratio v_1/w_{ss} , at which the process was the most efficient.

5. Conclusions

Laboratory tests were carried out on a physical model of a slotted separator, in which mineral particles with diameters from 0.15 to 12.0 mm and spherical particles with a diameter of 6.0 mm made of materials with a density range from 1000 to 2650 kg·m⁻³. The tests have shown that it is possible to create hydraulic conditions when the sediments are separated into two fractions and their further transport by means of two pipes. It allows to separate thicker mineral fractions of sediments (gravel, coarse and medium sand) from organic impurities and finer mineral fractions in the form of a slurry. The relations between the average water flow velocity above the slots and the settling velocity of particles were significant.

Laboratory tests also showed various structural defects of the slotted separator, affecting turbulence of flow (rapid changes in cross-section), as well as the efficiency of its work.

In laboratory tests, the diameters of pipes supplying mixture or water were equal to 0.05 m. Installation with such dimensions can be used in practice, but it can be pipes with larger diameters. It can be expected that installations that are geometrically two, five or ten times larger, in proportion to the increase in volume flow of water, will be able to remove many times more deposits from the bottom of the reservoir.

It has been assumed that the Hazen number is a good criterion for hydrodynamic similarity and allows the design of separators several times larger and forecasting the effectiveness of their work or the determination of the characteristic diameters of the separated sediment. This number takes into account both the variability of the velocity ratio v_1/w_{ss} and the change in the area of separator, resulting from different widths, spacing and number of slots.

The prototype installation on a technical scale will be examined in field condition and financed by the "Incubator of Innovation +" project, co-financed from funds for learning under the non-competition project

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Badania separatora szczelinowego instalacji hydromechanicznego usuwania osadów ze zbiornika wodnego

Streszczenie

Zamulanie zbiorników wodnych w Polsce postępuje w tempie 0,5-5% pojemności rocznie, stąd niezbędne są działania w kierunku ograniczenia tego niekorzystnego zjawiska, m. in. poprzez odmulanie. Stosunkowo tanią i wydajną metodą usuwania osadów ze zbiorników jest zasysanie uwodnionych osadów przez syfon lub lewar, wyposażony dodatkowo w separator cząstek stałych. Zadaniem prototypowej instalacji do hydromechanicznego usuwania i oczyszczania osadów jest rozdzielenie osadów pobieranych z dna zbiornika na dwa strumienie, zawierające: frakcje grube (pożądane), kierowane bezpośrednio do rzeki poniżej piętrzenia, oraz frakcje drobniejsze i lżejsze (niepożądane), które po odwodnieniu mogą być wykorzystane, np. rolniczo. Wyszortowane grube frakcje mineralne ograniczają erozję koryta cieków poniżej zbiornika.

Przeprowadzono badania laboratoryjne na modelu fizycznym separatora szczelinowego, w których użyto cząstek mineralnych o średnicach 0,15-12,0 mm oraz cząstek kulistych o średnicy 6,0 mm, wykonanych z materiałów o gęstości

od 1000-2650 kg·m⁻³. Badania wykazały, że jest możliwe stworzenie takich warunków hydraulicznych, w których zachodzi rozdzielanie osadów na dwie frakcje i ich dalszy transport dwoma przewodami. Istotne okazały się relacje prędkości przepływu hydromieszanki powyżej szczelin do prędkości opadania ziaren.

Abstract

The siltation of water reservoirs in Poland is progressing at the rate of 0.5-5% of capacity per year, hence the actions necessary to limit this unfavorable phenomenon are necessary, among others through desludging. A relatively cheap and efficient method of removing sediments from reservoirs is sucking in hydrated sludge through siphon or antisiphon, additionally equipped with a solid particle separator. The task of the prototype installation for hydromechanical removal and purification of sediments is the separation of sediments collected from the bottom of the reservoir into two streams, containing: coarse fractions (desirable), directed directly to the river below the damming, and finer and lighter (undesired) fractions that can be used after dehydration), e.g., agricultural. Sorted thick mineral fractions limit the erosion of the channel of the watercourse below the reservoir.

Laboratory tests were carried out on a physical model of a slotted separator, in which mineral particles with diameters of 0.15-12.0 mm and spherical particles with a diameter of 6.0 mm were used, made of materials with a density of 1000-2650 kg·m⁻³. The tests have shown that it is possible to create hydraulic conditions in which the sediments are separated into two fractions and their further transport by means of two pipes. The relations between the velocity of the water flow above the slits and the velocity at which the grains descended were significant.

Słowa kluczowe:

zbiornik wodny, sedymentacja, odmulanie, zasysanie osadów, separator szczelinowy

Keywords:

water reservoir, sedimentation, desilting, sediment hydrosuction, slotted separator



Vegetation Changes and Rare Plant Species in Grasslands in the Middle Wieprz Valley (PLH060005)

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1. Introduction

Middle Wieprz Valley comprises a mosaic of land and water habitats. The steep slopes of this valley are covered by remnants of xerothermic grasslands and shrubs while the lower terraces – mainly by meadows (Janiec & Rederowa 1992). Such a pattern of natural environment conditions favours the occurrence of varied plant associations (Stamirowska-Krzaczek 2008, Warda et al. 2013). However, similarly to other meadow sites in the Lublin Region (Baryła & Urban 1999, Kulik et al. 2016, Mosek & Miazga 2006), changes in the way of utilization or abandonment of use, and changes in the humidity of habitats, result in changes in the properties of the habitat and species composition of the plant communities (Czyż et al. 2013, Grzegorzczak et al. 1999, Kulik et al. 2017) occurring there as well as in the progressing succession (Kotańska et al. 2016, Stypiński & Grobelna 2000). These changes lead to decreasing floristic diversity of meadow communities (Klarzyńska & Kryszak 2015, Kryszak et al. 2010, Warda et al. 2013), reduced numbers or disappearance of characteristic species of typical plant communities (Myśliwy & Bosiacka 2009, Ratyńska 1997) as well as increased presence of species that previously occurred sporadically but are now appearing in greater numbers in transitional communities (Ratyńska et al. 2007, Stamirowska-Krzaczek 2015). The number of dicotyledon species is also

increasing, and grassy communities with a lower value score are spreading (Korzeniak 2012, Kozłowska & Burs 2013).

The basic objective of this study was to investigate the condition of the grassland vegetation, including the presence of rare and endangered plant species in the Middle Wieprz Valley (PLH060005). The investigation concerned the vegetation of rush meadows (*Mag/Phrag*), wet meadows (*Mol*) and fresh meadows (*Arr*), and the presence of characteristic and rare species in the communities under study, in the years 2005 and 2017.

2. Material and methods

2.1. The study area

The Wieprz Middle Valley is situated in the Nadwieprzański Landscape Park (Lublin Region). The Wieprz River is a right-hand tributary of the Vistula, and in its middle reaches is a natural, highly meandering river. Its valley has the character of a floodplain (Janiec & Rederowa 1992). In order to protect the natural values of the meadows and slopes of the Wieprz valley within the Park, a Natura 2000 area (PLH060005) was established in 2008. The meadow complex covers approximately 25% of the park area (Stamirowska-Krzaczek 2008).

2.2. Field study

The previous phytosociological studies were conducted in the years 2005–2007 (Stamirowska-Krzaczek 2008), using the Braun-Blanquet method (1964), while the previously investigated rush communities as well as wet meadow and fresh meadows communities are currently monitored (2017). Phytosociological relevés were made of an area of 25 m², representative of meadow phytocoenoses (Dzwonko 2007). In this study, 30 phytosociological relevés (*Molinio-Arrhenatheretea* class) were analysed. The adopted nomenclature of species was according to Mirek et al. (2002) while the taxonomy and nomenclature of communities according to Matuszkiewicz (2008).

2.3. Data analysis

The results of the phytosociological studies carried out in 2017 indicate trends in the species composition dynamics of investigated plant communities and let us locate all rare species occurring within a specified

habitat type in the Middle Wieprz Valley area. Rare plants are represented by species with low number of individuals or in very restricted areas (Lancaster 2000). Some plants are naturally rare while others have become rare or endangered through a loss or change in habitat affected by human practises. Thus, human actions towards biodiversity protection are needed to ensure continued existence of threatened plants.

Principal Component Analysis (PCA) (Jolliffe 2002) was used to examine the changes in the percentage share of various characteristic species in three different types of associations in 2005 and in 2017. This enabled the reduction of the number of explanatory variables in the dataset and identification of the characteristic plant species that best portray the changes in the composition of the particular phytosociological units/syntaxa. This method also enabled the identification of the correlations in the co-occurrence of the specific plant groups. Due to the comparable scale of the variables examined, the principal components were determined using the covariance matrix that provides a better image of the proportion of the specific characteristic species in the composition of communities. A MANOVA test was carried out for the determined principal components in order to verify the significance of the differences between the analysed types of plant communities during the period under study. Six categories of observation, i.e. a combination of community type and study year, were examined. Homogeneous groups were determined based on the Tukey's test for multiple comparisons. The significance level used in the test was $\alpha = 0.05$. Statistical analyses were carried out using StatSoft Statistica (version 13).

3. Results and discussion

Phytosociological investigations conducted in the years 2005-2007 revealed diversity of habitats and plant communities in grassland in the Middle Wieprz Valley area. There were distinguished various communities – from *Phragmitetea* class wetland communities to dry and poor habitat communities of the *Koelerio glauca-Corynopheretea canescentis* class, however features of transitional communities were characteristic for some of investigated meadow swards in the study area (Stamirowska-Krzaczek 2015). The results of the currently (2017) conducted phytosociological survey concern condition of the vegetation of rush meadows

(*Mag/Phrag* – *Magnocaricion/Phragmition*) and some communities of the *Molinio-Arrhenatheretea* class, and the presence of rare and endangered species in the communities under study (Fig. 1).

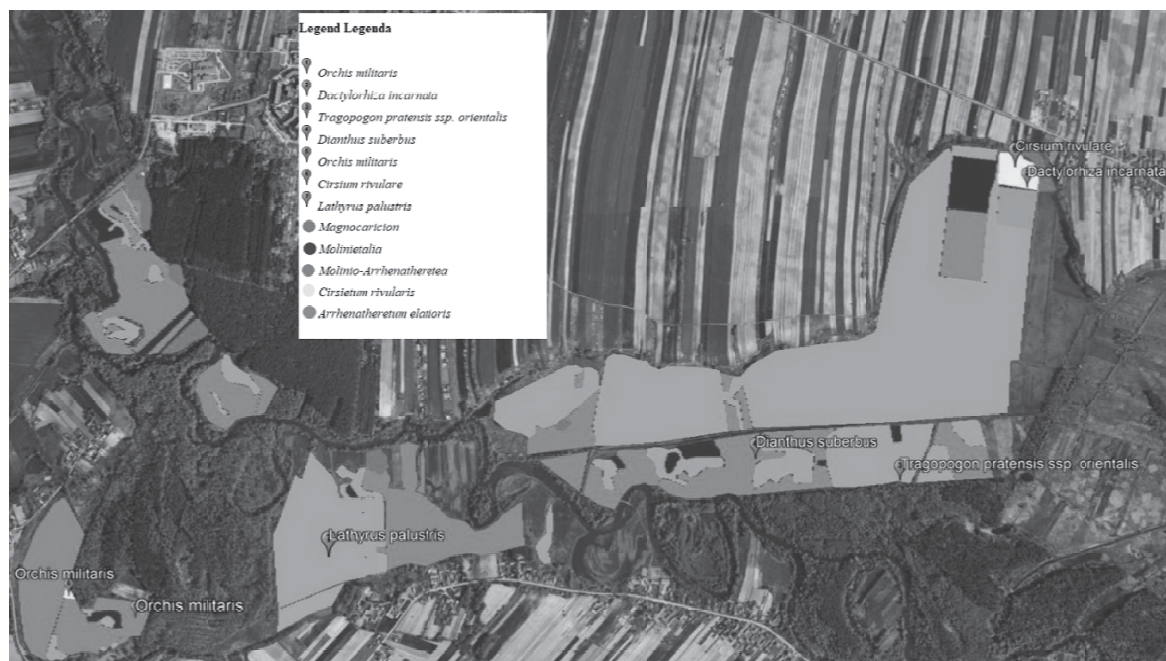


Fig. 1. Distribution of plant communities and rare and endangered species in the grasslands in the Middle Wieprz Valley

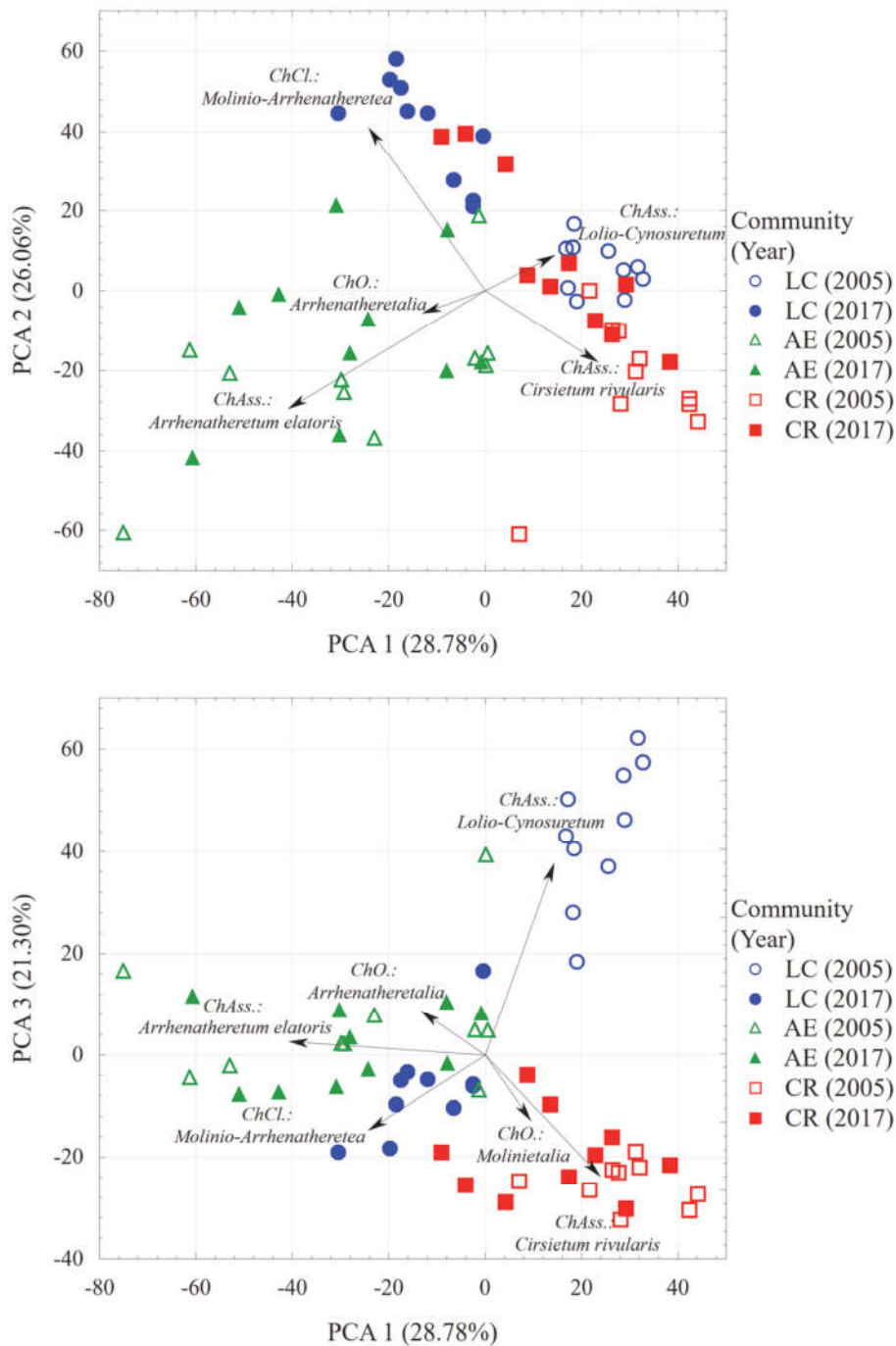
Rys. 1. Rozmieszczenie zbiorowisk roślinnych oraz rzadkich i zagrożonych gatunków roślin na użytkach zielonych w Dolinie Środkowego Wieprza

The extensive utilization of meadows or the lack of it pose a serious threat in the Middle Wieprz Valley. The smallest changes in the floristic composition of the sward occur in the rush and wet meadow communities although fluctuations of the number of some plant species can be observed there (unpublished results of own research). The more important changes in the species composition of meadow sward were particularly confirmed in the following associations of the *Molinio-Arrhenatheretea* class: *Lolio-Cynosuretum* R.Tx. 1937, *Cirsietum rivularis* NOWIŃSKI 1927 and *Arrhenatheretum elatioris* BR.-BL. ex SCHERR. 1925.

The Principal Component Analysis enabled the reduction of the plant groups considered in the study. The first three principal components (PCA1, PCA2, PCA3) obtained account for a total of 76.13% (28.78%, 26.06% and 21.30% respectively) of the total variance of the dataset.

The significance of characteristic plant species of the particular syntaxa in the determination of the principal components and their co-occurrence are shown in Fig. 2. The lines with an identical orientation denote a correlated share in the species composition of the syntaxa under study. After determining the principal components identifying the variability of objects to the greatest extent, the species composition for the particular sites was projected to the planes determined by the first three principal components. The sites are shown according to the type of community and study year. The graph shows a clear division of the groups according to type community. Characteristic species of the *Molinio-Arrhenatheretea* class and the *Lolio-Cynosuretum* association are dominant in the *Lolio-Cynosuretum* community, species of the *Arrhenatheretum elatoris* association, the *Arrhenatheretalia* order and the *Molinio-Arrhenatheretea* class are dominant in the *Arrhenatheretum elatoris* community, whereas species characteristic of the *Molinietalia* order and the *Cirsietum rivularis* association are dominant in the *Cirsietum rivularis* community.

Analysing the differences in the species composition of the sward that occurred in the studied communities between 2005 and 2017, it can be concluded that the biggest changes concern the *Lolio-Cynosuretum* association. Decreasing number, stability and cover abundance of characteristic species for association and increasing content of species characteristic for higher phytosociological units give an evidence of plant communities degeneration. A considerably greater presence of species characteristic of the *Molinio-Arrhenatheretea* class was found in the sward of this association in 2017 in comparison with the state of the vegetation cover in 2005. The lack of utilization of the sward for pasturage has probably contributed to the considerably decreased numbers of the characteristic species (Kryszak et al. 2007) and presence of *Cynosurus cristatus*. In the study area, this species can be regarded as very rare, even vulnerable, if the community for this association is not placed under active protection.



LC – *Lolio-Cynosuretum*, AE – *Arrhenatheretum elatoris*, CR – *Cirsietum rivularis*

Fig. 2. PCA ordination diagram of 60 relevés taken in the same study sites in the vegetation seasons of 2005 and 2017

Rys. 2. Diagram ordynacyjny PCA dla 60 zdjęć fitosocjologicznych wykonanych w tych samych miejscach w sezonie wegetacyjnym 2005 i 2017

A similar trend, but with less distinct changes, can be observed in the *Cirsietum rivularis* association where an increasing proportion of species characteristic for the *Molinio-Arrhenatheretea* class was confirmed. In the Middle Wieprz Valley, similar stability but less cover abundance of *Cirsium rivulare* (Jacq.). All. specimens (Table 1) were found at sites of its previous occurrence even though a clear decline in the number of sites of this species can be observed in Poland (Warda et al. 2014).

In the period under study, no significant changes in the vegetation cover of the *Arrhenatheretum elatoris* association were found, as evidenced by the distribution of points corresponding to the particular sites of this community, covering similar areas in both years compared. However, sward condition of this plant community was not good in the previous study period. According to the study results of Stamirowska-Krzaczek (2015), changes in the species composition of this association as a consequence of abandoned utilization usually lead to the disappearance or reduced presence of typical characteristic species and the development of *Poa pratensis-Festuca rubra* Fijałk. 1962 pro ass. and *Holcus lanatus* associations (Kulik et al. 2016, Myśliwy & Bosiacka 2009, Urban & Grzywna 2003). *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak is a species that is very rarely found among characteristic species of typical *Arrhenatheretum* meadows.

In order to confirm significant statistical differences between the communities and years under study, a single-factor multidimensional analysis of variance (MANOVA) was carried out for the obtained principal components; the results of this analysis are shown in Table 1.

The *Lolio-Cynosuretum* R.Tx. 1937 is another association where negative changes in the species composition have been observed. MANOVA analysis confirmed significant changes in the floristic composition of the sward of the *Lolio-Cynosuretum* association in the years 2005–2017. In the case of this association, all principal components for the particular years were assigned to other homogeneous groups according to Tukey's test. In the *Cirsietum rivularis* association, there are groups from different years which were assigned to the same homogeneous groups because of the first and third principal component, and the differences occurred in the second principal component.

Table 1. Mean values of principal components for the groups under study (determinations of communities, same as in PCA)

Tabela 1. Średnie wartości składowych głównych dla rozpatrywanych grup (oznaczenia zbiorowisk jak w PCA)

Group	PCA1 mean	PCA2 mean	PCA3mean
LC (2005)	23.7 ^B	5.9 ^B	43.9 ^C
LC (2017)	-12.6 ^A	40.7 ^C	-6.5 ^A
AE (2005)	-27.4 ^A	-21.3 ^A	6.5 ^A
AE (2017)	-28.5 ^A	-10.6 ^{AB}	1.8 ^A
CR (2005)	30.2 ^B	-23.4 ^A	-25.8 ^B
CR (2017)	14.7 ^B	8.8 ^B	-19.8 ^B
F(df = 5)	25.05	20.29	61.15
p-value	<0.001	<0.001	<0.001

^{A,B,C} – homogeneous groups within one principal component

^{A,B,C} – grupy jednorodne w obrębie jednej składowej głównej

The statistical analysis did not confirm differences in the condition of the vegetation cover of the *Arrhenatheretum elatoris* association in the particular study years with respect to every principal component.

Among species from studied grassland communities in the Middle Wieprz Valley, the following species were very rarely occurring: *Dactylorhiza incarnata* (L.) SOÓ, *Dactylorhiza majalis* s.l. (Rchb.) P.F. Hunt et Summerh., *Dianthus superbus* L. ssp. *superbus*, *Orchis militaris* L., *Lathyrus palustris* L., *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak, *Cirsium rivulare* (Jacq.) All. and *Cynosurus cristatus* L. In 2017, lower numbers but the similar stability of *Cirsium rivulare* (Jacq.) All. specimens were found at sites of its previous occurrence (2005) even though a clear decline in the number of sites of this species can be observed in Poland. An increased presence of *Dactylorhiza majalis* s.l. (Rchb.) P.F. Hunt et Summerh. was found in herbaceous communities (*Lythro-Filipenduletum ulmariae* Hadač et al. 1997 and *Valeriano-Filipenduletum* Siss. in Westh. et al. 1946), where the disappearance of *Orchis militaris* L., a species under strict protection (1.336), can be observed as well. *Dianthus superbus* L. ssp. *superbus*, also under strict protection (1.195), is another endangered species, previously occurring in these communities sporadically. However, the number of specimens of

this species has continued to fall recently. According to the Red List (Kaźmierczakowa et al. 2016), it is a vulnerable species (VU). *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak is a species that is very rarely found among characteristic species of typical *Arrhenatheretum* meadows during the current investigations. The most endangered pasture plant species is *Cynosurus cristatus* L. In the study area, this species can be regarded as very rare, even vulnerable, if the community for this association is not placed under active protection.

4. Conclusions

The phytosociological investigations carried out on the grasslands in the Middle Wieprz Valley revealed a serious threat for stability of plant communities. A consequence of extensive or abandoned utilization usually is the disappearance or reduced presence of typical characteristic species in the sward of meadow communities.

1. The most important changes in the species composition of meadow sward concern the *Molinio-Arrhenatheretea* class, particularly the *Lolio-Cynosuretum* association. A decreasing number of own characteristic species and a considerably greater presence of characteristic species of the *Molinio-Arrhenatheretea* class, found in the sward of this association in 2017 (in comparison with the state of the vegetation cover in 2005) can confirm negative dynamics of this association sward. A similar trend, but with less distinct changes can be observed in the *Cirsietum rivularis* association.
2. Changes in the vegetation cover of the *Arrhenatheretum elatoris* association were no significant. However, sward condition of this plant community was also not good enough in the previous study period.
3. Among plant species in studied grassland communities in the Middle Wieprz Valley there are some very rarely occurring species: *Dactylorhiza incarnata* (L.) SOÓ, *Dactylorhiza majalis* s.l. (Rchb.) P.F. Hunt et Summerh., *Dianthus superbus* L. ssp. *superbus*, *Orchis militaris* L., *Lathyrus palustris* L., *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak, *Cirsium rivulare* (Jacq.) All. and *Cynosurus cristatus* L. In the study area, *Cynosurus cristatus* L. can be regarded as very rare, even vulnerable, if the community for this association is not placed under active protection by grazing.

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Zmiany szaty roślinnej i rzadkie gatunki roślin na użytkach zielonych w Dolinie Środkowego Wieprza (PLH060005)

Streszczenie

Badania przeprowadzono w latach 2005 i 2017 metodą Braun-Blanqueta w Dolinie Środkowego Wieprza (PLH060005). Przedmiot fitosocjologicznych badań na tym obszarze stanowiła szata roślinna łąk szuwarowych, wilgotnych i świeżych oraz obecność w badanych zbiorowiskach – gatunków charakterystycznych, rzadkich i zagrożonych. Obecnie prowadzi się monitoring poprzednio badanych zbiorowisk szuwarowych oraz zbiorowisk łąk wilgotnych i świeżych w celu oceny zmian w szacie roślinnej badanych użytków zielonych. Obszar Natura 2000 (PLH060005) stanowi mozaikę środowisk lądowych i wodnych, a taki układ warunków środowiska sprzyja występowaniu różnorodnych zespołów roślinnych. Jednakże, ekstensywne użytkowanie łąk lub jego brak stanowią w Dolinie Środkowego Wieprza poważne zagrożenie dla zbiorowisk roślinnych. Do zbadania zmian w udziale różnych gatunków charakterystycznych w 3 różnych typach zbiorowisk między latami 2005 i 2017 wykonano również wielowymiarową analizę składowych głównych PCA. Wyniki obecnie prowadzonych badań fitosocjologicznych wskazują, że najmniejsze zmiany w składzie florystycznym runi obserwuje się w zbiorowiskach szuwarowych i łąk wilgotnych, chociaż dostrzega się tam wahania liczebności niektórych

gatunków roślin. Bardziej znaczące zmiany w składzie gatunkowym runi łąkowej potwierdzono w następujących zespołach roślinnych klasy *Molinio-Arrhenatheretea*: *Lolio-Cynosuretum* R.Tx. 1937, *Cirsietum rivularis* NOWIŃSKI 1927 i mniejsze zmiany w zespole *Arrhenatheretum elatioris* BR.-BL. ex SCHERR. 1925. Analizując różnice w składzie gatunkowym runi, które zaistniały w badanych zbiorowiskach w okresie między 2005 i 2017 rokiem można stwierdzić, że największe zmiany dotyczą zespołu *Lolio-Cynosuretum*. W runi tego zespołu stwierdzono w 2017 roku znacznie większą obecność gatunków charakterystycznych dla klasy *Molinio-Arrhenatheretea* niż w 2005 roku. Podobną tendencję, ale mniej wyraźne zmiany dotyczą zespołu *Cirsietum rivularis*. W badanych latach nie zaobserwowano znaczących zmian w szacie roślinnej zespołu *Arrhenatheretum elatioris*, o czym świadczy rozmieszczenie punktów odpowiadających poszczególnym stanowiskom występowania tego zbiorowiska, które zajmują podobne obszary w obu porównywanych latach. Wśród roślin kształtujących zbiorowiska użytków zielonych w Dolinie Środkowego Wieprza bardzo rzadko występowały następujące gatunki: *Dactylorhiza incarnata* (L.) SOÓ, *Dactylorhiza majalis* s.l. (Rchb.) P.F. Hunt et Summerh., *Dianthus superbus* L. ssp. *superbus*, *Orchis militaris* L., *Lathyrus palustris* L., *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak, *Cirsium rivulare* (Jacq.) All. i *Cynosurus cristatus* L. Brak pastwiskowego użytkowania runi przyczynił się prawdopodobnie do znacznego spadku liczebności gatunku charakterystycznego – *Cynosurus cristatus* L. W badanym rejonie gatunek ten można uznać jako bardzo rzadki, a nawet narażony na wyginięcie, jeśli zbiorowisko tego zespołu nie zostanie objęte czynną ochroną.

Abstract

The studies were conducted in the years 2005 and 2017 using the Braun-Blanquet method. The objective of studies was to investigate the condition of the grassland vegetation, including the presence of rare and endangered plant species in the Middle Wieprz Valley (PLH060005). The investigation in this area concerned the vegetation of rush meadows, wet and fresh meadows, and the presence of characteristic rare and endangered species in the communities under study. A Natura 2000 area (PLH060005) comprises a mosaic of land and water habitats and such a pattern of natural environment conditions favours the occurrence of varied plant associations. However, the extensive utilization of meadows or the lack of it pose a serious threat in the Middle Wieprz Valley to plant communities. The previously investigated rush communities as well as wet and fresh meadow communities are currently monitored to evaluate changes in vegetation of the studied grasslands. Principal Component Analysis was used to examine the changes in the percentage share of various characteristic species in three different types of

communities between 2005 and 2017. The results of the currently conducted phytosociological survey indicate that the smallest changes in the floristic composition of the sward occur in the rush and wet meadow communities although fluctuations of the number of some plant species can be observed there. The more important changes in the species composition of meadow sward were confirmed in the following associations of the *Molinio-Arrhenatheretea* class: Ass. *Lolio-Cynosuretum* R.Tx. 1937, Ass. *Cirsietum rivularis* NOWIŃSKI 1927 and lower changes in the association of the *Arrhenatheretum elatioris* BR.-BL. ex SCHERR. 1925. Analyzing the differences in the species composition of the sward that occurred in the studied communities between 2005 and 2017, it can be concluded that the biggest changes concern the *Lolio-Cynosuretum* association. A considerably greater presence of species characteristic of the *Molinio-Arrhenatheretea* class was found in the sward of this association in 2017 in comparison with the state of the vegetation cover in 2005. A similar trend, but with less distinct changes, can be observed in the *Cirsietum rivularis* association where an increasing proportion of characteristic species of the *Molinio-Arrhenatheretea* class was confirmed. In the period under study, no significant changes in the vegetation cover of the *Arrhenatheretum elatioris* association were found, as evidenced by the distribution of points corresponding to the particular sites of this community, covering similar areas in both years compared. However, sward condition of this plant association was not good enough in the previous study period. Among species from studied grassland communities in the Middle Wieprz Valley, the following species were very rarely occurring: *Dactylorhiza incarnata* (L.) SOÓ, *Dactylorhiza majalis* s.l. (Rchb.) P.F. Hunt et Summerh., *Dianthus superbus* L. ssp. *superbus*, *Orchis militaris* L., *Lathyrus palustris* L., *Tragopogon pratensis* L. ssp. *orientalis* (L.) Čelak, *Cirsium rivulare* (Jacq.) All. and *Cynosurus cristatus* L. The lack of utilization of the sward for pasturage has probably contributed to the considerably decreased numbers of the characteristic species *Cynosurus cristatus*. In the study area, this species can be regarded as very rare, even vulnerable, if the community for this association is not placed under active protection.

Słowa kluczowe:

użytki zielone, zmiany szaty roślinnej, rzadkie i zagrożone gatunki roślin, Dolina Środkowego Wieprza

Keywords:

grasslands, vegetation changes, rare and endangered plant species, Middle Wieprz Valley



The Disaster in Chernobyl Nuclear Power Plant and Tourism. Condition of and Prospects for the Development of Tourism in the Area of Radioactive Contamination

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1. Introduction

In the modern world tourism as a universal phenomenon (in which all age and social groups participate) is the most popular form of spending free time. Individual forms and types of tourism have specific impact on participants in tourist traffic serving a number of functions related to, among others: health, education, economy, leisure and culture (Kurek 2008, Boruszczak 2010, Noonan & Rizzo 2017, Talebi 2017). Importantly, the health function has been mentioned as the first one as when developing tourist offers or infrastructure global environmental issues are very often marginalized or totally ignored e.g. air pollution, greenhouse effect, degradation of natural ecosystem, the ozone hole or seismic and volcanic phenomena (Zarębski et al. 2015, Rzetala 2017). Apart from traditional facilities and places used for tourist purposes, it is more and more often that tourists look for more extreme places that are also more difficult to access. The response to the need of there being no barriers or limits in search of new tourist experiences is the area of radioactive contamination around the Chernobyl Nuclear Power Plant. Tourism practised in the area of the so-called Chernobyl Exclusion Zone is referred to in specialist literature as dark tourism – travelling to places of

death, human suffering and different sorts of tragedies (Foley & Lennon 1996, Seaton 1999, Miles 2002, Slade 2003, Stone & Sharpley 2008, Płomiński & Bakota 2017). Taking advantage of the area of radioactive contamination around the Chernobyl Nuclear Power Plant for tourist purposes is a new phenomenon. Its origin dates back to the beginning of the 21st century and shutting down (under the pressure of Western countries) the last working reactor on 15 December 2000 (Rzeczpospolita 2016).

2. Purpose, scope and methods

The aim of the paper is to analyse the condition of and prospects for the development of tourism in the area of radioactive contamination around the Chernobyl Nuclear Power Plant. The source basis for preparation of this work has been printed sources, field studies and reference books related to tourism, especially to dark tourism. As part of preparation of this study the following research methods have been used: analysis of printed sources, synthesis, induction, deduction and a comparative method.

The paper addresses research issues which have been put forward in the following questions:

1. To what extent is the tourist potential of the Alienation Zone around the Chernobyl Nuclear Power Plant used?
2. What factors influence progress of and decline in tourism in the Alienation Zone around the Chernobyl Nuclear Power Plant?
3. What is the nationality of tourists who most often visit the Alienation Zone around the Chernobyl Nuclear Power Plant?

3. Specific character of the study area in the context of use for tourist purposes

The Chernobyl Nuclear Power Plant (Ukr. Чорнобильська атомна електростанція) is located on the territory of Ukraine in the district of Kiev at the border with Belarus. It is 4 km away from the city of Pripjat and 18 km from Chernobyl, in the vicinity of the estuary of the Pripjat River into the Dnieper River (51° 23' 22.39" N, 30° 5' 56.93" E). The construction of the power plant began in the 1970s. Original plans provided for the construction of six nuclear reactors of the total power of 6,000 megawatts. By the time of the disaster four reactors were in opera-

tion (I – 1977, II – 1978, III – 1981, IV – 1983). The residential and social area for the employees of the power plant was the city of Pripyat established in 1970 (51°24'20"N 30°03'25"E). Built from scratch (in the place of the village called Semykhody) as the most modern city in the whole USSR (Nad'yarnyh et al 1989), it was full of conveniences for its residents. The cultural and social life flourished in its centre with the following facilities at the disposal of the inhabitants: the Palace of Culture „Energetik”; cinema „Prometheus”; café „Pripyat”, amusement park with e.g. the Ferris wheel, a merry-go-round and an electric car track (the opening celebration was scheduled for the holiday of 1 May 1986); music school with a concert hall; hospital; playgroups; nurseries; marinas with water equipment; sports halls, two sports stadiums and two swimming pools. In 1986 there were 49,360 residents of Pripyat and the average age was 26 (*Scenario for modelling changes in radiological conditions in contaminated urban environments, 2006*). The end of the existence of this „city of dreams” – which Pripjat undoubtedly was for the residents of the USSR, was the day of 26 April 1986. On that day at 01:24 am in the 4th reactor of the Chernobyl Nuclear Power Plant two explosions took place: of steam and released hydrogen. The explosion resulted in the destruction of the reactor and a part of the building structure. The plate covering the reactor was made to move making it partly exposed and resulting in the access of air to the fire place. Large amount of radioisotopes was released into the atmosphere. Approximately 8 out of 140 tonnes of fuel containing plutonium and other highly radioactive fission products were emitted from the reactor together with the remains of the moderator and were dispersed in the surrounding area (Trojanowski et al 2006). Several minutes after the explosion a fire brigade appeared on the spot and the rescue operation started whose main aim was to put out the fire threatening the remaining reactors of the power plant. Then, the focus was on the reduction of the emission of radioactive substances into the atmosphere. For this purpose it was decided to isolate the reactor from the external environment by enclosing it inside a huge sarcophagus of reinforced concrete. Simultaneously, the evacuation of the population from the endangered areas started and the thirty-kilometre exclusion zone was designated around the territories most adversely affected by the results of the disaster. On 27 April 1986 all residents of the city of Pripjat (49,360 people) and 254 residents of the neighbouring Yaniv were dis-

placed. In the period from 27 April to 7 May about 116 thousand people were evacuated. The total number of people displaced from the Exclusion Zone around the Chernobyl Nuclear Power Plant (within a 10-km radius from the power plant the "high risk zone" was established, and within a 30-km radius the zone of „the highest degree of contamination” – fig. 1) measuring approx. 2.5 thousand km² was nearly 350 thousand people.

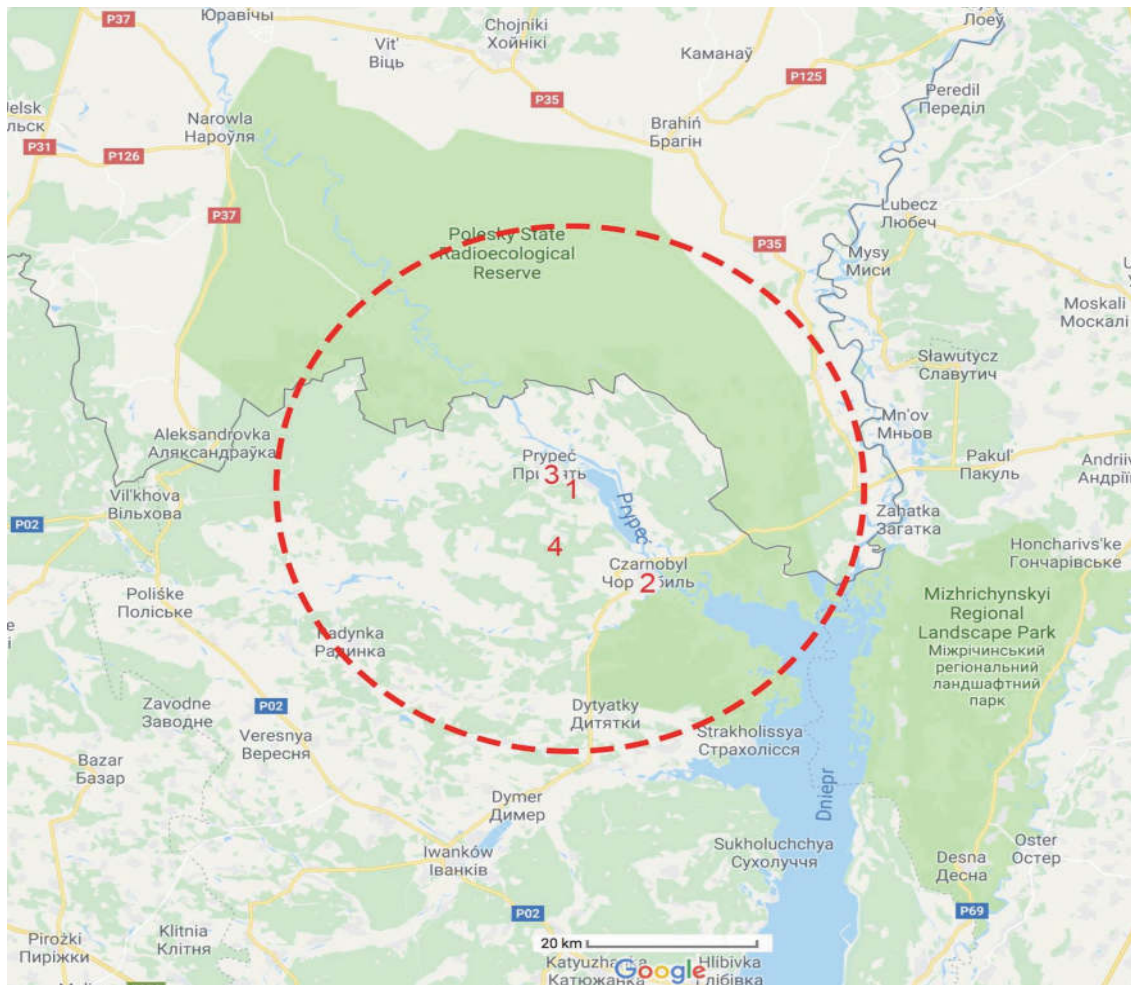


Fig. 1. The zone „of the highest contamination degree” designated within a 30-km radius, with the most important spots marked (1 – the Chernobyl Nuclear Power Plant, 2 – the city of Chernobyl, 3 – the city of Pripyat, 4 – „Duga” radar station)

Rys. 1. Strefa „o najwyższym stopniu skażenia” wyznaczona w promieniu 30 km, z zaznaczonymi najważniejszymi punktami (1 – Czarnobylska Elektrownia Jądrowa, 2 – miasto Czarnobyl, 3 – miasto Prypeć, 4 – stacja radarowa „Duga”)

To this day there is no clearly specified number of the disaster victims. According to the report of the „Chernobyl Forum” whose members are International Atomic Energy Agency (IAEA), World Health Organization (WHO), Agencies of UN (FAO, UNDP, UNEP, UN-OCHA, UNSCEAR) and the governments of Belarus, Russia and Ukraine, the death toll was 50 (two employees of the power plant, about 40 liquidators of the disaster results and persons who died of thyroid cancer which was proved to be associated with the disaster). Whereas the results of the studies presented by the Scientific Committee of the UN for the Effects of Nuclear Radiation talk about 28 victims of acute radiation sickness who were dead within 4 months from the accident, and the 3 victims who died from other causes (Trojanowski et al. 2006). All of these victims are commemorated with the monument at the road in Chernobyl with the inscription „To those who were saving the world”.

4. Tourism in the area of the Exclusion Zone around the Chernobyl Nuclear Power Plant

Pripyat, as well as the very power plant in Chernobyl are falling into ruin from day to day. Over the next decade or so – for natural reasons – the city is simply going to collapse. Thus it will fall into oblivion. The only remnant will be the so-called arch – a special structure, which the reactor no. 4 and the old steel and concrete sarcophagus were covered with at the end of 2016. It is a shelter which is 108 m high, 162 m long and 257 m wide. The whole structure weighs 36 thousand tonnes. Its cost amounts to 1.5 billion euros, which was collected from over 45 donor countries. The financing of the venture was managed by the European Bank for Reconstruction and Development which supported it with a greater funding than any of the remaining donors (0.6 billion euros). Considerable resources were also contributed to the Chernobyl Fund by, among others, the European Commission – 350 million euros, USA – 183 million, Germany – 80 million, United Kingdom – 65 million, France – 63 million, Japan – 45.7 million, Ukraine – 45 million, Italy – 42 million, Canada – 35 million and Russia – 25 million. In turn, Poland donated 2.5 million euros for this purpose (Rzeczpospolita 2017).

In the second half of the 20th century there were several accidents in nuclear power plants; e.g. in Windscale (United Kingdom, 1957), Three Mile Island (USA, 1979), Tsuruga (Japan, 1981), Tomsk (Russia, 1992) and Tokaimura (Japan, 1999); nevertheless it is Chernobyl that has become a destination for tourists from all over the world. What is the underlying phenomenon of this place then? The thing is that the cases mentioned did not receive so much coverage as the accident in Chernobyl. Also, the then tense political situation between the USSR and the USA added „taste” to all that. In addition, the number of victims and actual results of the disaster were open to doubt. All in all, the atmosphere created around Chernobyl had its aura of mystery. In this way, a place that was potentially regarded as dangerous and unfriendly has become attractive for tourists (Tomala 2010).

Travel agencies (especially Ukrainian ones) take advantage of this fact and organize day trips to Chernobyl (Tomala 2010). Whereas the first travel agency in Poland since 2007 organizing excursions to Chernobyl was the agency „Bis-Pol” with its seat in Jasło (the company also has its branch in Cracow).

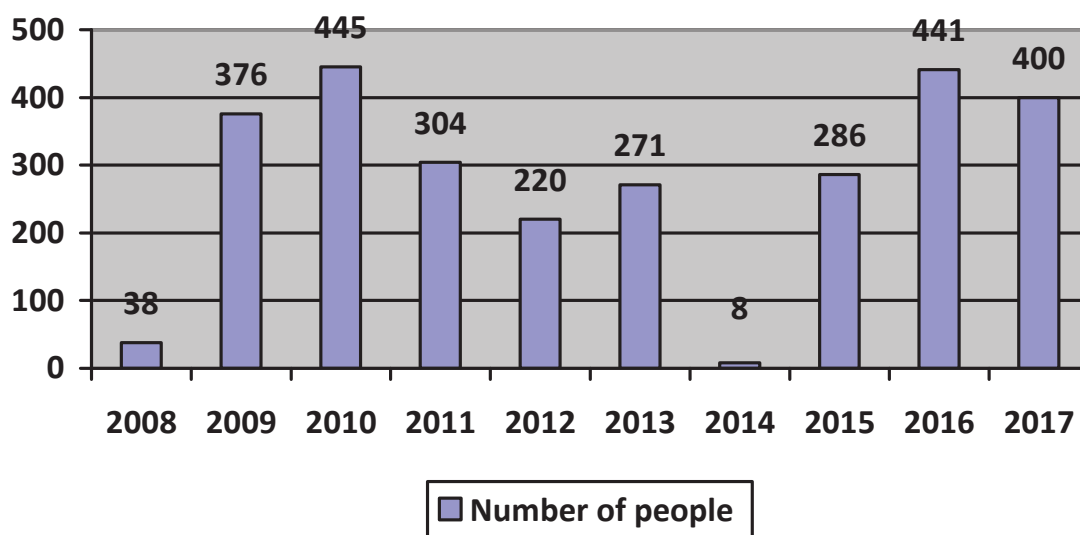


Fig. 2. Tourists visiting the Chernobyl Exclusion Zone with the Polish travel agency „Bis-Pol” in the years 2008-2017 (authors' own compilation based on information shared by an employee of the travel agency „Bis-Pol”)

Rys. 2. Turyści odwiedzający Czarnobylską Strefę Zamkniętą z polskim biurem podróży „Bis-Pol” w latach 2008-2017 (opracowanie własne na podstawie danych udostępnionych przez pracownika biura podróży „Bis-Pol”)

Based on the data obtained from the travel agency „Bis-Pol” it can be noted that since 2010 the number of tourist has been declining. According to the agency staff the reason was the emergence of other agencies on the tourist market which have undertaken to arrange trips to Chernobyl (e.g. Aliena Tours or StrefaZero.org). The year 2014, due to Euromaidan and annexation of Crimea by Russia was a total tourist failure. It was only in 2015 that the number of people wanting to visit Chernobyl started to grow.

Assistance in the organization of a trip to Chernobyl Exclusion Zone can be obtained from the Department for Visits, Trips and Events, to which, among others, travel agencies report their trips. The permits to enter the Zone are issued exclusively by the State Agency of Ukraine on the Exclusion Zone Management. People wishing to visit the Chernobyl Exclusion Zone must remember that visiting the zone takes place along designated routes which have been recognized as presenting no health hazard as long as appropriate safety measures are taken. Also, each visitor or group of visitors must be accompanied by a licensed guide and representative of the zone. It should also be remembered that visits are paid and require obtaining a written permit from the State Agency of Ukraine on the Exclusion Zone Management (Kruczek 2017).

Presently, in the Exclusion Zone the tourist routes are as follows:

- checkpoint „Dytiatky” – Czerewacz village – Zalesie village – city of Chernobyl,
- city of Chernobyl (place near the St. Elijah Church),
- city of Chernobyl (the monument „To those who were saving the world”, St. Elijah Church, remembrance complex „The Wormwood Star”),
- city of Chernobyl – Paryszew village (Opacici village, Kupuwate village),
- city of Chernobyl – the Chernobyl Nuclear Power Plant – Complex „Vector” (uncontaminated zone) – „Buriakówka” radioactive waste disposal site (uncontaminated zone),
- city of Chernobyl – the Chernobyl Nuclear Power Plant – the cooler,
- city of Chernobyl – city of Pripyat,
- city of Chernobyl – Chernobyl-2,
- city of Chernobyl – Krasne,

- city of Chernobyl – Poliśke,
- city of Chernobyl – „Skazocznyj” (Fairytale) pioneer camp (information from the website of the State Agency of Ukraine on the Exclusion Zone Management).

The most mysterious facility, recently opened to tourists and the media – an artefact of the cold war between the USSR and the West – is the „Duga” radar station (also dubbed „The Eye of Moscow”). It was a system of aerials in the shape of giant scaffolding whose aim was to detect incoming ballistic missiles on the territory of the then USSR. Owing to its characteristic rhythmic tapping in the air, which „Duga” generated, experts from the West also nicknamed it „the Russian Woodpecker”. It was not accidentally that Soviet engineers located the „Duga” radar station near the Chernobyl Nuclear Power Plant. Its energy consumption was very high. According to the intelligence of NATO member states it was about 10 megawatts of power.

The analysis of official statistical data referring to the number of tourist visitors to Chernobyl provided by the State Agency of Ukraine on the Exclusion Zone Management points to the fact that the number is growing each year. In 2016 35.1 thousand tourists visited Chernobyl, and in 2017 – over 50 thousand. (Fig. 3) It must also be noted that the vast majority of them are foreigners (more than 80%). According to the tour operators foreign tourists who visited Chernobyl in the years 2015-2017 leave about 10 million dollars a year in Ukraine. Currently, the most numerous groups of foreign tourists are: the Japanese, Americans and Germans (Fig. 4). Most tourists visiting Chernobyl are foreigners aged 20-50, wealthy or middle-class people.

On the basis of the data received it can be noted that in 2017, the greatest tourist activity – through the choice of Chernobyl as travel destination – was demonstrated by the Japanese. This interest is justified by the fact that their country is well aware of terrible consequences of excess radiation, so it is mainly associated with safety issues, in particular the technological condition of their own power plants.

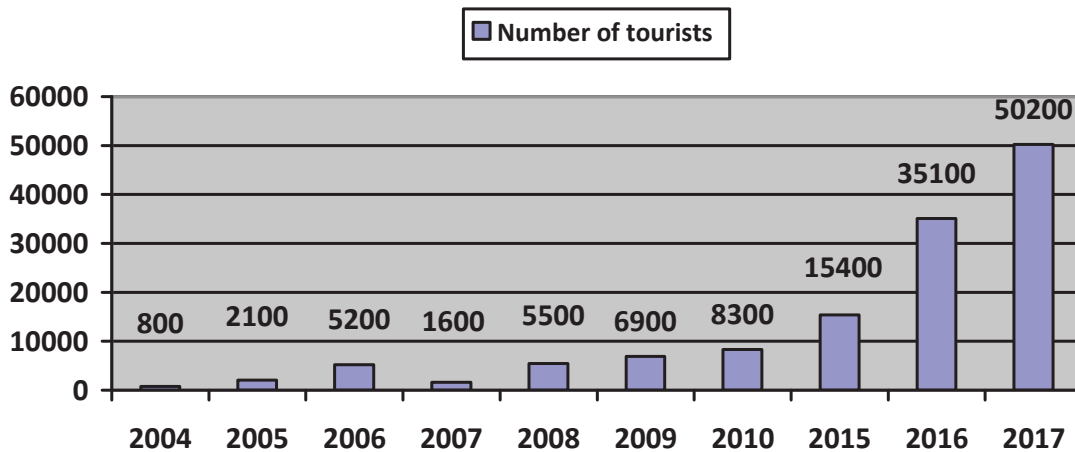


Fig. 3. Tourists visiting the Chernobyl Exclusion Zone in the years 2004-2017 (authors' own compilation based on information from the State Agency of Ukraine on the Exclusion Zone Management)

Rys. 3. Turyści odwiedzający Czarnobylską Strefę Zamkniętą w latach 2004-2017 (opracowanie własne na podstawie danych Państwowej Agencji Ukrainy ds. Zarządzania Strefą Wykluczenia)

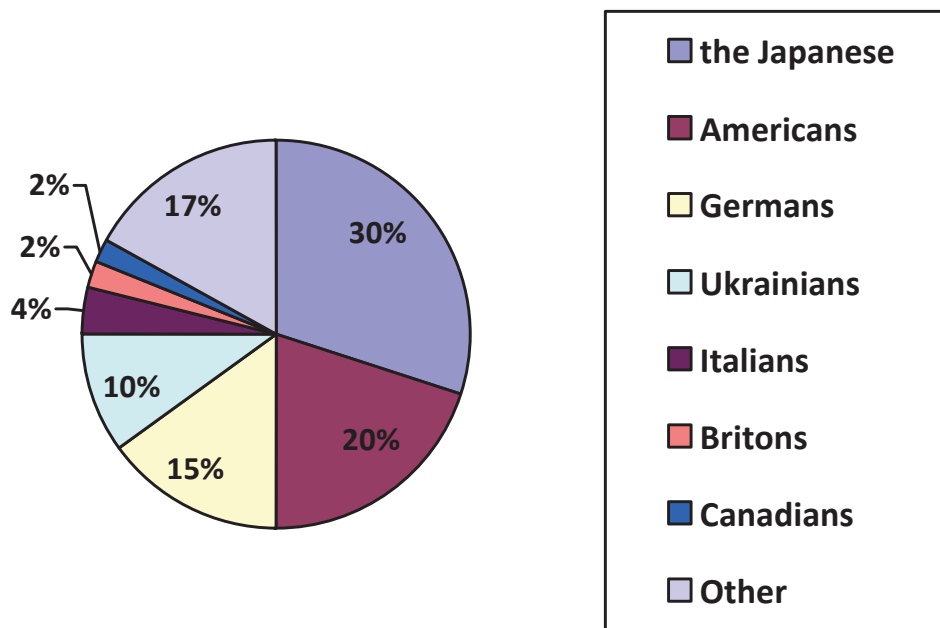


Fig. 4. Division of tourist by nationality, who in 2017 visited the Chernobyl Exclusion Zone (authors' own compilation on the basis of the data from the State Agency of Ukraine on the Exclusion Zone Management)

Rys. 4. Podział turystów, pod kątem narodowości, którzy w 2017 r. zwiedzili Czarnobylską Strefę Zamkniętą (opracowanie własne na podstawie danych Państwowej Agencji Ukrainy ds. Zarządzania Strefą Wykluczenia)

5. Prospects for the development of tourism in the area of the Exclusion Zone around the Chernobyl Nuclear Power Plant

In order to analyse the prospects for the development of tourism in the area of the Exclusion Zone around the Chernobyl Nuclear Power Plant, its strengths, weaknesses, opportunities and threats have been identified with the use of SWOT analysis.

Table 1. SWOT analysis of the prospects for the development of tourism in the Chernobyl Exclusion Zone

Tabela 1. Analiza SWOT perspektyw rozwoju turystyki w Czarnobylskiej Strefie Zamkniętej

Strengths	Weaknesses
<ul style="list-style-type: none"> • presence of the internationally recognized facility; • presence of unique species of plants and animals, which may become the basis for the development of scientific tourism; • yearly increase in the number of tourists, especially among foreigners; • additional tourist attractions unconnected with the disaster (e.g. „Duga” radar station). 	<ul style="list-style-type: none"> • no tourist infrastructure, accommodation and catering services; • not all facilities are made available to tourists; • frequent cases of pillage, especially among „illegal” tourists; • to visit the zone special permits from the authorities of the State Agency of Ukraine on the Exclusion Zone Management are required.
Opportunities	Threats
<ul style="list-style-type: none"> • convenient location and easy access for Ukrainian and foreign tourists (the facility is located 130 km from Kiev); • presence of „The Wormwood Star” Museum in Chernobyl; • promotion at international tourism fairs. 	<ul style="list-style-type: none"> • uncontrolled reproduction of wild animals and dogs which may spread diseases and attack people; • risk of exposure to radiation and of the related diseases; • tourists' fear of conflict in the east of Ukraine.

When calculating the results of SWOT analysis the ranking method of data formatting was used. The analysis conducted indicates a balance between the positive and negative sides. Eliminating weak sides of the discussed area's tourist attractiveness to a large extent depends on central authorities of Ukraine. It is necessary to work out conditions favourable to the development of tourism on the state level. Above all the following steps should be taken: awarding the Exclusion Zone around the Chernobyl Nuclear Power Plant the status of a museum reserve; granting financial support and introducing legal facilitation to create appropriate tourist infrastructure (accommodation, catering, renovation of roads); awarding in particular the city of Pripyat and other facilities located 10-15 km away from the Chernobyl Nuclear Power Plant the status of museum, which will allow to preserve Pripyat in its shape from 1986, and enhancing security that will prevent people engaged in theft and devastation of valuable historical monuments from accessing the area (Kapica & Grymanowski 2015). The undeniable asset of the Chernobyl Exclusion Zone is its ecosystem. The absence of human interference and the accompanying disappearance of risk factor have become an impulse for the Exclusion Zone to be colonized by wild animals. Over three decades in the area discussed species of animals which disappeared from this region as early as at the beginning of the previous century have re-emerged, e.g.: red deer, wolf, lynx, moose or brown bear (Znak 2016). The presence of unique plant and animal species could become the basis for the development of scientific tourism. Other elements increasing the attractiveness of the Exclusion Zone around the Chernobyl Nuclear Power Plant are unique facilities located on its territory, which, although not directly related to the disaster, can be used for tourist purposes. The structure of the Soviet strategic over-the-horizon „Duga” radar could serve as an example. Taking into account additional attractions and creating adequate infrastructure will allow the Chernobyl Exclusion Zone to become a unique tourist product.

As far as popularization of tourism is concerned the presentation of the offer at international tourism fairs plays an important role. Within this scope the most prominent commercial event of the tourism industry worldwide is Internationale Tourismus-Börse – organized annually in Berlin since 1966. During the 2018 Berlin fair the tourist offer of the Chernobyl Exclusion Zone was one of the most interesting ones (in view

of the authors of the paper). The stand was very popular with the visitors to the fair as well as other exhibitors. Well-chosen gloomy colours captured the atmosphere of the promoted product. Positive impressions were completed with promotional materials handed out to visitors to the stand, containing information, presented in a legible and clear manner, about tourist attractions and encouraging to visit the Chernobyl Exclusion Zone. In addition, some aspects influencing the increasing interest in tourism in the area discussed are documentaries (such as „The Battle of Chernobyl”, France 2006; „Chernobyl. Life in the Death Zone”, the Netherlands 2007; „Chernobyl. The Triumph of Nature”, France 2010) and research papers dedicated to various aspects of visiting the area discussed (Крапивенко 2006, Пестушко & Чубук 2010, Goatcher & Brunson 2011, Stone 2013, Yankovska & Hannam 2014, Kapica & Grymanowski 2015).

6. Summary and conclusions

The analysis of the condition of and prospects for the development of tourism in the area of radioactive contamination around the Chernobyl Nuclear Power Plant indicates that the tourist potential of the area discussed has been underused. In spite of the annual increase in the number of tourists visiting the Chernobyl Zone, the record result of 2017 (50,200 people), for the worldwide uniqueness of the place is quite modest. Apart from investments in the tourist infrastructure, awarding the museum status, enhancing security against devastation and robbery, introducing proper tourism-friendly legal regulations, great emphasis must be put on educational activity. The popularization of the Chernobyl Exclusion Zone as a safe place will allow potential tourists to overcome their fear of radiation and the related consequences of different diseases in the future. The awareness of danger dictated by the remembrance of the tragedy is especially visible among citizens of Ukraine and the countries of the former Eastern Block (which is reflected by the number of tourists from these countries). Not only will the educational activity conducted allow to show the tourist attractiveness of the area of radioactive contamination around the Chernobyl Nuclear Power Plant, but it will also serve a learning, ecological, social and cultural function, and above all could be a warning against possible consequences of irresponsible human activity both for people themselves and the natural environment.

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Katastrofa w Czarnobylskiej Elektrowni Jądrowej a turystyka. Stan i perspektywy rozwoju turystyki na obszarze skażenia promieniotwórczego

Streszczenie

Czarnobylska Elektrownia Jądrowa zlokalizowana jest na terytorium Ukrainy w obwodzie kijowskim, przy granicy z Białorusią (4 km od miasta Prypeć i 18 km od miasta Czarnobyl). Awaria IV reaktora czarnobylskiej elektrowni w dniu 26 kwietnia 1986 r. spowodowała niekontrolowaną emisję substancji promieniotwórczych do atmosfery. Równocześnie z akcją ratunkową rozpoczęto ewakuację ludności z zagrożonych terenów, wyznaczając trzydziestokilometrową zamkniętą strefę wokół terenów najbardziej dotkniętych skutkami katastrofy. Łącznie z zamkniętej Strefy Wykluczenia wokół Czarnobylskiej Elektrowni Jądrowej (w promieniu 10 km od elektrowni utworzono strefę „szczególnego zagrożenia”, a w promieniu 30 km strefę „o najwyższym stopniu skażenia”) mierzącej ok 2,5 tys. km² wysiedlono prawie 350 tys. osób. Wykorzystywanie do celów turystycznych obszaru skażenia promieniotwórczego wokół Czarnobylskiej Elektrowni Jądrowej rozpoczęło się z początkiem XXI w. kiedy to pod naciskiem państw zachodnich władze Ukrainy w 2000 r. zamknęły ostatni czynny reaktor. Pozwolenia na wjazd do Czarnobylskiej Strefy Zamkniętej wydawane są tylko przez Państwową Agencję Ukrainy ds. Zarządzania Strefą Wykluczenia. Osoby zwiedzające obszar skażenia promieniotwórczego wokół Czarnobylskiej Elektrowni Jądrowej muszą pamiętać o tym, że zwiedzanie strefy odbywa się wzdłuż określonych tras, które uznano za niezagrażające zdrowiu przy zachowaniu odpowiednich reguł bezpieczeństwa. Każdemu zwiedzającemu czy też grupie zwiedzających musi towarzyszyć licencjonowany przewodnik oraz przedstawiciel strefy. Obecnie w Strefie Wykluczenia istnieje 11 tras turystycznych: punkt kontrolny „Dytiatki” – wioska Czerewacz – wioska Zalesie – m. Czarnobyl; m. Czarnobyl (miejsce w pobliżu Cerkwi św. Eliasza); m. Czarnobyl (pomnik „Tym, którzy uratowali świat”, Cerkiew św. Eliasza, kompleks pamięci „Gwiazda Piołun”); m. Czarnobyl – wioska Paryszew (wieś Opacici, wieś Kupuwate); m. Czarnobyl – Czarnobylska Elektrownia Jądrowa – Kompleks „Wektor” (strefa czysta) – punkt składowania odpadów radioaktywnych „Buriakówka” (strefa czysta); m. Czarnobyl – Czarnobylska Elektrownia Jądrowa – chłodnica; m. Czarnobyl – m. Prypeć; m. Czarnobyl – Czarnobyl-2; m. Czarnobyl – Krasne; m. Czarnobyl – Poliśke oraz m. Czarnobyl – obóz pionierski „Skazocznyj” (Bajkowy). W 2017 r. obszar skażenia promieniotwórczego wokół Czarnobylskiej Elektrowni Jądrowej odwiedziło ponad 50 tys. osób z czego zdecydowaną większość stanowili obcokrajowcy (ponad 80%). Wśród

nich najliczniejszą grupą byli: Japończycy, Amerykanie oraz Niemcy. Według organizatorów wycieczek zagraniczni turyści, którzy odwiedzili Strefę Wykluczenia wokół Czarnobylskiej Elektrowni Jądrowej w latach 2015-2017, zostawili na Ukrainie ok. 10 mln dolarów w skali rocznej.

Abstract

The Chernobyl Nuclear Power Plant is located on the territory of Ukraine in the district of Kiev at the border with Belarus (4 km away from the city of Pripjat and 18 km from the city of Chernobyl). The failure of the reactor IV of the Chernobyl power plant on April 26, 1986, caused uncontrolled emission of radioactive substances into the atmosphere. Together with the rescue operation the evacuation of the population from the endangered areas started and the thirty-kilometre exclusion zone was designated around the territories most adversely affected by the results of the disaster. The total number of people displaced from the Exclusion Zone around the Chernobyl Nuclear Power Plant (within a 10-km radius from the power plant the "high risk zone" was established, and within a 30-km radius the zone of "the highest degree of contamination") measuring approx. 2.5 thousand km² was nearly 350 thousand people. Taking advantage of the area of radioactive contamination around the Chernobyl Nuclear Power Plant for tourist purposes began at the beginning of the 21st century when, under the pressure of Western countries, in 2000 the authorities of Ukraine shut down the last operating reactor. The permits to enter the Chernobyl Exclusion Zone are issued exclusively by the State Agency of Ukraine on the Exclusion Zone Management. People visiting the area of radioactive contamination around the Chernobyl Nuclear Power Plant must remember that visiting the zone takes place along designated routes which have been recognized as presenting no health hazard as long as appropriate safety measures are taken. Each visitor or group of visitors must also be accompanied by a licensed guide and representative of the zone. Presently, in the Exclusion Zone there are 11 tourist routes: checkpoint „Dytiatky” – Czerewacz village – Zalesie village – city of Chernobyl, city of Chernobyl (place near the St. Elijah Church); city of Chernobyl (the monument „To those who were saving the world”, St. Elijah Church, remembrance complex „The Wormwood Star”); city of Chernobyl – Paryszew village (Opacici village, Kupuwate village); city of Chernobyl – the Chernobyl Nuclear Power Plant – Complex „Vector” (uncontaminated zone) – „Buriakówka” radioactive waste disposal site (uncontaminated zone); city of Chernobyl – the Chernobyl Nuclear Power Plant – the cooler; city of Chernobyl – city of Pripjat; city of Chernobyl – Chernobyl-2; city of Chernobyl – Krasne, city of Chernobyl – Poliśke, city of Chernobyl – „Skazocznyj” (Fairytale) pioneer camp. In 2017 the area of radioactive con-

tamination around the Chernobyl Nuclear Power Plant was visited by more than 50 thousand people, of whom the vast majority were foreigners (over 80%). Among them the most numerous group was: the Japanese, Americans and Germans. According to tour operators foreign tourists who visited the Exclusion Zone around the Chernobyl Nuclear Power Plant Chernobyl in the years 2015-2017 left about 10 million dollars a year in Ukraine.

Słowa kluczowe:

Czarnobyl, dark tourism, Czarnobylska Strefa Zamknięta, elektrownia jądrowa, katastrofa, skażenie promieniotwórcze

Keywords:

Chernobyl, dark tourism, Chernobyl Exclusion Zone, nuclear power plant, disaster, radioactive contamination



Impact of Ultrasonic Pretreatment on the Anaerobic Fermentation of Dairy Waste Activated Sludge

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1. Introduction

Anaerobic digestion is the most commonly applied process for the stabilization of sewage sludge. Anaerobic digestion is generally considered to be an economic and environmentally friendly technology for the treatment of different organic waste. Indeed, the biological degradation process of organic matter, under anoxic conditions, led to the production of methane, which can be used as a renewable energy (Appels et al. 2011, Cesaro et al. 2012, Braguglia et al. 2012, Abe et al. 2011, Sadecka & Suchowska-Kisielewicz 2016). However, organic matters hydrolysis presents the rate-limiting step in sludge anaerobic digestion process (Hu et al. 2011, Galipoli & Braguglia 2012). Therefore, physical, chemical, biological process or their combination can be used to improve anaerobic treatment efficiency. Additionally, different types of pre-treatment methods can improve the degradation and thus result in higher methane production and a more stabilized end-product (Luste et al. 2012, Erden & Filibeli 2010, Xu et al. 2011, Braguglia et al. 2011, Carrere et al. 2010). Ultrasound processes are a potential option for promoting organic matter solubilisation, thus improving anaerobic digestion yields (Cesaro et al. 2012, Zawieja et al. 2015).

Ultrasound can be classified according to the frequency level into: (1) high frequency and low power (2-10 MHz range) ultrasound, also termed extended range or diagnostic ultrasound, which is used in medical imaging and chemical analyses; and (2) low frequency and high power (20-100 kHz) ultrasound, the conventional type of ultrasound, which is used for cleaning and welding and also for sonochemistry (Rokhina et al. 2009, Braguglia et al. 2012a). The ultrasonic power is the key parameter in sludge disintegration. The sludge type is very important to decide about the operational parameters (Kidak et al. 2009).

Ultrasound generated high acoustic energy, and when this energy is applied to a liquid system, it is possible to generate physical and chemical reactions that can significantly modify the character of dissolved and particulate substances present in the liquid. These reactions result from the generation and collapse of cavitation bubbles produced under this acoustic condition. While ultrasound shows great potential in environmental engineering, a number of scientific and technical questions exist, which include the influence of frequency, dissolved gases, and suspended solids on cavitation; optimal reactor design; economy, reliability, and life expectation of ultrasound equipment (Show et al. 2010). The ultrasound technique is well known for disrupting sludge floc and lysed biological cells, which can lead to solubilisation of organic matter, reduction of particle size and inactivation of sludge microorganisms (Huan et al. 2009, Wang et al. 2006). The mechanism of sludge destruction by ultrasound is divided into three stages. The first stage is the flocs loosing, where particle size decreases and extracellular materials are escaped from the surface of the flocs. The second stage is the cell breakage, where the intracellular organic materials inside the cells are set free, but most of them were macromolecular compounds. In the last stage, the macromolecular compounds were degraded into short chain organic micromolecular compounds (Chang et al. 2001, Khanal et al. 2007, Feng et al. 2009).

This research examines the effectiveness of ultrasound pretreatment on waste activated sludge (excess sludge)(WAS) disintegration at different specific energies and sonication time durations in the anaerobic digestibility of control, full stream sonicated WAS. Determine the effect the ultrasonic field on the efficiency anaerobic digestion of sewage sludge from dairy industry, that is increase in biogas production and the degree reduction of digested.

2. Methods

2.1. Materials

Sewage sludge was obtained from mechanical-biological treatment plant located in the dairy cooperative “Włoszczowa”. Substrate for the study was collected from recycled sludge inflow stub pipe to the circulation chamber sludge. The substrate was thickened by gravitational method to reach VS (volatile solid) concentration of approximately 16 g L⁻¹. The characteristic of the substrates and *inoculum* are shown in Table 1.

Table 1. Characteristics of raw substrates and *inoculum* mixtures used in the study

Tabela 1. Charakterystyka substratów badań: *inoculum*, mieszanin użytych w badaniach

Parameter	Unit	Substrates		
		Sewage sludge	Thickened sewage sludge	<i>Inoculum</i>
TS	[g L ⁻¹]	13.8	23.8	18.6
VS	[g L ⁻¹]	8.5	16.5	11.7

2.2. Sonication (ultrasonic disintegration)

Sonication was carried out with a low-frequency (20 kHz) ultrasonic processor VC750 (Sonics, USA), with a 19 mm titanium tip. Sludge samples with a volume of one liter was sonicated at ambient temperature. The quantity of the amplitude is set as a percentage of maximum amplitude and kept constant by generator. Four different amplitudes: $A_1 = 24.4 \mu\text{m}$ (40%), $A_2 = 36.6 \mu\text{m}$ (60%), $A_3 = 48.8 \mu\text{m}$ (80%) and $A_4 = 61.0 \mu\text{m}$ (100%), were tested in the study. Sludge sonication times were 18, 360, 540, 720, 900, 1080, 1200 s. The amount of acoustic energy that was being delivered to the probe was showed in Table 2. The acoustic energy (E) delivered to the sample was adjusted by varying the input amplitude (A) and sonication time (t_s). The acoustic energy was calculated by the integrated circuit with the Sonic VC750 device. The producer did not provide data on the efficiency of the transformation of electricity to acoustic energy. An external electrical power consumption counter was not used.

Table 2. Characteristics of sonication parameters**Tabela 2.** Charakterystyka parametrów nadźwiękawiania

Time	Amplitude	Acoustic energy	Amplitude	Acoustic energy
S	μm	kJ	μm	kJ
180 (3 min)	24.4	7.0	36.6	10.3
360 (6 min)		13.1		16.8
540 (9 min)		19.2		28.9
720 (12 min)		25.4		41.1
900 (15 min)		31.5		53.2
1080 (18 min)		37.6		65.4
1260 (21 min)		41.7		73.4
180 (3 min)	48.8	13.8	61.0	20.1
360(6 min)		31.8		46.7
540 (9 min)		52.1		73.3
720 (12 min)		72.4		99.9
900 (15 min)		92.8		126.6
1080 (18 min)		113.1		153.2
1260 (21 min)		126.7		170.9

2.3. Experimental setup

The study was performed in three stages (Figure 1). During the first stage, the effect of ultrasonic disintegration was characterized with ratio of total organic carbon concentrations (TOC) and acoustic energy as well as ratio of total carbon concentrations (TC) and acoustic energy (Table 2). The second stage was conducted in order to evaluate the effect of selected pre-treatment US parameters of sewage sludge on potential biogas production. Experiment was determined with the use of Oxi-Top Control AN6 measuring system. This system consists of glass vessels, measuring pressure heads, a controller, and shaking plateau. Pressure heads measure pressure variations in digestion vessels. The tests were performed in 12 vessels with continuous stirring at 37°C. Batch tests were carried out for 21 days. Based on the results of the first and second stage of the studies the best ultrasonic field parameters were determined, which were used in third stage of research. In this part of study, digestion

was carried out in 5.5 L glass reactor at 37°C (Fig. 1). Reactor was operated in draw-and fill mode (on a daily basis) with retention time of 10 days. The adaptation of the digester biomass in the reactor was achieved after 30 days. Initially reactor experiment was performed with sewage sludge without pretreatment (control). Subsequently, reactor was fed with sewage sludge pretreated at 36.6, 48.8. and 61 µm for 21, 18 and 15 respectively.

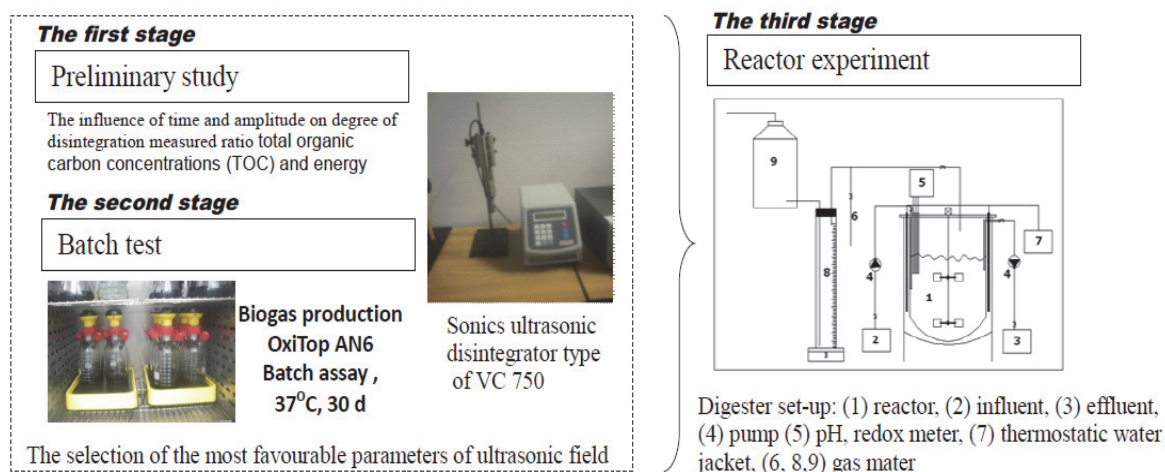


Fig. 1. Experimental setup

Rys. 1. Schemat doświadczenia

2.4. Analyses and calculations

Total carbon (TC) and total organic carbon (TOC) were measured by multi N/C analyzer (Analytik Jena UK). All measurements were done on soluble fractions of sludge. The soluble fraction was defined as the fraction resulting from the centrifugation and filtration. The samples were centrifuged at 10.000 rcf (relative centrifugal force) for 15 min. The supernatant was filtrated through a cellulose nitrate membrane (0.45 µm pore size). Total solids (TS), volatile solids (VS), pH (pH meter Cole Parmer Model No. 59002-00), alkalinity, chemical oxygen demand (COD), ammonium nitrogen and volatile fatty acids (VFAs) (steam distillation – BÜCHI K-355) were determined according to standard methods (APHA 1999). Biogas production was measured daily by the water displacement method and biogas composition (methane, carbon dioxide, ballast and oxygen) was analyzed by a portable gas analyzer (GA 2000,

Geotechnical Instruments (UK) Ltd.). All results was calculated at standard temperature and pressure.

3. Results

In the first stage, the selection of the most favorable sonication parameters of sewage sludge was selected. For this purpose, the concentration of total carbon (TC) and applied acoustic energy (E) ratio (TC/E) was used (Fig. 2). Moreover the TOC/E ratio was calculated (Fig. 3). It was found that, the highest value of TC/E and TOC/E ratios was observed for the highest tested amplitude (61.0 μm), and the lowest for the amplitude of 24.4 μm . This is evident by the fact that the maximum acoustic energy introduced into the sludge as a result of propagation of the ultrasonic wave at amplitude 24.4 μm was 41.7 kJ. However, in case of amplitude 61.0 μm application it was 170.9 kJ. At this stage the criterion for selection of the most favorable conditions for sonication was the maximum value of the TC/E and TOC/E ratios. Based on these results, it was decided that further research will be conducted using three amplitudes, i.e. 36.6 μm , 48.8 μm , 61.0 μm , respectively, and exposure times: 15, 18 and 21 minutes.

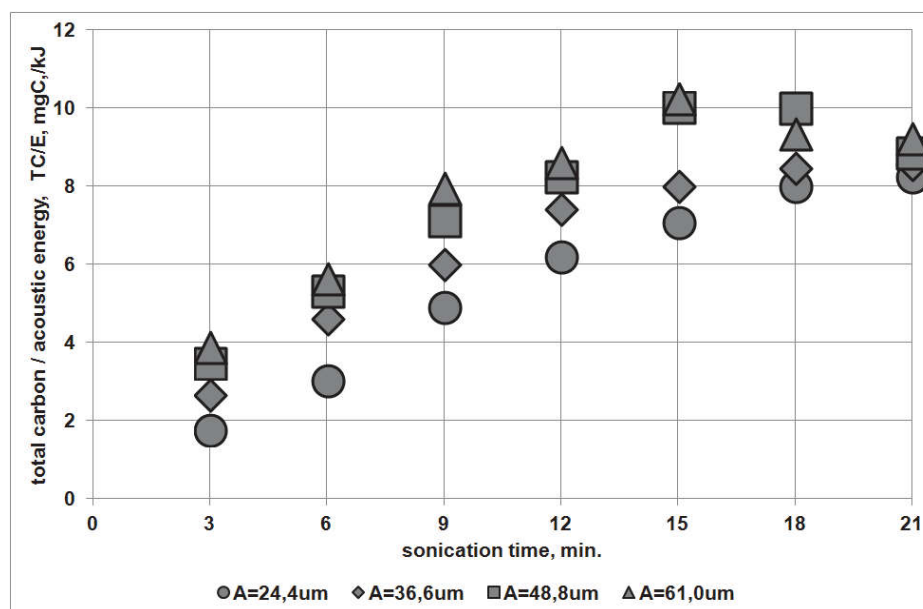


Fig. 2. Total carbon concentrations (TC) and acoustic energy (E) ratio as a function of sonication amplitude and time

Rys. 2. Całkowity stosunek stężenia węgla (TC) i energii akustycznej (E) w funkcji amplitudy nadźwiękawiania i czasu

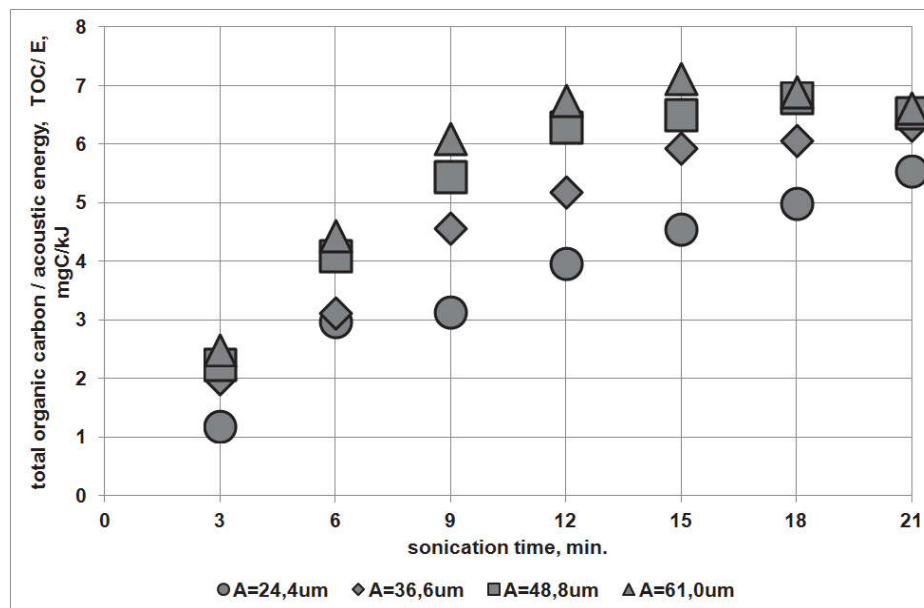


Fig. 3. Total organic carbon concentrations (TC) and acoustic energy (E) ratio as a function of sonication amplitude and time

Rys. 3. Całkowity stosunek węgla organicznego (TC) i energii akustycznej (E) w funkcji amplitudy nadźwiękawiania i czasu

3.1. Bach test

Figure 4 shows the change of biogas generation during anaerobic digestion carried out with OxiTop AN6. It was found, that only below listed sonication parameters allowed to increase the efficiency of biogas production in comparison to the control (non sonicated sludge). These were propagation of ultrasonic wave with amplitude $A = 36.6 \mu\text{m}$ at 21 minutes and also combinations $48.8 \mu\text{m}/18$ minutes and $61.0 \mu\text{m}/15$ minutes. The composition of biogas for each combination was presented in Figure 5. Compared to the control only sludge sonication with amplitude of $61 \mu\text{m}$ (regardless of the sonication time) allowed minimal increase in methane content in biogas. Specified combinations of sonication parameters were decided to test in the continuous fermentation process (third stage).

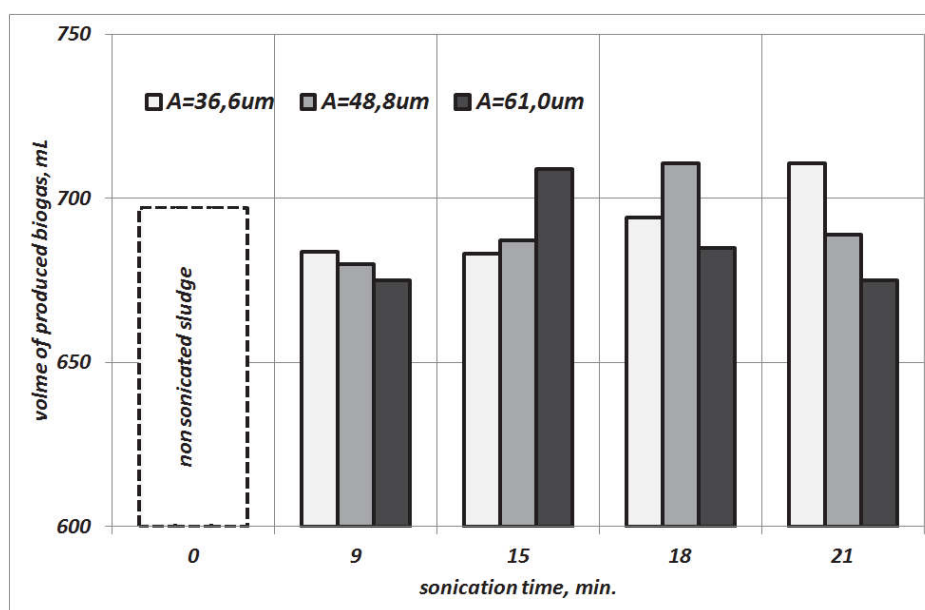


Fig. 4. The volume of biogas generated during the fermentation in set OxiTop AN6

Rys. 4. Objętość biogazu wytworzonego podczas fermentacji w zestawie OxiTop AN6

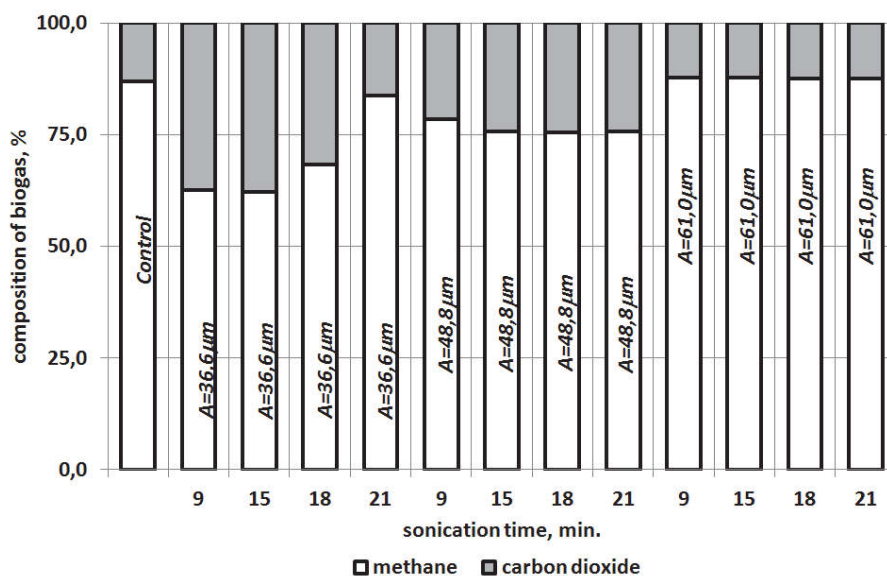


Fig. 5. The composition of biogas generated during the fermentation in set OxiTop AN6

Rys. 5. Skład biogazu wytworzonego podczas fermentacji w zestawie OxiTop AN6

3.2. Reactor experiment

The dynamic changes of the volatile fatty acids concentration during anaerobic digestion are shown in the Table 3. In the initial period (sludge not conditioned by US) the VFA concentrations ranged from 994 to 1.222 mg L⁻¹. From the day 50 the reactor was feed with US conditioned sludge (36.6 μm/21 minut). At the beginning of the experiment the increase of VFA (1428 mg L⁻¹) was observed, then the concentration of volatile fatty acids decreased to the level of 1120 mg L⁻¹. For the amplitude of 48.8 μm/18 min, the increase of organic loading rate cased the increase of VFA concentration in the reactor. For the last applied US field amplitude the concentration of VFA decreased to the level of 1,394 mg L⁻¹.

During the first period (without US conditioning) the total alkalinity changed from 3600 to 3900 mg L⁻¹. However, in case of the use of sonication to pretreat sewage sludge a steady growth of that index values was observed. The highest alkalinity (910 mg L⁻¹) was observed for amplitude of 48.8 μm and 18 minutes of exposure time. During the process, the VFA/ alkalinity ratio ranged from 0.25 to 0.36. However, it did not exceed the value recognized in the literature as alarming.

The highest ratio value was recorded in the 15 and 60 day trial. The highest ratio was recorded on the fifth day, the lowest in 10 days after the introduction of a new charge to the reactor. The pH of 7.33 to 7.61 was observed within the experience.

For the control the ammonium nitrogen concentration varied from 489 to 694 mg L⁻¹. After changing the conditions of the sewage sludge conditioning the N-NH₄ concentration increase of 62 mg L⁻¹ (36.6 μm/21 min), 247 mg L⁻¹ (48.8 μm/18 min) and 78 mg L⁻¹ (36.6 μm/21min). After application of ultrasonic disintegration the chemical oxidation demand (COD) increased from 698 to 1430 mg L⁻¹. In the last day of the process (61 μm/15 min) the concentration of COD stood at 1458 mg L⁻¹.

Figure 5 shows the daily biogas production during the digestion process. In the first stage of the study (fermentation without US) a steady increase in biogas volume produced per day was observed. During this period the highest biogas production of 2.84 L was observed in the day 41 of experiment.

Table 3. Characteristics of the digested material during the fermentation**Tabela 3.** Charakterystyka osadów przefermentowanych podczas procesu fermentacji

Pretreatment Amplitude	Day	VFA (mg L ⁻¹)	VFA/Alkalinity	pH	N-NH ₄ (mg L ⁻¹)	COD (mg L ⁻¹)	VS (g L ⁻¹)
—	1	977±247	0.25	7.61	694±6	385±55	8.96±0.20
	5	994±34	0.27	7.54	586±3	629±11	9.87±0.24
	10	1097±34	0.31	7.42	577±10	642±38	9.95±0.11
	15	1257±39	0.36	7.43	553±9	611±39	9.63±0.28
	20	1080±17	0.32	7.42	489±14	724±30	9.13±0.12
	25	1206±36	0.35	7.36	530±9	540±15	9.61±0.05
	30	977±45	0.27	7.4	547±3	840±40	10.37±0.10
	35	1223±71	0.33	7.37	579±3	760±1	11.86±0.23
	40	1177±50	0.30	7.38	657±12	964±19	12.92±0.09
	45	1017±49	0.26	7.33	669±3	698±37	12.95±0.09
36.6 μm	50	1429±36	0.35	7.48	735±9	923±29	11.50±0.08
	55	1120±20	0.27	7.54	732±3	1431±21	21.94±0.31
48.8 μm	60	1714±34	0.36	7.54	930±6	1278±82	11.64±0.12
	65	1703±20	0.34	7.61	978±3	1313±76	12.39±0.13
61 μm	70	1577±34	0.30	7.67	1036±6	1381±79	11.61±0.03
	75	1394±52	0.26	7.61	1057±6	1459±126	10.88±0.31

After the application of the ultrasound for sewage sludge pretreatment with amplitude of 48.8 μm and sonication time of 18 min an increase in the daily production of biogas compared to controls by 52% was observed. For all other amplitudes large fluctuations in the value of the measured parameter were observed. In their case, compared to controls it has been an increase in volume of gas produced by the fermentation of 16% ($A = 36.6 \mu\text{m}$) and 45% ($A = 61.0 \mu\text{m}$). The use of ultrasound has not significantly changed the composition of the biogas produced in the process. During the fermentation process, the methane content in the biogas is about 69%.

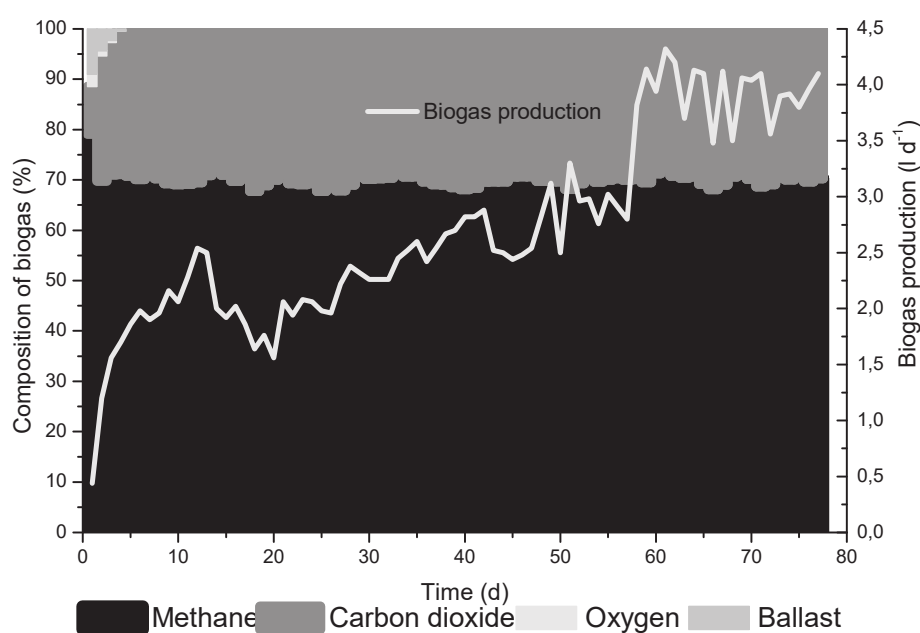


Fig. 5. Daily biogas production and its composition observed during study

Rys. 5. Dzienna produkcja biogazu i jego skład obserwowany podczas badań

Figure 6 shown biogas yield and OLR (organic loading rate) in the semi-continuous lab-scale reactor experiment. During the period when sludge was not conditioned by US organic loading rate remained at a level of $1.7 \text{ g L}^{-1} \text{ d}^{-1}$. After starting the ultrasound sludge pretreatment, for the first tested amplitudes ($36.6 \mu\text{m}$), a low (4%) reduction in the value of the parameter was observed. OLR was higher for all other amplitudes, $1.8 \text{ g L}^{-1} \text{ d}^{-1}$ for $A = 48.8 \mu\text{m}$ and 1.9 for $A = 61.0 \mu\text{m}$. Changes of OLR correlated with the production of biogas and specific biogas yield (Y). The value of this parameter for no prepared sludge ranged from 0.1

to 0.16 LgVS^{-1} . While the average value of Y for sludge conditioned by US field with an amplitude of $36.6 \mu\text{m}$, $48.8 \mu\text{m}$ and $61.0 \mu\text{m}$ was 0.18 , 0.22 and 0.21 respectively. It means that sonication of sludge at $A = 48.8 \mu\text{m}/18 \text{ min}$ causes a significant increase in the rate of biogas yield.

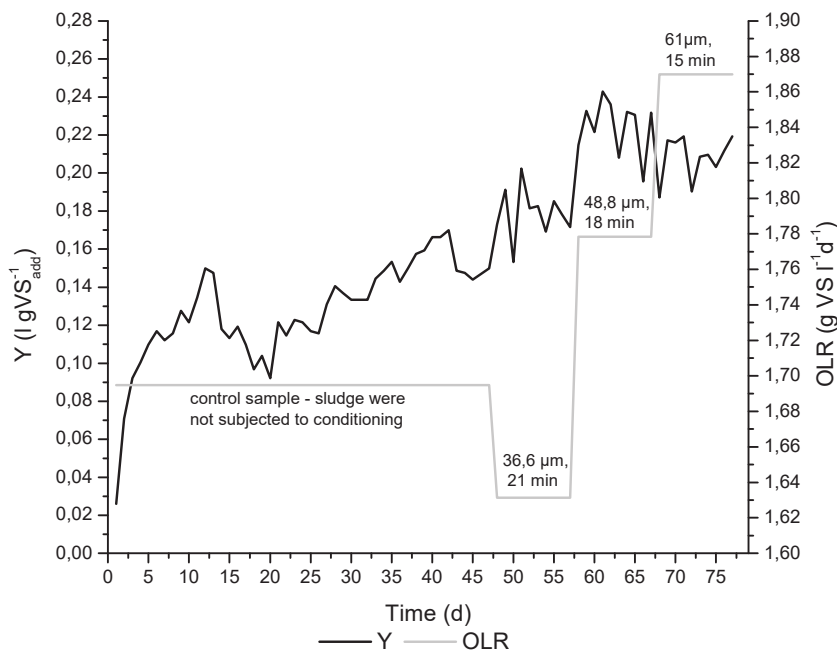


Fig. 6. Biogas yield and OLR in the semi-continuous lab-scale reactor experiment

Rys. 6. Wydajność biogazu i OLR w eksperymencie z reaktorem półciągłym w skali laboratoryjnej

Figure 7 shown the effect of sonication on composition of biogas, biogas yield and VS removal. During the fermentation of sewage sludge average methane content in the gas fermentation was at the level 70% and ultrasound conditioning of sewage sludge did not affected the biogas composition. The same situation was observed for the fermentation efficiency basis on VS removal. Only in the case of the highest amplitude VS removal was 2% higher as compare as the control test.

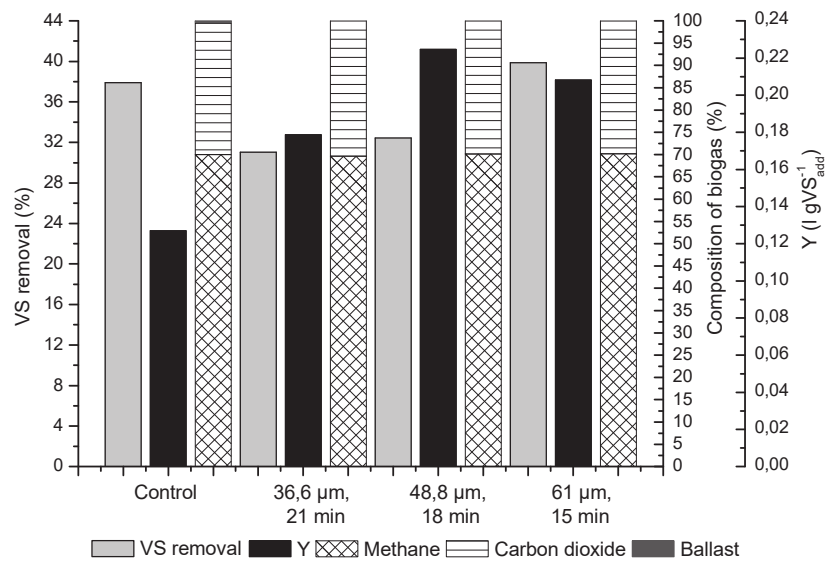


Fig. 7. Effect of sonication on composition of biogas, biogas yield and VS removal

Rys. 7. Wpływ nadźwiękawiania na skład biogazu, wydajność biogazu I usuwanie VS

4. Conclusions

The main objective of this study was to determine the most favorable US field parameters for preparation of sewage sludge generated in the dairy industry. Moreover the effect of sewage sludge sonication (for selected parameters) on the anaerobic digestion effects was determined.

Study of ultrasound pretreatment before anaerobic digestion showed that:

- ultrasound field had a positive impact on the effects of biogas production rate. Compared to the control reactor, during fermentation of dairy sludge conditioned with US field with amplitude 48.8 microns 52% higher biogas production was observed;
- UD field sludge conditioning did not significantly influence the extent and composition of biogas and VS removal (average methane content fluctuated in the range of 70%).

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Wpływ kondycjonowania polem ultradźwiękowym na fermentację metanową osadów ściekowych z przemysłu mleczarskiego

Streszczenie

W niniejszym artykule określono wpływ preparowania przemysłowych osadów ściekowych polem ultradźwiękowym na efekt fermentacji metanowej. Najkorzystniejsze parametry nadźwiękawiania dla preparowanych osadów, ustalono na podstawie zmian TOC w wodzie nadosadowej oraz efektów fermentacji metanowej w układzie ciągłym, wyrażonej wzrostem produkcji biogazu oraz ubytku suchej masy organicznej. Na podstawie uzyskanych wyników stwierdzono, że optymalne parametry nadźwiękawiania to czas ekspozycji wynoszący 18 minut i amplituda drgań 48.8 μm . Kondycjonowanie polem UD pozytywnie wpłynęło na efekty procesu, wyrażone współczynnikiem produkcji biogazu. W porównaniu do próby kontrolnej w osadach kondycjonowanych polem UD o amplitudzie 36.6 μm , 48.8 μm i 61.0 μm odnotowano zwiększenie ww. parametru odpowiednio o 38, 73 i 60%.

Abstract

In this paper, we focused on the effects of ultrasound (US) irradiation at different parameters on solubilization, biodegradation and anaerobic fermentation of sludge from the dairy industry. The changes of TOC in soluble fraction of sludge, the biogas yield, and the methane content in the biogas were used as control parameters for evaluating the effects of the US pretreatment. The optimal sonication parameters were found to be an exposure time of 18 min and ultrasound wave amplitude of 48,8 μm . The UD field conditioning positively influenced the process effects measured by the biogas production coefficient. In comparison to the control sample in sediments conditioned with a UD field with an amplitude of 36.6 μm , 48.8 μm and 61.0 μm , an increase was noted in the above-mentioned parameter by 38, 73 and 60%, respectively.

Słowa kluczowe:

biogaz, fermentacja metanowa, ultradźwięki

Keywords:

biogas, anaerobic fermentation, ultrasound



Assessing the Diameters of Water Pipes Using the k-Nearest Neighbours Method in the Calculations of Water Distribution Systems

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1. Introduction

Water distribution systems provide water in cities and in rural areas. The basic element through which water reaches the consumer are the water pipes, hence their correct design is extremely important. The choice of pipe diameter requires hydraulic calculations. Computer programmes may choose diameters, but usually, it is the designer's task. The aim of the work is to assess the correctness of the selection of water-pipe diameters assuming that the flows on the calculated sections have been determined correctly. This paper proposes a classifier, based on the k-Nearest Neighbours method, which, on the basis of a reliable flow, will assess the appropriateness of the diameter chosen. For this paper, calculations with a steady-state model, were carried out during the maximum water consumption times of the aforementioned consumers. Flows for these conditions are the basis for gauging the dimensions of the diameters of the water supply pipes (Knapik & Bajer 2010, Lansey & Mays 2000).

2. An overview of the application of artificial intelligence methods in the design of water distribution systems

The design and calculation of technical objects requires knowledge-based activities that are difficult to describe, using the classical computational algorithm. Artificial intelligence methods could become a great support in this type of task. Artificial neural networks, expert systems and the k -Nearest Neighbours method, or the Support Vector Machine are worthy of mention here. Computer programmes, used in calculations, may support the designer in his/her task, to some extent, through appropriate suggestions and prompts. In this article, the possibility of using the k -Nearest Neighbours method, to assess the diameters of water pipes, is analysed. The above method was used to assess pressure losses during the hydraulic calculations of water distribution systems (Biedugnis & Czapczuk 2018). In this article, (Oliveira & Boccelli 2017) the k -Nearest Neighbours method was used to forecast short-term, water demand periods. The k -NN approach is a pattern-recognition algorithm, where the predicted values are directly determined by previous observations which were most similar.

A review of artificial intelligence methods, in the design and operation of water supply systems, is provided in the article (Czapczuk et al. 2015). In the calculation of hydraulic water distribution systems, artificial neural networks are usually used. Suggestions for using them in the calculations themselves (Czapczuk et al. 2017, Brkić & Čojbašić 2016, Besarati et al. 2015, Bubić et al. 2011), in taring simulation models (Meirelles et al. 2017), as well as to evaluate the results of the hydraulic calculations obtained, (Dawidowicz 2017) are to be found. A method for estimating the diameter of water pipes using artificial neural networks of the multilayer perceptron type is presented in the paper (Dawidowicz 2018). One can also cite examples of expert systems used in the design stage (Dawidowicz 2012) as well as the actual operation (Changa et al. 2011). The application of RBF neural networks for the assessment of the water flow rate in the pipework is presented in the paper (Czapczuk & Dawidowicz 2018).

3. Introduction to the k -Nearest Neighbours Method

The k -Nearest Neighbours algorithm (k -NN) is used to predict the value of a random variable or classification (Triantaphyllou & Felici 2006). The method belongs to the group of lazy algorithms, that is, those algorithms which do not form the internal representation of the training data but look for a solution, only when a test pattern appears. In this work, the k -NN method was used to classify the diameter of water pipes. The task is to classify a new object, based on information as to which object or objects the new object is adjacent to. An important parameter in the method, is the value of k , that is, the number of teaching examples in the immediate environment. In the case of classification, the method takes into account, the values of most of the examples in the neighbourhood, that is, it sets the value of a new example by voting.

Choosing a neighbourhood, that is, the value of the k parameter, is essential. With a low k value, there will be a large variation in classification. Higher k values allow areas to be divided up, smoothly and noise to be removed; however, they can also lead to errors in the classification of rarer patterns. The problem then arises of generalising them, correctly. On the basis of the analyses, a k value must be chosen to minimise the likelihood of mis-classification. The k -Nearest Neighbour method proposes an optimal k value, based on the Cross-Check method.

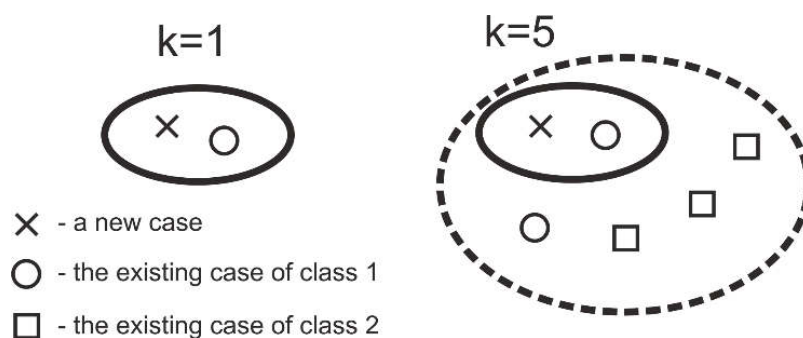


Fig. 1. Principle of the k -NN method for different neighbourhood values

Rys. 1. Zasada działania metody k -NN dla różnych wartości sąsiedztwa

If we consider $k = N$, where N is the number of all the elements of the set of teaching patterns, then the result of the classification will always be determined by the class most-represented in this set of teaching examples.

The Euclidean measure is usually used to evaluate the distance between the points describing the teaching examples:

$$D(x, p) = \sqrt{(x - p)^2} \quad (1)$$

where:

x – the new case to be classified,

p – one of the teaching cases.

4. Training examples for the assessment of the diameters of water lines by the k-Nearest Neighbours method

To use the k -Nearest Neighbours method, a set of teaching patterns is required, containing input data which define the object and are stored in vector X , as well as target values d . This corresponds to the teaching strategy under supervision.

A set of teaching examples was obtained on the basis of the hydraulic calculations of examples of water distribution systems. Diameters for the pipelines were chosen for conditions of maximum water consumption Q_{hmax} . Hydraulic calculations were made, taking into account the internal diameters of the pipelines. Each calculation option was checked and corrected where calculation irregularities appeared. Due to the large amount of data, a procedure was developed, in order to convert the results of the calculations of individual segments to an appropriate format and then to save them as a set of teaching examples.

11961 training examples were obtained containing the input variable in the form of a nominal flow, through water supply line Q_m , corresponding to the output variable DN, that is, the nominal diameter.

Nominal diameters were adopted as follows:

- DN90, DN110, DN160, DN225 for PE100 polyethylene pipes of the SDR17 series (EN 12201-2:2011),
- DN250, DN300, DN350, DN400, DN450, DN500 for ductile iron pipes (EN 545: 2010).

The amalgamated teaching examples have been divided into two subsets: teaching (75%) and testing (25%). The test group in the teaching process is not used at all; rather, it is intended for the independent determination of the accuracy of the k -NN method.

5. Development of the k-Nearest Neighbours model to assess the diameter of water pipes

On the basis of the set of teaching examples, a model was constructed and the diameters of the water pipes were classified using the k-Nearest Neighbours method, using various neighbourhood values.

The calculations for the neighbourhood in the scope of $k = 1-10$ were made in the work. Tables 1-3 summarise the results of the classification of the pipe diameters for the neighbourhood, where $k = 1$, $k = 5$ and $k = 10$. The Euclidean measure was used to calculate the distance between teaching examples; the best results are obtained in the vicinity of $k = 5$.

Detailed classification results are included in the Confusion Matrix. This is a square matrix, in which information, as to which classes the individual examples actually belong, are given in rows, as well as information as to which classes they were classified into, by the classifier, are given in columns. The diagonal contains examples that were correctly categorised, while those located beyond the diagonal were classified incorrectly. At the same time, examples lying beyond the diagonal, point to those classes which were incorrectly classified.

The matrix of classification errors, established by the k-Nearest Neighbours method, for neighbourhood $k = 5$, is shown in Table 4. Analysis of the results indicates the high quality of the classifier, which can select or assess the diameter of the pipeline, on the basis of the flow.

Table 1. Summary of the results for the classification of $k = 1$, pipe diameters
Tabela 1. Podsumowanie wyników klasyfikacji średnic rurociągów dla $k = 1$

	In total	Accurate	Incorrect	Relevant (%)	Invalid (%)
DN110	651	632	19	97.1	2.9
DN160	456	442	14	96.9	3.1
DN225	383	378	5	98.7	1.3
DN250	365	354	11	97.0	3.0
DN300	304	296	8	97.4	2.6
DN350	326	310	16	95.1	4.9
DN400	204	203	1	99.5	0.5
DN450	200	200	0	100.0	0.0
DN500	101	101	0	100.0	0.0

Table 2. Summary of the results for the classification of $k = 5$, pipe diameters**Tabela 2.** Podsumowanie wyników klasyfikacji średnic rurociągów dla $k = 5$

	In total	Accurate	Incorrect	Relevant (%)	Invalid (%)
DN110	652	635	17	97.4	2.6
DN160	457	445	12	97.4	2.6
DN225	380	377	3	99.2	0.8
DN250	370	360	10	97.3	2.7
DN300	296	295	1	99.7	0.3
DN350	323	309	14	95.7	4.3
DN400	211	207	4	98.1	1.9
DN450	200	200	0	100.0	0.0
DN500	101	101	0	100.0	0.0

Table 3. Summary of the results for the classification of $k = 10$, pipe diameters**Tabela 3.** Podsumowanie wyników klasyfikacji średnic rurociągów dla $k = 10$

	In total	Accurate	Incorrect	Relevant (%)	Invalid (%)
DN110	651	632	19	97.1	2.9
DN160	461	443	18	96.1	3.9
DN225	381	375	6	98.4	1.6
DN250	364	357	7	98.1	1.9
DN300	300	297	3	99.0	1.0
DN350	315	306	9	97.1	2.9
DN400	217	212	5	97.7	2.3
DN450	201	200	1	99.5	0.5
DN500	100	100	0	100.0	0.0

Table 4. Matrix of errors in the test subset for the $k = 5$ neighbourhood
Tabela 4. Macierz pomyłek dla sąsiedztwa $k = 5$ dla podzbioru testowego

	DN 110	DN 160	DN 225	DN 250	DN 300	DN 350	DN 400	DN 450	DN 500
DN110	635	5	0	0	0	0	0	0	0
DN160	17	445	0	0	0	0	0	0	0
DN225	0	7	377	1	0	0	0	0	0
DN250	0	0	3	360	0	0	0	0	0
DN300	0	0	0	9	295	3	0	0	0
DN350	0	0	0	0	1	309	4	0	0
DN400	0	0	0	0	0	11	207	0	0
DN450	0	0	0	0	0	0	0	200	0
DN500	0	0	0	0	0	0	0	0	101

6. Conclusions

The above method for classifying the diameter of water pipes was developed for the purposes of calculating hydraulic water distribution systems. Based on the data from hydraulic calculations, the k -NN algorithm can evaluate the diameter of the ducts on individually calculated sections of the water supply network and can then propose an appropriate value or accept the existing value. The k -NN method obtained, shows a high accuracy index in the classification of the diameters of the pipes in the $k = 5$ neighbourhood. It should be remembered, however, that there may be cases of incorrect classification, hence the solution should be treated as an additional tool in the selection or assessment of the diameters adopted. The final decision on the selection of the diameter, is down to the person performing the calculations.

The method is also quite simple from the point of view of theoretical assumptions; this is undoubtedly one of the advantages of this solution. The method for classifying water pipe diameters may only be used, however, for the automatic selection of pipe diameters, prior to undertaking the appropriate hydraulic calculations or evaluating the results obtained, because the target levels of pressure losses in the pipelines have not been achieved. Undoubtedly, this kind of module would be an interesting addition to any computational programme.

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Metoda oceny średnic przewodów wodociągowych za pomocą metody k-Najbliższych Sąsiadów w obliczeniach systemów dystrybucji wody

Streszczenie

Systemy dystrybucji wody dostarczają wodę w miastach i na terenach wiejskich. Podstawowym elementem, przez który woda dociera do odbiorców są przewody wodociągowe, stąd niezwykle istotne jest ich poprawne zaprojektowanie. Dobór średnic rurociągów wymaga przeprowadzenia obliczeń hydraulicznych. Programy komputerowe mogą automatycznie dobierać średnice, ale najczęściej zadanie to należy do projektanta. Obecnie opracowuje się metody, które wspomagałyby projektantów w realizacji powyższych zadań. W niniejszej pracy zaproponowano klasyfikator oparty na metodzie k-Najbliższych Sąsiadów (k-NN), który na podstawie przepływu miarodajnego Q_m będzie oceniał poprawność dobranej średnicy. W tym celu sporządzono 11961 przykładów uczą-

cych zawierających zmienną wejściową w postaci przepływu miarodajnego Q_m oraz odpowiadającą mu zmienną wyjściową zdefiniowaną jako średnica nominalna DN. Na podstawie zestawu przykładów uczących skonstruowano klasyfikator za pomocą metody k-Najbliższych Sąsiadów, stosując różne wartości sąsiedztwa. Uzyskana metoda k-NN pokazuje wskaźnik wysokiej dokładności w klasyfikacji średnic rur dla wartości sąsiedztwa $k = 5$.

Abstract

Water distribution systems provide water in cities and in rural areas. The basic element through which water reaches the consumer are the water pipes, hence their correct design is extremely important. The choice of pipe diameter requires hydraulic calculations. Computer programmes may choose diameters, but usually, it is the designer's task. This paper proposes a classifier, based on the k-Nearest Neighbours method, which, on the basis of a reliable flow, will assess the appropriateness of the diameter chosen. In the work 11961 training examples were obtained containing the input variable in the form of a nominal flow, through water supply line Q_m , corresponding to the output variable DN. On the basis of the set of training examples, a model was constructed and the diameters of the water pipes were classified using the k-Nearest Neighbours method, using various neighbourhood values. The k -NN method obtained, shows a high accuracy index in the classification of the diameters of the pipes in the $k = 5$ neighbourhood.

Słowa kluczowe:

system dystrybucji wody, obliczenia hydrauliczne, metoda k-Najbliższych Sąsiadów, średnice rurociągów

Keywords:

water distribution system, hydraulic calculations, k-Nearest Neighbours Method, diameters of water pipes



The Effect of Subsoiling on Changes of Compaction and Water Permeability of Silt Loam

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1. Introduction

Soil, or the surface layer of the earth's crust, is a natural medium for plant growth. Therefore, it is believed that food production is directly or indirectly dependent on the soil. In other words, life on Earth depends on the soil – it is a degradable and, unfortunately, non-renewable resource. Some 33% of the global acreage of soils is either moderately or heavily degraded by such factors as: erosion caused by water and/or wind, high salinity, compaction, sealing, contamination, acidification, and loss of organic carbon (Hillel 2007). Soil compaction is a significant problem of agriculture nowadays. It is directly connected with the mechanization of field treatments. Compaction is a physical form of soil degradation: it changes the soil structure, water and air permeability, porosity, and it inhibits penetration by plant roots (Hakl et al. 2007; Nawaz et al. 2013). The various ways to control the degree of soil compaction include soil improvement treatments, for instance, subsoil ploughing, which is also called subsoiling. Such treatments have a direct impact on the physical properties of soils and they indirectly affect the optimization of air-water conditions and the growth of crop plants (Matula 2003; Ragassi et al. 2012).

Water management in agricultural areas has gained more importance recently, mainly because the growing period has extended and the pattern of meteorological phenomena has become unpredictable: above all, the frequency of droughts and floods has increased (Szafranski et al. 2009, Trnka et al. 2013). Climate changes, connected with higher

air temperatures and lower total precipitation in the growing period, combined with its growing time-space irregularity, have led to the occurrence of water crises in various parts of the world (Ragab & Prudhomme 2002). On the other hand, suitable conditions for the provision of watering systems enabling the supplementation of water deficiency in crop plants do not exist everywhere.

Agriculture is the most water-consuming industry: it uses the highest volume of global water resources, affecting the crop yield (Qadir et al. 2003). If in good condition, the soils may play a strategic part, not only in solving the problem of food for the ever growing population but also in slowing down climate changes (Kružel et al. 2015, Szymanowski et al. 2018).

The results of previous research indicate that subsoil ploughing and other soil improvement treatments have a desirable effect on air-water conditions in soils with an exceedingly compacted subsoil. A loosened soil has a higher infiltration capacity and helps transform the surface runoff into the subsurface runoff.

The objective of this paper is to assess the effect of subsoiling on changes of the compaction and water permeability of silt loam.

2. Material and Methods

The effect of soil improvement by subsoiling on changes in the soil compaction and water permeability was investigated for arable land in two agricultural objects, situated in the south of Poland, in the localities of Strzybnik (Racibórz District, Śląskie Province, 50°8'13,33" N, 18°8'46,1" E) and Prusy (Kraków District, Małopolskie Province, 50°7'5,0" N, 20°4'49,9" E). In the region of Object 1, in the multi-annual period 1971-2000, average annual air temperature was 8.5°C and total precipitation was 616 mm (according to IMGW – Institute of Meteorology and Water Management – station in Racibórz). In the region of Object 2, the data were 8.1°C and 663 mm, respectively (IMGW station Kraków) – table 1. Depending on changes in meteorological conditions, there are soils with periodically too high moisture contents in both objects, depending on changes in meteorological conditions (Bogdał et al. 2016).

In the field experiment, a 7-tined passive subsoiler from Maschio was used in Strzybnik, and a 3-tined passive subsoiler was used in Prusy. The effective operating depth of the working elements of the two subsoilers was between 50 and 60 cm, and the tines/coulters were spaced every 50 cm.

The field soil tests were carried out in the years 2011-2015 (Table 2). The tests were carried out on brown- and black earth (chernozem), which are good/very good in terms of soil fertility classes. The soil samples were taken from a total of 8 sampling points: 4 samples before (S1, P1, P2 and P3) and 4 after the subsoiling (S1', P1', P2' and P3'), and the essential morphological features were determined based on them. From each genetic horizon, from 3 to 6 undisturbed samples were collected for laboratory analyses into 100 cm³ steel cylinders without disturbing the sample structures, and an approximately 1 kg sample with a disturbed structure was collected.

Table 1. The average sums of precipitations totals and air temperatures in the multi-annual period 1971-2000

Tabela 1. Średnie sumy opadów atmosferycznych i temperatur powietrza w wieloletniu 1971-2000

Station IMGW	Months												Jan- Dec
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
Precipitation total [mm]													
Racibórz	28	26	32	45	67	79	94	74	56	41	40	34	616
Kraków	35	30	35	50	74	94	81	76	60	50	40	38	663
Average air temperature [°C]													
Racibórz	-1,3	-0,2	3,8	8,2	13,5	16,1	17,8	17,7	13,6	9,0	3,6	0,2	8,5
Kraków	-2,3	-0,9	3,1	8,0	13,4	16,2	17,8	17,5	13,2	8,4	2,8	-0,6	8,1

Table 2. Characteristics of research stations**Tabela 2.** Charakterystyka stanowisk badawczych

Information	Object	
	Strzybnik (S)	Prusy (P)
Number of soil-sampling points	2	6
Date of subsoiling	10.2010	09.2014
Date of tests in the field (BS)	25.06.2012	7.04.2011/28.04.2015
Date of tests in the field (AS)	25.06.2012	4–5.10.2014/28.04.2015
Crop plant	maize	wheat

BS – field without subsoiling, AS – field with subsoiling

The field measurement of permeability of for the topsoil (10-20 cm) and subsoil horizons (40 cm) was performed using a double-ring infiltrometer from the Dutch manufacturer Eijkelkamp. The tests were carried out in three repetitions and the results of only two (most similar) of them were used in the analysis. Fluctuations in water permeability vs. time were plotted for each horizon. Moreover, linear trends and their corresponding equations (i) and coefficients of determination (R^2) were added. Infiltration rate was calculated for the respective time intervals ΔT , using the following formula (Gulliver & Anderson 2008):

$$i = \frac{864 \cdot 4 \cdot V}{3.14 \cdot D_r^2 \cdot \Delta T} [\text{m} \cdot \text{d}^{-1}] \quad (1)$$

where:

V – volume of water added in time (ΔT) into the measuring cylinder [cm^3],

D_r – diameter of the inner ring [cm^2],

ΔT – infiltration time for the water volume ΔV [s].

Average rate of infiltration of water vs. duration of measurement was described by the power function:

$$i_t = i_1 \cdot t^\varepsilon [\text{m} \cdot \text{d}^{-1}] \quad (2)$$

where:

i_t – infiltration rate at the time t from the beginning of the infiltration process [$\text{m}\cdot\text{d}^{-1}$],

i_1 – infiltration rate in the first time unit [$\text{m}\cdot\text{d}^{-1}$],

t – infiltration time [min],

ε – coefficient, depending on soil properties [–].

Infiltration classes for the various horizons were adopted according to the FAO classification (FAO 1971): infiltration is very slow – $<0.024 \text{ m}\cdot\text{d}^{-1}$; low – $0.024\text{-}0.12 \text{ m}\cdot\text{d}^{-1}$; moderately slow – $0.12\text{-}0.48 \text{ m}\cdot\text{d}^{-1}$; moderate – $0.48\text{-}1.56 \text{ m}\cdot\text{d}^{-1}$; moderately rapid – $1.56\text{-}4.20 \text{ m}\cdot\text{d}^{-1}$; rapid – $4.20\text{-}5.81 \text{ m}\cdot\text{d}^{-1}$; very rapid – $>5.81 \text{ m}\cdot\text{d}^{-1}$.

The following parameters were determined in three repetitions in order to assess the effect of subsoiling on changes of soil compaction: bulk density and moisture – by gravimetry (oven and balance); specific density – by pycnometry; organic carbon by the Tiurin's method (as organic matter); particle size distribution – by areometry. The names of soil texture classes were given according to the Polish Soil Science Society. Soil classification was established according to the Polish Soil Science Classification and the FAO–WRB classification.

Based on the results of laboratory analyses total porosity in the soil were found. Next, using the results of determination of actual moisture [% v/v], soil water resources [mm] were determined for all the genetic horizons of the soil profiles investigated (Landon 1991).

The significance of soil profile subsoiling to changes in the compaction and water permeability of silt loam was determined by means of statistical analyses using the *Statistica 12.5 PL* software. The parameters used for the purpose were bulk density (a measure of soil compaction) and steady infiltration. The statistical analyses were based on the results of determination of bulk density in all the repetitions. In the case of steady infiltration, the results of two repetitions were used. Basic descriptive statistics of the soil samples were determined, including the following: minimum value ($x_{\min.}$), maximum value ($x_{\max.}$), mean (\bar{x}), median (Me), percentile 25 and 75%, standard deviation (SD), and coefficient of variation (CV). Because of a lack of normality of distribution of the properties investigated, the significance of differences in the general population distributions in the respective soil horizons before and after

subsoiling were calculated using the non-parametric, statistical Mann-Whitney U test – the variant for two small independent samples at the significance level of $\alpha = 0.05$. This analysis was preceded by Stevens's series test to check the randomness of the data.

3. Results and Discussion

The soil composition in Strzybnik and in Prusy is highly uniform, with silt loam (SiL) in all its genetic horizons. With a high percentage of silt (61-74%), these soils are classified as heavy, silt soils. Silt soils are not easily cultivated as they tend to swell or shrink depending on their moisture content (Boivin et al. 2006). Moreover, secondary compaction often occurs in such heavy silt loams, causing an increased surface runoff, in particular on slopes, thus leading to erosion (Jourgholami et al. 2017). Their properties, especially air-water conditions, are frequently varied in time. The phenomenon is mainly caused by the pattern of meteorological conditions, landform features, and agrotechnical treatments.

Specific densities of the soils for the objects investigated ranged from 2.60-2.68 g·cm⁻¹ (Table 3) and tended to be lower in the topsoil horizons (Ap), which is normal for mineral soils (Hillel 1998). Bulk densities for the soils, affecting their porosity, ranged from 1.45 to 1.73 g·cm⁻¹; therefore, the soils are qualified as poorly compacted (pc) to heavily compacted (hc) (Table 3). As demonstrated by Berisso et al. (2012) commonly used agricultural machinery can compact the soil to 0.9 m depth, the effect may persist for at least 14 years, and important soil functions are affected. In mitigation of arable soil compaction a key role plays subsoiling (Chamen et al. 2015).

Total porosity of the soils in Strzybnik was higher in all the genetic horizons for the soil profile with subsoiling (39.3-41.6%) in comparison with same horizons for the soil without subsoiling (35.5-41.4%) (Table 3). In the case of Prusy, total porosity of the soils without subsoiling was not always the highest in the topsoil horizons. The fact may be accounted for by the soils' heavy texture (particle size distribution), leading often to what is called secondary compaction, as well as high activity of soil organisms, especially earthworms; they make their little canals which are visible in the soil profiles, thus improving the soil porosity and change its air-water conditions. The application of subsoiling improved

the soil porosity (40.9-44.5%) in comparison with the soil without subsoiling (39.3-43.5%), which is especially visible in the subsoil horizons below the Ap horizon – differences in the thickness of the genetic levels of soils before and after subsoiling were resulted from a change in porosity and from the fact that the pits were made at a certain distance from each other. Wang et al. (2014) observed that subsoiling affected on reduced soil bulk density in the 0-30 cm soil layer, but more importantly the treatment increased total porosity (Table 3).

The largest amounts of organic matter were recorded for the topsoil horizons (1.0-1.5%) in both Objects, and the lowest were recorded for the parent rock layer in Strzybnik (0.1-0.2%). In the soils in Prusy, the lowest content of organic matter was found for the subsoil horizons (Table 3). The soil organic matter is one of the parameter which influence to the physicochemical properties of soils (Widłak 2016).

Table 3. Selected physical and water properties of soils

Tabela 3. Wybrane właściwości fizyko-wodne gleb

Profile number	Genetic horizons	Depth	Specific density	Soil bulk density	Degree of compaction ¹	Total porosity	Organic matter	Soil moisture	Actual soil water resources
		[cm]	[g·cm ⁻³]		[-]	[%]		[% v/v]	[mm]
S1	Ap	0–27	2.63	1.54	c	41.4	1.1	16.9	46
	Bw	27–100	2.68	1.69	c	36.9	0.3	24.1	176
	C	100–150	2.68	1.73	hc	35.5	0.2	28.7	144
S1'	Ap	0–40	2.62	1.53	c	41.6	1.1	15.4	62
	Bw	40–90	2.68	1.59	c	40.7	0.2	18.9	95
	C	90–150	2.67	1.62	c	39.3	0.1	28.3	169
P1	Ap	0–30	2.61	1.50	c	42.5	1.0	38.6	116
	Bw	30–100	2.63	1.53	c	41.8	0.7	34.0	238
	C	100–150	2.62	1.52	c	41.9	0.7	40.4	202

Table 3. cont.

Tabela 3. cd.

Profile number	Genetic horizons	Depth	Specific density	Soil bulk density	Degree of compaction ¹	Total porosity	Organic matter	Soil moisture	Actual soil water resources
		[cm]	[g·cm ⁻³]		[-]	[%]		[% v/v]	[mm]
P1'	Ap	0–35	2.61	1.52	c	41.7	1.0	37.8	131
	Bw	35–105	2.63	1.48	pc	43.7	0.7	34.9	243
	C	105–150	2.62	1.45	pc	44.5	0.7	37.2	164
P2	Ap	0–35	2.62	1.54	c	41.2	1.2	37.1	130
	Bw	35–60	2.61	1.56	c	40.2	0.4	38.2	96
	Bw/C	60–94	2.61	1.48	pc	43.3	0.8	40.1	136
	C	94–150	2.60	1.49	pc	42.7	0.8	41.9	234
P2'	Ap	0–40	2.62	1.54	c	41.1	1.2	38.3	156
	Bw	40–65	2.61	1.54	c	40.9	0.4	35.2	86
	Bw/C	65–99	2.61	1.52	c	41.9	0.8	35.5	120
	C	99–150	2.60	1.48	pc	43.1	0.8	40.1	205
P3	Ap	0–27	2.61	1.58	c	39.5	1.5	36.2	98
	B	27–80	2.62	1.54	c	41.3	0.4	33.2	176
	B/C	80–100	2.60	1.58	c	39.3	0.8	37.1	74
	C	100–150	2.62	1.48	pc	43.5	1.0	36.1	181
P3'	Ap	0–32	2.61	1.45	pc	44.5	1.5	33.2	106
	B	32–85	2.62	1.46	pc	44.4	0.4	34.2	181
	B/C	85–105	2.60	1.47	pc	43.3	0.8	34.8	70
	C	105–150	2.62	1.47	pc	44.0	1.0	35.8	161

¹ Degree of compaction: pc – poorly compacted, c – compacted, hc – heavily compacted

In Strzybnik, higher actual moisture contents were recorded for the soil without subsoiling (S1: 16.9-28.7 % v/v; S1': 15.4-28.3% v/v) (Table 3). The highest moisture content was observed for the bedrock horizon and the values were getting lower toward the surface soil horizons. Lower moisture contents and higher porosities after subsoiling were also reported by Martínez et al. (2011). In Prusy, although it is rather hard to define an unambiguous trend in the distribution of actual moisture content for the soil with and without subsoiling, bulk moisture content is usually lower in soils after subsoiling as a rule (33.2-40.1% v/v) than before (33.2-41.9 % v/v). Strausbaugh & Windes (2006) reported that subsoiling resulted in higher soil moisture contents in the subsoil horizon and deeper soil profile horizons. In 1.50-m deep soil profiles, soil water resources [mm] were higher in the soil without subsoiling.

In the field with subsoiling in Strzybnik, in the topsoil horizon at 10 cm, the soil water permeability in steady conditions after 180 minutes was $i_{st} = 1.86 \text{ m}\cdot\text{d}^{-1}$ (Fig. 1b); according to the FAO classification, this corresponds to the moderately rapid infiltration class. Water permeability was 447% higher than that for the field without subsoiling where, after 180 minutes $i_{st} = 0.34 \text{ m}\cdot\text{d}^{-1}$; this corresponds to the moderately slow infiltration class (Fig. 1a). In the subsoil horizon at 40 cm, water permeability before and after subsoiling was lower than that in the topsoil horizon (Fig. 1). After some 110 minutes, values corresponding to the moderately slow infiltration class were obtained (Fig. 1c and 1d).

Soil compaction has an effect on the crop yield, it affects the ability of plants to take root and prevents water infiltration deep down into the soil profile (Hamza et al. 2011). According to Zhao et al. (2013), within its impact zone, subsoil ploughing has a major effect on its physical properties, especially its ability to infiltrate rainwater and transform surface runoff into subsurface runoff.

In Prusy, at the sampling point P1' in the field with subsoiling in the topsoil horizon at 20 cm, steady infiltration was $i_{st} = 4.80 \text{ m}\cdot\text{d}^{-1}$ (Fig. 2b) after 140 minutes, corresponding to the rapid infiltration class.

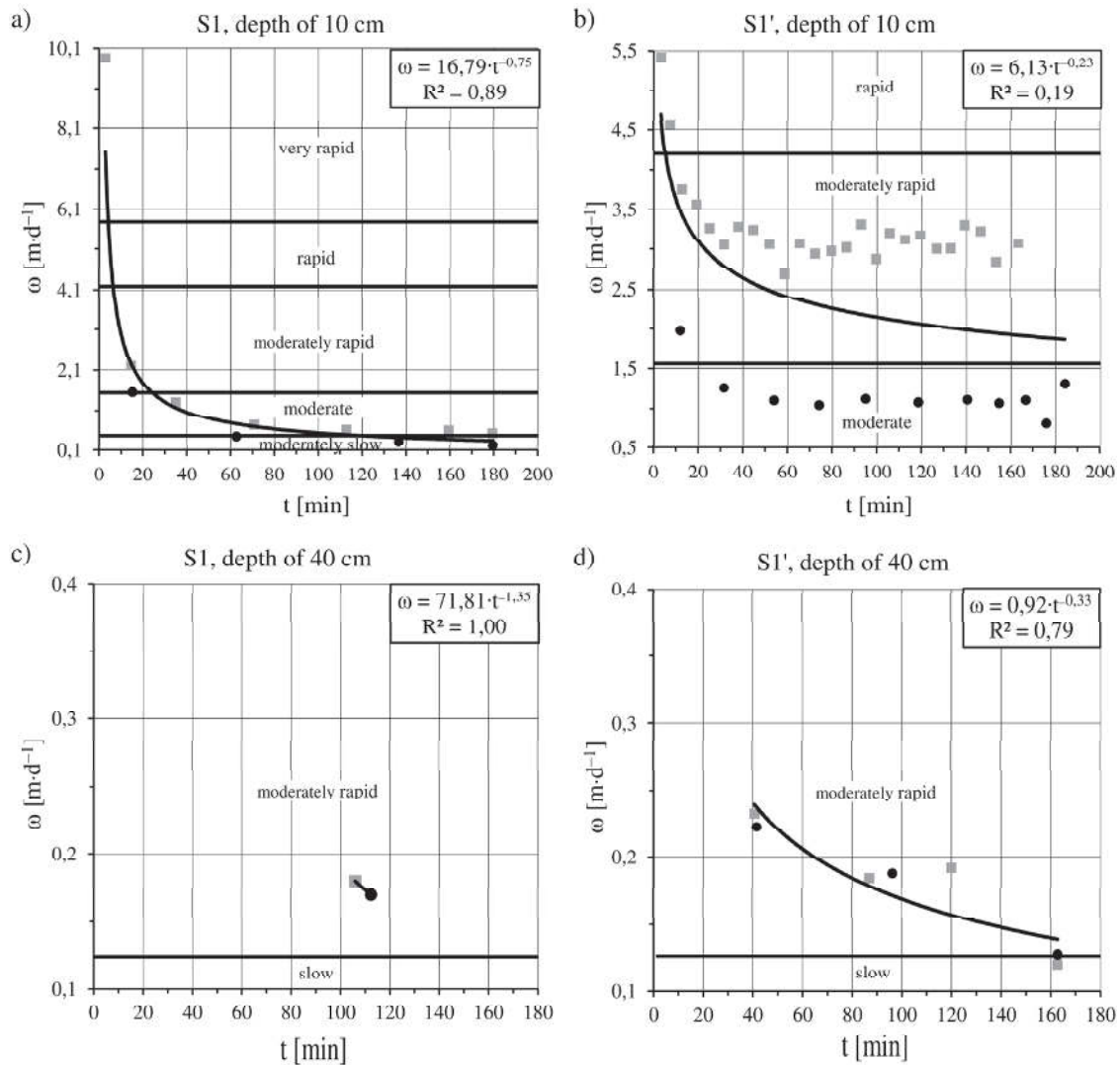


Fig. 1. Soil water permeability for the Strybnik object: a) and c) soil without subsoiling (S1), b) and d) soil with subsoiling (S1'); ● – first repetition, ■ – second repetition

Rys. 1. Przepuszczalność gleb na obiekcie Strybnik:

a) i c) gleba nie głęboszowana (S1), b) i d) gleba głęboszowana (S1');

● – pierwsze powtórzenie, ■ – drugie powtórzenie

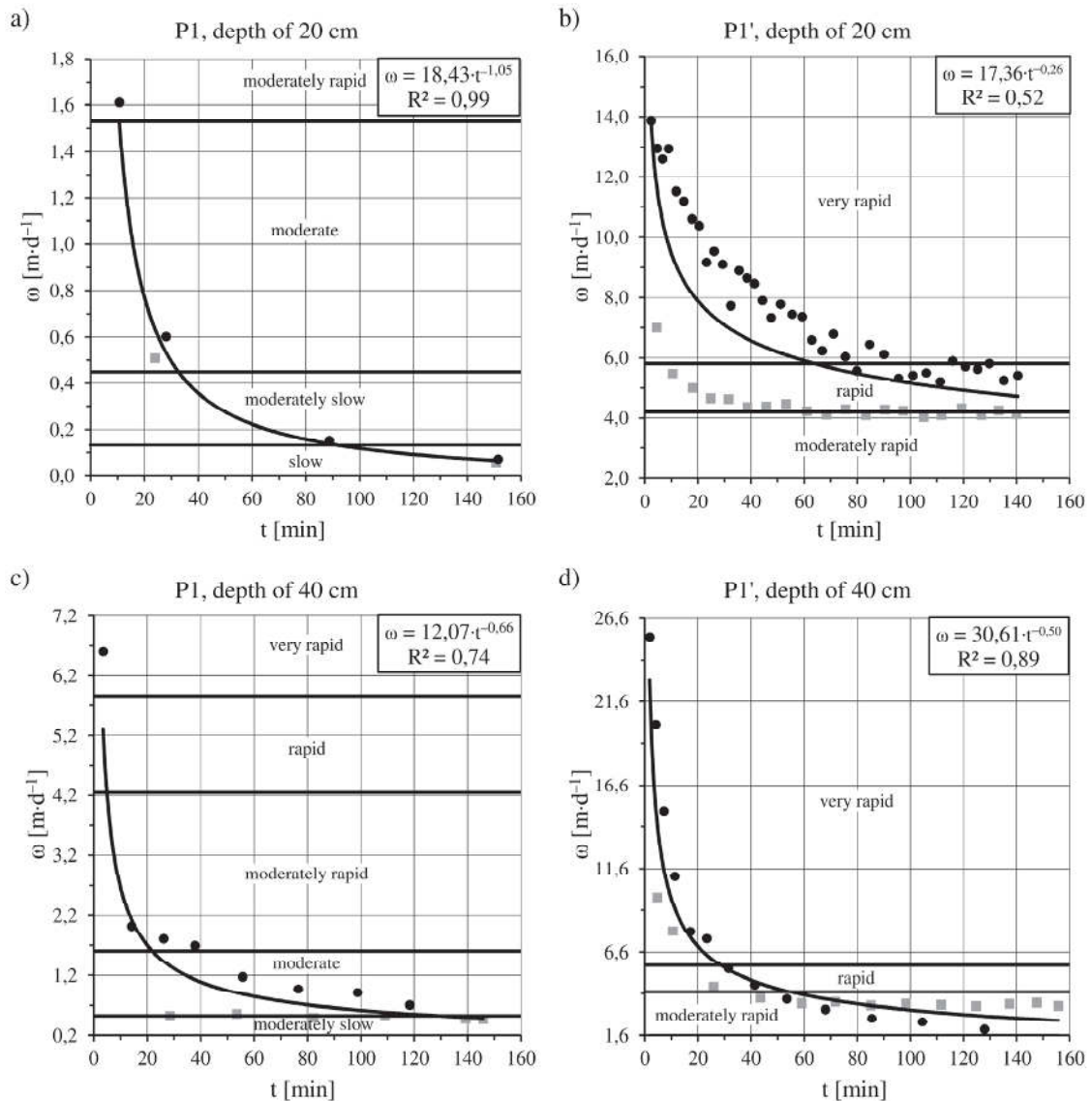


Fig. 2. Soil water permeability for the Prusy object: a) and c) soil without subsoiling (P1), b) and d) soil with subsoiling (P1'); ● – first repetition, ■ – second repetition

Rys. 2. Przepuszczalność gleb na obiekcie Prusy: a) i c) gleba nie głęboszowana (P1), b) i d) gleba głęboszowana (P1'); ● – pierwsze powtórzenie, ■ – drugie powtórzenie

The value was 48 times as high as that for the soil without subsoiling (P1), where infiltration after 150 minutes was about $0.10 \text{ m}\cdot\text{d}^{-1}$ (Fig. 2a), corresponding to the low infiltration class. In the subsoil horizon at 40 cm, steady infiltration after 150 minutes was 443% higher than that for the field with subsoiling ($i_{\text{st}} = 2.50 \text{ m}\cdot\text{d}^{-1}$), in comparison with that without subsoiling ($i_{\text{st}} = 0.46 \text{ m}\cdot\text{d}^{-1}$) and corresponded to the moderately rapid and moderately slow infiltration classes, respectively (Fig. 2c and 2d). The subsoil horizon of the soil without subsoiling showed 4.6-times as high infiltration capacities as the topsoil horizon; this is attributable to the presence in the horizon of earthworms (*Lumbricus terrestris*), which loosen and break up the soil by making canals in it (Mossadeghi-Björklunda et al. 2016). The subsoiling resulted in improved infiltration of the topsoil and subsoil horizons.

At the sampling point P2 in the field without subsoiling, in the topsoil horizon, steady infiltration after 110 minutes was $1.15 \text{ m}\cdot\text{d}^{-1}$, corresponding to the moderate infiltration class (Fig. 3a) according to the FAO classification. At P2' after subsoiling, in the same horizon, infiltration increased by 139% (Fig. 3b) and measurement time was as long as 160 minutes; this resulted in a steady infiltration of $2.75 \text{ m}\cdot\text{d}^{-1}$ and changed the infiltration class from moderate to moderately rapid. In the field without subsoiling, at P2, in the subsoil horizon, the value of steady infiltration after 100 minutes was $3.37 \text{ m}\cdot\text{d}^{-1}$, corresponding to the moderately rapid infiltration class (Fig. 3c). After subsoiling, infiltration which stabilized after some 160 minutes, was lower ($i_{\text{st}} = 1.90 \text{ m}\cdot\text{d}^{-1}$) than that recorded before subsoiling – this qualifies the soil infiltration capacity to the moderately rapid class (Fig. 3d).

In Prusy, before subsoiling, at the sampling point P3 at 15 cm, steady infiltration was $0.15 \text{ m}\cdot\text{d}^{-1}$ after 120 minutes, corresponding to the moderately slow infiltration class (Fig. 4a). After subsoiling, in steady conditions after 140 minutes infiltration was nearly 8 times as high, namely $i_{\text{st}} = 1.14 \text{ m}\cdot\text{d}^{-1}$, satisfying requirements for the moderate infiltration class (Fig. 4b). In the subsoil horizon without subsoiling, at 40 cm, after 120 minutes, steady infiltration was $1.72 \text{ m}\cdot\text{d}^{-1}$, which is higher than for the topsoil horizon (Fig. 4c and 4a); this classifies the soil water permeability as moderately rapid. However, that value of steady infiltration was clearly lower (by 338%) than that in the soil with subsoiling – $7.55 \text{ m}\cdot\text{d}^{-1}$ after 140 minutes, which corresponds to the very rapid water infiltration class (Fig. 4d).

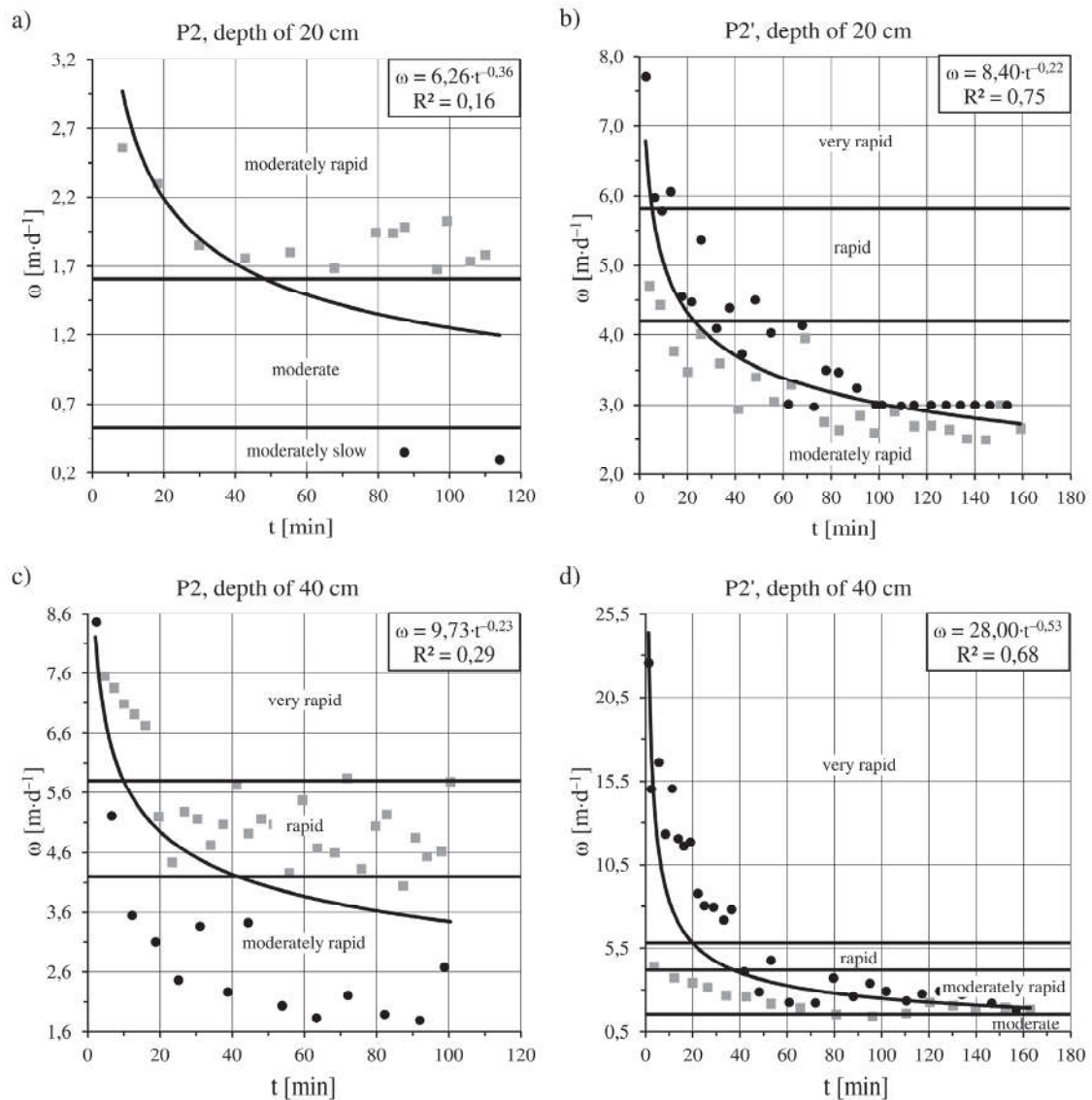


Fig. 3. Soil water permeability for the Prusy object: a) and c) soil without subsoiling (P2), b) and d) soil with subsoiling (P2'); ● – first repetition, ■ – second repetition

Rys. 3. Przepuszczalność gleb na obiekcie Prusy: a) i c) gleba nie głęboszowana (P2), b) i d) gleba głęboszowana (P2'); ● – pierwsze powtórzenie, ■ – drugie powtórzenie

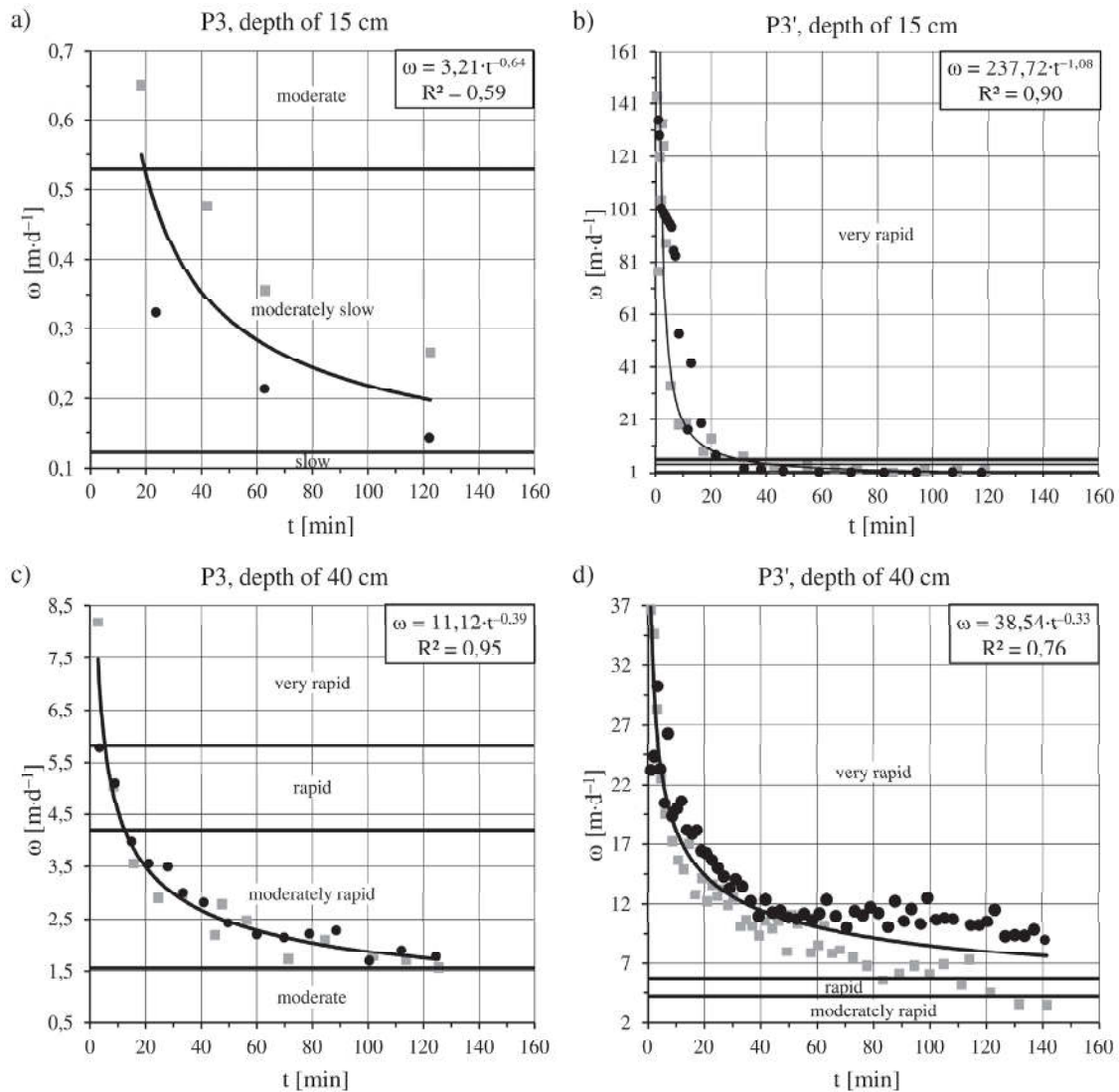


Fig. 4. Soil water permeability for the Prusy object: a) and c) soil without subsoiling (P3), b) and d) soil with subsoiling (P3'); ● – first repetition, ■ – second repetition

Rys. 4. Przepuszczalność gleb na obiekcie Prusy: a) i c) gleba nie głęboszowana (P3), b) i d) gleba głęboszowana (P3'); ● – pierwsze powtórzenie, ■ – drugie powtórzenie

In silt loam, the topsoil bulk density was statistically significantly lower ($P = 0.003$) after subsoiling than before subsoiling. Similarly in subsoil, despite a small difference in mean values, bulk density was statistically significantly lower after subsoiling: $P = 0.022$ (Table 4). This is confirmed in the report of Borghei et al. (2008) whose findings show that subsoiling as a soil improvement technique resulted in a significant decrease in the value of bulk density.

Table 4. Essential descriptive statistics of selected physical and water properties of soils without (BS) and with (AS) subsoiling and the Mann-Whitney U test results

Tabela 4. Podstawowe statystyki opisowe niektórych właściwości fizyko-wodnych gleb oraz wyniki testu U Manna-Whitneya

Statistical parameters:		x_{\min}	x_{\max}	n	x	Me	SD	CV [%]	Probability (P) in the Mann-Whitney U test
Soil bulk density [$\text{g}\cdot\text{cm}^{-3}$]									
Silt loam (SiL)	topsoil (BS)	1.51	1.63	18	1.56	1.56	0.036	2.3	0.003 ¹
	topsoil (AS)	1.43	1.58	18	1.51	1.51	0.051	3.4	
	subsoil (BS)	1.52	1.70	15	1.57	1.55	0.054	3.5	0.022 ¹
	subsoil (AS)	1.42	1.61	15	1.51	1.49	0.056	3.7	
Infiltration of water [$\text{m}\cdot\text{d}^{-1}$]									
Silt loam (SiL)	topsoil (BS)	0.09	1.73	8	0.41	0.23	0.307	128.1	0.002 ¹
	topsoil (AS)	1.00	5.42	8	2.80	2.83	2.170	49.2	
	subsoil (BS)	0.12	5.79	8	1.64	1.12	3.624	108.4	0.189
	subsoil (AS)	0.16	9.01	8	2.77	1.90	7.752	93.9	

¹statistically significant differences ($P < 0.05$) for the level of significance $\alpha = 0.05$

After the application of subsoiling in silt loams, steady infiltration for the topsoil was statistically significantly higher than that for the soils treated by conventional techniques only (Table 4). Also in the subsoil horizons, permeability was improved by subsoiling, on average, from 1.64 to 2.77 $\text{m}\cdot\text{d}^{-1}$, although the difference appeared to be statistically

insignificant for the assumed level of significance, $\alpha = 0.05$. The variability of steady infiltration values was high ($CV > 100\%$) for the soils without subsoiling and moderate for those with subsoiling (Table 4).

Drewry et al. (2000) report that subsoiling loosens and breaks up the topsoil, thus improving its porosity and hydraulic conductivity. Abu-hamdeh (2003) found that subsoil ploughing reduced the degree of soil compaction, which was reflected in lower bulk densities. Botta et al. (2006) report that the desirable effect of subsoil ploughing is noticeable for a maximum of 2 years, whereas Drewry et al. (2000) report a time limit of 2.5 years after subsoiling.

3. Conclusion

The assessment of the efficacy of subsoil ploughing of heavy soils indicates a statistically significant decrease in bulk densities for the topsoil and subsoil as well as an increase in steady infiltration for the two horizons, although it is statistically significant for the topsoil only. Improving the topsoil water permeability is expected to help control surface runoff and erosion. Therefore, the use of subsoiling in heavy, compacted arable land is justified, as it may be sufficient for improving its air-water conditions if the soil water resources are slightly lower or higher than necessary, without resorting to technical methods of soil improvement.

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Wpływ głęboszowania na zmiany zagęszczenia i przepuszczalność gleb pyłowo-ilastych

Streszczenie

Gleba jako naturalne środowisko rozwoju roślin w około 95% odpowiada za produkcję żywności. Około 33% światowego areału gleb jest średnio lub silnie zdegradowanych. Jedną z istotnych przyczyn degradacji gleb jest jej nadmierne zagęszczenie powodowane przez mechanizację prac polowych. Ograniczaniu zagęszczania gleb sprzyjają zabiegi agromelioracyjne – w tym głębokie spulchnianie, tzw. głęboszowanie – które wpływa na optymalizację warunków powietrzno-wodnych w glebie oraz na wzrost plonu roślin. W pracy oceniono wpływ zabiegu głęboszowania na zmiany zagęszczenia i przepuszczalności wodnej gleb pyłowo-ilastych. Badania prowadzono na gruntach ornych dwóch obiektów rolniczych położonych w powiecie raciborskim i powiecie krakowskim. W pracy wykazano, że zabieg głębokiego spulchniania spowodował statystycznie istotne zmniejszenie gęstości objętościowej (zagęszczenia) gleb zwięzłych w warstwach ornych i podornych oraz zwiększenie infiltracji ustalonej, które tylko w warstwie ornej okazało się statystycznie istotne. Uzyskane wyniki badań potwierdzają, że głęboszowanie zagęszczonych zwięzłych gleb uprawnych jest uzasadnione, ponieważ w przypadku wystąpienia niewielkich niedoborów lub nadmiarów wody w glebie może okazać się zabiegiem wystarczającym do uregulowania stosunków powietrzno-wodnych, bez konieczności wykonywania kosztownych melioracji technicznych. Ponadto, zwiększenie porowatości oraz wodoprzepuszczalności gleby powinno zmniejszać spływy powierzchniowe i tym samym ograniczyć zjawiska erozyjne.

Abstract

Soil, as the top layer of the Earth's surface, is a natural medium for the growth of plants. It is estimated that 95% of global food comes from our soils so we depend on the soil. About 33% of global soil is moderately to highly degraded. Soil compaction, caused by the mechanization of field treatments, is one of the major problems in agriculture nowadays. Subsoiling is one of the ways to reduce soil compaction and improve the air-water properties of arable soils. An assessment of the effect of subsoiling on the degree of compaction and water permeability of silt loam is presented in this paper. Soil tests were carried out in arable land, situated in the Racibórz and Kraków districts in the south of Poland. The results of the research show positive effects of subsoiling on the air-water relationship in the soil. In the majority of profiles, an increase in the percentage of total porosity in the first and second genetic horizons of the subsoiled soil was observed. The assessment of the efficacy of the subsoiling of heavy soils indicates a statistically significant decrease in bulk density for the topsoil and subsoil and a significant increase in steady infiltration only in the topsoil. The results show that subsoiling of arable compacted soils is justified, because in the case of slight deficiencies or excess water in the soil it may be a sufficient treatment to regulate air and water relationship, without the need for costly technical drainage. In addition, increasing the porosity and water permeability of soil should reduce surface runoff and thus reduce the phenomenon of erosion.

Słowa kluczowe:

zagęszczenie gleb, głęboszowanie, przepuszczalność gleb

Keywords:

soil compaction, subsoiling, soil water permeability



Effect of Dry Ice Modification of Excess Sludge on the Methane Fermentation Process

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1. Introduction

The essence of the methane fermentation process is its phase course. The efficiency of the process is determined by the rate of reactions taking place during the hydrolysis phase, occurring during the first days of the process. As a result of hydrolytic changes, the concentration of volatile fatty acids (VFAs) increases and correlates with it the increase in dissolved chemical oxygen demand (SCOD) and total organic carbon (TOC). Excess sludge, which are an important substrate for the methane fermentation process carried out in isolated closed fermentation chambers of sewage treatment plants, show limited susceptibility to the biochemical degradation process under anaerobic conditions. Excess sludge is an activated sludge isolated in secondary settling tanks. Excess sludge form clusters of microorganisms occurring in the form of flocks. In excess sludge live and dead organisms as well as spore forms can be observed. This sludge is characterized by a significant content of organic matter at the level of 65-75% of volatile suspended solids (VSS) (Wolski & Wolny 2011).

On the basis of our own research and literature reports, the application of thermal disintegration with dry ice as a method supporting the anaerobic stabilization process is a promising technological solution contributing to both sludge hygienization, reduction of sludge mass through the process of evaporation as well as intensification of the hydrolysis phase, phase determining the efficiency of methane fermentation (Nowicka et al. 2014, Grübel et al. 2013, Chen et al. 2014, Gao 2011).

The purpose of heat treatment of excess sludge is to facilitate biodegradation of organic substances contained in modified sludge (Elliott & Mahmood 2007, Wang 2009). Thermal disintegration acts supportively to the anaerobic stabilization process. The essence of thermal modification is the supply or removal of thermal energy to sludge, which determines the change of their structure and affects the increase in the value of indicators such as soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), as well as total organic carbon (TOC) (Stier & Fischer 1998, Zawieja & Wolski 2012). According to the literature data (Stier & Fischer 1998, Zawieja & Wolski 2012, Zawieja 2010) and the conducted own research, the effect of thermal disintegration of sludge depends not only on the temperature used, but also the processing time.

Dry ice is a natural product that does not cause secondary contamination of thermally modified sludge with its use. The property of dry ice is sublimation, i.e. the transition from the solid phase to the gas phase, omitting the liquid phase. Dry ice is carbon dioxide in the solid phase, produced, among others, in the form of granulate. Freezing point for CO₂ is -78.5°C. The sublimation temperature of dry ice is -78.5°C at 1013 hPa. Dry ice has no taste or smell, has bacteriostatic properties and removes oxygen from the surrounding air. Other important features of dry ice decisive for its wide application: it is a natural product, environmentally friendly, sublimates in a gas with no residue, has a high cooling efficiency, is non-flammable, is non-toxic (http://www.prokontech.pl/suchy_lod.html, Hu et al. 2011).

As reported Lygonie et al. (Leygonie et al. 2012) as a result of thermal modification of sludge with the use of dry ice, denaturation of microbial cells with a mechanical foundation takes place. The essence of the disintegrating effect of dry ice on sludge is the crystallization process occurring both in the case of sludge particles as well as microbial cells. This process leads to the loss of hydration water of proteins, that are a significant component of the cell walls of microorganisms and consequently the release of intracellular substances into the supernatant.

Mechanical damage to microbial cells and the occurring osmotic shock are responsible for the inactivation of excess sludge microorganisms following the destruction of biomembranes. The formation of crystals both inside the cells of microorganisms and in the environment surrounding them is responsible for the phenomenon of the release of intra-

cellular substances into the supernatant liquid (Thammavongsa et al. 2004, Nowicka & Machnicka 2013).

According to El – Kest and Marth (El – Kest & Marth 1992) with the rapid temperature reduction, microorganisms undergo the so-called "thermal shock". Frozen cells can be damaged mechanically. The formation of intra- and extra-cellular ice crystals causes mechanical damage to frozen cells of microorganisms. The effect of the freezing process is the increase in the concentration of dissolved cells, which can lead to the dissociation of cellular lipoproteins. On the other hand, the gradual heating of frozen cells increases the size of the ice crystals formed. The use of thermal disintegration, i.e. rapid freezing and gradual thawing, causes an increase in fastidiousness and changes in cellular morphology, as well as denaturation of macromolecules.

"Thermal shock" (a cold shock) is an effective method of cell damage caused by lowering the temperature. As reported Strange et al. (Strange et al. 1962) deactivation of microorganisms is the result of a rapid and not a gradual and slow change in the temperature value.

Freezing/thawing of excess sludge with dry ice affects the initiation of the lysis of microbial cells, resulting in an increase in the concentration of organic substances in dissolved form. With regard to mechanical or chemical methods of disintegration, thermal processes do not cause secondary sludge contamination, while with respect to mechanical methods, freezing/thawing of sludge does not require additional energy expenditure.

The process of freezing is dependent on the compartment nature of a microorganisms cellular system. Nucleation and growth of ice crystals in cells is conditioned by differences in water activity, nucleation sites, viscosity, membrane permeability, and other factors. As reported El – Kest and Marth (El – Kest & Marth 1992) most of enzymatically catalyzed reactions occur in living cells and to be effective, they must occur at the right temperature. Therefore a decrease in temperature is almost certain to disturb the balance and so modify cell function .

The aim of the study was to determine the effect of dry ice disintegration on the susceptibility of excess sludge to biodegradation. Studies have shown that thermal disintegration of excess sludge based on rapid freezing with dry ice, followed by gradual thawing at ambient temperature, compared to conventional methane fermentation, increases SCOD and TOC, as well as VFAs. Changes in the value of the indicators exam-

ined were recorded both at the stage of disintegration and during subsequent days of methane fermentation.

2. Experimental part

2.1. Substrate

Excess sludge, where the main substrate using during the research was sampled from the Central Wastewater Treatment Plant P.S.W. "Warta" in Czestochowa. Sludge was taken immediately before mechanical thickening. It is a mechanical and biological treatment plant with increased nutrients removal with a capacity of 90,000 m³/d, 314 835 PE. Table 1 shows the main physico-chemical characteristics of the excess sludge used during the research.

Tabela 1. Fizyczno-chemiczne wskaźniki osadów nadmiernych
Table 1. Physico-chemical indicators of excess sludge

Indicators	Excess sludge
Total Solids (TS)	16.32 g L ⁻¹
Volatile Solubled Solids (VSS)	12.68 g L ⁻¹
Chemical Oxygen Demand (COD)	110 mg O ₂ L ⁻¹
Volatile Fatty Acids (VFAs)	65 mg CH ₃ COOH L ⁻¹
Alkalinity	320 mg CaCO ₃ L ⁻¹
pH	7.04 g L ⁻¹
Kjeldahl Nitrogen	41 mg N L ⁻¹
Ammonium Nitrogen	27 mg N-NH ⁺ L ⁻¹
Total Organic Carbon (TOC)	26 mg C L ⁻¹

2.2. Methodology

In the study the following physico-chemical indicators were made: pH (PN-9/C-04540/05), the volatile suspended solids (VSS) (PN-EN-12879), volatile fatty acids (VFAs) by steam distillation (PN-75/C-04616/04), alkalinity (PN-91 C-04540/05), soluble chemical oxygen demand (SCOD) by dichromate method, using a colorimetric spectrophotometer Hach Dr 400 (PN-EN ISO 7027), Kjeldahl nitrogen (PN-73/C-04576/10), ammonium nitrogen (PN-73/C-04576/02), as well as total organic carbon (TOC) by spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena).

In the case of thermal modification used reagent i.e. dry ice, which is carbon dioxide in the solid phase. Dry ice, present in a granular form with a grain diameter of 0.6 mm, was mixed with excess sludge in a volume ratio of 0.05:1, 0.1:1, 0.15:1, 0.25: 1, 0.35:1, 0.5:1 and 0.75:1, respectively. Disintegration was carried out at ambient temperature. The time of the modification phases, i.e. freezing and defrosting, was determined by the size of the reagent dose and was increased with increasing it. For the doses of reagent used it ranged from 3 to 12 hours.

The disintegration degree was estimated according to the formula 1. The sludge was conditioned by means of 1-mol solution of NaOH for 10 min., at the temperature of 90°C, with unchanged volumetric proportion of the sludge and the solution (1:1). The SCOD of chemically modified excess sludge, which is the reference value for determining of the disintegration degree, was equal 2912 mg O₂ L⁻¹.

The degree of disintegration was estimated according the following formula (Tiehm et al. 2001):

$$DD_{\text{COD}} = (\text{SCOD}_1 - \text{SCOD}_2) / (\text{SCOD}_3 - \text{SCOD}_2) \cdot 100 \quad (1)$$

where:

DD_{COD} – disintegration degree, %,

SCOD₁ – SCOD level in the pretreatment sludge, mg O₂/l,

SCOD₂ – SCOD level in the non pretreatment sludge, mg O₂/l,

SCOD₃ – SCOD level in the sludge conditioned chemically 1-mol NaOH with ratio 1:1, temp. 90°C for 10 minutes, mg O₂/l.

In order to verify the effectiveness of the chosen disintegration method the sludge was subjected to eight-day anaerobic stabilization under the mesophilic condition. The process was periodic. Methane fermentation was subjected to non-processed excess sludge and thermally modified sludge using dry ice. A mixture consisting of 90% of excess sludge and 10% of digested sludge, serving as *inoculum* was prepared. The process of methane fermentation was carried out in eight models of fermentation chambers, placed in mesophilic conditions in temperature of 37°C in a laboratory thermostat. The mixture of excess sludge and digested sludge was placed in laboratory flasks with an active volume of 0.5 L, air-protected glass stopper with a manometric tube allowing the outflow of biogas produced. The contents of the flasks were mixed using mag-

netic stirrers, ensuring a continuous mixing throughout the day, preventing the formation of the skin and preventing the creation of areas overloaded with pollutants. The following mixtures of sludge i.e. excess sludge and digested sludge were subjected to anaerobic stabilization: Mixture I - non-prepared excess sludge + fermented sludge; (2) Mixture II - thermal pretreatment excess sludge with the reactant's dose equal in a volume ratio of dry ice to excess sludge 0.35/1 + digested sludge.

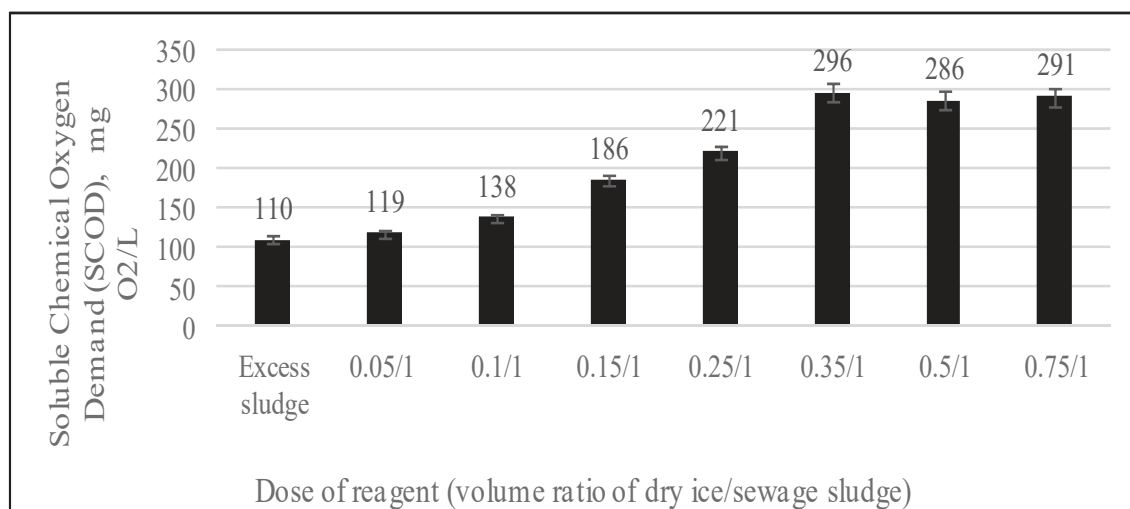
At this stage of the research, the course of the first days of methane fermentation was analyzed. Considering the phase limiting the hydrolysis proses, which is the first of the methane fermentation phases, the most favorable disintegration conditions were selected on the basis of the obtained values of the physico-chemical indicators. The selection made is the basis for conducting further research and in the next stage of optimization of biogas production.

3. Results and discussion

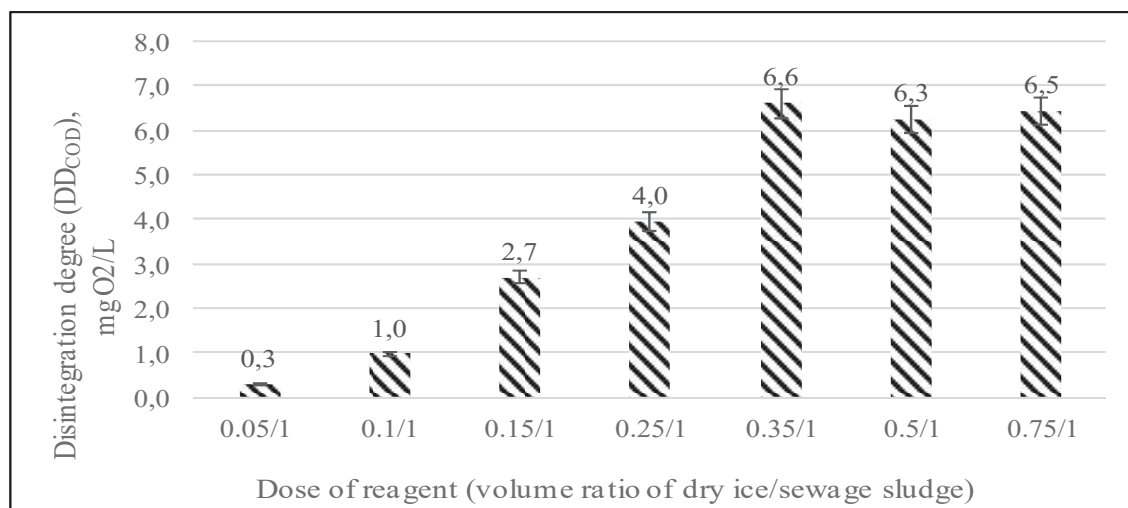
Subjecting the tested sludge to thermal modification using dry ice affect on the increase of organic compounds concentration in dissolved form, which was confirmed by the increase in the degree of disintegration of the prepared sludge. The increase of the disintegration degree of the modified dry ice excess sludge during the research conducted by Nowicka et al. and Chen et. al. (Nowicka et al. 2016, Chen et. al. 2014) was noted.

In order to assess the effectiveness of the dry ice disintegration process, the value of selected indicators was evaluated, which is a direct expression of the increased susceptibility of the prepared excess sludge to biodegradation. Pretreatment carried out using selected doses of reagent received a significant increase in the sludge disintegration, value of SCOD and TOC. With increasing degree of disintegration, an increase in the concentration of VFAs was observed, which confirms initiation already at the stage of modification of the hydrolysis process of organic substances bound intracellularly to soluble forms.

Figures 1-4 show the changes in the value of selected indicators of excess sludge during freezing with selected doses reagent i.e. in a volume ratio of dry ice to excess sludge equal 0.05:1, 0.1:1, 0.15:1, 0.25:1, 0.35:1, 0.5:1 and 0.75:1.



Rys. 1. Zmiany wartości chemicznego zapotrzebowania na tlen substancji rozpuszczonych w cieczy nadosadowej osadów kondycjonowanych suchym lodem
Fig. 1. Changes of soluble chemical oxygen demand (SCOD) values of pretreatment excess sludge with dry ice

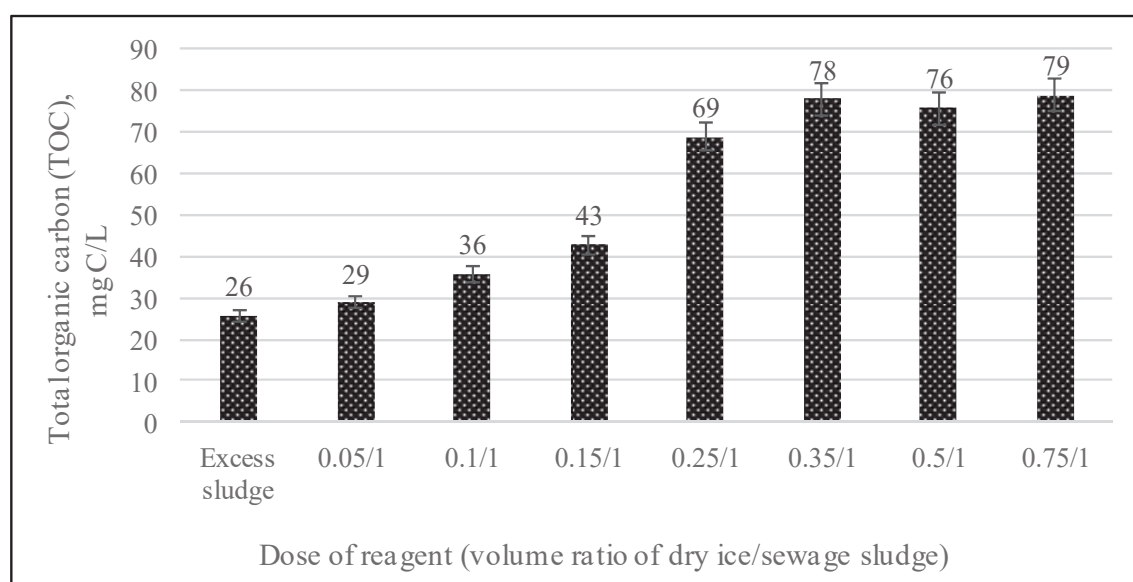


Rys. 2. Wpływ dawki suchego lodu na stopień dezintegracji (DD_{COD}) osadów nadmiernych w procesie wymrażania
Fig. 2. Effect of dry ice dose on the degree of disintegration (DD_{COD}) of excess sludge in the freezing process

According to the literature data (Kanh et al 1999), SCOD is one of the basic quality parameters of sewage sludge. With increasing the dose of the reagent, for the excess sludge subjected to modification in a volume ratio of dry ice to excess sludge in the range 0.05:1-0.35/1, a gradual increase in SCOD and a correlation of the increase in the sludge disintegration degree was noted (Fig. 1, 2). The linear correlation coefficient of the

dry ice dose dependence on the obtained SCOD value is 0.86. However, for the sludge modification of the reagent in a volume ratio of dry ice to sludge of 0.35/1, 0.5/1 and 0.75/1 did not show any significant increase in the value of the analyzed indicators. For the reagent doses mentioned above, a SCOD values of 298, 286, 291 and a degree of disintegration of 6.6, 6.3, 6.5 respectively were observed.

Determination of the effectiveness of disintegration of excess sludge by dry ice with total organic carbon (TOC) fully reflects the actual content of organic matter in the supernatant (Janiga & Michniewicz 2013), what was shown on the Fig. 3.

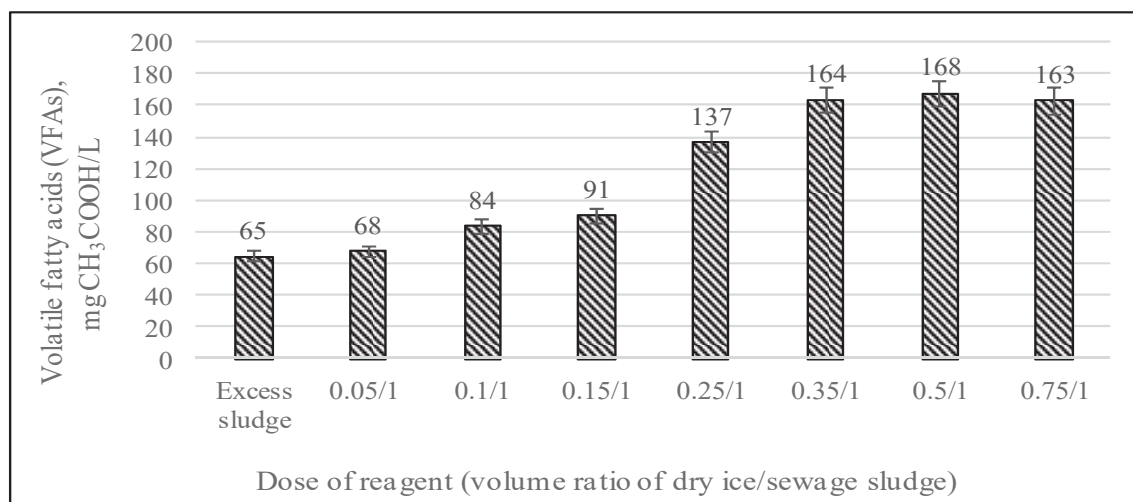


Rys. 3. Zmiany wartości ogólnego węgla organicznego (OWO) kondycjonowanych suchym lodem osadów nadmiernych

Fig. 3. Changes of total organic carbon (TOC) value of freezing excess sludge

There was a gradual increase in the TOC value. However, for doses of dry ice to sludge of 0.35/1, 0.5/1 and 0.75/1 the increase in the value of the indicator was similar.

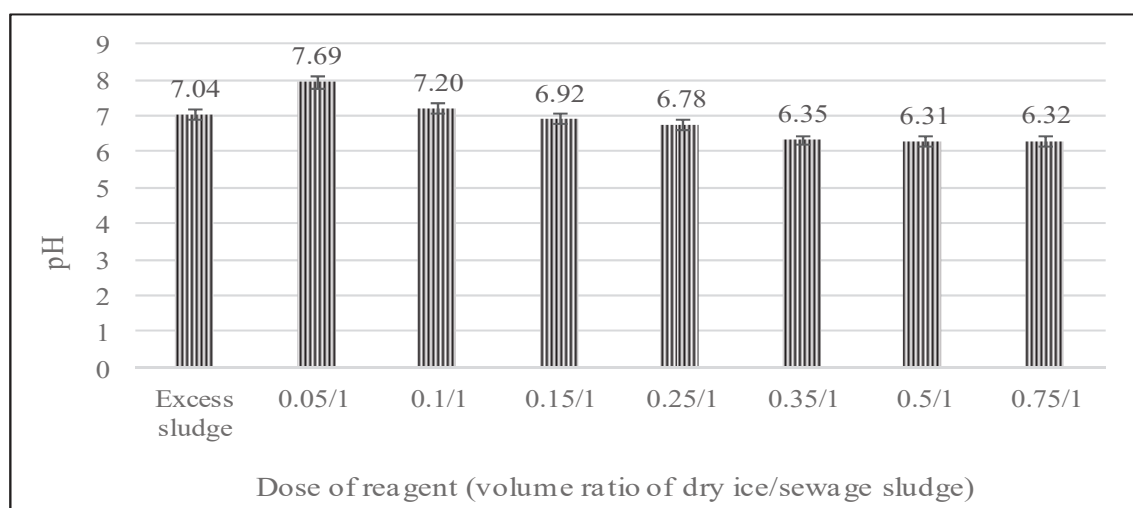
According to Hu et al. (Hu et al. 2011) in the case of sludge disintegration using freezing and thawing to the sludge supernatant of extracellular polymers are released. There was a correlation of the obtained TOC values with the SCOD values. In addition, a correlation coefficient of 0.84 was obtained for the dependence of the linear dose of dry ice on the obtained TOC value.



Rys. 4. Zmiany stężenia lotnych kwasów tłuszczowych (LKT) kondycjonowanych suchym lodem osadów nadmiernych

Fig. 4. Changes of the volatile fatty acids (VFAs) concentration of freezing excess sludge

The same tendency of gradual value increase along with an increase in the reagent dose was noted for the VFAs concentration. Changes in the VFAs concentration are indicative of lysing processes already taking place at the stage of modification and a correlation coefficient of 0.85 was obtained for the dependence of the linear dose of dry ice on the obtained VFAs value.



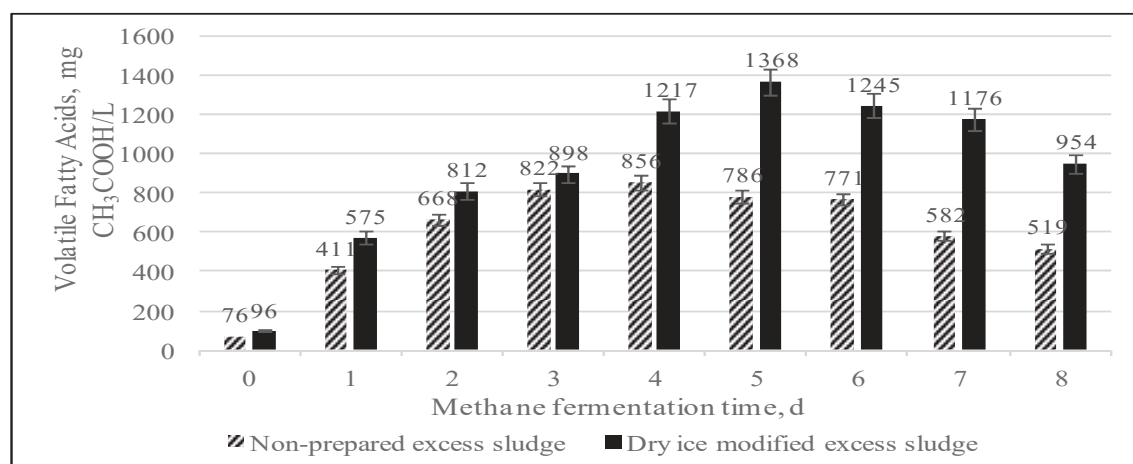
Rys. 5. Zmiany wartości pH kondycjonowanych suchym lodem osadów nadmiernych

Fig. 5. Changes of pH values of freezing excess sludge

During the disintegration of excess sludge, a gradual decrease in the pH value was noted with the increase of the reagent dose, which is conditioned by the acidifying nature of the dry ice action. The linear correlation coefficient of the dry ice dose dependence on the obtained pH value is 0.84.

As a result of the thermal modification of the sludge and the values of selected indicators such as SCOD, DD, TOC, and VFAs carried out at this stage, the most favourable modification conditions were selected. For the best dose in terms of the proposed technological solution, for further research, the dose of dry ice to the sludge was estimated to be 0.35 /1, respectively.

Figures 6, 7 and 8 show changes in the VFAs, SCOD and TOC values determined for dry ice modified excess sludge at a dose of 0.35/1, respectively, of the reactant to sludge.

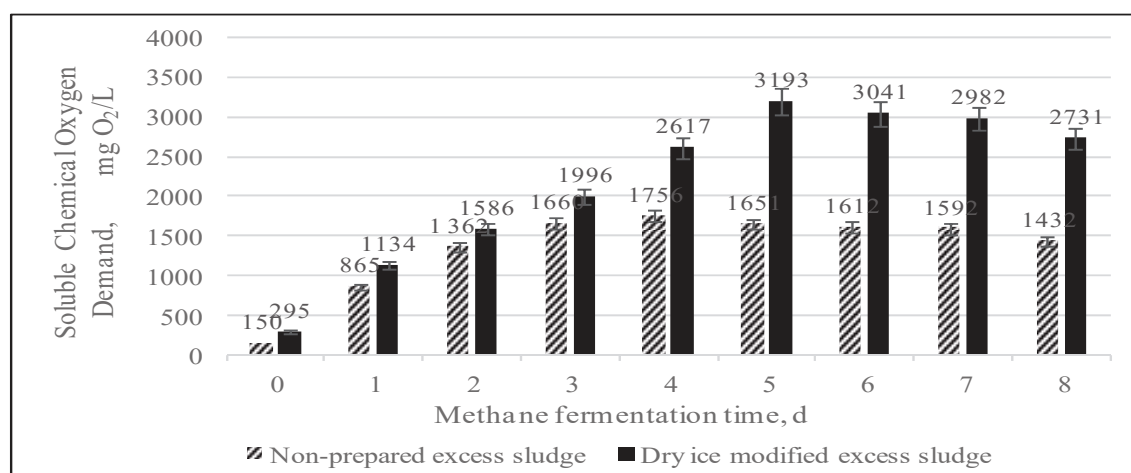


Rys. 6. Zmiany stężenia lotnych kwasów tłuszczowych (LKT) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych

Fig. 6. Changes of volatile fatty acids (VFAs) concentration during methane fermentation of non-prepared and dry ice modified excess sludge

During the methane fermentation process of modified excess sludge, in relation to the process of non-prepared sludge, intensification of the hydrolysis process was noted, the phases as reported by literature sources (Tiehm 2001, Kim 2003, Wolski & Małkowski 2014, Wolski 2016). and confirm own studies limiting anaerobic stabilization. For sludge subjected to disintegration with dry ice in the following days of the fermentation process, a gradual increase in the concentration of VFAs

was noted. The highest value of the indicator equal 1368 mg $\text{CH}_3\text{COOH/L}$ was obtained on the 5th day of the process, observing a gradual decrease in concentration in the next days. For non-prepared excess sludge, maximum VFAs concentration of 856 mg $\text{CH}_3\text{COOH/L}$ was recorded on 4th day of the process.



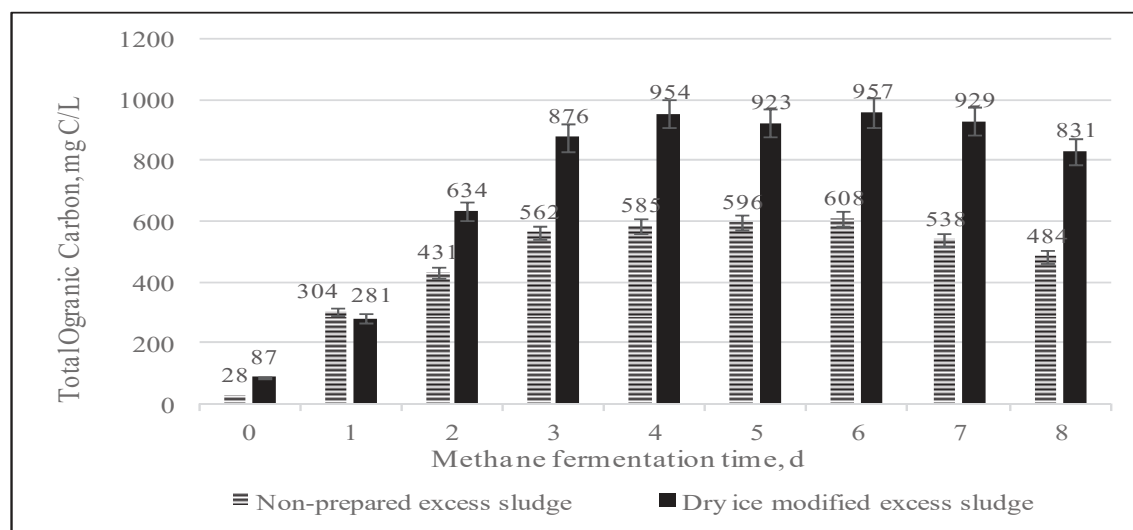
Rys. 7. Zmiany wartości rozpuszczonego chemicznego zapotrzebowania na tlen (ChZT) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych

Fig. 7. Changes of soluble chemical oxygen demand (SCOD) values during methane fermentation of non-prepared and dry ice modified excess sludge

A similar tendency of a gradual increase in value was noted in the case of the SCOD for both unprocessed and thermally modified sludge. The highest value of the SCOD equal 3193 mg O_2/L was obtained on the 5th day of the process, observing a gradual decrease of the value in the next days. For non-prepared excess sludge, maximum SCOD value of 1756 mg O_2/L was recorded on 4th day of the process. There was a close correlation between the changes in the SCOD value in relation to the VFAs concentration in subsequent days of methane fermentation.

Values of SCOD can be influenced of organic nitrogen compounds or reducing inorganic compounds. These compounds may influence on an increased demand for oxygen. Therefore the strictly defined parameter defining the content of organic substances of sludge is the total organic carbon (TOC). For sludge subjected to disintegration with dry ice in the following days of the fermentation process, a gradual increase of TOC value was noted. The highest value of the indicator equal 954 mg C/L was

obtained on the 4th day of the process, observing a gradual value decrease in the next days. For non-prepared excess sludge, maximum TOC value of 608 mg C/L was recorded during the 6th day of the process.



Rys. 8. Zmiany wartości ogólnego węgla organicznego (OWO) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych

Fig. 8. Changes of total organic carbon (TOC) values during methane fermentation of non-prepared and dry ice modified excess sludge

4. Summary and conclusions

According to the aim of the study the comparison of methane fermentation efficiency of thermal modified excess sludge using dry ice, as well as non-prepared excess sludge was made. The conducted research has shown an increase in the susceptibility of prepared excess sludge to biochemical degradation under anaerobic conditions. Already at the modification stage, the initiation of hydrolysing processes was noted, which resulted in an increase in the value of the analyzed indicators such as: solubled chemical oxygen demand (SCOD), volatile fatty acids (VFAs), as well as total organic carbon (TOC).

Based on the obtained research results, the following conclusions were formulated:

- With increasing doses of dry ice increase of SCOD and TOC values was observed which correlated with the increase of VFAs concentration.

- In the case of mixture of dry ice and excess sludge in a volume ratio of 0.35: 1, 0.5: 1 and 0.75: 1 respectively an increase of SCOD, TOC, DD_{COD} values as well as VFAs concentration was inadequate to the dry ice dose, there was no significant increase in the indicators values.
- As a result of the dry ice modification process, the combination of dry ice and excess sludge in a volume ratio of 0.35 to 1 was considered the most favourable mixture. The choice was confirmed by the value of the disintegration degree obtained for the modified sludge equal 6.6%.
- For sludge subjected to disintegration with dry ice, using the most preferred reagent dose, in the following days of the methane fermentation process, in relation to methane fermentation of non-prepared excess sludge, increase of SCOD and TOC values as well as VFAs concentration was noted.

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Wpływ modyfikacji osadów nadmiernych suchym lodem na proces fermentacji metanowej

Streszczenie

Specyficzna podatność osadów nadmiernych na proces fermentacji metanowej jest czynnikiem ograniczającym szybkość reakcji zachodzących w kolejnych etapach procesu. Na kinetykę przemian biochemicznych podczas zachodzących samorzutnie faz fermentacji metanowej wpływa bezpośrednio wzrost stężenia rozpuszczonych substancji organicznych dostępnych dla mikroorganizmów procesu. Modyfikacja osadów nadmiernych odmiennymi metodami dezintegracji, tj. chemicznymi, fizycznymi, hybrydowymi zwiększa efektywność procesu fermentacji metanowej. Spośród wymienionych powyżej metod modyfikacji należy podkreślić zalety metod fizycznych, zwłaszcza termicznych. Oprócz istotnej modyfikacji struktury osadów nadmiernych, nie powodują one wtórnego zanieczyszczenia preparowanych osadów i stanowią obiecujące rozwiązanie technologiczne. Celem przeprowadzonych badań było określenie wpływu dezintegracji osadów nadmiernych suchym lodem na wzrost podatności na biodegradację. Lotne kwasy tłuszczowe są ważnym produktem pośrednim fermentacji metanu, a zwiększona wydajność procesu stabilizacji zależy od ich stężenia. Ponieważ procesem limitującym fermentację metanową jest faza hydrolizy, pierwszy etap stabilizacji, dokonano analizy wybranych oznaczeń fizyczno-chemicznych w ciągu pierwszych ośmiu dni procesu fermentacji modyfikowanych osadów. Okresową fermentację metanową prowadzono w warunkach mezofilowych. Stworzono mieszaniny suchego lodu i osadów nadmiernych w stosunku objętościowym reagenta do osadów w zakresie od 0,05/1 do 0,75/1. Potwierdzeniem zwiększonej podatności dezintegrowanych osadów nadmiernych na proces fermentacji metanowej był zachodzący proces lizy osadów nadmiernych wyrażony wzrostem stopnia dezintegracji. W przypadku osadów nadmiernych poddanych dezintegracji suchym lodem, przy użyciu najkorzystniejszej dawki reagenta, w kolejnych dobach procesu fermentacji metanowej, w odniesieniu do fermentacji metanowej niepreparo-

wanych osadów nadmiernych, odnotowano wzrost wartości rozpuszczonego chemicznego zapotrzebowania na tlen (ChZT), ogólnego węgla organicznego (OWO) oraz stężenia lotnych kwasów tłuszczowych (LKT).

Abstract

The specific susceptibility of excess sludge to the methane fermentation process is a limiting factor for the rate of reaction occurring in the subsequent stages of the process. The kinetics of biochemical changes during spontaneous methane fermentation phases is directly influenced by the increase in the concentration of dissolved organic substances available to microorganisms in the process. Excess sludge deposition by different disintegration methods, ie: chemical, physical, combined increases the efficiency of the methane fermentation process. Among the modifications mentioned above, the advantages of physical methods, especially of thermal nature, should be emphasized. In addition to the significant modification of the excess sludge structure, it does not cause secondary contamination of the prepared sludge and therefore is a promising technological solution. The aim of the study was to determine the effect of dry ice disintegration on the susceptibility of excess sludge to biodegradation. Volatile fatty acids are an important intermediate product in methane fermentation and increased effects of the stabilization process is conditioned by their concentration. Since the phase limiting process is the hydrolysis phase, the first stage of the fermentation, the detailed analysis was carried out in the first eight days of the process by performing physicochemical determinations of the modified sludge. Periodic fermentation was carried out under mesophilic conditions. Excess sludge was prepared with dry ice in a volume ratio of dry ice to excess sludge in range from 0.05L^{-1} to 0.75L^{-1} . Confirmation of the increased susceptibility of the prepared excess sludge to the methane fermentation process was a modification of the sludge structure expressed by the increase of the disintegration degree. For sludge subjected to disintegration with dry ice, using the most preferred reagent dose, in the following days of the methane fermentation process, in relation to methane fermentation of non-prepared excess sludge, increase of SCOD and TOC values as well as VFAs concentration was noted.

Słowa kluczowe:

osady nadmierne, fermentacja metanowa, dezintegracja, suchy lód, lotne kwasy tłuszczowe (LKT), chemiczne zapotrzebowanie na tlen (ChZT), ogólny węgiel organiczny (OWO)

Keywords:

excess sludge, methane fermentation, disintegration, dry ice, volatile fatty acids (VFAs), soluble chemical oxygen demand (SCOD), total organic carbon (TOC)



Analysis of Fish Migration Potential Through the Seminatural Fish Pass on an Example the Skórka Barrage on the Głomia River

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1. Introduction

River valleys are very valuable landscape elements that, through the formation of ecosystems, create habitats for multiple organisms (Mazur et al. 2016, Walczak et al. 2013). Negligence in their protection can lead to a decrease in the population of some species living there. It is also worth mentioning that inappropriate actions aimed to regulate rivers and facilitate water management may have similar effects (Bombač et al. 2014). For instance, a result of the construction and impoundment of a river with a hydropower plant or water barrage is the interruption of fish migration routes (Marschall et al. 2011, Szoszkiewicz et al. 2016). Facilitating fish passage in fragmented river systems has been commonly focused on commercially important migratory species (e.g. salmonids) (Norrgård et al. 2013) and concerned popular technical solutions (e.g. vertical slot fishway) (Bermúdez et al. 2010, Marriner et al. 2014). Early fishway constructions targeted only a few fish species with strong swimming abilities, such as adult salmonids (Laine et al. 2002), but recent trends are directed at making fishways available for the passage of all species in all life stages (Bunt et al. 2012). The ecosystem-based approaches to river rehabilitation have been increasingly adopted and fishways are progressively being designed for fish assemblages.

From among the various types of fishways, nature-like ones are constructed with boulders, large wooden debris, and riparian vegetation

to imitate natural environments, instead of concrete or steel, thus producing hydrodynamic and morphological properties similar to those of natural rivers (Eberstaller et al. 1998, Tymiński and Kałuża 2013). Owing to these characteristics, unlike other fishways, those that are nature-like can be used by fish species with a wide range of sizes and swimming abilities (Calles and Greenberg 2005). Best-suited for the original purpose of fishways, nature-like ones are being constructed across the world in increasing numbers (DVWK 2002, Castro-Santos et al. 2009). In Poland too, nature-like fishways have attracted increasing attention.

These fishways, in contrast to the technical fish passages, are poorer described, and they are more difficult to design and build. Especially untypical solutions make a lot of trouble. The solution is continuous monitoring of fish behaviour in fishways and systematic hydraulic measurements in fish passages (Kim et al. 2016, Kasperek and Wiatkowski 2008, Hämmerling et al. 2016). By regularly monitoring the use of a fishway after its installation, not only its attraction and passage efficiencies can be checked, but useful data for its efficient management can also be obtained to better address fish movement issues (Knaepkens et al. 2006).

The study analysed hydraulic and geometric parameters of the fish pass at the Skórka barrage on the Głomia river in the context of its possible use by aquatic organisms for migration. This study is aimed to obtain accurate data necessary for evaluating the efficiency of a untypical nature-like fishway constructed on a small, lowland river.

2. Materials and methods

2.1. Fish pass efficiency

Technical parameters of a fish pass depend not only on hydraulic conditions of the riverbed, but also on migratory fish species present in a particular river. The key parameters that have to be taken into account to allow a given species pass through to the upper area of the barrage are: flow rate and water velocity, bottom slope of the fish pass, difference in the water level between adjacent chambers, minimum width of slots between chambers, length and width of chambers, minimum water depth.

It is very important to remember that, on the one hand, a fish pass is designed having in mind the requirements for the weakest organisms, and on the other hand – the largest individuals.

2.2. Requirements of fish

In order to systematise the above recommendations guidelines for designing fish passes have been devised. They include the characterization of main species of migratory fish, limiting values of dimensions for chambers and slots, and maximum velocity values that the fish are able to exceed. Depending on the species of fish (DVWK 2002, Mokwa 2010, Zgrabczyński 2007), two groups of different preferences regarding the topology and geometric dimensions of a fish pass are distinguished (Tab. 1).

Table 1. Dimensions of fish pass depending on fish species (DVWK 2002)

Tabela. 1. Wymiary przepławek w zależności od gatunku ryb (DVWK 2002)

Dimensions of fish pass		Grayling, bream, chub and others	
		Brown trout	Huchen, Trout
Slot width	s [m]	0.15-0.17	0.30
Chamber width	b [m]	1.20	1.80
Chamber length	l_b [m]	1.90	2.75-3.00
"Hook" length	c [m]	0.16	0.18
Deflector displacement	a [m]	0.06-0.10	0.14
Deflector width	f [m]	0.16	0.40
Maximal difference water level	Δh [m]	0.20	0.20
Minimum water depth	h_{\min} [m]	0.50	0.75
Water flow rates in chambers ^{a)}	Q [$m^3 \cdot s^{-1}$]	0.14-0.16	0.14
Maximum velocity	v [m/s]	1.50	2.00

2.3. Fish species found in the Głomia river

The biodiversity of species in the Głomia river depends on the section of the river. The greatest biodiversity was observed in the lower section of the river, while the largest number of fish was recorded in the middle of its run. In the Głomia river the most abundantly occurring fish are common roach and European perch, also frequent are Eurasian minnow (*Phoxinus phoxinus*), riffle minnow (*Alburnoides bipunctatus*), European

chub (*Squalis cephalus*), gudgeon (*Gobio gobio*), stone loach (*Barbatula barbatula*) grayling (*Thymallus thymallus*), brown trout (*Salmo trutta fario*) and European bullhead (*Cottus gobio*) (Penczak et al. 2008).

2.4. Research facility

The research facility is located in Wielkopolska, in the district of Złotów, Krajenka (commune), Skórka (locality). The barrage is located on the Głowia river. The barrage "Skórka" consists of four elements: weir, power plant, kayak crossing and fish pass.

The fish pass consists of two sections. Its upper part is a technical pass (Fig. 1b). The fish pass is located directly at the weir and separated with a retaining wall built of reticular-stone gabions. The water inlet (fish outlet) is a reinforced concrete dock structure with a profiled rectangular bed having a bottom width equal to 2.0 m. The technical part of the fish pass consists of three chambers. Then the fish pass becomes a semi-natural structure (Fig. 1a) consisting of 11 chambers with a length of approx. 3.50 m each and a bottom width of approx. 1.50 m. This part of the fish pass built with a 4% slope and a total decrease of 1.60 m and 39.0 m length. Its slots have a width of approximately 0.30 m and are located in baffles of wooden structure. The designed difference in levels of the water level between baffles is 0.15 m, and the depth of water in the fish pass ranges from 0.6 to 0.8 m.

At the design stage it was assumed that the amount of water needed to supply the fish pass was $Q = 0.30 \text{ m}^3 \cdot \text{s}^{-1}$, and the maximum speed was $v = 1.43 \text{ m} \cdot \text{s}^{-1}$. The escarpment of the fish pass constructed with a slope of about 1:1.5 is reinforced by grass. The bottom is strengthened with natural stone of different diameters, arranged irregularly. The fish pass at the "Skórka" barrage operates on the whole-year basis.

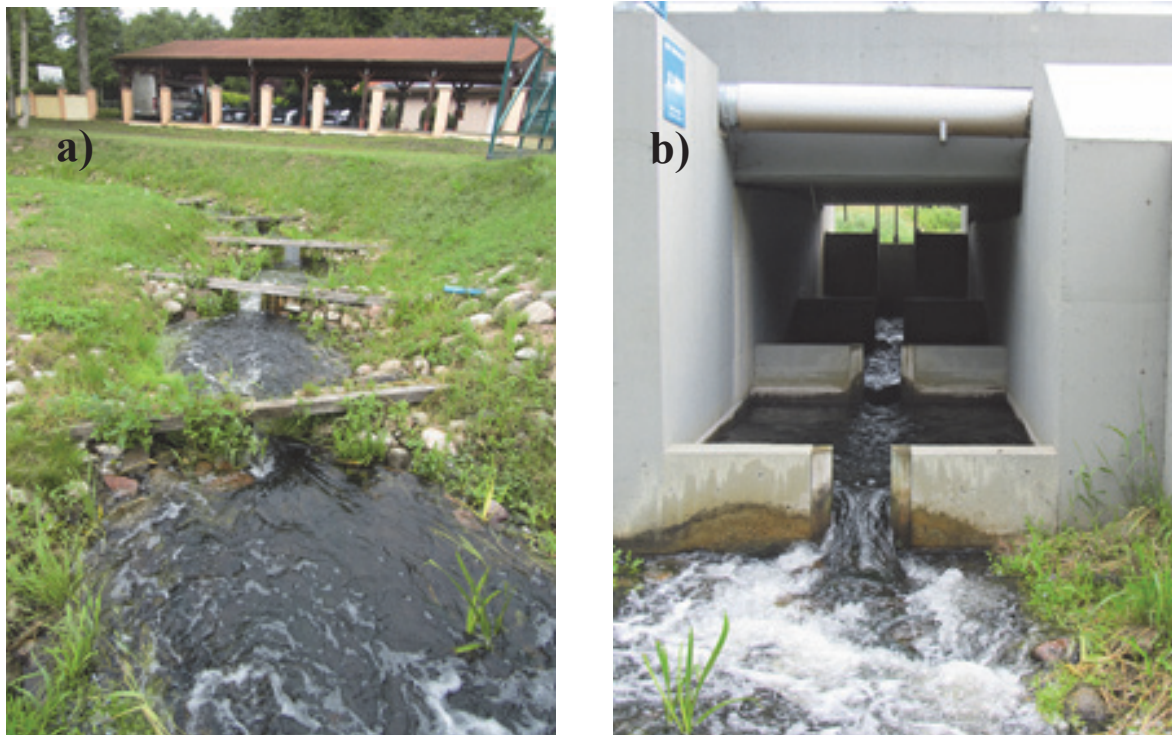


Fig. 1. The seminatural a) and technical b) parts of the fish pass at the Skórka barrage on the Głomia river

Rys. 1. Widok części seminaturalnej a) i technicznej b) przepławki na stopniu wodnym Skórka na rzece Głomi

The study was carried out in 2013 and 2014. The scope of the study included the levelling of the water level topology, velocity measurement in slots between chambers of the fish pass, velocity measurement in chambers of the fish pass and geometry measurement of the fish pass.

The water level results obtained from field tests in 2013 were compared to the theoretical model describing the difference between water levels in chambers of the fish pass:

$$\Delta h = \frac{H}{n+1} \quad (1)$$

where:

Δh – difference in water levels in chambers, m

H – difference in water levels between the inlet and outlet of the fish pass, m

n – number of fish pass chambers.

3. Results

3.1. Levelling and geometry measurement of the fish pass

During field measurements the ordinates of the water level in particular chambers and the differences between them were determined. Water surfaces elevation in 2013 was measured at the discharge $Q = 0.096 \text{ m}^3 \cdot \text{s}^{-1}$ and in 2014 it was measured at the discharge $Q = 0.030 \text{ m}^3 \cdot \text{s}^{-1}$ (table 2).

Table 2. Differences between the ordinates in chambers of the fish pass measured in 2013-2014

Tabela 2. Różnice pomiędzy rzędnymi zwierciadła wody pomierzonymi w komorach przepławki w latach 2013-2014

Number of chambers	Differences between ordinates in chambers	
	2013	2014
	Δh [m]	Δh [m]
1	–	–
2	0.110	0.012
3	0.015	0.030
4	0.015	0.020
5	0.028	0.020
6	0.027	0.010
7	0.070	0.100
8	0.004	0.060
9	0.091	0.100
10	0.060	0.080
11	0.132	0.100
12	0.266	0.270
13	–	0.230
14	–	0.060
15	–	0.180

The results obtained from levelling and geometry measurements are shown schematically in Figure 2. The above figure illustrates an uneven distribution of the water level topology in the fish pass. The water table measurements in the fish pass system were performed twice.

The greatest difference in water levels in 2013 was 0.266 m between chambers 10 and 11, and the smallest difference was between chambers 6 and 7, and reached the value 0.004 m. In 2014, the smallest difference between the water level was noted between chambers 4/5 and was 0.01, while the greatest one was 0.27 m between chambers 10 and 11. Significant differences in the water level between chambers 10 and 11 result from a steep slope of the fish pass bottom.

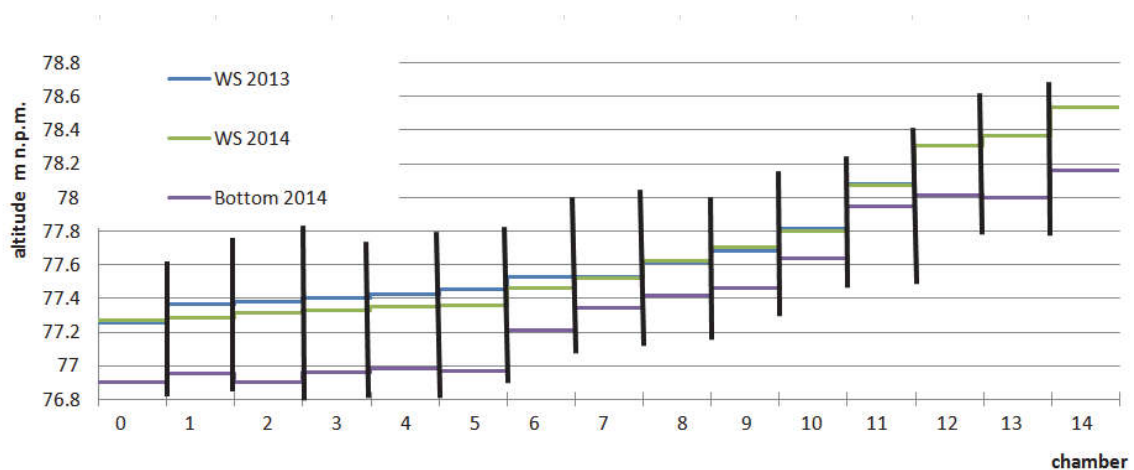


Fig. 2. Diagram of the water level topology of the fish pass semi-natural part in 2013 - 2014

Rys. 2. Schemat układu zwierciadła wody w części seminaturalnej przepławki w latach 2013 - 2014.

The differences between water levels in the chambers obtained from field research in 2013 were compared to the theoretical model describing the difference between water levels in chambers of the fish pass:

$$\Delta h = \frac{78.416 - 77.258}{15 + 1} = 0.072 \text{ m} \quad (2)$$

In the case of the analysed fish pass, the above formula (1) allows calculating an average difference in the water level between individual chambers, which does not exceed the limit value and amounts to 0.072 m (in 2013), and 0.066 m (in 2014).

3.2. Measurement of the water flow rate

On the basis of the water flow rate results obtained in the field measurements, the velocity curves were drawn for particular vertical measurement points. Because of low water levels in the fish pass cham-

bers, the analysis of vertical velocity distribution of flow rate was often based on measurements at 2-3 measuring points, assuming that at the bottom the flow rate was zero. From the point of view of fish migration possibility, the maximum values of flow rate are important. The results of examples flow velocity rate measurements in the fish pass (at the fish pass inlet and in chamber 6 – vertical measurement points on the left and right sides at a distance of 0.5 m from the central vertical measurement point) are presented below in Table 3. The flow rate analysis carried out in chamber 6 showed that the migration conditions were favourable even for the weakest individuals present in the river.

Table 3. Compilation of water flow rate measurements in the fish pass

Tabela 3. Zestawienie wyników pomiarów prędkości przepływu wody w przepławce

Measurement point in chamber 6 in 2013	Velocity [$\text{m}\cdot\text{s}^{-1}$]
The left vertical	0.14
The middle vertical	0.57
The right vertical	0.41

Table 4 presents the velocity values in the fish pass at all vertical points of measurement.

Table 4. Average water velocity values in the fish pass (no data available)

Tabela 4. Średnie prędkości przepływu wody w przepławce (brak danych)

No.	Section	Mean velocity 2013 year	Mean velocity 2014 year	Maximum velocity 2014 year
		$\text{m}\cdot\text{s}^{-1}$	$\text{m}\cdot\text{s}^{-1}$	$\text{m}\cdot\text{s}^{-1}$
1.	1.7 m down from partitions 1	No data available	0.06	0.18
2.	partitions 1	–	0.19	0.29
3.	partitions "2"	–	0.29	0.36
4.	partitions "3"	–	0.30	0.36
5.	partitions "4"	–	0.36	0.45
6.	partitions "5"	–	–	–
7.	partitions "6"	1.16	0.40	0.63

Table 4. cont.

Tabela 4. cd.

No.	Section	Mean velocity 2013 year	Mean velocity 2014 year	Maximum velocity 2014 year
		$\text{m}\cdot\text{s}^{-1}$	$\text{m}\cdot\text{s}^{-1}$	$\text{m}\cdot\text{s}^{-1}$
8.	partitions "7"	0.79	–	–
9.	partitions "8"	–	0.463	0.76
10.	partitions "9"	–	–	–
11.	partitions "10"	–	0.47	0.63
12.	outlet part of the concrete	0.36	0.31	0.41
13.	inlet part of the concrete	1.74	1.61	2.70

The average water velocity at the vertical point of the technical part outlet was $0.31 \text{ m}\cdot\text{s}^{-1}$, and the maximum value was $0.41 \text{ m}\cdot\text{s}^{-1}$. The average water velocity the vertical point of the concrete part outlet of the fish pass, due to its compact size, was $1.61 \text{ m}\cdot\text{s}^{-1}$ and the maximum was $2.70 \text{ m}\cdot\text{s}^{-1}$. These velocities far exceed the limit values, which may hinder fish migration.

4. Discussion

The principles of good design of fish passes have been established assuming that a fish pass should be efficient at all water levels enabling fish migration. Other additional conditions ensuring the optimal work of the fish pass should also be met, such as: proper filling, not exceeded velocity values admissible in slots and creation of an alluring stream in the lower area of the fish pass. Fish pass efficiency tests should be accompanied by some geometry measurements, and then compared to standards contained in DVWK (2002). According to the field tests, the chamber length varies from 3.08 m to 4.73 m, while the slot width in baffles changes from 0.2 m to 0.35 m. The total length of the semi-natural part of the fish pass is 39.87 m. The geometrical dimensions of chambers and slots provide the possibility of migration to all organisms present in the Głomia river.

The analysed fish pass within the Skórka barrage on the Głomia river is effective but to certain limits. Because of different slopes of the bottom for which the fish pass was designed and constructed, the condi-

tions of water flow during the vegetation season in multiple locations constitute a serious impediment to fish. The most unfavourable conditions are present at the interface between the technical and semi-natural part of the fish pass because the maximum difference in water elevations between the chambers is up to 20 cm. For example, due to the differences between the ordinates in chamber 12 where Δh is up to 27 cm, migration of small specimens can be significantly impeded (Marriner et al. 2014). This level difference also exceeds the recommendations of DVWK (2002). In contrast, in the semi-natural part of the fish pass the level differences are very small (in the order of a few centimetres). This translates into low flow velocities and no luring current.

The water velocities at slots are within the accepted range. The maximum water velocity at all studied points in semi-natural structure does not exceed $0.8 \text{ m}\cdot\text{s}^{-1}$. The flow rate right at the inlet to the concrete part of the fish pass is equal to $2.7 \text{ m}\cdot\text{s}^{-1}$, which makes an insurmountable barrier for most fish that use the fish pass. Similar problems have been studied by Bartnik et al. (2010) and Wierzbicki (2013). A separate issue is to provide an alluring stream in the lower area of the fish pass, where the fish pass joins the river. Based on observations and velocity measurements carried out in this area, the fish pass is hardly tempting to fish as the average water velocity value is there approx. $0.3 \text{ m}\cdot\text{s}^{-1}$. The stream of water flowing out of the fish pass cannot perish in the stream of the river, i.e. the water velocity in the fish pass should be much higher than in the river (alluring stream). The impact of alluring stream has been also considered by Bartnik et al. (2010) and Wyzga et al. (2014). Bartnik has shown the results of numerical modelling of 400-meter part of a river that includes coated weir, small hydroelectric power station and a fish pass. The action taken concentrated on such a formation of the water discharge in the ladder and modification of the bed configuration in the hydro-mouth that would make an alluring stream. Similarly as for the Skórka Barrage, the study by Bartnik et al. (2010) have shown that the velocity of water flowing out of the fish pass depends on the water velocity in the pass but also on the conditions of water movement in the main river bed.

The problem of semi-natural fish pass is to prepare a good project and its correct implementation (Zgrabczyński 2007). Another issue are the exploitation problems. The reason for such high water velocity rate may be the fact that on the day of field measurements (07.09.2014) the

valve regulating water supply to the fish pass at the upper area of the barrage was lowered to 0.10 m. With the valve being almost closed, it contributes to the phenomenon of water throttling. Therefore, high velocities are being generated preventing the fish from passing through the barrage. The measurements in 2013 indicate that water velocity values at the inlet slot exceeded the value admissible for the Trout family (Brown trout), which according to Mokwa (2010) is $1.5 \text{ m}\cdot\text{s}^{-1}$. Functionality of the fish pass would improve if the valve at the fish pass inlet was larger. This would result in reduction of water flow rate at the inlet, increase in the water level, as well as increase in depth and flow rate of the fish pass.

5. Summary

Analysis of the results of field measurements carried out in 2013 and 2014, has shown that the designed flow rate is not ensured during use. Increase in the flow rate would result in increase in the depth of water in the fish pass thereby increasing its water t ordinates and deepening the fish pass. The analysis of field data has indicated that differences in the water level between chambers are not significant except for the difference between chambers 10 and 11. The averaged difference between water levels in individual chambers is approx. 7 cm respectively. Analysis of geometry of the fish pass has indicated that all organisms present in the river may migrate if the opening of the inlet valve is larger. On the basis of the analyses it can be concluded that velocity values in the fish pass according to 2014 measurements oscillate within values that allow the free fish migration. The maximum velocity takes values allowing fish migration over the entire depth of tested hydrometric points.

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Analiza możliwości migracji ryb przez przepławkę seminaturalną na przykładzie stopnia wodnego Skórka na rzece Głómii

Streszczenie

Gospodarowanie wodą poprzez m.in. piętrzenie rzek powoduje zmiany w środowisku przyrodniczym. Jedną z nich jest ograniczenie możliwości migracji ryb i innych organizmów wodnych. W celu ułatwienia ich przemieszania buduje się przepławki. W pracy przedstawiono wyniki badań terenowych dotyczących parametrów hydraulicznych przepławki dla ryb zlokalizowanej w obrębie stopnia wodnego Skórka na rzece Głómii. Celem badań było rozpoznanie warunków przepływu wody w poszczególnych komorach przepławki seminaturalnej. Na podstawie wyników badań terenowych określono warunki hydrauliczne przepływu wody przez przepławkę, odnosząc uzyskane rezultaty do optymalnych parametrów pracy przepławki. Uzyskane wyniki stanowią podstawę do dyskusji na temat możliwych problemów budowy i eksploatacji „bliższych naturze” konstrukcji przepławek dla ryb.

Abstract

Water management by artificial water level increasing in rivers, results in environmental changes. One of them is the constraint on migration of fish and other aquatic organisms. In order to facilitate the passage, fish passes are built. The study analysed many parameters related to proper work of the fish pass. The article presents results of a field study of the fish pass located within the Skórka barrage on the Głomia river. The aim of the study was to identify water flow conditions in particular chambers of the fish pass. On the basis of results of the field study, the hydraulic conditions of water flow through the fish pass were determined and referred to the optimum performance parameters of the construction. The results obtained make a basis for discussion of possible problems related to construction and operation of the fish passes resembling „close to nature” structures.

Słowa kluczowe:

seminaturalna przepławka dla ryb, pomiary terenowe, rzeka Głomia

Keywords:

semi-natural fish pass, field measurement, Głomia river



Vermicomposting of Sugar Beet Pulps Using *Eisenia fetida* (Sav.) Earthworms

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1. Introduction

One-third of the world sugar production is manufactured from sugar beet (Roper 2002). From one ton of this raw material, approximately 150 kg of sugar and 250 kg of sugar beet pulps with the mean dry mass value of 20% are obtained (Spagnuolo et al. 1997). In 2016 in Poland, approximately 2.17 million tons of sugar were produced, and thus over 3.6 million tons of sugar beet pulps (www.stat.gov.pl).

Sugar beet pulps can be used as a feed for farm animals (Journal of Laws No. 16, item 137) on condition that they meet the quality requirements (Regulation EC No. 183/2005). When the standards are not met, in accordance with the regulation of the Minister of Environment of 9 December 2014 on waste catalogue (Journal of Laws of 2014, item 1923), sugar beet pulps are classified as group 02 waste: waste from agriculture, horticulture, aquaculture, fishery, forestry, hunting and food processing, 02 04 subgroups; Waste from sugar industry and 02 04 80 type: sugar beet pulps. The increasing amount of this waste generates a growing problem concerning its management (Bhat et al. 2015).

A large part of postproduction plant waste, such as for example apple pomace from apple processing, rapeseed cake from rape processing, soybean hulls and spelt husks from the processing or olive pomace are des-

ignated for energetic purposes (Wojdalski et al. 2016, Kraszkiewicz et al. 2017, Gołofit-Szymczak 2016), whereas some part of them, after neutralization, could be used as plant fertilizer.

Vermicomposting is one of biological methods of organic waste neutralization (Edwards 1995, 1998). It is an efficient process of nutrient recycling for plants, including a synergic action of earthworms and microorganisms. Although the microorganisms are responsible for the biochemical transformations occurring in this process, earthworms are of crucial importance for organic matter processing, because by fragmenting and aerating the substrate, they modify the activity of microorganisms (Aira et al. 2002, Fracchia et al. 2006, Lazcano et al. 2008).

Vermicompost is a material similar to peat, with high porosity, ability to aerate and retain water. It is characterised by the presence of various microorganisms and high content of nutrients for plants, so its use may be very important for sustainable agriculture, as an alternative for mineral fertilizers (Suthar 2012, Lim et al. 2015). However, waste neutralization time and the quality of the final product depend to a large extent on type and quality of the initial substrate (Singh et al. 2010).

The aim of the conducted studies was to assess the possibilities of using *E. fetida* for processing of sugar beet pulps in case of various ways of preparation of initial bedding in vermireactor.

2. Material and methods

The experiment was conducted in the Laboratory of the Department of Natural Theories of Agriculture and Environmental Education of the University of Rzeszów. *E. fetida* (Sav.) earthworms derived from the multiannual breeding line maintained at the above-mentioned Department were used in the experiment. Before the start of the experiment, only mature specimens (with well-developed *clitellum*) were selected from the culture and placed in containers filled with garden soil and feed for 7 days, for the acclimation period. It was done in order to eliminate any possible disturbances of the experiment caused by a sudden change in environmental conditions of earthworms.

Sugar beet pulps were obtained from the “Cukrownia Ropczyce” Sugar Plant. They were frozen in order to be stored. Before the onset of the experiment, sugar beet pulps were melted at temperature of $20\pm 1^{\circ}\text{C}$

and dried until dry mass was obtained, in order to apply the same waste weight to each vermireactor. Prior to placement in vermireactors, thoroughly weighed out waste was soaked in water for 2 hours.

The experiment was conducted in vermireactors of size of 300 x 200 x 200 mm (length x width x height). Vermireactors were constructed from plastic boxes. The bottom of each box was equipped with small holes in order to drain the excess water. Each vermireactor was placed in a slightly bigger box in such a manner, that their bottoms did not touch each other (a distance between the bottoms amounted to 30 mm), to store the excess water. Identical amount of plant waste (200 g of dry mass each) was put into the prepared nets of size of 150 x 200 x 150 mm (length x width x height). Nets with plant waste were placed in vermireactors and the remaining capacity of vermireactors was filled with initial bedding. Vermireactors were divided into two groups; in the first group, biologically active garden soil was used as the initial bedding (BAGS vermireactor), whereas in the second group the same bedding was applied, but it had been sterilised at 105°C (SGS vermireactor) (Fig. 1). The sterilised bedding was used to show the significance of soil microorganisms in the process of vermicomposting and the simulation of using in the vermiculture a soil degraded as a result of anthropopressure.

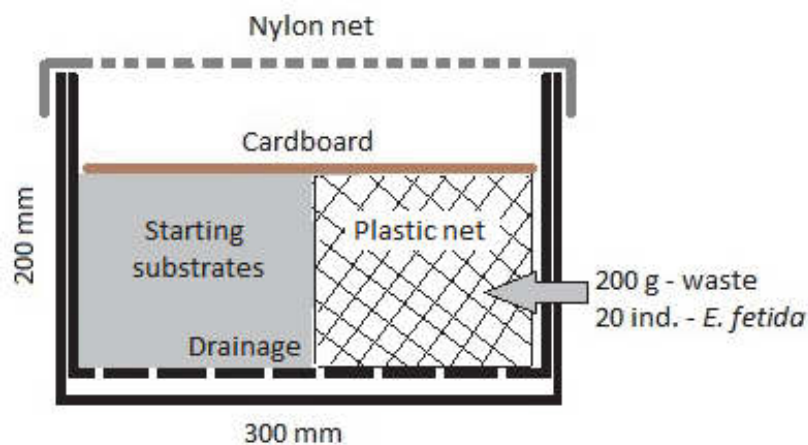


Fig. 1. Schematic diagram of vermireactors

Rys. 2. Schemat wermireaktorów

Only sexually mature earthworms balanced in terms of number and biomass were introduced to the previously prepared vermireactors. They were protected from the top with a nylon mesh that prevented earthworm escape, and with a paper cardboard that prevented drying out of the soil. Vermireactors were placed in the climatic chamber at constant temperature of $20 \pm 0.5^\circ\text{C}$. In order to maintain the proper humidity of waste, it was moistened every 10 days with the same volume (100 ml) of water (pH – 7.6, conductivity – $542 \mu\text{S}\cdot\text{cm}^{-1}$, nitrates V – $8.9 \text{ mg}\cdot\text{l}^{-1}$, Mg – $15.7 \text{ mg}\cdot\text{l}^{-1}$, hardness – $257 \text{ mg CaCO}_3\cdot\text{l}^{-1}$).

The experiment included 5 repetitions in each of the two groups, according to the following outline:

5 BAGS vermireactors (sugarbeet pulps 200 g + 20 mature *E. fetida* specimens 0.347 ± 0.02 g/specimen + biologically active garden soil)

5 SGS vermireactors (sugarbeet pulps 200 g + 20 mature *E. fetida* specimens 0.352 ± 0.01 g/specimen + sterilised garden soil)

Control examinations of the condition of earthworm populations were conducted every 10 days. They consisted in manual segregation of bedding and waste in order to analyse the count and biomass of earthworms and cocoons. After having recorded the above-mentioned characteristics, the cocoons were removed from the experiment. On the 20th day of the experiment and after its completion (on the 40th day) a control of the level of waste processing was carried out. For this purpose, the sugar beet pulp residues that have not been processed, were removed from the plastic nets, dried until dry mass was obtained and then weighed. Prior to returning them to vermireactors, the residues were soaked in tap water for 2 hours.

Macroelement (N, P, K, Ca, Mg) content was determined both in the waste material and in vermicompost. Nitrogen was assayed by Kjeldahl's method. Phosphorus was assessed by colorimetric vanadium-molybdenum method, potassium, magnesium and calcium were assessed using atomic absorption spectrophotometry after prior sample mineralization in a mixture of concentrated mineral acids ($\text{HNO}_3 : \text{HClO}_4 : \text{H}_2\text{SO}_4$ in a ratio of 20 : 5.1). Carbon was determined with the use of Vario EL-CUBE elemental analyzer. pH in water was evaluated by potentiometric method and salt concentration was determined by conductometric method.

All statistical analyses were expressed as mean of five replicates using the computer software package Statistica 13.1. Tukey's t test was

used as a post hoc analysis to compare the means. One-way analysis of variance (ANOVA) was used to analyze the significant difference between research groups for the observed monitoring parameters and the significance difference between macroelements contents in initial plant waste and vermicomposts.

3. Results and discussion

3.1. Changes in *E. fetida* populations and waste treatment rate

As it results from the conducted experiments, the count of mature *E. fetida* specimens was slightly decreasing in both groups of vermireactors (BAGS and SGS vermireactors) during the entire experiment (Fig. 2), that might have resulted from, among others, the stress associated with a change in habitat conditions or frequent controlling of the condition of earthworm population (Garczyńska & Kostecka 2012), but the differences between the groups were not statistically significant ($p > 0.05$) and, most probably, it did not have the effect on the plant waste treatment rate. Similar results were obtained by Bhat et al. (2016) who vermicomposted sugarcane waste. They demonstrated a decrease in count of *E. fetida* neutralizing exclusively sugarcane waste, with concurrent increase in the count of earthworms raised on the same waste with addition of cattle manure.

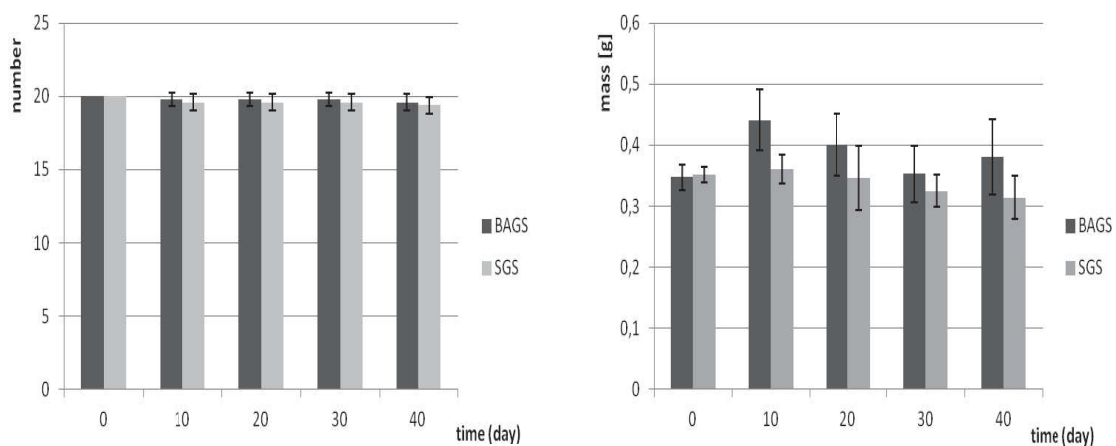


Fig. 2. The average number and mean weight of *E. fetida* specimens depending on the group of vermireactors

Rys. 2. Średnia liczebność oraz średnia masa osobników *E. fetida* w zależności od grupy wermireaktorów

However, pronounced differences were observed in the mean weight of *E. fetida* specimens (Fig. 2). Weight of specimens from the BAGS was higher (on average by 14%) compared to the earthworms from the SGS group. The greatest differences were showed on the 10th (18.2%) ($p < 0.05$) and on the 40th day of the experiment (17.6%) ($p < 0.05$), that might have affected the rate of vermicomposting of sugar beet pulps at that time. Bhat et al. (2015) demonstrated a positive effect of the addition of cattle manure to the neutralized sugar beet pulps on growth of *E. fetida*.

The applied vermicomposting technology affected the number of produced cocoons. The greatest and significant differences ($p < 0.05$) between BAGS and SGS groups were observed between the 10th and the 30th day of the experiment (Fig. 3). However, no differences were noted in the mean cocoon weight (except the 10th day of the experiment – when significant differences were observed ($p < 0.05$)) (Fig. 3). Bhat et al. (2015) noticed that a higher ratio of sugar beet pulps to cattle manure delays sexual maturity of *E. fetida* earthworms and has a negative effect on their reproduction.

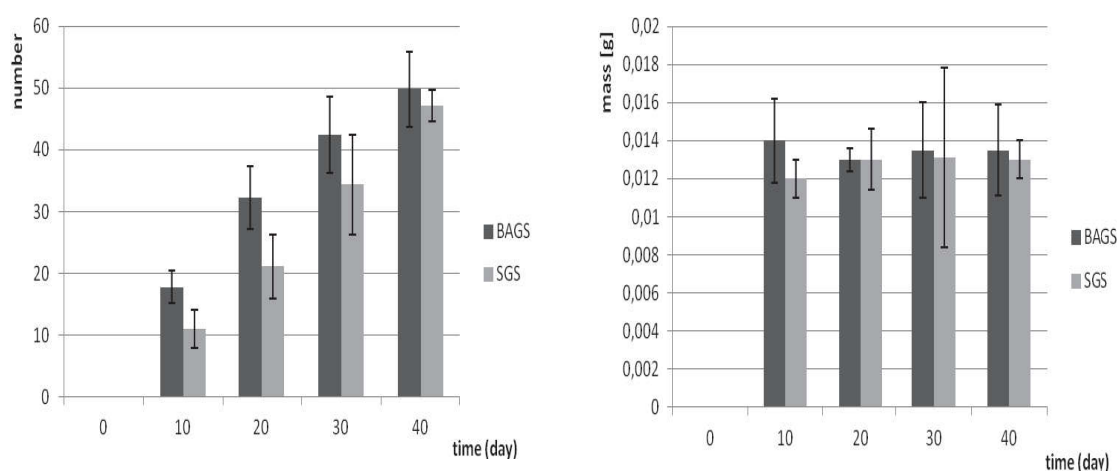


Fig. 3. The average number and mean weight of *E. fetida* cocoons depending on the group of vermireactors

Rys. 3. Średnia liczebność oraz średnia masa kokonów *E. fetida* w zależności od grupy wermireaktorów

Analysing the mean waste treatment rate, it was observed that in vermireactors with sterilised garden soil (SGS) this process occurred significantly slower compared to the group in which biologically active soil was used (BAGS). Both on the 20th and on the 40th day of the experiment, the earthworms from SGS group processed 44% ($p < 0.05$) and 27% ($p < 0.05$) of plant waste less compared to BAGS group (fig. 4). This could have been a result of lower biodiversity of microorganisms that play a crucial role in vermicomposting process, in the sterilised soil (Aira et al. 2002).

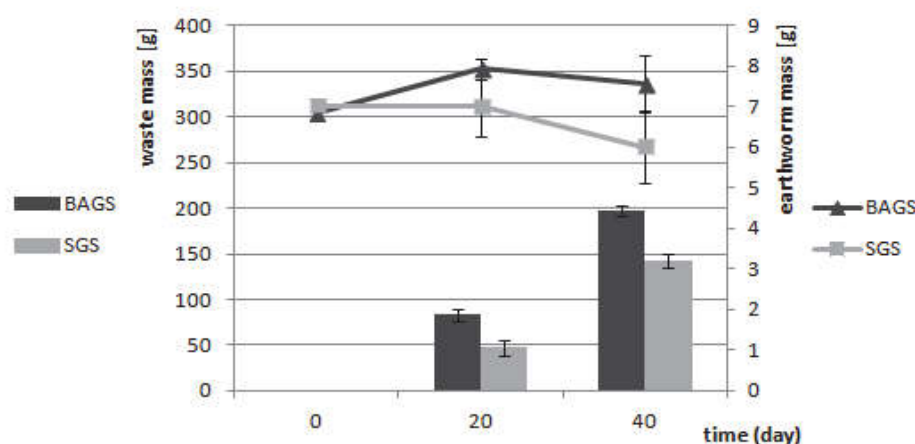


Fig. 4. Waste treatment rate and changes in the weight of *E. fetida* population depending on the type of used vermireactor

Rys. 4. Tempo przetwarzania odpadów i zmiany masy populacji *E. fetida* w zależności od rodzaju zastosowanego wermireaktora

3.2. Content of macroelements

As it was demonstrated in the studies by Dominguez et al. (2010), in the process of vermicomposting earthworms modify physical, chemical and biological properties of organic waste. Value of the obtained vermicompost depends on many factors, such as type and origin of organic waste, temperature, humidity and aeration of vermiculture, earthworm species and other elements. Thus, before starting the process of vermicomposting it is important to determine the physicochemical properties of waste, and after the completion of vermicomposting – to analyse these properties in vermicompost with regard to its usefulness as a fertilizer. Physicochemical properties of plant waste and vermicomposts are presented in Table 1.

Table 1. Macroelement content in sugar beet pulps and the obtained vermicomposts**Tabela 1.** Zawartość makroelementów w wysłódkach buraczanych oraz otrzymanych wermikompostach

Parameter	Units		BAGS	SGS
N		<i>Initial</i>	1413.7 ± 23.4a	
		<i>Final</i>	1785.3 ± 26.1b	1604.9 ± 28.5c
		<i>% of change</i>	26.3	13.5
P		<i>Initial</i>	119.2 ± 11.8a	
		<i>Final</i>	285.2 ± 30.2b	227.1 ± 26.8c
		<i>% of change</i>	139.3	90.5
K	mg kg ⁻¹ (d.m.)	<i>Initial</i>	2842.8 ± 21.1a	
		<i>Final</i>	3516.7 ± 36.5b	3309.1 ± 30.4c
		<i>% of change</i>	23.7	16.4
Ca		<i>Initial</i>	1514.4 ± 27.3a	
		<i>Final</i>	1891.8 ± 11.3b	1711.2 ± 23.4c
		<i>% of change</i>	24.9	12.9
Mg		<i>Initial</i>	179.6 ± 9.7a	
		<i>Final</i>	263.4 ± 10.8b	212.1 ± 14.2c
		<i>% of change</i>	46.6	18.1
C/N ratio	-	<i>Initial</i>	53.11 ± 3.16a	
		<i>Final</i>	19.72 ± 0.35b	28.41 ± 1.09c
		<i>% of change</i>	-62.9	-46.6
pH in H ₂ O	-	<i>Initial</i>	7.05 ± 0.04a	
		<i>Final</i>	6.28 ± 0.14b	6.01 ± 0.23b
		<i>% of change</i>	10.9	14.8
Electrical conductivity	mS·cm ⁻¹	<i>Initial</i>	1.74 ± 0.02a	
		<i>Final</i>	2.13 ± 0.04b	2.01 ± 0.08b
		<i>% of change</i>	22.4	15.5

Values designate mean ± standard deviation based on 5 samples

Mean value followed by different letters is statistically different ($p < 0.05$)

As a result of using various vermicomposting technologies, no significant differences in pH of vermicomposts from BAGS group and SGS group were found. However, significant ($p < 0.05$) changes in pH value between waste biomass of sugar beet pulps and the obtained fertilizers were noted (Table 1). Similar observations were obtained by Sangwan et al. (2008), by vermicomposting sugar beet waste mixed with biogas plant waste with the use of *E. fetida* earthworms. These authors demonstrated a decrease in pH value of the obtained vermicomposts. On the other hand, Bhat et al. (2014), in studies on vermicomposting of press-mud sludge sediment with cattle manure using *E. fetida*, showed a pronounced increase in pH value of the obtained vermicompost. These discrepancies in the obtained results may be explained by the use of different additives to the treated sugar beet pulp waste.

After 40 days of vermicomposting process a significant decrease in C/N ratio in the obtained vermicomposts was observed, compared to the initial waste biomass (in BAGS and SGS vermireactors - a decrease by 62.9% ($p < 0.05$) and 46.6% ($p < 0.05$), respectively. Significant differences in C/N ratio between the vermicomposts obtained using different technologies were noted as well (BAGS 19.72 ± 0.35 , SGS 28.41 ± 1.09) ($p < 0.05$) (Table 1). C/N ratio is the most often used indicator of vermicompost maturity that implies the degree of waste mineralisation and stability. Depending on the degree of advancement of vermicomposting process, loss of carbon in the form of CO_2 occurs as a result of respiration of microorganisms, with concurrent increase in nitrogen content resulting from, among others, physiological processes of earthworms (Suthar 2008).

Electrical conductivity (EC) of vermicomposts did not differ significantly between the groups but was significantly higher ($p < 0.05$) in comparison to the initial biomass (table 1). The increase in EC value was a result of release of various mineral ions, such as phosphates, ammonium ions, potassium ions and others, from the organic matter (Kaviraj & Sharma 2003).

A significantly increased macroelement content compared to the utilized waste biomass was also observed in the obtained vermicomposts (Table 1).

Nitrogen content in vermicompost obtained in BAGS group increased significantly by 26.3% (from 1413.7 ± 23.4 to 1785.3 ± 26.1 mg kg^{-1} ; $p < 0.05$), whereas in SGS group the content of this element increased

nearly by less than a half – by 13.5% ($p < 0.05$). As reported by Plaza et al. (2011) decreasing pH may lead to retaining nitrogen in vermicompost, whereas in increasing pH this element may be lost in the form of ammonia.

A similar situation was observed in case of phosphorus P, which content in the obtained vermicomposts was significantly higher in relation to plant waste (in BAGS group it increased by 139.3%, whereas in SGS group by 90.5%) ($p < 0.05$) (Table 1). Prakash & Karmegam (2010) claim that, among others, microorganisms dwelling in coprolites of earthworms are responsible for increasing phosphorus content in vermicompost.

Potassium content in vermicomposts in groups BAGS and SGS also significantly increased compared to the initial waste biomass (Table 1). Higher increase in the content of this element was also observed in BAGS group (from 2842.8 ± 21.1 to 3516.7 ± 36.5 mg kg⁻¹, (23.7%) ($p < 0.05$), whereas in SGS group the mentioned increase amounted to 16.4% ($p < 0.05$). Potassium content in vermicomposts obtained with the use of both technologies differed significantly (Table 1).

Calcium content in these vermicomposts was also different. A difference between the technologies was 12% ($p < 0.05$), whereas the difference between the initial biomass and fertilizers obtained using BAGS and SGS technologies amounted to 24.9% ($p < 0.05$) and 12.9% ($p < 0.05$), respectively. Similar observations were presented by Yadav and Garg (2011) in the studies on vermicomposting of various types of organic waste, but in their results Ca in vermicompost increased 1.15-3.57-fold.

A significant increase in Mg content in vermicomposts compared to the biomass of sugar beet pulps was also noted. In BAGS and SGS groups the content of this element increased by 46.6 and 18.1% ($p < 0.05$), respectively. Significant differences in Mg content between the vermicomposts obtained using different technologies were observed.

4. Conclusions

1. A possibility of using *E. fetida* earthworms in the treatment of sugar beet pulps in vermireactors with different characteristics of initial beddings (BAGS and SGS) was confirmed.
2. In both technologies of running vermireactors, vermicomposts with high nutrient content for plants were obtained. The collected vermicomposts were characterised by higher N, P, K, Ca and Mg content

compared to the initial waste biomass. The mean rate of waste treatment in vermireactors with biologically active soil (BAGS) was significantly higher compared to the group in which sterilised garden soil (SGS) was used.

3. During waste treatment in vermireactors, insignificant decreases in earthworm count were noted as well as significant differences in mean weight of specimens used in different technologies (BAGS and SGS). Earthworms reproduced that has been proved by the mean number of laid cocoons which was significantly increasing during the experiment conducted using both technologies.

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Wermikompostowanie wysłoków buraczanych z wykorzystaniem dżdżownic *Eisenia foetida* (Sav.)

Streszczenie

W artykule przedstawiono wyniki zastosowania różnych technologii procesu wermikompostowania odpadowej biomasy wysłoków buraczanych

przy użyciu dżdżownic *E. fetida*. Stwierdzono możliwość wykorzystania *E. fetida* do szybkiego unieszkodliwiania wysłodków w wermireaktorach o odmiennej charakterystyce podłoża startowych. Otrzymane wermikomposty charakteryzowały się wyższą zawartością N, P, K, Ca i Mg w porównaniu z inicjalną biomasą odpadową. Podczas unieszkodliwiania odpadu w wermireaktorach (BAGS i SGS) stwierdzano utrzymywanie się populacji dżdżownic przy nieistotnych spadkach ich liczebności. Zaobserwowano istotne różnice w średniej biomacie osobników z grup BAGS i SGS. Największe różnice (22 i 21%, $p < 0.05$) zaobserwowano w 10 i 40 dniu doświadczenia. Dżdżownice rozmnażały się, o czym świadczy średnia liczba składanych kokonów, która rosła istotnie w trakcie trwania doświadczenia w obu technologiach (średnio 36%; $p < 0,05$). Istotne różnice w średniej masie kokonów w zastosowanych technologiach stwierdzono jedynie w 10 dniu doświadczenia.

Abstract

The article presents results of application of various technologies of the process of vermicomposting of waste biomass of sugar beet pulps using earthworms *E. fetida*. A possibility of using *E. fetida* for quick utilization of sugar beet pulp in vermireactors with different characteristics of initial beddings was observed. The obtained vermicomposts were characterised by higher N, P, K, Ca and Mg content compared to the initial waste biomass. During waste utilization in vermireactors (BAGS and SGS) it was noted that the population of earthworms persisted, but earthworm count insignificantly decreased. Significant differences in the mean biomass of specimens from BAGS and SGS groups were also observed. The greatest differences (22 and 21%, $p < 0.05$) were observed on the 10th and 40th day of the experiment. Earthworms multiplied that has been proved by the mean number of laid cocoons which was significantly increasing during the experiment conducted using both technologies (on average by 36%; $p < 0.05$). Significant differences in the mean cocoon weight between the used technologies were noted only on the 10th day of the experiment.

Słowa kluczowe:

wysłodki buraczane, wermireaktor, technologia, *E. fetida*, makroelementy

Keywords:

sugar beet pulps, vermireactor, technology, *E. fetida*, macroelements



The Application of Integrated System in Dairy Wastewater Treatment

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1. Introduction

The dairy industry is generally considered to be the largest source of food processing wastewater in many countries. This sector has one of the highest water consumptions level and is one of the biggest producers of effluent per unit of production (Tikariha & Omprakash 2014). The dairy industry produces large quantities of wastewater often in the amount of thousand cubic meters per day. The wastewater from the dairy processing industry is characterized by: high concentrations of organic material (proteins, carbohydrates and lipids), high biological oxygen demand (BOD) and chemical oxygen demand (COD), high nitrogen concentrations and suspended solids (Wang et al. 2006). This all poses treat of envirnomanetal pollution (Banu et al. 2008). Several literature data suggest that appropriate treating of dairy wastewater are ecological treatment systems (aerobic and anaerobic reactors, clarifiers and wetlands) or physical-chemical treatment systems (membranes technology or an advanced oxidation proces-AOP) (Salazar et al. 2013). The AOPs are physical and chemical processes that involve the generation of transient species with a high oxidizing power, pointing out the hydroxyl radical ($\bullet\text{OH}$) among others. This radical has a high oxidizing capacity and can be generated by photochemical substances, mineralizing organic pollutants in CO_2 and H_2O . (Salazar et al. 2013). Many semiconductors like TiO_2 , ZnO , CdS , etc., have been used as photocatalysts. These processes have limitations which can potentially affect degradation efficiency through changing the pH, rapid organic-load variations, and also the ef-

fluent's physicochemical behavior. The efficiency of a photocatalytic system is also related to the form of TiO_2 and ZnO nanoparticle catalysts used as immobilized on surface or colloidal suspension (Mondal & Sharma IITK 2014, Chantes et al. 2015).

In the research, it was demonstrated which of the applied photocatalysts more effectively contributed to the oxidation of pollutants contained in dairy wastewater. The influence of both photocatalysts on the change in the efficiency and permeability of the assembly membrane was also evaluated.

2. Material and methods

The study examined industrial wastewater from one of the biggest dairy factories located in the Świętokrzyskie Voivodeship in Poland. The factory processes 400 000 litres of milk per day. The factory is equipped in its own wastewater treatment plant with capacity of up to 800 m³/d. The dairy wastewater was characterized by the alkaline reaction (pH 8.2). The value of COD used for the examination of wastewater was on average 4020 mg/dm³, with their mean value of BOD of 1750 mg/dm³. High contents of TOC and total w nitrogen (1200 mg/dm³ and 290 mg/dm³, respectively) were also observed.

The process of photocatalysis was conducted in a 250 cm³ photoreactor. The central part of the photoreactor contains a submersible medium-pressure UV-lamp with power output of 45 W, which emitted the waves with wavelength of 365 nm. The content of the reactor was mixed by supplying air from the bottom of the reactor and using the magnetic mixer (3000 rpm). The photocatalysts used in the study were titanium dioxide (TiO_2) and zinc oxide (ZnO). Both photocatalysts were in the form of nanopowders with particles smaller than 100 nm. Nanopowders were the materials of the puriss class of 99-100.5%, manufactured by Sigma-Aldrich (Germany).

Ultrafiltration posttreatment of the dairy wastewater was conducted using the research stand Millipore CDS-10. The system was operated in the dead-end one-directional arrangement at the pressure of 0.1 MPa. The membrane installation was composed of the ultrafiltration cell containing a flat membrane with active surface of 0.045 m². The cell was connected through a reducer with a gas cylinder (with oxygen). The

reducer allowed for adjustment of gas pressure in the range of 0.1 to 0.5 MPa. The study used hydrophilic ultrafiltration membrane made of polyethersulfone (PES) with cut-off of 50 kDa.

Dairy wastewater treatment was performed using two technological systems that combined photocatalysis with ultrafiltration (I – TiO_2 +UF and II – ZnO +UF). Before the proper photocatalysis process, a photolysis process was conducted in order to determine the most beneficial time of irradiation and the reaction of the dairy wastewater subjected to the photooxidation. Raw wastewater (pH 8.2) and initially acidified (to the level of pH 3.5) wastewater was used in the process. After determination of the above mentioned most beneficial conditions of the process, photocatalysis was performed using the titanium dioxide and zinc oxide. The dose of titanium dioxide was changed from 1 to 40 g/dm^3 , whereas the content of zinc oxide ranged from 1 to 6 g/dm^3 . Evaluation of the efficiency of photocatalysis was made every 15 minutes and the treated wastewater was centrifuged in the medical centrifuge by 10 minutes (10,000 rpm) and next filtered using the soft filter. This filtration was connected with the necessity of initial removal of photocatalyst from the treated wastewater. Since the photocatalysts (TiO_2 and ZnO) were supplied to the photoreactor in the form of a suspension, the membrane in the next reactor represented an efficient barrier for their particles.

The efficiency of the unit processes used in the study was controlled based on the changes in the levels of COD, TOC and total nitrogen. The HACH DR/4000 spectrophotometer was used to perform the measurements of chemical oxygen demand (COD). BOD was determined using the respirometric method by means of the measurement set OXI Top WTW. Kiper TOC 10C Analyser PX-120 with AS40-Dione3.11 autosampler was used for the determination of total organic carbon (TOC) and total nitrogen (TN). CP-401/CP-40 ph-meter was used to measure pH during the AOP process.

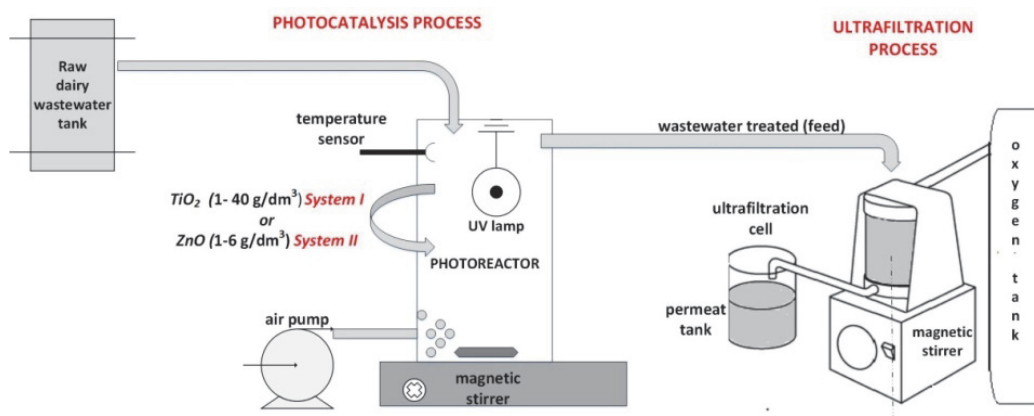
The effectiveness of the membranes was assessed based on surfactant retention coefficient and permeate relative flux (Table 1).

Table 1. Parameters for membrane process efficiency evaluation (Klimonda & Kowalska 2018)

Tabela 1. Parametry do oceny efektywności procesu membranowego (Klimonda i Kowalska 2018)

Parameter	Unit	Equation
Permeate flux	$\text{m}^3/\text{m}^2\text{s}$	$J = \frac{V}{t \cdot A}$
Retention coefficient	%	$R = \frac{C_f - C_p}{C_f} \cdot 100$
Relative flux	%	$RF = \frac{J}{J_0} \cdot 100$

The study design and methodology of determination is presented in Fig. 1.



Rys.1. Schemat oczyszczania ścieków mleczarskich w procesie fotokatalizy
Fig.1. The scheme of dairy wastewater treatment in the photocatalysis proces

4. Results and discussion

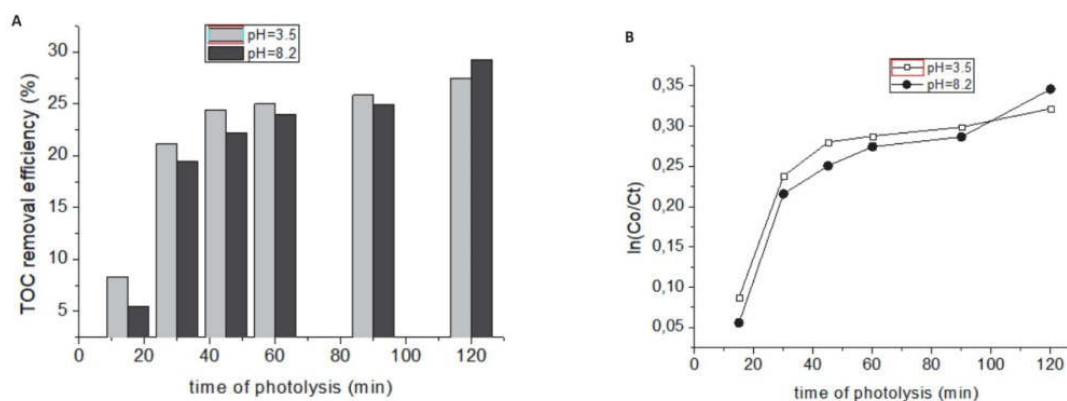
4.1. Dairy wastewater treatment using the photolysis process

The first step of the experiment examined the effect of initial value of pH of the wastewater subjected to photooxidation on the degree of degradation of TOC. Furthermore, the effect of the duration of the photolysis process on the value of TOC index in the treated wastewater

was determined. If the photolysis was performed for the initially acidified wastewater (pH 3.5), the degree of removal ranged from 8% (15 minutes of the process) to 25% (from 45 min to 120 min of the process) For the initially acidified wastewater TOC after 120 minutes of the process reduced from 1200 mg/dm^3 to 870 mg/dm^3 .

It was found that the rate of TOC removal from the alkaline wastewater (pH 8.2) was, until 90 minutes, by 4% lower on average compared to the dairy wastewater whose reaction was initially corrected. However, after 120 minutes of photooxidation, TOC removal from alkaline wastewater reached a higher level (29%). These changes are illustrated in Fig. 2a.

It was observed that elongation of the process to over 60 minutes did not significantly improve the effectiveness of oxidation of contaminants from the wastewater. At this stage, changes in the TOC removal rate were also analysed. Also in this case, the TOC degradation rate was insignificantly higher for the initially acidified wastewater. For certain durations (from 5 min to 30 min), the TOC degradation process was in both cases the first order reaction which was next transformed into a quasi-static reaction (Fig. 2b).



Rys. 2. Wpływ pH w procesie fotolizy na stopień usunięcia OWO (a) i $\ln C/C_0$ (b)
Fig. 2. Effect of pH on the photolysis proces in of removal TOC (a) and $\ln C/C_0$ (b)

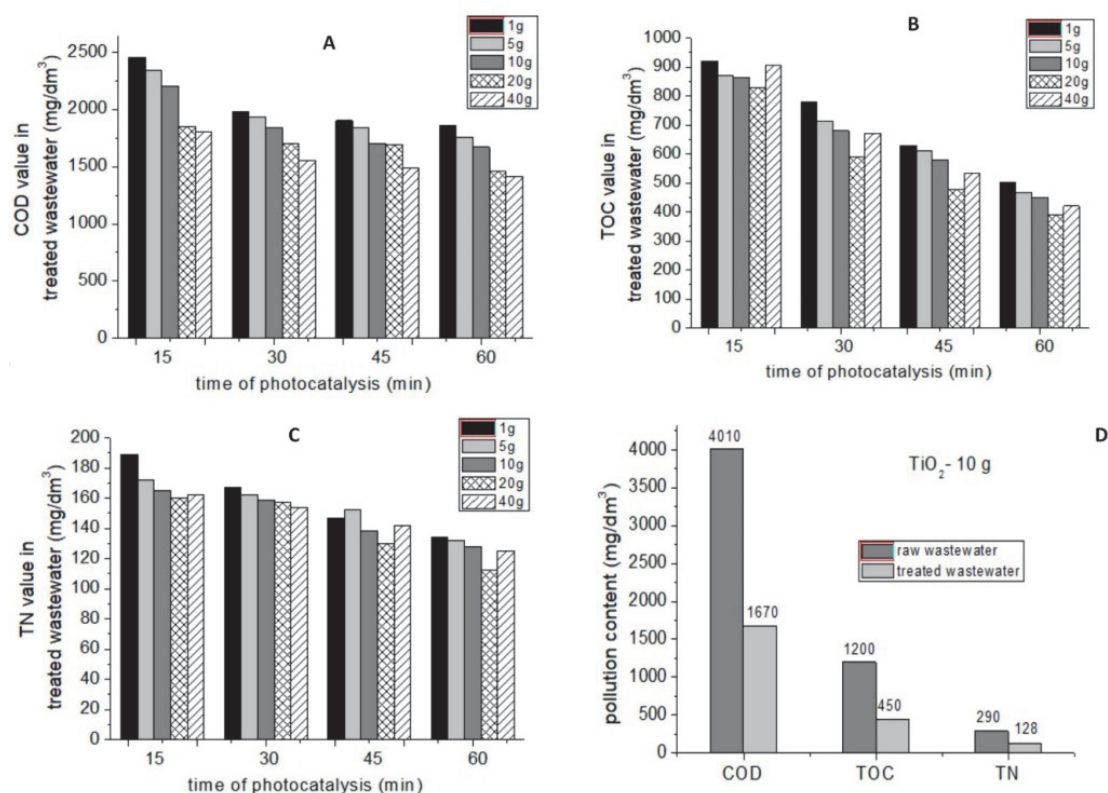
A constant reaction rate was determined based on the Langmuir–Hinshelwood formula (Kępa 2012). Analysis of the obtained results of constant TOC degradation rates revealed that oxidation of organic compounds contained in dairy wastewater occurs the fastest within the first 15 minutes. The value of k_{RTOC} for the wastewater with $\text{pH} = 3.5$ and

pH = 8.2 in the 15th minute of the process was 0.0079 min^{-1} and 0.0070 min^{-1} , respectively. In the 90th minute of the process, the values of these coefficients were substantially reduced, reaching 0.0026 min^{-1} (pH – 3.5) and 0.0028 min^{-1} (pH – 8.2), respectively. It was found that at the next stage of the examination, the dairy sewage would not be initially acidified and the photocatalysis process will be reduced to 60 minutes.

4.2. The use of titanium dioxide for dairy wastewater treatment

This stage of the examinations evaluated the effect of the amount of the titanium dioxide added to the reaction chamber on the degree of removal of contaminants from the dairy wastewater. Its dose was changed from 1 g/dm^3 to 40 g/dm^3 . The weakest effects in oxidation of contaminants determined as COD were observed if smaller doses of the photocatalyst (1 g/dm^3 and 5 g/dm^3) were used. The 60 minute duration of the photocatalytic oxidation of dairy wastewater led to the reduction in contaminants determined as COD at the doses of 1 g/dm^3 and 5 g/dm^3 by 53% (1860 mg/dm^3) and 56% (1770 mg/dm^3), respectively. When the highest dose was used, i.e. 20 g/dm^3 and 40 g/dm^3 , the COD removal rate after the same time of photocatalytic oxidation (60 min) was 63.5% (1460 mg/dm^3) and 64.8% (1410 mg/dm^3), respectively. In the case of TOC, it was found that its removal rate is more affected by the duration of the photocatalysis rather than the level of the photocatalyst dose. The TOC removal during photocatalysis increased on average from 23% (15 min) to 67% (60 min).

Oxidation of total nitrogen contained in the wastewater during photocatalysis occurred analogously to COD and TOC. After completion of the process (60 min), its level in the treated dairy wastewater with addition of 20 g/dm^3 and 40 g/dm^3 TiO_2 was 112 g/dm^3 (61%) and 125 g/dm^3 (57%), respectively. It was found that for all analysed doses of TiO_2 , extension of the process time to over 30 minutes does not substantially impact on the increase in oxidation of the contaminants contained in the wastewater. The changes were presented in Figs. 3a, 3b and 3c. It was found that the best solution is photocatalysis supported by TiO_2 if its dose is 10 g/dm^3 , with values of COD, TOC and total nitrogen in the treated wastewater after a 60 min process reaching $1,670 \text{ mg/dm}^3$, 450 mg/dm^3 and 128 mg/dm^3 , respectively (Fig. 3d).



Rys. 3. Wpływ dawki TiO₂ na stopień usuwania ChZT (a), OWO (b), azotu ogólnego (c) oraz na jakość ścieków oczyszczonych przy optymalnej jego dawce (d)

Fig. 3. Effect of the TiO₂ dose on the removal efficiency COD (a), TOC (b), TN (c) and the quality of treated wastewater at the optimal dose (d)

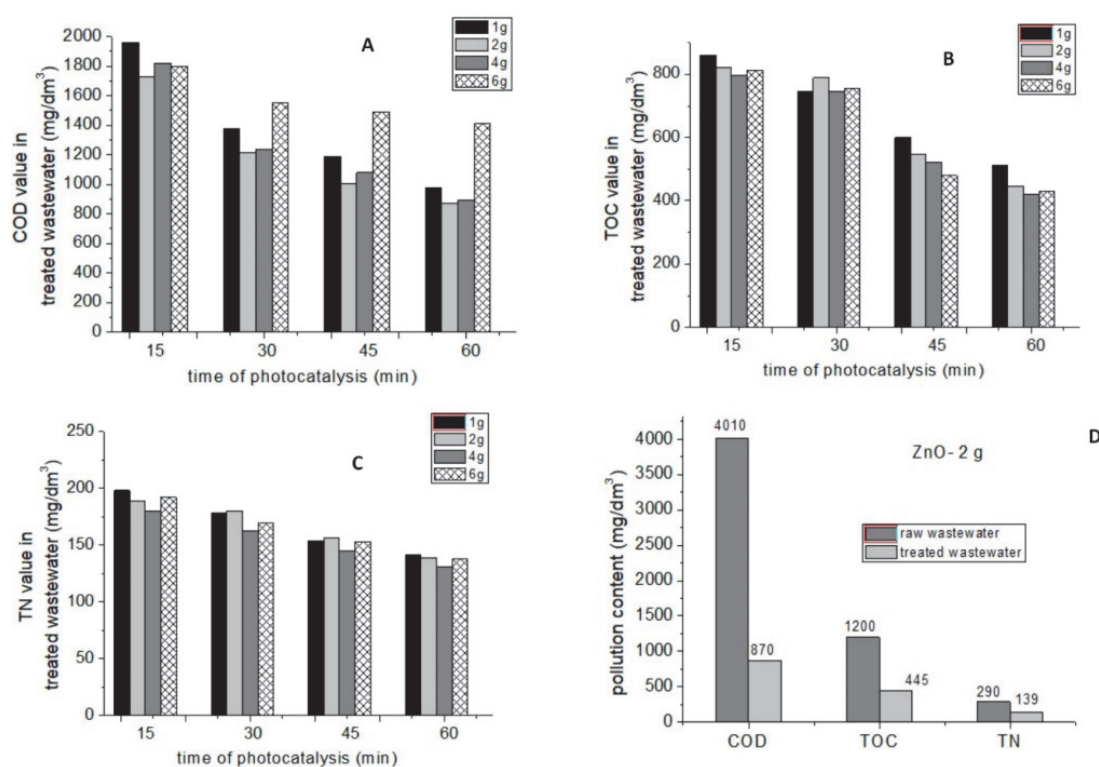
4.3. The use of zinc oxide for dairy wastewater treatment

The second photocatalyst used for oxidation of the contaminants contained in dairy wastewater was zinc oxide (ZnO). The doses were lower than in the case of TiO₂, and ranged from 1 g/dm³ to 6 g/dm³. It was found that the process of photocatalytic oxidation of the contaminants determined as COD occurred on average by 20% more effectively compared to the process conducted with titanium dioxide. In the case of the application of lower doses of ZnO i.e. 2 g/dm³ and 4 g/dm³, the degree of COD removal after 60 minutes of the process was 78.2% and 77.8%, respectively. It was also observed that the increase in the dose from 4 g/dm³ to 6 g/dm³ led to the reduction in the COD removal rate by 12% on average for all the analysed times (Fig. 4a). The 60 minute duration of the photocatalytic oxidation of dairy wastewater to the reduction

in contaminants determined as TOC at the smallest dose (1 g/dm^3) and the biggest dose (5 g/dm^3), by 57% (512 mg/dm^3) and 64% (430 mg/dm^3), respectively. These changes are illustrated in Fig. 4b.

In the case of TOC, it was found that its removal rate is more affected by the duration of the photocatalysis rather than the level of the photocatalyst dose. The TOC removal during photocatalysis increased on average from 28% (15 min) to 65% (60 min).

The efficiency of total nitrogen oxidation from the wastewater in the process of photocatalysis using the ZnO was closer to the effects obtained when the titanium dioxide was used (Fig. 4c). After completion of the process (60 min), its content in the treated wastewater with addition of 1 g/dm^3 and 6 g/dm^3 ZnO was 141 g/dm^3 (51.3%) and 138 g/dm^3 (52.4%), respectively.



Rys.4. Wpływ dawki ZnO na stopień usuwania ChZT (a), OWO (b), azotu ogólnego (c) oraz na jakość ścieków oczyszczonych przy optymalnej jego dawce (d)

Fig.4. Effect of the ZnO dose on the removal efficiency COD (a), TOC (b), TN (c) and the quality of treated wastewater at optimal dose (d)

It was observed that for all analysed doses of ZnO, the extension of the process time to over 45 minutes does not substantially impact on the increase in oxidation of the contaminants contained in the wastewater. It was concluded that the most favourable option of the photocatalysis process is when the dose is 2 g/dm³. The value of COD, TOC and total nitrogen in the treated dairy wastewater after 60 minutes of the process reached the value of 870 mg/dm³, 445 mg/dm³ and 139 mg/dm³ (Fig. 4d).

There is not much research on the use of ZnO in the form of a nanomaterial for the treatment of wastewater from the food industry. It is often immobilized on the walls of photoreactors. An example of this may be research (Samanamud et al. in. 2012) where used ZnO was immobilized on a metal plate (coating thickness ZnO 100 µm). Removal efficiency for TOC was lower (31.7%) at pH 8.0.

Action ZnO may also be intensified by the addition of H₂O₂ to the photoreactor. As shown by the study, the use of 1 g/dm³ ZnO and 30 mL H₂O₂ contributes to a significant removal of COD and total and thermo-tolerant coliforms from the wastewater (Abreu et al. 2013).

4.4. Ultrafiltration treatment of dairy wastewater

Combining the membrane process with photocatalysis along with improving the quality of treated wastewater is the ability to effectively separate the photocatalyst after the end of the degradation process. The separated photocatalyst can be used again (Zmudziński 2012, Moza et al. 2005, Mozia 2010).

Before the proper process of dairy wastewater treatment in the ultrafiltration process, the transport properties of the membrane used were determined (Bodzek et al. 1997). For the highest pressure used, i.e. 0.25 MPa, the ultrafiltration membrane was characterized by nearly 3 times higher ($24 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) volumetric water stream compared with the smallest pressure (0.1 MPa- $8.8 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$).

After determination of the transport properties of the membrane, the filtration of the initially treated system I and system II was performed. Process of ultrafiltration (UF) was conducted at the pressure of 0.1 MPa. It was found that regardless of the type of wastewater treated (system I or system II), the efficiency of the membrane gradually decreased with the duration of the ultrafiltration (UF) process. The cause of this phenomenon was the deposition of contaminants in the membrane

pores and formation of the filtration cake, which resulted in blocking the pores and a decline in the flux of permeate (Bodzek et al. 1997).

During the treatment of the wastewater initially treated during the photocatalysis, higher volumetric flux of permeate was obtained when the wastewater with titanium dioxide were supplied to the titanium dioxide (system I). After 5 minutes of the UF process, the flux of permeate was by 16% lower compared to the flux of deionized water. If the dairy wastewater was initially treated using ZnO (system II), a 30% reduction was observed after the same time. After 30 minutes, the flux of permeates in both cases were stabilized and reached the values of $4.6 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ (after TiO_2 $10 \text{ g}/\text{dm}^3$) and $4.1 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ (after ZnO; $2 \text{ g}/\text{dm}^3$).

Based on the determined initial values of the volumetric water flux and medium values of volumetric permeate flux, the relative permeability of membranes was determined for both types of feed material. It turned out that relative permeability of membranes after ultrafiltration treatment of initially treated wastewater using TiO_2 was nearly by 14% (0.65) higher compared to their efficiency when treatment concerned the wastewater with content of ZnO (0.56).

At this stage of examinations a change in the content of organic compounds was determined in filtrated samples (permeates) depending on the duration of the process, i.e. retention coefficient (Bodzek et al. 1997). As expected, the ultrafiltration process ensured a high degree of removal of the contaminants from the initially treated wastewater in both systems. It was found that the ultrafiltration process in the case of the feed material with TiO_2 led to the reduction in COD, TOC and total nitrogen by 78% ($370 \text{ mg}/\text{dm}^3$), 72% ($126 \text{ mg}/\text{dm}^3$) and 40% ($80 \text{ mg}/\text{dm}^3$), respectively. Slightly lower degree of retention and wastewater with higher quality was obtained when the feed material contained ZnO. Removal rates for COD, TOC and total nitrogen were 68% ($280 \text{ mg}/\text{dm}^3$), 66% ($143 \text{ mg}/\text{dm}^3$) and 42% ($76 \text{ mg}/\text{dm}^3$), respectively.

5. Conclusions

The results obtained in the study led to the following conclusions:

- Elongation of the duration of photocatalysis with TiO_2 and ZnO to over 30 min and 45 min, respectively, does not have a substantial effect on the increase in the degree of oxidation of the contaminants contained in the dairy wastewater.

- In the case of treatment of dairy wastewater with TiO_2 , the photocatalysis occurred most beneficially for its dose of 10 g/dm^3 . Removal rates for COD, TOC and total nitrogen were 58% (1670 mg/dm^3), 62% (450 mg/dm^3) and 56% (128 mg/dm^3), respectively.
- Replacing titanium dioxide with zinc oxide ($\text{ZnO} - 2 \text{ g/dm}^3$) in the photocatalysis allowed for obtaining higher degrees of removal of contaminants determined as COD, TOC and total nitrogen to the level of 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) and 52% (139 mg/dm^3), respectively.
- It was found that relative permeability of membranes after ultrafiltration treatment of initially treated dairy wastewater using TiO_2 was nearly by 14% (0.65) higher compared to their efficiency when treatment concerned the wastewater with content of ZnO (0.56).
- Furthermore, the permeate obtained during treatment of wastewater using the system II (with ZnO) was better. Degree of retention of the contaminants COD, TOC and total nitrogen were 68% (280 mg/dm^3), 66% (143 mg/dm^3) and 42% (76 mg/dm^3), respectively.

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Zastosowanie zintegrowanego systemu w oczyszczaniu ścieków mleczarskich

Streszczenie

W pracy zaprezentowano wyniki badań jakie otrzymano podczas oczyszczania ścieków mleczarskich w fotoreaktorze membranowy w którym sekwencyjnie skojarzono procesy fotokatalizę z niskociśnieniowym procesem

membranowymi. Celem badań było określenie skuteczności degradacji zanieczyszczeń znajdujących się w tego rodzaju wodach odpadowych w samodzielnie prowadzonym procesie fotokatalizy jak również w układzie kojarzącym go z procesem ultrafiltracji. Przeprowadzono szereg eksperymentów w celu ustalenia najkorzystniejszych warunków prowadzenia procesu fotokatalizy tj. dawka zastosowanych fotokatalizatorów (TiO_2 i ZnO), czas prowadzenia procesu oraz wartość pH ścieków poddawanych utlenianiu. Dawkę ditlenku tytanu zmieniano w zakresie od 1 do 40 g/dm^3 a tlenku cynku od 1 do 6 g/dm^3 . Na podstawie uzyskanych wyników badań stwierdzono, że wydłużanie czasu naświetlania powyżej 30 minut (TiO_2) oraz powyżej 45 min (ZnO) w procesie fotokatalizy nie wpływa na zwiększanie usunięcia zanieczyszczeń z oczyszczanych ścieków mleczarskich. Wykazano również, że zwiększanie stosowanych dawek obu fotokatalizatorów nie skutkuje wzrostu efektywności ich oczyszczania. W przypadku oczyszczania ścieków mleczarskich z TiO_2 proces fotokatalizy przebiegał najkorzystniej jego dawce wynoszącej 10 g/dm^3 . Stopień usunięcia ChZT, OWO i azotu ogólnego wynosił odpowiednio 58% (1670 mg/dm^3), 62% (450 mg/dm^3) i 56% (128 mg/dm^3). Zastąpienie ditlenku tytanu tlenkiem cynku ($\text{ZnO} - 2 \text{ g/dm}^3$) w procesie fotokatalizy pozwoliło na uzyskanie wyższych stopni usunięcia zanieczyszczeń oznaczanych jako ChZT, OWO i azotu ogólnego odpowiednio do poziomu 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) i 52% (139 mg/dm^3). Z uwagi na fakt, że oba dawkowano do fotoreaktora w formie zawiesiny to znajdująca się w kolejnym reaktorze membrana była skuteczną barierą dla ich cząstek. Zaobserwowano, że wyższy objętościowy strumień permeatu uzyskano w trakcie prowadzenia procesu niskociśnieniowej filtracji membranowej ścieków wstępnie podczyszczonych w procesie fotokatalizy z ditlenkiem tytanu ($4,6 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s} - \text{TiO}_2$ i $4,1 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s} - \text{ZnO}$). Stwierdzono że wykorzystany proces ultrafiltracji w przypadku nadawy z TiO_2 przyczynił się do obniżenia wartości wskaźników ChZT, OWO i azotu ogólnego odpowiednio o 78% (370 mg/dm^3), 72 % (126 mg/dm^3) i 40% (80 mg/dm^3). Nieznacznie lepszej jakości permeat otrzymano, gdy nadawa zawierała proszek ZnO . Stopień retencji zanieczyszczeń ChZT, OWO i azotu ogólnego wynosił odpowiednio 68% (280 mg/dm^3), 66 % (143 mg/dm^3) i 42% (76 mg/dm^3).

Abstract

The study presented the results of the examinations obtained during treatment of dairy wastewater in a membrane photoreactor where photocatalysis was sequentially combined with low-pressure membrane process. The aim of the study was to determine the effectiveness of degradation of the contaminants contained in such wastewater during photocatalysis and in the arrangement that combined photocatalysis with ultrafiltration.

Several experiments were performed in order to determine the most beneficial conditions of the photocatalysis process, e.g. the dose of the photocatalysts used (TiO_2 and ZnO), duration of the process and pH of wastewater subjected to oxidation. The dose of titanium dioxide was changed from 1 to 40 g/dm^3 , whereas the content of zinc oxide ranged from 1 to 6 g/dm^3 . The results obtained in the study showed that the extension of the irradiation time to over 30 minutes (TiO_2) and over 45 minutes (ZnO) during photocatalysis does not lead to increased removal of contaminants from the dairy wastewater. It was also demonstrated that the increase in the doses of both photocatalysts does not lead to the increase in the efficiency of their treatment. In the case of treatment of dairy wastewater with TiO_2 , the photocatalysis occurred most effectively for its dose of 10 g/dm^3 . Removal rates for COD, TOC and total nitrogen were 58% (1670 mg/dm^3), 62% (450 mg/dm^3) and 56% (128 mg/dm^3), respectively. Replacing titanium dioxide with zinc oxide ($\text{ZnO} - 2 \text{ g/dm}^3$) in the photocatalysis process allowed for obtaining higher degrees of removal of contaminants determined as COD, TOC and total nitrogen to the level of 77.8% (870 mg/dm^3), 62% (445 mg/dm^3) and 52% (139 mg/dm^3), respectively. Since both photocatalysts were supplied to the photoreactor in the form of a suspension, the membrane in the next reactor represented an efficient barrier for their particles. It was observed that higher volumetric stream of the permeate was obtained during the process of low-pressure membrane filtration of sewage initially treated in the process of photocatalysis with titanium dioxide ($4.6 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s} - \text{TiO}_2$ and $4.1 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s} - \text{ZnO}$). It was found that the ultrafiltration process in the case of the feed material with TiO_2 led to the reduction in COD, TOC and total nitrogen by 78% (370 mg/dm^3), 72% (126 mg/dm^3) and 40% (80 mg/dm^3). Slightly better quality of permeate was obtained when the feed material contained ZnO powder. Degree of retention of the contaminants COD, TOC and total nitrogen were 68% (280 mg/dm^3), 66% (143 mg/dm^3) and 42% (76 mg/dm^3), respectively.

Słowa kluczowe:

ścieki mleczarskie, fotokataliza, TiO_2 , ZnO , zaawansowane metody utleniania, ultrafiltracja

Keywords:

dairy wastewater, photocatalysis, TiO_2 , ZnO , advanced oxidation process, ultrafiltration



Effect of Chitin Modification on the Sorption Efficiency of Reactive Black 5 Dye

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1. Introduction

Wastewater treatment from various industries is now a big challenge for scientists. The regulations, which limit the amount of pollution discharged to receivers, are becoming stricter each year and definitely do not make this task easier. Industrial wastewater contains many organic and inorganic compounds that are by-products or residues of technological processes.

Colored wastewater from the textile industry are particularly problematic. Dyes are chemical compounds with a complex structure that significantly hampers the process of removing them from industrial wastewater. Around $7 \cdot 10^5$ tons of dyes are produced annually for the world's textile, paper and tanning industry (Robinson et al. 2001). Due to the low susceptibility to staining of some materials, only about 60-90% of the dye contained in the dyeing bath binds to the fiber, and what is more, the process consumes 80-250 dm³ of water for 1 kg of the colored product (Janeczko & Ay 2007). Due to the different susceptibility of materials to dyeing and high solubility of dyes, 10-50% of them get into sewage after dyeing process (Burkinshaw & Kabambe 2011). Conventional wastewater treatment systems are characterized by low efficiency of removal of this type of compounds, therefore 10-15% of dyes get to the natural environment (Robinson et al. 2001). Thus, large amounts of dyes with insufficiently purified waste water leak into the environment.

The penetration of dyes into the aquatic environment not only worsens the visual values, but above all disturbs the biological balance of the ecosystem, by limiting the light transmission and inhibiting photosynthesis in plants. Dyes are not biodegradable, and many of them have a toxic effect on living organisms (Machado et al. 2011). Therefore, it is very important to look for innovative methods that allow for the effective removal of these hazardous substances from wastewater.

Physical, chemical and biological methods of sewage discoloration have been proposed over the last few decades. Among these methods, adsorption is one of the most commonly used and provides satisfactory efficiency.

Until now, activated carbon was the most commonly used adsorbent. The use of this adsorbent on a technical scale is, however, unprofitable, as the production and regeneration costs are high (Filipkowska & Józwiak 2013). For this reason, many scientists conduct research in search of cheaper, widely available unconventional substitutes. Recently, chitin is becoming more and more popular among sorbents. Chitin is one of the most widespread biopolymers in nature (Filipkowska 2005). According to literature data, the annual global production of chitin by living organisms reaches even 10^{11} tons (Je & Kim 2006). However, all kinds of waste from various industry sectors are not always characterized by a high sorption capacity for dyes. Therefore, various methods of modifying potential sorbents are sought to improve this ability.

In this article, research was undertaken in order to increase the adsorptive capacity of chitin in relation to the Reactive Black 5 dye. For this purpose, the effects of microwaves, magnetic field, ultrasound and ozone was used to modify the sorbent.

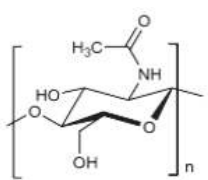
2. Materials and methods

2.1. Characteristics and sorbent preparation

2.1.1. Chitin

Chitin in the form of flakes were purchased from BioLog company. Characteristics of adsorbents were presented in Table 1.

Table 1. Characteristics of chitin
Tabela 1. Chatakterstyka chityny

Chitin	
Structural formula	
Deacetylation degree	< 15%
Origin of the material	Shrimp shells

2.1.2. Chitin modified with ultrasound

Two 200 ml beakers were filled with 5 g of unmodified chitin each and then 50 ml of distilled water was added to each of them. The beakers were then placed in the ultrasound generator for 15 minutes, setting the device's power to 350 W (beaker No. 1) and 700 W (beaker No. 2). Is-1K washer by InterSonic, which generates ultrasound at the frequency of 35 kHz, was used as the ultrasound source. After the process, the chitin was drained and dried.

2.1.3. Chitin modified with microwaves

The Amica microwave with a maximum power of 700 W was used for microwave emission. 5 g of chitin and 50 g of distilled water were weighed into beaker No. 3 and 4 in order to cause modification. The beakers were placed in the microwave for 5 minutes, setting its power to 50%, i.e. about 350 W, in the case of beaker 3 and 100%, i.e. about 700 W, in the case of beaker 4. After modification, the sorbent was drained and left to dry.

2.1.4. Chitin modifies with magnetic field

In order to perform modification of the magnetic field, 5 g of chitin was weighed and placed on watch glasses. The glasses were then placed for one hour in a magnetic field at the intensity of: 15 mT (glass nr 1) and 30 mT (glass nr 2).

2.1.5. Ozone modified chitin

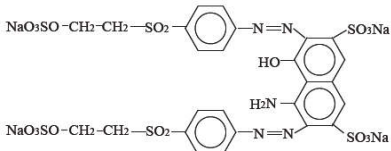
To each of two 200 ml beakers 5 g of chitin was weighted on an analytical balance and then 100 ml of distilled water was added to each of them. Both of the solutions were then transferred to the two separate reaction vessels of the ozonation plant. First sample was then subjected to ozone for 5 minutes, which gives 1 g of O₃, whereas the second sample was subjected to ozone for 10 minutes, which results in the dose of 2 g of O₃. After the ozonation process the chitin was filtered and dried at temperature of 100°C. The installation used for the process of ozonation in the research consisted of two oxygen generators, ozone concentration meter, rotameter, reaction vessel with a capacity of 200 ml and post-reaction ozone destructor.

2.2. Dye characteristics and preparation

The study was conducted with anionic dye Reactive Black 5 (RB5), the structure and properties of which were presented in Table 2.

Table 2. Characteristics of RB5 dye

Tabela 2. Chatakterstyka barwnika RB5

Name	Reactive Black – RB 5
Chemical structure	C ₂₆ H ₂₁ N ₅ Na ₄ O ₁₉ S ₆
Structural formula	
Molecular weight	991,82 [g/mol]
λ_{\max}	600 nm
Character of dye	Acidic (anionic - reactive)
Type of chromophore group	azo
Type of active groups	vinylsulfone

In order to prepare a working solution, 1 g of pure RB5 dye powder was weighed and transferred quantitatively into a 1 dm³ measuring flask. The flask was then filled up with distilled water. Dye concentration in the resultant solution reached 1000 mg/dm³.

2.3. Determination of the maximum sorption capacity

Unmodified and modified with each of the presented methods chitin was added to each of the five 100 ml Erlenmeyer flasks at a concentration of 1 g of dry mass/dm³ and then solutions of the dye with concentrations: 10, 20, 30, 50, 75, 100, 150, 200 and 300 mgRB5/dm³ were added at the pH of 4. Corrections of the reactions were carried out using aqueous solutions of NaOH and HCl. The flasks were then placed on a laboratory shaker whose rotational speed was set to 130 rpm.

2.4. Calculation methodology

The dependence was used to calculate the amount of sorbed dye:

$$Q_s = \frac{C_0 - C_s}{m} \quad (1)$$

Q_s – mass of the dye removed from the solution (mg/g d.m.),

m – concentration of chitin (g d.m./dm³),

C_0 – initial concentration of dye in the sample (mg/dm³),

C_s – concentration of the dye after the sorption process (mg/dm³).

The Langmuir adsorption isotherm (2) were used to determine the maximum sorption capacity of the sorbents tested.

$$Q = \frac{q_{\max} \cdot K_c \cdot C}{1 + K_c \cdot C} \quad (2)$$

Q – amount of dye adsorbed by 1 g d.m. of the sorbent (mg/g d.m.),

C – removed substance concentration in a steady state (mg/dm³),

K_c – constant (dm³/g d.m.),

q_{\max} – maximum sorption capacity (mg/g d.m.).

3. Overview and discussion on results

3.1. Maximum chitin sorption capacity

In the studies to describe the adsorption of RB 5 dye to chitin, the Langmuir model was used. Table 3 shows the constants determined with its application. Considering the values of the matching factor R^2 , it can be concluded that the Langmuir isotherm describes the results very well.

Table 3. Constants determined with the use of Langmuir adsorption model

Tabela 3. Stałe wyznaczone z zastosowaniem modelu adsorpcji Langmuira

Sorbent		Constant		
		q_{\max} [mg/g d.m.]	K_c [dm ³ /g d.m.]	R^2
Unmodified chitin		30,37	0,80	0,9856
Chitin modified with ultrasound	150 W	29,55	1,29	0,9825
	300 W	27,29	0,92	0,9948
Chitin modified with microwaves	350 W	27,32	1,17	0,9980
	700 W	27,79	1,05	0,9970
Chitin modified with magnetic field	15 mT	38,40	0,38	0,9611
	30 mT	33,66	0,70	0,9673
Ozone modified chitin	1 g O ₂	18,36	0,41	0,9800
	2 g O ₂	13,37	0,11	0,9783

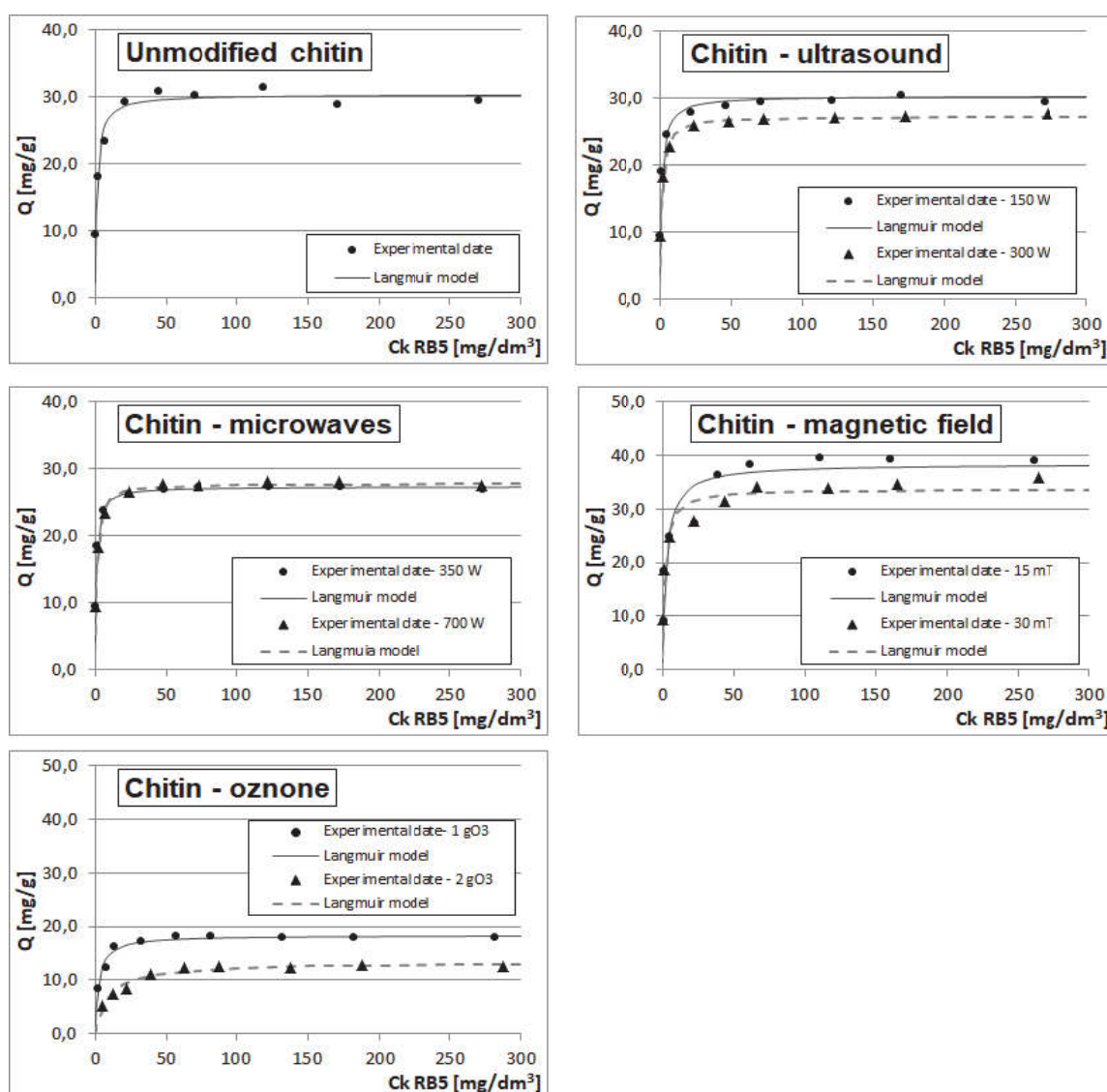


Fig. 1. Sorption capacities of unmodified and modified – RB5 dye
Rys. 1. Pojemności sorpcyjne chityny niemodyfikowanej i modyfikowanej – barwnik RB5

The highest sorption capacity was obtained during adsorption on chitin modified with magnetic field (Table 1, Figure 1). In the case of a field of 15 mT, it was 38.40 mg RB5/g d.m. and was over 25% higher than the maximum sorption capacity of unmodified chitin, whereas for modification with 30 mT field the result was 33.66 mg RB5/g d.m., which was higher by approx. 11% relative to the sorbent without modification. Slightly weaker results were noted in the case of dye removal using ultrasound-modified chitin and using microwaves (Table 1, Figure 1). In the

first case, a better effect was obtained for the ultrasound modified sorbent when setting the device power at 350 W. It was only less than 3% lower than the result obtained for unmodified chitin and was 29.55 mg RB5/g d.m. The sorption capacities obtained during the removal of RB5 on a sorbent modified with microwaves of 150 and 300 W were similar: 27.32 and 27.79 mg RB5/g d.m. Significantly lower sorption capacities were noted for ozone-modified chitin, the lowest of which was obtained with 2 g of O₃ (Table 1, Figure 1). It was only 13.17 mg RB5/g d.m. and it was 56.6% lower than the unmodified chitin capacity. Little more was detected during the sorption chitin treated with 1 g O₃ – 18.36 RB5 mg/g d.m.

3.2. Sorption using unmodified chitin

As an unconventional sorbent, chitin gives satisfactory results. The initial concentration of the solution had a major influence on the process efficiency, which was noticed by Yagub et al. (2014). Only at low concentrations of the dye in the solution more than 90% removal efficiency can be obtained. An increase in the initial concentration from 10 mg/dm³ to 300 mg/dm³ resulted in a decrease in dye removal from approx. 95% to 10%. Relatively to anionic dyes, chitin has good adsorptive properties. The structure of chitin contains mostly acetamide groups, whereas the amino groups are only about 15%. Both of those groups play an important role in dye adsorption. In acidic environment these groups are protonated according to the reaction: $R-NHCOCH_3 + H^+X^- \leftrightarrow R-NH_2^+COCH_3X^-$ and the affinity of proton to amino groups is bigger than to acetamide groups. In turn, the anionic dye contains negatively charged functional groups, which causes electrostatic attraction of the adsorbent and adsorbate (Filipkowska & Rodziewicz 2012). A similar sorption capacity in relation to the RB 5 dyestuff obtained in the tests is demonstrated by cotton stalks. Tunç Ö in his research, and others (2009) received an adsorption capacity of 30.70 mg/g d.m. with a solution of 1 pH and 35°C. They also noted the relationship between the initial dye concentration in the solution and the removal efficiency. At higher concentrations, efficiency decreases due to the almost complete use of active sites on the adsorbent surface.

3.3. Sorption with the use of ultrasound modified chitin

Seeking a way to increase the RB5 dye removing efficiency in the adsorption process on chitin, 4 modifications of this sorbent were carried out in this study. One of them was a modification using ultrasounds. The results obtained indicate that ultrasound does not improve the chitin adsorptive capacity. Considering the final concentrations of dyes in solutions obtained after the adsorption process on 150 W ultrasound-modified chitin and during adsorption on unmodified chitin, it can be concluded that in the first case only at concentrations of 10-30 mg/dm³ better results were obtained. For initial concentrations of 10, 20 and 30 mg/dm³ efficiencies were obtained successively: 95, 95 and 82% of dye removal on chitin treated with ultrasound and 94, 91 and 76% on chitin without modification. Analyzing the remaining results, during the sorption on chitin modified with ultrasounds, both 150 W and 300 W, the process efficiency is lower than during adsorption on the non-modified chitin. According to the values presented in Table 1, the maximum sorption volumes of the ultrasound modified chitin are 29.55 mg RB5/g d.m. for ultrasounds with a capacity of 150 W and 27.29 mg RB5/g d.m., i.e. by about 10% less, for ultrasounds with a power of 300 W. Thus, the power of the sound waves generated affects the sorptive capacity of the sorbent used in the studies. This is also confirmed by Lach J. et al. (2013) who studied cadmium sorption on activated carbon subjected to ultrasound with different vibration amplitudes. According to the researchers, ultrasounds with a higher sound power level during 10, 15 and 20 minutes cause changes in activated carbon resulting in reduced adsorption of cadmium ions. They explain that the effect of very high energy waves causes destructive changes in the residues of oxygen on the surface of activated carbon. They also observed the destruction of coal grains (dust in solution), especially at higher intensities (Lach and others 2013). Ultrasounds evoke a series of fast compresses and expansions in solid bodies, which create microscopic channels in their structure (Fijałkowska et al. 2015). J. Mason et al. (2011) noticed that cavitation bubbles forming and disintegrating during this process have a big influence on mechanical and chemical changes. In the case of chitin, this may lead to the breaking of hydrogen bonds or the disconnection of amide groups responsible for good sorption properties with respect to anionic dyes. The smaller the ultrasonic power,

the less physicochemical changes occur in the structure of chitin, therefore the efficiency of dye removal using 150 W ultrasound-modified chitin is higher than in the case of 300 W power.

3.4. Sorption on chitin modified with microwaves

Another modification carried out on the sorbent in the present studies was the microwave treatment of chitin. Only at lower initial concentrations of RB5 can there be a slight improvement in the efficiency of removal on modified chitin compared to normal chitin. At a concentration of 10 mg/dm³ during sorption on chitin modified with microwaves, when the device was set to 700 W, the result was 0.02 mg/dm³ lower. Higher efficiency was also obtained for a concentration of 20 mg/dm³ for both 350 W and 700 W, which increased by 14.13% and 1.1% respectively as compared to the unmodified sorbent. Also, about 7% of dye more was adsorbed on chitin modified with microwaves of 350 W at an initial concentration of 30 mg/dm³, where the result was 6.20 mg RB/dm³ in the final solution. Analyzing the results presented in Table 1, it can be noticed that sorption on 350 W modified chitin, compared to the 700 W microwaved chitin, was only more effective at initial concentrations of 20 and 30 mg RB5/dm³. At the remaining concentrations, better results were noted for higher power, which translates to a higher sorption capacity by 0.47 mg/g d.m. of the microwave-treated chitin with the device set to 700 W power. As noted by Połowiński (2001), the treated polymers undergo a degradation process, which may be accompanied by destruction processes. In this study, chitin was exposed to sonic degradation in the electromagnetic field and to thermal degradation associated with elevated temperature. The modified chitin was in an aqueous medium, which could cause the breaking of amide and hydrogen bonds during the operation of the microwave, responsible for good sorption properties. In addition, the elevated temperature may cause cracking of C-C bonds, which in turn leads to the formation of free radicals. The higher the temperature, the more intensive the process. Consequently, it is possible that free radicals improve the adsorptive capacity of chitin in relation to dyes. Perhaps this is why in our research during sorption on chitin modified with higher power microwaves, a slight increase in the efficiency of RB 5 removal in relation to sorption on chitin modified with 350 W microwaves was observed. Considering the fact that the sorption capacity of

modified chitin in relation to the unmodified one has decreased slightly, it can be concluded that the degradation process, including its accompanying phenomena, did not occur to a small extent. Bathen (2003) in his article noted that distilled water may limit the ability of microwave penetration, which may also explain the above observation. The lack of electromagnetic influence of microwave radiation on the adsorptive capacity of activated carbons was noticed by Ania et al. (2005). They showed that the heat-treated sorbent using the 2450 MHz microwave method retains its porous structure, and the size of the micropores did not differ significantly from those that the sorbent had before the modification. Nair and others (2016) came to a different conclusion. Microwave-treated bisected basal protein (*Prosopis juliflora*) significantly increased its porosity. Thanks to this, the sorption capacity of biocarbon with respect to Remazol Brilliant Blue R has more than doubled, reaching 83.33 mg/g d.m. Thus, it can be concluded that microwaves have different effects, depending on the initial structure of the material being treated.

3.5. Sorption on chitin modified with magnetic field

Adsorption of the dye on chitin modified with magnetic field gave the best results among all the methods used in this research. A little higher sorption efficiency on unmodified chitin in relation to chitin subjected to this modification was recorded only at the initial concentration of 10 and 50 mg RB5/dm³. The efficiency was 95.2% and 58.6% for unmodified chitin, and respectively 91.3 and 93.4% as well as 54.4% and 55.5% for the chitin modified magnetic field with the intensity of 15 mT and 30 mT were obtained. removing the dye. In the case of other concentrations, higher efficiency during adsorption on chitin modified with magnetic field was noted. These results are reflected in the maximum sorption capacity determined using the Langmuir model. For chitin treated with a field of 15 mT, it is 38.02 mg/g d.m. and is higher by 13% than the volume of chitin modified with a field of 30 mT, of 33.66 mg/g d.m. The effectiveness of RB5 removal is influenced by both the initial concentration in the solution and the type of sorbent used. It can be noted that in the case of concentrations of 10-50 mg/dm³, chitin modified with a magnetic field of higher intensity works better, whereas at concentrations of 75-300 mg/dm³ chitin modified with a smaller magnetic field gives better results. Differences in the amount of adsorbed dye from solutions with

lower concentrations are small – they differ a maximum of 0.53 mg/dm^3 with respect to both modifications by magnetic field. However, at higher concentrations these differences are more visible and range from 3 to 5.54 mg/dm^3 . This is reflected in the maximum sorption capacity, where for the chitin modified with a magnetic field of lower intensity, the result was 13% higher than for the chitin subjected to the magnetic field of higher induction. Positive influence of the magnetic field on the sorbent is also confirmed by Samonin et al. (2012), who investigated the effectiveness of sorption of benzene vapors on active carbon subjected to modification with a magnetic field. According to the present research, the magnetic field caused a 14% increase in the sorption of benzene vapors by activated carbon.

3.6. Sorption on ozone-modified chitin

The least effective modification of chitin carried out in this study was ozonation. Removal of the dye by using ozone-modified chitin in 1 g O_3 and 2 g O_3 was much less efficient than removal by using unmodified chitin. Depending on the initial concentration, differences in efficiency were very high. The biggest difference was observed for the initial concentration of 20 mg RB5/dm^3 . After adsorption on the unmodified chitin, less dye was left in the solution than after adsorption on chitin treated with 1 g and 2 g of O_3 , respectively 5.74 and 10.82 mg/dm^3 . The obtained maximum adsorptive capacities relative to RB5 amounted to: 18.36 mg/g d.m. in the case of modified chitin with 1 g ozone, and 13.17 mg/g d.m. in the case of modified chitin with 2 g ozone. Longer time of ozonation worsened the sorption capacity of chitin by almost 40% in relation to the shorter time. The highest removal efficiency, as with other modifications, was obtained at an initial concentration of 10 mg RB5/dm^3 . For chitin treated with 1 g O_3 it was 82.9%, whereas for chitin treated with 2 g O_3 only 52.4%. In comparison, at the same initial concentration unmodified chitin adsorbed as much as 95.2% of the dye. The biggest difference in the amount of removed RB 5 was observed for samples with an initial concentration of 150 mg/dm^3 . The ozone-modified chitin during 5 and 10 minutes removed respectively by 13.55 and $19.13 \text{ mg RB5/dm}^3$ less from the solution than chitin without modification. Significantly weaker results from among ozonated sorbents were obtained during sorption on chitin modified for 10 minutes. However,

taking the performances obtained in both cases into account, there is a reduction in differences with the increase in the initial concentration of the dye in solution. For example, with an initial concentration of 10 mg RB5/dm³, the difference was 30.5%, and at a concentration of 300 mg/dm³ only 1,8%. As is well known, ozone is a very strong oxidant. Direct or indirect, through the generation of radicals, it reacts with most organic compounds (Lucas et al. 2010). In contrast to the other modifications used in this study, which were physical modifications, ozonation qualifies as chemical modification. During this process, some of the hydroxyl groups of the glucose units are oxidized, thereby carboxyl or carbonyl groups are formed. The formation of carboxylic groups may particularly adversely affect the sorption of the anionic RB5 dye, as they have a negative charge. Therefore, there may be electrostatic repulsion between the dye molecule and modified chitin (Józwiak et al. 2016). Furthermore, ozonation leads to partial depolymerization of chitin and to the loosening or cracking of some bonds, which may also cause deterioration of sorption properties (Ostrowska-Czubenko and others 2016). Most likely, the bonds responsible for the good sorptive properties of chitin, such as hydrogen bonds, were ruptured. The intensity of these processes, as noted earlier, increases with the prolongation of the ozonation time and increasing the dose of O₃. Alvarez et al. (2004) in their research used activated carbon activated treated with ozone as a sorbent for phenol. As in these studies, it turned out that the longer modification time, the lower sorption capacity. In the study they explained that during ozonation acidic groups are formed on the surface of activated carbons, which in the case of phenol sorption is a detrimental phenomenon.

4. Conclusions

In this paper modifications of chitin were carried out using ultrasound, microwaves, magnetic field and ozone in order to investigate the possibility of increasing the adsorptive capacity of this sorbent in relation to the RB5 dye. As a result of proper modification, the maximum sorption capacity of chitin in relation to the RB5 anionic dye may change. Among all the modifications which were carried out, chitin modified with a magnetic field of 15 mT induction had the highest sorption capacity – 38.02 mg RB5/dm³. It was 25% higher than the maximum sorption

capacity of unmodified chitin. The lowest sorption capacity, 13.17 mg RB5/dm³, was observed for the chitin which was treated with ozone for 10 minutes. Ozonation has a negative effect on the sorption capacity of chitin by its partial depolymerisation and bond disruption, such as hydrogen bonds, which are responsible for this ability. The effectiveness of the RB5 dye sorption on chitin was affected by the initial solution concentration and the intensity of the modifying agent.

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Wykorzystanie niekonwencjonalnych systemów do usuwania barwnika RB5

Streszczenie

Na potrzeby światowego przemysłu włókienniczego, garbarskiego i papierniczego wytwarzanych jest rocznie około $7 \cdot 10^5$ ton barwników. Z powodu niskiej podatności niektórych materiałów na barwienie i wysokiej rozpuszczalności barwników nawet do 50% z nich po procesie barwienia przedostaje się do ścieków, z czego około 15% trafia do środowiska naturalnego. Substancje barwne w większości są trudno-biodegradowalne, więc dekoloryzacja ścieków za pomocą metod biologicznych stosowanych na konwencjonalnych oczyszczalniach ścieków nie jest skuteczna.

Jedną z efektywniejszych, tańszych i przyjaznych dla środowiska metod usuwania barwników ze ścieków jest proces adsorpcji. Pomimo tego jej praktyczne zastosowanie napotyka na szereg ograniczeń, głównie z uwagi na wysoki koszt komercyjnych sorbentów i trudności w ich regeneracji. W związku z tym wiele badań koncentruje się na poszukiwaniu sorbentów tanich a zarazem efektywnych.

W ostatnim czasie coraz większym zainteresowaniem wśród sorbentów cieszy się chityna, która jest jednym z najbardziej rozpowszechnionych biopolimerów w przyrodzie. Według danych literaturowych roczna światowa produkcja chityny przez organizmy żywe osiąga nawet 10^{11} ton, a z odpadów przetwórstwa bezkręgowców morskich rocznie na świecie pozyskuje się 120 000-200 000 ton chityny. Jednak wszelkiego rodzaju odpady z różnych sektorów przemysłu nie zawsze charakteryzują się wysoką pojemnością sorpcyjną względem barwników. W związku z tym poszukuje się różnych metod modyfikacji potencjalnych sorbentów w celu poprawienia tej zdolności.

W pracy zbadano możliwość zwiększenia zdolności adsorpcyjnej chityny względem barwnika RB5 poprzez wstępną modyfikację sorbentu. Jako czynnik modyfikujący chitynę przed sorpcją wykorzystano ultradźwięki, mikrofałę, pole magnetyczne i ozonowanie. W wyniku odpowiedniej modyfikacji maksymalna pojemność sorpcyjna chityny względem barwnika anionowego Reactive Black 5 uległa zmianie. Stwierdzono, iż na efektywność sorpcji barwnika RB 5 na chitynie miały wpływ początkowe stężenie roztworu oraz rodzaj czynnika modyfikującego. Spośród testowanych sorbentów największą pojem-

nością sorpcyjną wynoszącą 38,02 mg/dm³ charakteryzowała się chityna modyfikowana polem magnetycznym o indukcji 15 mT. Efektywność usuwania barwnika anionowego na tym sorbencie była wyższa od maksymalnej pojemności sorpcyjnej chityny niemodyfikowanej o 25%. W celu określenia dokładnego wpływu pola magnetycznego na chitynę, należałoby przeprowadzić dodatkowe i bardziej szczegółowe badania. Natomiast najniższą pojemność sorpcyjną odnotowano dla chityny poddanej działaniu ozonu w ilości 2 g O₃, gdzie uzyskano wynik 13,17 mg/dm³. Ozonowanie negatywnie wpłynęło na zdolność sorpcyjną chityny poprzez jej częściową depolimeryzację oraz rozrywanie wiązań, takich jak wiązania wodorowe, odpowiedzialnych za sorpcję zanieczyszczeń w formie anionów.

Abstract

Around $7 \cdot 10^5$ tons of dyes are produced annually to supply for the needs of the global textile, tanning and paper industry. Due to the low susceptibility of some materials to dyeing process and high solubility of dyes, up to 50% get into sewage, about 15% of which goes to the natural environment. Colored substances are mostly difficult to biodegrade, so decolorization of wastewater using biological methods used on conventional wastewater treatment plants is not effective. One of the most effective, cheap and environmentally friendly methods of removing dyes from wastewater is the adsorption process. However, the practical application of this process encounters a number of limitations, mainly due to the high cost of commercial sorbents and difficulties in their regeneration. Therefore, many studies focus on the search for cheap and effective sorbents. Recently, chitin, which is one of the most widespread biopolymers in nature, is becoming more and more popular among sorbents. According to literature data, the annual global production of chitin by living organisms reaches up to 10^{11} tons and 120,000-200,000 tons of chitin are obtained in the world from the waste of marine invertebrates processing annually. However, not all kinds of waste from various industry sectors are characterized by a high sorption capacity for dyes. That encourages seeking various methods of modifying potential sorbents to improve this ability. The study investigated the possibility of increasing the adsorption capacity of chitin in relation to the RB5 dye by initial modification of the sorbent. Modifying factors such as ultrasound, microwaves, magnetic field and ozone were used. Due to appropriate modification, the maximum sorption capacity of chitin in relation to the anionic dye Reactive Black 5 has changed. It was found that the effectiveness of the RB5 dye on chitin was influenced by the initial concentration of the solution and the type of modifying agent. Among the tested sorbents, the highest sorption capacity of 38.02 mg/dm³ was obtained for chitin modified with magnetic field at an induc-

tion of 15 mT. The efficiency of removing the anionic dye on this sorbent was higher than the maximum sorption capacity of unmodified chitin by 25%. In order to determine the exact effect of the magnetic field on chitin, additional and more detailed studies would have to be carried out. The lowest sorption capacity was obtained for chitin treated with ozone in the amount of 2 g of O₃, where the result of 13.17 mg/dm³ was obtained. Ozonation affected negatively the sorption capacity of chitin by its partial depolymerisation and disruption of bonds, such as hydrogen bonds, responsible for the sorption of impurities in the form of anions.

Słowa kluczowe:

sorpcja, barwnik, RB5, ultradźwięki, pole magnetyczne, mikrofałe, ozon, chityn

Keywords:

sorption, dye, RB5, ultrasounds, magnetic field, microwaves, ozone, chitin



Influence of Leachate Quality on Reverse Osmosis Performance

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1. Introduction

Landfills are still the most popular method for municipal waste disposal. One of the main environmental problems arising from solid waste landfilling is the generation of landfill leachate from original moisture in solid waste and percolation of rainwater through the final cover soil (Theepharaksapan et al. 2011). Production of landfill leachate begins with introducing moistened waste into disposal area and continues for several decades following the landfill closure (Hasar et al. 2009). The chemical and microbiological composition of landfill leachate is complex and variable, since apart from being dependent upon features of residual deposit, it is influenced by environmental conditions, the operational manner of the landfill and by dynamics of the decomposition process that occurs inside the cells (Yao 2017, El-Fadel et al. 2002, Kjeldsen et al. 2002). According to Christensen et al. (2001) and Moravia et al. (2013) one of characteristic features of leachate is presence of four groups of pollutants: dissolved organic matter, macro inorganic compounds, heavy metals and xenobiotic organic compounds originating from chemical and domestic residue present at low concentrations (aromatic hydrocarbons, phenols, pesticides, etc.) and microorganisms. Since the composition of leachate consists of a wide range contaminants, it can be toxic for environmental and human health (Hasar et al. 2009). For this reason, leachate treatment is a major issue in the context of landfill management and treating design should take into account not only quantity and quality but also variation over time, in line mainly with landfill age (Morello et al.

2016). For young leachate (from landfills under 5 years of exploitation), which contains mostly organic substances in biodegradable form, nutrients and suspended solids, a conventional biological process could be effective (Rukapan et al. 2012, Theepharaksapan et al. 2011, Yahmed et al. 2009, Nowak et al. 2016). For old landfills, most of the leached organic compounds are hardly- or non-biodegradable forms and such a leachate should be treated by physico-chemical processes or by a combination of biological and physico-chemical processes (Fudala-Książek et al. 2016, Rukapan et al. 2012). Among another process, the reverse osmosis (RO) seems to be one of the most promising and efficient method for landfill leachate treatment. The application of RO for treatment of stabilized leachate from Lipówka landfill (Poland) gave for COD a 97% removal efficiency (Peters 1998). During the treatment of stabilized leachate from Hedekosga (Sweden), the maximum removal of COD and N-NH₄⁺ with initial concentrations of 1,254 and 541 mg/l was found to be 95 and 82%, respectively (Thörneby et al. 2003). Reverse osmosis was also employed for the treatment of leachate from Wijssler landfill (The Netherlands) The reduction of COD and N-NH₄⁺ was found to be 98% with the initial concentrations of 335 and 140 mg/l, respectively (Kurniawan et al. 2006).

Even though literature review indicates that leachate treatment by RO process is well studied topic, there are no wider and systematic investigations and comparison on the RO performance for young and stabilized leachate. Fouling of reverse osmosis membrane, during leachate treatment, differs for young and stabilized leachate due to the fact, that chemical composition of these leachate differs from each other. The differences in RO performance influence on efficiency of reverse osmosis system. Besides, most of the papers describe the efficiency of RO systems based on laboratory tests conducted on lower flows and lower pressures, which does not reflect the actual operating conditions of the system (Hasar et al. 2009, Theepharaksapan et al. 2011, Rukapan et al. 2015). In addition, most studies are conducted on easy-to-use flat membranes while in the actual leachate treatment conditions most commonly recommended are tubular membranes with parallel flow (Bohdziewicz et al. 2010, Wang et al. 2014). Therefore the main objective of this work is to evaluate the influence the two kind of leachate (young and stabilized) on reverse osmosis performance during their treatment by the use of the

RO system which reflects the actual operation circumstances of reverse osmosis units exploited on municipal landfills.

The use of reverse osmosis for landfill leachate treatment may involve various difficulties associated with both the nature of the leachate (variable quantity and quality over time) and the specificity of the reverse osmosis process (scaling, fouling, adsorption on the membrane surface). Therefore realization of this study is of practical importance to the operator of the leachate treatment plant, because it will evaluate the effectiveness of the unit reverse osmosis process in the treatment of landfill leachates and validity of its use for both young and stabilized leachate.

2. Materials and methods

The leachate samples used in this study were collected directly from the municipal landfill site localized in northern-eastern part of Poland, at the northern latitude 53°50'55'' and the eastern longitude 22°19'02''. The young leachate (ON) was taken from landfill cell, which is exploited since three years. The mature stabilized leachate (OS) was taken from landfill cell with over 20 years of exploitation. The samples both of young and mature leachate were collected three times. Collected samples were transported to the laboratory and stored in dark at 4°C to minimize biological and chemical changes.

In leachate samples the following parameters were determined: electro-conductivity (EC), chemical oxygen demand (COD), biological oxygen demand (BOD), nitrogen ammonia N-NH₄; total nitrogen (TN), total phosphorus (TP), sulfate (SO₄²⁻), chloride (Cl⁻), calcium (Ca²⁺) and manganese (Mg²⁺). All determination were done in accordance with APHA (APHA 1995).

The evaluation of the reverse osmosis system operating parameters was carried out separately for young leachate and stabilized leachate. The reverse osmosis process was carried out using the RO20NS.1 – a laboratory reverse osmosis system, which was designed and constructed in such a way as to reflect the actual operation of reverse osmosis units running in municipal waste landfills. The basic elements of the laboratory system were the Micro 240 PCI membrane module and the high pressure pump. In addition, the system was equipped with a pump pulsation damper, a flow meter, safety valve and two pressure gauges enabling

pressure measurement on the liquid entry side to the system and to control the RO process pressure. The leachate treatment process was carried out in a cross-flow system with concentrate recirculation to the tank supplying the effluents to the RO system. The recovery rate was set at 60/40 (60% permeate and 40% concentrate). Before entering the RO system, landfill leachate were acidified to pH 6.5 and subjected to filtration successively on a 50 and 5 μm filter. The RO process was carried out at the feed rate of 18 dm³/min, 25 ° C and constant pressure of 3.8 MPa. The scheme of research installation is given in Figure 1.

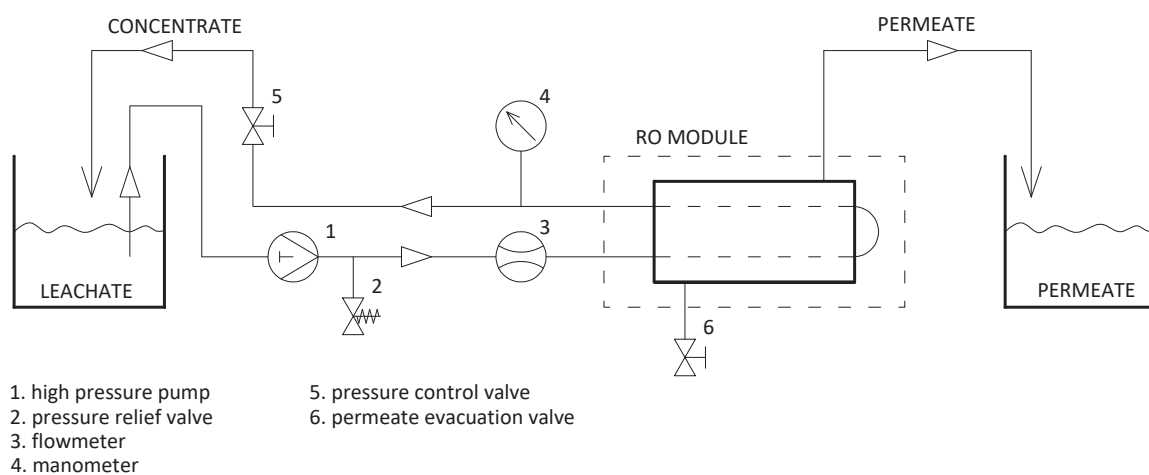


Fig. 1. Scheme of RO installation

Rys.1. Schemat instalacji RO

The performance characteristics of the reverse osmosis system were made on the basis of the following calculations:

- permeate flux (J):

$$J = k \cdot \left(\frac{V_p}{t \cdot S} \right) \quad (\text{L/m}^2 \cdot \text{h}) \quad (1)$$

where: V_p – permeate volume (L), t – time (h), S – membrane area (m²), k – temperature correction factor;

- removal (retention) rate of salt expressed as a electroconductivity value (R_{EC}):

$$R_{EC} = \left(1 - \frac{EC_p}{EC_n} \right) \cdot 100\% \quad (\%) \quad (2)$$

where: EC_p – electroconductivity of permeate (mS/cm),
 EC_n – electroconductivity of inlet (leachate) (mS/cm);

- concentration factor of EC in concentrate (CF_{EC}):

$$CF_{EC} = \frac{EC_c}{EC_n} \quad (3)$$

where: EC_c – electroconductivity of concentrate (mS/cm).

In order to assess the relationship between the quality of leachate directed to the RO system and its operating parameters, the analysis of variance (ANOVA) was carried out. The one-way ANOVA with one independent variable: kind of leachate (with two levels: young leachate, stabilized leachate) and 5 dependent variables (filtration time, J_{min} , J_{aver} , J_{max} , R_{EC}) was used for test. To facilitate the interpretation of the results, the average, minimum and maximum permeate flux during reverse osmosis process was also calculated.

3. Results and discussion

Table 1 presents the basic characteristics of young and stabilized leachate directed to the reverse osmosis system.

The leachate from the new disposal field (ON) are characterized by more than three times higher COD value and six times higher value of BOD compared to stabilized leachate (OS). This indicates a high share in the leachate of readily biodegradable organic substance with high molar mass (Rosik-Dulewska 2002). Younger leachate also had higher concentrations of total and ammonia nitrogen as well as total phosphorus as well as a higher value of conductivity. In both effluents, the concentration of magnesium and calcium ions, chlorides, sulphate and iron is maintained at a similar level.

The collected leachate samples were directed to the reverse osmosis system, with the osmotic filtration being carried out in three series, separately for young and stabilized leachate. The results obtained are shown in Figure 2 and Table 2.

Average permeate flux for stabilized leachate was 38.61 L/m²·h, and the time required to achieve the assumed 60% recovery rate was

5.27 h (Table 2). The biggest decrease in permeate flux occurred in the first hour of the system's operation, indicating the membrane blocking. In the final phase of the process permeate flux was on average 28.83 L/m²·h (50% of maximum permeate flux). At the 60% recovery rate, the EC concentration factor was reached at 2.01, which means that at 2.5 times the reduced volume of the concentrate, a two-fold increase in the electrolytic conductivity was achieved. The average rate of EC removal was 99.1%.

Table 1. Basic parameters of young (ON) and stabilized (OS) leachate directed to the reverse osmosis system

Tabela 1. Podstawowe parametry odcieku młodego (ON) i ustabilizowanego (OS) kierowanego na układ odwróconej osmozy

Parameter	Young leachate (ON) (mg/L)		Stabilized leachate (OS) (mg/L)	
	Average	Stand. dev.	Average	Stand. dev.
EC	15.37	2.73	7.89	3.71
COD	4623.3	1985.6	1443.3	1782.3
BOD	579.3	191.7	92.0	70.2
N-NH ₄ ⁺	763.3	127.4	231.7	145.8
TN	826.7	176.2	275.0	152.1
TP	16.13	1.62	0.82	1.04
SO ₄ ²⁻	235.7	152.5	376.9	278.0
Fe	2.73	1.97	4.30	1.75
Cl ⁻	1959.3	469.9	1388.8	825.6
Mg ²⁺	387.5	120.9	376.7	135.3
Ca ²⁺	469.5	50.2	446.8	23.7

All in mg/dm³ apart EC (mS/cm)

In the case of young leachate, the filtration time required to achieve the 60% recovery rate was longer and amounted to nearly 7 h, which was the result of a lower average permeate flux – 29.35 L/m²·h. As in the case of stabilized leachate, the largest drop in flux occurred in the first hour of filtration. However, the observed drop in permeate flux during filtration of young leachate was much larger; the final value of permeate flux was on average 19.39 L/m²·h (29% of maximum permeate flux). The value of concentration factor was 1.97 and the EC removal rate – 98.8%.

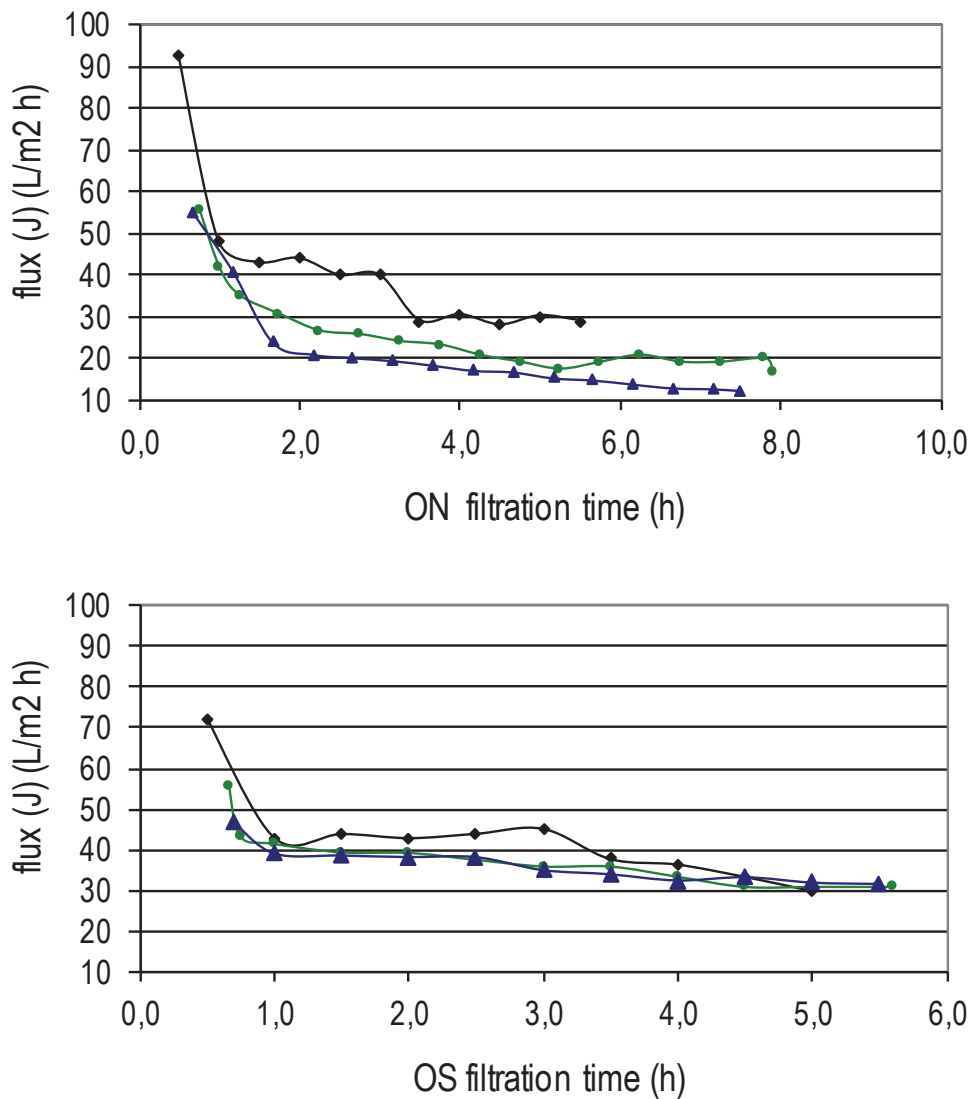


Fig. 2. The value of permeate flux during young (ON) and stabilized (OS) leachate filtration in reverse osmosis process

Rys. 2. Przepływ permeatu podczas filtracji odcieku młodego (ON) i ustabilizowanego (OS) w procesie odwróconej osmozy

Table 2. Characteristic of membrane performance according to kind of leachate
Tabela 2. Parametry pracy membrany w zależności od rodzaju kierowanych na nią odcieków

Parameter		Stabilized leachate (OS)	Young leachate (ON)	Average for all groups
		N = 3	N = 3	N = 6
Filtration time t (h)	Average	5.27	6.97	6.12
	Stand. dev.	0.49	1.29	1.28
Flux minimum J_{\min} (L/m ² ·h)	Average	28.83	19.39	24.11
	Stand. dev.	4.21	8.58	7.95
Flux average J_{aver} (L/m ² ·h)	Average	38.61	29.35	33.98
	Stand. dev.	3.25	10.60	8.65
Flux maximum J_{\max} (L/m ² ·h)	Average	58.05	67.82	62.94
	Stand. dev.	12.95	21.63	16.82
EC removal rate R_{EC} (%)	Average	99.1	98.6	98.8
	Stand. dev.	0.26	0.40	0.40
concentration factor CF	Average	2.01	1.97	1.99
	Stand. dev.	0.11	0.02	0.07

The main reason for the drop in permeate flux, observed both during osmotic filtration of young and stabilized leachate, was the process of fouling/scaling and the increase in osmotic pressure, caused by the increasing concentration difference between permeate and leachate/concentrate mix (Costa and Pinho 2005). Kabsch-Korbutowicz and Majewska-Nowak (1996) explain increased membrane blocking during filtration of young leachates by humic substances present in leachate. Their polyelectric nature facilitates binding of cations by these compounds (including Ca^{2+} , Mg^{2+}), which neutralizes their negative charge resulting from the deprotonation of H^+ ions and facilitates blocking of pores in negatively charged membrane. The carried out research shows that an important role in the neutralization of the charge of humic substances can also be played by N-NH_4^+ ions. Formed in this way complexes of inorganic ion with humic substances have, in addition to a neutral electric charge, a smaller solubility than free humic macromolecules, hence the polarization layer is formed faster at the membrane surface (Kabsch-Korbutowicz and Majewska-Nowak, 1996). For this reason, the filtration of solutions containing humic substances and inorganic cations

causes a decrease in membrane permeability. In addition, surface membrane studies carried out by Chon et al. (2012) indicated that N-NH_4^+ along with Fe^{3+} , Al^{3+} , Si^{4+} and Ca^{2+} are the main inorganic foulants on RO membranes. The conducted research indicates that the process of filtration of stabilized leachate is characterized by higher flow rates and smaller values of flux decline. When RO system receives leachate rich in humic substances, the removal of ammonium cations from it may bring beneficial effects in the form of reducing the membrane blocking and increasing value of permeate flux.

In order to assess the effect of leachate age on RO system performance, the analysis of variance (Tab. 3) and average values of RO system parameters were conducted (Tab. 2, Fig. 3).

Although the analysis of variance indicated the lack of statistically significant differences between the parameters of the reverse osmosis system work during filtration of young and stabilized leachates (Tab. 3), the analysis of average parameters of the system performance indicated a shorter filtration time – by more than one hour - of stabilized leachate, higher average permeate flux, higher EC removal rate and better concentration factor. The observed differences indicate that the filtration of stabilized leachate affects the better performance of the RO system compared to filtration of young leachate (Tab. 3, Fig. 3).

Table 3. Influence of kind (age) of leachate on reverse osmosis performance – variance analysis

Tabela 3. Wpływ rodzaju (wieku) odcieków na parametry pracy odwróconej osmozy – analiza wariancji

Parameter	SS Effect	df Effect	MS Effect	SS Error	df Error	MS Error	F	p
Filtration time t (min)	4.33	1	4.33	3.8	4.0	0.9	4.6	0.10
J_{\min} ($\text{L}/\text{m}^2\cdot\text{h}$)	133.7	1	133.7	182.6	4.0	45.7	2.9	0.16
J_{aver} ($\text{L}/\text{m}^2\cdot\text{h}$)	128.8	1	128.8	245.6	4.0	61.4	2.1	0.22
J_{\max} ($\text{L}/\text{m}^2\cdot\text{h}$)	143.1	1	143.1	1271	4.0	317.8	0.5	0.54
EC removal rate (%)	0.350	1	0.350	0.5	4.0	0.1	3.1	0.16

SS Effect – sum of squares between groups, MS Effect – mean square between groups, SS Error – sum of squares inside group, MS Error – mean sum of squares inside group, df – degrees of freedom, F – value of Test F, p – probability level

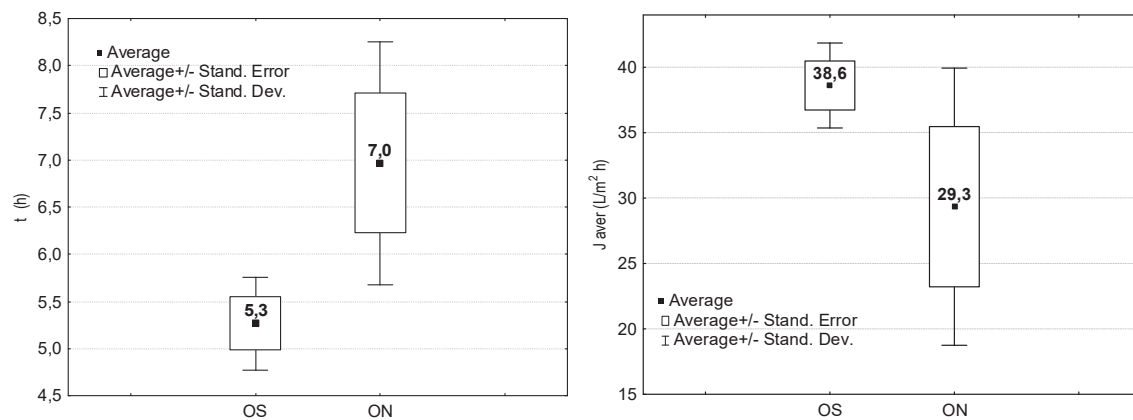


Fig. 3. Filtration time (t) and permeate average flux (J_{aver}) according to the kind of leachate

Rys. 3. Czas filtracji (h) i średni przepływ permeatu (J_{aver}) w zależności od rodzaju odcieków

4. Conclusions

Osmotic filtration of young leachate with high organic content is characterized by lower permeate flux rates and higher flux decline in comparison with stabilized leachate. Directing leachate from old disposal fields to the RO system caused an increase in the permeate flux (J_{aver} , J_{min}) and shortening the leachate filtration time. Higher ionic strength, characteristic for leachate from young landfills (ON), tends to block the pores of the membrane. In addition, the rate of salt retention is lower then. Moreover, high organic content in the leachate from young landfills, with a high concentration of cations, leads to an unfavorable phenomenon of neutralization of the membrane surface. The lower concentration of cations in the feed (including $N-NH_4^+$) limits the process of neutralization of humic substances. The humic substances not neutralized by cations, maintain their negative electric charge and do not deposit on the negatively charged surface of the membrane.

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Wpływ jakości odcieków na parametry pracy odwróconej osmozy

Streszczenie

W pracy przedstawiono wpływ odcieków ze składowisk o różnym czasie eksploatacji na parametry pracy odwróconej osmozy podczas ich oczyszczania. Do badań przyjęto niestabilizowane odcieki ze składowiska o 2-letnim czasie eksploatacji oraz odcieki ustabilizowane ze składowiska o czasie eksplo-

atacji przekraczającym 10 lat. Analizy prowadzono na układzie odwróconej osmozy, skonstruowanym w ten sposób by odzwierciedlać rzeczywiste warunki pracy układów eksploatowanych na składowiskach odpadów. Odcieki skierowano na układ RO zachowując podczas ich filtracji te same parametry pracy (temperatura, ciśnienie, przepływ, stopień odzysku oraz odczyn odcieków). Uzyskane wyniki wskazały, że proces filtracji odcieków ustabilizowanych charakteryzuje się lepszymi parametrami pracy układu RO, tj. krótszy czas filtracji, wyższy przepływ permeatu oraz wyższy stopień retencji soli. Większa zawartość substancji organicznych zawartych w odciekach młodych (nieustabilizowanych) przyczynia się do blokowania porów membrany i obniża wydajność układu osmotycznego. Ponadto wyższa zawartość substancji organicznej w odciekach z młodych składowiska oraz wyższe stężenie w nich kationów prowadzi do niekorzystnego zjawiska neutralizacji powierzchni membrany.

Abstract

In paper an influence of leachate from landfills with different exploitation time on reverse osmosis performance during their treatment was presented. An unstabilized leachate from landfill of two years exploitation and stabilized leachate from landfill with operation time over 10 years were taken to analysis. The analyses were conducted with use of RO system constructed to reflect the actual operating conditions of the reverse osmosis system exploited on municipal landfills. These two kind of leachate was directed to the reverse osmosis system by maintaining during their filtration the same operating parameters (temperature, pressure, flow rate, recovery rate and pH of leachate). The obtained results indicated that filtration of stabilized leachate is characterized by better performance of the RO system, i.e. shorter filtration time, higher permeate flow and higher salt retention. The higher concentration of organic matter in unstabilized leachate contributes to membrane pores blocking decreases the efficiency of the osmotic system. Moreover, high organic content in the leachate from young landfills, with a high concentration of cations, leads to an unfavorable phenomenon of neutralization of the membrane surface.

Słowa kluczowe:

oczyszczanie odcieków, składowisko odpadów, odwrócona osmoza

Keywords:

leachate treatment, municipal landfill, reverse osmosis



Ballast Water Management Systems on Vessels. The Water Cleanliness Requirements of New D-2 Standard Versus the Expectations

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1. Introduction

International shipping causes many hazards to the environment. Transport by sea is the most efficient (it needs the lowest energy demand). A contribution of transport by sea (in all types of transport) is about 90% taking into account transported mass (cargo) and the distance. Even during normal operation processes of vessels the environment is contaminated by bilge water, slops from cargo tanks, sewage, exhaust gases, ballast water and leakages from vessel systems (for example refrigeration gases). The main hazard are vessels accidents and disasters leading to serious sea pollution from cargoes, marine fuels, lubrication oils and many others.

It was estimated that international voyages transfers about three to five billion tons of ballast water every year. Ballast water is essential for safe and efficient ships' operations (to compensate the change of cargo quantity, its different density and allocation).

Due to the transfer of invasive aquatic species poses a serious ecological, human health and economic threat. In February 2004 the International Maritime Organization (IMO) adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention). There are regulations of ballast water discharges and methods of risk reducing the introduction of non-native

species (Herdzik 2016-1, Herdzik 2017, *International Convention...* 2016). To complement the BWM Convention, IMO has adopted the guidelines prepared as resolutions and circulars by the Maritime Environment Protection Committee (MEPC) (MEPC 10-23). In addition to IMO, other national or regional bodies have introduced their own regulations e.g. the United State Coast Guard rules (2012).

The BWM Convention has entered into force on 8th September 2017 after one year when the minimal conditions were fulfilled: ratification by 30 states (members of IMO), representing 35 percent of world's merchant shipping tonnage (*Understanding...* 2016, Chorab 2013).

All ships of capacity 400 and above will be required to have on board approved a Ballast Water Management Plan and Ballast Water Record Book, and to be surveyed and issued with an International Ballast Water Management Certificate. For existing ships it ought to be done during the International Oil Pollution Plan (IOPP) Certificate renewal survey (required every five years), for ships constructed after 7th September 2017 the compliance ought to be fulfilled on delivery. The plan of implementation the BWM requirements approved by MEPC 71 is presented in Fig. 1. After 8th September 2024 the BWM Convention requirements should be implemented in all vessels.

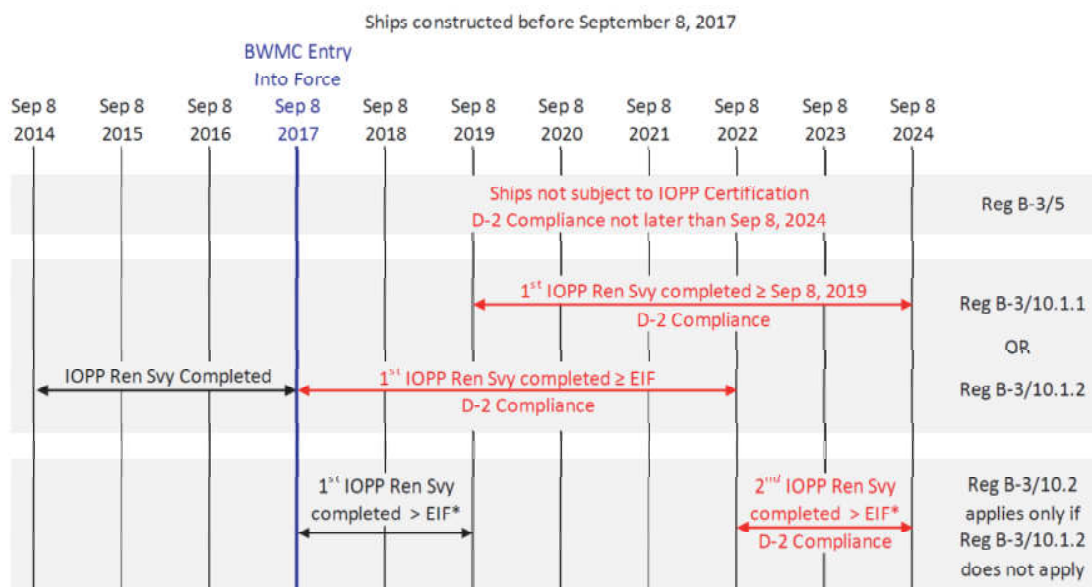


Fig. 1. Approved BWM implementation scheme according to MEPC 71 (IMO 2017)
Rys. 1. Zatwierdzony przez MEPC 71 plan wprowadzania konwencji BWM

Some exemptions are possible for ships which operate exclusively within one “Captain of the Port” (COTP) zone, non-seagoing vessels, vessels that takes on and discharge ballast water exclusively in one COTP zone or without any water ballast tank or with only closed ballast tanks.

2. Ballast water treatment standards required by the BWM Convention

The D-1 standard was the first one required from February 2004 by BWM Convention. The method for fulfillment of D-1 standard was the ballast water exchange at mid-ocean (over 200 nautical miles from shore). There are two possibilities to achieve it:

- the sequential method – in each ballast tank, water should be discharged until suction of the pumps is lost, and stripping pumps or eductors should be used, if possible. The emptied tanks are then refilled. Emptying and filling three times allows for at least 95% water exchange,
- “flow-through” method – tanks are overfilled by pumping. There is little change to the condition of the ship. It is necessary to pump in three times the volume of the tank to achieve at least 95% change of water.

It should be noted that clean seawater does not make a problem but many non-native species living inside. Some species may survive in water and sediment of ballast water tanks. For the reason, some port states do not allow to use stripping pumps when emptying a ballast tank in the harbor, even if the ballast water was exchanged in mid-ocean. The routine ought to be the cleaning the ballast tank to remove sediments, possible in mid-ocean or under controlled arrangements in port or a dry dock. The tank cleaning should be logged in the Ballast Water Record Book also.

From 1st January 2017 the BWM Convention requires regulation D-2 as standard for discharged ballast water. The requirement for D-2 standard is presented in Table 1.

Ballast water treatment systems must have an approval certificate in compliance with the IMO Guidelines (MEPC.125(53) 2005, MEPC.174(58) 2008). It should be noted the difference between the USCG treatment discharge standard and the BWM Convention D-2 standard. The BWM Convention standard specifies measurement of “vi-

able” organisms, while the USCG standard specifies measurement of “living” organisms.

Table 1. The IMO D-2 standard for discharged ballast water (PRS 2016, Lloyd’s Register 2016)

Tabela 1. Wymagania standardu D-2 usuwania wody balastowej za burzę

Organism category	Regulation
Plankton, >50 µm in minimum dimensions	<10 cells/m ³
Plankton, 10-50 µm	<10 cells/ml
Toxicogenic <i>Vibrio cholera</i> (O1 and O139)	<1 colony forming unit (cfu)/100 ml or less than 1 cfu/g (wet weight)
<i>Escherichia coli</i>	<250 cfu/100 ml
Intestinal Enterococci	<100 cfu/100 ml

3. Generic ballast water treatment technology

Many manufacturers of marine equipment have tried to solve the problems of ballast water treatment. The classification societies (*A guide...* 2016, *Guidelines...* 2016, *Understanding...* 2016, *International Convention...* 2016) give their own propositions. The generic ballast water treatment technology process option is presented in Fig. 2 (*Understanding...* 2016). The process is divided into two stages:

- physical solid-liquid separation (mainly filtering) with possibility of chemical enhancement,
- disinfection by using different methods (presenting in Fig. 2).

Similar proposition is presented in Fig. 3. There are three stages of ballast water treatment that may work singularly or in combination. The arrangement of cleaning process has essential influence on the standard for discharged ballast water (outboard).

A small quantity of ballast water may be used for water injection into burning process in marine boilers (Szkarowski et al. 2017) in aim of decreasing the nitrogen oxide emission to the atmosphere. Ballast water used for this purpose may be without the required cleaning process.

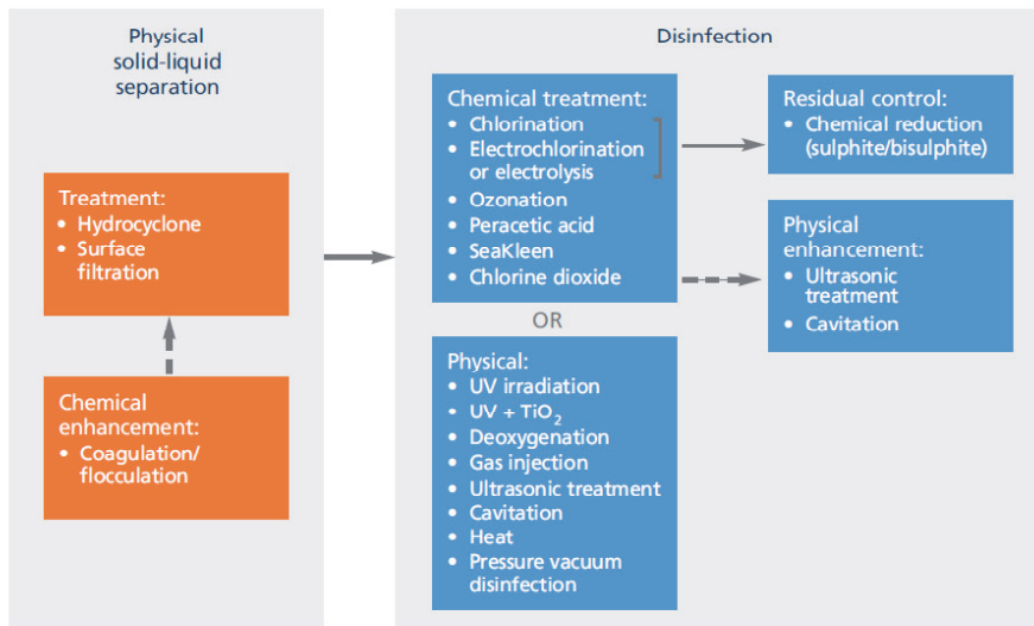


Fig. 2. Generic ballast water treatment technology process option (Lloyd's Register 2016)

Rys. 2. Podstawowe technologie obróbki wód balastowych

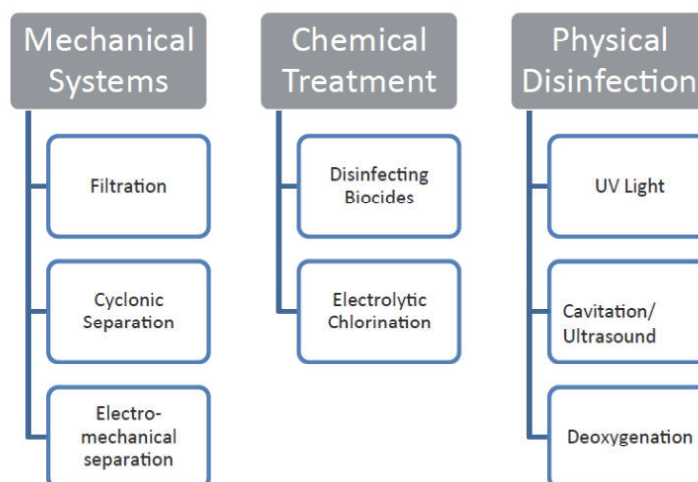


Fig. 3. Ballast water cleaning systems – singularly or in combination (A guide... 2016)

Rys. 3. Systemy oczyszczania wód balastowych – pojedyncze i w kombinacji

Marine market is so considerable and important for manufacturers that they prepared completely ready systems and tried them to develop as to:

- the effectiveness of cleaning process,
- the fulfillment of cleanliness standard,
- the minimal mass and dimensions of the pack,
- the minimal required electric energy,
- automatic operation with very little crew attention,
- series of types (different capacities) – the most often proposition is only with one capacity, for bigger capacity there is a possibility by using more than one pack,
- the long term life,
- the total cost of investment and operation.

An example of cleaning system of Hyde Marine based on mechanical filters and UV lamps is presented in Fig. 4.

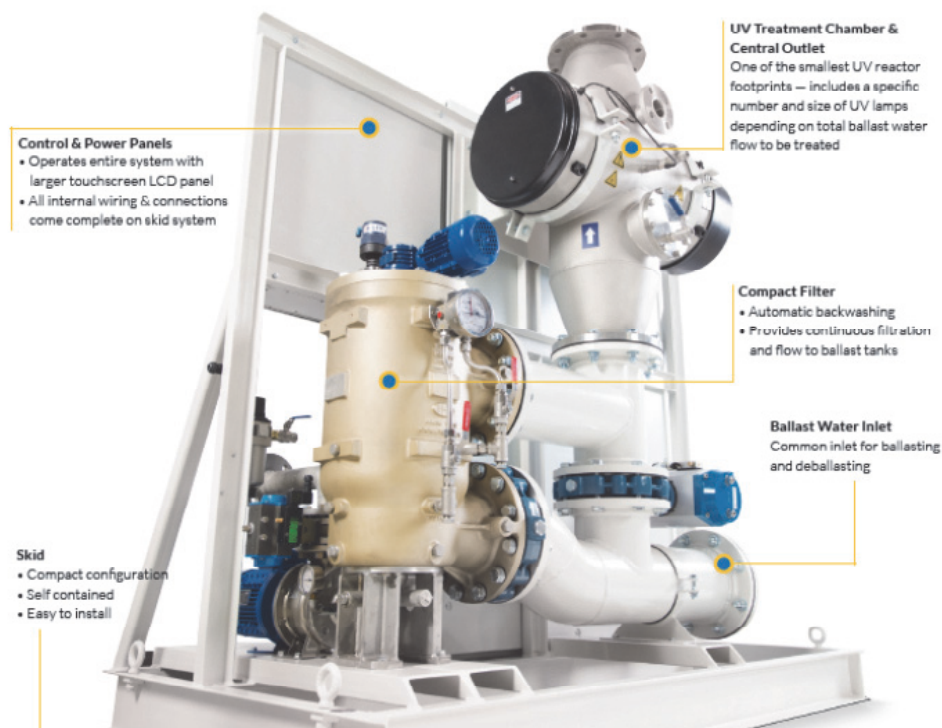


Fig. 4. HG250GS BWMS, Hyde Marine (*Hyde Guardian...* 2017)

Rys. 4. System HG250GS firmy Hyde Marine

The cleaning system used in HG250GS is the most popular at present. An automatic backwashing filter with continuous filtration and flow to ballast tanks is the first stage. The second stage uses a high intensity of ultraviolet (UV) treatment for disinfection. UV dosage depends on a combination of lamp power flow path and exposure time. The cleanliness of UV lamp glasses is very important, so the washing systems for lamp glasses ought to be installed. The advantages of UV disinfection are:

- low corrosion risk (without using of chemical oxidants),
- use of no chemicals,
- no danger for overdosing (no effect on killed organisms),
- no harmful toxic or significant nontoxic products after disinfection process,
- safe to the crew and environment.

The mechanical filtering of ballast water may be efficient. The zooplankton removal efficiency is 20 μm or 40 μm (on request). An example of such system is presented in Fig. 5.

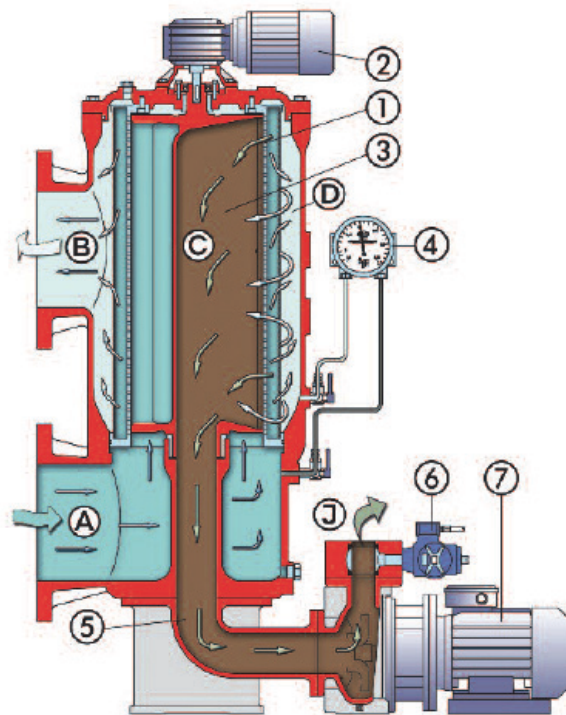


Fig. 5. Filtration and cleaning of ballast water (*Ballast Water Filters...* 2016)

Rys. 5. Proces filtracji mechanicznej wody balastowej

<i>A – entrance of ballast water</i>	<i>1 – filter element</i>
<i>B – exit of ballast water</i>	<i>2 – backwashing system</i>
<i>C – cleaning chamber (inside)</i>	<i>(electric motor in “on” position)</i>
<i>D – cleaning chamber (outside)</i>	<i>3 – backwashing shaft,</i>
<i>J – cleaning duct (outlet)</i>	<i>4 – pressure gauge</i>
	<i>5 – duct of filter cleaning,</i>
	<i>6 – backwashing valve</i>
	<i>7 – backwashing pump</i>
	<i>with electric motor (optional)</i>

There is presented the process of filtration of ballast water and parallel process of filter cleaning (when the pressure drop on filter activated the cleaning process of the filter).

4. Cleanliness of ballast water tanks. Possibility of checking

The cleaning process is always active during ballasting operations. Some ballast water systems work only during ballasting operation, others during ballasting and de-ballasting operations. Ballast Water Managements Systems (BWMS) arrangement depends on a method approved by the Administration. The idea of BWMS, which does not require an after treatment, is presented in Fig. 6.

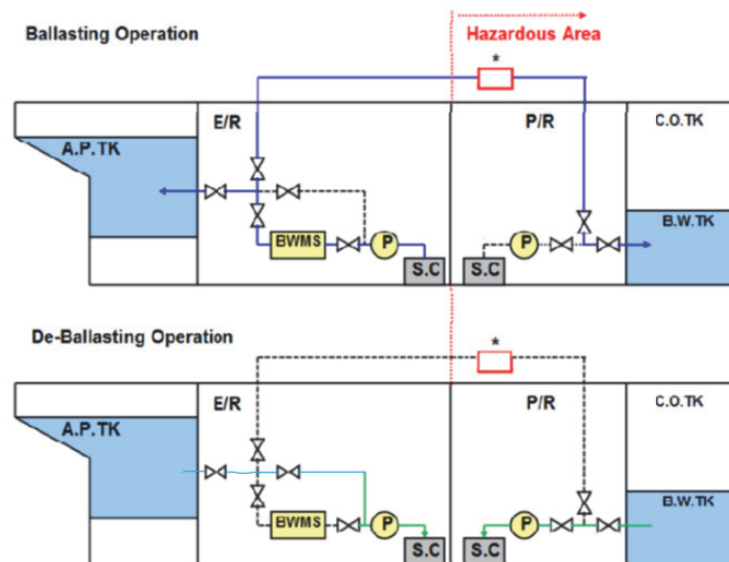


Fig. 6. BWMS which does not require after treatment (*Guidelines... 2016*)

Rys. 6. System BWM niewymagający dodatkowej obróbki wód balastowych

S.C – sea chest, *P* – ballast water pump, *E/R* – engine room compartment, *P/R* – pump room compartment, *A.P.TK* – after peak ballast tank, *B.W.TK* – ballast water tank

During a de-ballasting operation the ballast pump works directly from ballast tank to the sea chest.

The idea of BWMS, which require the after treatment, is presented in Fig. 7. There is a small difference during de-ballasting process. The ballast water is pumped again through the BWMS pack.

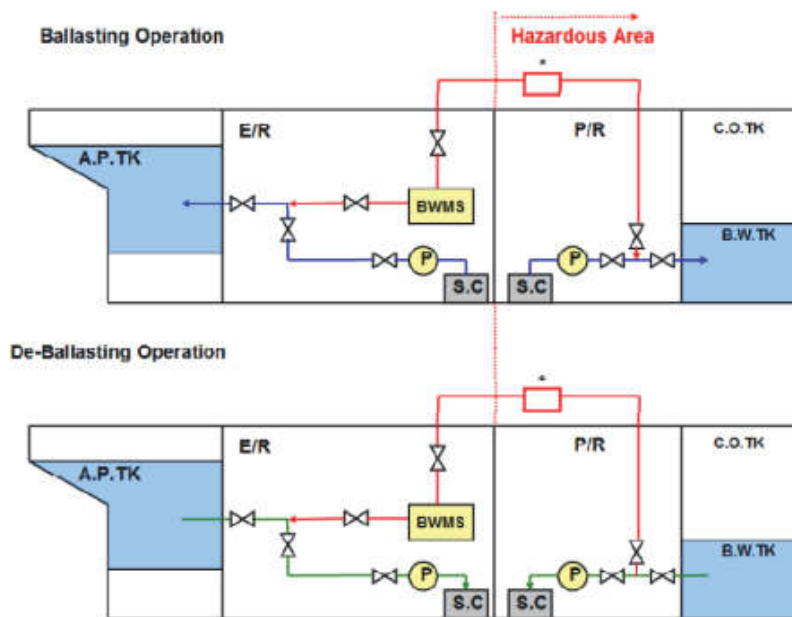


Fig. 7. BWMS which require after treatment (injection type) (*Guidelines...* 2016)

Rys. 7. System BWM wymagający obróbki wody balastowej przed odpompowaniem za burtę

The standard D-2 of ballast water cleanliness should be reached after proper treatment through the BWMS. Certificates of BWMS inform that the cleanliness requirements were fulfilled during certification process at first examined installation of such type and such manufacturer. For other installations we received in reality the copy of mentioned certificate (*Wärtsilä Aquarius*® 2016).

The effectiveness of ballast water treatment depends on many factors:

- type of BWMS,
- the degree of water contamination,
- proper parameters of BWMS work,
- autoregulation system of BWMS pack on different temperature, salinity of sea water, etc.

The final effect should be reached during the de-ballasting operation by measuring cleanliness of ballast water in the outboard outlet pipeline. At sea during ballast operation there is a big problem to measure continuously cleanliness of discharged water (see Table 1). It is possible that cleanliness of ballast water may change during de-ballasting operation. A first time of pumping the parameters will be proper only if at the end they will be over the permitted limits. The ballasting operation should be done to the end. The ballast tank should be empty or full of water, never partly filled up. And additional question – what to do when the parameters of cleanliness exceeds the limits and the vessel is deep at sea? It is time for preventive exchange of ballast water or cleanliness processes at tanks.

5. Operational problems of ballast water systems

An exchange of ballast water and the process of cleanliness may be the reasons for potentially dangerous situations for ship safety and crew. It should be done where the sea state, vessel operational state etc. allow for such operations (Herdzyk 2016-1, Herdzyk 2016-2).

Due to the International Safety Management Code (ISM Code) the BWMS needs to prepare appropriate procedures to avoid the above mentioned threats and to provide proper operation, service and routine maintenance (*Wärtsilä Aquarius*® 2016).

The unsolved problem is the cleanliness state inside the ballast tanks and inside the ballast water pipelines. There is a real possibility of corrosion (contact with seawater), contamination of plankton, bacteria and viruses not killed by BWMS, other substances (chemicals) produced in the ballast tanks during a voyage. It should decrease the effectiveness of BWMS and make under the question mark the reasonableness of utilization necessity such systems.

The possible solution is a frequent inspection of ballast tanks but it may be done only when the ballast tank is empty. How to check the tank cleanliness (and the pipelines) when there is no visible contamination but still possible from the bacteria and viruses? If a ballast tank is contaminated it is necessary to wash it (only by water or with chemicals?) and what to do with the tank washings. The next questions is who will decide about the evaluation of ballast water tank cleanliness, when and where to do it.

The simplest solution is to treat ballast water during ballasting and de-ballasting operation (it doubles the time of BWMS work, waste energy etc.) but it does not still recognize a state inside the tank.

6. Will the expectations be fulfilled? Final remarks

The expectation is minimizing the threats of transport to the sea and environment. The hot discussion will be about the new required parameters, the limits decreasing, procedures, additional processes etc.

The BWMS is and will be installed on vessels according to required regulations (being in force in day of renewal survey – Table 1). Some answers to the above mentioned questions should be done before the decision of BWMS type choice. It needs some calculations to choose the best (maybe the cheapest) solution. The experience and opinions about considered type (and manufacturer) from crew or superintendents may be helpful for the correct decision.

The BWMS should be friendly to the environment and the crew. The next essential cost for ship-owners or operators should be justified by benefits for the environment and all of us.

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Systemy zarządzania wodami balastowymi na statkach. Wymagania czystości wód nowego standardu D-2 w porównaniu do oczekiwań

Streszczenie

W lutym 2004 roku Międzynarodowa Organizacja Morska (IMO) wprowadziła Międzynarodową konwencję o kontroli i zarządzaniu statkowymi wodami balastowymi oraz osadami z wód balastowych (Konwencja BWB). Przedstawiono w niej regulacje możliwości usuwania wody balastowej za burtę oraz metody zmniejszenia ryzyka wprowadzania do środowiska obcych gatunków. Dopełnieniem Konwencji są przewodniki, rezolucje i okólniki przygotowane przez Komitet Ochrony Środowiska Morskiego (MEPC). Dodatkowo, oprócz IMO, narodowe lub regionalne administracje morskie mogą wprowadzać własne regulacje np. wymagania Amerykańskiej Straży Granicznej (USCG). Początkowo standard D-1 wód balastowych był obligatoryjny. Po wejściu wymogów Konwencji BWB w dniu 8 września 2017 roku, wymaga się spełnienia standardu D-2 czystości wód balastowych.

W artykule przedstawiono systemy zarządzania wodami balastowymi, wymagania czystości, rozwiązania obróbki wód balastowych oraz oczekiwania związane ze zwiększeniem jakości wód balastowych i zmniejszeniem ryzyka dla środowiska. Poddano dyskusji standard D-1 obowiązujący od lutego 2004 roku oraz jego niedoskonałości. Czynnością rutynową winno być czyszczenie zbiorników balastowych z osadów, możliwe do przeprowadzenia na otwartym oceanie lub pod kontrolą urządzeń portowych lub suchego doku.

Rynek urządzeń okrętowych jest tak istotny i ważny dla producentów, że są oni w stanie przygotować w pełni gotowe systemy, będą je rozwijać, aby spełnić wymagania efektywności procesu czyszczenia, wymagania standardów czystości, jak najmniejszej masy i gabarytów urządzenia, jak najmniejszego zapotrzebowania na energię elektryczną, automatyzacji procesu z jak najmniejszą pracochłonnością dla załogi, budowy typoszeregu (o różnych wydajnościach – obecnie propozycje dotyczą jednego typu urządzenia z jedną wydajnością, można zastosować kilka urządzeń w celu zwiększenia wydajności), wieloletniego okresu użytkowania, całkowitych kosztów inwestycji i eksploatacji.

Jako przykład przedstawiono system HG250GS firmy Hyde Marine. Ważnym rozwiązaniem jest zastosowanie w pierwszym stopniu automatycznego filtra umożliwiającego pracę urządzenia podczas jego czyszczenia. Jako drugi stopień stosuje się intensywne napromieniowanie ultrafioletem (lampami UV) w celu dezynfekcji wody balastowej. Dawka promieniowania lamp UV jest ustalana jako kombinacja mocy lampy UV i czasu naświetlania. Czystość

szkieł lampy UV ma decydujące znaczenie dla skuteczności procesu, dlatego zainstalowano system ich czyszczenia. Wskazano na wiele parametrów, od których zależy efektywność obróbki wody balastowej. Istniejącym i nierozwiązanym problemem jest stan czystości zbiorników balastowych i rurociągów obsługujących tą instalację w czasie eksploatacji. Kończącą uwagą jest, że oczekiwania dotyczące skutecznej obróbki wód balastowych nie zostały w pełni zweryfikowane.

Abstract

In February 2004 the International Maritime Organization (IMO) adopted the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM Convention). There are regulations of ballast water discharges and methods of risk reducing of introducing non-native species. To complement the BWM Convention, the IMO has adopted the guidelines prepared as resolutions and circulars by Maritime Environment Protection Committee (MEPC). In addition to the IMO, other national or regional bodies have introduced own regulations for example the United State Coast Guard rules. At first the D-1 standard of ballast water was obligatory. The BWM Convention has entered into force in 8th of September, 2017 and it needs the D-2 standard of ballast water cleanliness.

The article presents the ballast water managements systems, the cleanliness requirements, solutions of ballast water treatment and expectations for improvement the quality of ballast water pumped outboard and the decreased risk for the environment. It was discussed the D-1 standard of ballast water required from February 2004 and its imperfections. The routine ought to be the cleaning of the ballast tank to remove sediments, possible in mid-ocean or under controlled arrangements in port or dry dock.

The marine market is so considerable and important for manufacturers that they prepared full ready systems and still tried them to develop as to the effectiveness of cleaning process, the fulfillment of cleanliness standard, the minimal mass and dimensions of the pack, the minimal required electric energy, automatic operation with very little crew attention, series of types (different capacities) – the most often proposition is only with one capacity, for bigger capacity there is a possibility by using more than one pack, the long term life, the total cost of investment and operation etc.

As an example it was presented the HG250GS system of Hyde Marine. As an very important solution is an automatic backwashing filter with continuous filtration and flow to ballast tanks is the first stage. The second stage uses high intensity of ultraviolet (UV) treatment for disinfection. UV dosage results from a combination of lamp power flow path and exposure time. The cleanli-

ness of UV lamp glasses is very important, so the washing systems for lamp glasses ought to be installed. The effectiveness of ballast water treatment depends on many factors – they were indicated. The existing and unsolved problem is the cleanliness state inside the ballast tanks and inside the ballast water pipelines. As a final remark – the expectations concerning to ballast water treatment systems are not properly verified.

Słowa kluczowe:

woda balastowa, system zarządzania, Konwencja BWM, standard D-2, czystość wody

Keywords:

ballast water, management system, BWM Convention, D-2 standard, water cleanliness



Supporting Sustainable Agriculture: the Potential to Reduce GHG Emissions – the Case of Agricultural Biogas Production in Poland

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1. Introduction¹

Since the publication of the Brundtland report (WCED 1987) Sustainable Development became one of the key concepts in economic development. Agriculture belongs to the most important sectors of the economy from the sustainability perspective, due to its twofold impacts as a “user” of the natural environment – depleting natural resources and causing threats to the environment, but also as a “protector” of nature due to its environmental services and mitigation potential. In numerous attempts to define "Sustainable Agriculture" (e.g. Tilman et al. 2002, Pretty 2008), definitions are derived from various dimensions of "sustainability", as Majewski (2008) points out, focusing on environmental, technological or socio-ethical aspects (e.g. emphasis on satisfying the needs of the present generation without undermining the prosperity of future generations).

Renewable energy production in agricultural sector corresponds with all those aspects allowing for reduced consumption of fossil fuels and improvement of the balance of greenhouse gases (GHG) emissions, identified as important challenges that agriculture faces (Pedroli & Langeveld 2011, Olesen et al. 2011, Pawłowski & Pawłowski 2016) in

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fulfilling its sustainability responsibilities and helping to solve some food, energy and environment related problems (Iotti and Bonazzi 2016). Production of renewable energy that reduces the use of fossil fuels may be considered the most essential move toward the Sustainable Development paradigm. It is also a response to the EU climate and energy policy which for the year 2020 sets three main targets for the European Union: 20% reduction in GHG emissions from the 1990 level, 20% of the EU energy produced from renewable energy sources (RES) and 20% improvement in energy efficiency (European Parliament 2009). Established in 2014 the climate and energy policy framework of the EU imposes further reduction of greenhouse gas emissions in 2030 by 40% compared to 1990 and an increase in the share of renewable energy to at least 27% of total consumption (European Commission 2014). Given the rather slow pace of the GHG emissions reduction the European Commission has prepared a Proposal for a Regulation (European Commission 2016), which establishes additional targets for GHG emissions from the non-ETS sector² in the perspective of the year 2030. An average 30% reduction of GHG emissions from the 2005 level is expected in the EU (7% in the case of Poland). Taking into account that non-ETS includes agriculture we can expect that the issue of emissions from agriculture will become increasingly important in the coming years.

One of the ways to increase the role of agriculture in reducing GHG emissions may be the production of biogas from manure and agricultural wastes.

The assessment of the potential to reduce GHG emissions in Poland by manure-based biogas production in the farming sector is the main aim of this paper.

2. GHG Emissions from agriculture

Agricultural production is responsible for about 15% of the total Worldwide GHG emissions (WRI 2017) and about 10.3% in the EU (17.5% if only non-ETS sector is taken into account). In the case of the

² These targets concern emissions from most sectors not included in the EU Emissions Trading System (EU ETS), such as transport, buildings, agriculture and waste [https://ec.europa.eu/clima/policies/effort_en].

EU about half of the GHG emissions from agriculture comes from crop production, and another half from livestock sector (Eurostat 2015).

The main greenhouse gases emitted by agriculture are methane (CH₄) and nitrous oxide (N₂O), which have respectively 45% and 46% share in global GHG emissions from agriculture in CO₂ equivalent, while the share of CO₂ is estimated at only 9% of global agricultural emissions (EAT 2015). For comparison, the share of CO₂ in the total global structure of GHG (measured in kg of CO₂e) is estimated at 82.4% (European Environment Agency 2013). The animal production sector is the main source contributing to agricultural emissions of methane in the EU (mainly enteric fermentation and manure storage), while application of manure and mineral nitrogen fertilizers is responsible rather for N₂O emissions (IPCC 2014). The importance of methane and nitrous oxide in the total emissions results from the fact that the impact of these compounds on the greenhouse effect is approximately 23 (CH₄), and almost 300 (N₂O) times stronger than the impact of carbon dioxide (IPCC 2007, Thomson et al. 2012). Recently, particularly great attention has been paid to the issue of methane emissions because of the rapid increase in the concentration of this gas in the atmosphere in the last few years (Dlugokencky 2016). At the same time a lower growth rate in CO₂ emissions and rather stability in the case of N₂O are observed (Thomson et al. 2012).

The largest emitters of methane from agriculture in the EU are France, Germany, the United Kingdom and Poland (Table 1).

Table 1. Methane and nitrous oxide emissions in selected EU countries

Tabela 1. Emisja metanu i podtlenku azotu w wybranych krajach europejskich

Country	Total greenhouse gas emissions ¹	Emissions from agriculture ²			
		Methane (CH ₄)	Nitrous oxide (N ₂ O)	Methane and nitrous oxide	Share of countries in EU emissions from agriculture [%]
[million tonnes of CO ₂ equivalent]					
EU-28	4 548.4	198.8	271.9	470.6	100.0
France	490.3	38.4	50.8	89.3	19.0
Germany	939.1	25.8	43.7	69.5	14.8

Table 2. cont.

Tabela 1. cd

Country	Total greenhouse gas emissions ¹	Emissions from agriculture ²			
		Methane (CH ₄)	Nitrous oxide (N ₂ O)	Methane and nitrous oxide	Share of countries in EU emissions from agriculture [%]
		[million tonnes of CO ₂ equivalent]			
United Kingdom	582.9	22.1	29.7	51.8	11.0
Poland	399.3	11.5	25.2	36.7	7,8
Italy	461.2	15.3	20.1	35.4	7.5
Spain	340.8	17.9	19.8	37.7	8.0
Romania	118.8	8.7	9.5	18.2	3.9
Ireland	58.5	11.0	6.9	18.0	3.8
Netherlands	191.7	9.2	6.7	15.9	3.4
Denmark	51.6	4.2	5.4	9.6	2.0
Rest	1023.3	40.4	59	88.5	18.8

¹Excluding Land Use, Land Use Change and Forestry (LULUCF) net removals.

² Emissions from agricultural transport and energy use are excluded, as these sectors are not defined as part of the agriculture sector by the current IPCC (The Intergovernmental Panel on Climate Change) reporting guidelines.

Source: Eurostat 2015, Eurostat 2016

3. Biogas production – a way to reduce GHG emissions from agriculture

Production of agricultural biogas from manure and other wastes from agricultural production may be considered the most sustainable way of producing clean energy. Much more controversial is biogas production from crops normally used for food, because as substrates they compete for agricultural land with food crops (Paterson et al. 2016, Pawłowski 2015). Production of agricultural biogas from manure not only contributes to the reduction of methane emissions which would take place during traditional manure storage but also replaces energy from fossil fuels with renewable energy (Shih et al. 2012, Bentley et al. 2010, IPCC 2006, Oenema et al. 2007).

Agricultural biogas has an advantage over other forms of renewable energy because its production is independent of natural conditions such as availability of wind, running water or sunlight. Some authors (e.g. Pöschl et al. 2010, Persson et al. 2014, Jacobson 2009) indicate a higher stability of supply of energy from biogas in comparison to other renewable energy sources [RES].

It is worth mentioning that the digestate, a by-product of the anaerobic fermentation of manure has a high fertilizing value. Using digestate as a natural fertilizer has also some disadvantages from the sustainability perspective such as worsening of the balance of soil organic matter. Although the amount of nutrients in the digestate and manure used in the process are comparable, the carbon content in digestate is lower (Möller and Stinner 2009).

From the economic point of view there is a problem of the relatively high costs of energy generated from biogas. Numerous analyses carried out in many countries indicated a rather low profitability of agricultural biogas production, particularly in small farms (van Foreest 2012, Kost et al. 2013, Delzeit and Britz 2012, Sulewski et al. 2016). One of the disadvantages of small biogas plants is the lack of economies of scale that can be achieved in larger businesses (Bruins and Sanders 2012, Jacobsen et al. 2014). However, small biogas plants have some advantages which are particularly important from the point of view of sustainability such as independence from fluctuations of biomass prices, simpler and less costly administrative procedures and securing the energy self-sufficiency of farms (Dobbelaere et al. 2015, Paterson et al. 2016). On the other hand logistics of big biogas plants usually requires transportation of substrates and products over long distances which limits the positive impact of biogas on reduction of GHG emissions (Szabó et al. 2014). Despite the existing controversies, the development of agricultural biogas production based on anaerobic fermentation of manure seems to be the most effective way to reduce methane emissions from agriculture, which is particularly important for countries with a high number of livestock, such as Poland.

4. Method

The evaluation of the potential of GHG reduction by manure anaerobic fermentation is based on the prior estimations of potential production of agricultural biogas in Poland (Majewski et al. 2016). The basis for the estimations was the number of animals of main groups of livestock converted to Livestock Units (LU)³ and normative amounts of natural fertilizers (solid and liquid manure, slurry) per 1 LU.

The potential for biogas production was estimated for the sample of farms represented in the Polish FADN (Farm Accountancy Data Network) database. The average production of solid manure, liquid manure and slurry per 1 LU in specified regions was multiplied by the number of animals in the FADN population⁴ and aggregated to the country level.

Parameters published by KTBL⁵ (average values for indicated ranges) that characterize specific types of manure were used for estimation (Table 2).

Table 3. Yields of biogas from selected substrates [m³/t of organic dry matter]

Tabela 2. Produkcja biogazu z wybranych substratów [m³/t suchej masy]

Source of substrate	Cattle	Pigs	Poultry	Horses
Solid manure	255	360	521	315
Liquid manure	350	450	–	–
Slurry	370	370	–	–

Source: KTBL (2005) – modified

³ Livestock Unit - is a reference unit which facilitates the aggregation of livestock from various species and age as per convention, via the use of specific coefficients. The reference unit used for the calculation of livestock units (= 1 LSU) is the grazing equivalent of one adult dairy cow producing 3 000 kg of milk annually, without additional concentrated foodstuffs [EUROSTAT]

⁴ The farm population represented in FADN consist of about 731 thousand entities which generate nearly 90% of all agricultural production in Poland using 88% of agricultural land and keeping 99,7 % of farm animals (in terms of LU) (Floriańczyk et al. 2016).

⁵ Kuratorium für Technik und Bauwesen in der Landwirtschaft

The potential for biogas production from manure was estimated in three scenarios, namely:

- hypothetical scenario – assuming the total amount of manure from all animals represented by farms in the FADN population is processed to biogas,
- theoretically workable scenario – taking into account only farms with animal herds greater than 30 LU that may provide substrates for installation with electrical capacity of 10 kWe,
- realistic scenario – assuming that only a half of farms with animal herds greater than 30 LU would undertake biogas production.

Estimated values of the potential for biogas production based on manure from specified groups of animals are presented in Table 3.

A total hypothetical potential was estimated at the level of approximately 2 762 million m³ of biogas, while the theoretically workable and realistic potentials were less than 30% and about 15% of the hypothetical value respectively (appr. 797 and 399 million m³) (Majewski et al. 2016). These amounts differ significantly. However, the dispersed structure of livestock production and the fact that the majority of the animals are kept in relatively small herds can be considered the key factors limiting real opportunities for biogas production from animal wastes in Poland.

Table 4. Potential of agricultural biogas production from different types of manure in Poland*

Tabela 3 Potencjał produkcji biogazu z nawozów naturalnych w Polsce*

Livestock	Hypothetical scenario		Theoretically workable scenario		Realistic scenario	
	mln. m ³	% of total	mln. m ³	% of total	mln. m ³	% of total
Cattle	1379.6	50.0	417.6	52.4	208.8	52.4
Pigs	1193.1	43.2	352.2	44.1	176.1	44.1
Other	189.8	6.8	27.6	3.4	13.8	3.4
Total	2762.4	100.0	797.4	100	398.7	100.0

* based on 2013 livestock numbers

Source: own calculations

Based on the estimated potential of biogas production the possible reduction of methane emissions from the livestock sector in Poland has been calculated. Because production of agricultural biogas does not eliminate emissions from enteric fermentation the analysis was limited to the storage of manure only, considering:

- direct reduction of GHG emissions due to processing manure into biogas in the process of anaerobic fermentation,
- indirect reduction of GHG emissions in a form of emissions avoided due to less electricity produced from conventional energy sources balanced by electricity from biogas converted in CHP installations.

In order to assess the potential to reduce emissions resulting from manure storage the methane conversion factors (MCF)⁶ developed by the IPCC (2006) for specified types of manure were applied. Methane conversion factors indicate the share of methane, which is emitted to the atmosphere during storage of specific types of manure (maximum methane capacity). A possible reduction of methane emission from Polish agriculture due to eliminating storage of natural fertilizers used directly in biogas production was estimated with the use of the following formula:

$$E_r = \sum_m Q_m \times MCF_m \quad (1)$$

where:

E_r – emission reduction in CO₂e,

Q_m – country level total methane-producing capacity of the specified natural fertilizer type (m) expressed in CO₂ equivalent,

MCF_m [%] – Methane Conversion Factor for the specified natural fertilizer type (m) is the percentage of natural fertilizer's maximum methane-producing capacity that is actually achieved during storage in annual average temperature.

⁶ MCFs – (methane conversion factors) are determined for a specific manure management system and represent the degree to which the maximum methane-producing capacity of the manure is achieved. The maximum methane-producing capacity of the manure varies by species and diet [IPPC 2006].

In other words MCF is a part of organic matter actually converted into methane – for the assessment the default level of 2% for solid manure and 17% for slurry and liquid manure has been applied after IPCC (2006).

In order to estimate the emissions avoided, the amount of CO₂ emitted at the existing level of conventional electricity production has been reduced proportionally, as if the demand for conventional energy was lower due to introducing the substitute in a form of electricity from biogas plants.

For the estimation of the emission avoided the following formula has been used:

$$E_a = E_{el\ RES} \times U_e \quad (2)$$

where:

E_a – emission avoided in tonnes CO₂ equivalent,

$E_{el\ RES}$ – amount of electricity from Renewable Energy Sources (RES) [MWh],

U_e – emission of CO₂e in electricity generation in CO₂e/ MWh.

The CO₂ emission factors recommended by The National Centre for Emissions Management (KOBIZE) have been applied in the analysis. The unit emission of CO₂ in the case of electricity generation in Poland according to KOBiZE is equal to 0.812 Mg CO₂e/MWh (KOBiZE 2014).

5. Results

The total value of GHG emissions from Polish agriculture was estimated at 30244,6 thousand tonnes of CO₂ equivalent in the year 2010 (Eurostat 2012). Animal husbandry (mainly enteric fermentation and manure storage) was responsible for about 50% of the total agricultural emissions.

Eliminating storage of manure and producing biogas converted further into electricity and heat in CHP installations (instead of spreading manure on the fields) would result with a noticeable reduction of methane emissions (Table 4).

Table 5. Reduction of GHG emissions due to elimination of manure storage and emission avoided after transforming manure into energy in farm biogas installations

Tabela 4. Redukcja emisji gazów cieplarnianych w efekcie zaniechania przechowywania nawozów naturalnych i zastąpienia energii ze źródeł konwencjonalnych energią z biomasy

Scenario	Potential reduction of GHG emissions [thousand tonnes CO ₂ e] due to:		Reduction of GHG emissions due to processing manure into energy in relation to:	
	Elimination of manure storage	replacing fossil fuels (emissions avoided)	Reference point	[%]
Hypothetical	1032.1 (24.3%)	4239.5 (75.7%)	Total GHG emissions at country level	1.54
			Total GHG emissions from agriculture	17.4
			Emissions from livestock production	43.0
Theoretically workable	303.1 (24.8%)	1223.7 (75.2%)	Total GHG emission at country level	0.45
			Total GHG emission from agriculture	5.0
			Emissions from livestock production	12.5
Realistic	151.6 (24.8%)	611.9 (75.2%)	Total GHG emission at country level	0.22
			Total GHG emission from agriculture	2.5
			Emissions from livestock production	6.22

Source: own research and Eurostat data (2012, 2016).

Eliminating manure storage would reduce GHG emissions from Polish agriculture by about 1032.1 thousand tonnes of CO₂ equivalent in the hypothetical scenario and about 303.1 or 151.6 thousand tonnes respectively in the theoretically workable and realistic scenarios.

Saving fossil fuels due to converting biogas into electricity would result with much greater reduction of GHG emissions in a form of emissions avoided – 4239.5; 1223.7 and 611.9 thousand tonnes of CO₂ equivalent in respective scenarios.

In order to illustrate the importance of reductions, estimated values of potential GHG emission reductions were referred to total emissions at different scales: of the country level, agricultural sector and livestock production as recorded in official statistics (Eurostat 2012, 2016). At the country level reduction of GHG emissions in relation to the total emissions is relatively small (1.54%, 0.45% and 0.22% in respective scenarios).

Relative reductions of GHG emissions due to converting natural fertilizers into renewable energy are much more significant if the agricultural sector or livestock production are considered as a reference levels. The total reduction of GHG emissions in Poland due to elimination of the storage of natural fertilizers and partial replacement of electricity generated from fossil would result in a reduction of emissions equal to 17.4% of GHG emission from the agricultural sector in the case of the hypothetical and approximately by 5.0% and 2.5% in the case of the theoretically workable and realistic scenarios respectively.

6. Conclusions

A number of analyses confirm that production of biogas can effectively reduce GHG emissions as well as the carbon footprint of livestock production, and provide a number of other environmental and social benefits (Massé et al. 2011). The scale of emission reduction is determined by the method of biogas utilization. Uusitalo et al. (2014) compared three ways of producing biogas (biowaste, waste water treatment plant sludge and agricultural biomass) and various ways of its utilization. They found that the reductions of GHG emission would achieve the highest values if the biogas is used as a fuel in transportation (reduction at the level of 65-72% compared to the use of fossil fuels which is generally coherent with results noted by Tuomisto and Helenius 2008). De-

tailed analyses that confirm that agricultural biogas production could be one of the most environmentally effective ways of generating energy was also carried out by Szabó et al (2014), who studied the case of the biogas plant in Tiszaszentimre (Hungary).

The examples cited as well as many other studies (Kimming et al. 2011, Jury et al. 2010; Rehl and Müller 2013) suggests that the effectiveness of minimizing GHG emissions through biogas production depends on many factors, including such of greater importance as the source of substrates and the way biogas is utilized.

Considering sources of substrates the highest reduction of GHG emissions occurs when biogas is produced from waste materials. This is the case of our estimation of the GHG emissions' reduction assuming natural fertilizers, instead of being stored before application on fields, are processed into biogas, next into electricity and heat in small scale on-farm biogas plants. An additional gain from producing and consuming this energy on farm is elimination of GHG emissions related to the transportation of energy and substrates, typical for large scale operations.

According to the estimates presented in the paper, the use of natural fertilizers for energy production would reduce greenhouse gas emissions by 5271.6 thousand tonnes of CO_{2e} (17.4% of GHG emissions from agriculture and 1.28% of the total country emission) in the hypothetical scenario. Respective values in the theoretically workable scenario are 1526.8 thousand tonnes of CO_{2e} emission reduced (5% and 1.54% respectively of total emissions from agriculture and from various sources nationwide). In the realistic scenario it would be half as much. It can be concluded, that producing agricultural biogas from natural fertilizers, further converted to electricity and heat, improves sustainability of the agricultural system, particularly in the environmental dimension.

The present potential of GHG emissions' reduction based on biogas production estimated at the country level in Poland is limited, despite the fairly large size of the livestock sector. This is mainly because the fragmented farm structure in Poland is an important constraining factor - many farms are too small to run efficiently even the smallest micro scale biogas plants. However, taking into account the on-going concentration processes in Polish agriculture, the number of larger livestock farms with the potential to be profitable in renewable energy production from biogas will increase in a long-term perspective.

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Wspomaganie zrównoważonego rolnictwa: potencjał redukcji emisji gazów cieplarnianych – przypadek produkcji biogazu rolniczego w Polsce

Streszczenie

Sektor rolnictwa może stać się znaczącym producentem energii odnawialnej ze źródeł rolniczych, takich jak odpady z produkcji zwierzęcej (nawozy naturalne). Wzmocniłoby to możliwy wkład energii odnawialnej w łagodzenie negatywnych efektów zewnętrznych generowanych przez sektor rolny. Należy do nich emisja gazów cieplarnianych, w której znaczny udział ma rolnictwo, głównie sektor produkcji zwierzęcej. W Unii Europejskiej rolnictwo polskie jest czwartym co do wielkości emitentem metanu i tlenu azotu z produkcji rolniczej, z udziałem 7,8%.

W artykule dokonano oceny potencjalnej redukcji emisji gazów cieplarnianych w Polsce dzięki produkcji biogazu na bazie fermentacji beztlenowej nawozów naturalnych (obornik, gnojówka, gnojowica), przetworzonego następnie na energię elektryczną. Możliwość produkcji biogazu została oszacowana dla populacji 731 tys. gospodarstw ze zwierzętami z wykorzystaniem danych z próby FADN, co stanowi około 97% sektora produkcji zwierzęcej w Polsce. Potencjalne zmniejszenie emisji metanu zostało obliczone jako ekwiwalent CO₂.

Szacunek produkcji biogazu rolniczego sporządzono dla trzech scenariuszy:

- hipotetycznego, zakładając wykorzystanie nawozów naturalnych od wszystkich zwierząt gospodarskich w Polsce,
- teoretycznie wykonalnego – zakładającego, że minimalna skala produkcji zwierzęcej dla inwestycji w produkcję biogazu w gospodarstwie rolniczym przekracza 30 dużych sztuk przeliczeniowych zwierząt,
- realistycznego – zakładającego, że jedynie połowa gospodarstw posiadających co najmniej 30 dużych sztuk przeliczeniowych podejmie produkcję biogazu.

Według sporządzonych szacunków wykorzystanie nawozów naturalnych do produkcji energii zmniejszyłoby emisję gazów cieplarnianych z rolnictwa o 17,4% w przypadku scenariusza hipotetycznego, o 5% w scenariuszu teoretycznie wykonalnym oraz o około 2,5% w scenariuszu realistycznym (odpowiednio o 1,54%, 0,45; oraz 0,22 całkowitej emisji z różnych źródeł w skali kraju). Zmniejszenie emisji GHG nastąpiłoby z tytułu redukcji emisji metanu poprzez wyeliminowanie składowania nawozów naturalnych, a także ze względu na zwiększony udział "czystej energii" w całkowitym zużyciu energii. Po-

zwołyby to zatem na niższe zużycie paliw kopalnych (np. węgla) w konwencjonalnych elektrowniach. W obecnej sytuacji rynkowej w Polsce, głównie wobec relatywnie niskich cen energii elektrycznej, produkcja energii elektrycznej z biogazowni rolniczych nie jest opłacalna ekonomicznie bez subsydiów. Niewystarczające wsparcie dla produkcji biogazu wskazuje, że korzyści z produkcji energii z nawozów naturalnych są niedoszacowane co dotyczy zwłaszcza redukcji emisji gazów cieplarnianych. Produkcja biogazu rolniczego ułatwiłaby osiągnięcie celów strategii energetycznej UE i uczyniłaby sektor rolny bardziej zrównoważonym.

Abstract

Agricultural sector can become a major producer of renewable energy from different sources, including such as animal wastes (natural fertilizers). It is important due to its potential role in mitigating negative externalities generated by agricultural sector, among other greenhouse gas emissions, mainly from the livestock sector. Within the European Union the Polish agriculture is the fourth largest producer of methane and nitrogen oxide from agricultural production, with a share of 7.8%. This paper aims to assess the potential reduction of GHG emissions in Poland due to biogas production based on manure anaerobic fermentation. Possible biogas production was estimated for a population of 731 thousand Polish livestock farms with the use of data from the FADN sample, which represents about 97% of the animal production sector in Poland. The potential reduction of methane emissions was calculated as CO₂ equivalent for three scenarios:

- hypothetical, assuming the use of natural fertilizers from all livestock in Poland,
- theoretically workable, assuming that the minimum scale of animal production for viable investment in biogas production in the farm exceeds 30 Livestock Units,
- realistic scenario – assuming that only a half of farms with animal herds greater than 30 LU would undertake biogas production.

Reduction of GHG emissions can be achieved through elimination of manure storage and processing natural fertilizers into biogas, next converted into electricity and heat, as well as due to emissions avoided as a result of the increased share of “clean energy” in the total energy consumption and a lower use of fossil fuels (e.g. coal) in conventional power plants.

According to the estimates, the use of natural fertilizers for energy production would reduce greenhouse gas emissions from agriculture by 17.4% in the hypothetical scenario, 5.0% in the theoretically workable and about 2.5% in

realistic scenario (1.54%, 0.45% and about 0.22% respectively of total emissions from various sources nationwide).

In the current market situation mainly due to relatively low energy prices production of electricity from small scale agricultural biogas plants in Poland is not profitable without subsidies. Growth of the agricultural biogas industry would facilitate meeting the EU Energy Strategy targets making the agricultural sector more sustainable.

Słowa kluczowe:

biogaz, gazy cieplarniane, emisja, rolnictwo zrównoważone

Keywords:

biogas, greenhouse gasses, emission, sustainable agriculture



Effects of Mulching with Forest Litter and Compost Made of Sewage Sludge on the Presence of Oribatida as Bioindicators of Soil Revitalization in Larch and Pine In-Ground Forest Nurseries

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1. Introduction

In-ground forest nurseries operating for over 20 years often suffer from degradation processes involving e.g. decreasing biological diversity of ectomycorrhizal fungi (ECM) (Aleksandrowicz-Trzcińska 2004). This is usually accompanied by lower quality of the produced seedlings. ECM fungi are a small but very important for trees part of the edaphon. In natural conditions, the microorganisms of forest soil form a web of relationships, often of trophic nature, with abundant soil micro- and mesofauna.

The main cause of nursery soil degradation is drastically decreasing content of organic matter. This results in reduced microbial activity and a shortage of ectomycorrhizal fungi (Kropp and Langlois 1990, Aučina et al. 2014). Biological condition of these soils may be improved by enriching them with organic matter, e.g. by fertilization with a compost or inoculation with edaphon, including zooedaphon, from forest soils. In the forest nurseries composts from sewage sludge (with addition of bark or sawdust) can be useful (Boruszko 2011, Klimek et al. 2013a). Mulching is one of effective methods of soil enrichment. Apart from supplying organic matter, this treatment restores natural layered structure of forest soil (Leski et al. 2009, Aučina et al. 2014). Therefore, mulching creates optimal conditions for the development of microorganisms and

soil mesofauna (Forge et al. 2003). Spreading forest litter allows also for reintroduction of multiple microorganisms and arthropods, such as oribatid mites (Oribatida).

These small soil arthropods including Acari and especially Oribatida, are known to play many important functions in terrestrial ecosystems, they improve pedogenic processes and a propagation of bacteria and fungi, and they indirectly affect the formation of endo- and ectomycorrhizas (Klironomos & Kendrick 1996, Behan-Pelletier 1999, Schneider et al. 2005, Remén et al. 2010). They are also good bioindicators of soil biological activity (Behan-Pelletier 1999, 2003, Gulvik 2007).

The aim of the study was to determine the effects of mulching with forest litter and organic fertilization (compost prepared from sanitized sewage sludge supplemented with bark or sawdust) on the presence of oribatid mites in the nurseries producing European larch (*Larix decidua* L.) and Scots pine (*Pinus sylvestris* L.). The oribatid mites were treated as bioindicators of the effectiveness of soil revitalization treatments in in-ground nursery.

2. Material and Methods

The study was conducted in the years 2006-2007 in Białe Błota nursery belonging to Bydgoszcz Forest Inspectorate (53°06'12.3"N; 17°55'41.5"E), Poland. The experiment was established in the spring 2006 in the nurseries producing European larch and Scots pine. Each nursery included 16 experimental plots (4 variants x 4 repetitions) with the area of 2 m² each. The experiment included the following variants: Cb – compost made of sanitized sewage sludge ($\frac{2}{3}$) + pine bark ($\frac{1}{3}$), Cs – compost made of sanitized sewage sludge ($\frac{2}{3}$) + pine sawdust ($\frac{1}{3}$), M+Cb – mulching with forest litter + compost made of sanitized sewage sludge ($\frac{2}{3}$) + pine bark ($\frac{1}{3}$), M+Cs – mulching with forest litter + compost made of sanitized sewage sludge ($\frac{2}{3}$) + pine sawdust ($\frac{1}{3}$).

Detailed description of the investigated soils was presented in earlier works (Klimek et al. 2011, 2012). The compost contained 49% of organic matter, 56% of dry weight and its pH was 7.82. It was applied at a dose of 100 t·ha⁻¹ and mixed with surface soil layer (to the depth of 10 cm) before sowing the seeds.

The entire experimental area was irrigated with “Nelson” micro sprinklers. Irrigation times and precipitation rates were determined as recommended in the guidelines for open area forest nurseries (Pierzgalski et al. 2002). Aggregate water doses in subsequent growing seasons were 88 and 65 mm, in 2006 and 2007, respectively. Plants grown in the areas around Bydgoszcz, as well as in entire central Poland, need intense irrigation (Żarski & Dudek 2009, Stachowski & Markiewicz 2011, Żarski 2011).

Soil samples for acarological studies were collected four times in mid-June and mid-October. Twelve samples (three from each plot) were always collected per each experimental variant on each collection date. In total, 384 soil samples were collected. The soil was sampled from the area of 17 cm² and down to 3 cm deep. The mites were extracted over 7 days using Tullgren funnels, fixed in 70% ethanol, prepared and classified into species or genera. A total of 2,622 juvenile and adult oribatid mites were classified. Their mean density (N) was given per 1 m² of soil. Oribatida aggregations in each variant were described using a domination ratio D (%), total number of species (S), average number of species per sample (s) for a series of 48 samples, and Shannon's diversity index (H').

Prior to statistical analysis, the numerical data were subjected to a logarithmic transformation – $\ln(x+1)$ (Berthet and Gerard 1965). The statistical analysis was performed using Statistica 10.0: a compliance of the measurable parameters with the normal distribution was assessed using Kolmogorov-Smirnov test. As the normal distribution was not confirmed, a non-parametric analysis of variance (Kruskal-Wallis) was performed. For statistically significant differences ($p < 0.05$) a analysis for each pair was carried out (Mann-Whitney U test) to identify significantly different means.

3. Results

The number of oribatid mites in larch and pine nurseries fertilized with the compost enriched with bark (Cb) or sawdust (Cs) ranged from 240 to 1,000 individuals per m² (Table 1). Differences between these variants were not significant. Oribatida density was markedly improved following mulching, and it was 3,560-4,150 individuals m⁻² in larch nursery and 10,660-12,320 individuals m⁻² in pine nursery. In both nurse-

ries, the highest density of oribatid mites was observed on the plots that were both mulched and fertilized with bark-enriched compost (M+Cb).

On non-mulched plots evaluated in June 2006, the mite density was low and ranged from 0 to 300 individuals per m^2 (Table 2 and 3). On the last sampling date, an increase in the density up to 850 individuals m^{-2} was observed in larch nursery. In pine nursery on Cb and Cs plots assessed over the two-year study, the increase in Oribatida density was greater than in larch nursery and ranged from 2,410 to 3,760 individuals m^{-2} . Contrary to that, the density of oribatid mites in June 2006 on mulched plots where edaphon was reintroduced was high (3,010-11,790 individuals m^{-2}). In the next season (autumn 2006), a significant decrease in this parameter was observed on most of the mulched plots. In the spring of 2007, oribatid mites were significantly more abundant on these plots than in the previous season, and in the autumn 2007 their density was usually higher than at the beginning of the study. The only exception was M+Cs variant in larch nursery. It is worth mentioning that in autumn 2007 the density of oribatid mites on the mulched plots was many times higher in pine than in larch nursery. The highest Oribatida density was observed for M+Cb variant where it amounted to 37,470 individuals m^{-2} .

Table 1. The density of oribatid mites (N in 10^3 individuals m^{-2}) in the variants of the experiment for the forest nursery cultivations: larch (L) and pine (P)

Tabela 1. Liczebność mechowców (N w 10^3 osobników m^{-2}) w wariantach doświadczenia w uprawach szkółkarskich modrzewia (L) i sosny (P)

Taxon	Species of seedlings	Experiment variant				Kruskal-Wallis test	
		Cb	Cs	M+Cb	M+Cs	H	p
<i>Carabodes subarcticus</i> Tragardh	L	0	0	0.24 ^{Aa}	0.23 ^{Aa}	25.5	0.001
	P	0	0	0.45 ^{Aa}	0.43 ^{Aa}		
<i>Eremaeus oblongus</i> C.L. Koch	L	0	0	0.04 ^{Aa}	0.09 ^{Aa}	22.7	0.002
	P	0	0.01 ^A	0.14 ^{Ba}	0.70 ^{Ba}		
<i>Metabelba pulverulenta</i> (C.L. Koch)	L	0	0	0.09 ^{Aa}	0.10 ^{Aa}	15.8	0.027
	P	0	0	0.04 ^{Aa}	0.51 ^{Aa}		
<i>Oppiella nova</i> (Oudemans)	L	0.01 ^{Aa}	0.03 ^{ABa}	0.26 ^{Ba}	0.05 ^{ABa}	32.8	0.000
	P	0.01 ^{Aa}	0.09 ^{Aa}	4.06 ^{ABa}	2.23 ^{Bb}		

Table 1. cont.

Tabela 1. cd.

Taxon	Species of seedlings	Experiment variant				Kruskal-Wallis test	
		Cb	Cs	M+Cb	M+Cs	H	p
<i>Oribatula tibialis</i> (Nicolet)	L	0	0.03 ^{Aa}	0.16 ^{Ba}	0.71 ^{Ca}	52.3	0.000
	P	0.01 ^A	0.03 ^{Aa}	0.26 ^{Ba}	0.70 ^{Ca}		
<i>Pergalumna nervosa</i> (Berlese)	L	0	0	0.21 ^{Aa}	0.21 ^{Aa}	24.5	0.001
	P	0	0	0.29 ^{Aa}	0.28 ^{Aa}		
<i>Rhysotritia duplicata</i> (Grandjean)	L	0	0	0.06 ^{Aa}	0.01 ^{Aa}	18.3	0.011
	P	0	0	0.28 ^{Aa}	0.11 ^{Aa}		
<i>Scutovertex sculptus</i> Michael	L	0.11 ^{Aa}	0.10 ^{Aa}	1.23 ^{Ba}	0.35 ^{Aa}	98.6	0.000
	P	0.56 ^{Aa}	0.77 ^{Ab}	2.92 ^{Bb}	1.08 ^{Bb}		
<i>Steganacarus carinatus</i> C.L. Koch	L	0	0	0.15 ^{Aa}	0.24 ^{Aa}	29.88	0.000
	P	0	0	0.15 ^{Aa}	0.29 ^{Aa}		
<i>Tectocephus velatus</i> (Michael)	L	0.11 ^{Aa}	0.09 ^{Aa}	1.37 ^{Ba}	1.15 ^{Ba}	60.1	0.000
	P	0.06 ^{Aa}	0.09 ^{Aa}	3.19 ^{Ba}	3.71 ^{Ba}		
*Other species of Oribatida	L	0.00	0.06	0.34	0.41	-	-
	P	0.00	0.03	0.54	0.61		
Oribatida total	L	0.24 ^{Aa}	0.30 ^{Aa}	4.15 ^{Ba}	3.56 ^{Ba}	100.3	0.000
	P	0.65 ^{Ab}	1.00 ^{Ab}	12.32 ^{Ba}	10.66 ^{Ba}		

*Other species of Oribatida ($N < 200$ individuals per m^2): *Camisia biurus* (C.L. Koch) – L: M+Cb; *C. horrida* (Hermann) – L: M+Cb; *C. segnis* (Hermann) – P: M+Cs; *C. spinifer* (C.L. Koch) – L: M+Cb, M+Cs; P: M+Cb, M+Cs; *Carabodes forsslundi* Sellnick – P: M+Cb, M+Cs; *C. minusculus* Berlese – L: M+Cb, M+Cs; P: M+Cb, M+Cs; *Chamobates schuetzi* (Oudemans) – L: M+Cb, M+Cs; P: M+Cb, M+Cs; *Eupelops torulosus* (C.L. Koch) – L: M+Cb, M+Cs; P: M+Cb, M+Cs; *Galumna lanceata* (Oudemans) – P: M+Cb; *Lauropia neerlandica* (Oudemans) – L: M+Cs, P: M+Cs; *Licneremaeus licnophorus* (Michael) – L: M+Cs; P: M+Cs; *Liochthonius* sp. – P: M+Cs; *Micreremus brevipes* (Michael) – P: M+Cb; *Peloptulus phaenotus* (C.L. Koch) – L: M+Cb, P: M+Cb; *Phthiracarus longulus* (C.L. Koch) – L: M+Cb, M+Cs; P: M+Cb, M+Cs; *Protoribates variabilis* Rajski – L: M+Cs, P: M+Cb; *Quadroppia quadricarinata* (Michael) – L: M+Cs, P: M+Cb; *Ramusella mihelcici* (Pérez-Íñigo) – L: Cs, M+Cb, M+Cs; P: Cs, M+Cb, M+Cs; *Suctobelba* sp. – L: M+Cs, P: M+Cb, M+Cs; *Trhypochthonius tectorum* (Berlese) – L: M+Cb, P: M+Cb; *Trichoribates trimaculatus* C.L. Koch – L: M+Cb, P: M+Cb

^{AB} – the same letter for a seedling species means lack of significant differences among the variants of the experiment – a the Mann-Whitney U test at $p < 0.05$, ^{ab} – the same letter for a single variant of the experiment means lack of significant differences between the species of the seedlings – a the Mann-Whitney U test at $p < 0.05$)

Table 2. The dynamic changes in the density (N in 10^3 individuals m^{-2}) of oribatid mites over the 2-year course of the study in the forest nursery cultivation of larch

Tabela 2. Dynamika liczebności (N w 10^3 osobników m^{-2}) wybranych gatunków mechowców w 2-letnim cyklu badań w uprawie szkółkarskiej modrzewia

Taxon	Variant	Research data				Kruskal-Wallis test	
		VI. 2006	X. 2006	V. 2007	X. 2007	H	p
<i>Oppiella nova</i>	Cb	0	0	0	0.05	65.1	0.000
	Cs	0	0	0	0.10		
	M+Cb	0	0	0	1.05		
	M+Cs	0	0.05 ^A	0	0.15 ^A		
<i>Oribatula tibialis</i>	Cb	0	0	0	0	77.5	0.000
	Cs	0.05 ^A	0.05 ^A	0	0		
	M+Cb	0.55 ^A	0	0.10 ^A	0		
	M+Cs	1.76 ^A	0.10 ^B	0.85 ^{AB}	0.15 ^B		
<i>Scutovertex sculptus</i>	Cb	0.05 ^A	0	0	0.40 ^B	71.3	0.000
	Cs	0	0	0	0.40		
	M+Cb	0.10 ^A	0.40 ^A	1.15 ^A	3.26 ^B		
	M+Cs	0.15 ^A	0	0.15 ^A	1.10 ^A		
<i>Tectocephus velatus</i>	Cb	0	0	0.05 ^A	0.40 ^A	92.7	0.000
	Cs	0	0	0	0.35		
	M+Cb	0.40 ^A	0.55 ^A	1.30 ^A	3.21 ^A		
	M+Cs	2.06 ^A	0	0.80 ^A	1.76 ^A		
Oribatida total	Cb	0.05 ^A	0	0.05 ^A	0.85 ^B	127.9	0.000
	Cs	0.30 ^{AB}	0.05 ^A	0	0.85 ^B		
	M+Cb	3.01 ^A	2.01 ^A	3.71 ^{AB}	7.88 ^B		
	M+Cs	7.63 ^A	0.40 ^B	2.61 ^A	3.61 ^A		

Explanations see Table 1.

In total, the investigated area harbored 31 species of oribatid mites. Non-mulched plots yielded from 3 to 6 species, and after mulching this number increased to 21-26 species (Table 4). Statistical analysis based on the average number of species per sample (s) indicated significant increase in the number of species following mulching. Maximum values of this parameter in M+Cb and M+Cs variants were found in pine nursery. On non-mulched plots, s parameter was low (0.1-0.3) in the first year of the study, and it significantly increased by the last sampling date, particularly in pine nursery, up to 1.2-1.6 (Figure 1). Contrary results

were obtained on the mulched plots, where initially high average number of species s was reduced by the last sampling date. In pine nursery this decrease was significant. Shannon's diversity index (H') was relatively low on non-mulched plots (0.50-1.47) (Table 4), and it markedly increased in both nurseries (1.80-2.21) following mulching treatment.

Table 3. The dynamic changes in the density (N in 10^3 individuals m^{-2}) of oribatid mites over the 2-year course of the study in the forest nursery cultivation of pine

Tabela 3. Dynamika liczebności (N w 10^3 osobników m^{-2}) wybranych gatunków mechowców w 2-letnim cyklu badań w uprawie szkółkarskiej sosny

Taxon	Va-riant	Research data				Kruskal-Wallis test	
		VI. 2006	X. 2006	V. 2007	X. 2007	H	p
<i>Oppiella nova</i>	Cb	0	0	0	0.05	73.7	0.000
	Cs	0	0	0	0.35		
	M+Cb	0.05 ^A	0.05 ^A	0	16.15 ^B		
	M+Cs	0.90 ^A	0.05 ^A	0.25 ^A	7.73 ^B		
<i>Oribatula tibialis</i>	Cb	0.05	0	0	0	80.4	0.000
	Cs	0.05 ^A	0	0.05 ^A	0		
	M+Cb	0.90 ^A	0.05 ^A	0.05 ^A	0.05 ^A		
	M+Cs	1.61 ^A	0.45 ^A	0.75 ^A	0		
<i>Scutovertex sculptus</i>	Cb	0	0	0.10 ^A	2.16 ^A	119.3	0.000
	Cs	0	0	0	3.06		
	M+Cb	0	0.10 ^A	0.85 ^A	10.74 ^B		
	M+Cs	0	0	0.10 ^A	4.21 ^B		
<i>Tectocephus velatus</i>	Cb	0	0	0.05 ^A	0.20 ^A	104.6	0.000
	Cs	0	0	0	0.35		
	M+Cb	1.81 ^A	0.35 ^A	1.51 ^A	9.08 ^B		
	M+Cs	3.81 ^A	0.40 ^A	1.00 ^A	9.63 ^B		
Oribatida total	Cb	0.05 ^A	0	0.15 ^A	2.41 ^B	135.7	0.000
	Cs	0.20 ^A	0	0.05 ^A	3.76 ^B		
	M+Cb	7.17 ^A	1.15 ^B	3.46 ^C	37.47 ^D		
	M+Cs	11.79 ^A	1.51 ^B	7.32 ^C	22.02 ^D		

Explanations see Table 1.

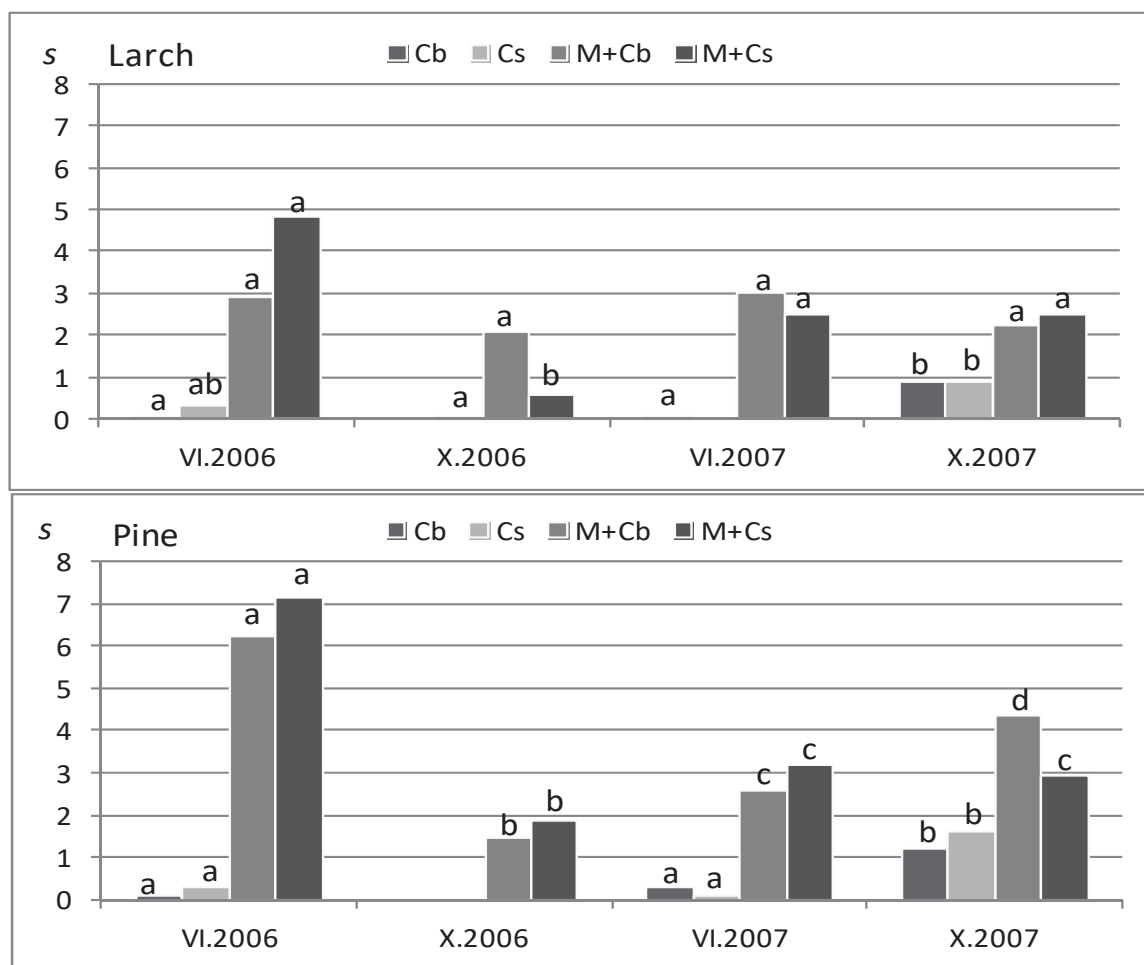


Fig. 1. Average number of species per sample (s) of oribatid mites over the 2-year course of the study (2006-2007) in the variants of the experiment at the forest nursery, ^{abc} – the same letter for a single variant of the experiment means lack of significant differences – a the Mann-Whitney U test at $p < 0.05$)

Rys. 1. Średnia liczba gatunków mechowców na próbkę (s) w 2-letnim cyklu badań (2006-2007) w wariantach doświadczenia w szkółce leśnej, ^{abc} – te same litery w ramach jednego wariantu doświadczenia oznaczają brak istotnych różnic – test U Manna-Whitneya, $p < 0.05$)

Only three Oribatida species, *Oppiella nova*, *Scutovertex sculptus* and *Tectocephus velatus* were present in all experimental variants (Table 1). Oribatida communities on non-mulched plots were dominated by *Scutovertex sculptus* with D index ranging from 33 to 87%. Depending on the variant, the most abundant oribatid mites on mulched plots were *Tectocephus velatus* (three times, D 32-35%) or *Oppiella nova* (once, D = 33%). Another species fairly common in the investigated area was

Oribatula tibialis that was absent in only one variant, and its mean domination rate was 7%. The other Oribatida species were less abundant and no effects of the experimental variants on their occurrence were observed.

Table 4. Number of oribatid mite species (S), average number of species (s) and Shannon index (H') in the variants of the experiment for the forest nursery cultivations: larch (L) and pine (P)

Tabela 4. Liczba gatunków mechowców (S), średnia liczba gatunków na próbkę (s) i wskaźnik ogólnej różnorodności gatunkowej Shannona (H') w badanych wariantach doświadczenia w uprawach szkółkarskich modrzewia (L) i sosny (P)

Index	Species of plant	Experiment variant				Kruskal-Wallis test	
		Cb	Cs	M+Cb	M+Cs	H	p
S	L	3	5	20	21	-	-
	P	4	6	26	22	-	-
s	L	0.3Aa	0.3Aa	2.6Ba	2.6Ba	93.5	0.000
	P	0.4Aa	0.5Aa	3.6Ba	3.8Ba		
H'	L	0.86	1.47	2.01	2.21	-	-
	P	0.50	0.87	1.80	2.08	-	-

Explanations see Table 1.

Scutovertex sculptus was the most abundant oribatid mite on non-mulched plots, and it was particularly common in pine nursery (560-770 individuals m^{-2}). Mulching positively affected its density, especially in M+Cb variant (1,230-2,920 individuals m^{-2}). This species preferred pine nursery. Pine seedlings attracted also numerous representatives of *Oppiella nova*, which in M+Cb variant achieved its maximum density (4,060 individuals m^{-2}) and was twice as abundant as in M+Cs variant. Mulching considerably improved the density of *Tectocephus velatus*.

This species, similarly to the previously described ones, preferred pine nursery but 3-fold difference between pine and larch nursery was too low to be significant. However, significant differences in its numbers between both nurseries were found for mulched and non-mulched plots. *Oribatula tibialis* was the most abundant species in both nurseries in M+Cs variant (700-710 individuals m^{-2}).

Oppiella nova, *Scutovertex sculptus* and *Tectocephus velatus* were the most numerous on the last sampling date, i.e. in October 2007, achiev-

ing the count of 16,150, 10,740 and 9,630 individuals m^{-2} , respectively (Table 2). The first two species were the most abundant in the last season in all experimental variants, and only once *Tectocepheus velatus* was the most abundant at the beginning of the study (larch nursery, M+Cs).

3. Discussion

Our earlier reports on the same experiment revealed no effects of various composts enriched with bark or sawdust on the growth of larch (Klimek et al. 2011) and pine seedlings (Klimek et al. 2012). However, their growth was considerably affected by mulching. This treatment reduced pH and increased the content of organic carbon and general nitrogen. Also ECM fungi on the seedling roots were found to be well developed and the use of the compost made of sewage sludge did not bring about any negative effects.

Therefore, increased abundance of oribatid mites after mulching observed in this study corresponded to improved quality of the produced seedlings. This confirmed proper course of soil revitalization processes. A study carried out in Lithuania that tested different forest litters revealed improvements in plant growth and ECM formation in pine seedlings fertilized with this substrate (Aučina et al. 2014). The results of this study indicated a key role of forest litter in improving environmental conditions conducive to the development of ECM fungi previously present in the soil. The forest litter probably did not serve as an inoculum for specific fungal species.

In our study, the forest litter introduced into the nurseries was most probably the source of numerous mesofauna species. However, not all populations from the soil of matured stands survived in new ecological conditions of the nurseries. Dynamics of mean number of species per samples s over the two-year study cycle indicated at first a drop in this parameter and then its gradual growth. In autumn 2007, 57% of the species present in the spring 2006 were detected. It should be remembered that oribatid mites do not have as many spreading options as fungi. Literature reports indicated that the colonization of initial soils is a slow process that may last for many months or even years (Wanner & Dunger 2002, Lehmitz et al. 2011).

Oribatid mites indirectly affect a nursery performance as they speed up the processes of organic matter decomposition (Wallwork 1983) and improve the activity of soil microorganisms including ECM fungi (Klironomos & Kendrick 1996, Behan-Pelletier 1999, Schneider et al. 2005, Remén et al. 2010). Some studies suggested that oribatid mites feed mainly on mycelium (Lindberg & Bengtsson 2005, Renker et al. 2005), and environmental conditions beneficial to the mycelium development are also favorable for Oribatida populations (Blakley et al. 2002, Pollierer et al. 2007). Good or improving condition of Oribatida communities and populations may therefore indicate their optimal performance.

After mulching, in both nurseries but particularly in the pine one, high density of fungivorous (Luxton 1972, Ponge 1991) *Oppiella nova* and *Tectocephus velatus* were observed. According to literature data, *Oppiella nova* is a parthenogenetic species with short life cycle (20 days), and its population grows very rapidly (Siepel 1994, Skubała & Gulvik 2005). Similar survival strategy is exercised by *Tectocephus velatus* (Gulvik 2007) but its life cycle is slightly longer. *T. velatus* is a eurytopic soil species (Weigmann & Kratz 1981), characterized by high reproduction rate and capability of colonizing new environments. Moreover, Remén et al. (2010) claimed that *Oppiella nova* feeds mainly on active ECM fungi, while *Tectocephus velatus* is rather a general fungivore. It is worth mentioning that these species were also numerous at a similar experiment on the linden nursery cultivation (Klimek et al. 2013a). Both species were the most abundant on the last sampling date, and this may suggest progressive soil revitalization also within fungal communities.

The density of another oribatid mite, *Oribatula tibialis*, which was fairly high in the beginning of the study, considerably decreased or it was not detected at all on the last sampling date. Interestingly, similar trends in density changes over time were observed for these species when forest litter was added to containers during the production of pine seedlings (Klimek et al. 2013b).

The sites fertilized with the compost alone (no mulching) were dominated by *Scutovertex sculptus*. This species is adapted to initial soils and high solar radiation and is commonly found in Poland e.g. on wastelands and industrial waste heaps (Skubała 1999, Rolbiecki et al. 2006). Therefore, it was not introduced from a forest but it had been probably

present in the nursery soil before the experiment was established. However, its abundance increased in all experimental variants and it reached its maximum density on the last sampling date.

This study mainly indicated very positive effects of mulching with forest litter on the presence of oribatid mites. The changes in their density indicate their affinity to the compost enriched with pine bark, especially at the end of the study. The highest density of oribatid mites, unprecedented in forest nurseries, was obtained in pine nursery by combined treatment involving mulching and fertilizing with the compost enriched with pine bark. Given high bioindicative value of this group of arthropods (Behan-Pelletier 1999, 2003, Gulvik 2007) it can be assumed that the implemented treatments resulted in desired soil revitalization that affected the quality of the produced seedlings.

4. Conclusions

The study showed a strong positive effect of mulching larch and pine nurseries with forest litter on the abundance and species diversity of oribatid mites. Dynamics of changes in Oribatida presence in this two-year study revealed positive effects of mulching on soil revitalization, particularly in pine nursery and when combined with fertilization with bark-enriched compost.

High abundance and growing population of such fungivores as *Oppiella nova* and *Tectocephus velatus* may indicate positive changes in fungal communities. The study suggests that these species may be good bioindicators of soil biological activity in in-ground forest nurseries.

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Wpływ ściółkowania ektopróchnicą leśną i nawożenia kompostowanym osadem ściekowym na mechowce (Acari: Oribatida) jako bioindykatory rewitalizacji gleb w uprawach szkółkarskich modrzewia i sosny

Streszczenie

Badania terenowe prowadzono w latach 2006-2007 w należącej do Nadleśnictwa Bydgoszcz gruntowej szkółce leśnej Białe Błota. Ich celem było określenie wpływu ściółkowania ektopróchnicą leśną i nawożenia kompostem przygotowanym na bazie higienizowanych osadów ściekowych z dodatkiem kory lub trocin na występowanie mechowców w uprawach szkółkarskich modrzewia europejskiego i sosny zwyczajnej. Mechowce traktowano jako bioindykatory zabiegów rewitalizacji gleb szkółki. Z przeprowadzonych badań wynika, iż ściółkowanie upraw modrzewia i sosny miało wyraźny dodatni wpływ na liczebność i różnorodność gatunkową mechowców. Przebieg dynamiki występowania tych roztoczy w 2-letnim cyklu badań świadczy o pozytywnym wpływie ściółkowania na rewitalizację gleb, szczególnie w uprawie sosny i w połączeniu z nawożeniem kompostem z dodatkiem kory. Liczne występowanie i rosnąca liczebność populacji mykofagów – *Oppiella nova* i *Tectocephus velatus* – może świadczyć o pozytywnych zmianach w obrębie zbiorowisk grzybów. Wymienione gatunki mogą być dobrymi bioindykatorami aktywności biologicznej gleb w gruntowych szkółkach leśnych.

Abstract

The study was conducted in the years 2006-2007 in Białe Błota nursery belonging to Bydgoszcz Forest Inspectorate (53°06'12.3"N; 17°55'41.5"E), Poland. The aim of the study was to determine the effects of mulching with forest litter and organic fertilization (compost prepared from sanitized sewage sludge supplemented with bark or sawdust) on the presence of oribatid mites in the nurseries producing European larch (*Larix decidua* L.) and Scots pine (*Pinus sylvestris* L.). The oribatid mites were treated as bioindicators of the effectiveness of soil revitalization treatments in in-ground nursery. The study showed a strong positive effect of mulching larch and pine nurseries with forest litter on the abundance and species diversity of oribatid mites. Dynamics of changes in Oribatida presence in this two-year study revealed positive effects of mulching on soil revitalization, particularly in pine nursery and when combined with fertilization with bark-enriched compost. High abundance and growing population of such fungivores as *Oppiella nova* and *Tectocepheus velatus* may indicate positive changes in fungal communities. The study suggests that these species may be good bioindicators of soil biological activity in in-ground forest nurseries.

Słowa kluczowe:

osady ściekowe, ściółkowanie, rewitalizacja gleb, bioindykacja, Oribatida

Keywords:

sewage sludge, mulching, soil revitalization, bioindicators, oribatid mites



The Potential Application of Effluent after Microalgae Anaerobic Digestion for Fertilization of Lettuce

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1. Introduction

Recently, it is observed growing trend in many EU countries to use of natural and organic fertilizers that are environmentally friendly. The societies' awareness resulting from dangers of using chemical fertilizers is still growing. Also, food industry noticed dynamic growth of organic food products. Therefore, demand for organic farming production will increase and role of different kind natural and organic fertilizers will gain importance. Worth noticing is fact that, the matter of third generation biofuels production is willingly discussed among scientists (Pawłowski, 2015). Thus, it should be highlighted that not only production of biogas is the ultimate goal but safe management of effluent after microalgae anaerobic digestion (algal effluent) as valuable organic fertilizer (Zabochnicka-Świątek, 2010; Zabochnicka-Świątek, 2013).

Due to the fact that food demand will be constantly growing, the maintenance of soil fertility will be key issue to face it. Currently soil degradation concerns approximately 50% of arable land in the world and it is projected to intensify in the future years (FAO, 2015). Despite that share of arable land in Poland equals 60% in total land use, the soil quality in Poland remain low. For instance, production properties of Polish soil from 1 hectare is comparable to 0.6 hectare of European Union arable land (Skłodowski & Bielska, 2009). The soil analysis indicates on decreasing level of organic matter content, with the average value of

1.94% in 2015 (EPI, 2017). Polish soils are characterized by high level of acidification – about 50% of arable land. Majority of soils belong to IV valuation class – 40%, with the surface area of 7 572 thousand ha (CSO, 2016). Diminishment of soil fertility may be the result of overusing chemical fertilizers. In 2014/15 the consumption of chemical fertilizers reached up to 39.2 and 123.2 kg/ha in terms of pure ingredient.

Taking into consideration negative effects of chemical fertilizers on the environment such as nitrogen leaching, depletion of nutrients, loss of organic matter and acidification it is desirable to explore for innovative, organic fertilizers which will not pose negative impact on environment. Algal biomass used for agricultural purposes will act in accordance with agricultural sustainable manner. Studies to date indicate that algae can be utilized as biofertilizers, seed primers, biostimulants and influence the growth of plants; improvement of physicochemical characteristic of soil (Lichner et al., 2013; Godlewska et al., 2016; Michalak et al., 2017). Different forms of algae such as dry biomass, extracts or post-fermentation residues are discovered to bring the value as effective fertilizer due to high micro and macronutrients content, phytohormones and vitamins (Blunden et al., 2010; Papenfus et al., 2013; Garcia-Gonzalez & Sommerfeld, 2016; Zabochnicka-Świątek, 2017). Organic fertilizers obtained from algal biomass are not toxic and do not pollute the environment unlike mineral fertilizers. The anaerobic digestion of microalgae provides biogas and effluent (Ward et al. 2014). Research on the impact of dry and living algal biomass on plant yielding and soil fertility was carried out, however algal effluent after microalgae anaerobic digestion as organic fertilizer has not been examined so far.

The main aim of the work was to assess the potential application of the algal effluent for fertilization of lettuce. Influence of the algal effluent fertilization on growth parameters of lettuce was also examined. The changes in physicochemical characteristics of sandy soil after application of algal effluent were determined, too.

2. Materials and methods

The pot experiment was conducted using 3 fertilization combinations in triplicate in the laboratory conditions. The experiment was set up on very light soil of valuation class VI, with granulometric composition

of loose sand (PSSS, 2008). The soil samples were taken from the Czestochowa steelworks area. At laboratory soil was dried and mixed in order to homogenize the soil material and sieved through 2.0 mesh for further preparation for analysis. Prior application of fertilizers, soil samples were taken from soil layer of 15 cm and analyzed. All results are given on a dry mass content.

In the soil samples were determined: the dry matter content according to PN-ISO 11465:1999. pH was measured according to PN-ISO 10390:1997. Kjeldahl's nitrogen was analyzed according to PN-ISO 11261:2002. Total carbon was determined by means of Multi N/C 2100 Analytik Jena. Measurement of Total Organic Carbon (TOC) concentration was conducted according to PN-ISO 14235:2003, by means of Spectrophotometer HACH DR/4000 V. Macro elements (P, K, Ca, Mg) and microelements (Cu, Zn, Fe) were analyzed according to PN-ISO 11047:2001 by means of plasma spectrometer – Spectro Arcos ICP-OES. Determination of available phosphorus and potassium content was carried out according to Egner-Riehm method (Karczewska & Kabała, 2017). The available magnesium content was examined by Schachtschabel method (Karczewska & Kabała, 2017). Measurement of humic acids content was carried out by means of method described by Stevenson (1994). Hydrolytic acidity and sum of alkaline cations were analyzed according to modified Kappen method (Karczewska & Kabała, 2017).

In our previous study biogas production from algal biomass digestion was performed and algal effluent was obtained. The effluent after 3-week anaerobic digestion of algal biomass *Scenedesmus acutus* was utilized for fertilization of lettuce. The macro elements as well as microelements contained in algal effluent could be more available to plants than in raw dry algal biomass. Measurements of pH, Kjeldahl's nitrogen, Dissolved Organic Carbon (DOC) concentration and macro elements (P, K, Ca, Mg) and microelements (Cu, Zn, Fe) in algal effluent were done.

The widely used mineral fertilizer Azofoska in this experiment was used as reference fertilization with dose of 1.1 g/kg of the soil recommended by manufacturer.

Plants for the experiment were selected based on short vegetation period and need of rational fertilization. *Lactuca sativa* chosen for the pot experiment exhibits sensitivity for salinity in the soil and nitrates accumulation.

Fertilization was carried out based on nitrogen content in the tested soil as the most significant macronutrient for plants growth and nutritional requirements for plants. The experiment was conducted based on the principles of good agricultural practice (GAP) and protecting plants against over-fertilization.

Before foundation of experiment, homogenous seeds were selected and used to produce the seedlings of lettuce which lasted around 15 days. Fertilization of plants took place in the time of seedlings transferring for the 0.5 kg pots. Plants were watered regularly throughout the entire experiment and leachate was collected in plastic bottles. Lettuce seedlings were provided with artificial conditions with the lightening of 12h per day with appropriate temperature of 18°C. While experiment was over, the plants were harvested and measured. The fertilized soil was analyzed in terms of pH, Kjeldahl's nitrogen, total carbon, total organic carbon, C/N ratio, macro (P, K, Ca, Mg) and microelements content (Zn, Cu, Fe), available forms of P, Mg and K.

The fertilization treatments for experiment are following:

- Mineral fertilizer Azofoska with N/P/K ratio of 13/6/17 in the dose of 1.1 g/kg,
- Algal effluent in the dose of 33.61 g/kg,
- Control sample – tap water without any additive.

3. Results and discussion

3.1. Characteristics of soil and fertilizers

The examined soil exhibits alkaline character in KCl – 7.60, which exceeds the maximum value of pH for Polish soils which is 7.4 (IUNG, 2017). The value of pH measured in H₂O is the same as maximum pH measured in Polish soils. TOC measured in soil is in the level of 7493 mg/kg which is placed at the lower limit in the range for Polish soils (3600-38400) mg/kg. Similarly, the value of Kjeldahl's nitrogen is assessed as low ($N_{Kjeld} - 7493$ mg/kg) because the value is close to the lower limit of range for Polish soils 400-3600 mg/kg. The content of macro elements in examined soils considerably below the average level of Polish soil, with exception of calcium. Particularly the soil suffers from potassium deficit, 21.3 times less than the average value recorded for Polish soils. The available forms of macro nutrients, phosphorus and

potassium content place the soil in the average soil fertility class. In the light of above mentioned properties of tested soil can be concluded that soil needs to be fertilized in order to restore nutritional values.

Mineral fertilizer Azofoska is characterized by specific content of nutrients presented in the Table 1. pH of this fertilizer was amounted to 5.6, which indicates on acidic character.

Table 1. Characteristics of mineral fertilizer Azofoska

Tabela 1. Charakterystyka nawozu mineralnego Azofoska

Nutrient	Compound name	[%]
Nitrogen	Total nitrogen	13.3
	Nitrate nitrogen	5.5
	Ammonium nitrogen	7.8
Phosphorus	Phosphorus pentoxide soluble: in neutral ammonium citrate and water	6.1
	Phosphorus pentoxide soluble: in water	4.0
Potassium	Potassium oxide soluble in water	17.1
Magnesium	Total magnesium oxide	4.5

The characteristic of the algal effluent is presented in the Table 2. The algal effluent effluent has a basic character (pH – 8.30). Kjeldahl's nitrogen of tested additive is at the level of 79938 mg/kg. The measured parameter of dissolved organic carbon indicated on high level of organic matter content (15151 mg/kg). The content of macronutrients is varied but the highest amount is recorded for calcium – 24030 mg/kg. There is twice predominance of phosphorus to potassium content (17084 mg P/kg and 8007 mg K/kg).

Table 2. Characteristic of the algal effluent after anaerobic digestion
Tabela 2. Charakterystyka odcieku pofermentacyjnego z glonów

Parameter/Nutrient	Unit	Algal effluent
pH _{H2O}	–	8.30
N _{Kjeld.}	mg/kg	79938
DOC	mg/kg	15151
P	mg/kg	17084
K	mg/kg	8007
Mg	mg/kg	3969
Ca	mg/kg	24030
Cu	mg/kg	150
Zn	mg/kg	579
Fe	mg/kg	7841

3.2. Effect of fertilization on soil

The applied fertilizers influenced on physicochemical characteristic of the soil. Application of mineral fertilizer caused decrease of pH from 7.60 to 7.40, while pH after addition of the algal effluent did not change. In both cases the fertilized soil has not change the alkaline character. In general, recommended pH for most of the plants is within the range 5.5-7.2 (Dyśko et al., 2014) It is documented that acidic and alkaline soils may disturb nutrients uptake by plants, particularly influence on deficiencies of phosphorus. In very acidic soils, at pH (in 1M KCl) below 4.5-5.0 the absorption of phosphorus rapidly decreases and phosphorus turns into practically insoluble compounds with plant-toxic aluminum. Inversely, when pH is above 6.8, absorption of phosphorus decreases. Systematic organic fertilization promotes stabilization of soil pH due to high organic matter content and increased buffering properties. Mineral fertilizers such as Azofoska used in this experiment exhibit acidifying properties and therefore should be used deliberately to not pollute the environment by toxic aluminum ions (Barak et al., 1997).

The Kjeldahls' nitrogen has increased in fertilized soil compared to control but the change was inconsiderable. Upward trend was noticed in case of mineral fertilization, change of Kjeldahl's nitrogen by 133 mg/kg compared to control. Other literature sources obtained results confirming that biogas digestate is the source of easily available forms of nitrogen for plants uptake and influenced on the greater biomass growth by approximately 30% compared with mineral fertilizers (Nabel et al., 2014). It is worth noticing that plants can absorb only mineral forms of nitrogen (NO_3^- , NH_4^+) which is several percent of total nitrogen (Bednarek & Tkaczyk, 2003; Zawadzki, 2003). Additionally, long-term application of the algal effluent as organic fertilizer prevents total nitrogen loss and thus prevents surface and groundwater against nitrates contamination. In this experiment, similar values of nitrogen achieved by two different types of fertilizers confirms that application of the algal effluent may constitute good source of nitrogen as well as commonly used Azofoska.

There is observed increase of TOC after application of the algal effluent 1.2 fold increase of TOC and decrease of the same amount of TOC in case of mineral fertilization. It resulted from the fact that the algal effluent is significant source of organic matter content. According to the literature, with the increase of organic matter, the sorption capacity also increased up to 40.10 mol/kg due to seaweed extract application (Habashy & Abdel-Razek, 2011). On the contrary, reduction of organic carbon by mineral fertilizer is in accordance with other literature sources (Dziadowiec et al., 2003; Rynowska-Hryńczuk, 1992). Crucial is fact that organic fertilizers decompose slowly in the soil, allowing for continuous release of nutrients and sustain the microbial activity for long time in comparison to mineral fertilizers (Murphy et al., 2007). Rural Development Program 2014-2020 assumes that soil analysis should be extended to twice TOC analysis which is regarded as necessary as well as providing positive organic matter balance due to fertilization (RDP, 2017).

C/N ratio has increased after treatment with the algal effluent, from 9.08 to 11.22. Differently, decrease of C/N ratio was recorded for mineral fertilization, change by 2.3 unit compared to control. Widening the C/N ratio is found to have positive effect on the balanced mineralization and immobilization processes in the soil. The application of mineral fertilizers favors mineralization processes and increase the availability of

nitrogen and subsequently may be the reason of nitrate leaching deep into the soil profile and groundwater.

The obtained results of macro elements analysis revealed that both organic and mineral fertilization caused increase of potassium, phosphorus, calcium and magnesium content compared to control. The highest increase was recorded for application of mineral fertilizer, although the change is regarded as not significant. The growing trend was also observed for the content of micro elements. The increase of zinc, copper and iron has inconsiderably increased after organic and mineral fertilization. It can be explained by short experiment time. The summarized physicochemical characteristic of fertilized soil is given in Table 3.

Table 3. Effect of the algal effluent fertilization on physicochemical characteristic of soil (Mean \pm SD)

Tabela 3. Wpływ nawożenia odciekiem pofermentacyjnym z glonów na właściwości fizykochemiczne gleby (Odchylenie standardowe \pm SD)

Parameter	Unit	Control sample	Azofoska	Algal effluent
pH _{KCl}	mg/kg	7.6 \pm 0.02	7.4 \pm 0.04	7.6 \pm 0.01
pH _{H₂O}	mg/kg	7.8 \pm 0.02	7.4 \pm 0.01	7.6 \pm 0.01
N _{Kield.}	mg/kg	939 \pm 61	1072 \pm 31	944 \pm 36
TOC	mg/kg	8527 \pm 835	7261 \pm 380	10593 \pm 2607
C/N ratio	–	9.1	6.8	11.2
P	mg/kg	140 \pm 1	175 \pm 4	167 \pm 11
K	mg/kg	574 \pm 17	762 \pm 15	629 \pm 47
Mg	mg/kg	895 \pm 8	990 \pm 16	952 \pm 57
Ca	mg/kg	4278 \pm 38	4350 \pm 110	4461 \pm 202
Cu	mg/kg	20 \pm 0.4	24 \pm 0.5	22 \pm 1.4
Zn	mg/kg	403 \pm 5	419 \pm 7	425 \pm 28
Fe	mg/kg	13841 \pm 110	13983 \pm 92	13655 \pm 524

Regarding the available forms of nutrients (P_2O_5 , K_2O , Mg), its values show changes to a relatively great extend in soil (Fig. 1).

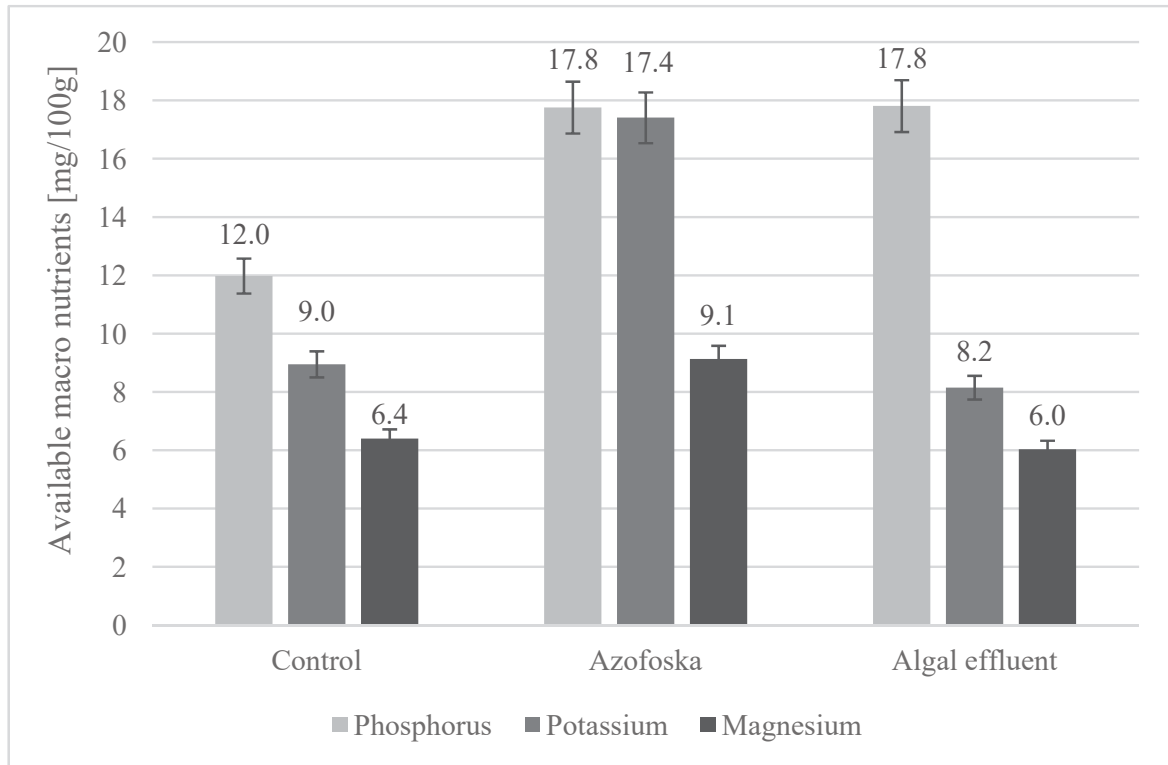


Fig. 1. Changes of available macro nutrients in soil after organic and mineral fertilization

Rys. 1. Zmiany zawartości łatwo przyswajalnych form makroelementów w glebie po zastosowaniu nawożenia

Considering available phosphorus content, its value was the same after treatment of the algal effluent and Azofoska – 17.8 mg P_2O_5 /100 g. The limit numbers established for available phosphorus content are: 0.1-15 (average fertility); 15.1-20.0 (high fertility); above 20.1 mg P_2O_5 /100 g (very high fertility). The soil fertility class for both organic and mineral treatment increased from average to high. Completely different effect was observed in case of potassium fertilization. The limit numbers for available K_2O content are as following: 7.6-12.5 (average fertility); 12.6-17.5 (high fertility); above 17.6 mg K_2O /100 (very high fertility). According to these intervals, application of mineral fertilizer resulted in the highest increase of available potassium with the value of 17.4 mg K_2O /100 g and changed soil fertility class from average to high.

Also, available magnesium content increased after application of mineral fertilizer, change from 6.4 to 9.1 mg Mg/100 g. The algal effluent added to the soil resulted in slight decrease of available potassium and magnesium content compared to control. It is mainly caused by nutrients utilization by plants and microorganisms during the experiment. However, it indicates that organic matter included in the algal effluent should be subjected to mineralization processes in order to become more available for plants uptake. Despite changes of available magnesium values, the soil fertility class maintained the same as in the control soil (very high fertility class above – 6.1 mg Mg/100 g).

3.3. Effect of fertilization on growth parameters of lettuce

The algal effluent influenced all growth parameters of lettuce. Number of leaves changed significantly from 5 to 7. Parameters such as leaves length and leaves width increased respectively, by 2.03 cm and 0.8 cm. However, roots length was inconsiderably shorter than in control lettuce. Plants looked healthy, without symptoms of over fertilization or plant diseases. Plants fertilized by mineral fertilizer did not survive until the end of pot experiment. The results of the experiment are presented in the Fig. 2.

Different authors draw attention to negative effects caused by using chemical fertilizers on the environment, e.g. nitrate pollution, loss of organic carbon and relatively high cost of given fertilizers. At the same time, literature sources provide alternatives which are organic fertilizers, such as compost, manure, sewage sludge and others (Diacono & Montemurro, 2010; Hatfield & Stewart, 2002; Kot & Frąc, 2014; Styszko et al., 2017; Ciesielczuk et al., 2015). Recently, scientists are interested in using alternative energy sources e.g. biogas, but utilization of biogas effluent and its impact on the environment has not been investigated (Möller, 2015). The application of biogas effluent and digestate as organic fertilizer and soil amendment is still taken under debate (Nkoa, 2014). Usually, feedstock of biogas production constitute animal manure or different kind wastes, therefore further experiments should be carried out to explore the potential use of algal effluent (Tambone et al., 2010; Murto et al., 2004). So far, obtained fertilization results within this experiment cannot be compared with other literature sources. The conducted experiment proved beneficial influence of the algal effluent on soil fertility and

enhancement the growth of lettuce. Properly handled and managed bio-gas effluent has great but still untapped potential to be safely used in organic farming without inducing any negative aspects on the environment.

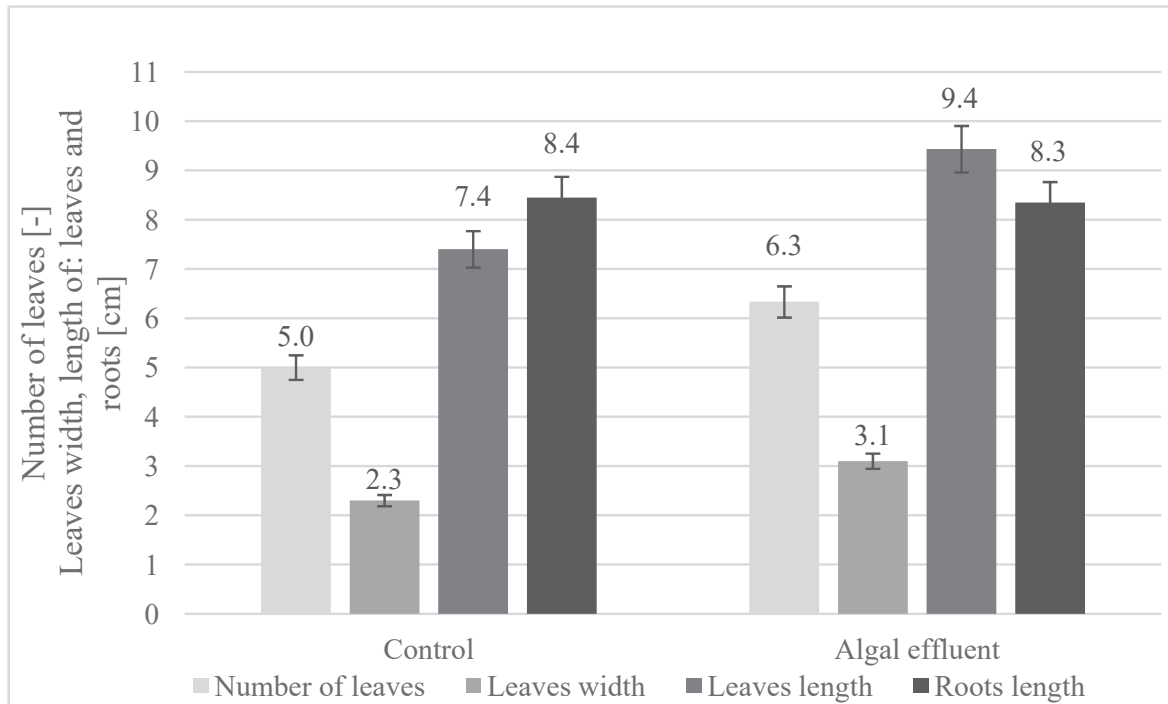


Fig. 2. Influence of the algal effluent fertilization on growth parameters of lettuce

Rys. 2. Wpływ nawożenia odciekami pofermentacyjnymi z glonów na parametry wzrostu sałaty

4. Conclusions

The conducted experiment draws attention on utilization of effluent after microalgae anaerobic digestion as a valuable fertilizer, characterized by high level of nutrients: N_{Kjeld} – 79938 mg/kg; DOC – 15151 mg/kg; P – 17084 mg/kg; Ca – 24030 mg/kg.

According to the obtained results the following conclusions can be drawn:

1. Both fertilizers (algal effluent and Azofoska) increased in the soil key macronutrients essential for plants growth: nitrogen, potassium and phosphorus to similar degree, which means that post-fermentation residues can replace chemical fertilizers.

2. Despite of higher content of macronutrients and their available forms in the fertilized soil by mineral fertilizer, the utilization of the algal effluent is beneficial due to enrichment the soil in total organic carbon (10593 mg/kg), available phosphorus (17.8 mg P₂O₅/100 g), widening C/N ratio (11.2) and counteracting pH changes.
3. Application of algal effluent resulted in significant increase of lettuce growth parameters: increase of number of leaves up to 6, leaves width up to 3.1 cm, leaves length up to 9.4.
4. The algal effluent can act as organic fertilizer which slowly decompose and release nutrients in prolonged time in accordance to sustainable agricultural approach in comparison to fast-acting mineral fertilizers.

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Możliwości zastosowania odcieku pofermentacyjnego na bazie glonów do nawożenia sałaty

Streszczenie

W ostatnich latach obserwuje się wzrost stosowania nawozów pochodzenia naturalnego, które są przyjazne dla środowiska naturalnego. Użyty w badaniach odciek pofermentacyjny po beztlenowej fermentacji glonów zawierał substancje organiczne i związki mineralne niezbędne do uprawy sałaty. Dzięki ww. składowi odciek może stanowić konkurencyjny produkt dla nawozów naturalnych i alternatywę dla nawozów mineralnych. Badania prowadzono w warunkach laboratoryjnych. Głównym celem badań była ocena możliwości wykorzystania odcieku pofermentacyjnego z glonów jako nawozu organicznego pod uprawę sałaty masłowej. W pracy przeanalizowano również wpływ ww. odcieku pofermentacyjnego na właściwości fizykochemiczne gleby i wzrost roślin. Eksperyment założono na glebie biellicowej, lekkiej, klasy VI, o składzie granulometrycznym luźnego piasku. Roślinami użytymi w doświadczeniu była sałata masłowa, odmiana "Attractie". Doświadczenie przeprowadzono w trzech powtórzeniach. Dawki nawozów ustalono ze względu na następujące czynniki: zawartość azotu jako głównego makroelementu determinującego wzrost i rozwój roślin oraz wymagania pokarmowe badanych roślin i aktualną żyzność gleby. Przeprowadzona kompleksowa analiza gleby i eksperyment doniczkowy wykazały, że pofermentacyjny odciek z glonów można z powodzeniem stosować w celu poprawy żyzności gleby i zwiększenia wzrostu roślin. Dodatek pofermentacyjnego odcieku glonów spowodował wzrost całkowitego węgla organicznego o 2066 mg/kg, fosforu całkowitego o 27 mg/kg, całkowitego potasu o 55 mg/kg, całkowitego magnezu o 57 mg/kg, całkowitego wapnia o 183 mg/kg. Wskaźnik C/N wzrósł z 9,1 do 11,2. Wartość pH pozostała niezmienną.

Abstract

In recent years, it is observed an increase in the use of natural fertilizers that are environmentally friendly. The effluent after microalgae anaerobic digestion (algal effluent) contained organic substances and mineral compounds necessary for lettuce cultivation, hence it is a competitive product for natural fertilizers and an alternative to mineral fertilizers. The experiment was conducted under laboratory conditions. The main objective of the research was to assess the possibility of using the algal effluent as an organic fertilizer for the cultivation of butterhead lettuce. The study also analyzed the effect of the algal effluent on physicochemical properties of soil and plant growth. The experiment was

established on podzolic, light soil of VI fertility class, under granulometric composition of loose sand. Plants used in the experiments are butterhead lettuce, variety 'Attractie'. The experiment was conducted in three replicates. Doses of fertilizers have been established due to factors: the content of nitrogen as the main macro element determining the growth and development of plants, nutritional requirements of tested plants and current soil fertility. The performed complex soil analysis and pot experiment showed that the algal effluent can be successfully used to improve soil fertility and enhance plants growth. Addition of the algal effluent caused increase of total organic carbon by 2066 mg/kg, total phosphorus by 27 mg/kg, total potassium by 55 mg/kg, total magnesium by 57 mg/kg, total calcium by 183 mg/kg. C/N ratio has increased from 9.1 to 11.2. pH maintained at the same level.

Słowa kluczowe:

mikroglony, odciek pofermentacyjny, nawożenie

Keywords:

microalgae, algal effluent after microalgae anaerobic digestion, fertilization



Decomposition of Carcinogenic Hydrocarbons in an Integrated Oxidation – Sorption System

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1. Introduction

At present no law sets limits for concentration of organic micropollutants, such as polycyclic aromatic hydrocarbons (PAHs). Simultaneously these compounds are listed among the pollutants which should be removed from wastewater because of their carcinogenic and mutagenic effect on water organisms (Regulation... 2014). These compounds are included in the list of the priority substances for water environment, which should be monitored in surface water (Regulation... 2016). Up to now, the research studies have shown that despite of the high rate of COD (or BOD₅) degradation, effectiveness of organic micropollutants removal in wastewater treatment plants is unsatisfactory (Włodarczyk-Makula 2011, Litter & Quici 20103). This applies to both municipal and industrial wastewater. In the case of industrial wastewater, part of micropollutants load is removed in company sludgeworks. Efficiency of micropollutants removal does not meet rising requirements for the quality of environment. This brings us to the necessity of using advanced methods of pollutants removal and degradation. It concerns mainly the pollutants which are resistant to degradation, such as PAHs, organochlorine derivatives or dyes (Zhang et al. 2012, Dąbek et al. 2013). Some of these pollutants show carcinogenic, mutagenic or/ and teratogenic effect to organisms and are relatively persistent in the environment (Abdel-Shafy & Mansour 2016). Both literature data and our own research indicate that effective removal of PAHs from wastewater is possible by sorption or by using advanced oxidation processes (AOPs)

(Włodarczyk-Makuła 2011, Brandli et al. 2008, Smol et al. 2014, Trapido et al. 1995, Beltrán et al. 1999). Use of these processes meets the requirements of IED Directive (Industrial Emissions Directive 2010/75/EU). This directive aims in integrated prevention and reducing emissions of pollutants from the industry by using the Best Available Techniques (BAT) (Directive 2010/75/EU). Among commonly used sorbents the activated carbons are the ones most carefully examined. Many researchers is now also focusing on using of some waste materials as sorbents (Brandli et al. 2008, Smol et al. 2014, Pan & Baoshan 2008). Few studies exist on sorption of PAHs from wastewater on activated carbons. In earlier own studies it was confirmed that PAHs can be removed from sewage by sorption (Smol et al. 2014). Use of granular activated carbon allowed for 97% removal of carcinogenic hydrocarbons whereas on mineral sorbents removal efficiency of these compounds did not exceed 84%. Literature review has show that also powdered activated carbons can be successfully used for removal of organic micropollutants from aqueous solutions. However it should be noted that in real life situations various organic and inorganic pollutants are present in wastewater, both in form of sediments, colloids and dissolved. Taking into consideration competitive sorption on suspended solids, effectiveness of adsorption of organic compounds on activated carbons can be limited. Because of this in the case of wastewater treatment other methods are recommended, including AOPs. Advanced oxidation processes allow for degradation of the organic pollutants instead of removal them (Trapido et al. 1995, Beltrán et al. 1999, Nkansah et al. 2012, Rubio-Clemente et al. 2014). High efficiency of AOPs in degradation of organic substances is widely discussed in research literature. These methods are based on generation of hydroxyl radicals – OH^\bullet , which nonselectively oxidize most organic compounds. The most frequently used oxidant is hydrogen peroxide, both alone, or as a component of Fenton's reagent (Neyens & Baeyens 2003, Pouran et al. 2014). Effectiveness of PAHs degradation depends on initial concentration of the compounds, kind and dose of reagents, pH of the environment, presence of the other pollutants and temperature (Rubio-Clemente et al. 2014). Presence of the catalysts is the factor which supports degradation of organic pollutants via free radical reactions. Also UV radiation increases the effectiveness of degradation processes. Titanium dioxide is frequently used as a catalyst, but also oth-

er chemicals are used for these purpose, including cobalt or wolfram compounds (Rubio-Clemente et al. 2014, Turek et al. 2016). In Fenton's process Fe^{2+} is used as catalyst. Information on two stage (oxidation plus sorption) removal of pollutants are also available in scientific literature. In this case sorption allows for preliminary removal of organic compounds, whereas oxidation is used as main degradation process. Sorption and oxidation can also be conducted simultaneously by using activated carbon as adsorbent and catalyst for generation of hydroxyl radicals. Under these conditions both soluble and adsorbed compounds can be oxidized (Ayranci & Duman 2010, Huang et al. 2003, Yuan et al. 2010). In the studies on advanced oxidation of PAHs conducted to date mainly symulant solutions were used. The solutions contained individual compounds or a mixture of several compounds. In wastewater PAHs are, however, mainly present as a mixture of various compounds. The composition of the mixture is affected by the kind of production processes. High concentrations of PAHs are reported in coke plant wastewater, also this pretreated in company sludgeworks. Despite of high efficiency of COD removal concentration of PAHs in treated wastewater is still high. Previous coauthored research works on this topic involved:

- oxidation of PAHs by hydrogen peroxide, also in the presence of catalysts, in water solutions (Turek et al. 2016),
- photooxidation of PAHs with hydrogen peroxide in municipal and coke plant effluents (Włodarczyk-Makuła 2011, Włodarczyk-Makuła et al. 2016),
- oxidation of selected PAHs by Fenton's reagent using CaO_2 as a source of hydroxyl radicals (Kozak & Włodarczyk-Makuła 2018),
- oxidation of selected PAHs in the presence of activated carbon (Włodarczyk-Makuła & Popenda 2018).

Because the results of PAHs removal/degradation using the processes mentioned above were satisfactory, research on carcinogenic hydrocarbons removal by integrated oxidation/ sorption have been undertaken. The aim of the study was to evaluate the effectiveness of carcinogenic PAHs removal during simultaneous oxidation-sorption process.

2. Research methods

2.1. Technological studies

Technological studies were performed with coke plant wastewater. Wastewater were taken from the secondary settlement tank of company sludgeworks. Biological processes (organic compounds removal plus nitrification) are used for sewage treatment in this plant. Wastewater was analyzed for total organic compound content (COD) and for initial PAHs concentration. 30% solution of hydrogen peroxide (H_2O_2) at dose equal to 2.5 g/L was used. The dose was selected taking into consideration the results of the previous research works (Litter & Quici 2010, Yuan et al. 2010). Powdered activated carbon C2186 (Merck) was used as a sorbent. Also catalyst (titanium dioxide – TiO_2) was added to support oxidation of PAHs. The doses of active carbon and catalyst were equal to 0.5 g/L and 1.0 g/L, respectively. The following samples were prepared:

- with H_2O_2 (control sample) (H),
- with H_2O_2 and TiO_2 (catalyst and sorbent) (H+T),
- with H_2O_2 , TiO_2 catalyst and powdered activated carbon (H+T+C).

Simultaneous oxidation and adsorption in all samples were performed for 24 hours. Analysis of COD and selected PAHs were done after 2 and 24 hours. The initial concentration of PAHs was equal to 6615 $\mu\text{g/L}$.

2.2. Qualification and quantification of PAHs

In order to determine concentration of PAHs in wastewater (both before and after simultaneous oxidation-sorption process) the samples were treated as follows. At the beginning extraction of organic matrix from wastewater was performed using liquid-liquid extraction. To extract organic matrix from wastewater cyclohexane: dichloromethane mixture (v/v – 5:1) was spiked into wastewater. After this, the extract was separated from wastewater in glass separator. In order to drain the separated extract anhydrous sodium sulphate was added followed by purification on silica gel (liquid-solid extraction). Cleaned extracts were concentrated under nitrogen stream to 2 mL. Such prepared extracts were qualified and quantified by GC-MS chromatograph Fisons. It was calibrated with AccuStandard mixture. Analysis of PAHs was performer for 50 min. Sample flow rate was equal to 1.5 mL/min. Recovery rates for individual

PAHs were evaluated using standard solution and based on this average concentration of the compounds was calculated. Concentration of the following PAHs was determined: benzo(a)anthracene (BaA), chrysene (Ch), benzo(b,k)fluoranthene (BbF, BkF), benzo(a)pyren (BaP), dibenzo(ah)anthracene (DahA), benzo(ghi)perylene (BghiP) and indeno (123cd)pirene (IP). These compounds contain 18, 20 or 22 carbon atoms in the particle, as well as 12 or 14 atoms of hydrogen in 4-6 ring system. BbF, BkF and IP have not only benzene, but also cyclopentane ring in their structure. All analyzed compounds are considered as carcinogenic or potentially carcinogenic.

3. The results

COD of coke plant effluents was at average equal to 689 mg/L. Table 1 presents COD changes after simultaneous oxidation – sorption in the presence of catalyst (titanium dioxide).

Table 1. Changes in the COD of wastewater

Tabela 1. Zmiany wartości ChZT w ściekach

Sample	After 2 h		After 24 h	
	COD, mg/L	Effectiveness %	COD, mg/L	Effectiveness %
H	426	38	192	71
H+T	358	48	146	79
H+T+C	273	60	94	86

Removal efficiency of COD after 24 h simultaneous sorption-oxidation process reached 86%. Use of hydrogen peroxide alone (H) or catalyzed oxidation without sorption (H+T) allowed to obtain efficiencies by several percent lower, compared to integrated oxidation-sorption system. This is an indication of the effect of sorption on activated carbon and of presence of catalyst, accordingly. Effectiveness of degradation and/or sorption of COD was comparable with the results obtained by other authors given in research paper by Rubio et al. (Rubio-Clemente et al. 2014).

3.1. Effectiveness of 4-ring PAHs degradation

Initial concentration of 4-ring PAHs was equal to 2359 $\mu\text{g/L}$. In the sample treated with hydrogen peroxide in the presence of catalyst, PAHs removal was about 31% after 2 h and 53% after 24 h. Removal rate of these compounds in catalyzed system increased as the time of reaction increased. Additive of activated carbon allowed for 84% removal of PAHs. Catalyst increased 4-ring PAHs removal rate by 16-18%, whereas sorbent by 6 to 13%, compared to control sample. Fig. 1 presents the changes in benzo(a)anthracene and chrysene concentration during oxidation or simultaneous oxidation-sorption.

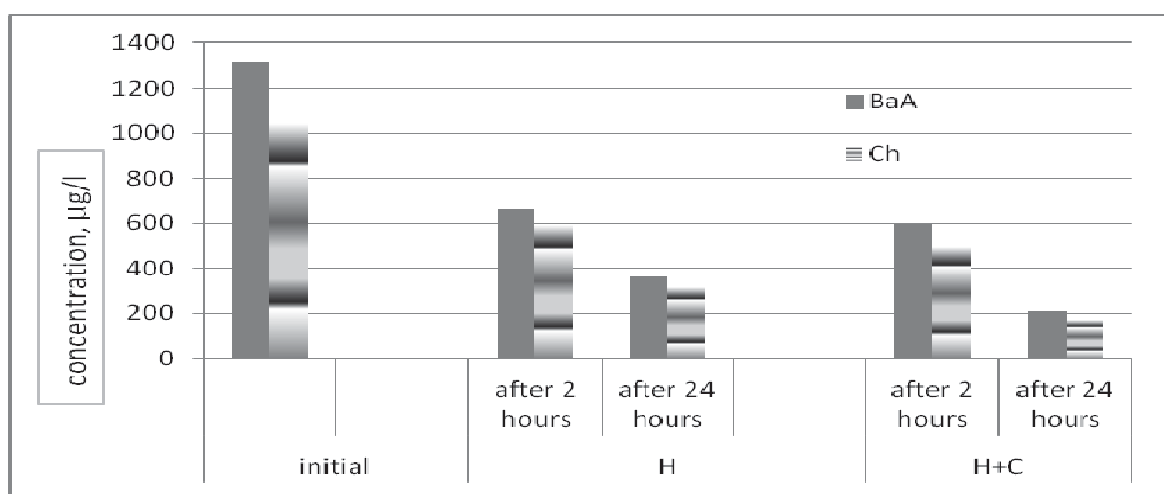


Fig. 1. Changes in the concentrations of benzo(a)anthracene and chrysene during integrated processes

Rys. 1. Zmiany stężenia benzo(a)antracenu i chryzenu w procesie zintegrowanym

3.2. Effectiveness of 5-ring PAHs degradation

In Fig. 2 and 3 changes in concentration of benzofluoranthenes, benzo(a)pirene and dibenzo(ah)anthracene are presented. Initial total concentration of 5-ring compounds was equal to 3235 $\mu\text{g/L}$. Benzo(a)pirene represented about 30% of total 5-ring compounds concentration. This compound is considered as the most carcinogenic PAH. Trend in concentration changes of 5-ring compounds was similar to the 4-ring ones. PAHs were progressively oxidized. Addition of activated carbon allowed to remove part of PAHs by sorption process. PAHs removal effectiveness did not exceed 43% in the case of (H) sample and 57% in the case of (H+T) sample. It increased to 80% when activated

carbon was present in the sample. Degradation of 5-ring PAHs was slower than 4-ring ones which would seem to indicate higher resistance of benzo(b)fluoranthenes, benzo(a)pyrene and dibenzo(ah)anthracene to the degradation. Hydrocarbons which contain cyclopentane ring (it means benzo(b)fluoranthenes) were better adsorbable on activated carbon, but less vulnerable to oxidation than other 5-ring compounds.

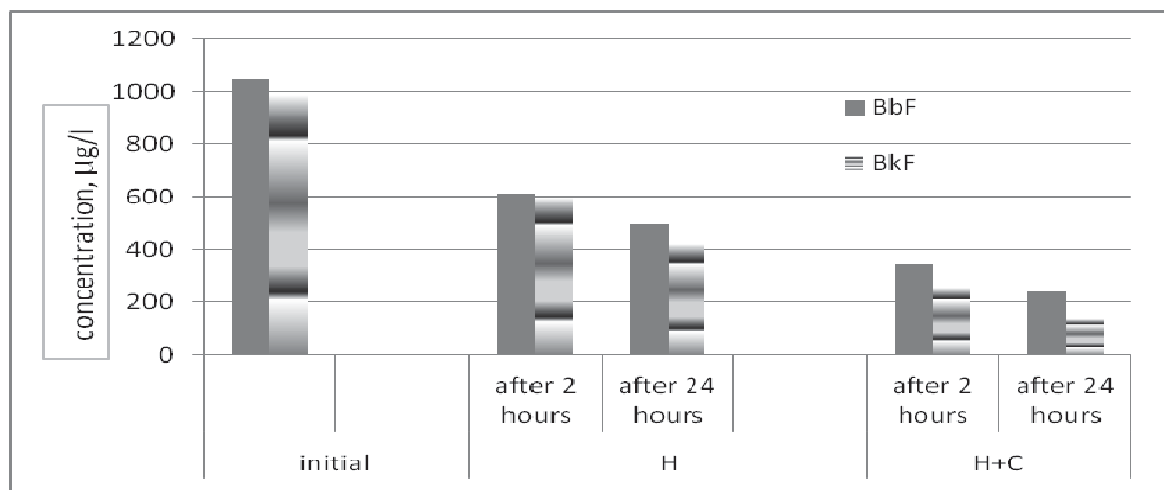


Fig. 2. Changes in the concentrations of benzo(b)fluoranthene and benzo(k)fluoranthene during integrated processes

Rys. 2. Zmiany stężenia benzo(b)fluorantenu i benzo(k)fluorantenu w procesie zintegrowanym

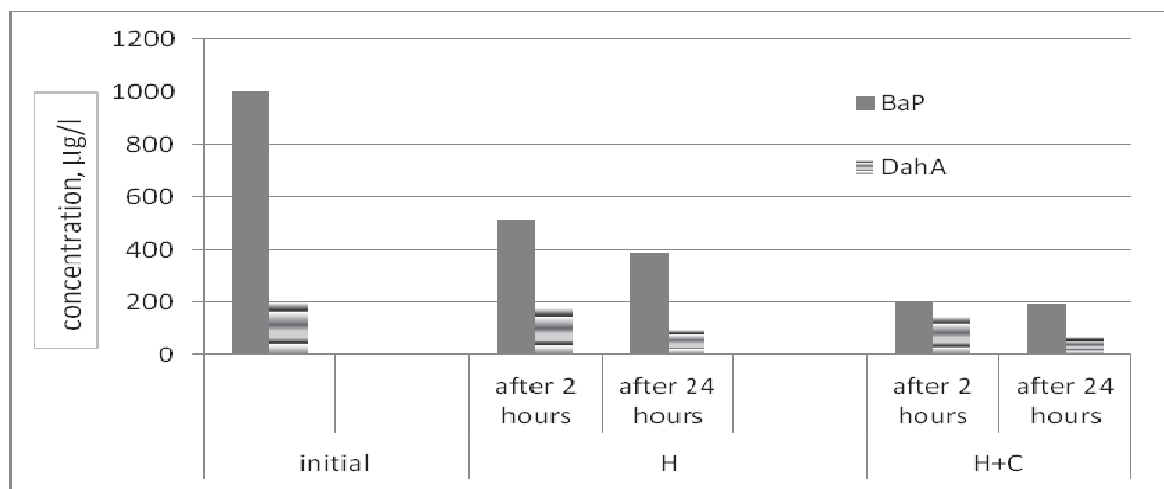


Fig. 3. Changes in the concentrations of benzo(a)pyrene and dibenzo(ah)anthracene during integrated processes

Rys. 3. Zmiany stężenia benzo(a)pirenu i dibenzo(ah)antracenu w procesie zintegrowanym

3.3. Effectiveness of 6-ring PAHs degradation

In Fig. 4 changes in concentration of indeno(123cd)pyrene and benzo(ghi)perylene during oxidation and simultaneous oxidation-sorption are presented. Initial total concentration of analyzed 6-ring PAHs was 1021 $\mu\text{g/L}$. After 24 h of hydrogen peroxide oxidation it decreased by 27%. Addition of catalyst increased the effectiveness of 6-ring PAH removal by 15%, use of activated carbon by another 26%.

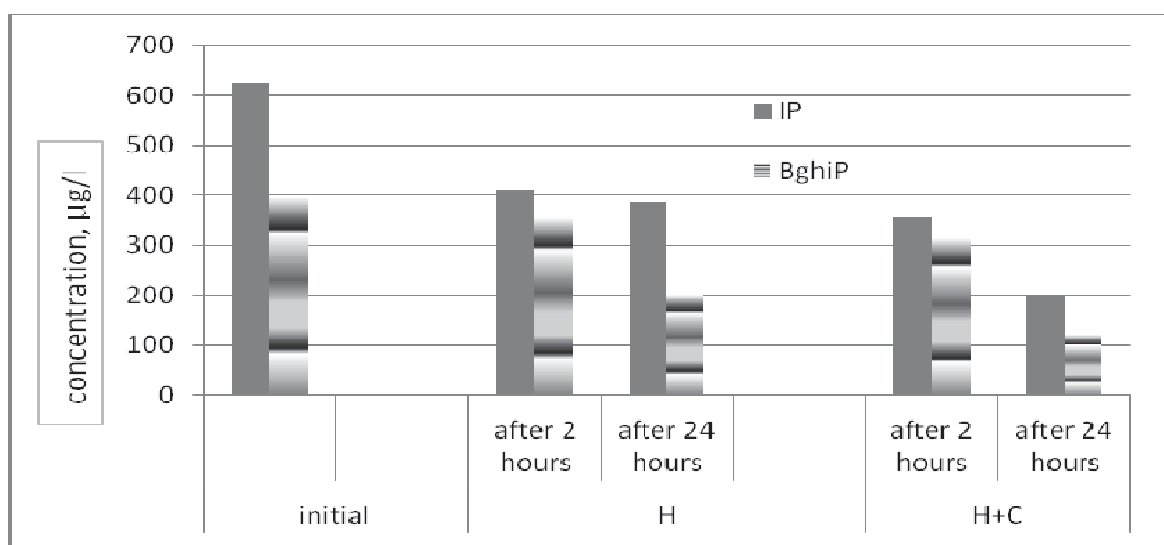


Fig. 4. Changes in the concentrations of indeno(123cd)pyrene and benzo(ghi)perylene during integrated processes

Rys. 4. Zmiany stężenia indeno(123cd)piranu i benzo(ghi)perylenu w procesie zintegrowanym

In so doing, the highest degradation efficiency of 6-ring PAHs was achieved under simultaneous catalytic oxidation-sorption. It was characteristic for all carcinogenic compounds. Effectiveness of PAHs removal decreased as the number of rings in PAH congeners increased.

4. Summary and conclusions

The results of research work indicate that the most preferable conditions for removal of carcinogenic hydrocarbons from coke plant wastewater are ensured in integrated catalyzed oxidation-sorption system. It can be emphasized that under conditions of the experiment significant removal of 4 and 5-ring was achieved, which was a result of oxidation of these compounds. In the case of 6-ring PAH removal sorption

played more important role. It can be explained by higher octanol/water values of 6-ring PAHs. Higher removal efficiency was achieved for the PAH compounds which contain cyclopentane ring in molecule structure. It can be assumed that they contain in the molecule larger number of persistent bounds than other. Based on the obtained results the following points can be made:

- Removal rate of individual hydrocarbons depended on their structure, as well as on the presence of catalyst and activated carbon in the sample.
- Effectiveness of the oxidation of carcinogenic hydrocarbons were in the range of 27 to 55%, addition of catalyst (TiO₂) increased it to 38-72%.
- Integrated catalytic oxidation – sorption ensured the efficiency of removal in the range 67-86%.

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Rozkład rakotwórczych węglowodorów w zintegrowanym układzie: utlenianie-sorpcja

Streszczenie

Celem badań było określenie efektywności degradacji rakotwórczych WWA w zintegrowanym procesie utleniania i sorpcji. Badania technologiczne prowadzono z wykorzystaniem biologicznie oczyszczonych ścieków koksowniczych. Utlenianie prowadzono z wykorzystaniem ditlenku diwodoru. Proces adsorpcji polegał na wprowadzeniu pylistego węgla aktywnego. Katalizatorem reakcji utleniania był ditlenek tytanu. Badania prowadzono przez 24 godz. Stężenia WWA oznaczano przed procesem oraz po 2 godz. i 24 godz. trwania procesu utleniania. Efektywność degradacji WWA wyliczono na podstawie zmian stężenia WWA przed i po procesie. Analizę jakościowo-ilościową WWA prowadzono z wykorzystaniem układu chromatografu gazowego i spektrometru masowego. Badania prowadzono przy stałym odczynie środowiska i stałej temperaturze. Efektywność degradacji analizowanych węglowodorów w warunkach utleniania była w zakresie od 27 do 55%. Obecność katalizatora tytanowego wspomagała utlenianie, co powodowało, że efektywność degradacji węglowodorów była w zakresie od 38 do 72%. W procesie zintegrowanym (utlenianie katalityczne w warunkach sorpcji) efektywność degradacji WWA była w granicach od 67 do 86%. Wyniki badań potwierdzają że proces utleniania i sorpcji może być skuteczny w doczyszczaniu ścieków przemysłowych i zapewniać ograniczenie ładunku WWA wprowadzanego do środowiska.

Abstract

The aim of the study was to evaluate the removal of carcinogenic PAHs during integrated processes: catalytic oxidation and sorption. Technological research was conducted using biologically treated industrial wastewater (coke plant wastewater). Oxidation was carried out with dihydrogen peroxide. The adsorption process was carried out onto powdered activated carbon. TiO_2 was added to the wastewater as a catalyst of oxidation reaction. The experiment was carried out for 24 hours. The concentration of PAHs at the beginning, after 2 and after 24 hours of integrated processes was analyzed. The effectiveness of PAHs degradation was evaluated based on the the individual compounds concentration changes before and after process. Quantitative and qualitative determination of

polycyclic aromatic hydrocarbons was conducted using gas chromatograph - mass spectrometer system. The experiments were conducted under constant pH as well as under constant temperature. The efficiency of oxidation of the analyzed hydrocarbons under oxidation conditions ranged from 27 to 55%. In the presence of the titanium catalyst the efficiency of PAHs degradation was enhanced to 38-72%. During the integrated process (catalytic oxidation and adsorption on activated carbon) the PAHs removal was in the range 67-86%. The results lead to the conclusion that simultaneous oxidation and adsorption can be successfully apply in the final treatment of industrial wastewater and results in the minimizing PAHs load discharged to the environment.

Słowa kluczowe:

WWA, ścieki koksownicze, utlenianie, sorpcja, TiO₂

Keywords:

PAHs, coke wastewater, oxidation, sorption, TiO₂



Thermal Insulation Materials with High-porous Structure Based on the Soluble Glass and Technogenic Mineral Fillers

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1. Statement of the problem

Alkali-silicate porous materials obtained by means of thermal or cold foaming of alkali metals silicates aqueous solutions (soluble glass) or solid alkali silicate hydrogels (Pavlenko & Koshlak 2015a,b, Koshlak et al. 2016, Leonovich 2012, Pavlenko & Pietrowski 2017, Fei et al. 2007), are referred to the present-day, efficient inorganic insulants, promising due to the ability to achieve low values of the relative density and thermal conductivity while maintaining sufficient structure strength and easy handling of foaming and induration processes within a wide range of composition formulations. The above benefits are based on the equilibrium and homogeneity of the main raw mixture component: soluble glass and hydrogels based on it.

Composite alkaline-silicate porous thermal-insulating materials, both granulated and block-type, contain significant amounts of the gas phase. There are various technological approaches to obtaining such materials at gas development directly in the strata of the formed composition. Moreover, the process of gas development at high temperatures can be based both on the special additives reactions, and on the crystallization and chemically bound water vapors liberation.

2. Recent research analysis

To manufacture foam glass, special gas forming agents are used. Normally, the process of making the foam glass lies in preparing the batch, consisting of 95-97% of powdered glass and 5-3% of the gas forming agents (carbonate, such as limestone, or carbon, such as charcoal, coke, carbon dust), heating the batch to the temperature of silicates' pyroplastic state. At this temperature glass grains are sintered and gases formed as a result of the gas-forming agents decomposition, blow highly viscous glass melt. After annealing and cooling, porous material is formed with high thermal insulation properties and high mechanical strength (Koshlak 2017a). General issues to obtain the foam glass, including granular one, are described in monographs (Koshlak 2017b, Demidovich 1975). The foaming temperature of foam glass usually lies between 750°C and 900°C.

Another method is the heat processing of glassy silicates containing water, which gasifies at high temperatures and foams the silicate base. Raw material in this process can be both natural (Meizel & Sandler 1988) and synthetic water-containing materials.

To obtain blocks of heat-insulating material, the granular thermal insulating silicate filler can be used, as suggested by the authors (Patent No. 2161142). In this case, the use of a silicate binding component permits forming blocks of the required size and shape, and dehydration of the latter occurs at temperatures within 100-350°C.

The feed silicate composition can be obtained by artificial means. In this case, it is often possible to avoid energy-intensive and technologically costly operation of obtaining highly dispersed silicate powders. The raw materials basis for such technical solutions, are water soluble silicates, most frequently sodium silicates. Obtaining of sodium silicates solutions is performed in compliance with the schemes of the technical product synthesis: soluble glass, or by means of silicon oxide dissolution in a strong caustic, or by autoclave dissolution of pre-fused silicate (silicate-blocks). Further, aqueous solution of sodium silicate in one way or another is converted into a gel, for example by the adding acids or strong electrolytes, and the resulting material is accessible to heat treatment, when water is removed from it and the product foams, increasing its volume significantly. In this case, if heat treatment of the material is performed in a rigid

metal form, then while foaming, the material fills the entire free volume of the form, forming blocks of the given configuration.

Amorphous silica is frequently used to produce sodium silicate with the required $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. Normally, microsilica-wastes from the production of crystalline silicon are used for these purposes (Patent No. 2097362).

Another option to obtain light porous silicate blocks is mixing the finished granulated lightweight silicate with any binding material, followed by hardening of the composition and obtaining the required blocks. Both of the described approaches to obtaining light silicates have been implemented in numerous technical solutions. At the same time, examples of the particular lightweight products manufacture may have some differences both in the composition of the starting materials and in their processing technology.

As it was noted above, one of the ways to obtain foamed silicate in the form of blocks or slabs is heat treatment in rigid forms of sodium silicates pre-transformed into the gel state with various additives.

For the raw material transformation from the fluid to the thickened pasty state and the subsequent granulation, it is possible to add not only the hydrophobic agent, but also the acidic components to it. Thus, in (Patent No. 2220927), the option of adding boric acid is suggested. In (Patent No. 2220928), it is suggested to increase the content of acid oxides in the composition due to adding not only mineral acid, but dispersed acid oxides as well, preferably SiO_2 and Al_2O_3 , due to adding burnt clay: naturally burnt clay (which constituents content is close to that of the TPP fly ash); in (Patent No. 2246463) – fly ash of thermal power plants is directly suggested.

Modification of additives to soluble glass is also proposed in the study (Patent 2134668). In the invention described, soluble glass is mixed with portland cement and sodium hexafluorosilicate. The resulting mass is filled in the forms and undergoes heat treatment in the furnace, where the raw mass is additionally blown up and acquires the necessary properties.

Currently, the two technologies for thermal insulating materials manufacturing of rare-glass compositions are suggested. The main difference between them is the method of the starting rare-glass composition preparation. These are process flow diagrams with the use of liquid (Pa-

tent No. 2268248) and mechanical granulation. The both technologies are two-staged and include stages of the prepared rare-glass composition granulation and the subsequent granules heating in a closed form at the temperatures within 400-450°C.

With the use of technologies for liquid granulation of composite systems, there arise difficulties connected with the large fillers granulation, which are difficult to pass through the bushing openings; with maintaining the necessary concentration of Al, Ca, Mg chlorides solutions and their mixtures in the operation cycle and with the worked-out brine utilization. The indicated problems do not occur at the use of mechanical granulation, it is possible to use standard equipment. At the moment, the processing technical procedure, which includes mechanical granulation, is the most processable, promising and used in our suggested developments.

An interesting technical solution of the set assignment is the suggested variant of using the starting raw materials mix and the technology used in the production of alkaline-silicate insulation material: “aerated glass” TOV “Stroyevolutsia” (Żelazna 2012). Under its regulations, heat treatment of the soluble glass mixture, a creaming agent (slightly hydrated sodium silicate) and hydrophobe agents are provided. The process of obtaining a granulated “aerated glass” includes homogenizing by mixing the components of the above starting mixture and subsequent heat treatment at 110-115°C. In the course of the transformation, the mass viscosity is significantly growing and the initial liquid system is transformed into a plastic-solid mass. Cooled to the room temperature, the product is completely solidified and acquires fragility, necessary for the subsequent crushing into pieces. After crushing, it is fractionated and “beads” are obtained. The air-entrainment to such “beads” is performed in a boiling layer or in a drum oven at 350-600°C.

The use of such a procedure causes a number of technological problems connected with rheological and environmental difficulties of introducing in this way hydrophobe agents into the composite system, with the possibility to reproduce the dimensions and regularity of pores, the granules macrostructure strength in general and the reduction of internal tension in the products.

3. Identification of previously unsettled parts of the general problem

Analysis of the existing suggested raw mixtures formulations and methods of obtaining thermal insulating materials proves that introducing a significant gel formers amount has a serious drawback: the gelling agent breaks the soluble glass structure to form hydrosilicic acid gel, which is capable of retaining less water than soluble glass. This adversely affects the porosity of the resulting rare glass compositions. Therefore, there is a need to introduce such substances that are inert to soluble glass at the normal temperature.

In addition, a significant drawback of the known methods is performing air-entrainment at fixed temperatures in the furnace within the range of 300-700°C. Such a mode of heat treatment reveals several contradictory trends. At relatively low temperatures, the air-entrainment process is complicated due to the low warming-up rate of the raw mass internal areas, resulting in the increased duration of its air-entrainment process.

At the same time, the slow warming up of rare-glass mixtures also leads to significant losses of chemically bound water, due to which air-entrainment of the mixtures occurs. The high rate and unevenness of their heating is manifested in the size, regularity of the pores and the strength of the entire porous structure, in the internal tensions of the products. Therefore, an important prerequisite for obtaining the expanded material possessing a set of required properties and their reproduction is compliance with the principle of correspondence between the rate of crystallization and chemically bound water isolation and the rate of new solid silicate structures formation.

In all of the above-described methods, the first stage is to obtain a solid or plastic composition from soluble glass which can then be subjected to heat treatment. At the same time it is not necessary to use different additives that cause coagulation of silicates. It is possible to obtain a plastic composition using soluble glass simply by means of adding an inert disperse component.

4. Statement of assignment and methods of its solving

The study performed is aimed at the search and development of an optimized raw material mixture variant of the silicon oxide containing

technogenic component: fly ash of thermal power plants and methods of obtaining the fly ash based porous alkaline-silicate composite thermal insulating materials of extended application, differing from the analogues by their composition, the content of the starting raw mass, the sequence and modes of the target product formation, the applied technological equipment.

5. Study results and their discussion

In the present project, the set task of making the targeted porous thermal insulating material is achieved by means of the raw mass hot foaming technology, which procedure includes the four main stages:

- 1) preparation of the starting raw mixture components and homogenization of the latter;
- 2) the composite system “gaging” by soluble glass and formation of a persistent gel; fragmentation of the hardened raw mass and placement of the granulate into lined dismountable molds;
- 3) heating and transferring of the workpieces’ substance into the pyroplastic state (110-115°C);
- 4) further hot foaming and reproduction of the regular porous macrostructure of composite systems (130-220°C) and formation of the targeted processed product’s properties (500-550°C).

The blowing agent in this case is water (mainly silanol or molecular, strongly bound by hydrogen bonds with unbridged oxygen atoms), which is released during heat treatment of composite systems.

In the raw mixture, the industrial soluble glass, thermal power plants fly ash of the mixed chemical composition (see Table 1), sticky portland cement and, additionally, a thickener (pre-staged partially dehydrated hardened “dry glass”) are used.

Table 1. Chemical composition of the thermal power plants fly ash, % mass

Tabela 1. Skład chemiczny popiołu lotnego elektrowni, % mas.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Mn ₃ O ₄	TiO ₂	SO ₃	P ₂ O ₅
51,68	16,75	14,47	0,88	4,38	0,35	2,58	0,04	0,86	4,24	0,49

In the prepared samples, the fly ash is manifesting good reinforcing properties, high thermal stability, sufficient resistance to aggressive media, has a small bulk density. At the same time, the results of the authors' studies (Breck 1976, Ovcharenko 2000) (on the ability of alkaline-silicate systems with Al_2O_3 in alkaline media to form insoluble products of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{Si}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) permit to consider aluminum oxide contained in ash to be a modifying component that provides the raw mix with the properties necessary for the targeted product formation.

In forming the raw mix, the results were taken into account on improving the water resistance of alkali silicate composition by means of replacing the two-calcium silicate (belit) hydrophobe components with the sticky Portland cement; the results are presented in (Maliavsky & Zvereva 2015).

The "setting" rate control of the suggested raw mix during the formation of hydrosilicic acid xerogel (depending on the executed tasks purposes) was performed by means of varying properties of the thickener used and by means of regulating the hardened processed mass fragmentation in the further processes and its subsequent hot foaming.

The raw mix prepared according to the optimized formulation, in contrast to the previously considered analogues, starts hardening at the usual temperature from the moment of its "gaging" with soluble glass and forms a plastic cake with the properties necessary for further fragmentation.

The suggested raw mix also permits to overcome the difficulties associated with drying of viscous rare-glass mix to remove a large output amount of water (56-62%) to the water content of 33-38% needed to obtain a rigid hydrogel capable of thermal blowing.

The optimized formulation of the raw mix allows processing of the compositions in various ways, with the formation of thermal insulating materials of extended application. An important prerequisite for their reproduction with the necessary properties system is strict compliance with the regulatory requirements established by the previous empirical studies.

In parallel with the formulation development, the technology of samples manufacturing was being tried. Thereat, the decisive factor, in contrast to the regulations, the exclusion of the raw mix granulation stage after heat treatment 110-115°C and the use of sealed closed forms at their temperature annealing.

The suggested hot air entrainment of the silicate compositions structure “blowing” of the systems in a xerogel form passes quickly, avoiding the viscous-adhesive state. The determining factor in the process of the systems thermal activation was the technical performing of their heating reproduced rate (Pat. 43549).

The conscious choice of its optimal mode is motivated by empirical data to determine the thermal foaming features of composite systems obtained by the method of differential-thermal analysis (DTA) presented in Fig. 1.

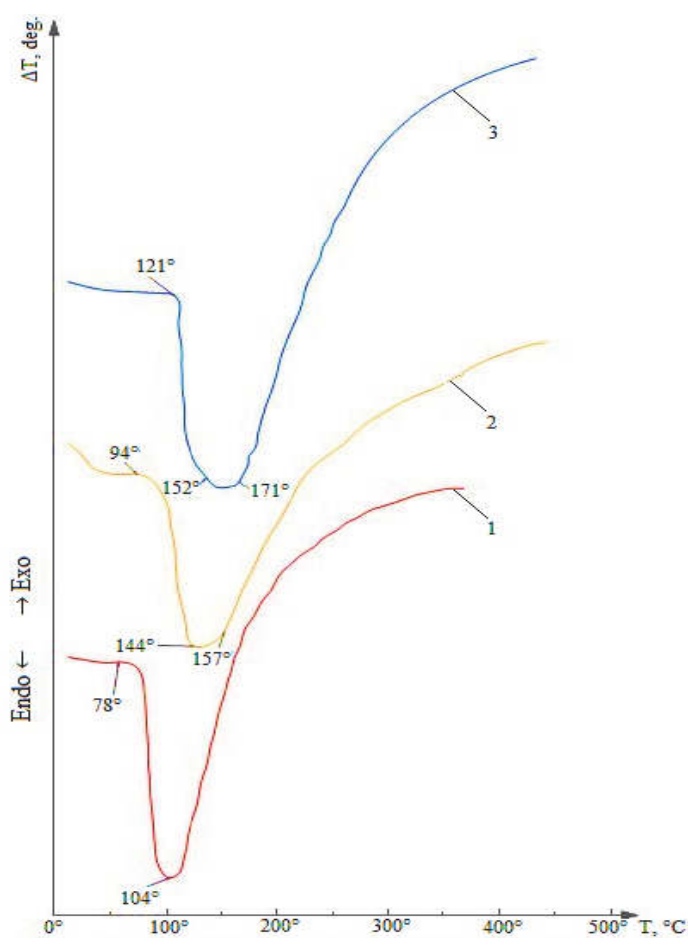


Fig. 1. DTA thermograms of sodium rare-glass composites xerogels in coordinates $\Delta T-T$, recorded at heating the samples in adequate conditions at different rates: curve 1 – 4 deg./min.; curve 2 – 7 deg./min.; curve 3 – 20 deg./min.

Rys. 1. DTA termogramy kserożeli kompozytowych z metali ziem rzadkich we współrzędnych $\Delta T-T$, zapisany podczas grzania próbek w tychże warunkach przy różnej prędkości: krzywa 1 – 4°C/min.; krzywa 2 – 7°C/min.; krzywa 3 – 20°C/min.

The air entrainment process includes the three main stages, the duration and nature of which depends on the type and amount of water containing the raw mix:

- within the range of 100-110°C, the hardened composite system partially transforms into the pseudopyroplastic state and begins to deform with increasing volume;
- within the range of 130-147°C, an intensive release of free and adsorbed water and intensive air entrainment of the sample mass occurs;
- at the temperature values above 147°C, the removal of constitutional moisture, the completion of restructuring, physical and chemical transformations of composite systems are observed.

Based on the analysis of the thermographic data and the macrostructure of the samples obtained, it can be concluded that the greatest contribution to the formation of the product's structure with maximum homogeneity is made by the constitutional water, while removal of the excess adsorption moisture at the initial stages leads to the formation of large through pores and capillary channels in the raw mass. Therefore, the initial rare-glass composition should contain a minimum amount of free and adsorbed water.

As the efficient ways to reduce the free water's effects, the following ones can be recommended:

- direct thermal dehydration and transformation of soluble glass into xerogel (the basis of the present variant of the suggested technical solution);
- liquid granulation of composite systems (for example, in Al, Ca, Zn, Mg chlorides solutions or their mixtures);
- introducing of mineral fillers or chemical additives into the rare-glass composite system, which leads to the development of gelation processes.

According to the results of the study (Bohdal 2013), alkaline-silicate compositions in solutions at heating form a number of hydrated associates with differing properties. This permits modifying the properties of the raw mix thickener – grated “dry glass” – by means of the partial unwatering of the purchased product in a liquid state at different temperature values, in the conditions of the technological cycle for the target

product formation, simultaneously with the same equipment, without the use of additional equipment. Meanwhile, the empirically determined physicochemical behavior of composite silicate systems, the features of unwatering and the viscosity state passing, strong adhesion of the intermediate transformation products to metals, ceramics, glass allow to suggest technological regulations, stages, sequence of operations during processing, development and selection of the equipment materials, variations in the methods of obtaining and using porous targeted composites.

Laboratory practice proves that the excess amount of the soluble glass introduced in a liquid state during the “gaging”, on the one hand improves the rheological properties, the plasticity of the treated raw mix, and on the other hand, during the subsequent heat treatment, causes additional viscosity of the system, deteriorates the heat transfer conditions, requires more prolonged temperature holding at higher temperature values and leads to the increased energy costs. Therefore, a necessity arises to find an efficient way of regulating the rate of gelling, using the method of shifting the equilibrium of physical and chemical processes of the disperse systems dehydration by adding less hydrated forms of the dried soluble glass; with the degree of the grated “dry glass” dispersion, with its dosage and regulating the processes of the hardened processed mix fragmentation during the granulate formation and the subsequent hot air entrainment.

The improved formulation of the raw mix preparing allows processing compositions in various ways with the formation of insulating materials of extended application: granular insulating filler (Fig. 2), materials for thermal insulation for the structures complicated in the form (Fig. 3), the plate and film-like types of insulating materials (Fig. 4) This task (depending on the purpose and features of the performed tasks) is solved by the capability of performing the final stages by means of several different ways of the products obtaining.

The use of the two stages procedure of the suggested renovation in the technology of preparing the porous thermal insulating materials determines: 1) the nature and the behavior peculiarities of the rare-glass composite systems components during the heat treatment, their strong adhesion manifestation related to most structural materials; 2) the necessity to solve the problem of easy workpieces removal from the formation molds; 3) the choice of the method for lining the internal surfaces of dis-

mountable equipment molds; 4) thermophysical and chemical properties of the used lining material.

The features of the suggested project are:

- ease and availability of obtaining components and preparing the raw mix,
- formation of the raw mix directly at its “gaging” with soluble glass under the normal conditions,

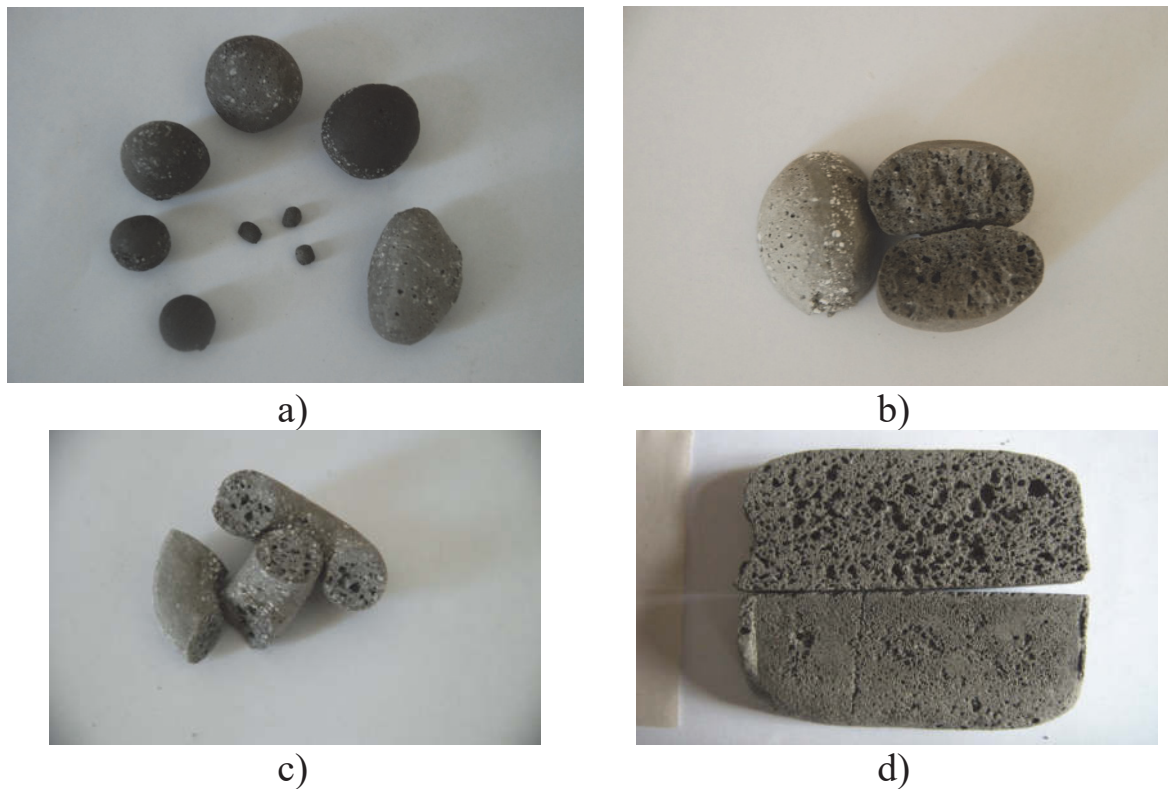


Fig. 2. Illustration of the granular thermal insulating fillers' samples, obtained in the lined molds without limitation of formation volume: a), b) – cutting of iso-sized elements; c) – cutting elements of plastic hardened raw cake of the set preformed thickness; d) – of workpieces, formed in separate dismountable molds

Rys. 2. Wygląd próbek granulowanych wypeiniaczy termoizolacyjnych, otrzymanych w formach z wykiadziną bez ograniczania objętości formacji: a), b) – przekroje elementów izometrycznych; c) – przekroje elementów w plastikowych foremkach z utwardzoną powierzchnią o wstępnie ustalonej grubości; d) – przekroje elementów, uformowanych w oddzielnych rozbieralnych formach

- the thermal insulation method is fast,
- the possibility of easy formation and fragmentation of the raw workpieces, their inherent properties makes it possible to spread in time and space separate stages of thermal insulation: the stage of preparation, formation of granulate (possibly, in a specialized site); storage; transportation; technological packing in the working area complying with the increased resistance requirements to the heat transfer (possibly, in the construction site),



Fig. 3. Illustration of fragments of thermal insulation zones sections in complicated form structures performed by the working zone filling with fragmented elements and the subsequent heat treatment in dismountable equipment of varying complexity: a) - without limiting the free volume of formation; b) - with restriction of formation space

Rys. 3. Wygląd przekrojów elementów izolacji termicznej o złożonym kształcie, wykonanych przez wypełnianie strefy roboczej fargmentowanymi elementami z następną obróbką termiczna, w rozbieralnym sprzęcie o różnych złożonościach: a) – bez ograniczenia objętości formacji; b) – z ograniczeniem objętości formacji

- processing of complicated working areas: selection of the raw mix cake thickness, the size and shape of the starting fragmented elements (depending on the target task and in order to provide more tight packing),
- the versatility of the thermal insulation method (based on the manifestation of significant adhesion ability of alkaline-silicate composite systems in relation to most structural materials: metals, ceramics, glass, wood),

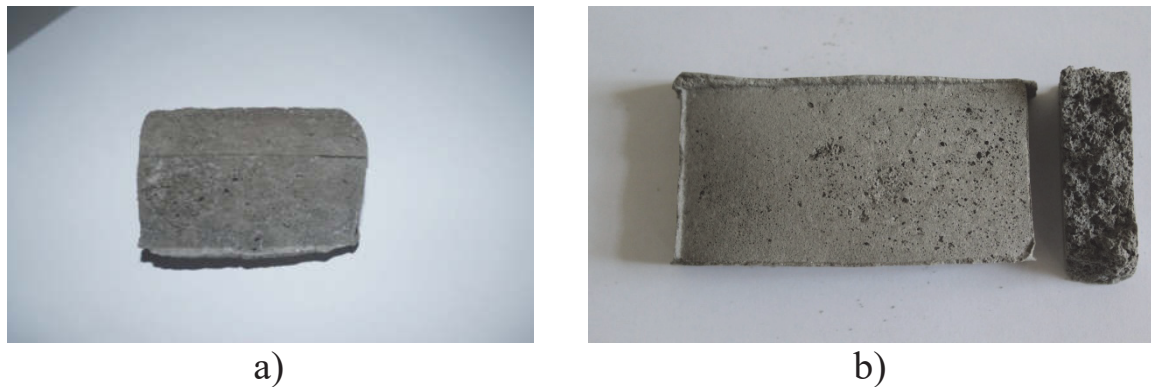


Fig. 5. Illustration of the items fragments formed: a) – in the form of plates; b) – in the form of films

Rys. 5. Wygląd fragmentów próbek ukształtowanych: a) – w postaci płyty; b) – w postaci folii

- low shrinkage with the suggested formulation of the raw mix and the method of treatment,
- indifference to most components and stability of the thermal insulation material properties, high thermal and chemical resistance, non-combustibility, ability to withstand significant temperatures;
- combination of the valuable properties set: low thermal conductivity factor, thermal stability, incombustibility, durability, low cost.

6. Conclusions

The raw mix of silica-containing technogenic component – fly ash of thermal power plants – and the methods of preparing waterproof porous thermal insulating materials of extended application on its base according to the powder low-temperature technology has been developed using multifunctional properties of soluble glass as: a) a binding component; b) blowing agent; c) the raw mix hardening rate regulator. The physical and chemical, technological aspects of obtaining and using the suggested alkaline-silicate compositions have been considered.

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Izolacja termiczna o strukturze wysokoporowatej na bazie szkła wodnego i wypełniaczy mineralnych o pochodzeniu poprodukcyjnym

Streszczenie

Przekazujemy wyniki badań procesów powstawania porowatej struktury metodą termicznego wzdęcia żelowej mieszaniny surowców. Badaliśmy przemiany fizyko-chemiczne surowej mieszaniny po jej ogrzaniu, co umożliwiło określenie początkowej zawartości wody w surowej mieszaninie, optymalnej dla

tworzenia się kserożelu i resztkowej zawartości żelu, wystarczającej do skutecznego pęcznienia. Surowa mieszanina zawiera lotny popiół z elektrowni ciepłej, jak również sposoby wytwarzania porowatych materiałów wodoodpornych, wytrzymałych materiałów izolacyjnych na bazie technologii proszek o niskiej temperaturze zostały opracowane przy użyciu właściwości wielofunkcyjnych szkła wodnego jako: a) element łączący; b) środek porotwórczy; c) regulator szybkości utwardzania dla surowej mieszaniny. Uwzględniono fizyko-chemiczne, technologiczne aspekty wytwarzania i stosowania proponowanych kompozycji alkaliczno-krzemianowych. Zaproponowaliśmy zoptymalizowany skład surowej mieszaniny, która wykorzystuje maksymalną dopuszczalną ilość popiołu jako wypełniacza mineralnego; rozważane są tryby obrzęku termicznego. Na podstawie uzyskanych danych opracowano nową technologię produkcji porowatych materiałów termoizolacyjnych.

Abstract

We report results of research into processes of formation of porous structure by the method of thermal bloating of the gel-like mixture of raw materials. Regularities of the course of physical-chemical transformations are considered in the material when it is heated; as a result, we established the initial water content in the raw mixture, optimal for the formation of xerogel, and the residual water content in gel, sufficient for effective bloating. The raw mix of silica-containing technogenic component – fly ash of thermal power plants – and the methods of preparing waterproof porous thermal insulating materials of extended application on its base according to the powder low-temperature technology has been developed using multifunctional properties of soluble glass as: a) a binding component; b) blowing agent; c) the raw mix hardening rate regulator. The physical and chemical, technological aspects of obtaining and using the suggested alkaline-silicate compositions have been considered. We proposed the optimized composition of the raw mixture that employs maximally permissible amount of ash as a mineral filler; the thermal modes of bloating are studied. Based on the data obtained, a new technology for the production of porous thermal insulation materials is created.

Słowa kluczowe:

popiół lotny, szkło wodne, kompozytowe materiały termoizolacyjne, krzemiany alkaliczne, termiczne wzdęcia

Keywords:

fly ash, soluble glass, composite insulation materials, alkaline silicate, thermal bloating



Progress in the Production of Biogas from Maize Silage Following Alkaline and Thermal Pre-Treatment

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1. Introduction

Lignocellulose can be converted into biofuels such as biogas, ethanol or hydrogen. However, it needs to be pre-prepared due to numerous factors limiting the process of lignocellulosic material biodegradation (Hendriks & Zeeman 2009, Zhang et al. 2016).

In recent decades, many pre-treatment processes have been developed which are being continuously tested and improved. Effective pre-treatment should meet several criteria, *inter alia* ensure lignin separation from cellulose, increase the percentage of amorphous cellulose, ensure the greater porosity of substrates, eliminate sugar losses, reduce the formation of inhibitors and minimise the energy costs. In order to increase the efficiency of production of energy from biomass, physical, physico-chemical, chemical and biological treatments are conducted. An important issue is to determine the technological conditions allowing an efficient, economically viable and safe conditioning process. Where the treatment is not effective enough, it may become a cause of the formation of toxic compounds inhibiting the metabolism of methanogenic bacteria (Jönsson et al. 2016, Sindhu et al. 2016, Bechera et al. 2014).

Among the chemical methods of pre-treatment, acid and alkaline treatments are distinguished. The advantage of the alkaline methods is the removal of lignin and acetyl groups which inhibit the saccharification and reduce the availability of cellulose (Pandey et al. 2000). The

solubility of hemicellulose and cellulose is lower than that for hydrothermal acid treatment. Alkali treatment results in swelling and increases the biomass porosity. The ester bonds between lignin and xylan are broken, which intensifies the delignification processes (Zheng et al. 2014). The advantages of the application of alkaline treatment also include a lower temperature of the process, as the alkaline treatment can be successfully conducted at room temperature with no need for carrying out the reaction in special vessels. A disadvantage of the method is the long duration of the process, which lasts from several hours to several days. In an alkaline treatment, sodium, potassium, calcium and ammonium hydroxides are most frequently used. The most commonly used sodium hydroxide successfully disrupts the lignin structure and increases the availability of cellulose and hemicellulose (Fox et al. 2003, Hartmann et al. 1999, Delegens 2002, Gregg 1996, Kumar & Wayman 2009). A new method for preparing the substrate which is attracting increasing interest among researchers is microwave and chemical pre-treatment, which combines the advantages of both thermal and chemical methods. Microwave pre-treatment is considerably more effective than pre-treatment using conventional heating (Balat 2011, Du et al. 2016). This is due to an increase in the reaction rate of the occurring processes, which is similar to the microwave treatment supported by the action of chemical agents. Microwave radiation is applied during the treatment using acids, bases or hydrogen peroxide. A substrate subjected to microwave treatment exhibits a fast reaction rate and a high content of glucose in the hydrolysate (Kaur & Phutela 2016, Delegens 2002).

The aim of the presented study was to analyse the simultaneous effects of microwave radiation and sodium hydroxide on the destruction of lignocellulosic plant biomass and on its susceptibility to the anaerobic decomposition in the methane fermentation process.

2. Materials and methods

2.2. Plan of the study

During the study, the effects of microwave-heating-based disintegration of plant biomass (maize silage) were compared to the results obtained during biomass heating in a conventional manner. During the preliminary tests aimed at the determination of parameters of the thermal hydrolysis process depending on the applied heating method, work was

carried out to determine the shortest duration and the lowest temperature of the disintegration process at which the highest effectiveness of the anaerobic biomass conversion was obtained. Preliminary tests demonstrated the efficiency of the application of a temperature of 150°C and a duration of 20 minutes.

The study involved the alkaline-thermal treatment of a lignocellulosic substrate at a temperature and for the duration determined in the preliminary tests; the criterion differentiating particular variants was the dose of a chemical agent used. The addition of a 10% solution of NaOH in the amounts of 0.02, 0.05, 0.1, 0.2, and 0.4 g/g_{d.m.} was tested. The pre-prepared substrate was subjected to biogas tests in respirometric units.

2.2. Research material

The raw material used in the experiment was maize silage originating from crops cultivated at the research station of the University of Warmia and Mazury. The characteristics of the research material used are presented in Table 1.

Table 1. Characteristics of maize silage applied in the experiment

Tabela 1. Charakterystyka kiszonki kukurydzy użytej podczas eksperymentu

Parameter	Unit	Value
Dry matter	[mg/g _{d.m.}]	360.0±11.0
Organic dry matter	[mg/g _{d.m.}]	326.0±9.1
Mineral dry matter	[mg/g _{d.m.}]	34.0±2.0
Cellulose	[% _{d.m.}]	20.1±0.5
Hemicellulose	[% _{d.m.}]	14.6±0.3
Lignin	[% _{d.m.}]	2.6±0.1

2.3. Pre-treatment of the substrate

The substrate was broken up in a device in the form of a mill with a perforated drum placed in a sealed housing. During the disintegration of the research material, the rotational speed of the drum was 30 rpm. Thanks to mechanical breakage of the substrate, a material with particle sizes ranging from 2 to 5 mm was obtained. The broken up native sub-

strate was hydrated to the level of 90%, which was followed by the thermal and chemical treatment.

Sodium hydroxide was introduced into thermo-reactors at five different doses: 0.02 g/g_{d.m.}; 0.05 g/g_{d.m.}; 0.10 g/g_{d.m.}; 0.20 g/g_{d.m.}; 0.40 g/g_{d.m.}, and the obtained results were compared to the control sample with no addition of chemical reacting substances. The treatment of the substrate with a chemical agent involved placing the prepared raw material with the addition of NaOH in pressure vessels, and heating it for 20 minutes at a temperature of 150°C.

Thermal hydrolysis was carried out based on two heating technologies. The hydro-thermal microwave treatment was carried out using a Mars-Solvent Extraction system by CEM with the power output regulated up to 1600 W, and the microwave radiation frequency of 2.45 GHz. The tests were carried out in Easy Prep Teflon vessels with a volume of 115 cm³ (Fig. 1).

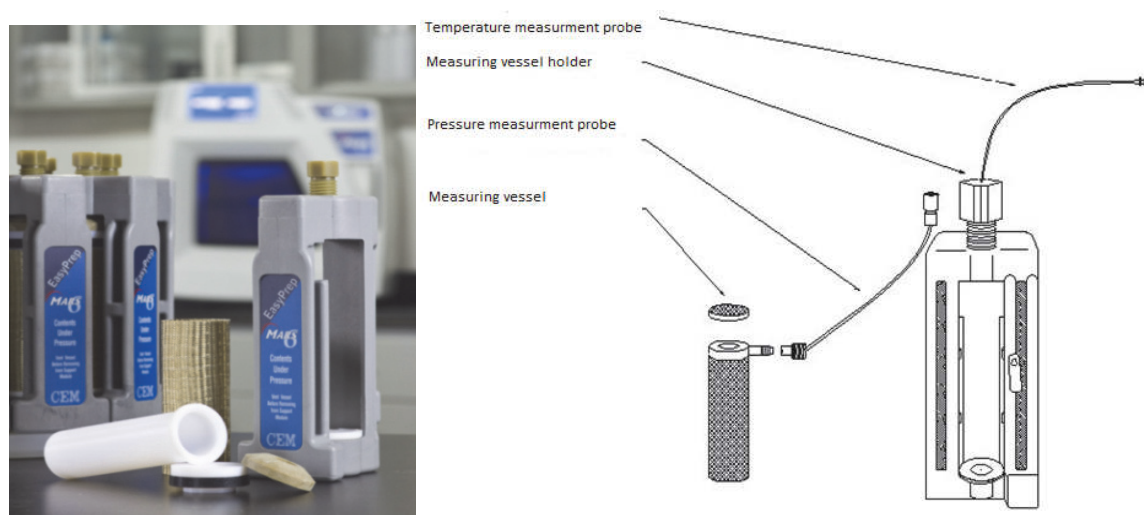


Fig. 1. Utensils for microwave digestion of samples

Rys. 1. Naczynia do mikrofalowej dezintegracji próbek

The thermal hydrolysis under conventional heating conditions was carried out using thermo-reactors of the authors' own design. The thermo-reactors were made of acid-proof steel and designed so the dimensions did not differ from the Easy Prep vessels used during the microwave digestion of samples (Fig. 2). In order to conventionally heat the plant material, a four-station Laboplay O420E oil bath was used, in which silicone oil was the heating medium. The conditions prevailing

during the thermal hydrolysis carried out based on both conventional and microwave heating were identical. In order to obtain identical parameters of the course of the process in both devices, the heating duration and the thermal hydrolysis temperature were occasionally controlled.

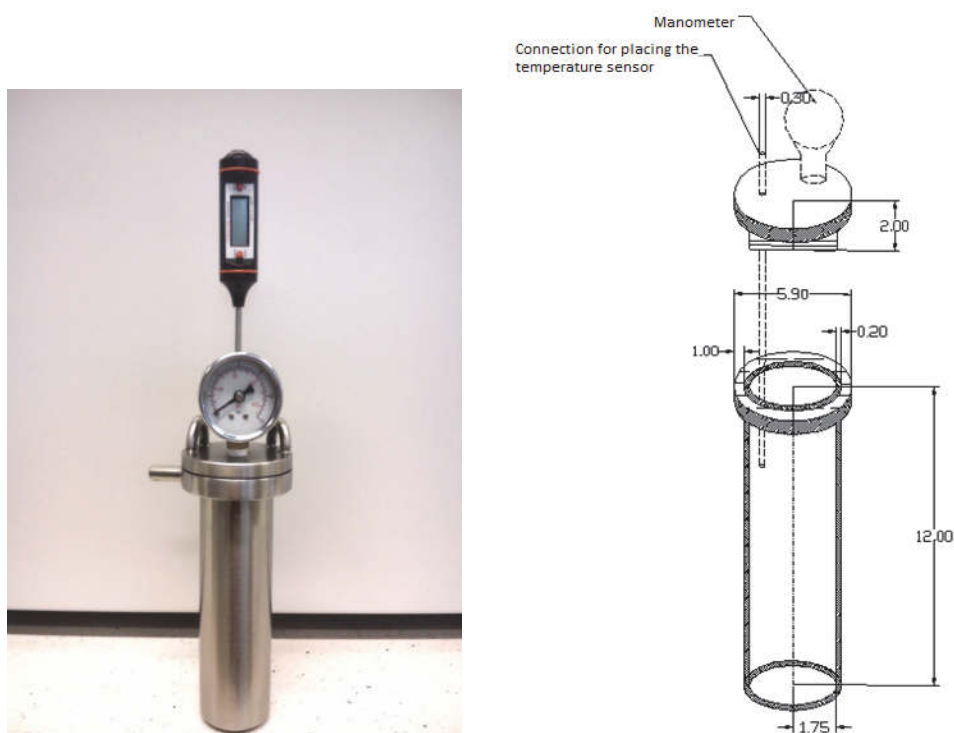


Fig. 2. Utensils for conventional digestion of samples

Rys. 2. Naczynia do konwencjonalnej dezintegracji próbek

2.4. Research procedures

The scope of analyses included the direct and indirect determination of the effectiveness of disintegration process. Directly, the effectiveness of the applied conditioning methods was tested through an analysis of glucose content using a YSI 2300 analyser. The determination of theoretical efficiency of hydrolysis process was tested using an analysis of the chemical oxygen demand (COD) value using the colorimetric method according to Hach (LCK 914), Measurements of the amounts of total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were tested using a TOC Shimadzu analyser. Samples for the above determinations were prepared by filtering the thermally and chemically digested

plant material through a membrane filter with a pore diameter of 1.2 μm using the method according to Hach (LCK 914).

The following formula (Świątek et al. 2012) was used as a basis for the calculations of the hydrolysis process efficiency:

$$\text{efficiency} = \frac{c \times 0.9}{p} \times 100 [\%] \quad (2.1)$$

where:

c – concentration of reducing sugars [g/dm^3],

p – the contents of cellulose and hemicellulose in the native material [%],

0.9 – conversion factor for simple sugars to polysaccharides.

The effectiveness of hydrothermal depolymerisation was analysed in an indirect manner through respirometric measurements of the decomposition of the digested biomass under conditions of mesophilic methane fermentation. The substrate following the thermal hydrolysis was directed to OxiTop control-and-recording units by WTW, comprising reaction chambers connected to measuring and recording devices. The reaction chambers were inoculated with an inoculum, i.e. anaerobic sludge originating from an agricultural biogas plant fed with maize silage. To 100 cm^3 of the sludge, such an amount of the prepared raw material was added so that the initial load was 5 $\text{g}_{\text{o.d.m.}}/\text{l}$, and the samples were then blown through with nitrogen in order to provide anaerobic conditions. The substrate retention time was 40 days; the necessary duration of measurement was determined based on the amount of biogas being generated. It was assumed that all decomposable matter was processed when three subsequent values of the daily biogas production did not differ by more than 2%. Measurement units analysed changes to partial pressure in the chamber, caused by the production of biogas in anaerobic processes carried out by microorganisms. A measurement unit comprised a reaction chamber and a measuring-and-recording device placed in a thermostatic cabinet with hysteresis not exceeding $\pm 0.5^\circ\text{C}$. The measurements were carried out at a temperature of 36°C ; pressure values in the reaction chamber were recorded every 15 minutes.

An analysis of the quality of the generated biogas was conducted using a 7890A GC gas chromatograph with a TCD detector, in which the measurement was performed through an analysis of changes to electric conduction resulting from changes to thermal conduction of the atmosphere surrounding the thermocouple at the moment when the tested chemical compounds appeared in the carrier gas (helium). The value of changes to thermal conduction was directly proportional to the concentration of the tested biogas components. The chromatograph determined the percentages of biogas components, i.e. methane CH₄, carbon dioxide CO₂, oxygen O₂, hydrogen H₂, and nitrogen N₂.

3. Results

The progress of hydrolysis of maize silage conditioned using NaOH depending on the applied heating method was analysed by determining the amount of glucose released to the solution and calculating the theoretical efficiency of hydrolysis in relation to the polysaccharides contained in the native substrate. In all analysed variants differing in the dose of NaOH, the amount of released glucose (and thus the efficiency of the process) was higher when using microwave heating by at least 14% as compared to the conventional heating. All obtained results were significantly different at the significance level $\alpha = 0.05$. Following the introduction of NaOH dose of 20% into the solution, a large amount of glucose was released and, for the microwave heating, the glucose concentration in the solution was 142 ± 11.25 mg/dm³, which accounted for $0.75 \pm 0.07\%$ of the theoretical efficiency of hydrolysis (Table 2). For conventional heating, the generated amount of 92.1 ± 9.02 mg/dm³ of glucose accounted for $0.49 \pm 0.06\%$ of the theoretical efficiency. The amounts of glucose obtained for the considered dose, were higher by 79% and 39% compared to the sample with no NaOH added, respectively for the microwave and conventional heating. Following an increase in the NaOH dose to 0.4 g/g_{d.m.} in the variant of pre-treatment using microwave radiation, a 40% decrease in glucose concentration was noted in relation to the dose of 0.2 g/g_{d.m.}. In the conventional variant, the decrease was by 21% (Fig. 3).

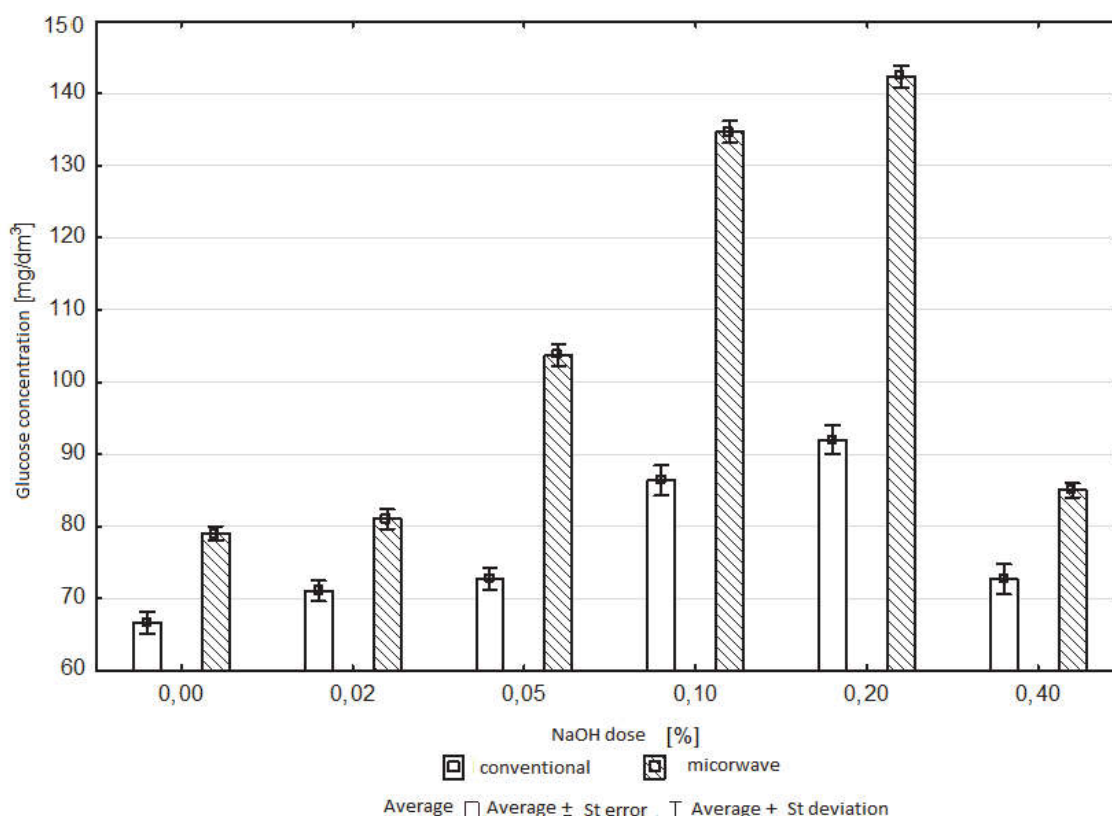


Fig. 3. Concentration of glucose released after maize silage pre-treatment with the addition of NaOH

Rys. 3. Stężenie wydzielonej glukozy po obróbce kiszonki kukurydzy z dodatkiem NaOH

The heating method had a significant effect on the value of the COD of the solution following the process of hydrothermal hydrolysis with the used of sodium hydroxide. In each of the tested variants of the NaOH doses, higher values of the COD were observed when using the microwave heating. The amount of released organic compounds was greater as compared to the tests using the conventional heating by a minimum of 13.9% (at a dose of 0.4 g/g_{d.m.}) to a maximum of 31% at a dose of 0.1 g/g_{d.m.}. A change in the NaOH dose affected, to the greatest extent, the value of the COD of the solution when using microwave heating in the case of an increase from 0.1 g/g_{d.m.} to 0.2 g/g_{d.m.}, and the COD value then increased from 17,873±31 mg/dm³ to 18,620.3±101 mg/dm³. When analogous doses of NaOH were used for the substrate heated conventionally, the COD value increased by 15.7% from the amount of 13,619±19 mg/dm³ obtained for the dose of 0.01 g/g_{d.m.} to

16,068±28 mg/dm³ obtained for 0.2 g/g_{d.m.}. An increase in the dose of sodium base to 0.4 g/g_{d.m.} had no significant effect on the increase in the value of the COD released and the results were not statistically different at the level $\alpha = 0.05$ (Fig. 4).

Table 2. Theoretical yield of hydrolysis process with the use of NaOH

Tabela 2. Teoretyczna wydajność procesu hydrolizy z użyciem NaOH

NaOH dose [g/g _{d.m.}]	Concentration of released glucose [mg/dm ³]	Efficiency [%]
Conventional heating		
0.0	66.7±1.52	0.35±0.01
0.02	71.1±3.0	0.37±0.02
0.05	72.6±4.52	0.38±0.03
0.1	86.3±7.81	0.44±0.04
0.2	92.1±9.02	0.49±0.06
0.4	72.7±7.08	0.37±0.05
Microwave heating		
0.0	79.2±2.82	0.42±0.02
0.02	82.1±6.63	0.43±0.04
0.05	103.7±10.25	0.54±0.07
0.1	134.7±10.35	0.71±0.07
0.2	142.3±11.25	0.75±0.07
0.4	85.2±3.81	0.45±0.02

Another tested parameter which demonstrated the efficiency of the applied method of pre-preparation of the substrate was an analysis of the amounts of total organic carbon, inorganic carbon, and total carbon released to the solution. In the analysed series of the study, an increase dose of NaOH added during the hydrothermal treatment of the raw material resulted in a considerable increase in the contents of carbon compound in the solution (Table 3).

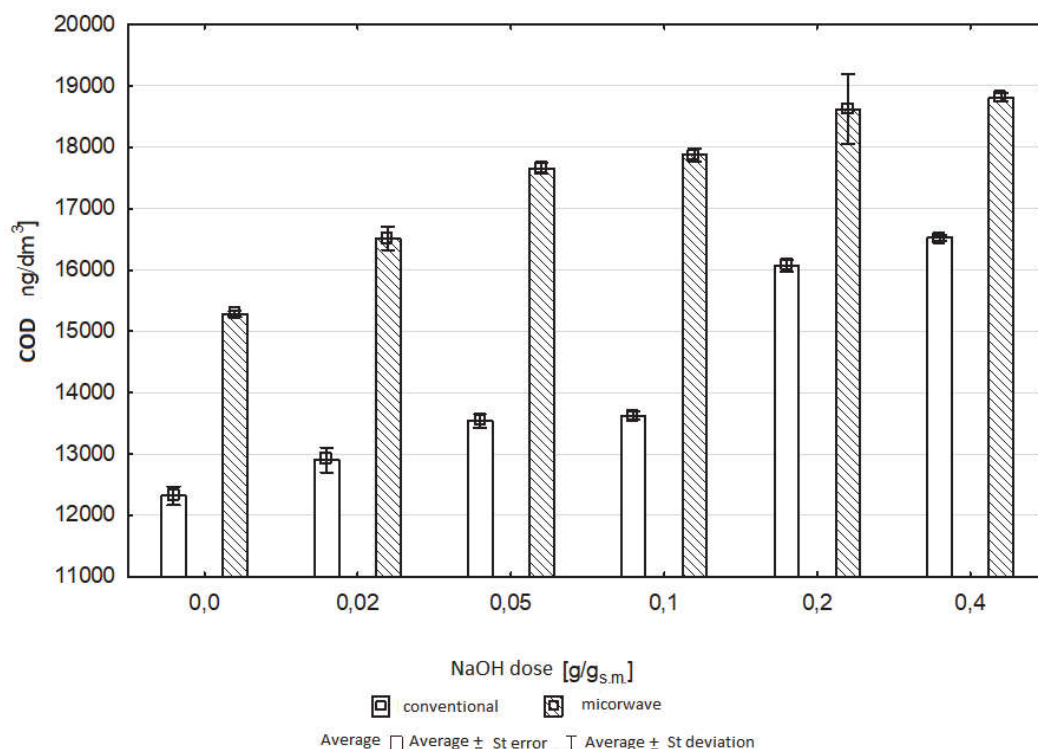


Fig. 4. Value of COD coefficient in the solution after maize silage pre-treatment with the addition of NaOH

Rys. 4. Wartość współczynnika ChZT w roztworze kiszonki kukurydzy po wstępnej obróbce z dodatkiem NaOH

The values of TC, TOC, and IC for the sample heated with microwaves, with no addition of NaOH, amounted to, respectively, $6,313 \pm 97$ mg/dm³, $6,145 \pm 81$ mg/dm³ and 168 ± 9 mg/dm³; following the application of the chemical treatment, the values increased, and the highest concentrations of TC, TOC and IC, respectively, ($9,178 \pm 93$ mg/dm³, $8,780 \pm 481$ mg/dm³ and 398 ± 21 mg/dm³) were noted in the variant with a 0.4 g/g_{d.m.} dose of NaOH. The trend in the results in the variants using the conventional heating method was similar; the contents of TC, TOC and IC in the zero sample amounted to, respectively, $6,293 \pm 68$ mg/dm³, $6,145 \pm 81$ mg/dm³, and 148 ± 6 mg/dm³. As in the case of microwave heating, the greatest release of carbon compounds to the solution occurred following the use of the highest NaOH dose (TC amounted to $8,824 \pm 120$ mg/dm³, TOC to $8,496 \pm 104$ mg/dm³, and IC to 328 ± 19 mg/dm³). For all analysed doses of NaOH, the results between the use of conventional heating and microwave heating were statistically

different at the significance level $\alpha = 0.05$ Microwave heating contributed to the release of a greater amount of TOC and TC than conventional heating did in each of the variants applied. For total organic carbon, the values obtained using microwave heating were higher from 1.44% (for a dose of 0.02 g/g_{d.m.}) to 31.0% (obtained when using NaOH at an amount of 0.1 g/g_{d.m.}). For total carbon, these amounts were from 1.81% when using a dose of 0.02 g/g_{d.m.} to 23.27% at a dose of 0.1 g/g_{d.m.}.

Table 3. Content of total organic carbon, total carbon and inorganic carbon in the solution after maize silage pre-treatment with an addition of NaOH

Tabela 3. Zawartość całkowitego węgla organicznego, węgla całkowitego i węgla nieorganicznego w roztworze kiszonki kukurydzy po wstępnej obróbce z dodatkiem NaOH

NaOH dose [g/g _{d.m.}]	TOC [mg/dm ³]	TC [mg/dm ³]	IC [mg/dm ³]
Conventional heating			
0.0	6,145±81	6,293±68	148±6
0.02	6,241±99	6,421±74	180±18
0.05	7,526±104	7,743±109	217±15
0.1	7,699±112	7,967±115	268±11
0.2	7,996±105	7,971±86	302±17
0.4	8,496±104	8,824±120	328±19
Microwave heating			
0.0	6,145±81	6,313±97	168±9
0.02	8,179±107	8,369±102	190±7
0.05	7,691±105	7,916±81	225±13
0.1	7,810±98	8,111±79	301±10
0.2	8,578±68	8,932±110	354±15
0.4	8,780±81	9,178±93	398±21

The direct susceptibility of the substrate to anaerobic decomposition was assessed by carrying out respirometric tests on the digested substrates with an initial load of the active volume of the reactor of 5 g_{o.d.m.}/dm³. In all discussed variants of this part of the study, the course of the process of biogas production was a first-order reaction. With each

considered dose of NaOH, a greater amount of the produced biogas per unit of the substrate weight was obtained thanks to hydrothermal pre-treatment using microwave radiation. The highest effectiveness of biogas production was obtained during the fermentation of maize silage conditioned using microwave radiation with the addition of NaOH in an amount of 0.2 g/g_{d.m.}, at the rate of biogas production of 0.146 dm³/d, with a process efficiency of 1155±34 dm³/kg_{o.d.m.}, and this amount was higher by 11.3% than the sample with the same addition of NaOH, heated conventionally. It was also higher by 29.4% than the sample subjected to no chemical treatment (Fig. 5, Table 4).

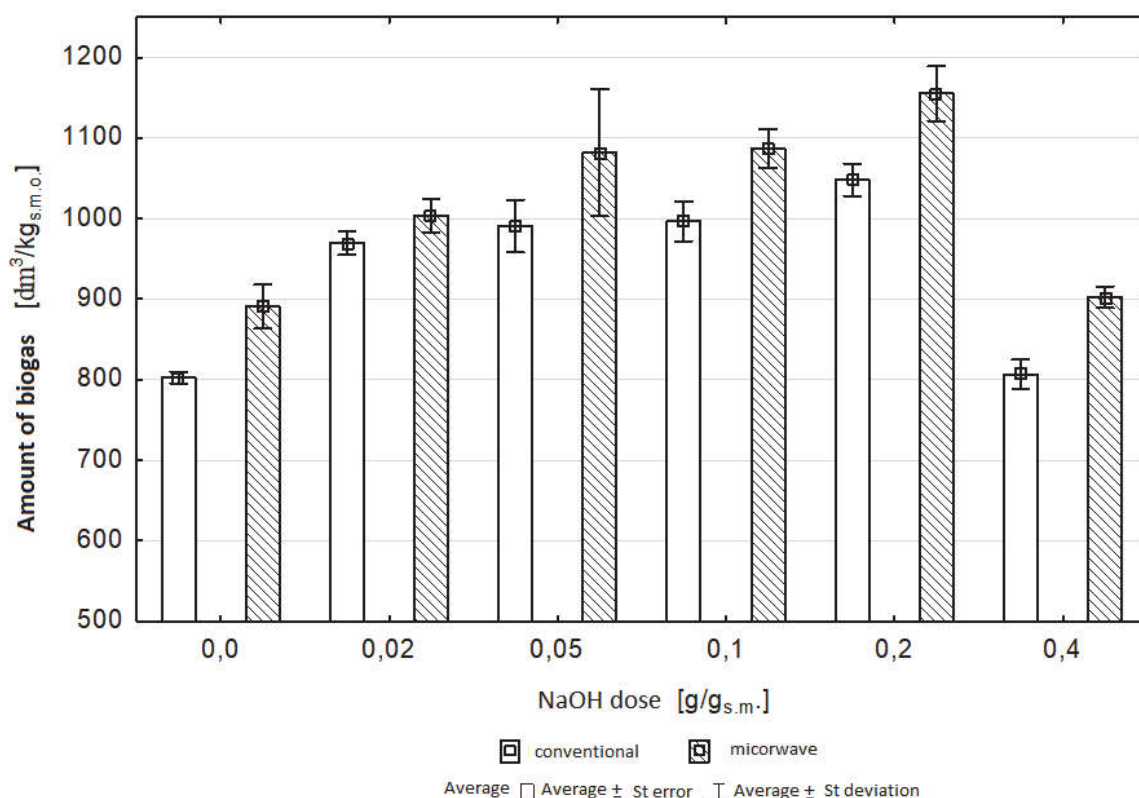


Fig. 5. Biogas production from maize silage pre-treated with the addition of NaOH

Rys. 5. Produkcja biogazu z kiszonki kukurydzy po wstępnej obróbce z dodatkiem NAOH

Increasing doses of NaOH, from 0.02 g/g_{d.m.} to 0.2 g/g_{d.m.}, using both the microwave heating and conventional heating during hydrothermal depolymerisation, resulted in an increase in biogas production. In both methods of heating, a decrease was observed in the amount of produced

biogas, with an increase in NaOH dose to 0.4 g/g_{d.m.}. For microwave pre-treatment, the production of biogas decreased by 27.8%, while for the treatment using conventional heating it decreased by 28.8% (Fig. 5).

The percentage of methane in the gaseous products of bacteria metabolism was, irrespective of the applied dose of the chemical agent and the type of heating, at a level of approx. 59%. A statistical analysis indicated no significant differences between the content of methane in the biogas produced following the conditioning of maize silage using various doses of NaOH; similarly, no statistically significant differences were noted between the content of methane produced following the treatment using various types of heating (Fig. 6). The composition of biogas was supplemented with up to 99% carbon dioxide, the residual components accounted for up to 1% of biogas.

Table 4. Biogas production rate in respirometric analysis of maize silage pre-treated with the addition of NaOH

Tabela 4. Współczynnik produkcji biogazu w pomiarach respirmetrycznych kiszonki kukurydzy po obróbce wstępnej z dodatkiem NAOH

NaOH dose [g/g _{d.m.}]	Reaction rate constant k [d ⁻¹]		The rate of biogas production r [dm ³ /d]	
	Conventional heating	Microwave heating	Conventional heating	Microwave heating
0.0	0.29	0.33	0.10	0.13
0.02	0.32	0.23	0.13	0.10
0.05	0.29	0.27	0.14	0.12
0.1	0.19	0.28	0.08	0.14
0.2	0.3	0.28	0.14	0.14
0.4	0.29	0.22	0.10	0.13

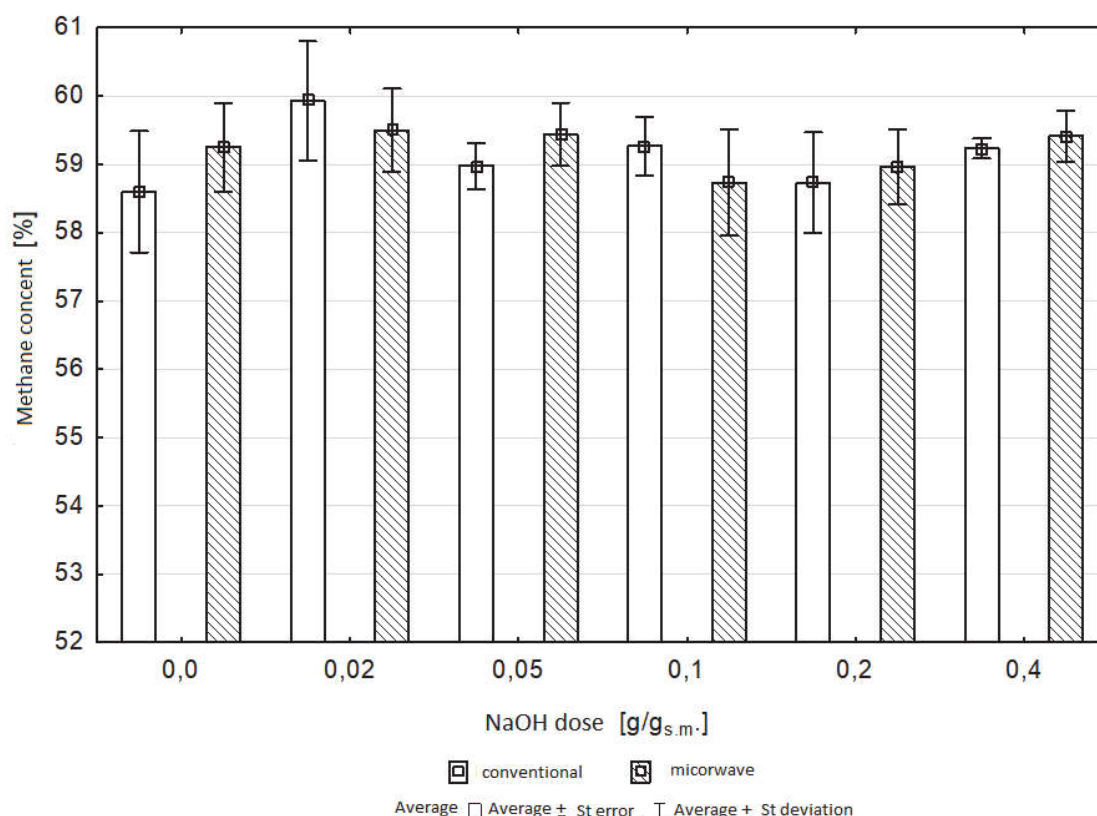


Fig. 6. Percentage content of methane in biogas produced from maize silage pre-treated with the addition of NaOH

Rys. 6. Procentowa zawartość metanu w biogazie z kiszonki kukurydzy poddanej obróbce wstępnej z dodatkiem NaOH

4. Discussion

The presented study aimed to determine the impact of the simultaneous effects of microwave radiation and sodium hydroxide on the destruction of maize silage and its susceptibility to anaerobic decomposition in the methane fermentation process.

The alkaline treatment of plant biomass is usually carried out in the presence of sodium, potassium or ammonium hydroxide (Balat 2011). According to Fengel and Wegner, during alkaline treatment a solvation process occurs which results in a kind of biomass swelling, which renders it more accessible to the action of enzymes and bacteria (Fengel & Wegner 1984). In the author's own study, the chemical reacting substance used for the pre-treatment was sodium hydroxide. In the series with the microwave alkaline treatment of maize silage using the most effective

NaOH dose of 0.2 g/g_{d.m.} (7.1 g/100 g glucose) expressed as an amount of fresh biomass, was released to the solution. The obtained results correspond to the literature data. Hu and Wen (2008) studied the alkaline microwave pre-treatment prior to enzymatic hydrolysis of the switchgrass (*Panicum virgatum*). During the study, the amount of reducing sugars released to the solution was investigated. Based on the obtained data, the most favourable parameters for conducting the treatment in a microwave device were selected. The most sugar was released following microwave pre-treatment with the addition of NaOH at an amount of 0.1 g/g, carried out for 30 minutes at a temperature of 190°C; the amount of the released reducing sugar was 11.4 g/100 g biomass (Hu & Wen 2008).

Alkaline treatment leads to the breakage of the ester bond between lignin and xylan, which intensifies the delignification process – therefore, as claimed by Zheng et al. (2014) and by Liew et al. (2011), the action of the alkaline treatment is more effective where it is applied for the preparation of biomass characterised by a high lignin content of the lignocellulosic complex (Zheng et al. 2014, Liew et al. 2011). As regards the amount of polysaccharides contained in the native substrate, treatment with the addition of NaOH was characterised by low theoretical efficiency of hydrolysis. Such trends in the results could have been due to the low content of lignin in maize silage, as the amount of lignin in the native material was 2.6%. Compared to the literature data characterising the composition of lignocellulosic biomass, the obtained value is very low. As reported by Manlau et al. (2012), the maize stems contain from 3.5 to 10.5% lignin (Monlau 2012). More lignin (from 19 to 25%) is contained in miscanthus (Li et al. 2010), in the sunflower stems – up to 30% (Ruiz et al. 2013), or in coniferous tree shoots – up to 35% (Sun & Cheng 2002). Higher effectiveness of the fermentation process following the application of alkaline treatment is obtained by fermenting biomass with a higher lignin content. Mirahmadi et al. (2010) studied the alkaline treatment of the birch and spruce at a temperature of 100°C and found that alkaline treatment with the addition of NaOH results in an increase in the effectiveness of methane fermentation by 83% for the birch and 74% for the spruce (Mirahmadi et al. 2010).

In the author's own study, it was noted that the amount of biogas produced in respirometric tests increased with an increase in the amount

of NaOH added for the pre-treatment; this relationship was maintained to a dose of 0.2 g/g_{d.m.}, while following an increase in the dose to 0.4 g/g_{d.m.} the production of biogas decreased. The obtained results developed in the same manner using both types of heating. The obtained results could have been affected by the Na⁺ ions formed during the pre-treatment; the literature data indicate the possibility for the inhibition of methane fermentation process due to an excessive amount of these cations. Jabłoński et al. (2014) report that the presence of Na⁺ ions in an amount exceeding 3,500 mg/dm³ is dangerous to the process of methane fermentation, and a concentration exceeding 8,000 mg/dm³ becomes toxic (Jabłoński et al. 2014).

In the author's own study, in all test variants of the alkaline and thermal pre-treatment, the heating of substrate using microwaves resulted in greater biogas production than from conventional heating. Studies of the use of electromagnetic microwave radiation for the pre-treatment of lignocellulosic biomass indicated that microwave radiation is able to change the ultrastructure of cellulose and lead to the degradation of lignin and hemicellulose in the lignocellulosic complex, thus increasing the susceptibility to the biodegradation process. It was also observed that microwave pre-treatment in the presence of water increased the efficiency of hydrolysis of lignocellulosic structures (Binod et al. 2012).

Reports on the use of microwave treatment in order to intensify the methane fermentation of lignocellulosic biomass do not clearly indicate the efficiency of the method applied. Sapci (2013) investigated the production of biogas from barley straw, spring wheat, winter wheat and oats. As a method of pre-treatment, he used microwave radiation at temperatures of 200°C and 300°C and, following the preparation of the substrate, he carried out methane fermentation under mesophilic conditions for 60 days. The results of that study demonstrated that the microwave treatment did not improve the temperature of the process and resulted in a reduction in biogas production (Sapci 2013). Completely different study results were obtained by Jackowiak et al. (2011), who focused on analysing the process of microwave optimisation of the methane fermentation of wheat straw. During the experiment, four process temperatures were tested: 100°C, 120°C, 150°C and 180°C, with the highest amount of biogas obtained from non-microwave-treated biomass reaching 270 dm³/kg_{o.d.m.}, which is a result very similar to that obtained by Sapci (277 dm³/kg_{o.d.m.}) also from

wheat straw. However, in Jackowiak's study, the amount of biogas following the microwave treatment increased considerably, with the most effective temperature option (150°C) the efficiency of methane production improved by 28%. As indicated by Sapci, the failure of his study was most probably caused by an increase in the content of dissolved lignin formed at a temperature exceeding 160°C. The compounds generated as a result of lignin dissolution are very reactive and, in many cases, have a toxic effect on bacteria and the archaea. They trigger the inhibition of enzymes responsible for the degradation of the lignocellulosic complex, cellulase, xylanase and glycosidase (Jackowiak et al. 2011, Sapci 2013).

To improve the efficiency of the conversion processes of lignocellulosic materials to energy, it is necessary to learn and understand the mechanism of the action of microwave radiation on the structural components of plants, mainly on the structure of a lignocellulosic complex. Literature reports indicate that low-temperature (< 200°C) microwave treatment is able to increase the energy value of biomass. In low-temperature microwave treatment, the efficiency of the process is, to a large extent, determined by the type of the material subjected to treatment, its physical parameters, structural arrangement, conductivity and dielectric properties. In the conventional thermal treatment, heat is supplied by means of convection and conduction, while the use of microwave radiation results in the energy being supplied directly to the material being heated. The application of microwave technology for heating has many potential benefits as microwaves penetrate the material, accumulate energy and generate heat within the entire volume. The use of microwave energy shortens the duration of additional heating of the material, allows the process to be controlled, and increases energy efficiency. Budarin et al. (2009) studied the process of microwave support of cellulose decomposition; it follows from their study that the interaction between cellulose and microwave radiation is enormous and has a decisive effect on the disintegration of a cellulose molecule. As a result of these interactions, during the low-temperature of microwave treatment, products are generated which, under the conditions of conventional heating, require the use of considerably higher temperatures (> 200°C) (Budarin et al. 2009).

5. Conclusions

The use of microwave heating simultaneously with alkaline treatment resulted in a greater volume of produced biogas. The highest efficiency of biogas production was obtained during the fermentation of maize silage conditioned using microwave radiation with the addition of NaOH in an amount of 0.2 g/g_{d.m.}, the process efficiency was 1,155±34 dm³/kg_{o.d.m.}, and this amount was higher by 11.3% than for a sample with the same addition of NaOH heated conventionally, and was 29.4% higher than a sample subjected to no chemical treatment. For both types of heating, a decrease in the amount of produced biogas was observed with an increase in the dose of NaOH to 0.4 g/g_{d.m.}. The inhibition of the methane fermentation process at the highest dose of the tested chemical agent could have been caused by the generated inhibition of the methane fermentation process due to an excessive amount of Na⁺ ions.

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Postęp produkcji biogazu z kiszonki kukurydzy po wstępnej obróbce alkaliczno-termicznej

Streszczenie

Celem opisanych badań była analiza oddziaływania promieniowania mikrofalowego oraz wodorotlenku sodu na destrukcję lignocelulozowej biomasy roślinnej (kiszonka kukurydzy) oraz określenie podatności wstępnie przygotowanego substratu na beztlenowy rozkład w procesie fermentacji metanowej. W toku prac porównano efekty dezintegracji w oparciu o ogrzewanie mikrofalowe z wynikami uzyskanymi podczas ogrzewania konwencjonalnego. Najwyższą efektywność produkcji biogazu uzyskano podczas fermentacji substratu kondycjonowanego przy pomocy promieniowania mikrofalowego z dodatkiem NaOH w ilości 0,2 g/g_{s.m.}, otrzymany wynik był o 11,3% większy od próby ogrzewanej konwencjonalnie i o 29,4% większy od próby nie poddanej obróbce chemicznej.

Abstract

This study analysed the effects of microwave radiation and sodium hydroxide on the destruction of lignocellulosic plant biomass (maize silage) and determined the susceptibility of a pre-treated substrate on anaerobic decomposition in the methane fermentation process. The effects of microwave heating-based disintegration were compared to conventional heating. The highest effectiveness of biogas production was obtained during the fermentation of a substrate conditioned using microwave radiation with the addition of NaOH in an

amount of 0.2 g/g_{d.m.}, and the obtained result was 11.3% higher than a sample heated conventionally and was 29.4% higher than a sample subjected to no chemical treatment.

Słowa kluczowe:

biogaz, kiszonka kukurydzy, biomasa lignocelulozowa, hydroliza termiczna, promieniowanie mikrofalowe

Keywords:

biogas, maize silage, lignocellulosic biomass, thermal hydrolysis, alkaline treatment, microwave radiation



The Influence of Sludge on Thermal Performance of Heat Exchanger Tubes Inside in an Anaerobic Digester

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1. Introduction

In recent times, we have been observing an increase in energy demand, which results in the deepening devastation of the natural environment. One of the effective ways to mitigate this phenomenon is the use of biogas plants (Wandera et al. 2018). Biogas plants in which waste is used as an alternative source of energy as opposed to sources of conventional energy sources makes these green technologies as pro-ecological investments. By using waste after sewage treatment and agricultural waste (Kogut et al. 2012, Montusiewicz 2014, Sadecka & Suchowska-Kisielewicz 2016), biogas plants contribute to the improvement of the quality of the environment, which makes them an integral part of environmental protection. The Polish government program “Innovative Energy – Powering Agriculture” assumes that by 2020 one biogas plant will be built in each municipality. However, this goal is very difficult to implement currently. According to the data of the Energy Regulatory Office – Department of Renewable Energy, there are approximately only 300 biogas plants in Poland (data from September 30, 2016). About 30% of these facilities are the agricultural type. For comparison, in China there were more than 30 000 middle and large agricultural biogas plants in 2010 (Guo et al. 2013). However, it can be stated that there is a continuous increase in the power of installations using biogas in Poland (Fig. 1).

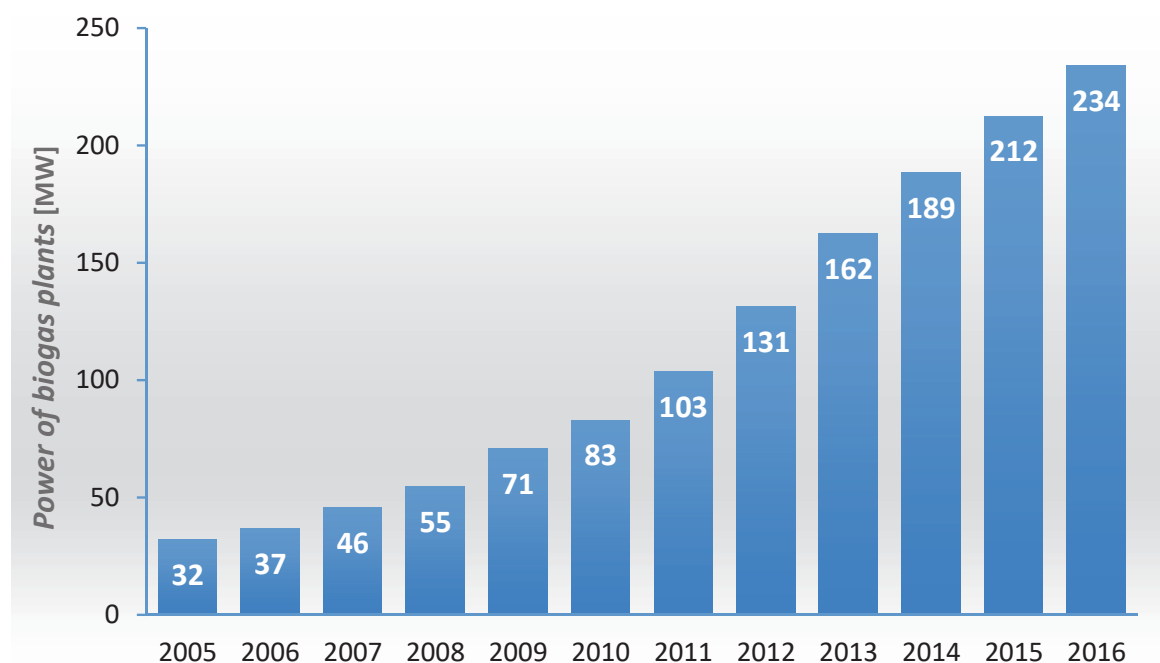


Fig. 1. Installed capacity for power generation in biogas plants in Poland (prepared on the basis of data from the Energy Regulatory Office – Department of Renewable Energy)

Rys. 1. Zainstalowana moc do wytwarzania energii w biogazowniach w Polsce (przygotowana na podstawie danych Urzędu Regulacji Energetyki – Departament Źródeł Odnawialnych)

According to Igliński et al. (2015), the energy amount that can potentially be obtained from biogas in Poland is around 11 million MWh. This potential is made up of 82 million m³ of municipal waste, 20 million m³ sewage sludge, 1 600 million m³ of farm animal droppings, and, according to Piwowar et al. (2016), over 244 million m³ of all agricultural biogas production plants per year.

One of the most important problems related to the operation of biogas plants in Poland is the drop in the temperature of the bed at times of low temperature of the outdoor air. A frequent cause of this phenomenon is the insufficient power of the heat exchanger placed inside the anaerobic digester. This article analyses the impact of sludge on decreasing the heat transfer efficiency in these devices.

Teng et al. (2017) investigated the effect of mineral scale deposition on heat exchanger pipes. They experimentally tested the progressive build-up of deposits, the rate of deposition, and the crystal morphology of

the mineral deposits on tubes made of stainless and carbon steel, brass, copper, and aluminium. In this work, many interesting conclusions were given allowing the optimal design of heat exchangers operating in difficult conditions.

The phenomenon of the deposition of organic and inorganic compounds in heat exchangers used in refineries was studied by Diaz-Bejarano et al. (2017). They developed a model based on thermo-hydraulic methodology, which was used to analyse the operation of shell-and-tube heat exchangers. The authors of this research stated that the new comprehensive model can be a very useful tool for diagnosis, monitoring, and troubleshooting of fouling in refinery heat exchangers.

Heat pumps are often used for energy recovery from urban wastewater. Unfortunately, the microbiological contaminants in sewage negatively affect the operation of the heat exchangers. The influence of many factors on the fouling formation by iron and sulphate-reducing bacteria were analysed by Xiao et al. (2018). The researchers formulated a number of conclusions regarding the effect of microbial fouling on the efficiency of heat exchangers.

Markowski et al. (2013) developed a new calculation algorithm for determination of the thermal resistance of fouling on heat exchangers. This method was validated by comparison calculation results with measurement data obtained from a heat exchanger connected to a distillation system. As the authors claim, applying of this algorithm and methodology can help in determining of fouling thermal resistance and its influence on the thermal performance of heat exchangers used in industry.

One important problem of a biogas plant is to maintain a constant temperature inside the fermentation chamber, especially during the winter. The basic component responsible for setting a constant temperature inside the digester is the heat exchanger. Operation of this device may be disturbed by deposition of sludge on the external heat transfer surface. As it turned out, in the literature there is no information nor any research results related to the operation of heat exchangers used in an anaerobic digester. The purpose of this work is to investigate the influence of sludge accumulation on the efficiency of the heat transfer process.

2. Description of the research object under investigation

The biogas plant (Fig. 2), located near the village of Ryboly (Poland), consists of two anaerobic digesters, a storage tank, co-generator and an administrative building.



Fig. 2. The storage tank and fermentation chamber located in the Ryboly Biogas Plant

Rys. 2. Zbiornik i komora fermentacyjna w biogazowni w Rybołach

The research object consists of four heating loops connected in parallel. These are made of stainless steel pipes with an outer diameter of 60.3 mm and a wall thickness equal to 2 mm. The entire construction of the heat exchanger is attached to the walls of the tank in its lower part, as shown in Fig. 3a. Supply and return manifolds (Fig. 3b) are placed on the external wall of the chamber. Photos on Figs. 3a and 3b were taken during the installation of two additional heating loops in autumn 2017, after the analysis demonstrating the insufficient power of the heat exchanger when there is a low external temperature.

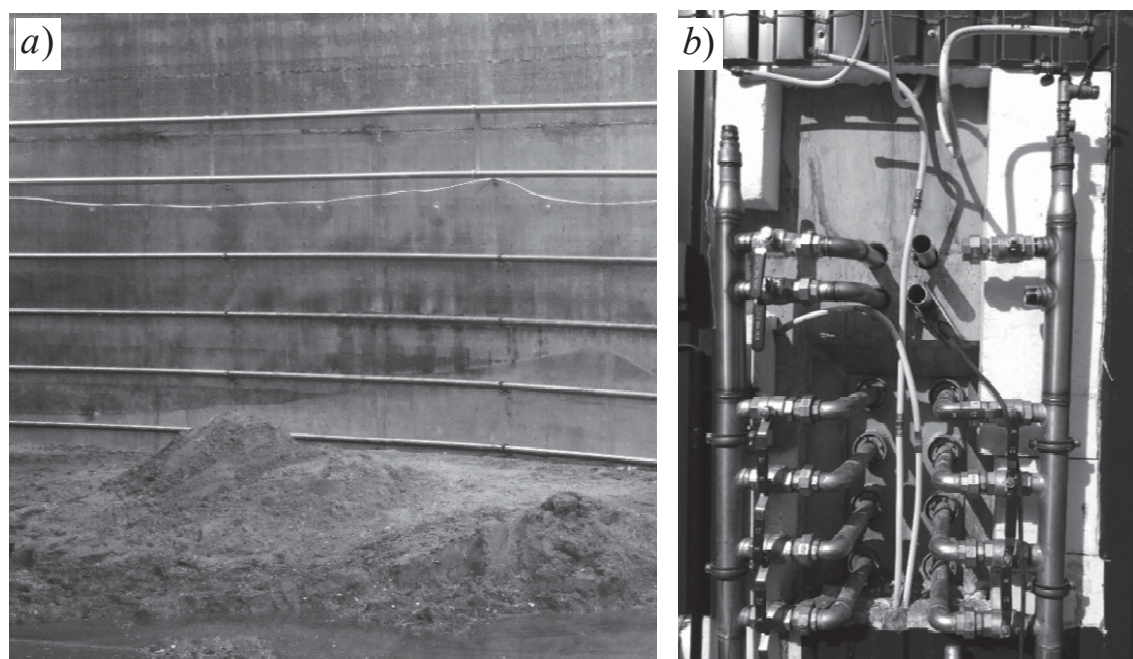


Fig. 3. Heat exchanger in Ryboly Biogas Plant: (a) heat exchanger attached to the digester wall (deposits formed during the operation of the digester are visible at the bottom of the chamber), (b) manifolds during mounting of two additional loops of the heat exchanger

Rys. 3. Wymiennik ciepła w biogazowni w Rybołach: (a) wymiennik ciepła przymocowany do ściany komory fermentacyjnej (osady powstałe podczas pracy komory fermentacyjnej są widoczne w dolnej części komory), (b) rozdzielacz podczas montażu dwóch dodatkowych pętli wymiennika ciepła

3. Model of determining the influence of sludge on the thermal performance of the heat exchanger

In order to determine the influence of sludge thickness on the thermal efficiency of the exchanger, a forced convection heat transfer model for the external and internal flow was used. The physical model of the heat exchanger is shown in Fig. 4. The following assumptions were made for the computer simulations: steady-state conditions, fully developed flow, incompressible liquid, and negligible viscous dissipation. Additionally, it was assumed that the sludge uniformly covers the walls of the heat exchanger tubing in such a way that it creates an additional layer of cylindrical wall with diameter d_3 (Fig. 4). Tab. 1 presents the basic geometric data of the heat exchanger (one loop) and the properties of the working medium and substrate.

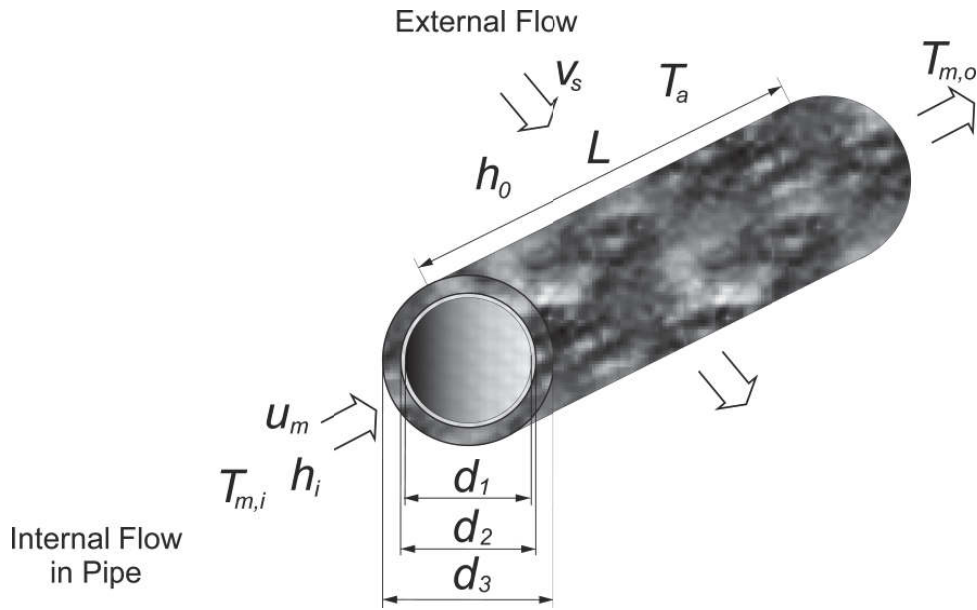


Fig. 4. Physical model of the heat exchanger

Rys. 4. Model wymiennika ciepła

The Reynolds number of the flow inside the heat exchanger is described by the following formula:

$$\text{Re}_{d_1} = \frac{4m}{\pi d_1 \mu_m} \quad (1)$$

Therefore, assuming a fully developed flow ($\text{Re} = 26393$) through the heat exchanger, the convection coefficient h_i can be determined from the definition of the Nusselt number (2) and the Dittus-Boelter correlation (3):

$$h_i = \frac{\text{Nu}_{d_1} k_m}{d_1} \quad (2)$$

$$\text{Nu}_{d_1} = 0.023 \text{Re}_{d_1}^{4/5} \text{Pr}^{0.3}, \quad \text{Re}_{d_1} \geq 10000, \quad 0.6 \leq \text{Pr} \leq 1600, \quad (3)$$

$$\text{Pr} = \frac{c_{pm} \mu_m}{k_m}$$

The Churchill-Bernstein correlation was used for determination of the external convective heat transfer coefficient h_o :

$$h_o = \frac{\text{Nu}_{d_3} k_s}{d_3} \quad (4)$$

$$\text{Nu}_{d_3} = 0.3 + \frac{0.62 \text{Re}_{d_3}^{1/2} \text{Pr}^{1/3}}{\left[1 + (0.4/\text{Pr})^{2/3}\right]^{1/4}} \left[1 + \left(\frac{\text{Re}_{d_3}}{282000}\right)^{5/8}\right]^{4/5}, \quad (5)$$

$$\text{Re}_{d_3} \text{Pr} \geq 0.2$$

where the Reynolds number (6) and the Prandtl number (7) are defined as:

$$\text{Re}_{d_3} = \frac{\rho_s v_s d_3}{\mu_s} \quad (6)$$

$$\text{Pr} = \frac{c_{ps} \mu_s}{k_s} \quad (7)$$

where v_s is the substrate velocity around the heat exchanger tubes.

The temperature at the outlet from the exchanger was determined according to the following relationship (Bergman et al. 2011):

$$T_{m,o} = T_a - (T_a - T_{m,i}) \exp\left[-\frac{\pi d_1 L U}{m c_{pm}}\right], \quad [^{\circ}\text{C}] \quad (8)$$

where an overall heat transfer coefficient is defined as:

$$U = 1 / \left(\frac{1}{h_i} + \frac{r_1}{k_w} \ln \frac{r_2}{r_1} + \frac{r_1}{k_{sl}} \ln \frac{r_3}{r_2} + \frac{r_1}{r_3} \frac{1}{h_o} \right), \quad \left[\frac{\text{W}}{\text{m}^2 \text{ } ^{\circ}\text{C}} \right] \quad (9)$$

where $r_1 = d_1/2$, $r_2 = d_2/2$ and $r_3 = d_3/2$ (Fig. 5).

The total heat transfer rate of the heat exchanger is determined by the formula:

$$q = m c_{pm} (T_{m,o} - T_{m,i}), \quad [\text{W}] \quad (10)$$

Two issues were considered to investigate the influence of the sludge on the heat transfer rate of the heat exchanger. In the first case, two examples were solved. The first example is the dependence of the outlet temperature from the exchanger as a function of the thickness of the sludge on the piping and the thermal conductivity of the sludge at a constant substrate velocity. The second example is the dependence of the thermal efficiency of the heat exchanger as a function of the thickness

of the sludge on the piping and the thermal conductivity of the sludge at a constant substrate velocity.

Table 1. Parameters used to calculate the influence of sludge on the thermal efficiency of the exchanger installed in the digester

Tabela 1. Parametry stosowane do obliczania wpływu osadu na wydajność cieplną wymiennika zainstalowanego w komorze fermentacyjnej

Description	Symbol	Value	Unit
Inner diameter of the heat exchanger	d_1	0.0563	m
Outer diameter of the heat exchanger	d_2	0.0603	m
Thickness of the sludge layer on the heat exchanger	s	0.005-0.01	m
Mass flow of heat exchanger medium	m	0.594	kg/s
Length of a single heat exchanger loop in the digester	L	94.25	m
Inlet temperature for the heat exchanger	T_{mi}	70	°C
Temperature substrate in the fermentation chamber	T_a	40	°C
Specific heat capacity of the working medium in the exchanger	c_{pm}	4180	J/kg/°C
Dynamic viscosity of the working medium in the exchanger	μ_m	0.000509	kg/m/s
Thermal conductivity of the working medium in the exchanger	k_m	0.64	W/m/K
Thermal conductivity of the steel wall of the heat exchanger (1.4301 Austenitic Corrosion Resistant Steel)	k_w	15	W/m/K
Thermal conductivity of the sludge on the heat exchanger	k_{sl}	0.2-1.1	W/m/K
Specific heat capacity of the substrate	c_{ps}	4184	J/kg/°C
Dynamic viscosity of the substrate	μ_s	0.03	kg/m/s
Thermal conductivity of the substrate	k_s	0.62	W/m/K
Substrate velocity in the fermentation chamber	v_s	0.001-0.1	m/s

In the second issue, the temperature at the outlet from the exchanger and heat transfer rate of the heat exchanger were determined as a function of the velocity of the substrate around the heat exchanger tubing at a constant thermal conductivity of the sludge. The properties of the working medium (water) in the heat exchanger were assumed for the average inlet and outlet temperature (Tab. 1).

The thickness of the sludge appearing on the piping changes with the time of operation of the digester. In the case of the tested real object, after three years of exploitation of the digester the thickness of the sludge layer was about 1 cm (Fig. 5a). The view of the exchanger after purification from the sludge on the piping wall is presented on Fig. 5b. The heat transfer coefficient, specific heat and sludge viscosity depend on the type of substrate used in the digester. The substrate properties presented in Tab. 1 were adopted on the basis of tests carried out by the manager of the biogas plant in Ryboly, while the sludge properties for different substrate forms were adopted on the basis of literature data (Poloski et al 2002, Dewil et al. 2007, Wu 2013, Terradas et al 2014).

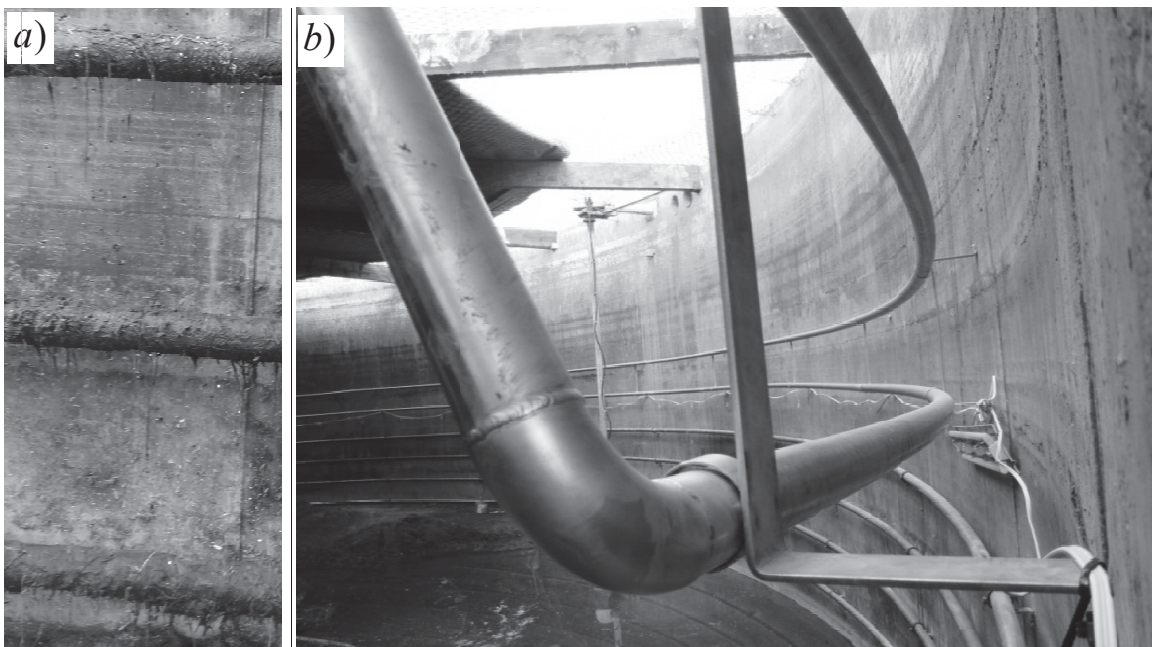


Fig. 5. Piping of the heat exchanger in the digester: (a) after three years of operation, (b) view after cleaning the exchanger

Rys. 5. Orurowanie wymiennika ciepła w komorze fermentacyjnej: (a) po trzech latach eksploatacji, (b) widok po oczyszczeniu wymiennika

The mass flow rate through the heat exchanger was determined on the basis of actual measurements and amounted to 0.594 kg/s. Due to the lack of the ability to measure the flow velocity of the substrate around the piping, the velocity range from 0.001 to 0.1 m/s was adopted based on the literature results (Meroney & Colorado 2009, Bridgeman 2012, Barbarinsa et al 2013, Wu 2014).

4. Results and discussion

The effect of various fouling from the working medium inside the piping on the operation of heat exchangers was described extensively in the literature (Mitrovic 2012). There are no studies on the influence of sludge from the working substrate on the thermal efficiency of the heat transfer in the digester chamber. In 2015-2017, the heat demand of the fermentation chambers and outside temperature were measured. Fig. 6a shows the average monthly outside temperature in 2015-2017 near biogas plants, which did not differ significantly in subsequent years, while Fig. 6b shows the average annual energy for heating the fermentation chambers in the same range of years. Energy consumption for heating purposes in 2016 was higher by 12.66% than in 2015, while in 2017 energy consumption was higher by 12.06% than in 2016. According to the authors, the increasing trend of heat consumption for heating the substrate in the digester is probably related to the increase in thermal resistance of heat transfer.

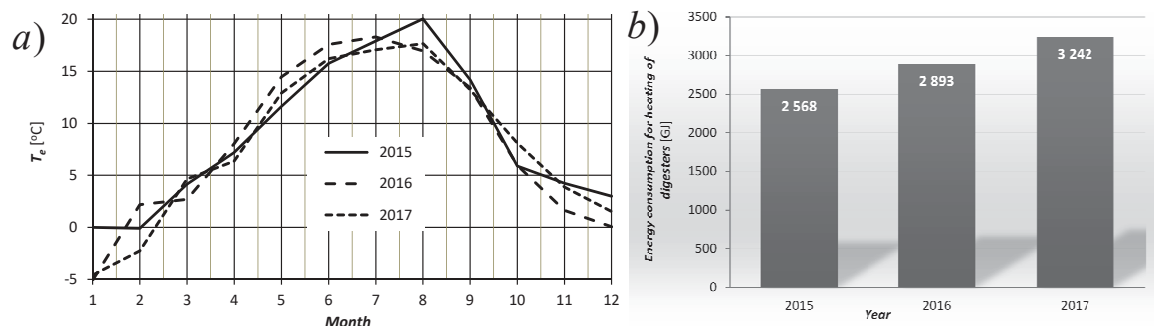


Fig. 6. The results of tests of the heat exchangers inside the digesters in Ryboly: (a) average monthly outdoor temperatures measured in 2015-2017 near the biogas plant, (b) energy consumption for heating of digesters in 2015-2017

Rys. 6. Wyniki badań wymienników ciepła wewnątrz komór fermentacyjnych w Rybołach: (a) średnie miesięczne temperatury zewnętrzne mierzone w latach 2015-2017 w pobliżu biogazowni, (b) zużycie energii do ogrzewania komór fermentacyjnych w latach 2015-2017

Figs. 7a-b show the dependence of the outlet temperature from the heat exchanger (Fig. 7a) and the heat transfer rate of the exchanger (Fig. 7b) depending on the thickness of the sludge layer and the thermal conductivity coefficient of the sludge. For the calculations a constant flow velocity of the substrate $v_s = 0.001$ m/s, and the following thermal

conductivity coefficients of the sludge were assumed: 0.3, 0.5, and 1.0 W/(mK). Along with the increase of the thickness of the sludge layer on the exchanger wall, the outlet temperature from the exchanger rises, which leads to the decrease in the heat transfer rate of the exchanger. For example, an increase of the sludge layer from 0.002 to 0.01 m with a thermal conductivity coefficient of 0.5 W/(mK) leads to a decrease in thermal efficiency by 47%.

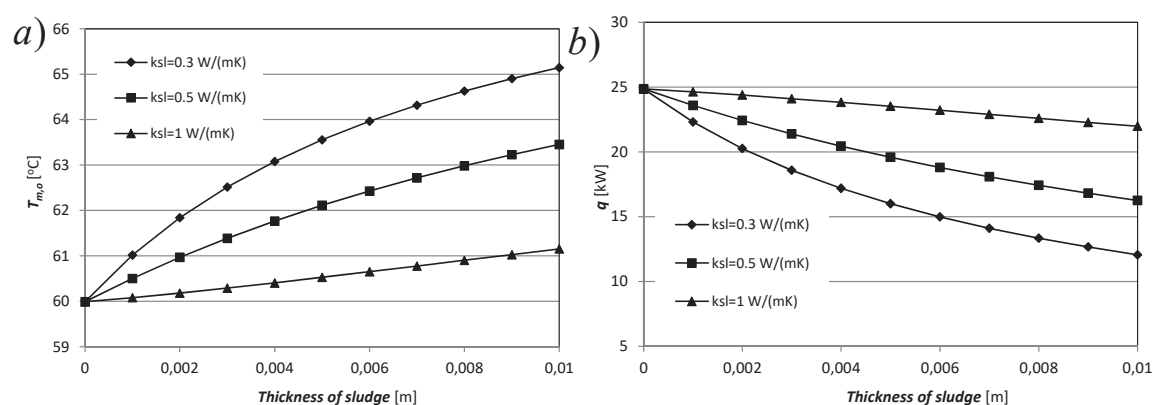


Fig. 7. Change of the heat exchanger operation parameters depending on the thickness of the sludge layer s and the thermal conduction coefficient of the sludge k_s : (a) $T_{m,o}=f(s)$, (b) $q=f(s)$

Rys. 7. Zmiana parametrów pracy wymiennika ciepła w zależności od grubości warstwy osadu i współczynnika przewodzenia ciepła osadu k_s : (a) $T_{m,o}=f(s)$, (b) $q=f(s)$

The next charts show the dependence of outlet temperature from the heat exchanger (Fig. 8a) and the heat transfer rate (Fig. 8b) depending on the substrate velocity around the heat exchanger tubing and the thickness of the sludge layer. A constant thermal conductivity coefficient of the sludge ($k_s=1$ W/(mK), piping of the exchanger without sludge, and the heat exchanger with sludge–thickness 0.005 m and 0.01 m were assumed for calculations. As the velocity of the substrate increases, the outlet temperature from the exchanger decreases, while the heat transfer rate increases. In the case of the increase in the thickness of the sludge, the characteristics $T_{m,o}=f(v_s)$ rise, i.e. the outlet temperature from the exchanger increases, while the reverse effect can be observed in the case of $q=(v_s)$. Figs. 8a and 8b show that the increase in substrate velocity around the piping increases heat transfer. It should be noted that the

tested exchanger is installed close to the wall of the fermentation chamber. In this case the substrate velocity, according to the literature (Poloski et al 2002, Dewil et al. 2007, Wu 2013, Terradas et al 2014), is not too high.

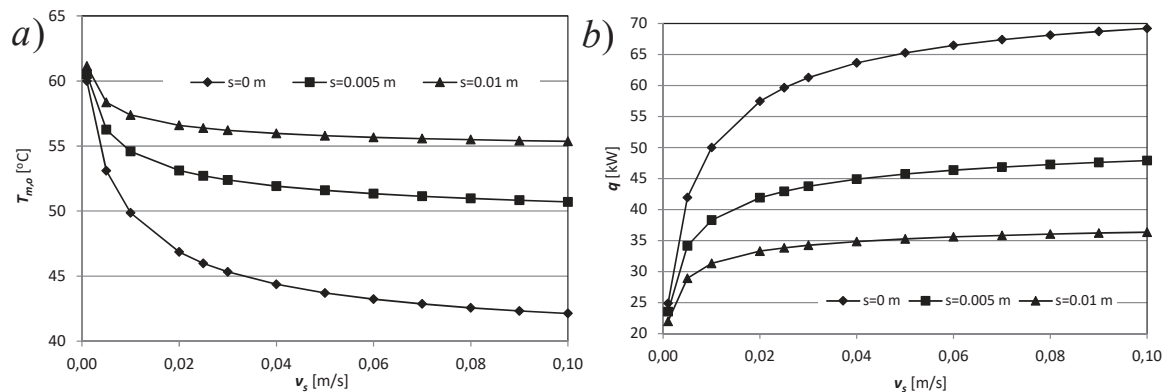


Fig. 8. Changing the parameters of the heat exchanger operation depending on the substrate velocity for different sludge layer thicknesses s : (a) $T_{m,o}=f(v_s)$, (b) $q=f(v_s)$

Rys. 8. Zmiana parametrów pracy wymiennika ciepła w zależności od prędkości przepływu substratu dla różnych grubości warstw osadu s : (a) $T_{m,o}=f(v_s)$, (b) $q=f(v_s)$

5. Conclusion

The reason for writing this article were problems related to the operation of the biogas plant in Ryboly during the winter season. The paper presents the model for determining the influence of sludge on the operation of the heat exchanger in the anaerobic digester depending on the geometry, operating parameters, and fouling properties. This approach was implemented in the form of a computer program that allows one to specify the influence of sludge on the pipe walls on the efficiency of the heat exchanger inside the anaerobic digester. Based on the simulations and the results of measurements, the following conclusions can be drawn:

1. The existence of sludge on the external walls of the heat exchanger causes a decrease in the thermal efficiency of the heat transfer. It should be noted here that increasing the supply temperature of the heat exchanger in order to overcome the effects of lowering the heat

- transfer can lead to the death of microorganisms around the heating system as a result of local excessive increase of substrate temperature. One of the possible solutions to this problem is to increase the heat exchange surface by adding additional loops of tubes in the existing biogas plant.
2. The increase in flow rate around the piping in the fermentation chamber increases the heat transfer between the exchanger and the substrate. Therefore the negative effect of the fouling layer on the heat transfer can be overcome by increasing the velocity around the piping by intensifying the reactor mixing process e.g. by increasing the rotational speed of agitators in the anaerobic digester.
 3. The thermal conductivity of the fouling depends on the type of working substrate in the digester. This coefficient has a direct effect on the efficiency of the heat exchanger. The subject of the influence of the substrate sludge on the external surface of the heat exchanger in the anaerobic digester is new, and therefore requires further testing for different types of substrates. However, it should be noted that implementing this type of an experimental research in such a difficult environment is highly complex and expensive.

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Wpływ osadu na wydajność cieplną wymiennika ciepła w beztlenowej komorze fermentacyjnej

Streszczenie

Biogazownie w Polsce są obecnie jednym z najbardziej dochodowych alternatywnych źródeł energii. Wysoką wydajność biogazowni zapewnia przede wszystkim odpowiedni dobór wymienników ciepła w beztlenowej komorze fermentacyjnej. W literaturze brak jest danych dotyczących działania wymienników ciepła stosowanych w beztlenowej komorze fermentacyjnej. Osad w komorze fermentacyjnej często osadza się na rurach wymiennika ciepła, zmniejszając tym samym efektywność wymiany ciepła, co może prowadzić do niebezpiecznego spadku temperatury wewnątrz komory fermentacyjnej. W pracy omówiono wpływ osadu na pracę wymiennika ciepła w biogazowni. W celu wyznaczenia współczynnika przenikania ciepła dla opływającego poprzecznie orurowania wymiennika przyjęto korelacje zaproponowane przez Churchilla i Bernsteina, natomiast wewnątrz orurowania wymiennika ciepła współczynnik przejmowania ciepła obliczono z korelacji Dittusa-Boeltera. Do obliczeń przyjęto zmierzone, rzeczywiste parametry pracy biogazowni. W pierwszym zagadnieniu wyznaczono zależność temperatury na powrocie z wymiennika ciepła oraz wydajności cieplnej wymiennika w zależności od grubości warstwy osadu i współczynnika przewodzenia ciepła osadu. Do obliczeń przyjęto stałą prędkość opływu orurowania substratem: 0.001 m/s oraz następujące współczynniki przewodzenia ciepła osadu: 0.3, 0.5 oraz 1.0 W/(mK). Wraz ze wzrostem grubości warstwy osadu na ścianie wymiennika temperatura na powrocie z wymiennika rośnie, co prowadzi do obniżenia wydajności cieplnej wymiennika. W drugim zagadnieniu wyznaczono funkcję temperatury na powrocie z wymiennika ciepła i wydajności cieplnej w zależności od prędkości przepływu

substratu w obrębie orurowania wymiennika ciepła oraz od grubości warstwy osadu. Do obliczeń przyjęto stały jednostkowy współczynnik przewodzenia ciepła osadu oraz orurowanie wymiennika bez osadu i z osadem o grubości warstwy osadu 0.005 m i 0.01 m. Wraz ze wzrostem prędkości przepływu temperatura na powrocie z wymiennika maleje, natomiast wydajność cieplna wymiennika rośnie. Orurowanie wymiennika ciepła jest zainstalowane blisko ściany komory fermentacyjnej, gdzie prędkości przepływu substratu są niewielkie. Wszystkie rezultaty obliczeń zostały przedstawione w formie wykresów. Jednym ze sposobów zwiększenia wydajności cieplnej wymiennika jest zwiększenie temperatury zasilania. Należy tu zaznaczyć, że zbyt duża temperatura w obrębie orurowania wymiennika może doprowadzić do zniszczenia mikroorganizmów w komorze fermentacyjnej. W pracy przedstawiono również pomiary zużycia energii na cele ogrzania komory fermentacyjnej w latach 2015-2017. Ilości zużytego ciepła na cele ogrzania komory fermentacyjnej rosła wraz z czasem eksploatacji komory fermentacyjnej w wyniku gromadzącego się na komorze fermentacyjnej osadu. Publikację uzupełniają zdjęcia przedstawiające osady na ścianach wymiennika ciepła.

Abstract

Biogas plants in Poland are currently one of the most profitable alternative energy sources. The high efficiency of the biogas plant is guaranteed first of all by the appropriate selection of heat exchangers inside the anaerobic digester. There is no data in the literature regarding the operation of heat exchangers used in an anaerobic digester. The sludge in the digester is often deposited on the tubes of the heat exchanger, thereby reducing the efficiency of the heat transfer which can lead to a dangerous temperature drop inside the digester. This paper discusses the influence of sludge on the operation of the heat exchanger in a biogas plant. In order to determine the heat transfer coefficient for the heat exchanger tubing flowing around, the correlations proposed by Churchill and Bernstein were adopted, while inside the heat exchanger tubing the heat transfer coefficient was calculated from the Dittus-Boelter correlation. The measured actual parameters of the biogas plant operation were used for the calculations. In the first issue, dependence of return temperature from the heat exchanger and thermal efficiency of the exchanger was determined depending on the thickness of the sludge layer and the thermal conductivity of the sludge. For the calculations a constant flow velocity of the substrate was assumed: 0.001 m/s and the following thermal conductivity of sludge were assumed: 0.3, 0.5 and 1.0 W/(mK). Along with the increase of the thickness of the sludge layer on the exchanger wall, the return temperature from the exchanger increases, which leads to a decrease in the thermal efficiency of the exchanger. In the second

issue, the function of return temperature from the heat exchanger and thermal efficiency was determined depending on the substrate flow velocity and the thickness of the sludge layer. A constant unit thermal conductivity coefficient of the sludge and piping of the exchanger without sludge and sludge with the thickness of the sludge layer 0.005 m and 0.01 m were assumed for calculations. With the increase of the flow velocity, the return temperature from the exchanger decreases, while the thermal efficiency of the exchanger increases. The heat exchanger piping is installed close to the wall of the digester where the substrate flow rates are small. All calculation results are presented in the form of graphs. One of the ways to increase the thermal efficiency of the exchanger is to increase the supply temperature. It should be noted that too high temperature within the exchanger's piping can lead to the destruction of microorganisms in the fermentation chamber. The paper also presents measurements of energy consumption for heating the digester in 2015-2017. The amount of heat consumed to heat the fermentation chamber increased with the time of exploitation of the fermentation chamber as a result of the sludge accumulating on the fermentation chamber. The publication is supplemented with photographs showing deposits on the walls of the heat exchanger.

Słowa kluczowe:

beztlenowa komora fermentacyjna, wymiennik ciepła, osad

Keywords:

biogas anaerobic digester, heat exchanger, sludge



Supporting the Coagulation Process with Shale – Preliminary Studies

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1. Introduction

The amount and variety of anthropogenic pollutants and contaminants in the natural environment have increased in recent years. Searching for new effective materials and technological solutions to prevent the growing threats to the environment is still one of the most important tasks of today's engineering. One of the basic processes used in water and sewage treatment is coagulation (Nawrocki & Biłozor 2000; Girczys & Caban-Pabian 1999; Jiang 2015), which is increasingly improved through the use of various supporting materials (Bina et al. 2009, Aygun & Yilmaz 2010). These include, first of all, various ballasts of floc. They can be minerals such as bentonite (Góra et al. 2016), montmorillonite (Lagaly & Ziesmer 2003) or kaolinite (Li et al. 2016), chitosan (Bhalkaran & Wilson 2016, Zhang et al. 2018), activated silica (Sinha & Mathur 2015), activated carbon (Furlan et al. 2009), organic polyelectrolytes (Kozminykh et al. 2016) or mineral polyelectrolytes (Thakur & Choubey 2014). Adjuvants are used to accelerate floc formation and sedimentation, reduce the negative effects of low temperatures, extend of the optimal pH range for coagulation and lower the dose of coagulant (Nawrocki & Biłozor 2000). Often, these substances also have adsorptive properties. It is significant that most of natural ballasts have a charge of sign opposite to the one of basic coagulant. The beneficial effect of small amounts of dissolved silica as an adjuvant to aluminum sulfate in the coagulation of opacifying pollutants was confirmed in water of low turbidity. The test results demonstrated the participation of silicon complex-

es in modifying the method of colloid charge neutralization by the products of hydrolysis of the coagulant (Duan & Gregory 1996). Moreover, the presence of silica may reduce the bioavailability of aluminum remaining after the coagulation (Birchall et al. 1989).

Thus, substances opacifying water such as bentonites, clays, montomorylonites can be used to enhance the rate of coagulation. They are applied mostly in conjunction with primary coagulants. In such conditions, the presence of fine clay particles increases the number of condensation centers in the gel, which causes a faster adsorption of colloidal particles and the formation of highly loaded and easily sedimenting floc (Nawrocki & Biłozor 2000). The resulting post-coagulation sediment is a complex mixture of pollutants and clayey substances held together by the van der Waals and electrostatic forces (Abdelaal 2004).

The world's attention is mainly focused on the use of bentonites and bentonite clays, the resources of which are unfortunately small in Poland (about 2.9 million Mg), and this is the reason for their import (Burkowicz 2015). However, there are other rocks which could partially replace them. One of them could be gangue (shale, claystone, mudstone), which accompanies the coal beds in Polish mines and is treated as waste during coal extraction. Artificially deposited rocks are mostly clays, shales, mudstones and carbon shales (Skarżyńska 1997). The Central Statistical Office (GUS) gives that 7.66 million Mg of waste rocks from non-metalliferous extraction were generated in Poland in 2015 (Ochrona Środowiska 2016). The greatest amount of gangue in the world are mined in China – around 300-350 million Mg per year (Yu et al. 2016). Presently, the mining waste rocks are used mainly in civil engineering (hydro-engineering, roads) as aggregate, in the restoration of degraded lands and for the production of building materials (Kozioł et al. 2016). In the world, gangue is also used for energy production, in agricultural fertilizer industry and the production of bricks, cement and concrete (Wang et al. 2016). The quality of the extractive wastes, mainly their physical and chemical properties, is largely due to their mineral and petrographic composition. Currently, the waste is increasingly seen as a waste mineral resource. Besides, a comprehensive approach in management of various types of mining waste for a range of applications is observed depending on their quality and taking into account their diverse lithology. This can be done by modifying existing technologies or development of new technologies

aimed in the use and processing of the mining wastes themselves. One of such applications of clayey waste materials could be using them for water treatment in the coagulation process. Their addition during coagulation, particularly in low turbidity water, can cause ballasting the floc and improve the sedimentation properties. Moreover, previous studies have shown that the rock in its natural form can adsorb some organic substances, e.g. phenol (Jabłońska 2012), and inorganic ones, e.g. heavy metals (Jabłońska & Siedlecka 2015, Sikora & Budek 1996).

The paper shows the preliminary results of research on the assessment of usefulness of waste rock (shale) originating from one of Polish coal mines to support the process of coagulation in low turbidity water. Raw shales as well as modified with simple thermal treatment, which could cause favorable changes in the structure of the materials (Jabłońska et al. 2017), were studied.

2. Materials and methods

The water was taken from the Warta River in Częstochowa on the day of testing. Then it was standing for 30 minutes to remove easily falling suspended matter.

The material supporting the process of coagulation was shale taken from a Polish coal mine extracting the coal in the area of Chief Saddle of the Upper Silesian Coal Basin. According to the Regulation of the Ministry of Environment of 9 December 2014, the waste rock is classified under code 01 01 02 (wastes from extracting non-metalliferous minerals). The waste is collected on dumps as rock material. The material for study was shale in its natural state. Then it was crushed in the vibration mill (TESTCHEM) to the grains less than 0.1 mm and dried to air-dry state. To obtain shale calcined at 600°C and 800°C, the material was introduced into a cold muffle and heated to the desired temperature at a rate of 10°C/min in an electrically heated muffle furnace.

The coagulant was aluminum sulfate – $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ p.a. – produced by a chemical plant Kemipol Ltd. as a clear colorless solution. It is characterized by a density of $1\,310 \pm 10$ g/dm³, pH = 2.4 ± 0.5 , with the percentage of Al_2O_3 of 7.9 ± 0.4 (data sheet by Kemipol Ltd.).

The coagulation process was carried out in 2 dm³ glass beakers, into which a volume of 1 dm³ of the water was introduced and then the coagulant was added. The coagulant dose of 30 mg/dm³ was established

based on Stępniaak (2006). After addition of the coagulant, a mechanical stirring was applied at 200 r.p.m. for 1 min. followed by 20 r.p.m. for 15 min. After this time, the samples were left for 1 hour sedimentation. Then 100 cm³ of water were decanted and the turbidity was determined (nephelometric method using HACH 2100 IS turbidimeter according to ISO 7027). The final result was assumed the arithmetic mean of three determinations varying no more than 10% of the highest reading.

The second series of tests was performed as above, except that the raw shale was introduced during the coagulation and rapid stirring. The adjuvant doses ranged from 10 to 80 mg/dm³. In the third step, the effect of thermal modification was tested by introducing the shale calcined in 600°C and 800°C. The coagulation with use of the material after the thermal modification was performed in the same manner as in the case of raw material. In every case, pH was specified by the natural pH of the treated water and the introduced shale and acidic solution coagulant.

The turbidity removal percentage (efficiency), E , was determined as the percentage change in the turbidity

$$E = \left(1 - \frac{T}{T_0}\right) \cdot 100\%, \quad (1)$$

where T and T_0 are turbidities of water after and before coagulation, respectively.

The chemical composition was determined with use of XRF spectrometry (Philips PW 1404). Trace elements were detected using ICP-AES spectrometry (Thermo Elemental IRIS Intrepid II XSP DUO). The leaching tests were carried out in accordance with PN-EN 12457-4:2006. The following determinations were made in the water filtrate: concentration of sulfate ions – with gravimetric method (PN-ISO 9280:2002), concentration of chlorate ions – with titration method (PN-ISO 9297:1994), concentration of phosphates – with spectrophotometric method with ammonium molybdate (PN-EN ISO 6878:2006), concentration of sodium, potassium and magnesium – using ICP-AES spectrometry in accordance with PN-ISO 9964-2:1994P and PN-EN ISO 7980:2002P. pH was measured using a CPC-401 type Elmetron pH meter. Determination of ash content was made in accordance with PN-ISO 1171: 2002P.

3. Results and discussion

3.1. Characteristics of shale used in tests

Shale in its natural state is characterized by a dark gray tint; it locally shows clear cleavage and is laminated with organic matter (carbon). The mineralogical composition of the rocks is dominated by kaolinite and quartz. The larger amounts of illites, hematite and mica are observed, too. There are also traces of smectites and chlorites. The chemical composition shown in Table 1 reflects the mineralogical composition of the examined rocks. The relatively high content of SiO_2 , Al_2O_3 and K_2O indicates mainly the presence of quartz, kaolinite and illite, and sometimes feldspar. A significant part in the composition of the shale belongs to Fe_2O_3 , which is attributed to the presence of hematite in the rock. Other elements present in the chemical composition can be associated with clayey minerals such as mica, smectites, chlorites and carbonates: calcite and siderite. The non-combustible constituents of the rock are 84.7% of the mass, and the combustible part is 15.3%.

Table 1. Chemical composition of shale used in tests
Tabela 1. Skład chemiczny badanego łupka ilastego

Constituent	Content, mass %	Constituent	Content, mass %
SiO_2	53.4	K_2O	2.7
Al_2O_3	20.1	TiO_2	0.6
Fe_2O_3	4.5	P_2O_5	0.05
CaO	1.1	SO_3	0.1
MgO	1.8	Loss on ignition	15.3
Na_2O	0.2	Others	0.05

The content of trace elements in the shale and permissible limits in soils and land surface (at a depth of 0 to 0.3 m below the surface) are shown in Table 2. The levels of trace metals are much lower than the limit values permissible in surface soils belonging to the group B areas (i.e. areas classified as agricultural land, forest land and wooded shrub, and built and urbanized areas with the exception of industrial areas).

Table 2. The content of trace elements in the tested shale and their permissible limits in soils of group B as specified in the Regulation of the Ministry of Environment of 9 September 2002

Tabela 2. Zawartość pierwiastków śladowych w badanym łupku i ich dopuszczalne wartości w gruntach grupy B podanych w Rozporządzeniu Min. Środ. z dnia 9 września 2002

Element	Content, mg/kg of dry mass									
	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sn	Zn
Determined	12	<0.5	4.5	33	44	<2	19	<0.5	2	171
Limit	20	4	20	150	150	10	100	100	20	300

The tested rocks characterize a low level of leaching of constituents soluble in water (Tables 3 and 4). Among leached anions, SO_4^{2-} and Cl^- can be found, whereas the leached cations were mainly Na^+ , K^+ and Mg^{2+} . Among detected heavy metals, the highest mobility was observed for iron ions. Concentrations of Cd(II), Cr(III) and Ni(II) were below the limits of quantification. pH was weakly alkaline. The determined values were below the permissible limits and pH was in the permissible range.

Table 3. The concentration of heavy metals in water extract from shale and limits given in the Regulation of the Minister of Environment of 18 November 2014

Tabela 3. Stężenia metali ciężkich w wyciągu wodnym z łupka ilastego i wartości dopuszczalne wg Rozporządzenia Min. Środ. z 18 listopada 2014

Element	Concentration, mg/dm ³							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Determined	<0.007	<0.004	0.02	0.28	0.09	<0.003	0.015	0.05
Limit	0.4	0.5	0.5	10	–	0.5	0.5	2.0

Table 4. Selected parameters of aqueous extract of shale and limits given in the Regulation of the Minister of Environment of 18 November 2014

Tabela 4. Wybrane parametry wyciągu wodnego z łupka ilastego i wartości dopuszczalne wg Rozporządzenia Min. Środ. z 18 listopada 2014

Parameter	pH	Concentration, mg/dm ³					
		Na^+	K^+	Mg^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}
Determined	7.5	46	12	14	31	24	0.14
Limit	6.5-9	800	80	–	1000	500	–

3.2. Effect of shale dose and calcination

The effect of shale dose on decreasing the turbidity in coagulation is shown in Table 5.

Table 5. Effects of coagulation with use of aluminum sulfate aided with raw and calcined shale

Tabela 5. Efekty koagulacji siarczanem glinu wspomaganą materiałem ilastym surowym i kalcynowanym

	Turbidity, NTU			
	Series 1		Series 2	
Raw water	9.9	(pH = 7.32)	11.8	(pH = 7.53)
Water and coagulant	4.68	(pH = 4.69)	6.65	(pH = 4.89)
Shale dose, mg/dm ³	Water with coagulant and shale			
	Raw shale	Shale calcined at 600°C	Raw shale	Shale calcined at 800°C
10	3.09	2.69	2.61	4.94
20	4.06	2.11	5.62	4.66
30	4.09	3.07	5.55	4.09
40	4.69	3.55	5.51	4.22
50	3.91	2.87	4.92	6.10
80	7.11	3.47	5.81	5.75
pH range	4.62-4.78	4.68-4.93	4.68-4.95	5.07-5.53

Aiding the coagulation with the raw shale decreased the turbidity of the water compared to the treatment without the shale. Typically, the turbidity was reduced to about 30-40% of the initial value, and the highest reduction was obtained for the lowest tested doses of the shale (10 mg/dm³). Greater doses of shale did not cause a further reduction in turbidity. Using the shale calcined at 600°C gave usually better results than the raw shale – the turbidity was decreased to about 20-30% of its initial value, with the highest reduction for shale dose 10-20 mg/dm³. Introducing the shale calcined at 800°C did not improve the reduction, and even sometimes worsened it.

The percentage turbidity removal is shown in Figure 1 and summarized in Table 6. Introducing the coagulant alone resulted in reduction of the turbidity by about 40-50%. Addition a portion of raw shale gave

a further decrease in turbidity with the exception of one case (shale dose 80 mg/dm³). The highest efficiency (78%) was obtained for 10 mg/dm³, i.e. for the smallest of the doses tested. A similar percentage turbidity removal (74.3-98.2%) was obtained by Bina et al. (2009), who used alum as a coagulant combined with chitosan as an adjuvant. The colloidal particles of shale are endowed with a negative charge, which is opposite to the charge of Al(III) hydroxides. During the mutual coagulation, the shale fragments are centers of condensation, which accelerate the flocculation and the formation of heavy, complex and rapidly falling floc. However, larger shale doses resulted in lower turbidity removal efficiency, although usually slightly higher than in the absence of the shale. Higher doses of the adjuvant increase the stability of the colloidal particles. Most likely, they cause the formation of a mesh of associated particles that interacts with the colloidal particles and impedes their coagulation. Comparison of Figures 1a and 1b for raw shale shows a significantly higher turbidity removal in the first sample than in the second. This indicates additional substances having an effect on the reduction of turbidity were present in the samples. Nevertheless, the results of the study showed the ability of shales to improve the effect of aluminum sulfate as an agent reducing water turbidity.

The use of clay calcined at 600°C gave better results than using the raw shale – the turbidity removal efficiency was 65-79%, the highest for 20 mg/dm³. The results obtained for shale calcined at 800°C are not clear – the turbidity removal efficiency increased in some cases, but decreased in other (compared to the raw shale efficiency of turbidity removal). Shale calcination is likely to cause favorable shifts in the crystalline shale structure, resulting in additional active centers (Heller-Kallai 2006), thus increasing the sorption surface of the sediment flocs. However, too high temperature of calcination can again weaken the shale properties to support of coagulation.

To summarize, the highest turbidity removal was obtained for shale calcined at 600°C in small doses. It seems that the ratio of coagulant and adjuvant doses should be not less than 3:1, and the adjuvant dose should not exceed 10-20 mg/dm³.

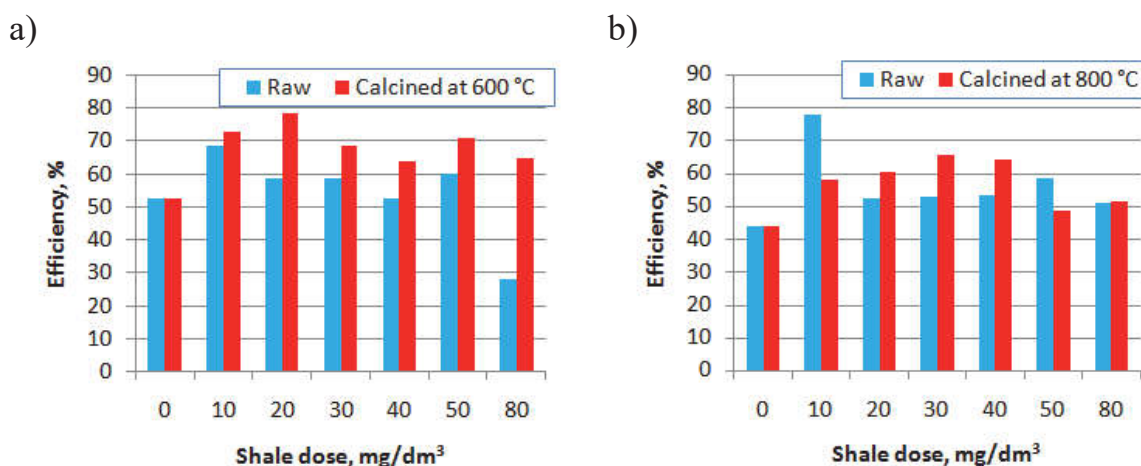


Fig. 1. Turbidity removal vs. shale dose for initial turbidity 9.9 NTU (a) and 11.8 NTU (b)

Rys. 1. Procent usunięcia mętności w funkcji dawki łupka ilastego dla mętności początkowej 9,9 NTU (a) i 11.8 NTU (b)

Table 6. Turbidity removal efficiency with aluminum sulfate (30 mg/dm^3) aided with shale ($10\text{-}80 \text{ mg/dm}^3$)

Tabela 6. Skuteczność obniżania mętności siarczanem glinu w dawce 30 mg/dm^3 wspomaganiej materiałem ilastym ($10\text{-}80 \text{ mg/dm}^3$)

Initial turbidity, NTU	Turbidity removal efficiency, %			
	Coagulant	Coagulant + raw shale	Coagulant + shale calcined at 600°C	Coagulant + shale calcined at 800°C
9.9	53	28-69	65-79	–
11.8	44	51-78	–	48-65

4. Conclusions

Based on carried out experiments and achieved results it was possible to draw the following conclusions:

- The use of shale as a substance aiding the process of coagulation with aluminum salts improves the quality of treated water of low turbidity. Supporting the coagulation process with raw shale resulted in higher turbidity removal than the use of coagulant alone.
- Using the shale calcined at 600°C improved the turbidity removal efficiency. The shale calcined at 800°C gave ambiguous results.
- The highest turbidity removal was obtained for low doses of shale ($10\text{-}20 \text{ mg/dm}^3$).

- The shale could be used as an adjuvant in coagulation, especially in low turbidity waters. Its grains are crystalline nuclei for the flocs, they increase the number of contacts, accelerate the formation of flocs, ballasting them and facilitating sedimentation.

However, the assessment of the efficiency of supporting the coagulation process with shale requires further research on removing other impurities (color, organic substances and heavy metals) from surface water depending on the order of introduction of the coagulant, shale and their doses.

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Wspomaganie koagulacji łupkiem ilastym – badania wstępne

Streszczenie

W pracy rozważono możliwości zastosowania płonnych skał ilastych (łupków ilastych) z kopalni węgla kamiennego do wspomaganie procesu koagulacji. Badano surowe i kalcynowane w temperaturze 600°C i 800°C łupki ilaste towarzyszące pokładom węgla kamiennego z kopalni położonej w południowej części Polski. Jako koagulantu użyto siarczanu glinu. Analizowano efekty obni-

żenia mętności w próbkach wody pobranej z rzeki Warty. Wspomaganie procesu koagulacji łupkiem surowym przyniosło większą efektywność zmniejszenia mętności w wodzie niż w przypadku zastosowania samego tylko koagulantu. Efektywność obniżania mętności była najwyższa w przypadku zastosowania łupka kalcynowanego w temperaturze 600°C. Użycie łupka kalcynowanego w temperaturze 800°C przynosiło nieco gorsze rezultaty, w niektórych przypadkach efektywność obniżania mętności była niższa niż z użyciem łupka surowego. Wyniki badań wskazują, że proces koagulacji może być efektywnie wspomagany łupkami ilastymi. Wcześniejsze badania (Jabłońska, B., Siedlecka, E., Removing heavy metals from wastewaters with use of shales accompanying the coal beds, *Journal of Environmental Management*, 155 (2015), 58-66) wykazały, że łupki ilaste mają stosunkowo dobre właściwości sorpcyjne, co może dodatkowo pozytywnie wpływać na jakość oczyszczanej wody.

Abstract

In the paper, clayey gangue (shale) accompanying coal beds was considered to support the coagulation process. The raw shale from a mine located in the southern part of Poland as well as the shale calcined at temperatures of 600°C and 800°C were tested. The coagulant was aluminum sulfate. The effects of turbidity reduction in water samples taken from the river Warta were analyzed. Aiding the process of coagulation with the raw shale increased the efficiency of reducing turbidity in water in comparison with the use of coagulant alone. The turbidity reduction was highest when using the shale calcined at 600°C. Applying the shale calcined at 800°C brought slightly worse results, and in some cases the turbidity reduction was lower than for the raw shale. The results indicate that the shale could be an effective adjuvant in the coagulation process. In addition, previous research (Jabłońska, B., Siedlecka, E., Removing heavy metals from wastewaters with use of shales accompanying the coal beds, *Journal of Environmental Management*, 155 (2015), 58-66) has shown that shale has relatively good adsorptive properties, which may further contribute to the quality of the treated water.

Słowa kluczowe:

oczyszczanie wody, koagulacja, mętność, łupki ilaste

Keywords:

water treatment, coagulation, turbidity, shale



Analysis of Energy Demand in the Process of Continuous and Pulse Sonication of Sewage Sludge

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1. Introduction

The problem of disposal and management of sewage sludge has been and is still valid. The increasing number of them requires the use of more and more efficient devices that meet certain standards, thus affecting the greater financial outlay. For these reasons, various methods are being sought to intensify the stabilization and drainage process. One of the known methods that helps to neutralize sewage sludge is ultrasonic disintegration. Depending on the parameters used, this method may have a coagulating or dispersive effect on the floc structure. It is a process that can be used at various stages of wastewater treatment.

The process of disintegration consists in the decomposition of solids contained in sewage sludge. Flocs are formed by various microorganisms, mainly bacteria and organic and inorganic matter. With the disintegration process, microorganism cells are decomposed, which leads to the release of intracellular fluids. This allows for easy removal of organic compounds that are contained in the cells during further processes of biological treatment of waste and processing of sewage sludge (Zhang et al. 2017, Guan et al. 2016, Grosser 2017). Disintegration enhances the decomposition of organic substances which are contained in the sludge and accelerates the process of transformation into biogas while reducing the final amount of sludge to be managed (Zawieja 2016, Gonze et al. 2003).

Disintegration of sewage sludge can be performed using various technologies. Methods differ from each other in the agent used for disintegration. Accordingly, they can be divided into mechanical, thermal, biological and chemical methods, freezing, oxidation and the ultrasonic method (Zhang et al. 2017, Zhou et al. 2014, Chang et al. 2001).

The elastic medium in which ultrasounds propagate can be liquids, gases and solids. Each medium differs from each other in their structure and velocity of wave propagation, whereas the mechanism of generation and propagation of the wave is the same. The effect of elastic wave with organic matter is particularly affected by the wave length and the process can occur in various manners. The use of the ultrasound field offers opportunities for generating processes with varied character, such as coagulation, agglomeration and fragmentation (Zielewicz 2016, Wolski et al. 2012, Feng et al. 2009).

Wave length and wave frequency represent the basic parameters used for the description of the ultrasound waves. The first parameter, i.e. wave length, depends on the medium where the process occurs (Zhang et al. 2008). The relationship between wave length and frequency can be defined by the equation:

$$\lambda = \frac{v}{f}, m \quad (1)$$

where:

v – velocity of ultrasound wave propagation in the medium, m/s,

f – vibration frequency, Hz.

The longest ultrasound wave can be observed in solids, whereas the shortest waves propagate in gases.

The characteristic energy values of the ultrasound field determine transfer of energy through acoustic wave. Energy transported over a time unit is defined as acoustic power. If this energy is related to the unit of volume V of the sonicated medium, it is termed energy density. Density of energy stream is defined as energy per unit of area of the surface S which is perpendicular to the direction of wave propagation (Zielewicz 2016, Bień et al. 2015, Zhou et al. 2017).

According to Śliwiński (Śliwiński 2001), the acoustic field can be described by energy values that describe transport of energy through waves. The amount of energy which is transported by the acoustic waves

over time of 1 s per area of the surface which is perpendicular to the direction of wave propagation is termed sound intensity. It is given by the equation:

$$I = \frac{N}{S} \quad (2)$$

where:

N – power transported by the waves, W,

S – surface of wave propagation, m².

The application of the ultrasonic field is connected with incurring some energy expenditure, the amount of which depends on the intensity of the field and the duration of the sonification. Therefore, the aim of the research was to determine the amount of energy introduced into the system depending on the wavelength (intensity) used, the time of exposure of the UD field and the type of process (continuous and pulsed). The research was preliminary (basic), therefore their scope was limited. In order to determine the effect of disintegration on the ability to drain, only the capillary suction time test was performed. Disintegration carried out periodically was limited to two intensity values (2.2 and 3.2 W/cm²), and three exposure times (10, 30 and 60 seconds).

2. Methodology

The sewage sludge for the examinations was sampled from processes of treatment of residential waste water. The samples were taken after the process of anaerobic stabilization but before the process of dewatering and polyelectrolyte station. Dry matter content was 21.2 g/dm³, whereas initial hydration was 97.88%. Dry mass content and initial hydration of sludge was determined based on the standard PN-EN-12880. Continuous disintegration was conducted using the energy of ultrasound field with intensity of 1.6, 2.2, 2.7, 3.2, 3.8 W/cm², with the wave length of 7.88, 15.77, 23.65, 31.54, 39.42 μm, respectively. Sonication of the sludge samples was conducted under static conditions for the period of 2, 5, 10, 20, 30, 45, 60 and 120 seconds. Periodical disintegration of sewage sludge was performed using ultrasound field energy with intensity of 2.2 and 3.2 W/cm², for 10, 30 and 60 seconds. The process of sewage sludge sonication used ultrasound processor Sonics VCX-1500 with maximal

power output of 1500 W. Frequency of ultrasound field vibration was 20 kHz whereas maximal wavelength for the amplitude of 100% was 39.42 μm . The device is used to transform electricity into mechanical energy supplied to the titanium tip in the form of wave. The amount of energy supplied to the system was read after each measurement. Volume of the samples exposed to ultrasound field was 100 cm^3 .

Simultaneously to the examinations aimed at the determination of the amount of energy supplied to the system, the capillary suction time (CST) was also determined. Capillary suction time of the fermented sonicated sludge was 436 seconds. Capillary suction time was measured using the Baskerville and Galle methodology, which is based on the measurement of time of transition of frontal boundary layer of filtrate as a result of the effect of suction forces in the paper used (Whatman 17). The result presented in the study was time of absorption of the sludge by the filtration paper between the rings with diameter of 32 and 45 mm.

3. Results and discussion

The examinations were aimed to determine the amount of energy supplied to the system (sewage sludge) in the process of continuous pulse sonication. Simultaneously, dewatering capacity of the sludge conditioned with ultrasonic wave was determined based on the capillary suction time.

The analysis of the results obtained in the study demonstrated the increase in the demand of the energy with elongation of the time of exposure to the ultrasound field (Fig. 1). The value of the energy supplied in the case of the 2-second continuous exposure, with ultrasonic wave length of 7.88 μm was 140 J. The 5-time elongation of sonication time for the discussed wave length caused an over 6-time increase in the demand for energy (889 J). In the next examinations, energy demand increased proportionally to sonication time. In the case of 120-second exposure, the amount of energy supplied was 8985 J.

For other wave length values, the analogous relationships were obtained as in the case of the amplitude of 20%. With the wave length of 15.77, 23.65, 31.54 and 39.42 μm , the amount of energy supplied to the system also increased with sonication time. The highest value of the energy supplied (25108 J) was recorded for the highest wave length (39.42 μm) and exposure time of 120 s.

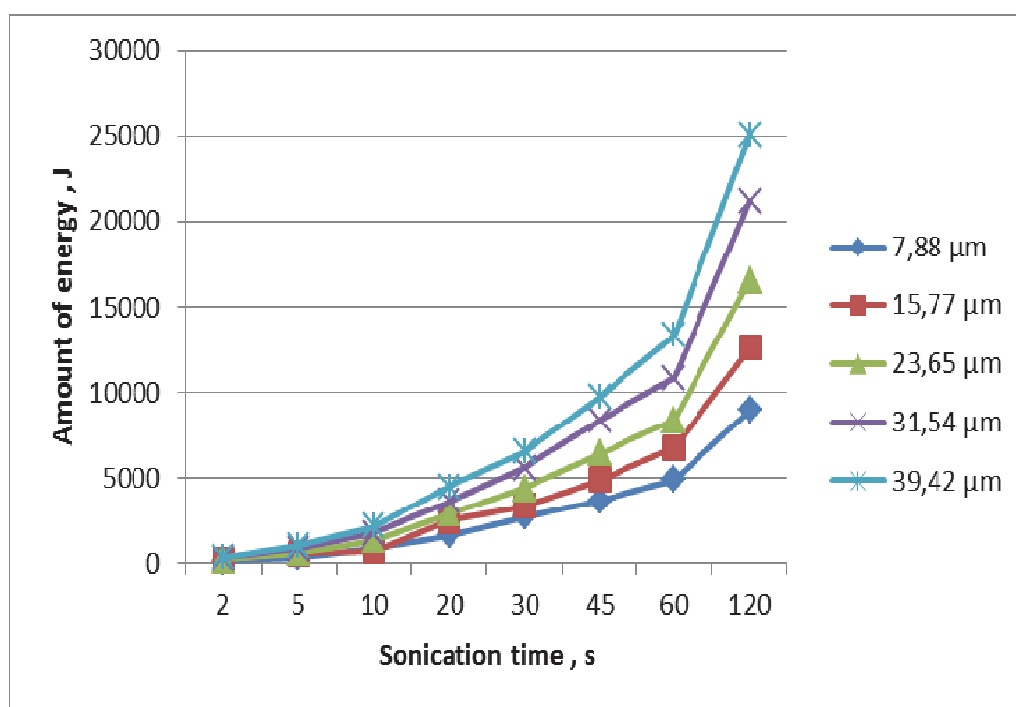


Fig. 1. Effect of continuous sonication time on the amount of energy supplied to the system depending on the ultrasound field wave length

Rys. 1. Wpływ czasu nadźwiękawiania ciągłego na ilość wprowadzonej energii do układu w zależności od zastosowanych długości fali pola ultradźwiękowego

The amount of the energy supplied to the system had an effect on dewatering capacity of sewage sludge, determined based on the capillary suction time. The lowest values of capillary suction time were obtained for sonication of sewage sludge with ultrasound field with wave length of 7.88 μm compared to four other amplitudes of the ultrasound field (Fig. 2).

With 2-second exposure, CST was 457 s and was insignificantly higher with respect to non-sonicated sludge. Elongation of sonication time led to the deterioration of the dewatering capacity expressed in higher values of capillary suction time. After 120 seconds, its value for the lowest amplitude (20%) was 1057 seconds. Higher values were found for other wave lengths and they were proportional to sonication time. With the highest wave length (39.42 μm) and sonication time of 120 seconds, the CST was 1323 s and was 3 times greater with respect to the non-sonicated sludge.

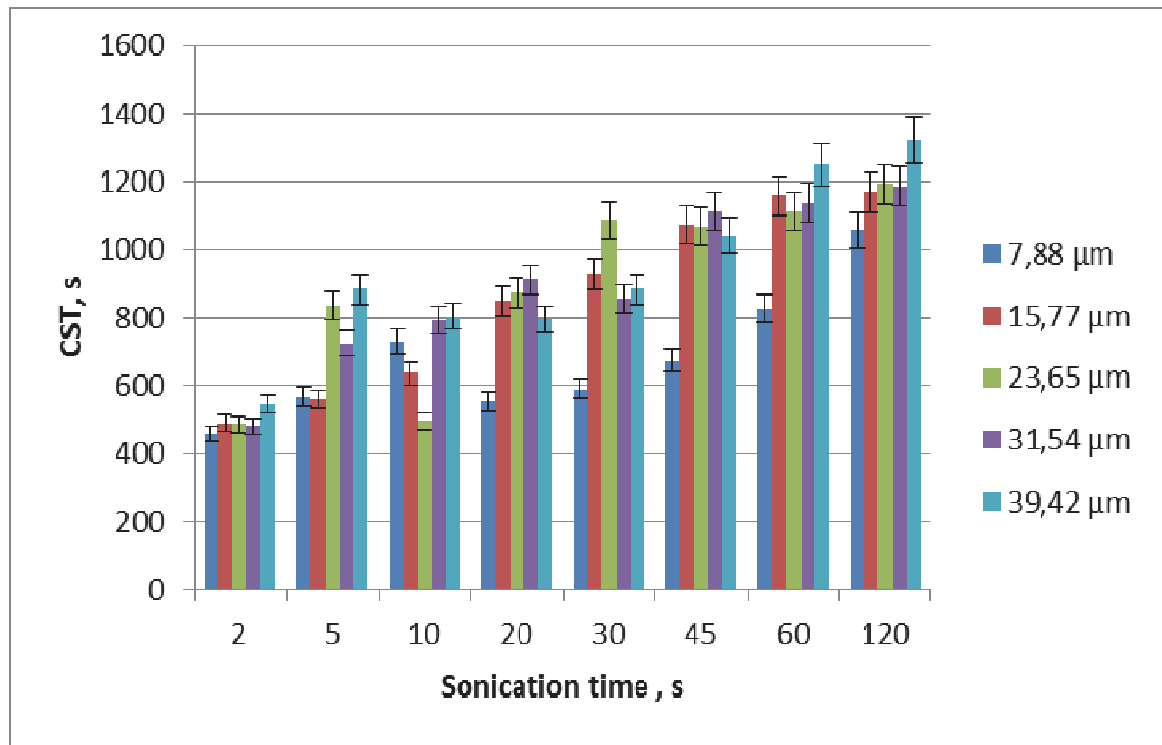


Fig. 2. The effect of continuous sonication time on capillary suction time depending on the ultrasound field wave length

Rys. 2. Wpływ czasu nadźwiękawiania ciągłego na wartości czasu ssania kapilarnego osadów ściekowych w zależności od zastosowanych długości fali pola ultradźwiękowego

The pulsating exposure led to the reduction in the amount of energy supplied to the system compared to the same parameters as in continuous sonication. Using the wave length of the ultrasound field of 15.77 and 31.54 μm , the amount of energy supplied to the system was, after 10 s, 1157 J and 1647 J, respectively (Fig. 3).

In the case of higher sonication time (60 s), the amount energy supplied to the system was 5298 J (15.77 μm) and 8967 J, respectively (31.54 μm). These values were lower than the amount of energy supplied continuously. The differences in the values of the amount of energy at the wave length of 31.54 μm was, after 10 minutes of exposure: 130 J; after 30 minutes of exposure: 1103 J; after 60 minutes of exposure: 1853 J.

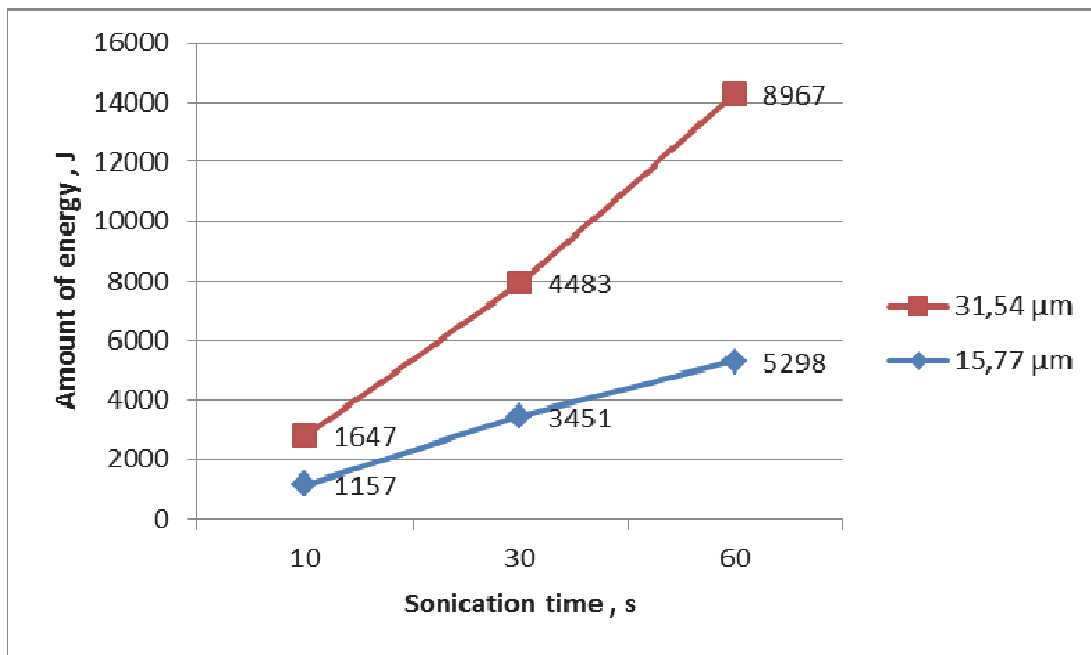


Fig. 3. Effect of pulse sonication time on the amount of energy supplied to the system depending on the ultrasound field wave length

Rys. 3. Wpływ czasu nadźwiękawiania pulsacyjnego na ilość wprowadzonej energii do układu w zależności od zastosowanych długości fali pola ultradźwiękowego

Lower energy supplied to the system during pulse sonication led to lower capillary suction times (Fig. 4). Improved dewatering capacity is connected with lower dispersion of sludge flocs and, consequently, clogging the pores in the filtration partition (Whatman 17). Furthermore, CST after 10 minutes of ultrasound exposure for the wave length of 15.77 μm was 623 seconds, whereas for the wave length of 31.54 μm, this value was 772 s. After 60 seconds of sonication, these values rose to 1041 s (15.77 μm) and 933 s (31.54 μm).

Changes in capillary suction time were correlated with changes in sludge structure caused by disintegration with exposure to ultrasound field. Non-conditioned sludge was characterized by the compact and homogeneous structure, without the likelihood of observation of free water (Fig. 5a). During exposure of the sludge to ultrasound field, single clusters of sludge flocs were observed, with zones of free water (Fig. 5b). The sludge flocs in the vision field were extended. The ten-day fermentation process caused homogenization of the structure observed (Fig. 5c). Flocs with free water were mixed, forming a uniform mass with individual clusters of the sewage sludge.

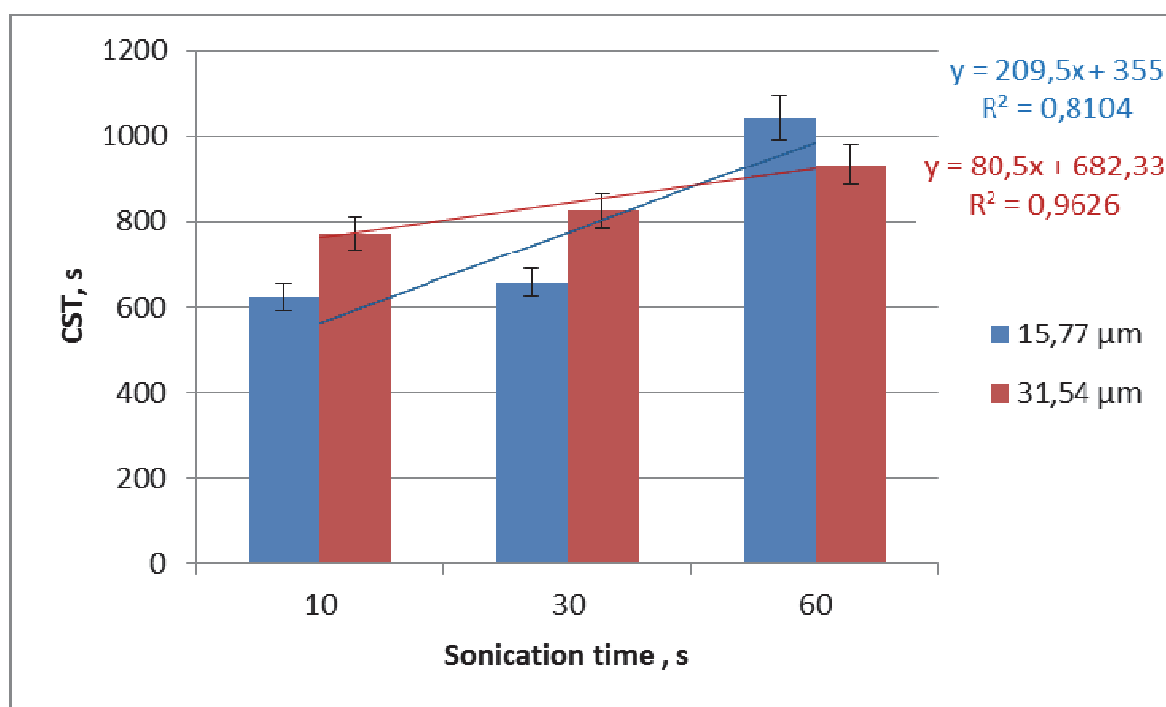


Fig. 4. The effect of pulse sonication time on capillary suction time depending on the ultrasound field wave length

Rys. 4. Wpływ czasu nadźwiękawiania pulsacyjnego na wartości czasu ssania kapilarnego osadów ściekowych w zależności od zastosowanych długości fali pola ultradźwiękowego

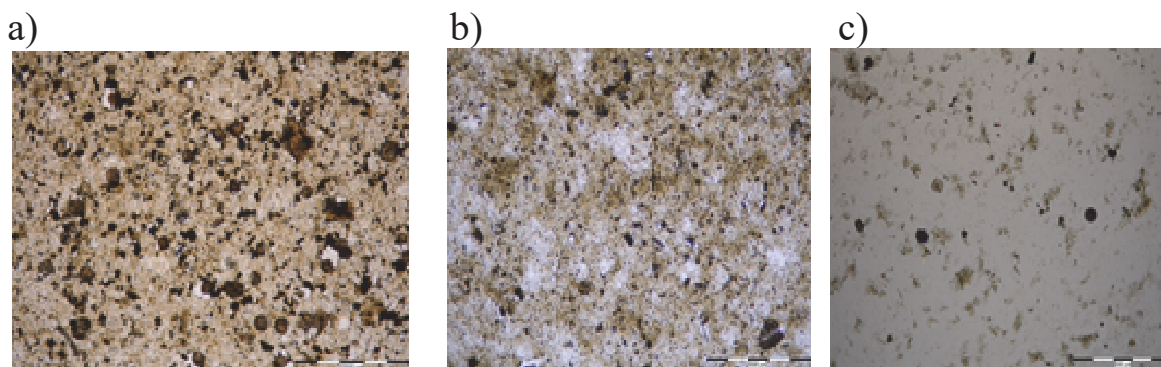


Fig. 5. Sewage sludge structure: (a) non-conditioned sewage sludge; (b) sewage sludge initially conditioned with ultrasound field; (c) sewage sludge initially conditioned with ultrasound field on the 10th day of fermentation

Rys.5. Struktura osadów ściekowych; a) niekondycjonowanych osadów ściekowych; b) wstępnie kondycjonowanych polem ultradźwiękowym; c) wstępnie kondycjonowanych polem ultradźwiękowym w 10 dniu fermentacji

4. Conclusions

The study evaluated the amount of energy supplied to the system depending on the wave length and sonication time. Analysis also concerned the effect of the adopted methodology on capillary suction time. The examinations revealed the amount of energy generated with the increase in time and ultrasonic wave length. Sonication also led to the increase in capillary suction time. These relationships were observed in the case of both continuous and pulse sonication. During pulse sonication and the same parameters, lower amount of energy was supplied compared to the continuous ultrasound disintegration. The disintegration carried out in a pulsating manner influenced the smaller dispersion of sludge flocs, which ultimately had less influence on clogging of the filtration partition and obtaining lower values of the capillary suction time.

The results obtained in this study lead to the following final conclusions:

- 1) ultrasound field intensity determines the amount of energy supplied to the system. The increase in intensity and time of exposure to the ultrasound field causes an increase in the amount of energy supplied to the system,
- 2) amount of the energy supplied during the process of ultrasonic disintegration to sewage sludge impacts significantly on the value of capillary suction time. Its value of 1323 s, was the highest for the use of ultrasound field with intensity of 39.42 μm and sonication time of 120 s,
- 3) pulse sonication leads to a lower amount of energy generated. For the sonication time of 60 s and wave length of 31.54 μm , the amount of energy supplied through pulse sonication was 8967 J, whereas this value for continuous sonication was 10820 J.

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Zapotrzebowanie energetyczne w procesie ciągłej i pulsacyjnej sonifikacji osadów ściekowych

Streszczenie

Jednym ze sposobów kondycjonowania osadów ściekowych jest zastosowanie energii pola ultradźwiękowego. W wyniku jego działania w zależności od zastosowanych parametrów (natężenia pola UD, czasu działania) może dojść do koagulacji lub dyspersji kłaczków osadowych. Ilość dostarczonej energii do układu wynika z czasu działania i natężenia pola ultradźwiękowego.

Celem prowadzonych badań było określenie ilości wprowadzonej energii w zależności od czasu działania i natężenia energii pola ultradźwiękowego, oraz jego wpływu na ocenę efektywności odwadniania wyrażoną czasem ssania kapilarnego.

Jako substrat badań zastosowano przefermentowane osady ściekowe, które poddano działaniu pola ultradźwiękowego o natężeniu 3,8, 3,2, 2,7, 2,2, 1,6 W·cm⁻² (co odpowiadało amplitudą 100, 80, 60, 40, 20%). W badaniach przyjęto czas sonifikacji z przedziału od 2 do 120 s. Na podstawie przeprowadzonych badań odnotowano wzrost zapotrzebowania na energię oraz wydłużenie czasu ssania kapilarnego wraz ze wzrostem amplitudy i czasu ekspozycji pola UD.

Abstract

One of the ways of sewage sludge conditioning is the use of ultrasonic field energy. As a result of its operation, coagulation or dispersion of sludge flocs may occur depending on the parameters used (UD field strength, operating time). The amount of energy supplied to the system results from the operating time and intensity of the ultrasonic field.

The purpose of the research was to determine the amount of energy introduced depending on the time and intensity of the ultrasonic field energy and its effect on the evaluation of the dehydration efficiency expressed by the capillary suction time.

Fermented sewage sludge was used as the substrate for the study, which was subjected to an ultrasonic field of 3.8, 3.04, 2.28, 1.52, 0.75 W·cm⁻² (corresponding to amplitude 100, 80, 60, 40, 20%). The sonication time was from 2 to 120 s. On the basis of the research, the increase in energy demand and the increase of the capillary suction time with increasing amplitude and time of exposure of the UD field were recorded

Słowa kluczowe:

osady ściekowe, energia, nadźwiękawianie, czas ssania kapilarnego

Keywords:

sewage sludge, energy, sonication, capillary suction time



The Relationship Between the Economic Development of the Country and Food Security

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1. Introduction

The food industry is a source of significant dangers to the natural environment – soil, water, air, plants, animals and humans. The problem of environmental protection in the light of dangers from chemical substances used by the food industry include water and sewage management, waste management, air protection against pollution as well as soil and noise protection. Globalisation, which also affects changes in the food chain, presents new challenges and brings unknown risk factors determining, among others, drug resistance in the treatment process, chemical contamination of food, which can influence the quality of life of the consumers. Accession of Poland to the EU has initiated a series of dynamic changes in food-processing sectors, involving not only quality standards and food safety, but also the protection of the natural environment. The consequence of accession are changes in the adjustment of Polish regulation to the standards binding in the EU. Consistent with the *acquis communautaire*, environmental legal pacts impose on the mentioned parties the obligation to prevent and to reduce the risks throughout the food production cycle.

The use of chemical substances in food processing is necessary in order to obtain products with higher nutritional value, stability that ensures microbiological safety, better sensory properties and reduced content of substances with potentially harmful effects on human health. The

chemical compounds that are added to foods during the processing practice must be safe to human health and the amount of additives and processing aids added is strictly limited by the provisions of feed and food law. It must also be borne in mind that despite these undisputable benefits, it may also result in the formation of compounds with adverse effects on the quality of human life.

The aim of the article is to analyse the impact of the natural environment on food safety using critical literature analysis and analysis of the Global Security Index (food quality and safety sub-indicator) and its relations with the country's PKB on the example of the European Union.

2. Environmental contaminants and food safety

The natural environment, a habitat for living organisms, has a significant impact on the safety of food – quality of life. The development of the industry (Bober et al. 2017, Wolniak & Skotnicka-Zasadzień 2014), in the nineteenth and twentieth centuries seriously contaminated the water and soil environment and the degradation of the air continues. Air contamination is detrimental to nature, and after reaching plants and animals, primary sources of food, poses a major hazard to the human organism. Surface waters are contaminated by a variety of substances deteriorating its quality, which impact negatively on its expiration date and on the use in production (Kołożyn-Krajewska 2007). Soil, which together with air and water constitute the main element of the natural environment, affect primarily the quality of raw materials used for food production. It contains high level of minerals, which, according to the origin of the soil, are used by plants which, in turn, are the main source of micro- and macro-elements for humans and animals. Environmental pollution has an effect on changes in the soil chemical, physical and biological properties. These factors are the crucial elements of the environment through which micro- and macro-elements are transferred to the living matter, where they are accumulated in tissues and organs. Concentration of specific pollutants causes food contamination, which is a risk to the safety of food being consumed. The quality of food has a significant impact on human live and health. The changing environment also generates new threats in the food chain causing exposure of the consumers to new unknown risk factors. Because they are not always aware of what

the food might contain, they might be exposed to chemical compounds, in particular those that can be found in food. In addition to microbiological purity, the percentage of chemical contaminants is the health safety criterion of food products. Among the chemical hazards we can distinguish those that can be commonly found in the environment (heavy metals, pesticide residues, dioxins, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons) and those which presence in food can be avoided or reduced to an acceptable level as a result of the use of systems providing food health safety (medical products, plant protection products, technological auxiliary agents and preservatives, substances which result from the improper food storage or processing technologies used). Currently the dynamics of food products development continuous to grow. New technologies, security management tools, the changing expectations of customers, lifestyle, changes in the state of the environment and the development of international food markets, are essential determinants for creating the new quality of food, which provides both nutritional value and health security. The fundamental responsibility to ensure food safety (Olkiewicz 2015) and environmental protection (Olkiewicz et al. 2015) falls not only on producers and distributors, but also on state authorities that supervise the food production chain – “from farm to fork”. Management through traceability of food and its labelling should be a significant tool used for monitoring the security of an integrated food chain, while taking into account the present-day threats, i.e. bioterrorism or chemical terrorism using food products. The concept of hygiene that deals with studying the effects of environmental pollution on food safety is also an important element in the analysis of the impact that environmental factors have on the human body. Therefore, maintaining high hygiene during food production determines the conditions for the production of both healthy and safe products for human health in terms of health quality (Dzwolak 2011).

3. Food safety measurement

According to Codex Alimentarius, hazards are understood as undesirable contaminations, inter alia the chemical ones. By the analysis of the risk and threats in accordance to the ISO 9001 standard, a process-oriented approach can be taken into account to (Gadula 2008, Wolniak 2013):

- raise customer satisfaction,
- ensure ongoing surveillance (over the links between the processes, combination of processes, mutual interaction between the processes),
- stress the importance (to understand and meet the requirements),
- the need to consider processes in terms of an added value, the effectiveness of the processes,
- continuous improvement of the processes on the basis of an objective measure.

Therefore, fixing limit values of the daily intake and Acceptable Daily Intake (ADI) tolerance are the basis for the prevention against potential poisoning of the consumers. This serves as an indicator of the maximum amount of the substances that, in accordance to the current state of knowledge, people can intake daily without any adverse effects (Czerwiecki 2005).

For instance, pesticides can cause acute poisoning and chronic poisoning as a result of their accumulation in small doses in the body. Therefore, the biggest threat of poisoning and an adverse effect are insecticides, and in particular organophosphorous and carbamides. They are the cause of, inter alia, the defects in development, i.e. limb defects or infertility, hydronephrosis, cleft palate and DNA damage. It is very important because they are introduced into the body with food and skin pores (Juszczak 2008).

Food additives that have been approved, demonstrate applications that, inter alia, aim to increase health safety and substance protection against changes during storage or warehousing and transport. The attractiveness of the quality of products is additionally boosted along with the consumer attractiveness and availability if new features to products are added.

One of the most commonly used indicator to measure food safety in the world is the so-called *Global Food Security Index*, which measures issues related to food safety in three categories: affordability, availability and quality & safety. The Global Food Security Index consist of a set of indicators from 113 countries and measures food security across most of the countries of the world. The indicator was first published in 2012 and is managed and updated annually by The Economist's intelligence unit (Economist 2018). The index is a dynamic quantitative and qualitative

benchmarking model, constructed from 28 unique indicators that measures these food safety factors across both developing and developed countries. It is the first index to comprehensively study food safety. The use of a composite indicator has the advantage to summarise a significant amount of information in one unique score (Thomas et al. 2017). The advantages of composite indicators are as follows (OECD-JRC2008):

- can summarise complex, multi-dimensional realities to support decision makers,
- are easier to interpret than a number of separate indicators,
- can assess progress of countries over time,
- can reduce the size of a set of indicators without dropping the basic information base,
- makes it possible to include more information within the existing size limit,
- places issues of the country's performance and progress at the heart of the policy arena,
- facilitates communication with general public (i.e. citizens, media) and promotes accountability,
- helps to construct/underpin narratives for lay and literate audiences,
- enables users to compare complex dimension.

The indicator on the food quality and safety index is the objective of this paper. In Table 1 data concerning the value of this indicator for 2017 for the EU together with the GDP was collected. In the research only those EU countries which can be found in the Global Security Index Database (Food security index 2018) were used. Twenty countries were included in the table: Austria, Belgium, Bulgaria, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Portugal, Romania, Slovakia, Spain, Sweden and United Kingdom.

Taking into consideration the food quality and safety, Poland is ranked 29th in the world. Figure 1 shows the value of this indicator among European Union countries. Compared to the rest of EU, Poland is on the 16th place and the food quality and safety index has the value of 74.9. This is not a good result when we take into account that only twenty countries were used in the analysis. However, if we compare Po-

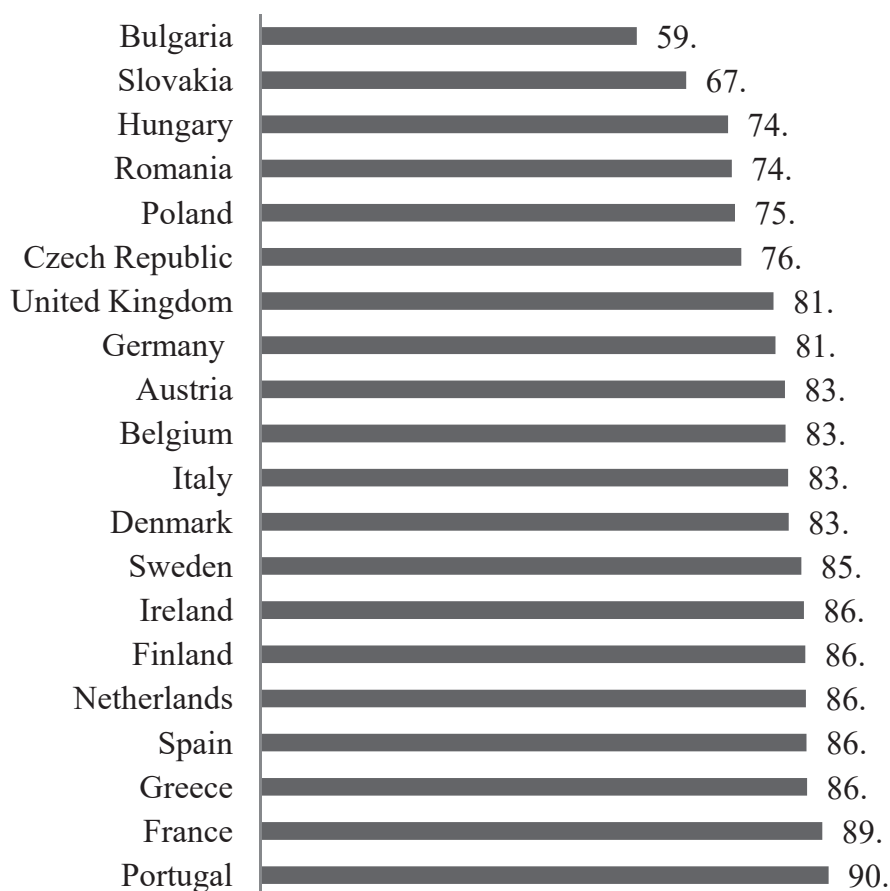
land to similar countries, i.e. the countries belonging to the Visegrad Group, its position is not so bad. From four countries of the Visegrad Group, Poland is ranked 2nd. Only the Czech Republic obtained better results when the researched problem is considered (index value at 75.9). The index value of other countries of the Visegrad Group, i.e. Hungary (73.8) and Bulgaria (67.2), is significantly worse compared to Poland.

Tabela 1. Wskaźnik jakości i bezpieczeństwa żywności i PKB

Table 1. Food quality and safety index and GDP

No	Country	Food quality and safety index 2017	GDP per capita [\$]
1	Austria	82.8	43435
2	Belgium	82.9	43243
3	Bulgaria	59.4	7924
4	Czech Republic	75.9	19818
5	Denmark	83.4	56335
6	Finland	86.0	45693
7	France	88.7	39673
8	Germany	81.3	44184
9	Greece	86.3	18945
10	Hungary	73.8	13459
11	Ireland	85.8	68604
12	Italy	83.3	31618
13	Netherlands	86.1	48271
14	Poland	74.9	13429
15	Portugal	89.7	20575
16	Romania	74.4	10372
17	Slovakia	67.2	17491
18	Spain	86.2	28212
19	Sweden	85.4	53248
20	United Kingdom	81.0	38847

Source: Own research (based on the data from: www.foodsecurityindex.eiu.com/Resources, [date of access 08/03/2018]; World Economic Outlook Database. International Monetary Fund, www.imf.org/external/index.htm, 24 October 2017, [date of access 08/03/2018]).



Rys. 1. Indeks jakości i bezpieczeństwa żywności 2017 – Kraje Unii Europejskiej

Fig 1. Food quality and safety index 2017 – European Union Countries

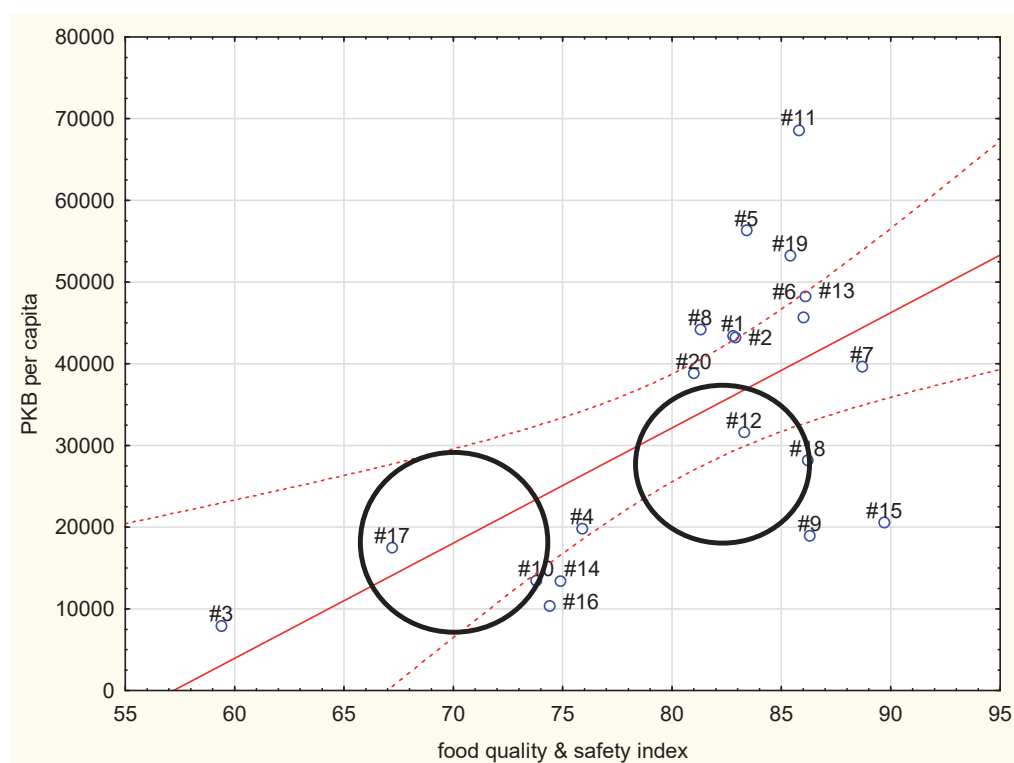
Source: own study based on the data: foodsecurityindex.eiu.com/Resources, [date of access 08/03/2018].

Figure 2 shows the analysis of the differences between the studied countries. The statistical analysis of the data at the level of significance at $\alpha = 0.05$ proves the existence of a positive correlation between the variables of a 0.62 value. National prosperity affects the food quality and safety level in its area. In the figure, most of the surveyed relevant nations are in the 95% confidence interval. By analysing the data, two coherent groups of countries can be distinguished:

- Countries with similar average level of the food quality and safety index and low wealth measured by the GDP per capita index. This group includes four nations: Czech Republic, Hungary, Poland, and Romania.

These countries are on medium level of economic growth and cannot achieve a high level of food security due to the low level of their wealth. In the case of this group of nations can be difficult to afford a high level of security related to food safety, including chemical safety. Improvement of food safety can be difficult to achieve for those countries without further economy growth. Improvement of food safety in those countries requires financial outlays, which should be raised along with further economic growth of the analysed countries.

- An interesting group of countries are Greece, Portugal and Spain. In these nations, the level of food quality and safety index is much higher than their level of wealth might suggest. It should be noted that they are Mediterranean countries with a specific climate, which are focused on the production of healthy, natural food. For nations such as Poland, with completely different geographical conditions, following their path seems to be slightly more difficult.



Rys. 2. Wykres rozproszenia PKB na mieszkańca oraz wskaźnik jakości i bezpieczeństwa żywności

Fig 2. A scatter plot of GDP per capita and food quality & safety index

Source: own research.

Globally, based on the analysis, it can be concluded that a high level of food quality and safety can be achieved in the situation of high national wealth and it is very difficult to adopt technically highly advanced methods that would address the threats to food safety without considerable financial commitments.

The report on drug resistance (EFSA & ECDC 2016) is the basis of the addressed issue of the presence of chemical substances within the food processing industry. It was based on the analysis of data obtained from twenty-eight EU countries under the aegis of the European Food Safety Authority (EFSA) together with the European Centre for Disease Prevention and Control (ECDC). The report includes the results of studies that draw attention to the gravity of the current situation concerning infections with pathogenic microorganisms and the rapidly growing problem of resistance to bactericides (chemical contaminants present in food).

According to the authors of this report (European Union Summary Report 2014), pathogenic bacteria, which causes infections for humans and animals and are present in food, show an increased resistance to commonly used bactericides. Resistance to ciprofloxacin, which is essential in the treatment of human infections, is very high among *Campylobacter* species. The consequence of this situation is the reduction of the effectiveness of the treatment process of serious food borne infections. Furthermore, the phenomenon of a continuous expansion of the *Salmonella* bacteria resistant to a number of drugs is evident across Europe. The report also shows the issue of the resistance of *E. coli* and *Salmonella* strains (poultry microorganisms within the EU) to colistin.

Mike Catchpole, a scientific director of the ECDC, expressed his concern about the present situation because colistin is the last effective bactericide that may soon lose its efficiency in the treatment of severe *Salmonella* infections. The report further indicates the increasing differences in antibiotic resistance depending on the region. The highest Anti-Microbial Resistance (AMR) level can be observed in Eastern and Southern Europe, while bacteria living in poultry with lower resistance in the Northern Europe region, especially in countries where the application of germicides in animals is at a low level. According to Vytenis Andriukaitis, the European Union Commissioner for Health and Food Safety, around 25 000 deaths occur every year in the EU as a result of complications after infections caused by micro-organisms resistant to treatment.

It is not a problem that only concerns Europe but has become a global threat that requires a global solution. The European Union has long been a leader in the fight against resistance to bactericides.

Measures in this area are also being taken in Poland. Tests for the presence of harmful chemicals in food has shown that unauthorised substances have been detected only in individual cases. The hygienic and sanitary status in the production and food trade entities controlled by the National Sanitary Inspection, has improved significantly (2% of facilities supervised by the National Sanitary Inspection did not meet the sanitary requirements) (National Sanitary Condition 2007-2008 & 2015-2016). Therefore, food safety as result of the use of chemical agents in food-processing as well as the increasing resistance to bactericides should be one of the priority areas for national policy. The existing legal conditions impose restrictions on the food-processing industry, thanks to which a consumer can feel secure on the food market.

4. Discussion

The obtained results determine the conclusions that are not very optimistic. Apart from the undisputed advantages of using chemical compounds in the food-processing chain, there are also negative factors:

- Campylobacteriosis is the most commonly reported food borne infectious disease. Resistance to antimicrobials, i.e. ciprofloxacin among bacteria isolated from people may amount to as much as 60.2%, and in the case of animals (broilers) up to 69.8%.
- Salmonellosis is the second most commonly reported food borne illness. It has been noted that the resistance of bacterial strains isolated from people to commonly used bactericides is at the level of: 30% relative to tetracycline, 28.2% to sulfonamides and 28.2% to ampicillin. The overall multidrug resistance of bacteria is assessed at 26% for people, and in the case of broilers and turkeys – 30.5% and 24.8% respectively. Certain strains of salmonella (*Salmonella Kentucky* and *Salmonella Infantis*) have relatively high levels of resistance to ciprofloxacin and overall high multidrug resistance.
- The strains of *Salmonella* and *E. coli*, isolated from poultry originating from the EU, are characterised by significant resistance to colistin.

- At low levels of *Salmonella* originating from poultry, a wide spectrum of beta-lactamases (ESBL) was observed. The clones of *Salmonella* *Infantis* showing multidrug resistance and ESBL-producing were found in both people and poultry. However, no carbapenemase-producing *Salmonella* was found in poultry and meat.

Therefore, agencies such as EFSA or ECDC (through the combination of experience, theoretical and practical knowledge) for the protection and prevention of human and animal health should serve as databases, which provide a lot of valuable scientific information to policymakers responsible for food policy in a given country or a region.

Food chemical pollution should become a significant element in the process hazard analysis, which is a tool in health safety management, taking into account different stages of the food supply chain, which includes primary production, processing and distribution as well as packaging and storage.

The presence of undesirable substances (chemical contaminants in food) poses a risk to the safety of the consumers. Therefore, according to the Codex Alimentarius and Food Hygiene Basic Texts, food safety is understood as an assurance that food will not cause prejudice to consumer health if prepared and / or consumed in accordance with the intended use. In the preventive part, it serves as an important element of the human health protection system (Łozowicka 2009).

The present paper described food chemical contaminants as critical quality of food and food safety factors. They were classified as:

- industrial – heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls,
- technological – PAHs, mycotoxins, heterocyclic amines (HCAs),
- environmental – heavy metals, pesticides, fertilizers and radioactive elements.

The majority of them, which are detected in food, fall within a group of pollutants that are difficult or even impossible to avoid due to their prevalence in the natural environment, durability and the ability to accumulate in individual links of the food chain.

The second group consists of chemical compounds which presence in the food processing process can be avoided by, inter alia, good manufacturing practice (GMP), good hygiene practice (GHP), and hazard analysis and critical control points (HAACP) – a method that ensures health security of food.

The last group are chemical agents that are added in the processing processes, i.e.: certain colourants, artificially sweeteners that are formed from improper storage of agricultural raw materials or in technological processes.

5. Conclusions

Taking care of environmental protection by reducing the risks and water and energy consumption during food processing may prove to be, on the one hand, a complex process that requires substantial financial resources and, on the other hand, can lead to increased economic outcomes and improved image of companies that use environmentally friendly technologies. This can be often achieved through the monitoring of each stage of the technological process and an analysis of the capacity to implement measures which may lead to the reduction of the negative effects of the production process and thus the whole entity on the natural environment. Food safety can be mainly ensured through a preventive approach based on the implementation of good hygiene practice and procedures related to Hazard Analysis and Critical Control Point principles. The nature of food safety is based on a risk analysis of which one of its elements is risk assessment. The use of additives in the food industry brings benefits to both food producers, facilitation of production and storage processes, and consumers who receive a product with better quality of health and hygiene, often with a higher nutritional value.

On the one hand, their application is favourable for expanding the range of foodstuffs that can contribute to the diversification of food and the reduction of the risk of drug-resistant or diet-related diseases. On the other hand, given the low content of additives in food and thus the low intake, the risk to human health resulting from the use of additives appears to be minimal when compared to harmful effects, i.e. toxins produced by micro-organisms that can develop in foods that do not contain any additives with preserving effect.

It can be stated that the current state of knowledge indicates, among others, that the use of food additives in amounts consistent with the recommendations of the Codex Alimentarius and good production practice offers more significant benefits than possible threats to the quality of human life.

The main aim of the paper was to analyse the impact of the natural environment on food safety. On the basis of conducted research on the European Union countries we found that exist a positive correlation between food quality and safety and GDP per capita. Normally the high level of food quality and safety can be achieved in the situation of high national wealth. The identification of this relation is main contribution of presented research to the theory.

We think that if we want to improve the quality and safety of food in countries such as Poland, Czech Republic and Hungary it needs more investment to achieve this goal and is difficult without continuous development of the whole economy of the countries. Also we found that Mediterranean countries (Greece, Portugal and Spain) are specific because their quality and safety of food index is higher than their level of wealth can suggest. The cause of the phenomenon is specific climate of those countries, which are focused on the production of healthy, natural food.

The main limitation of the paper is that we analysed only European Union countries. In the future researches it would be good to analyse all world countries to check if the founded relations exist also on the global level. Other limitation is connected with the GDP per capita indicator. In the research we could use other indicators connected with development of the country – for example innovativeness indicators.

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Związek między rozwojem gospodarczym kraju a bezpieczeństwem żywności

Streszczenie

W publikacji przedstawiono kwestie dotyczące wpływu środowiska naturalnego na bezpieczeństwo żywności. Zaprezentowano w nim zagadnienia dotyczące występujących zanieczyszczeń środowiska w kontekście ich wpływu na

bezpieczeństwo żywności. W publikacji skoncentrowaniu się na analizie związków pomiędzy rozwojem gospodarczym kraju a bezpieczeństwem żywności. Celem artykułu jest analiza wpływu środowiska naturalnego na bezpieczeństwo żywności przy wykorzystaniu krytycznej analizy literatury oraz analizy wskaźnika Global Security Index (subwskaźnik jakości i bezpieczeństwa żywności) oraz jego związków z zamożnością kraju na przykładzie Unii Europejskiej.

Abstract

The publication presents issues concerning the impact of the natural environment on food safety. It presents problems regarding existing environmental pollutants in the context of their impact on food safety. The publication focuses on the analysis of the relationship between the economic development of the country and food security. The aim of the article is to analyse the impact of the natural environment on food safety using critical literature analysis and analysis of the Global Security Index (food quality and safety sub-indicator) and its relations with the country's PKB on the example of the European Union.

Słowa kluczowe:

jakość, bezpieczeństwo żywności, zanieczyszczenie środowiska, rozwój gospodarczy

Keywords:

quality, food safety, environment pollution, economic development



Alternative Fuels and Their Impact on Reducing Pollution of the Natural Environment

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1. Introduction

Climate policy pursued by the European Union, aims to limit climate change and strongly affects the transport industry through i.a. among others reduction of greenhouse gas emissions (Ministry of Energy 2016, Bauer et al. 2014). According to the estimates of the European Environment Agency in 2015, the transport industry, including urban transport and municipal services, accounted for over 25% of greenhouse gas emissions in the entire European Union (European Environment Agency 2018). A large share in CO₂ emissions is due to urban transport which accounts for 25% of gas emissions in total transport. The European Union guidelines, recorded in the White Paper of Transport in 2011 relate to pollution reduction and efficiency improvement in transport. Moreover, they focus on increasing the importance of public transport and reducing the role of oil-derived fuels for alternative fuels (Müller-Hellmann 2001), (Jacyna et al. 2015).

According to the adopted transport policy, by 2030, greenhouse gas emissions should be reduced to 20% in relation to 2008 and carbon dioxide emissions by approx. 60% compared to data from 1990. This goal should be achieved by a 50% reduction of conventional vehicles in urban transport and their elimination in the perspective of 2050 (European Commission 2011).

The objective of low-emission transport is to be supported among other things by implementing solutions provided for in the European Parliament Directive on the development of alternative fuels infrastructure, aimed at increasing the availability of infrastructure and amending the Directive 2009/33/EC on the promotion of ecologically clean and energy-saving road transport vehicles (Polish Alternative Fuels Association 2018).

2. Analysis of the alternative fuels market

The growing need to reduce dependence on imports and declining oil resources are the main factors increasing the growth of the global alternative fuels market. In addition, these factors affect energy companies and national governments in increasing investment in the alternative fuels market.

Alternative mobility solutions improve fuel supply security while opening the way for improved sustainability. Alternative fuels have significant advantages in reducing greenhouse gas emissions and pollution. In addition, they help reduce dependence on the use of fossil fuels in the transport sector.

Pursuant to Directive 2014/94/EU of the European Parliament and of the Council of 22 October 2014 on the development of alternative fuels infrastructure, alternative fuels are fuels or energy sources that serve, at least partially, as a substitute for crude oil sources of energy in transport and which can potentially contribute to the decarbonisation of transport and the improvement of the environmental performance of the transport sector. These include, but are not limited to: electricity, hydrogen, biofuels as defined in art. 2 (i) Directive 2009/28/EC, synthetic and paraffin fuels, natural gas, including biomethane, in gaseous form (compressed natural gas - CNG) and in liquid form (liquefied natural gas – LNG), and liquid gas (LPG), (European Parliament 2014).

The transition from petroleum fuels to alternative fuels requires a change in fuel infrastructure, as most alternative fuels are not drop-in fuels (e.g. electricity, CNG, LNG, ethanol, hydrogen).

In the coming years alternative fuels will play a very important role in the development of the transport sector around the world, including in European Union countries. One of the key objectives of the EU is that alternative fuels become a widely available substitute for fossil fuels. Thanks

to the popularization of alternative fuels, it will be possible to achieve the benefits of reducing harmful emissions to the atmosphere, increase energy security through diversification of raw materials supply as well as obtain socio-economic benefits, including the creation of thousands of new jobs (Brooke 2010), (Pyza & Ziembicki 2016), (van Haaren 2011).

One of the most widely used varieties of alternative fuels is CNG, i.e. compressed natural gas, whose energy value of 1 m³ is equal to 1 liter of gasoline. It is used primarily as a high octane fuel in internal combustion engines. CNG is a low-emission fuel that is an alternative to conventional car fuels, yet still clearly cheaper than them. Its ecological values are also connected with lower noise emission accompanying the combustion of CNG and that is more, its use is safer than eg gasoline, as it has a higher lower explosion limit.

LNG (Liquefied Natural Gas) is also a fuel that is becoming more and more important in transport. LNG can be used both in liquefied form, mainly in means of transport, offering i. a. higher octane number than conventional fuels, as well as in the volatile form after being subject to regasification, eg as a network gas, or in areas outside the reach of gas distribution network. LNG as motor fuel has similar properties as CNG, combining ecological and economic values. This allows for a significant reduction of pollutant and noise emissions as well as a reduction in fuel purchase costs. Currently, the share of LNG in the global gas trade is over 25% (Energy Information Administration 2018).

LPG (Liquefied Petroleum Gas) is a mixture of propane and butane, which is obtained in the refining of crude oil and at the stage of oil production. LPG is widely used in transport, primarily in passenger cars, as motor fuel with an octane number of 90-120. In comparison to conventional fuels, LPG combustion results in significantly lower exhaust emissions, although it is usually associated with higher consumption (10-20%).

Hybrid systems combine two vehicle propulsion systems and usually consist of a gasoline engine that works in conjunction with an electric one. The use of such a system allows to reduce exhaust emissions up to 50% and significantly reduce noise. Although hybrid drives have been operating on a larger scale for around 20 years, when the Toyota Prius model hit the market, their popularity is limited, mainly due to the much higher price of vehicles available on the market. It should also be remembered that hybrid vehicles continue to use traditional fuels, so their

impact on reducing exhaust emissions is more limited than in the case of other types of alternative fuels.

Currently, one of the main and most widely promoted directions of automotive industry development is the electric vehicle segment, in which almost all leading manufacturers offer models of this type of vehicles. The use of electricity allows for low operating costs with low emissivity, depending on the source of energy.

Motor drives based on electrochemical fuel cells using hydrogen are relatively low-tech technology in the automotive industry. Due to insufficient level of advancement and costs, this technology has not been used on a mass scale so far. Hydrogen is defined in the long term as fuel of the future. It is renewable and at the same time ecological fuel. The market is in a very early stage of development and it was not until 2004 that the Japanese concern Toyota introduced the first serial vehicle powered by a hydrogen fuel cell, under the name Toyota Mirai.

The increasing demand for alternative fuels applies to several segments: passenger cars, vans, vehicles used in public transport and those used by municipal services. The degree of development of the electric car market in Europe varies significantly from country to country. The development of the electric car market is also evident in public transport and in transport used by municipal services. The share of individual fuels for passenger cars in individual EU countries in 2015 is shown in Figure 1.

The share of passenger electric cars powered by electricity in the European Union countries is at the level of 0.00%-0.4% of the total number of vehicles. The smallest share of personal electric cars in circulation may be observed in Greece, Poland, Romania, Slovakia and Slovenia. The largest share, however, occurs in the Netherlands and the United Kingdom. In the area of personal hybrid cars, their market share is at 0.00%-2.3%. The smallest share can be noted for Slovakia and Slovenia, while the largest for the Netherlands (2.3%). Among the European countries belonging to and not belonging to the European Union, the greatest development of electromobility has been noticed in Norway. The share of personal electric cars (battery powered and hybrids) is 23.63%.

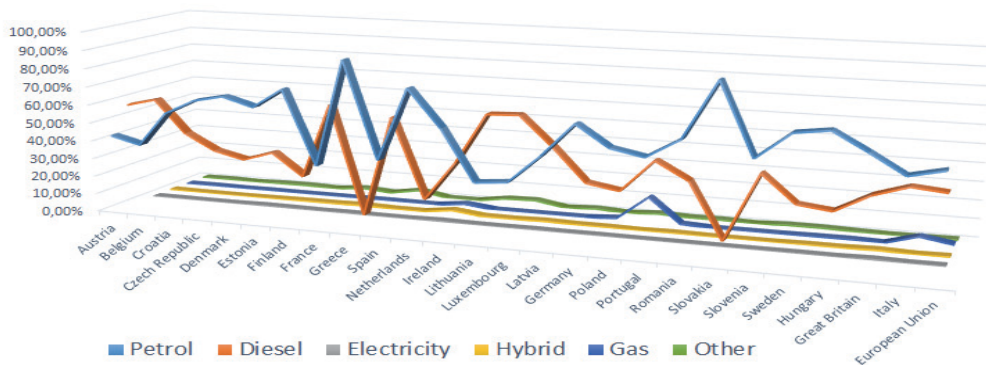


Fig. 1. Share of individual fuels for passenger cars in individual EU countries in 2015

Rys. 1. Udział poszczególnych rodzajów paliw dla samochodów osobowych w poszczególnych krajach Unii Europejskiej w roku 2015

Source: own study based on data from ACEA Report: Vehicles in use – Europe 2017.

The largest share of passenger cars fueled by gas can be noted in Poland (14.4%), Italy (5%) and the Netherlands (almost 2%), while the smallest share is in Croatia, Denmark, Estonia, Spain, Ireland and the United Kingdom (0, 00%). The countries with the highest share of other alternative fuels used in passenger cars are Greece (3.1%), Lithuania (2.9%), Ireland (2.5%), Finland (1.7%), and Poland and Latvia (about 1%).

The share of individual fuels for trucks and buses in individual EU countries in 2015 is shown in Figure 2.

The largest share of heavy electric cars and electric buses can be observed in Italy (1.9%), while the smallest is in Croatia, the Czech Republic, Finland, Greece, Latvia, Romania, Slovakia and Slovenia (close to 0.00%). Poland's share in the use of trucks and electric buses (including the hybrid) is at 0.01%. The average value for the European Union is low - the share of electric trucks and buses is at 0.3%, while hybrid ones at 0.04%. On the other hand, the use of gas in trucks and buses has the highest share in Slovenia (over 11%), Sweden (2.5%) and the Netherlands (1%). The largest share in the use of other alternative fuels can be noted for Greece (44%), while the smallest share for Austria, Croatia, Spain, Germany, Slovakia, Hungary or Italy (close to 0.00%).

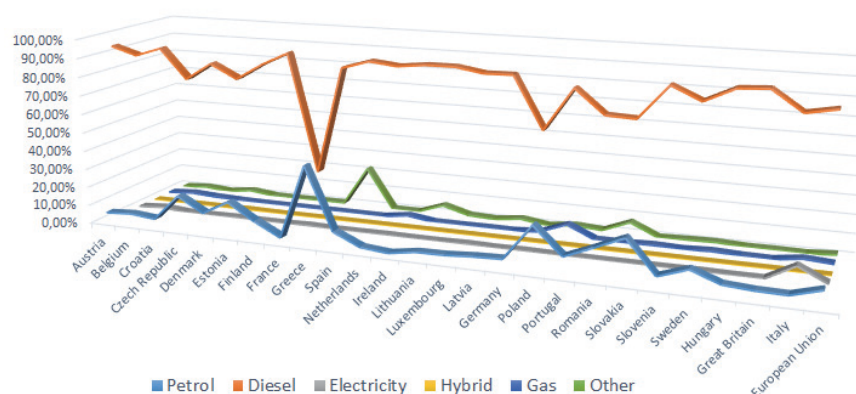


Fig. 2. Share of individual fuels for trucks and buses in individual EU countries in 2015

Rys. 2. Udział poszczególnych rodzajów paliw dla samochodów ciężarowych I autobusów w poszczególnych krajach Unii Europejskiej w roku 2015

Source: own study based on data from ACEA Report:

Vehicles in use – Europe 2017.

3. Pollution of the natural environment in the aspect of means of transport

The quality of the natural environment is an important factor affecting societies and thus indirectly affecting economic development (Ambroziak et al. 2014). Transport, which stimulates economic and social development, contributes to environmental pollution at the same time. Particularly high air pollution is caused by road transport, the share of which in transport of cargoes in 2016 was 85.2%, while in transport work it was 78.7%. A similar situation occurs in passenger transport, whose share in passenger transport amounted to 56.2%, while in passenger-kilometers it was 35.4%.

The presented data and the specificity of road transport, indicate the need to implement pro-ecological solutions in this branch of transport.

Air pollution from road transport depends on many factors. These include: the type of fuel, the type and basic features of the vehicle, the condition of the infrastructure, the vehicle's driving speed, the location of congestion, etc. (Ambroziak et al. 2014, Gołda & Zieja 2015, Jacyna et al. 2015, Jacyna-Gołda et al. 2016, Jacyna-Gołda et al. 2014, Pyza et al. 2017, Zieja et al. 2017).

The measure of air pollution is the degree of emission and concentration of individual primary pollutants, i.e. harmful exhaust gas compounds generated during driving. Among them there are: nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO_2), lead (Pb) and solid particles (PM10) and (PM2,5) as well as dust and soot. Data from the Central Statistical Office show that road transport is responsible for more than 28% of the total emission of nitrogen oxides (NO_x), more than 27% of carbon monoxide (CO) emissions and more than 15% of dusts.

A much larger share of road transport and public transport in the emission of pollutants into the environment occurs in large urban agglomerations, especially well-developed cities and in city centers heavily burdened with traffic (Pyza et al. 2017).

Within the European Union, a European standard for exhaust emissions has been introduced for all new cars. The introduction of the EURO standard limits the emission of several of the most important harmful exhaust components – nitrogen oxides (NO_x), hydrocarbons (HC), carbon oxides (CO) and particulate matter (PM). Tables 1-2 show emission limit values for new vehicles with different engine types. Vehicles that do not meet the following standards are classified in the EURO 0 standard.

Table 1. Emission limit values from vehicles powered by gasoline, natural gas or LPG

Tabela 1. Graniczne wartości emisji pochodzącej z pojazdów zasilanych benzyną, gazem ziemnym lub gazem płynnym

Standard	CO [g/km]	HC [g/km]	NO_x [g/km]	HC + NO_x [g/km]	PM [g/km]
EURO 1	2.72	–	–	0.97	–
EURO 2	2.20	–	–	0.5	–
EURO 3	2.30	0.20	0.15	–	–
EURO 4	1.00	0.10	0.08	–	–
EURO 5	1.00	0.10	0.06	–	0.005
EURO 6	1.00	0.10	0.06	–	0.005

Source: own development based on (Regulation (EC) No 715/2007)

Table 2. Limit values for emissions from vehicles equipped with diesel engines
Tabela 2. Graniczne wartości emisji pochodzącej z pojazdów wyposażonych w silniki diesel

Norma	CO [g/km]	HC [g/km]	NO _x [g/km]	HC + NO _x [g/km]	PM [g/km]
EURO 1	3.16	–	–	1.13	0.14
EURO 2	1.00	0.15	0.55	0.70	0.08
EURO 3	0.64	0.06	0.50	0.56	0.05
EURO 4	0.50	0.05	0.25	0.30	–
EURO 5	0.50	0.05	0.18	0.23	0.005
EURO 6	0.50	0.09	0.08	0.17	0.005

Source: own development based on (Regulation (EC) No 715/2007)

Limiting the negative impact of transport on the environment and the local community requires undertaking two types of actions. On the one hand, these are activities promoting the use of ecological forms of transport, including means of transport, and on the other hand aimed at limiting traffic in areas with high saturation of means of transport.

Pro-ecological activities may have both local and national range. Activities on a national scale are regulations, among others in the area of lower road tolls for vehicles meeting higher emission standards and promoting the use of alternative fuels in transport.

In the field of local activities, it is necessary to distinguish aimed at limiting traffic in urban areas for vehicles fueled with traditional fuels, which is undertaken in some of European cities, including Poland. The development of vehicles fueled with alternative fuels significantly affects the reduction of air pollution, and in some cases noise. These vehicles use alternative fuels in relation to petrol and diesel.

The development of vehicles powered with alternative fuels is dynamic, especially in highly developed countries, which contributes to the improvement of the air condition. Poland, as a member of the European Union, also promotes this direction of motorization development by undertaking various types of activities, among others legislative. Following the Directive of the European Parliament and the Council 2014/94/EU on October 22, 2014 on the development of alternative fuels infrastructure, the Polish government has prepared the Act on electromobility and alternative fuels, which was adopted on January 11, 2018.

An important area that has an impact on reducing environmental pollution is electromobility, dynamically developing in European countries. The development of electromobility in Europe is stimulated by various incentives for electric car buyers. In most cases, they take the form of tax incentives (reductions or reliefs), often also in the form of direct surcharges to purchase vehicles. The types of incentives in selected European countries are presented in Table 3. The incentives vary depending on the country and they are (PwC Polska Sp. z o.o., 2017):

- Surcharges to purchase:
 - Austria: companies can receive a surcharge: up to EUR 1 500 for an electric vehicle and EUR 750 for a plug-in hybrid,
 - Germany: a surcharge program for the purchase of 400,000 vehicles: for electric vehicles up to EUR 4,000 and for hybrids up to EUR 3,000, wherein the price of a vehicle may not exceed EUR 60,000. The program lasts until 2020.
 - United Kingdom: surcharges for the purchase of electric vehicles and hybrids (plug-in). Vehicles with emissivity below 50 g CO₂/km and a range of over 70 miles may receive co-financing covering 35% of the cost of purchasing a passenger vehicle, up to GBP 4,500 or GBP 25,000 (depending on the vehicle category) and 20% of the purchase cost of the van vehicle, but not more than 8,000 GBP. Hybrid vehicles with a range of less than 70 miles and CO₂ emissions of 50-75 g/km can receive a purchase grant of GBP 2 500 (if the price of the vehicle does not exceed GBP 60,000).
- Reductions in registration fees relate to the exemption from the registration fee.
- Relief in fees/taxes borne by the owner:
 - Austria: exemption from car tax for electric passenger cars, the amount of which depends on the engine capacity,
 - Germany: exemption from car tax for electric cars for 10 years, period counted from the date of registration,
 - Norway: exemption from the tax on the purchase of an electric vehicle (which also means an exemption from import tax) and concessions for a hybrid vehicle (up to EUR 10,000),
 - United Kingdom: exemption from road tax.

- Additional tax/fees reliefs paid by enterprises:
 - Germany: limitation of unfavorable taxation of income from using a company vehicle for private purposes based on the price of an electric car,
 - Norway: a tax on electric company cars reduced by half
 - United Kingdom: excise duty exemption for electric cars and some hybrid cars. Exemption from corporate income tax, calculated on the basis of CO₂ emissions.
- Discounts in VAT apply to Norway and include the exemption from 25% VAT when leasing an electric vehicle.
- Other reliefs of a financial nature:
 - Austria: exemption from the CO₂ emission fee levied by companies when using a company car for private purposes,
 - Norway: exemption from annual toll for cars for electric cars,
 - United Kingdom: zero tax on electric cars.
- Discounts granted locally, e.g. in municipalities:
 - Austria: free parking,
 - Germany: free parking, separate parking spaces, the possibility of using bus lanes,
 - Norway: exemption from tolls for urban roads – urban toll, free parking, possibility of using bus lanes, free charging stations – 3,200 stations in office buildings, shopping centers and car parks,
 - Great Britain: in London, electric cars are exempt from road tolls, in some districts, their owners pay lower parking fees.
- Payments for investments in infrastructure:
 - Austria: co-financing for the construction of charging station installations intended for commercial use,
 - Germany: co-financing for the construction of a charging station (program value is EUR 300 million),
 - Norway: co-financing for the construction of fast charging stations, located every 50 km on the main roads.
 - United Kingdom: 500 GBP surcharge to cover the cost of installing electric car charging stations in homes.

Table 3. Catalog of incentives for buyers of electric cars used in selected European countries**Tabela 3.** Katalog zachęt dla nabywców samochodów elektrycznych stosowanych w wybranych krajach europejskich

Type of incentive	Country			
	Austria	Germany	Norway	Great Britain
Subsidies for purchase	YES	YES	NO	YES
Discounts in registration fees	YES	NO	YES	YES
Relief in fees/taxes paid by the owner	YES	YES	YES	YES
Additional tax reliefs/fees paid by enterprises	NO	YES	YES	YES
Discounts in VAT	NO	NO	TAK	NO
Other financial relief	YES	NO	YES	YES
Discounts granted locally, e.g. in municipalities	YES	YES	YES	YES
Surcharge for investment in infrastructure	YES	YES	YES	YES

Source: own development based on (Rozwój elektromobilności w Polsce, Opracowanie PwC Polska Sp. z o.o., 2017)

Another area where solutions that reduce the emission of harmful compounds or noise should be sought for, is public transport. CNG installations are often used for public transport buses, but you can also point to examples of using electric and hybrid drives (London, Chicago, San Francisco, Rome, Warsaw, Krakow). All these activities are aimed at reducing emissions of compounds harmful to the environment, but they require not only legislative measures, but also financial support and actions aimed at public awareness in this area.

4. Environmental research in the field of using alternative fuels

Despite various types of activities supporting the development of alternative fuels, in subsequent years the main type of drive used in cars will remain gasoline engines and diesel engines. Nevertheless, their share will steadily decline in favor of vehicles powered by alternative energy sources.

In 2016, 15,982 electric vehicles were registered in Poland. Passenger cars accounted for 91.42% of this value, 6.44% heavy goods vehicles, 0.38% truck tractors, 1.14% buses, and special cars 0.62%.

According to the Electromobility Development Plan in Poland, by 2025, a million electric vehicles are to travel on Polish roads, which is supposed to drive the expansion of innovative industry. In addition, the replacement of combustion cars with electric cars should reduce the emission of harmful compounds both in the corridors of the TEN-T base network as well as locally in the area of cities and urban agglomerations.

The studies on the environmental effects of the development of electric vehicles in Poland in relation to air pollution were carried out taking into account their development forecasts until 2025.

Three scenarios for the development of electric vehicles were assumed in the analyzes: aggressive, moderate and conservative. It was assumed that the base year for analysis is 2025. In the aggressive scenario for the base year, an achievement of $LP_{2025}^{aggressive} = 1\,000\,000$ electric vehicles was assumed, in the moderate scenario, it was assumed to reach fifty percent of the number of electric vehicles for the base year of the aggressive scenario $Lp_{2025}^{moderate} = 50\%LP_{2025}^{aggressive}$, while in the conservative scenario, it was assumed to achieve twenty-five percent of the number of electric vehicles of the base year of the aggressive scenario $Lp_{2025}^{conservative} = 25\%LP_{2025}^{aggressive}$. Taking into account the number of registered electric vehicles in 2016 and adopted development scenarios, forecasts of the number of electric vehicles in particular years were estimated using the exponential regression function (Figure 3). The values of the regression function were estimated using a Microsoft Excel spreadsheet. Expression regression models have the form:

- Aggressive scenario

$$y = 715,54e^{0,8047x} \quad (1)$$

- Moderate scenario

$$y = 780,3e^{0,7181x} \quad (2)$$

- Conservative scenario

$$y = 850,93e^{0,6314x} \quad (3)$$

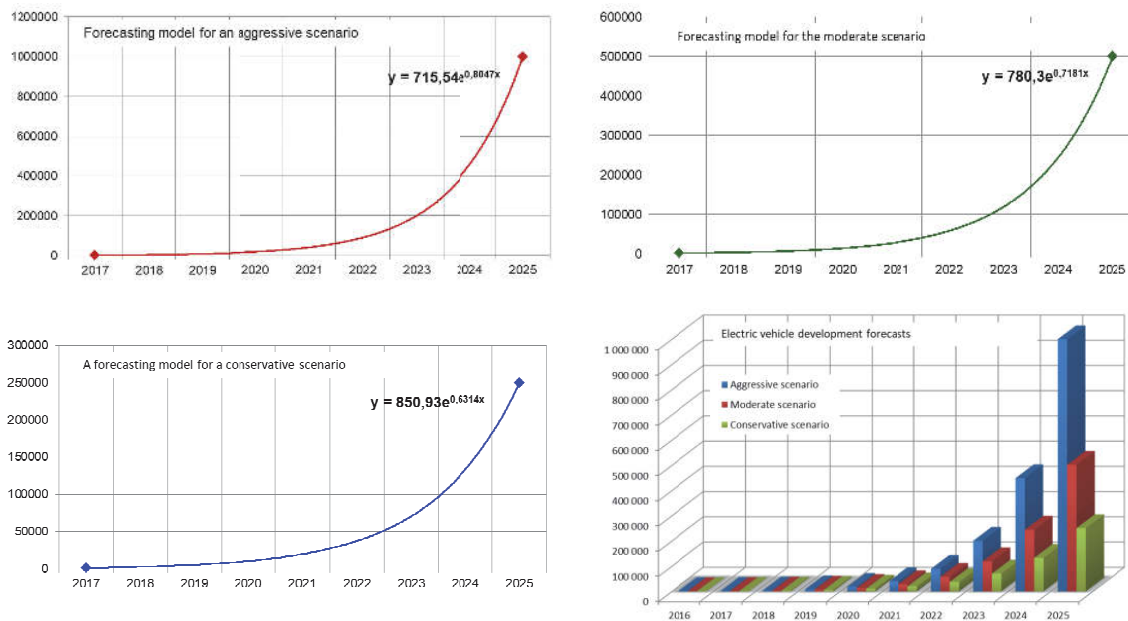


Fig. 3 Electric vehicle development forecasts in Poland together with forecasting models

Rys. 3 Prognozy rozwoju pojazdów elektrycznych w Polsce wraz z modelami prognostycznymi

Source: own development

It should be assumed that with the development of electromobility there will be a systematic reduction of the number of vehicles powered by petrol and diesel. The developed forecasts for three scenarios for the development of electric vehicles have been used in further studies for analyses related to the reduction of the emission of pollutants.

As part of the analysis, it was estimated to what extent the increase in the number of electric vehicles for the three development scenarios will translate into the volume of pollutant emissions from the transport sector. The limit values of emissions from petrol-powered vehicles and from vehicles equipped with diesel engines were adopted for the analyzes (Tables 1-2).

The analyses were carried out according to the following procedure:

- Estimation of the number of electric vehicles for particular years, using exponential regression models,
- Estimation of the number of vehicles, which will be reduced as a result of the development of electromobility, powered by petrol and equipped with

- diesel engines. The following vehicle shares are assumed: 78.4% – gasoline-powered vehicles, 21.6% – vehicles equipped with diesel engines,
- Estimation of the annual mileage of vehicles in total, assumed the average annual mileage of the vehicle at 13 700 km,
 - Estimation for individual types of vehicles (petrol-powered and diesel-powered) vehicle share structures with specific EURO standards,
 - Estimation of the annual mileage of vehicles for individual EURO standards,
 - Taking into account the annual mileage of vehicles for individual EURO standards and the limit values of emissions from petrol-powered vehicles and diesel engines, estimation of emission limits for individual pollutants.

The analysis refers to three pollution compounds, which are nitrogen oxides (NO_x), carbon oxides (CO) and solid particles (PM). Analyzes in the scope of limiting the emissions of pollutants from the transport sector for three scenarios for the development of electric vehicles in Poland are shown in Figure 4.

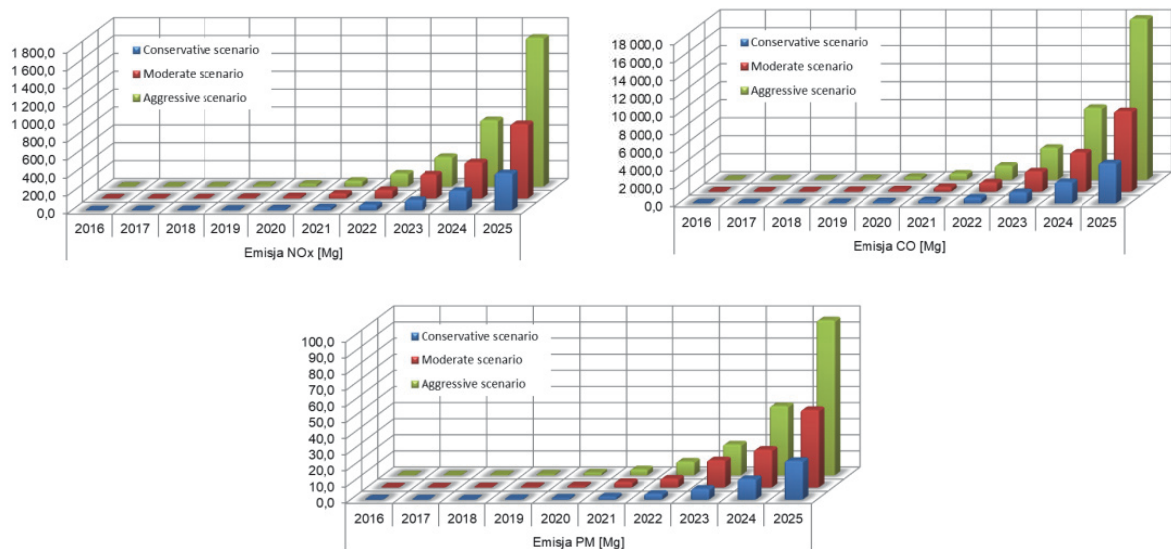


Fig. 4. Restrictions on the emission of pollutants from the transport sector for three scenarios for the development of electric vehicles by 2025

Rys. 4. Ograniczenia wielkości emisji zanieczyszczeń z sektora transportu dla trzech scenariuszy rozwoju pojazdów elektrycznych do roku 2025

Source: own development

The analysis carried out for three development scenarios of electric vehicles by 2025 showed that the limitations on the volume of pollutant emissions from the transport sector are growing exponentially. Due to the specifics of electric vehicles, it should be assumed that in the initial period of electromobility development, the largest pollutant emission limitations will occur in cities and urban agglomerations, smaller in the corridors of the TEN-T base network and other public roads. Due to the gradual development of charging infrastructure for electric vehicles, it is expected that these proportions will change in the perspective of further development of electromobility.

5. Conclusions

The development of electromobility is a priority of the European Union, which translates into a series of activities promoting and supporting this area of transport. Also in Poland, this area of transport is widely promoted, which should bring in the next years a number of tangible benefits both in terms of reducing environmental pollution and the development of innovative industry.

The research shows that the limitations in environmental pollution in the first years of implementing electromobility in Poland will be small, which is related to the low number of electric vehicles and the slow persuasion of vehicle users to this type of vehicle. A significant increase in environmental pollution restrictions should take place in the following years, together with a dynamic increase in the number of electric vehicles, this increase will be in exponential mode and for example for carbon monoxide the limit in 2025 will be: for aggressive scenario 17,899.1 Mg, moderate 8,960.6 Mg, conservative 4,469.9 Mg.

The development of electromobility will occur in two areas, the first is the development of electric vehicles in individual transport, the second concerns public transport and electric buses, an example of which is the government e-bus program under which actions aimed at purchasing electric buses by local government will be supported.

Electromobility and the development of alternative fuels are activities that effectively affect the natural environment, which requires support under various sectoral programs. These are activities that contribute to environmental protection not only on a local or continental scale, but also globally.

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Paliwa alternatywne i ich wpływ na ograniczenie zanieczyszczenia środowiska naturalnego

Streszczenie

W pracy odniesiono się do zagadnienia ochrony środowiska w aspekcie rozwoju paliw alternatywnych. Zgodnie z Dyrektywą Parlamentu Europejskiego i Rady 2014/94/UE z dnia 22 października 2014 r. w sprawie rozwoju infrastruktury paliw alternatywnych, paliwa alternatywne to paliwa lub źródła energii, które służą, przynajmniej częściowo, jako substytut dla pochodzących z ropy naftowej źródeł energii w transporcie i które mogą potencjalnie przyczynić się do dekarbonizacji transportu i poprawy ekologiczności sektora

transportu. W tym aspekcie dokonano analizy dokumentów normatywnych istotnych z punktu widzenia stosowania paliw alternatywnych w obszarze transportu. Odniesiono się również do obecnego stanu rynku paliw alternatywnych jak również przedstawiono perspektywy jej rozwoju. Przedstawiono problematykę zanieczyszczenia środowiska przez pojazdy samochodowe oraz wskazano na działania promujące elektromobilność w wybranych krajach europejskich. W ostatniej części pracy przedstawiono wynik badań środowiskowych w zakresie wykorzystania paliw alternatywnych w Polsce. Przedstawiono prognozy dla pojazdów elektrycznych z uwzględnieniem trzech scenariuszy ich rozwoju a następnie przy założonych warunkach brzegowych oszacowano wielkości ograniczeń emisji zanieczyszczeń z sektora transportu do roku 2025.

Abstract

The paper refers to the issue of environmental protection in the aspect of the development of alternative fuels. Pursuant to Directive 2014/94 / EU of the European Parliament and of the Council of 22 October 2014 on the development of alternative fuels infrastructure, alternative fuels are fuels or energy sources that serve, at least partially, as a substitute for crude oil sources of energy in transport and which can potentially contribute to the decarbonisation of transport and the improvement of the environmental performance of the transport sector. In this aspect, the analysis of normative documents relevant to the use of alternative fuels in the area of transport was made. Reference was also made to the current state of the alternative fuels market as well as prospects for its development. The problems of environmental pollution by motor vehicles were presented and actions promoting electromobility in selected European countries were pointed out. The last part of the work presents the result of environmental research on the use of alternative fuels in Poland. The forecasts for electric vehicles are presented, taking into account three scenarios of their development and then, with the assumed boundary conditions, the values of pollutant emission limitations from the transport sector were estimated until 2025.

Słowa kluczowe:

elektromobilność, paliwa alternatywne, ochrona środowiska

Keywords:

electromobility, alternative fuels, environmental protection



Assessment of the Effect of Struvite on the Growth of *Sinapis alba*

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1. Introduction

Struvite has fertilizing properties and is a source of phosphorus, nitrogen and magnesium. More and more scientific studies concerning recovery of phosphorus from recycled materials have been devoted to this compound. Current research aimed at identification of optimal chemical conditions for the recovery of phosphorus in the form of struvite from various recycled materials, especially those generated in the wastewater treatment plant and wastewater from the meat industry (Worwąg & Mędrala 2017, Wzorek 2008, Wzorek 2008a). Raw materials which represent alternative sources of phosphorus include: sewage sludge from municipal wastewater, slaughter house waste from the meat industry, manure and liquid manure from animal production (Wzorek 2008).

Struvite can be a good fertilizer since it contains basic biogenic elements needed for plant growth. Furthermore, due to low solubility, its components are not washed to ground waters or inside the soil, thus limiting availability for plants. After previous granulation, struvite can be added to the soil with greater amounts than other fertilizers with phosphorus and it is safe for plants (Gorazda et al. 2008, Faucon et al. 2015).

Despite the benefits of using struvite as a fertilizer, the processes of its recovery have not gained much popularity to date. The processes of struvite recovery include: CSIR, Phosnix UNITIKA.

The CSIR process was developed in the South Africa and consists in crystallization in the fluidized bed. Struvite is recovered in the reactor from supersaturated solutions at $\text{pH} > 8$ and in the presence of yellow slate and fly ash as crystallization nuclei. NaOH was used for maintaining adequate value of pH. The CSIR process consists in removal of the compounds of phosphorus in the form of granulated struvite (Wzorek 2008, Jodko et al. 2003). In a three-step Phosnix Unitika process, precipitation of struvite occurs to greater scale. The process is conducted in the fluidized-bed reactor, where the level of magnesium and phosphorus is constantly equalized by adding Mg^{2+} in the form of magnesium chloride. The high level of $\text{pH} = 9$, is maintained by the addition of NaOH. The whole process takes 1 to 2h and allows for the recovery of phosphorus, even with the efficiency of 94% (Hudziak et al. 2012).

The aim of the preliminary study was to analyse the effect of addition of struvite on plant growth and chemical and physical parameters of the soil. Struvite used in the present study was obtained in laboratory settings. For this purpose, optimal concentrations were evaluated for selected ions (PO_4^{3-} , Mg^{2+} , NH_4^+) at which maximal sediment mass was precipitated. Next, the surface composition of the obtained sediments was determined by means of X-ray spectra analysis.

2. Material and methods

2.1. Substrate for the analysis

The following substrates were used in the study:

- synthetic struvite, obtained in laboratory settings,
- soil from a house garden,
- mixture of soil with various struvite doses: 0.1 g, 0.5 g and 1 g to the same soil volume.

2.2. Research procedure

Preparation of synthetic struvite

The research stand was composed from the beaker with volume of 500 ml located on a plate of a magnetic mixer and a pH-meter. Solutions were prepared based on distilled water and phosphate salt in the form of KH_2PO_4 , ammonium salt in the form of NH_4Cl and magnesium salt in the

form of $\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$. A constant value of $\text{pH} = 10$ was used, determined based on the literature data. This value represents a point of precipitation of struvite sediment for almost any concentration of ammonium and phosphate ions if adequate amount of magnesium ions is ensured. 1M solution of NaOH was used for correction of $\text{pH} = 10$. The examinations were conducted for PO_4^{3-} ions (50 mg/dm^3 , 100 mg/dm^3 , 150 mg/dm^3 , 200 mg/dm^3 and 250 mg/dm^3) and NH_4^+ ions (100 mg/dm^3 , 200 mg/dm^3 , 300 mg/dm^3 , 400 mg/dm^3 , 500 mg/dm^3). Concentrations of Mg^{2+} were 10 mg/dm^3 , 20 mg/dm^3 and 30 mg/dm^3 . At this stage of the research, the most beneficial proportion of ions was determined, for which the highest struvite mass was obtained. The surface composition of the precipitated sediment was evaluated using the X-ray diffractometer.

Preparation of soil and mixtures of soil and struvite

The air-dry soil used for the examinations was sieved on a sieve with 2 mm mesh. After preparation, the soil was used to obtain mixtures with various doses of struvite:

- 1) 250 g soil + plants,
- 2) 250 g soil + 0.1 g struvite + plants,
- 3) 250 g soil + 0.5 g struvite + plants,
- 4) 250 g soil + 1.0 g struvite + plants.

Each combination was prepared in five replicates.

Growing mustard in a phytotron chamber

Pots with 250 g and the prepared mixtures were used for the pot experiment. Certified white mustard (*Sinapis alba*) was used as a biomass, with 0.5 g seeds put in the pots with soil and mixtures. The pots with the sown white mustard were placed in the phytotron chamber (P.H.U. Biogenet) for the period of four weeks, during the process the air temperature in the chamber was 21°C and during the night 18°C . In addition, the air humidity ranged between 60-100%. Level and time of exposure – (day and night cycle 16/8) day 6:00-22:00. Intensity of light during the day 40,000 lux. Wetting of the research material – watering 3 times a week. The plants were watered with distilled water in order to avoid introduction of additional components such as mineral salts and other contaminants. After four weeks, the experiment was completed and the obtained biomass

was weighed, dried and the dry biomass was again determined. Soil was also dried and subjected to further analysis.

Harvesting of the plants and preparation of soil for analyses

Plants were harvested after 4 weeks of the experiment. The over-ground biomass was cut at the height of 0.5 cm. It was weighed and next dried at the temperature of 70°C for 48 hours and weighted in order to evaluate biomass growth from each pot (g d.m./pot). Furthermore, the air dry soil material was sieved through the sieve with mesh diameter of 2 mm and next prepared for physical and chemical analyses.

2.3. Physical and chemical analyses of substrates

2.3.1. Struvite

XRD – Bruker D8 Advance X-ray diffractometer was used to examine the precipitated sludge. The X-ray photoelectron spectroscopy (XPS) methodology was employed. The methodology uses the effects of interactions of electrons, photons, ions or neutral particles with atoms of the examined specimen. X-ray photoelectron spectroscopy analyses the electrons that escape from the material being analysed due to irradiation with monochromatic soft X-ray radiation (<8 keV). Kinetic energy of photoelectrons allows for identification of elements and analysis of their binding. Furthermore, photoelectron intensity allows for the evaluation of concentrations of elements and the analysis of contribution of various bindings.

2.3.2. Soil and mixtures of soil and struvite

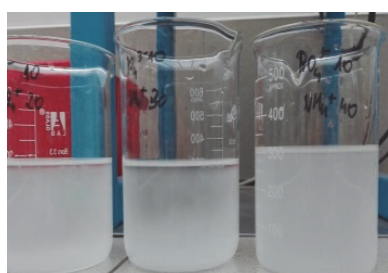
The physicochemical analysis of the substrates was performed according to the methodology developed by Karczewska and Kabała "Methods of Laboratory Analyses of Soil and Plants" (2008). Analyses included: dry mass, content of hygroscopic water, loss on ignition, ash content, reaction, hydrolytic acidity, total alkaline cations, nitrogen content, carbon content, total phosphorus, available phosphorus, heavy metal content.

3. Results of the analysis of research substrates

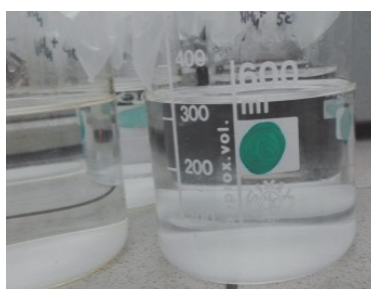
3.1. Characteristics of substrates: struvite

3.1.1. Amount of precipitated struvite sediment

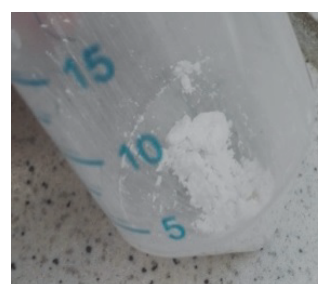
The experimental design is presented in Fig. 1. Immediate opaqueness was observed for all combinations used after addition of all solutions. However, it took around one hour for the precipitated sediment to be observed on the bottom of beakers. Due to insignificant differences during formation of the sediments for individual concentrations, in order to evaluate the mass of obtained struvite sediments, the samples were centrifuged and left for drying at room temperature and next they were weighed.



Opaqueness of the samples after adding all reaction substrates



Sediment precipitated after 1 hour



Sediments obtained after centrifuging and drying at room temperature

Fig. 1. Stages of precipitation of struvite sediment

Rys. 1. Etapy wytrącania osadów struwitu

Table 1 present the struvite sediments obtained for various combinations of concentration of NH_4^+ , PO_4^{3-} and Mg^{2+} ions. The results led to the conclusion that the increase in ammonium ions concentration causes a decreasing concentration of magnesium ions necessary for precipitation of struvite, which is consistent with the findings presented by Czajkowska and Siwiec (2011, Czajkowska 2015). The obtained mass of struvite sediments at a specific ion concentration of PO_4^{3-} and NH_4^+ , and concentration of ions of Mg^{2+} 10 mg/dm^3 are substantially lower than for Mg^{2+} ion concentration of 20 mg/dm^3 . The highest struvite mass (0.338 g) was obtained

at concentrations of 500 mg NH_4^+ /dm³, 100 mg PO_4^{3-} /dm³ and 20 mg Mg^{2+} /dm³.

Table 1. Amount of struvite precipitated for a given concentration of PO_4^{3-} and NH_4^+ ions, pH=10 and concentration Mg^{2+} ions of 10, 20, 30 mg/dm³

Tabela 1. Ilość strącanego struwitu dla danego stężenia jonów PO_4^{3-} i NH_4^+ jonów, pH=10 i stężenia jonów Mg^{2+} : 10, 20, 30 mg/dm³

Concentration ions		PO_4^{3-} [mg/dm ³]				
Mg^{2+} [mg/dm ³]	NH_4^+ [mg/dm ³]	50	100	150	200	250
10	100	0,093	0,109	0,093	0,096	0,099
	200	0,059	0,088	0,105	0,096	0,121
	300	0,055	0,105	0,097	0,101	0,152
	400	0,082	0,098	0,094	0,173	0,198
	500	0,069	0,105	0,088	0,099	0,141
20	100	0,140	0,203	0,200	0,198	0,201
	200	0,128	0,215	0,198	0,299	0,202
	300	0,154	0,196	0,194	0,200	0,200
	400	0,169	0,189	0,191	0,205	0,218
	500	0,233	0,368	0,281	0,198	0,236
	600	0,122	0,186	0,167	0,184	0,173
	700	0,118	0,180	0,160	0,181	0,165
30	100	-	0,203	-	-	-
	300	-	0,215	-	-	-
	500	-	0,196	-	-	-

3.1.2. Analysis of the surface composition of struvite sediments

Fig. 2 shows the results of the analysis of the surface composition of the sediments obtained in laboratory settings from an X-ray diffractometer. The results of the analysis demonstrate that the sediments contain 99% of the mixture of struvite, its amorphous forms and trace contents of compounds used for synthesis of the compound, and NaOH used for correction of pH.

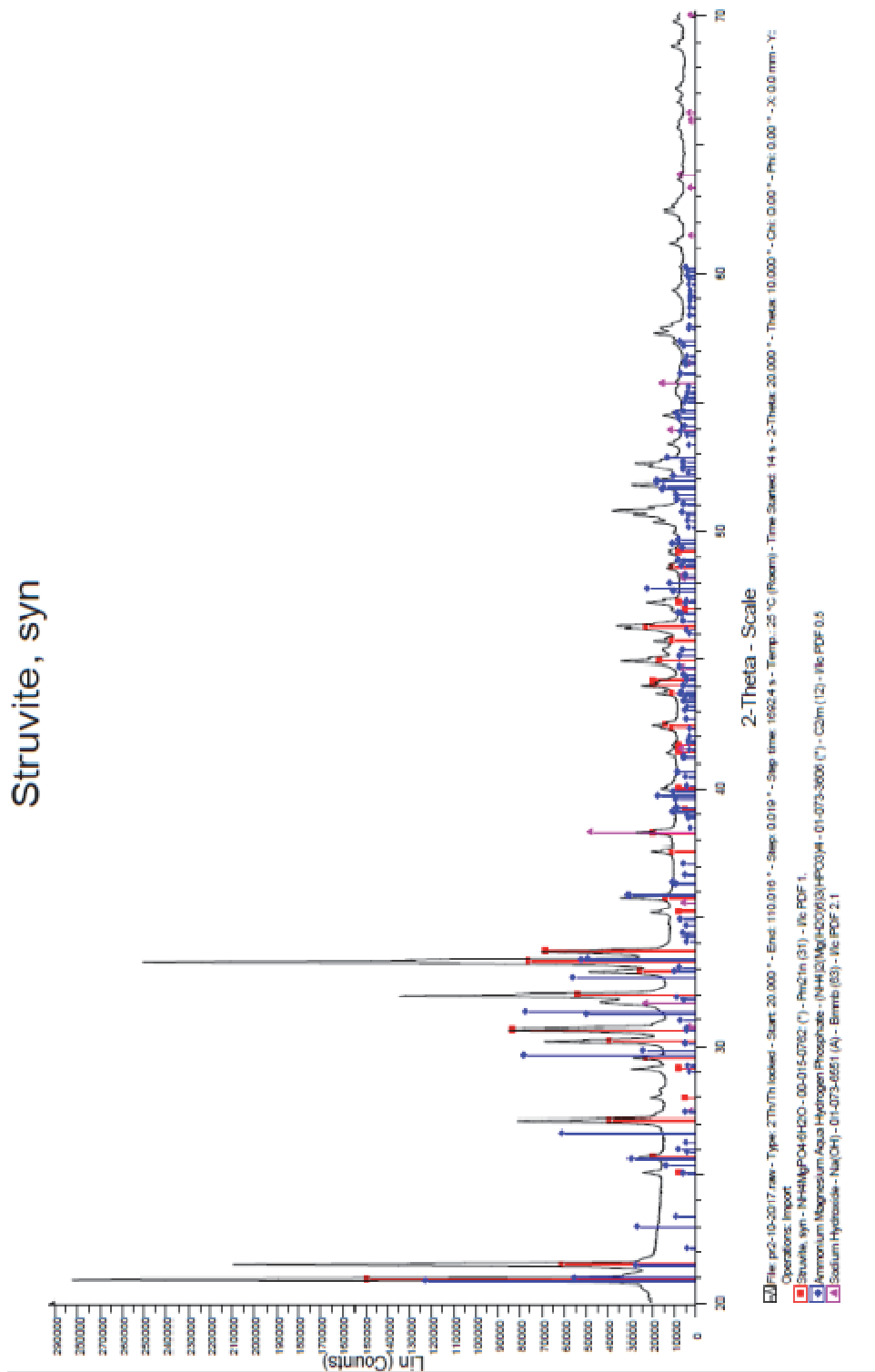


Fig. 2. Results of the analysis of struvite by means of the X-ray diffractometer
Rys. 2. Wyniki analizy osadów struwitu za pomocą dyfraktometru rentgenowskiego

4. Results

4.1. Characteristics of research substrates: soil and soil mixtures

Tables 2 and 3 present an overall characterization of the soil and soil mixtures with various doses of struvite. Percentage of the organic fraction for the soil was 3.44%, whereas for the mixtures, it ranged from 2.29% to 2.36%. All the substrates were characterized by a slightly alkaline reaction. Content of total nitrogen for the soil was ca. 439.2 mg/kg, whereas the contribution of the available forms represented 63%. Total phosphorus content and available forms in the mixtures increased with the increasing struvite percentage. A noticeable increase in the content of available forms of phosphorus (93%) was observed for the mixtures with addition of 0.5g and 1g struvite. The content of total carbon for soil and the mixtures ranged from 1.3% to 1.5%, whereas percentage of total nitrogen was at a low level, from 0.085% to 0.098%. Addition of struvite to soil led to the increase in the content of biogenic elements: total nitrogen and phosphorus, especially in the mixture of soil with 1g struvite.

Table 2. Results of physico-chemical analysis of substrates: soil, mixtures

Tabela 2. Wyniki analizy fizyko-chemicznej substratów: gleba, mieszaniny

Parameters	Soil	Soil + 0.1 g struvite	Soil + 0.5 g struvite	Soil + 1.0 g struvite
Dry matter [%]	0.38	0.69	0.80	0.78
Content of hygroscopic water [%]	99.62	99.31	99.20	99.22
Loss on ignition [%]	3.44	2.29	2.36	2.26
Ash content [%]	96.56	97.71	97.64	97.74

Table 2. cont.

Tabela 2. cd.

Parameters	Soil	Soil + 0.1 g struvite	Soil + 0.5 g struvite	Soil + 1.0 g struvite
pH	H ₂ O: 7.61 ± 0.049	H ₂ O: 7.62 ± 0.007	H ₂ O: 7.73 ± 0.035	H ₂ O: 7.94 ± 0.014
	KCl: 7.36 ± 0.007	KCl: 7.39 ± 0.007	KCl: 7.40 ± 0.014	KCl: 7.47 ± 0.007
Hydrolytic acidity	pH = 8.29	pH = 8.37	pH = 8.47	pH = 8.72
Total alkaline cations [mmol(+)/100 g]	0.2	0.25	0.2	0.05
Total carbon [mg/g]	13.64 ± 0.09	14.35 ± 0.58	14.28 ± 0.57	14.76 ± 0.76
Total phosphorus [mg/kg]	439.2	463.3	535.7	823.5
Available phosphorus [mg P/kg]	278	305	500	760
Total nitrogen [mg/g]	0.85	0.83	0.86	0.98

The results of the analysis of the content of heavy metals in substrates are shown in Table 5. The results reveal an increase in macro- and microelements in the soil mixtures with struvite compared to pure soil, with particular focus on contents of B, Ca, Cu, K, Fe, Mg, Na and Pb. Three metals were not found: Ag, Cd and Co. Not all the tests revealed presence of As and Cr.

Table 3. Results of the analysis of heavy metals content in substrates of soil and mixtures**Tabela 3.** Wyniki analizy zawartości metali ciężkich w podłożach z gleby i mieszanin

Heavy metals content [mg/kg]	Soil	Soil + 0.1 g struvite	Soil + 0.5 g struvite	Soil + 1.0 g struvite
Ag	–	–	–	–
Al	6179.2	6297.2	5698.3	7087.0
As	–	1.177	–	1.162
B	4.792	4.6	4.511	5.61
Ba	45.7	46.2	38.9	50.9
Ca	5812.4	6525.6	5735.1	6074.4
Cd	–	–	–	–
Co	–	–	–	–
Cr	–	11.5	8.49	12.3
Cu	11.7	14.8	12.4	16.6
Fe	6054.4	6138.5	7781.0	7656.1
K	938.8	964.0	834.8	1103.6
Mg	1055.6	1088.3	1130.8	1561.6
Mn	254.5	260.1	235.1	261.6
Na	200.4	177.5	202.6	250.3
Ni	1.561	1.682	1.772	3.217
P	439.2	463.3	535.7	823.5
Pb	40.9	72.8	49.6	55.4
Zn	59.8	63.3	83.4	66.9

4.2. Observation of plant growth

Fig. 3 presents a comparison of seven-day mustard growth for soil and its individual mixtures. It can be observed from the plant size and the number of shooting seeds, that struvite had a positive effect on all samples. At this stage of the research, no significant differences were found for all the plants grown on the mixtures of soil with struvite.



Fig. 3. Comparison of the growth of mustard after 7 days of growing: (from the left) control sample, soil with addition of 0.1 g struvite, soil with addition of 0.5 g struvite, soil with addition of 1.0 g struvite

Rys. 3. Porównanie wzrostu gorczycy po 7 dniach uprawy: (od lewej) próbka kontrolna, gleba z dodatkiem 0,1 g struwitu, gleba z dodatkiem 0,5 g struwitu, gleba z dodatkiem 1,0 g struwitu

Fig. 4 presents a comparison of fourteen-day mustard growth for soil and its individual mixtures. It can be observed that addition of 1.0 g struvite led to the biggest increase in the length of mustard shoots. No significant differences in the length of plants were found in other cases compared to the control sample.



Fig. 4. Comparison of the growth of mustard after 14 days of growing: (from the left) control sample, soil with addition of 0.1 g struvite, soil with addition of 0.5 g struvite, soil with addition of 1.0 g struvite

Rys. 4. Porównanie wzrostu gorczycy po 14 dniach uprawy: (od lewej) próbka kontrolna, gleba z dodatkiem 0,1 g struwitu, gleba z dodatkiem 0,5 g struwitu, gleba z dodatkiem 1,0 g struwitu

The twenty-day growth of mustard is presented in Fig. 5. Comparison of individual samples in terms of mustard shoot length revealed similarities in growing in soil and the soil mixture with addition of 0.1 g struvite. Similarly, no significant differences in the length of mustard plants were observed for the soil mixtures with addition of 0.5 g and 1.0 g struvite. Furthermore, plants grown on the soil with 0.5 g and 1g of struvite were substantially higher than the plants in the control sample and with the dose of struvite of 0.1 g.



Fig. 5. Comparison of the growth of mustard after 21 days of growing: (from the left) control sample, soil with addition of 0.1 g struvite, soil with addition of 0.5 g struvite, soil with addition of 1.0 g struvite

Rys. 5. Porównanie wzrostu gorczycy po 21 dniach uprawy: (od lewej) próbka kontrolna, gleba z dodatkiem 0,1 g struwitu, gleba z dodatkiem 0,5 g struwitu, gleba z dodatkiem 1,0 g struwitu

4.3. Analysis of the plant biomass

Fig. 6 contains the results for plant biomass obtained after 28 days of growing in the phytotron chamber for each combination. The highest value of mean plant biomass and dry mass was obtained for the mixture of soil with 1g struvite. In the case of the mixture of soil with 0.5 g struvite, lower values of the analysed parameters were obtained compared to the control sample. Table 4 presents the results for individual repetitions and the means with standard deviations for each combination.

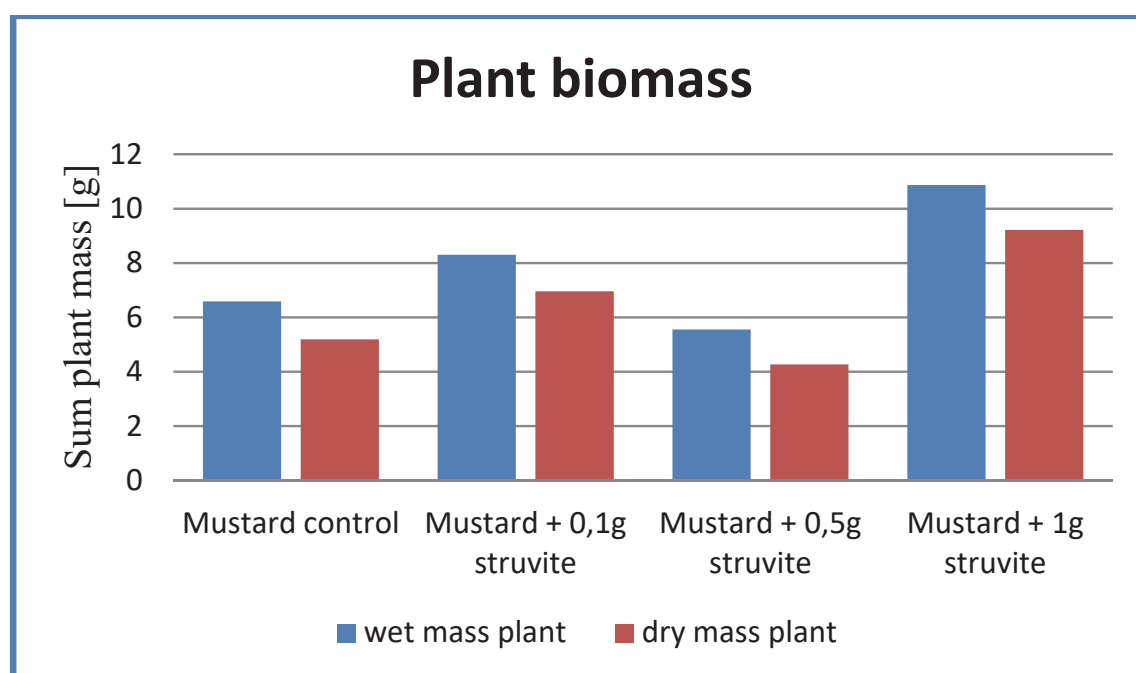


Fig. 6. Comparison of plant biomass

Rys. 6. Porównanie biomasy roślinnej

Table 4. Plant biomass

Tabela 4. Biomasa roślinna

Type of combination	Wet mass plant	Dry mass plant
	Average \pm SD	
Mustard control	2.197 \pm 1.17	1.730 \pm 1.03
Mustard + 0.1 g struvite	2.767 \pm 1.34	2.320 \pm 1.21
Mustard + 0.5 g struvite	1.853 \pm 1.06	1.423 \pm 1.15
Mustard + 1.0 g struvite	3.623 \pm 1.90	3.073 \pm 1.81

4.4. Analysis of the soil after completion of the experiment

Tables 5 and 6 contain the results of the physico-chemical analysis for all combinations (soil and soil mixtures) after 28 days of growing mustard. Similarly to soil and control mixtures, the samples were characterized by a slightly alkaline reaction, with the value of pH ranging from 7.58 to 7.85 in distilled water, whereas these values of KCl ranged from 7.23 to 7.39. The values of pH decreased with increasing struvite dose in the samples. Reaction of soil and mixtures is adequate for growing plants. Hydrolytic acidity for all samples was similar. Availability of

nutrients for plants depends on acidity of soil they grow in (Mocek 2015, Zawadzki 1999). Some nutrients in acid soils transform into hardly available forms e.g. molybdenum, boron and phosphorus. Furthermore, the amount of organic matter is reduced in these soils while activity of heavy metals, such as iron, manganese, zinc, copper and lead, and their availability for plants increase (Handzel et al. 2017).

Total organic content increased with the struvite dose in the mixture and was: 15.5 mg/g for soil without additions, 15.34 mg/g for the mixture with the dose of 0.1 g struvite and 16.55 mg/g and 17.88 mg/g for samples with 0.5 and 1.0 g struvite. After completion of the experiment, it was observed that total content of all metals in the soil material declined in all control combinations. The basic factor that impacts on mobility of elements in soil is water, where, depending on the natural or anthropogenic environment, pH and chemical composition are formed (Nowińska & Adamczyk 2013). The increase in pH and content of loamy minerals and organic matter usually improves capacity of soil to absorb heavy metals (Gorlach & Gambuś 1991).

Table 5. Results of physico-chemical analysis of soil: control soil and mixtures (after pot experiment)

Tabela 5. Wyniki analizy fizykochemicznej gleby: kontrola gleby i mieszanin (po doświadczeniu wazonowym)

	Plant control	Plant + 0.1 g struvite	Plant + 0.5 g struvite	Plant + 1.0 g struvite
pH	H ₂ O: 7.85 ± 0.09	H ₂ O: 7.66 ± 0.06	H ₂ O: 7.70 ± 0.03	H ₂ O: 7.58 ± 0.08
	KCl: 7.39 ± 0.04	KCl: 7.25 ± 0.04	KCl: 7.29 ± 0.03	KCl: 7.23 ± 0.09
Hydrolytic acidity	pH = 8.49	pH = 8.47	pH = 8.49	pH = 8.36
Total alkaline cations [mmol(+)/100 g]	0.2	0.2	0.1	0.2
Total carbon [mg/g]	15.90 ± 0.81	15.34 ± 0.15	16.55 ± 0.32	17.88 ± 0.67

Table 5. cont.**Tabela 5.** cd.

	Plant control	Plant + 0.1 g struvite	Plant + 0.5 g struvite	Plant + 1.0 g struvite
Total phosphorus [mg/kg]	415.8	471.0	584.6	688.8
Available phosphorus [mg P/kg]	253	308	490	680
Total nitrogen [mg/g]	0.97	0.91	1.03	1.05

Table 6. Results of heavy metals analysis for soil and mixtures (after pot experiment)**Tabela 6.** Wyniki analizy metali ciężkich dla gleby i mieszanin po zakończeniu doświadczenia wazonowego)

Heavy metals content [mg/kg]	Soil	Soil + 0.1 g struvite	Soil + 0.5 g struvite	Soil + 1.0 g struvite
Ag	–	–	–	–
Al	5991.1	6151.0	6269,7	5381.6
As	1.331	1.406	1.304	1.445
B	5.14	5.06	6.73	4.148
Ba	51.5	44.6	48.9	44.2
Ca	5675.1	5073.6	5761.1	7009.8
Cd	–	–	–	–
Co	–	–	–	–
Cr	10.1	9.47	9.5	7.83
Cu	11.1	10.3	12.5	12.1
Fe	5836.2	6225.0	5896.8	5408.8
K	859.0	876.7	893.7	768.3
Mg	1248.3	1051.1	1323.7	1342.5
Mn	222.4	311.2	224.9	227.0

Table 6. cont.

Tabela 6. cd.

Heavy metals content [mg/kg]	Soil	Soil + 0.1 g struvite	Soil + 0.5 g struvite	Soil + 1.0 g struvite
Na	75.4	218.6	90.7	85.4
Ni	1.147	1.886	2.385	2.496
P	415.8	471.0	584.6	688.8
Pb	30.2	30.0	38.8	37.3
Zn	65.7	58.8	61.7	62.4

5. Summary

At the end of the 20th century, a discussion was started among people who are involved in agricultural production concerning technologies of plant nutrition. It was found that previous fertilization method do not meet their role since a barrier of efficiency of the nutrient doses used was already reached. The increasing physical and chemical degradation of soil has led to changes in the physiological status of plants, resulting in the decrease of yield and its quality. First and foremost, one should care for adequate soil status as a basic and the only source of nutrients, water, growth substances for plants.

Soil additions, composed of specific mixtures of mineral compounds, should impact on activation of the processes of cellular metabolism and soil microflora which is best prepared for the environment. Adequate fertilization has a mild effect on processes that occur in humus. This leads to several reactions which are conducive to the development of soil and plants, thus allowing for compensation of the degrading effect of intensive agricultural production.

The research studies were started in order to develop fertilizers rich in microelements, growth regulators or amino acids with extended period of release of biogenic elements (Ciesielczuk et al. 2015, Ciesielczuk et al. 2016). An important factor of using fertilizers is their dose, which is closely related to specific expected soil parameters.

6. Conclusions

The focus of this study was on comparison of the effect of various synthetic struvite doses used as a fertilizer on the growth and biomass of mustard. A pot experiment was conducted in controlled conditions of a phytotron chamber. The analysis of the results obtained in the study leads to the following conclusions:

- It was found that physico-chemical properties of soil such as: pH, acidity, content of biogenic elements (N, P), content of micro- and macro-elements improved with the increasing struvite dose.
- Comparison of the length of mustard shoots, grown on the mixtures with struvite leads to the conclusion that the dose of 0.5 g is sufficient for maintaining a maximal length of the plants.
- The highest value of plant biomass (10.87 g) and dry biomass (9.22 g) was obtained for the dose of 1g struvite to soil.
- Based on the results of physicochemical analysis of soil and the obtained biomass, it was found that the most beneficial struvite dose was 1.0 g.
- It should be noted that the most beneficial dose of struvite was considered the largest of the experiments, so in the future the research should be extended with more than 1.0 g doses, also taking into account the extension of the experiment duration to determine the time of action and release of struvite components as a fertilizer.

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Ocena wpływu struwitu na wzrost gorczyicy *Sinapis alba*

Streszczenie

Struwit to uwodniony fosforan amonowo-magnezowy o wzorze chemicznym $MgNH_4PO_4 \cdot 6H_2O$, odkryty w 1845 roku. Mineralek charakteryzuje się barwą przejrzysta/półprzejrzysta biała o szklistym połysku, twardością według skali Mohsa wynoszącą 2, masą właściwą $1700 \text{ kg} \cdot \text{m}^{-3}$. Jego krystaliczna forma tworzy się przy odpowiednich stężeniach jonów magnezowych, fosforanowych oraz amonowych. W środowisku naturalnym jego obecność stwierdzono głównie w rozkładające się materii organicznej. Jednak kryształy struwitu mogą się także tworzyć na oprzyrządowaniu instalacji do oczyszczania ścieków (w rurociągach, wirnikach pomp itp.). Odbywa się w to sposób niekontrolowany i niesie za sobą problemy techniczne w oczyszczalni. Najczęstsze występowanie stwierdzono w osadach ściekowych po oczyszczaniu metodami biologicznymi oraz osadach ściekowych pochodzenia zwierzęcego po fermentacji beztlenowej. Jednak z racji tego, że dany związek stanowi źródło fosforu, zauważono możliwość wykorzystania struwitu w celach nawozowych. Jako granulatu nawozowy ma niską rozpuszczalność przez co uważany jest za bardziej przyjazny środowisku. Wolno rozpuszcza się w glebie co powoduje, że rośliny same mogą dozwalać jaką jego ilość pobiorą z otoczenia. Technologie odzysku tego minerału nie są jednak jeszcze powszechnie stosowane ponieważ są wymagające pod względem ekonomicznym. Nad struwitem prowadzone są ciągle intensywne badania mające na celu zoptymalizowanie jego procesu wytrącania.

Niniejsza praca skupiała się na porównaniu wpływu różnych dawek (0,1; 0,5; 1,0 g/250 g gleby) struwitu syntetycznego zastosowanego jako nawozu na wzrost oraz biomasę gorczyicy. Doświadczenie, miało charakter wazonowy i było prowadzone w kontrolowanych warunkach komory fitotronowej. Stwierdzono, że właściwości fizycznochemiczne gleby takie jak: pH, kwasowość, zawartość pierwiastków biogennych (N, P), zawartość makro i mikroelementów; poprawiały się wraz z wzrastającą dawką struwitu. Na podstawie uzyskanych wyników dla poszczególnych kombinacji, stwierdzono, że dawka 0,5 g jest wystarczająca, do uzyskania maksymalnej długości plonów. Jednakże, nie korelowało to z uzyskaną świeżą oraz suchą biomasą, gdzie najwyższą wartość (10,87 g dla świeżej biomasy oraz 9,22 g dla suchej biomasy) uzyskano dla dawki 1,0 g struwitu.

Abstract

Struvite is a hydrated ammonium magnesium phosphate of chemical formula $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$, discovered in 1845. Mineral is characterized by a transparent / translucent white color with a glossy gloss, a Mohs hardness of 2, a specific weight of $1700 \text{ kg} \cdot \text{m}^{-3}$. Its crystalline form is formed at appropriate concentrations of magnesium, phosphate and ammonium. In the natural environment its presence was mainly found in decomposing organic matter. However, struvite crystals may also be formed on the equipment of sewage treatment plants (piping, pump impellers, etc.). This is done in an uncontrolled manner and carries with it technical problems in the treatment plant. The most frequent occurrence was found in sewage sludge after biological treatment and sewage sludge of animal origin after anaerobic digestion. However, due to the fact that a given compound is a source of phosphorus, the possibility of using struvite for fertilization has been noted. As the fertilizer granule has low solubility, it is considered to be more environmentally friendly. It slowly dissolves in the soil, which causes the plants themselves to dispense the amount that they take from the environment. The recovery technologies of this mineral are not yet widely used because they are economically demanding. There are still intensive researches on the struvite to optimize its precipitation process.

This work focuses on comparing the effects of different doses (0.1, 0.5, 1.0 g/250 g of soil) of a synthetic struvite used as a fertilizer for growth and biomass of *Sinapis alba*. The experiment was vase-shaped and was carried out under controlled conditions of the phytotron chamber. It was found that the physical physico-chemical properties of soil such as: pH, acidity, content of biogenic elements (N, P), content of macro and microelements; they improved with the increasing dose of struvite. Based on the results obtained for each combination, it was found that a dose of 0.5 g is sufficient to obtain the maximum yield length. However, this did not correlate with the obtained fresh and dry biomass, where the highest value (10.87 g for fresh biomass and 9.22 g for dry biomass) was obtained for a dose of 1.0 g of struvite.

Słowa kluczowe:

struwit, nawozy mineralne, biomasa roślinna, gleba, nawożenie

Keywords:

struvite, mineral fertilizers, plant biomass, soil, fertilization



Effectiveness of Coagulation in Contaminants Removal from Biologically Treated Landfill Leachate

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1. Introduction

Landfilling is the most used final waste disposal method, because of its lower costs of operation and maintenance. One of the main concerns in landfill site exploitation is production of highly contaminated wastewater – landfill leachates. Highly variable composition of leachate depends on several factors, among others: characteristics of the solid waste dumped, the degree of separation of the moisture fraction in the municipalities served by the landfill site, the seasonality, the degree of solid waste stabilisation and technical treatment at landfills (Kurniawan et al. 2006, Kulikowska & Klimiuk 2008, Szymański & Nowak 2012, Talalaj & Biedka 2015). Municipal and industrial waste landfill sites creates potential hazard of groundwater pollution (Szymański et al. 2017).

To treat landfill leachate several methods are used: leachate transfer (recycling and combined treatment with domestic sewage), biodegradation (aerobic and anaerobic process), chemical and physical methods (chemical oxidation, adsorption, chemical precipitations, coagulation/flocculation, air stripping), membrane process (microfiltration, ultrafiltration, nanofiltration, reverse osmosis) (Renou et al. 2008). One of the method is also landfill leachate treatment in a multi-stage subsurface flow constructed wetland (Wojciechowska 2015, Wojciechowska 2017). The right choice of treatment method depends on the composition of leachate (Fudala-Książek et al. 2016, Nowak et al. 2016).

Complete leachate treatment is complicated, mostly expensive, and generally require various process applications due to high loads of contaminants and complex composition. Hybrid treatment methods: stripping – Fenton – SBR – coagulation (Guo et al. 2010), coagulation – nanofiltration (Mariam & Nghiem 2010), coagulation – UF – NF/RO and adsorption/UF/NF-RO (Dolar et al. 2016), aerobic activated sludge biological pre-oxidation (ASBO) – coagulation/sedimentation – photo-oxidation through a photo-Fenton (PF) reaction combining solar and artificial light (Silva et al. 2017), and many others, are the subject of scientific studies.

Due to its reliability, simplicity and high cost-effectiveness, biological treatment is commonly used for leachate containing high concentrations of BOD. When the BOD/COD ratio has value >0.5 , process is very effective in removing organic and nitrogenous matter. Coagulation-flocculation may be used successfully to remove non-biodegradable compounds (Renou et al. 2008).

The aim of this study was to evaluate coagulation-flocculation process in removing contaminants from biologically treated leachate from a municipal landfill.

2. Materials and methods

2.1. Leachate characteristics

The effectiveness of the coagulation process was determined in leachates from the Siedliska landfill near Ełk (north-eastern Poland). The landfill has been in operation since 1983 storing municipal, non-hazardous waste. The facility consists of two cells, of which one (A) is closed and reclaimed, and the other (B) is in operation. In this study leachate from the cell B was used. The cell B has an area of 5.1 ha (enabling the deposition of 280,000 Mg of waste), is operated since 2012 and equipped with drainage. The amount of generated leachate is in the range of 50-90 m³/d. The leachate is treated in a reverse osmosis system. The RO concentrate is recirculated to the landfill cells, which was supposed to ensure adequate humidity of the bed and intensification of the distribution of organic matter.

The leachate samples for this study were taken in March 2017, directly from the collective drainage well. In laboratory conditions, the leachate underwent a biological pretreatment process in the SBR system. The characterization of raw and biologically treated leachates is presented in Table 1.

Table 1. Properties of raw and biologically pretreated leachates

Tabela 1. Właściwości odcieków surowych i podczyszczonych biologicznie

accuracy	TSS mg L ⁻¹ (± 1%)	EC mS cm ⁻¹ (± 0,5%)	TOC mg L ⁻¹ (± 1%)	BOD ₅ mg O ₂ L ⁻¹ (± 1%)	COD _{Cr} mg O ₂ L ⁻¹ (± 1,6%)
Raw	23	15.45	1210	347	3585
Biologically pretreated	84	13.61	1170	50	3390
accuracy	pH (±0,02 pH)	Turbidity NTU (± 2%)	Colour PtCo (± 2%)	TP mg P L ⁻¹ (± 1,2%)	P-PO ₄ ³⁻ mg P L ⁻¹ (± 0,5%)
Raw	7.58	5.1	11842	17.2	9.83
Biologically pretreated	8.94	10.2	10750	16.0	8.71
accuracy	TKN mg N L ⁻¹ (± 1%)	N-NO ₃ ⁻ mg N L ⁻¹ (± 0,5%)	N-NO ₂ ⁻ mg N L ⁻¹ (± 0,5%)	N-NH ₄ ⁺ mg N L ⁻¹ (± 0,5%)	
Raw	935	0.35	-	921.4	
Biologically pretreated	168	0.85	-	16.08	

2.2. Biological treatment

Biological treatment of leachate was conducted as a bench-scale test, in a sequential biological reactor system (SBR), with nitrification and denitrification assisted by metering of an external carbon source (methanol). The stand comprised a tank with a total volume of 25 L, peri-

staltic pumps dosing raw sewage and methanol and discharging treated wastewater and biological sludge, mechanical mixer CAT R50D with adjustable speed, aeration system: electromagnetic piston pump Hailea ACO-208 with a diffuser placed on the bottom of the tank, pH, ORP, dissolved oxygen (Hach HQ30D, HQ40D multiparameter) instruments. The operation of the pumps, the mixing and aeration system was controlled automatically, developed individually for the needs of the model by an electronic system based on the ATMEGA328P microcontroller.

The activated sludge used in the reactor came from municipal wastewater treatment plants. Before the actual experiment, it was gradually adjusted to work in leachate for 4 weeks.

The operation cycle of the SBR reactor has been developed in a way that allows obtaining a high degree of ammonium nitrogen removal (average 98.2%) – Table 2.

Table 2. Operating parameters and schedule of SBR reactor

Tabela 2. Parametry i cykl pracy reaktora SBR

Phase	Time / volume
filling	2.0 L
mixing (denitrification)	120 min
mixing and aeration – nitrification	240 min
dozing of metanol	3.0 mL
mixing (denitrification)	180 min
mixing and aeration – nitrification	240 min
dozing of metanol	3.0 mL
mixing (denitrification)	180 min
mixing and aeration – nitrification	240 min
sedimentation	30 min
decantation	1.8 L
removal of excess sludge	0.2 L
duration of phase, t_C	20.5 h
reaction time, t_R	18.0 h / phase
aeration time, t_{aero}	12 h / phase
active volume, V_R	10.0 L
concentration of active sludge, TS_{BB}	3.5-4.5 mg s.m. / L

The biologically pretreated leachates, as compared to the raw leachates, were characterised mainly by the lower concentration of ammonium nitrogen and Kieldahl nitrogen (the removal rate of 98.3 and 82.1%, respectively). The removal rate of organic matter expressed as BOD, amounted to an average of 85.6%. The remaining indicators in the SBR reactor were removed to a lesser extent (Table 1).

2.3. Coagulation experiment

The coagulation process was carried out by dosing three aluminium coagulants to the leachates: polyaluminium chloride $\{Al_n(OH)_mCl_{(3n-m)}\}_x$, aluminium sulphate ($Al_2(SO_4)_3$, (ALS), sodium aluminate ($NaAlO_2$) and one iron coagulant: iron (III) chloride ($FeCl_3$, PIX111). PAX18, ALS, PIX111 were used as ready coagulants produced by Kemipol Ltd., Poland, $NaAlO_2$ – as solution of sodium aluminate. The dose volume of preparations was chosen based on metal ions ($mg\ Me\ L^{-1}$). Each coagulant was added in varying doses – Table 3.

Table 3. Doses of coagulants used in leachate pretreatment process

Tabela 3. Dawki koagulantów stosowane w procesie podczyszczania odcieków

Coagulant	Doses, $mg\ Me\ L^{-1}$				
polyaluminium chloride	125	250	500	750	1000
aluminium sulphate	100	200	400	600	800
sodium aluminate	120	240	480	720	960
iron (III) chloride	200	400	600	800	1000

Before adding the coagulant, the pH of the leachate was adjusted by adding sulphuric acid in an amount sufficient to achieve a coagulation pH in the range 6.0-7.0. The obtained reaction in which the process was carried out is presented in Fig. 1.

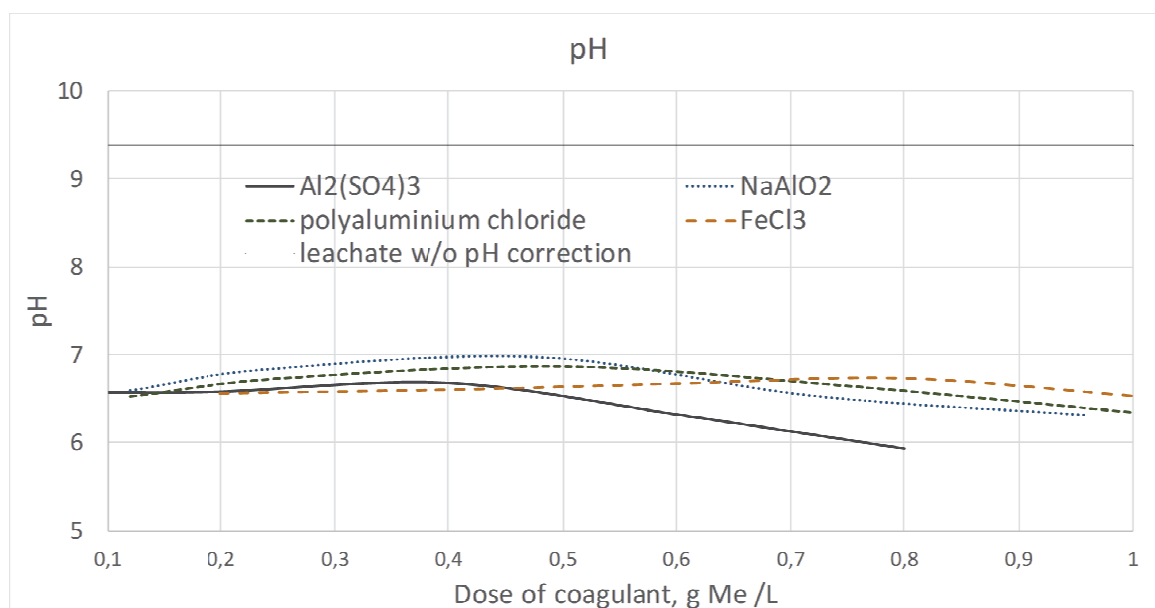


Fig. 1. Changes pH of coagulation process

Rys. 1. Zmiany odczynu pH procesu koagulacji

Coagulation was carried out in cylindrical glass beakers, in 0.5-liter samples. The process included two mixing phases: rapid (150 RPM) for 30 seconds and slow (20 RPM) for 30 min. A Velp Scientifica JLT 6 flocculator was used for mixing. After the mixing was completed, the samples were allowed to settle for 4 hours. Liquid from a height of approx. 2 cm from the surface was taken for testing (sample volume: 100 mL).

2.4. Analytical methods

Several analytical parameters were selected: pH, conductivity (mS/cm), colour (PtCo), turbidity (NTU), chemical oxygen demand (COD, mg O₂ L⁻¹) phosphorus total (TP, mg P L⁻¹). The conductivity and the pH were measured by a conductivity and potentiometric method, respectively, using a portable pH meter (HACH HQ40). The chemical oxygen demand was analyzed using a colorimetric method with a HACH spectrophotometer (620 nm) after a 2-hour reactor digestion (a K₂Cr₂O₇ method). The phosphorus total was measured using test'N Tube Vials (molybdate method) on the HACH spectrophotometer (880 nm) after a 1-hour acid persulfate digestion. Colour was analyzed by 455 nm (HACH). For turbidity measurement, the WTW Turb® 550 turbidity meter was used. The obtained results were the mean value of three determinations carried out simultaneously.

3. Results and discussion

The conducted research allowed to determine the degree of removal of selected indicators of leachate contamination depending on the coagulant used and its dose. The reaction of the process was to be maintained in the range of 6.0-7.0, which is higher than optimal for removing COD and turbidity. This assumption resulted from the potential for further leachate purification in membrane processes, in which the capacity of the membranes is reduced by a high sulphate content (Wiszniowski et al. 2006). The actual pH values are presented in Fig. 1. In the assessment of the effectiveness of the coagulation process, selected indicators were taken into account, i.e. the concentration of organic matter, colour, turbidity and total phosphorus.

Organic matter

Due to the concentration of easily and non-easily decomposable organic matter expressed as a BOD/COD ratio, which amounting to 0.098 in raw leachate, these leachates should be classified as stabilized (Kang et al. 2002). In biologically pretreated leachates, the value of this ratio was 0.015. Due to the low BOD values, only the COD indicator was taken into account in the assessment of the coagulation process.

The degree of removal of organic matter, using the above-mentioned doses of metal ions, reached approx. 60% in the case of aluminium coagulants, and less than 40% in the case of iron coagulant. However, a different molar concentration of iron and aluminium with the same weight concentration of metals should be taken into account, which for aluminium is 2.07 times higher. The dependence of the indicator removal rate on the coagulant dose, for aluminium sulphate, polyaluminium chloride and ferric chloride, was similar to linear. The dose of sodium aluminate up to approx. 0.5 g Al L⁻¹ allowed the COD to be reduced by about 20%, only higher doses allowed for more effective removal of organic matter.

In the work of other authors (Silva et al. 2004, Rivas et al. 2003, Monje Ramirez & Orta de Velasquez 2004, Tatsi et al. 2003, Leszczyński 2011), the effectiveness of COD removal in the coagulation process was estimated in the range of 10-90%. At the dose of iron and aluminium coagulants amounting to approx. 18 mmol Me L⁻¹, there were

no clear differences between them in the effectiveness of COD removal. When treating old landfill leachate applying coagulation –flocculation with iron trichloride or with aluminium polychloride, it was possible to reduce the non-biodegradable organic matter by 73-62%, also reducing turbidity and colour by more than 97% (Castrillón et al. 2010). In the combined treatment system including a coagulation process, followed by a Fenton oxidation, obtained result of COD removal was 65.3% (Barbusiński & Pieczykolan 2010).

Colour

The use of polyaluminium chloride and aluminium sulphate gave a similar effect in colour removal. The dependence of the degree of colour removal on the applied dose of coagulant (similarly as in the case of COD) was similar to the linear one. At the highest dose, the values of 89.8 and 89.9% were achieved, respectively. The use of sodium aluminate at a dose of up to 0.5 g Al L^{-1} resulted in a slight degree of colour removal (by approx. 20%), only a higher dose (0.96 g Al L^{-1}) enabled colour removal in 89%. Iron (III) chloride at a dose of 0.2 g Fe L^{-1} caused a colour increase, only doses above 0.6 g Fe L^{-1} allowed a reduction of this index (up to 54.8% at a dose of 1.0 g Fe L^{-1}). Similar degrees of colour removal from landfill leachate (55 ÷ 70%) were obtained by Zamora et al. (2000), at doses of $\text{Al}_2(\text{SO}_4)_3 + \text{FeCl}_3$ of $0.738 + 1.136 \text{ g L}^{-1}$. Using doses of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 g/L at pH 8.0) and $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (12 g/L at pH 7.5) Liu et al. (2012) obtained 93.31% and 74.65% colour removal, respectively. Investigation the efficiency of coagulation and flocculation processes for removing colour from a semi-aerobic landfill leachate from one of the landfill sites in Malaysia (Aziz et al. 2006) using four types of coagulant namely aluminium (III) sulphate (alum), ferric (III) chloride, ferrous (II) sulphate and ferric (III) sulphate result that ferric chloride was superior to the other coagulants and removed 94% of colour at an optimum dose of 800 mg/l at pH 4. The effect of coagulant dosages on colour removal showed similar trend as for COD, turbidity and suspended solids.

Phosphorus total

The biological treatment process used in the experiment, optimized to remove nitrogen compounds, did not allow achieving a high total phosphorus removal rate of 7%. By coagulation, this contamination is removed from the leachate usually with high efficiency, because of forming by orthophosphate sparingly soluble complexes with coagulants.

In the case of biologically treated leachates, the use of four coagulants has resulted in a different removal effect of phosphorus compounds. A high degree of removal was already observed at the smallest doses of polyaluminium chloride, sodium aluminate and iron chloride. It amounted to 54.7%, 67.2% and 68.7% respectively. Increased doses allowed further phosphorus removal to reach the maximum values of 96.9%, 95.3% and 82.8%. The dependence of the effectiveness of aluminium sulphate in the removal of phosphorus on the applied dose was similar to the linear course, as in the case of other indicators – Fig. 2.

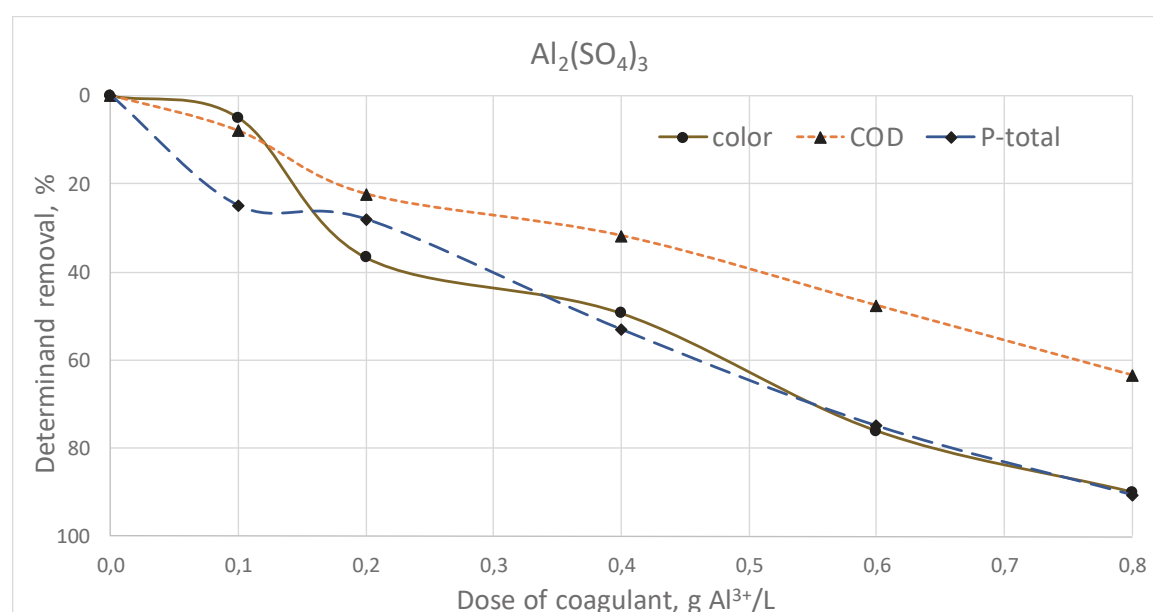


Fig. 2. The effect of contaminants removal depending on the applied dose of aluminium sulphate

Rys. 2. Stopień usunięcia zanieczyszczeń w zależności od zastosowanej dawki siarczanu glinu

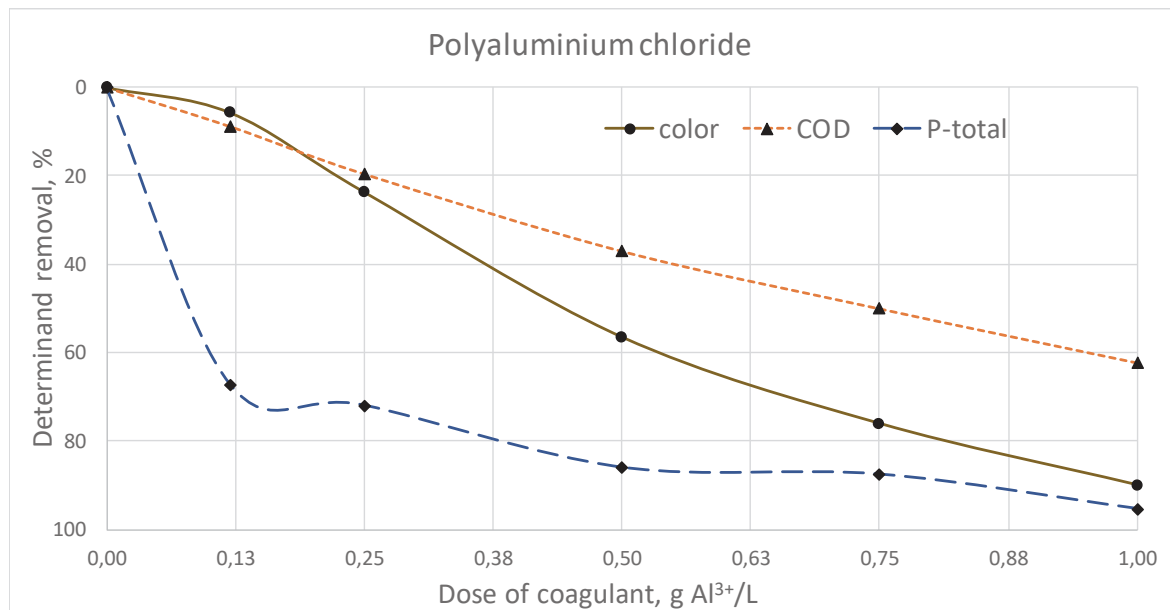


Fig. 3. The effect of contaminants removal depending on the applied dose of polyaluminium chloride

Rys. 3. Stopień usunięcia zanieczyszczeń w zależności od zastosowanej dawki chlorku poliglinu

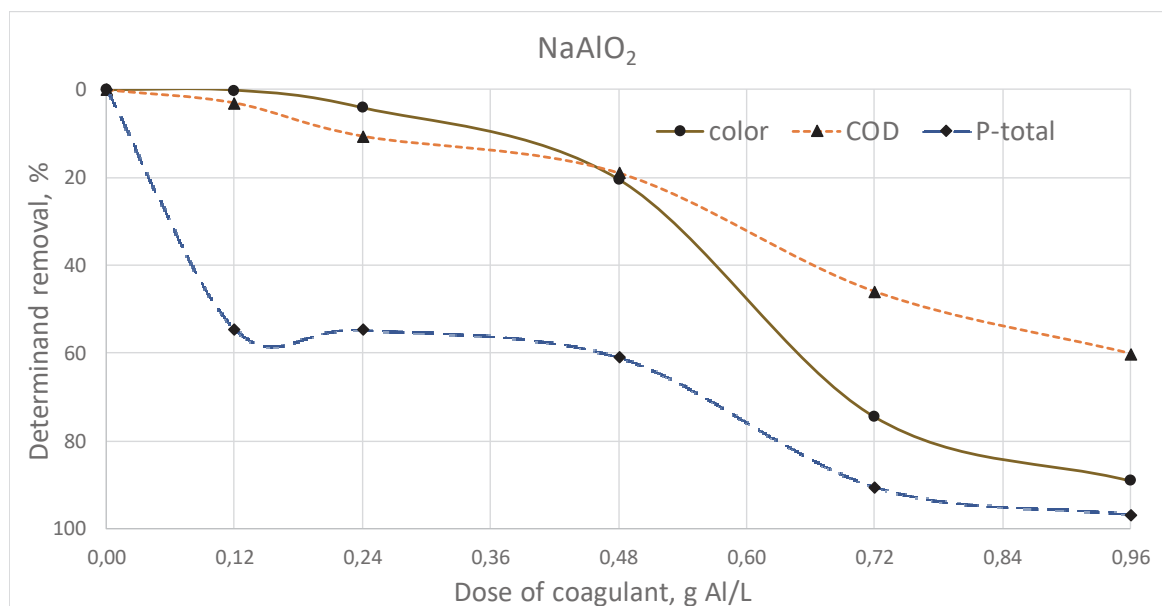


Fig. 4. The effect of contaminants removal depending on the applied dose of sodium aluminate

Rys. 4. Stopień usunięcia zanieczyszczeń w zależności od zastosowanej dawki glinianu sodu

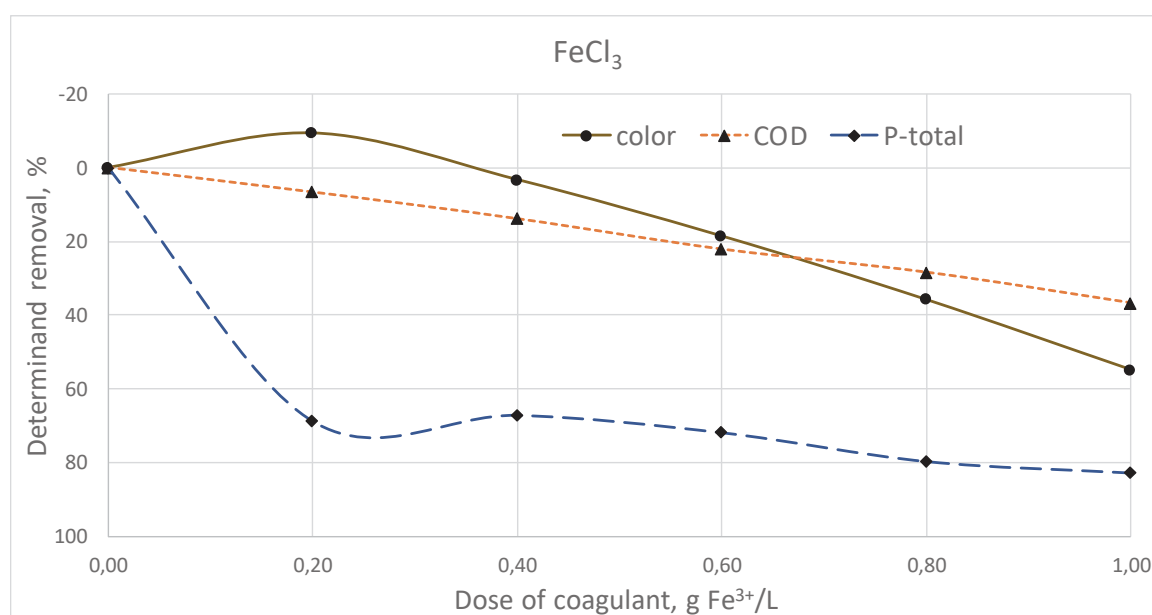


Fig. 5. The effect of contaminants removal depending on the applied dose of iron chloride (III)

Rys. 5. Stopień usunięcia zanieczyszczeń w zależności od zastosowanej dawki chlorku żelaza (III)

Turbidity

The biologically treated leachates manifested twice higher turbidity (10.2 NTU) than the raw leachate (5.1 NTU). These values are smaller than those presented in other works (Tatsi et al. 2003). The addition of aluminium coagulants in doses lower than the maximum adopted in the described experiment caused an increase in turbidity, that is the opposite of those in the case of leachates characterized by higher turbidity (Tatsi et al. 2003). Only higher doses (aluminium sulphate – 0.8 g Al L⁻¹, polyaluminium chloride – 0.75 g Al L⁻¹, sodium aluminate – 0.96 g AL⁻¹) allowed obtaining clear leachates with turbidity lower than initially. The maximum turbidity was observed at doses of: aluminium sulphate – 0.2 g Al L⁻¹, polyaluminium chloride 0.25 g Al L⁻¹, sodium aluminate 0.72 g Al L⁻¹. Additive iron (III) chloride in all applied doses caused an increase in turbidity – Fig. 6. Using doses of FeCl₃·6H₂O (10 g/L at pH 8.0) and Fe₂(SO₄)₃·7H₂O (12 g/L at pH 7.5) Liu et al. (2012) obtained 98.85% and 94,13% turbidity removal from landfill leachate, respectively. High turbidity removal efficiencies may be obtained in coagulation flocculation (CF) process. Doses of coagulant (ferric chloride) and flocculant (cationic polymer): 4.4 g/L and 9.9 mL/L respectively, reached

69±4.8% removal in leachate treated by anaerobic process (Bakraouy et al. 2017).

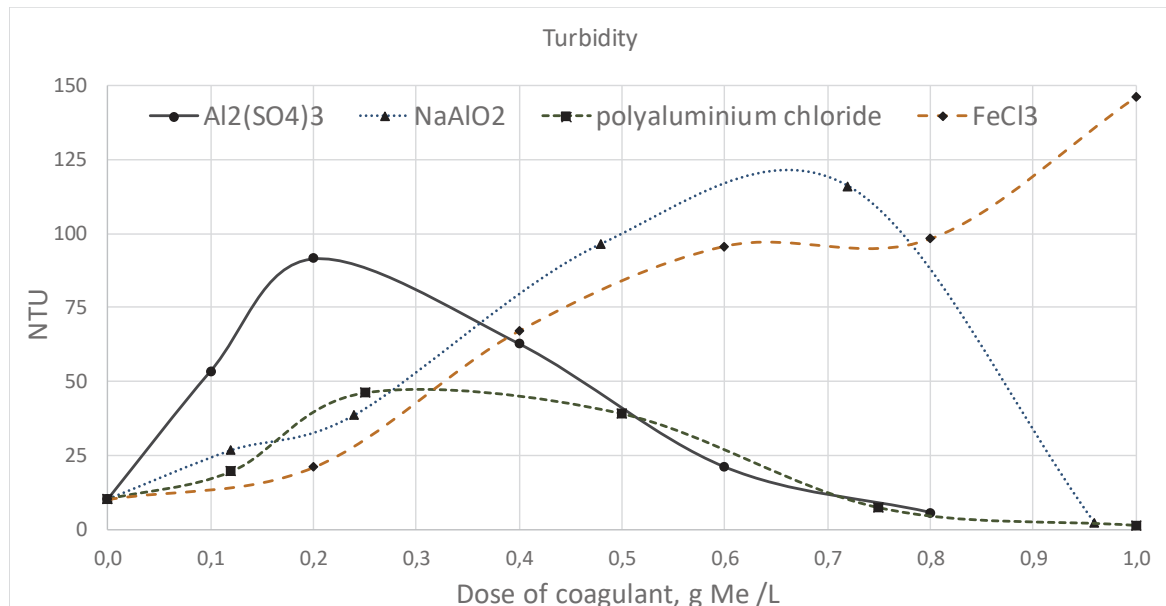


Fig. 6. Changes in turbidity of leachates at different doses of coagulants
Rys. 6. Zmiany mętności odcieków w zależności od dawki koagulantu

4. Conclusions

Treatment of landfill leachates, due to the degree of their contamination, usually requires the use of several technological processes. Obtained results of the tests carried out on biologically pre-treated leachate indicate the possibility of using a coagulation process to partially remove the remaining contamination. Leachates thus prepared, devoid of most nitrogen compounds in the biological process and organic matter that are difficult to decompose in the coagulation process, can then be directed, for example, to membrane processes.

Coagulation of stabilised, biologically pretreated leachates, allows for a high removal rate of organic matter. When aluminium coagulants were used in the doses of 0.8-1,0 g Al L⁻¹, a removal effect of more than 60% was obtained, whereas with iron coagulate (Fe³⁺) in the dose of 1 g Fe L⁻¹, the effect was lower and amounted to only 36.6%. A high removal degree, reaching 89.0-89.9% using aluminium coagulants and 54.8% in the case of iron coagulant was also obtained for the colour, at the maximum doses used in the experiment.

All the substances used enabled obtaining a high degree of phosphorus removal: 82.8% for iron (III) and 90.6-96.8% for aluminium.

High doses of coagulants resulted in the formation of large amounts of sludge that must be removed before being subjected to subsequent pretreatment processes. Maintaining the assumed pH of the coagulation process carried out using sodium aluminate required the use of increased volumes of H₂SO₄. A similar effect of leachate treatment with the use of other aluminium coagulants, without the need to introduce significant amounts of additional substances, leads to conclusion that the aluminate is less effective in leachate pretreatment.

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Efektywność procesu koagulacji w usuwaniu zanieczyszczeń z odcieków składowiskowych oczyszczonych biologicznie

Streszczenie

W artykule zaprezentowano wyniki badań skuteczności procesu koagulacji w usuwaniu zanieczyszczeń z podczyszczonych biologicznie odcieków pochodzących ze składowiska odpadów komunalnych. Ocieki podczyszczone biologicznie charakteryzowały się niskim stężeniem NH_4^+-N ($16,08 \text{ mg N L}^{-1}$), oraz TKN ($167,8 \text{ mg N L}^{-1}$). Zawartość substancji organicznej wyrażonej jako BZT_5 wynosiła $50 \text{ mg O}_2 \text{ L}^{-1}$, stężenie związków organicznych trudno rozkładalnych ChZT wynosiło $3390 \text{ mg O}_2 \text{ L}^{-1}$. Proces koagulacji prowadzono w warunkach laboratoryjnych, przy zastosowaniu zmiennych dawek koagulantów glinowych: polyaluminium chloride, aluminium sulfate, sodium aluminate oraz żelazowego: iron (III) chloride. Maksymalne dawki wynosiły $0,8-1,0 \text{ g Me L}^{-1}$. pH procesu utrzymywało się w granicach 5,93-6,97. Efekt usunięcia substancji organicznej (ChZT) uzyskano na poziomie 60-63% dla koagulantów glinowych oraz 37% dla iron (III) chloride. Zmniejszenie barwy nastąpiło o 90%, a zawartość fosforu całkowitego obniżona została maksymalnie o 97%.

Abstract

The effectiveness of the coagulation process in removing contaminants from biologically treated leachates from a municipal waste landfill was investigated. The biologically treated leachates were characterized by a low concentration of $\text{NH}_4^+\text{-N}$ ($16.08 \text{ mg N L}^{-1}$), and TKN (168 mg N L^{-1}). The organic matter concentration, expressed as BOD (Biological Oxygen Demand) was $50 \text{ mg O}_2 \text{ L}^{-1}$, the concentration of hard-to-break COD (Chemical Oxygen Demand) organic compounds was $3390 \text{ mg O}_2 \text{ L}^{-1}$. The coagulation process was carried out in laboratory conditions, using variable doses of aluminium coagulants: polyaluminium chloride, aluminium sulphate, sodium aluminate and iron: iron (III) chloride. The maximum doses were $0.8\text{-}1.0 \text{ g Me L}^{-1}$. The process was maintained between 5.93-6.97. The removal effect of the organic matter (COD) was obtained at 60-63% for aluminium coagulants and 37% for iron (III) chloride. The colour reduction occurred in 90% and the total phosphorus concentration was reduced to a maximum of 97%.

Słowa kluczowe:

odcieki, oczyszczanie biologiczne, koagulacja

Keywords:

leachate, biological treatment, coagulation



Environmental Flows of Lowland Rivers with Disturbed Hydrological Regime on the Example of Mała Wełna River

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1. Introduction

To achieve good water status in rivers it is necessary to establish their volume of environmental flows. Environmental flows are defined as a part of the watercourse's flow volume which must be maintained to keep high values of aquatic ecosystems and water-dependent ecosystems with respect to requirements of environmental protection (Tharme 2003, Młyński et al. 2015). According to hydrological practice, the flow which ensures sufficient conditions for biological life is called a contractual flow, i.e. in-stream flow. The obligation to maintain hydrological instream flow is imposed in water legal permits (UPW 2001), and since 2017 according to the new Polish Water Law (UPW 2017) also in water agreements covering water permits, water applications and water assessments. The water assessment is required for all investments and actions which might affect environmental goals' achievement. Instream flow is calculated as a product of k-coefficient and annual mean low flow. It relates only to flow capacity within riverbed, therefore does not include the requirements of wetlands and other water-dependent ecosystems (Fabjański 2003, Pullin 2005), while flows fulfil water requirements of water and water-dependent ecosystems. Additional factors affecting water's biological life are: water quality, riverbed's and river valley's hydromorphological conditions and anthropogenic transformation of a habitat (Dunbar et al. 2012, Parasiewicz et al. 2013, Pusłowska-Tyszewska & Rychalski 2015).

2. Research area

The Mała Wełna river is a left-bank tributary of the Wełna river and its outlet is located in Rogoźno village. The field studies and analysis of water management within the boundaries of the Mała Wełna river catchment up to Kyszkowo cross-section (area of 339.41 km²) were conducted by Poznań University of Life Sciences' Institute of Land Improvement, Environmental Development and Geodesy in 2000-2010 period.

According to the hydrographic division of Poland, the catchment of Mała Wełna river up to Kyszkowo cross-section is divided into 9 Surface Water Bodies (SWB), which are as follows: PLRW6000251866539 Mała Wełna to the outflow from the Gorzuchowskie Lake (covers the major share of this catchment's area – 265.51 km²), PLRW600024186675 Mała Wełna from the outflow from the Gorzuchowskie Lake to the Rejowiec's inflow (only partially within the catchment's boundaries, covers an area of 94.09 km²) and 7 other SWB (catchments of the Mała Wełna's inflows, which cover an area from 10.55 km² to 29.16 km²) (Fig. 1).

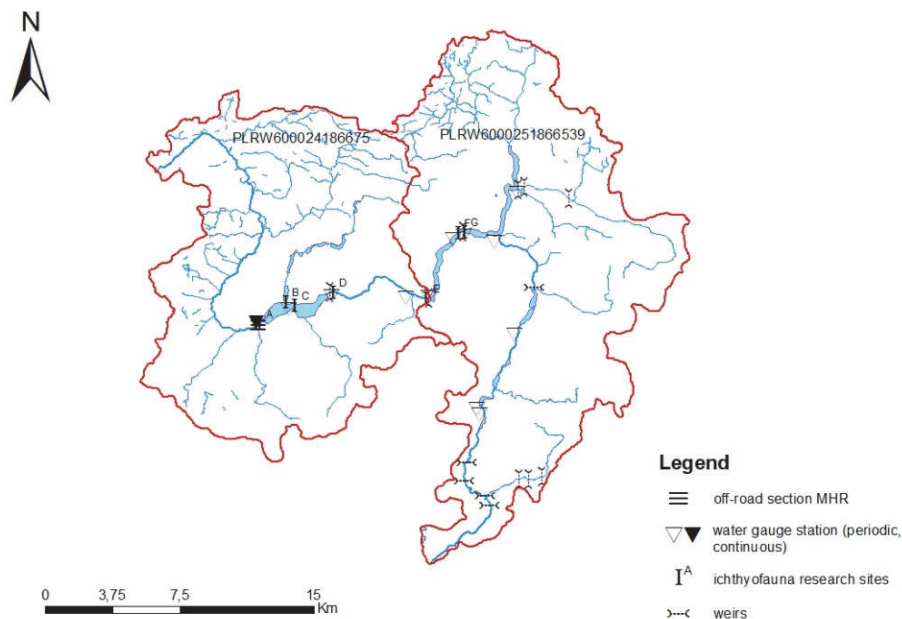


Fig. 1. Catchment area of Mała Wełna to an outflow from the Gorzuchowskie Lake and Mała Wełna from an outflow from the Gorzuchowskie Lake to the Rejowiec's inflow

Rys. 1. Położenie zlewni rzeki Małej Wełny do wypływu z Jeziora Gorzuchowskiego i Małej Wełny od wypływu z Jeziora Gorzuchowskiego do dopływu z Rejowca

Physiographic conditions and abiotic types of the analysed SWB are varied. Table 1 presents metric parameters for two largest SWB in the Mała Wełna river catchment up to Kiszkowo cross-section. The abiotic type of the Mała Wełna river from its source to the outflow of the Gorzuchowskie Lake was determined as the 25th type (natural waters and waters connecting lakes), while the next section up to the Rejowiec's inflow as the 24th type (river in the area under the influence of peat-forming processes).

Table 1. Physiographic conditions of chosen Surface Water Bodies within Mała Wełna river catchment

Tabela 1. Charakterystyka warunków fizjograficznych zlewni badanych JCWP Małej Wełny

Characteristics	Symbol or formula	Unit	SWB Mała Wełna	
			to an outflow from the Gorzuchowskie Lake	from an outflow from the Gorzuchowskie Lake to the Rejowiec's inflow
Area	A	km ²	265.51	94.09
River length	L	km	31.974	22.711
Maximum elevation	H_{max}	m above sea level	129.60	132.20
Outlet's height (minimum elevation)	$H_o = H_{min}$	m above sea level	92.00	77.50
River's source's elevation	H_s	m above sea level	108.00	94.70
Average elevation	$H_{av} = \frac{H_{max} + H_{min}}{2}$	m above sea level	110.80	104.85
Elevation difference	$H_{max} - H_{min}$	m	37.60	54.70
River longitudinal slope	$\frac{H_s - H_o}{L} \cdot 1000$	‰	0.50	0.76

Approx. 18% of the Mała Wełna to the outflow from Gorzuchowskie Lake SWB is urbanized, while 35% is covered by agricultural lands, 29% by forests, 12% by meadows and only 6% by water bodies. Whereas the dominant share of the Mała Wełna from the outflow from Gorzuchowskie Lake to the Rejowiec's inflow SWB is covered by agricultural lands (65%). Forests and meadows cover approx. 31% of this SWB, while both urbanized area and water bodies cover 2%.

3. The aim, scope and methodology

The aim of this paper was to analyse the characteristic and contractual flows of a lowland river with disturbed hydrological regime and their impact on the ecological status of this river's water.

Daily, characteristic and contractual flows were calculated based on the field studies which included daily water level measurements at the Kizskowo cross-section and monthly hydrometric measurements at several cross-sections along the course of the river.

The ecological status of water in this river was determined based on biological (ichthyofauna), hydromorphological and physicochemical conditions. The research of ichthyofauna structure in Mała Wełna river were conducted by Poznań University of Life Sciences' Department of Inland Fisheries and Aquaculture in 2008 (Murat-Błażejewska et al. 2010) (Fig. 1). Hydromorphological conditions of the river were analysed based on MHR (hydromorphological monitoring of rivers) methodology developed by Ilnicki et al. (2009) with respect to four elements: hydrological regime, river continuity, riverbed's and river valley's morphology. Physicochemical conditions of Mała Wełna river were diagnosed based on concentration of 14 parameters indicating thermal and oxygen conditions, salinity, acidity and presence of biogenic compounds (Sojka et al. 2010).

Environmental flow rate was calculated with three following methods: Tennant's, Tessmann's and method based on flow duration curves ($Q_{70\%}$ and $Q_{90\%}$). In the Tennant's method the water-habitat conditions of water ecosystems and water-dependent ecosystems depend on multiannual mean flow in winter season (since October to March) and summer season (since April to September).

According to the Tessmann's method the environmental flow values are related to multiannual monthly mean flow (SSQ_{mc}) and multiannual mean flow (SSQ). Instream flow was calculated as a product of annual mean low flow and k-coefficient which relates to river's hydrological type and catchment's area.

According to the Resolution of the Regional Water Management Authority (RZGW) Director in Poznan of 2 April 2014 r. on the conditions of use of the waters of the Warta water region, the proven method for environmental flow calculation is specified in the first and currently the only regulation defining conditions upon which the water can be used within the boundaries of water regions. The proper methodology is proposed for each water region individually with respect to its distinctive conditions.

The requirement is set to maintain environmental flow in all natural watercourses as the necessary condition to achieve their good ecological state or potential. The minimal acceptable flow in the given cross section of the natural watercourse must not be lower than calculated with the presented method unless other regulations decide otherwise:

$$Q_e = k \cdot SNQ \quad (1)$$

where:

Q_e – environmental flow [$m^3 \cdot s^{-1}$],

k – coefficient “k”,

SNQ – average men low flow [$m^3 \cdot s^{-1}$].

$$Q_e > NNQ \quad (2)$$

where:

Q_e – environmental flow [$m^3 \cdot s^{-1}$],

NNQ – the lowest low flow [$m^3 \cdot s^{-1}$].

The values of the coefficient “k” for given rivers in each water region. The values of the coefficient “k” for the same watercourse between the neighboring cross-sections are interpolated proportionally to the increase of the basin area (Operacz et al. 2018).

4. Results and discussion

The flow rates at Kiszkowo cross-section in 2000-2010 period were ranging from $0.021 \text{ m}^3 \cdot \text{s}^{-1}$ (multiannual low flow) to $3.183 \text{ m}^3 \cdot \text{s}^{-1}$ (multiannual high flow), while multiannual mean flow was equal to $0.644 \text{ m}^3 \cdot \text{s}^{-1}$ (Fig. 2).

The largest amplitude of flow variability occurred in February and March (Fig. 3).

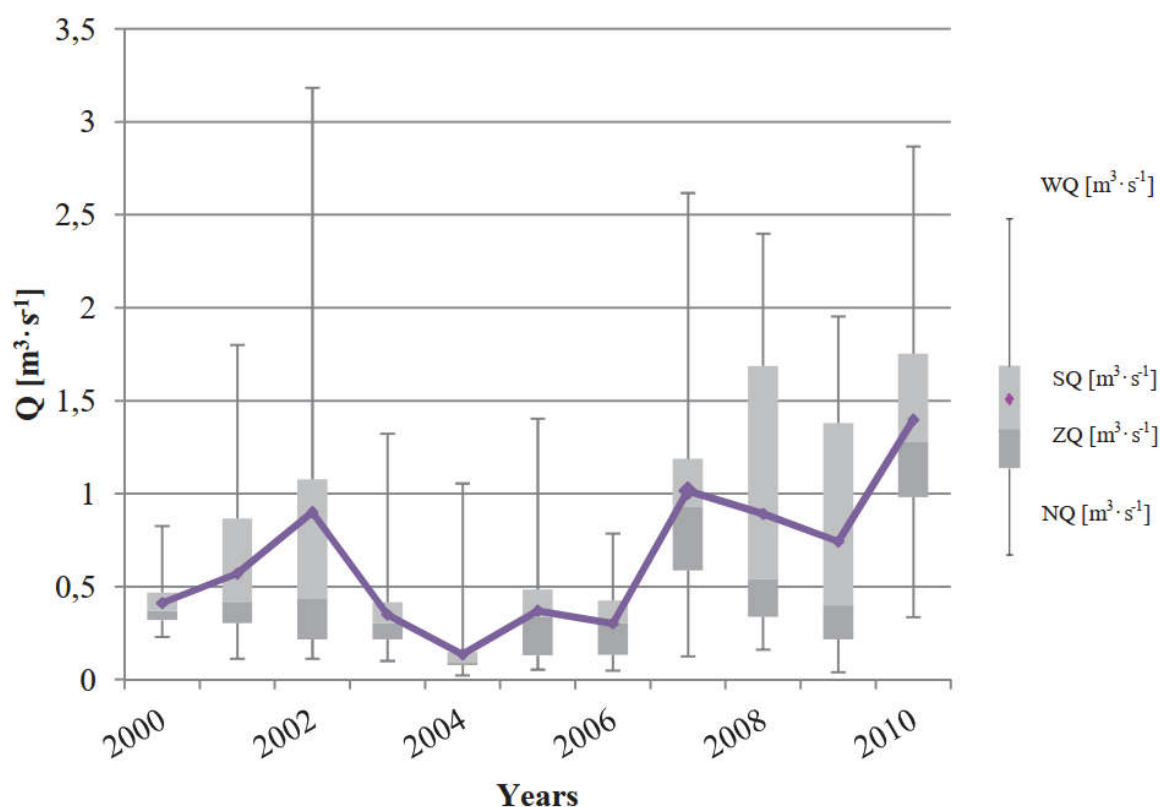


Fig. 2. Annual flow course in Mała Wełna river at Kiszkowo cross-section in 2000-2010 period

Rys. 2. Hydrogram charakterystycznych rocznych przepływów rzeki Małej Wełny w profilu Kiszkowo w latach 2000-2010

Results showed that water management of fish ponds (112 ha) located in Kiszkowo within the course of Mała Wełna river not only affects discharge rates in the river and its distribution curve, but also water quality (Murat-Błażejewska & Kanclerz 2005, Sojka et al. 2010, Murat-Błażejewska et al. 2009). According to the Polish Regulation of the Minister of the Environment of 22 August 2008 on the on the method of clas-

sification of the state of surface water bodies (Journal of Laws no. 162 item 1008, 2008) in the analyzed period, the waters of Mała Wełna did not meet the standards due to the physicochemical state of water.

Analysis of the ichthyofauna structure in seven sections located along the course of the river showed that both their number and biomass were varied.

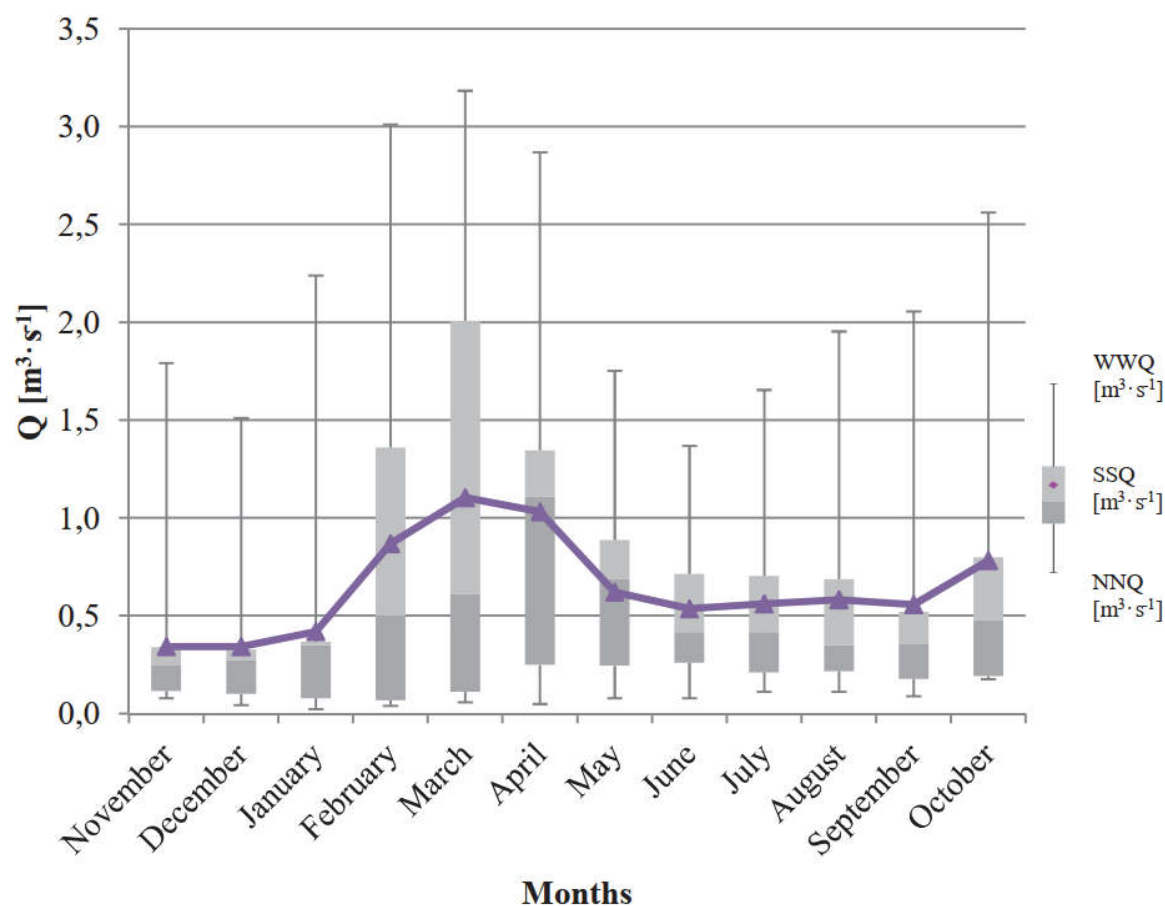


Fig. 3. Monthly flow course in Mała Wełna river at Kizskowo cross-section in 2000-2010 period

Rys. 3. Hydrogram charakterystycznych miesięcznych przepływów rzeki Małej Wełny w profilu Kizskowo w latach 2000-2010

Among 18 fish species found in the Mała Wełna river, 5 were qualified as low-risk endangered species and 3 as endangered with extinction. Water's ecological state was evaluated as moderate based on ichthyofauna structure and water quality (Sojka et al. 2010). Hydromorphological conditions of the Mała Wełna river's two Surface Water Bodies (Mała Wełna to an outflow from the Gorzuchowskie Lake SWB and Mała Wełna from an outflow from the Gorzuchowskie Lake to the Rejowiec's inflow SWB) were moderate mainly due to interrupted continuity of the river (Sojka et al. 2010). The results of State Environmental Monitoring for Surface Water Bodies (SWB) carried out since 2013 (PIEP Report 2014) indicate that ecological status or potential of Mała Wełna SWB doesn't fulfil environmental goals due to physicochemical and biological elements classification.

By the Tennant's method favourable water-habitat conditions of water ecosystems and water-dependent ecosystems are created depending on multiannual mean flow. Environmental flow rate in Mała Wełna river in Kiszkowo cross-section in winter season (since October to March) was equal to $0.129 \text{ m}^3 \cdot \text{s}^{-1}$ and in summer season (since April to September) – $0.258 \text{ m}^3 \cdot \text{s}^{-1}$.

Recommended rates for environmental flow calculated by Tessman's method was $0.258 \text{ m}^3 \cdot \text{s}^{-1}$ since November to January and since May to September with respect to multiannual mean flow ($0.644 \text{ m}^3 \cdot \text{s}^{-1}$), while in February, March, April and October it reached 40% of multiannual monthly mean flow rates equal to: 0.347 ; 0.441 ; 0.413 ; $0.313 \text{ m}^3 \cdot \text{s}^{-1}$ (Table 2).

Environmental flow rate in Mała Wełna river at Kiszkowo cross-section, calculated with method based on flow duration curves for 70% cut-off level ($Q_{70\%}$) was equal to $0.24 \text{ m}^3 \cdot \text{s}^{-1}$ and for 90% cut-off level ($Q_{90\%}$) – $0.121 \text{ m}^3 \cdot \text{s}^{-1}$ (Fig. 4).

Table 2. Environmental flow volume in Mała Wełna river in Kizskowo cross-section calculated with Tessman's method

Tabela 2. Wartości przepływów środowiskowych rzeki Mała Wełna w profilu Kizskowo obliczonych metodą Tessmana

Month	Multiannual monthly mean flow [$\text{m}^3 \cdot \text{s}^{-1}$]	40% of multiannual monthly mean flow [$\text{m}^3 \cdot \text{s}^{-1}$]	Category	Recommended minimal monthly flow volume [$\text{m}^3 \cdot \text{s}^{-1}$]
November	0.343	0.137	SSQ _{mc} >0.4 SSQ	0.258
December	0.342	0.137		
January	0.418	0.167		
February	0.868	0.347	0.4 SSQ _{mc} >0.4 SSQ	0.347
March	1.103	0.441	0.4 SSQ _{mc} >0.4 SSQ	0.441
April	1.032	0.413	0.4 SSQ _{mc} >0.4 SSQ	0.413
May	0.620	0.248	SSQ _{mc} >0.4 SSQ	0.258
June	0.536	0.214		
July	0.561	0.224		
August	0.582	0.233		
September	0.556	0.222		
October	0.782	0.313	0.4 SSQ _{mc} >0.4 SSQ	0.313

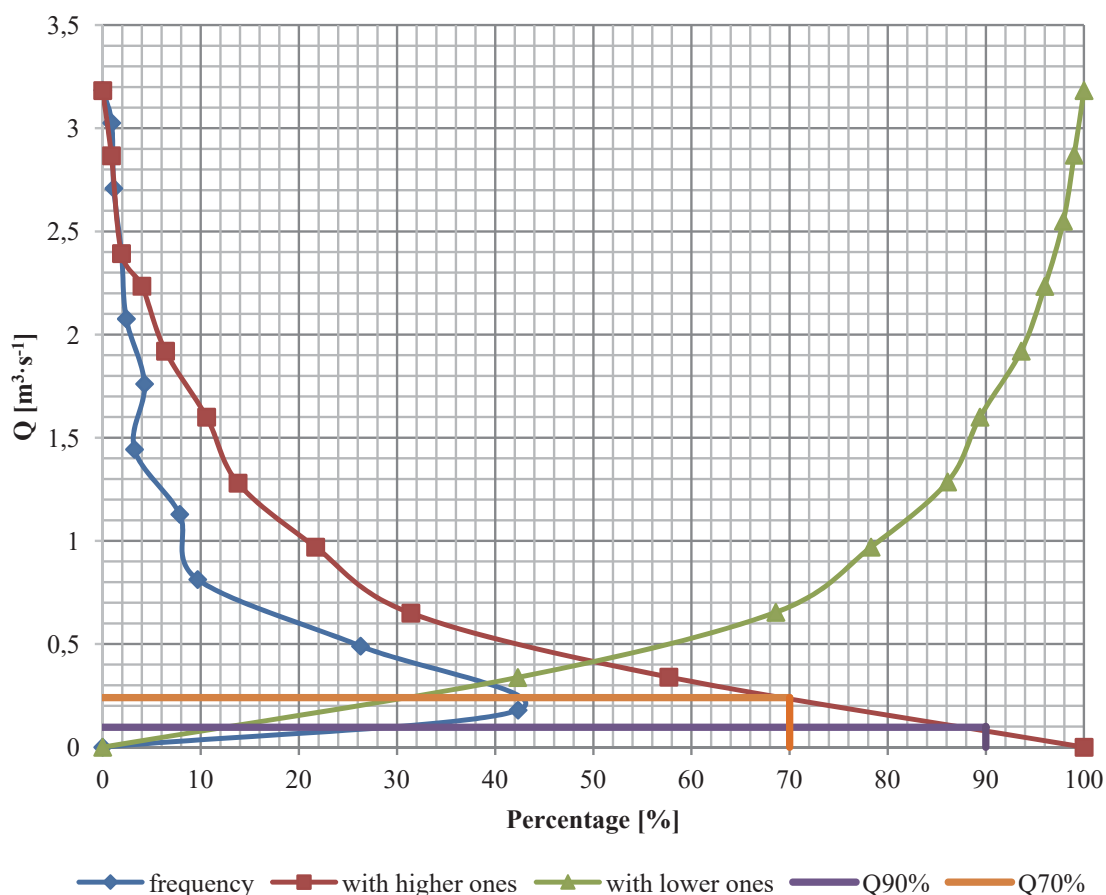


Fig. 4. Flow duration curves for Mała Wełna river at Kiskowo cross-section in 2000-2010 period

Rys. 4. Krzywa sum czasów trwania przepływów wraz z wyższymi i niższymi w latach 2000-2010 dla rzeki Małej Wełny w profilu Kiskowo

Environmental flow volumes calculated by the three methods were ranging from $0.121 \text{ m}^3 \cdot \text{s}^{-1}$ to $0.441 \text{ m}^3 \cdot \text{s}^{-1}$ (Fig. 5). The highest flow rates were obtained by the Tessman's method (Q_{Tessman}) which in March and April were equal $0.441 \text{ m}^3 \cdot \text{s}^{-1}$ and $0.413 \text{ m}^3 \cdot \text{s}^{-1}$ respectively and were three-times higher than instream flows ($0.121 \text{ m}^3 \cdot \text{s}^{-1}$) and two-times higher than in other months ($0.258 \text{ m}^3 \cdot \text{s}^{-1}$). Environmental flow rates calculated with Tennant's method (Q_{Tennant}) since October to March were equal $0.129 \text{ m}^3 \cdot \text{s}^{-1}$ and since April to September – $0.258 \text{ m}^3 \cdot \text{s}^{-1}$, which is even to Q_{Tessman} for 8 months. Whereas environmental flow volumes calculated with method based on flow duration curves for 90% cut-off level ($Q_{90\%}$) was $0.121 \text{ m}^3 \cdot \text{s}^{-1}$ which was equal the instream flow.

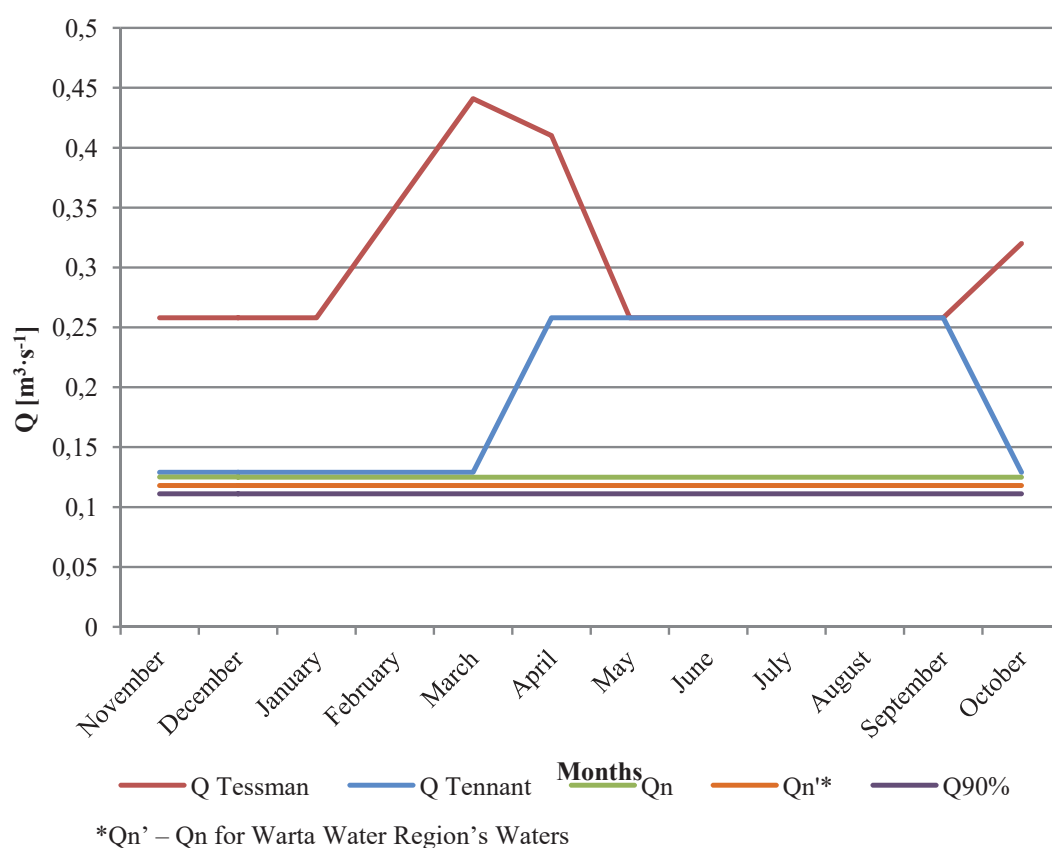


Fig. 5. Environmental and instream flow rates in Mała Wełna river at Kizskowo cross-section

Rys. 5. Zestawienie wartości przepływów środowiskowych i przepływu nienaruszalnego dla rzeki Małej Wełny w profilu Kizskowo

5. Summary

In order to achieve a good ecological status of water in rivers with disturbed hydrological regime and those which do not fulfil water quality environmental goals it is crucial to determine environmental flows in those rivers. Environmental flow rates in Mała Wełna river at Kizskowo cross-section calculated by the three following methods: Tennant's, Tesson's and method based on flow duration curves ($Q_{70\%}$ and $Q_{90\%}$) were ranging from $0.121 \text{ m}^3 \cdot \text{s}^{-1}$ to $0.441 \text{ m}^3 \cdot \text{s}^{-1}$. Results showed that it is necessary to develop a methodology for calculating environmental flows in cross-sections closing the SWB of flowing waters. According to data collected in diagnostic monitoring of rivers in 2010-2015 period approx. 75% of the SWB of flowing waters did not achieve good ecological status or potential.

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Przepływy środowiskowe rzeki nizinnej o zaburzonym reżimie hydrologicznym na przykładzie Małej Wełny

Streszczenie

W pracy, na podstawie obserwacji i pomiarów hydrologicznych, badań hydrochemicznych wody oraz struktury ichtiofauny rzeki Mała Wełna w okresie 2000-2010 określono przepływy charakterystyczne i umowne w tym hydrologiczne: przepływy nienaruszalne oraz przepływy środowiskowe. Wielkości przepływów nienaruszalnych określono według wymagań warunków korzystania z wód regionu wodnego Warty, zaś przepływów środowiskowych obliczono trzema metodami: Tennanta, Tessmana oraz metodą odcięcia poziomów 70% i 90% krzywej czasów trwania wraz z wyższymi. Przeprowadzona analiza wyników obliczeń wykazała, że natężenia przepływów środowiskowych były znacznie wyższe od obecnie wymaganych natężeń przepływów nienaruszalnych.

Abstract

This work presents the rates of characteristic and contractual flows of Mała Wełna river, including hydrological instream flows and environmental flows based on hydrological observations, hydro-chemical analyses and ichthyofauna structure accomplished in the years 2000-2010. The volume of instream flows were established according to requirements for the usage conditions of the Warta water region's waters, while environmental flows were calculated by three following methods: Tennant's, Tessman's and method based on flow duration curves ($Q_{70\%}$ and $Q_{90\%}$). Results showed that the environmental flow rates were significantly higher than currently required instream flow rates.

Słowa kluczowe:

rzeka nizinna, stan ekologiczny wód, przepływy środowiskowe

Keywords:

lowland river, ecological water status, environmental flows



Influence of Catchment Use on the Degree of River Water Pollution by Forms of Phosphorus

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1. Introduction

Contamination in surface waters is common, due to the tremendous human impact on the natural environment. Currently, it is very difficult to determine, what content of particular chemical compounds in water reservoirs can be considered as natural, therefore as contamination are considered substances in such quantities, in which they can potentially be a threat to ecosystems or humans. These are mostly soluble in water substances, organic or mineral origin, occurred in chemical compounds or less frequently in unbounded elements. Some of them undergo transformations in water and changes their chemical character or oxidation state (Ribeiro et al. 2014).

One of the most important element, which gets into the water, as a consequence of human activity is phosphorus (Palanisamy & Parthasarathy 2016). Phosphorus naturally occurs in mineral forms, mainly as apatites ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), but also as strengite ($\text{Fe}(\text{PO}_4)\cdot 2\text{H}_2\text{O}$) ($\text{Ca}_3(\text{PO}_4)_2$), vivianite ($\text{Fe}_3[\text{PO}_4]_2\cdot 8\text{H}_2\text{O}$) and berlinite (AlPO_4) (Pagliari et al. 2017). Those minerals are used as a source of phosphorus in fertilizers. Natural source of phosphorus in waters, is decomposition of organic matter and also erosion from minerals and soils. It occurs in living organisms cells, as an important component of nucleotides (compounds of phosphoric acid, nitrogen bases and carbohydrates: ribose and deoxyribose), which are main component of nucleic acids compounds as DNA and RNA. Another important nucleotide is adenosine triphosphate (ATP), the universal unit of intracellular energy transfer in living cells. It

is also occurred in vertebrate cells as tricalcium phosphate in about 60% of bone mass. It is natural part of proteins and in consequence of transformations of organic compounds, it circulates between living organisms and non-living matter (Mackey 2009).

Rivers as a specific type of surface waters, among the typical characteristics for watercourses, also have features which belong only to them. Water flow speed have influence on mixing water in whole river profile, on increasing erosion of soils through which the river flows and lower threat of eutrophication in comparison to lake waters. Rivers are also able to transfer contamination on long distances, especially those which are not reduced in self-cleaning processes ex. heavy metals (Zieliński & Jekatierynczuk-Rudczyk 2015, Krasowska & Banaszuk 2011).

The most important parameter influencing the increase of phosphorus amount in rivers is density of population. Human activities cause the increase of concentration of all forms of phosphorus in surface waters (including rivers), where they get into with wastewater, in which important source of phosphorus are detergents and other surfactants (Nedwell et al. 2002).

Surfactants which are used in detergents and other cleaning products, are the following source of phosphates in water. In detergents surfactants are used as extender to increase efficiency in binding divalent cations and to maintain proper pH. Phosphates in detergents usually occurs in the forms of: sodium triphosphate, sodium pyrophosphate, sodium silicate, sodium sulfate. Amount of surfactants could reach 15-20% of the mass of detergent, in particular cases even 50%. Currently, the amount of phosphates in surfactants is being reduced (UC 2002, 2003).

Nowadays the main source of phosphorus in surface waters is discharge of communal and industrial wastewater and elution from fertilizers (agriculture runoff) (Czechowska-Kosacka 2016). In domestic wastewater amount of phosphorus may occur 2-8 g/l, wherein human within a day excrete about 1.5 g of phosphorus. In fertilizers amount of phosphorus may be miscellaneous and it is assumed that average loss in fertilizing are 0.1-5%. Amount of phosphorus which is eluded from soils and goes to watercourses is about 0.05-1 mg/l. This amount may be higher, depending on amount and type of used fertilizer. The considerable amount of phosphorus may be contained in waters which flows through forested areas which can occur even 0.25 mg/l of phosphates.

Phosphates may occur in water in soluble or insoluble forms. Phosphorus occurs in water mainly as orthophosphates (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}). Surface waters occur also condensed forms of phosphorus – polyphosphates and metaphosphates which are created through connection of orthophosphates (Haygarth et al. 1998). Intensity of transformations of phosphorus compounds in water environment depends on many factors. The concentration of phosphorus is variable over time. The highest concentrations shall be observed in lower temperature seasons and insolation: winter, spring and autumn; the lowest in the season of most intense vegetation, which is summer. In summer the highest concentration of phosphorus is observed in the bottom area and sediments. In clear surface waters concentration of phosphorus is very low (Gomez et al. 1999, Kentzer 2001).

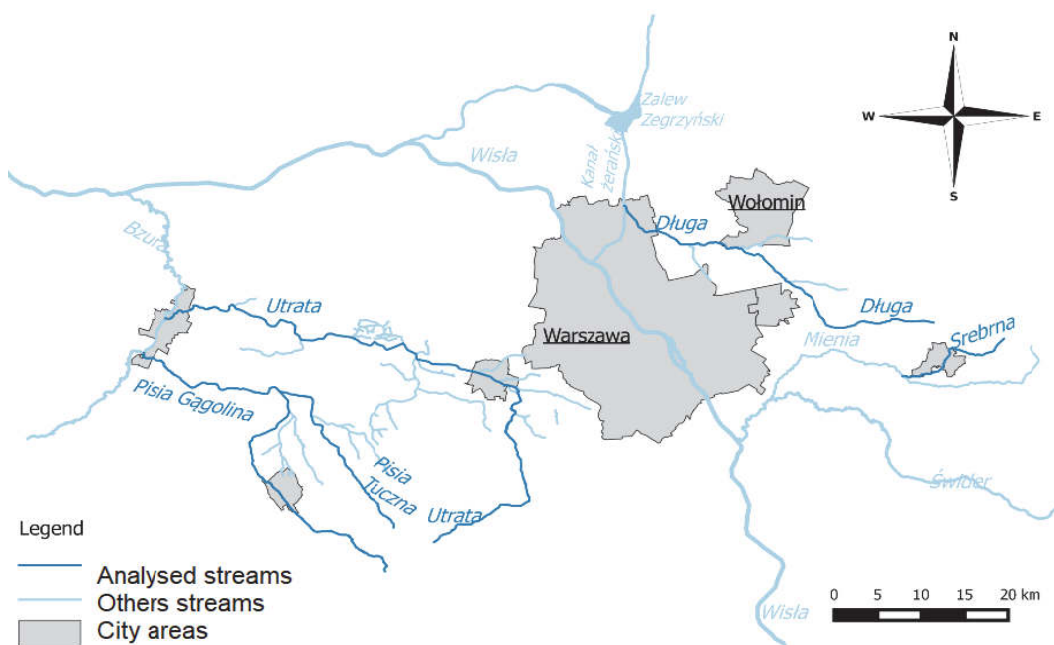
As a part of organic matter phosphates are important for development of living organisms, both terrestrial and aquatic. The deficiency of phosphorus shall be supplemented by correct fertilizing. It is observed to supplement phosphates to water to reduce its corrosivity and ability to precipitate iron and calcium salts. The excess of phosphorus carries a threat of eutrophication. In case, where relation of concentration of nitrogen and phosphorus is lower or equal to 14:1, the phosphorus is the factor which limits the growth of algae. That is why concentration of phosphorus is limited in surface waters. It is assumed that 1 mg of phosphorus which is introduced to environment, leads to growth of 100 mg of algae dry weight (Dodds & Smith 2015, Dojlido 1995).

Polish legal standards do not establish the limits of phosphates concentration in drinking water, however in treated wastewater limit is 1 mg P/l. For watercourses the limit of concentration of phosphates depends on water class and type of watercourse, and it fits between 0.005-0.065 mg P/l for class I water, 0.026-0.101 mg P/l for class II water (orthophosphates) and 0.03-0.2 mg P/l for class I and 0.14-0.4 for class II (total phosphorus). For standing waters the limits are mainly 10-times lower, which is caused by lower ability to self-cleaning and threat of eutrophication (Journal of Laws of 2014, Item 1800).

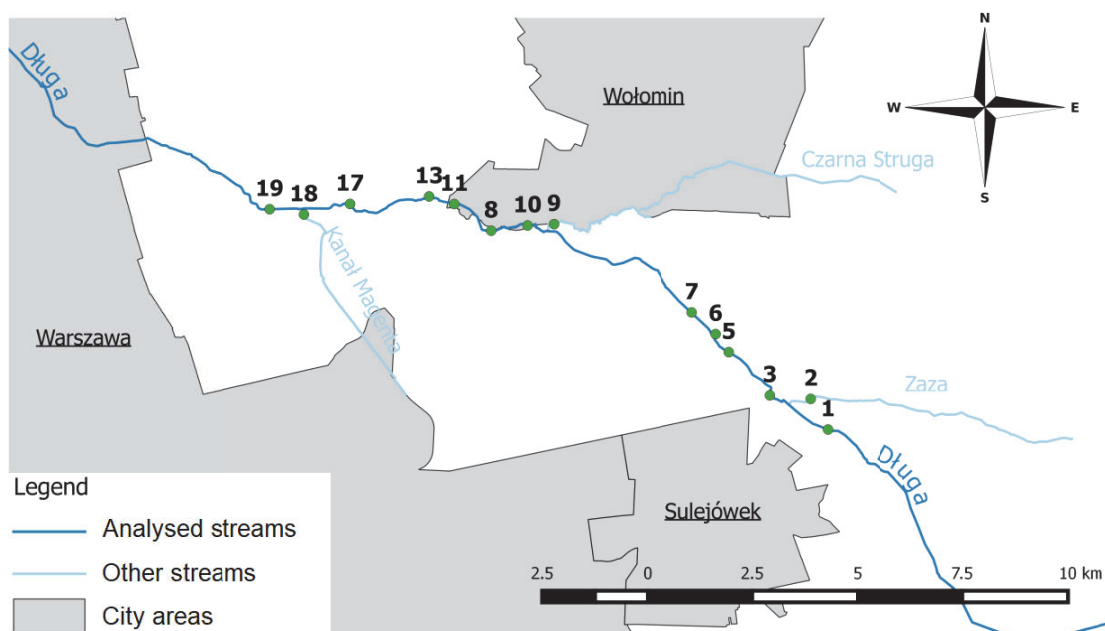
The aim of research was assessment of concentration of dissolved compounds of phosphorus and estimation of influence of municipal sewage treatment objects which are located in area of selected rivers on possibility of eutrophication process basing on concentrations of phosphorus forms.

2. Methodology and area of research

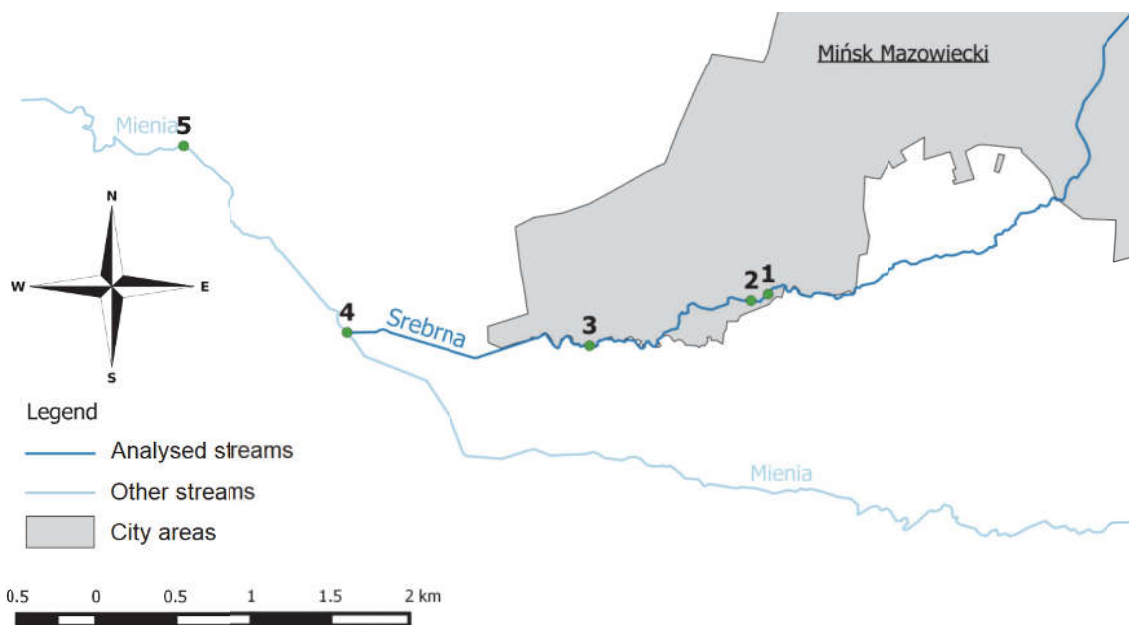
Research was conducted from May to July of 2016. As a part of research phosphorus forms were analyzed: total phosphorus without filtration after mineralization in acidic environment with the use of ammonium persulfate. All samples were taken from the depth of 20 cm. Total hydrolyzable phosphorus (P, hydro) – phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}, \text{etc.}]$. Dissolved Phosphorus (P-D)-all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size. Total Orthophosphate (P, ortho) – inorganic phosphorus $[PO_4^{3-}]$ in the sample as measured by the direct colorimetric analysis procedure. Total Organic Phosphorus (P, org) – phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. All forms after transformation into orthophosphates (P- PO_4^{3-}) were analyzed with the use of a spectrophotometric method (reaction involving with ammonium molybdate and tin(II) chloride) using Hach 4000 spectrophotometer.



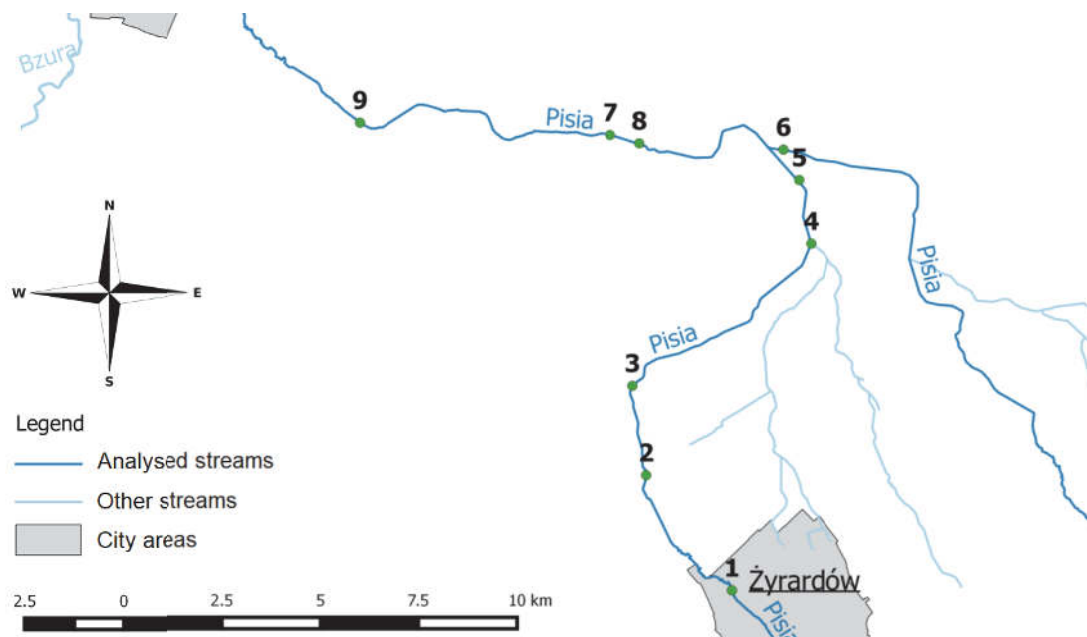
Rys. 1. Mapa sytuacyjna badanych obiektów
Fig. 1. Map of researched objects



Rys. 2. Punkty pomiarowe na rzece Długiej
Fig. 2. Points of research in the Długa river

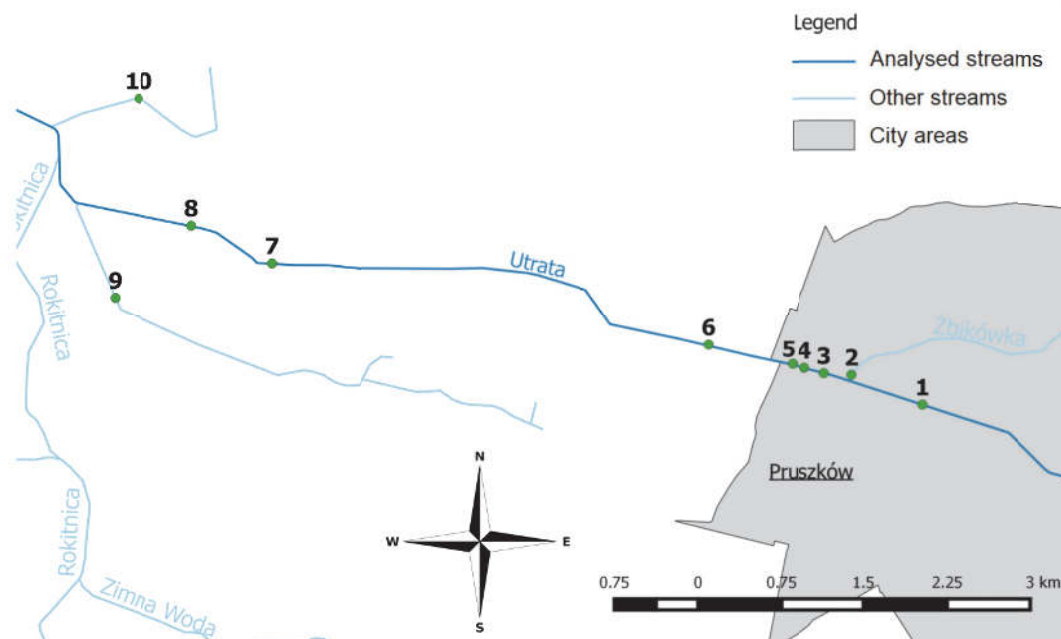


Rys. 3. Punkty pomiarowe na rzece Srebrnej
Fig. 3. Measurement points on Srebrna river



Rys. 4. Punkty pomiarowe na rzece Pisia Gąolina

Fig. 4. Measurement points on the Pisia Gąolina river



Rys. 5. Punkty pomiarowe na rzece Utracie

Fig. 5. Measurement points on the Utrata river

The results obtained were referred to the ordinance of the Minister of the Environment (Journal of Laws of 2016 position 1187) for the Single Parts of Surface Water (JCWP).

3. Characteristic of analyzed objects

To complete the subject of dissertation, four watercourses were selected. All of them are placed in the Masovian Voivodeship: Długa, Pisia Gągolina, Utrata rivers and Srebrna stream (Fig. 1). All of them have several common features. Those are lowland rivers, located near to Warsaw agglomeration. Długa and Srebrna have sources near to Mińsk Mazowiecki (city placed to the east from Warsaw). Pisia Gągolina and Utrata flow through districts on west from Warsaw and flows into Bzura near Sochaczew city. Sources of contamination in all river were mainly: disposal of wastewater from water treatment plants, leaks from septic tanks (damaged or intentionally leaked), surface runoff from agricultural areas and roads, landfill leachate. The ecological state of all watercourses, according to WIOŚ (Regional Inspectorate for Environmental Protection) monitoring was bad.

Długa – is lowland river about 50 km long. Source of river is located near to Mińsk Mazowiecki. Długa flows into Kanał Żerański. It is divided on two sections, classified to Single Parts of Surface Water: from source to Kanał Magenta and from Kanał Magenta to mouth. Upper section of the river is classified as natural, downer section as strongly changed. Upper section is classified by Regional Inspectorate for Environmental Protection as III class of biological elements, II class of hydromorphological elements, II class of physicochemical elements. Ecological state was classified as moderate, chemical state is below good. The general water condition is bad. Downer section meets the water requirements of IV class of biological elements, II class of physicochemical elements and II class of hydromorphological elements. The ecological potential of watercourse was low. Overall rating is bad state of water. Długa is the recipient of wastewater from the following objects: Przedsiębiorstwo Wodociągów i Kanalizacji Sp. z o.o. in Wołomin (“Krym” treatment plant), Miejski Zakład Wodociągów i Kanalizacji in Sulejówkę, Zakład Komunalny in Halinów, Wojskowa Agencja Mieszkaniowa Oddział Terenowy Nr 1 in Warsaw.

Srebrna – is a stream, which have a source near to Mińsk Mazowiecki and flows into Mienia river – located near this city. Total length of Srebrna is about 16 km. It is recipient of wastewater from treatment plant for Mińsk Mazowiecki. It is not classified as Single Part of Surface

Water, according to the Water Act (Journal of Laws of 2001 OJ L 115, Item 1229 with subsequent amendments). It means, that Srebrna is not classified by PMS (State Monitoring of Environment). Srebrna is recipient of wastewater from treatment plants in Minsk Mazowiecki, Barcząca and Janów.

Pisia Gągolina – source of Pisia is placed near to Mszczonów, the mouth is located in Sochaczew. The recipient is Bzura. Total length is about 58 km. The greatest tributary of Pisia Gągolina is Pisia Tuczná river, which flows into Pisia Gągolina about 13 km from mouth. Both rivers are classified as three natural parts of Single Parts of Surface Water: Pisia Gągolina from source to Okrzesza, Pisia Gągolina from Okrzesza to mouth and Pisia Tuczná. Regional Inspectorate for Environmental Protection classified Pisia Gągolina as IV class of biological elements, I class of hydromorphological elements, and physicochemical were evaluated as below good. The ecological state was bad, overall rating was bad. Pisia Tuczná meets the requirements which allows it, to be classified as III class of biological elements, I class of hydromorphological elements and II class of physicochemical elements. Ecological state was moderate. Overall rating was bad. The most important objects which discharge wastewater to Pisia are: Bakoma Sp. z o.o., Zakład Gospodarki Komunalnej in Żyrardów, Zakład Gospodarki Komunalnej i Mieszkaniowej Gminy Mszczonów in Mszczonów, Gminny Zakład Gospodarki Komunalnej in Teresin, City of Mszczonów (treatment plant in Grabce Józefpolskie), Zakład Wodociągów i Kanalizacji – Sochaczew Sp. z o.o.; Mars Polska.

Utrata – the river has its source near to Tarczyn and mouth near to Sochaczew (recipient is Bzura). Total length is about 76.5 km. It is divided on three segments classified as Single Part of Surface Water: from source to Żbikówka, from Żbikówka to Rokitnica and from Rokitnica to mouth. All three parts are classified as natural. According to Regional Inspectorate for Environmental Protection those segments were classified as IV class of biological elements, II class of hydromorphological elements and the physicochemical elements are below good. The most important objects which discharge wastewater into Utrata are: Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji w m. st. Warszawy S.A. in Warsaw, Zakład Wodociągów i Kanalizacji sp. z o.o., Grodzisk Mazowiecki, Zakład Wodociągów i Kanalizacji – Sochaczew Sp. z o.o., Miej-

skie Przedsiębiorstwo Wodociągów i Kanalizacji w Błoniu Sp. z o.o., Przedsiębiorstwo Gospodarki Wodno-Ściekowej GEA-NOVA Sp. z o. o., Przedsiębiorstwo Komunalne Nadarzyn sp. z o.o., Lesznawskie Przedsiębiorstwo Komunalne Sp. z o.o., Gminne Przedsiębiorstwo Komunalne "Eko-Raszyn" sp. z o.o., Mars Polska.

4. Results and discussion

4.1. Długa River

On the Długa river 19 points of collection of the water samples were selected (Fig. 2). Obtained results proved, that in all points of research on Długa river, the limits of total phosphorus for class I and II waters were exceeded. High range of results of total phosphorus (between 0.93 mg P/l and 8.11 mg P/l) may indicate a local contaminations which occur at single points. Average concentration of total phosphorus was 0.23 mg P/l.

In Długa waters, concentration of organic phosphorus and polyphosphates was dominant, especially in points 9 and 10, which were located near to mouth of Czarna Struga, the recipient of wastewater from treatment plants in Wołomin, and near to fish ponds in Ossowo. High concentration of organic phosphorus also may be caused by high influence of agriculture runoff. North segment of Długa, flows through farmlands area. Runoff from this area may be the reason of high concentration of organic phosphorus in the river.

According to Regional Inspectorate for Environmental Protection river monitoring data in 2013, on the river Długa average concentration of total phosphorus was 0.3 mg P/l in the segment from source to Kanał Magenta and 0.244 in the segment from Kanał Magenta to mouth. Concentration of orthophosphates occurred 0.074 in the segment from source to Kanał Magenta and 0.071 in the segment from Kanał Magenta to mouth. Analysis of researched segment of the river indicates, that from Kanał Magenta to mouth, are not any objects which may influence on increase of concentration of phosphates. The course of concentration of polyphosphates through the river on analyzed segment is also important: increases of polyphosphates concentration occur at single points and are reduced with the river course. Concentrations of orthophosphates are the lowest in points, which represent disposal of contamination and highest

in point which are located far from them. Average amount of orthophosphates occurred 50% of polyphosphates and 10% of total phosphorus (Fig. 6).

According to conducted research it may be concluded that Długa in the segment between Sulejówek and Rembertów does not meet the requirements of the Regulation of the Minister of Environment (Journal of Laws of 2016, Item 1187) for Single Part of Surface Water like lowland stream sandy (code 17). The level of eutrophication is very high. The reason of that state may be inflow of organic contamination from agricultural runoff and fish ponds and in lesser extent inflow of municipal wastewater.

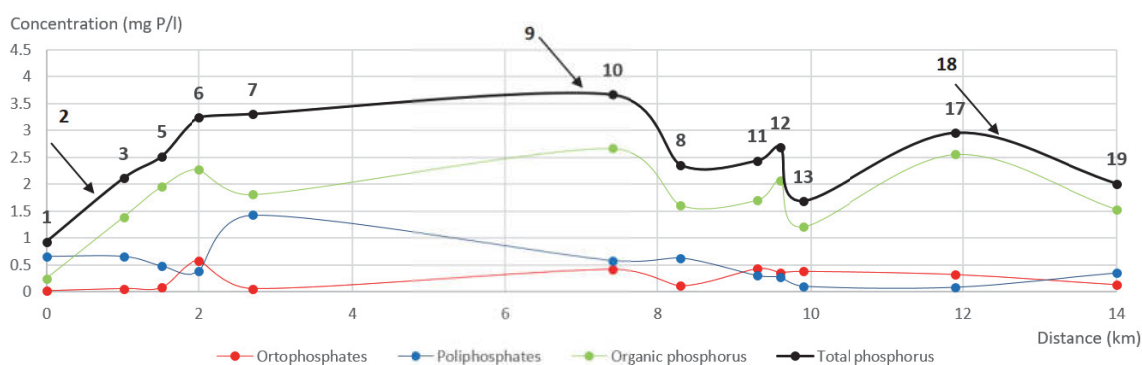


Fig. 6. Concentration of phosphorus forms in the Długa river

Rys. 6. Stężenie form fosforu w rzece Długa

4.2. Srebrna stream

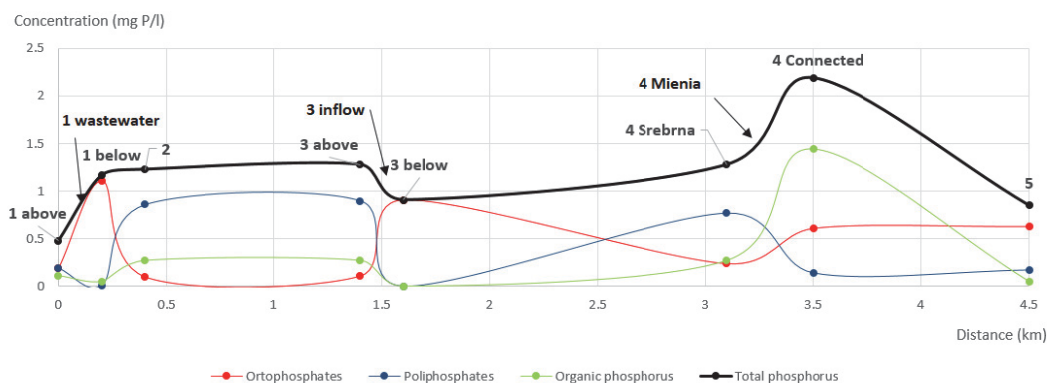
For Srebrna 5 points of research were selected. All of them were located on the down segment of the river (Fig. 3).

First point was located in the near to tributary of wastewater from local treatment plant, fifth point was located on the river Mienia, a few kilometers behind the mouth of Srebrna. Among the analyzed samples only one had concentration of total phosphorus below the limit and it was 0.16 mg P/l. The highest concentration of total phosphorus was noticed in point located at mouth of Srebrna – 2.19 mg P/l. Highest concentration was only in sample which was wastewater from treatment plant. The amount of ortophosphates was between 0.09 mg P/l and 1.11 mg P/l (Fig. 7).

The average results for all points indicate on high level of phosphate contamination of waters of Srebrna. The main identified source of phosphorus compounds was water treatment plant located on the south of

Mińsk Mazowiecki. Concentration of phosphate in wastewater is high and its influence on Srebrna is noticeable. Polyphosphates concentrations are highest in points which represent tributaries, organic phosphorus occur in single points – in wastewater from treatment plant and next points behind tributary. Beyond these point concentration of organic phosphorus is low, which may indicate on its fast mineralization to ortophosphates, especially in waters of Srebrna and Mienia.

Total phosphorus concentration near to its mouth is similar to contamination in near point of research at the Mienia. Two kilometers behind the Srebrna's mouth, concentration of phosphates reduces significantly. According to Regional's Inspectorate for Environmental Protection data in place of Mienia's mouth to Świder, concentration of orthophosphates occurred 0.084 mg P/l and total phosphorus occurred 0.259 mg/l.



Rys. 7. Stężenie form fosforu w rzece Srebrna

Fig. 7. Concentration of phosphorus forms in the stream Srebrna

The average share of three phosphorus forms (polyphosphates, organic phosphorus and orthophosphates) indicates the greatest share of orthophosphates and polyphosphates in most of research points, which allows to conclusion, that the main source of phosphates in Srebrna was wastewater from treatment plant.

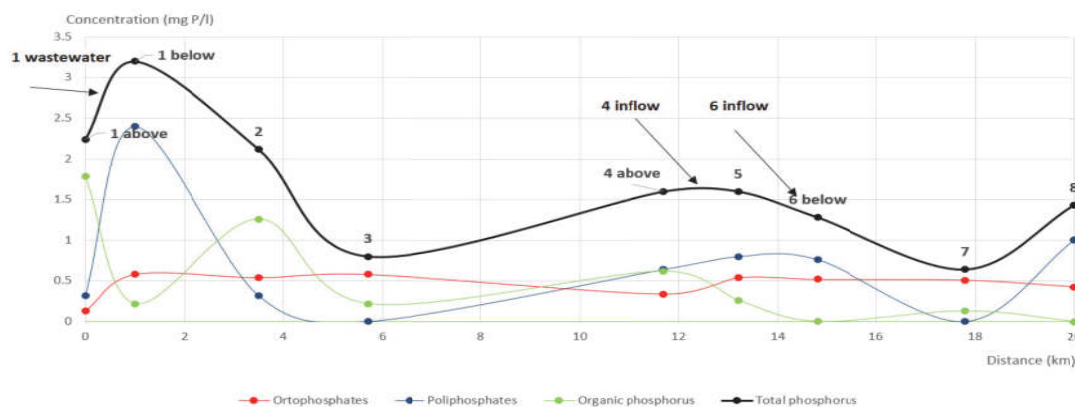
4.3. Pisia Gągolina River

Concentration of total phosphorus in samples from Pisia Gągolina was between 0.64 mg P/l to 3.2 mg P/l (Fig. 8) and that was over the limit established in the Regulation of the Minister of Environment (Journal of Laws of 2016, Item 1187). Average concentration was 1.6 mg P/l and the highest concentration was noticed in upper segment of river, near to

wastewater inflow from Żyrardów treatment plant (Fig. 4). Orthophosphate concentration on analyzed segment was between 0.13-0.58 mg P/l (average 0.45 mg P/l). The lowest concentrations was noticed in tributary from Żyrardów treatment plant. Average concentration of polyphosphates was 0.58 mg P/l. Concentration of polyphosphates was between 0.01 and 2.4 mg P/l. Concentration of organic phosphorus increased in single points, especially near to sources of contamination and reached to maximum concentration 2.02 mg P/l near to Żyrardów treatment plant.

According to Regional's Inspectorate for Environmental Protection data which were based on research point localized in Radziejowice (upper segment of Pisia Gągolina) average concentration of total phosphorus was 0.12 mg P/l and orthophosphates concentration was 0.06 mg P/l. That concentration do not exceed limits for class I waters. That point was localized beyond the segment analyzed in dissertation.

Provided data indicates, that on the analyzed segment of Pisia Gągolina, river was highly contaminated by phosphorus compounds and it results eutrophication of this river. Reason of that state may be influence of pollution from treatment plant in Żyrardów and Mszczonów and also agriculture runoff. Important source of contamination may also be industrial wastewater (in the area of Pisia there are 6 points of industrial wastewater tributaries).



Rys. 8. Stężenie form fosforu w rzece Pisia Gągolina

Fig. 8. Concentration of phosphorus forms in the Pisia Gągolina river

4.4. Utrata River

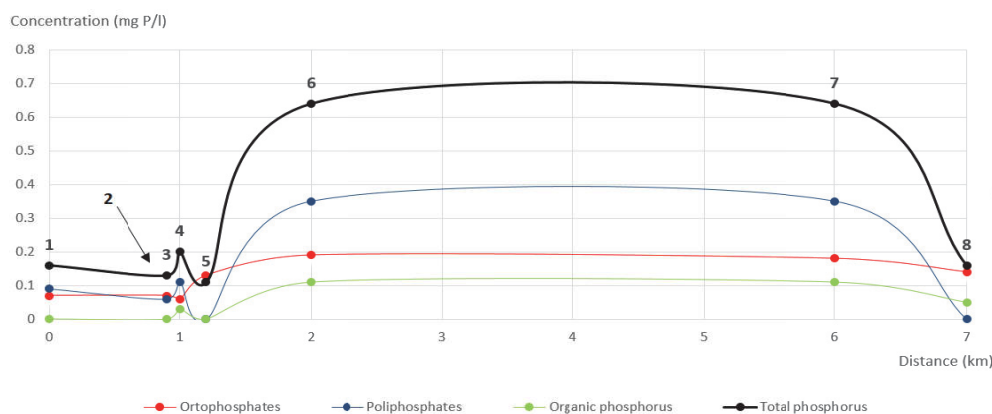
Analyzed segment of Utrata included points of research between south-east border of Pruszków and Rokitnica tributary (Fig. 5). In representative point of research according to Regional's Inspectorate for Environmental Protection data, which was located next to mentioned tributary, concentration of total phosphorus was 0.39 mg/l and concentration of orthophosphates was 0.127 mg P/l.

Conducted research proved that concentration of total phosphorus was between 0.16 and 0.8 mg P/l and orthophosphates was between 0.05 to 0.32 mg P/l. Highest concentrations of total phosphorus occurred in upper part of analyzed segment and the lowest near to the border of Pruszków (nearby to treatment plant).

Among the phosphates forms, in most points share of orthophosphates and polyphosphates was the highest in share of total phosphorus and their concentrations were similar. Organic phosphorus reached increased concentration in water from sample nr 10 and in the other points was small share of total phosphorus. Average share of total phosphorus in analyzed points was 0.38, which was amount very similar to Regional's Inspectorate for Environmental Protection data.

Reason of high concentration of phosphorus in Utrata may be agricultural runoff. The fact that concentration of orthophosphates through the analyzed segment is stable and concentration of polyphosphates and organic phosphorus is changing, is important.

Except the agriculture runoff, source of phosphorus may be industrial wastewater. Utrata was recipient of at least 9 industrial plants located in the area of river. Influence of municipal treatment plant in Pruszków was probably insignificant – concentration of phosphates near to the plant was the lowest.



Rys. 9. Stężenie form fosforu w rzece Utrata

Fig. 9. Concentration of phosphorus forms in the Utrata river

4.5. Discussion

Conducted research and data from Regional Inspectorate for Environmental Protection indicates on water states, which need improvement of concentration of phosphates forms:

- Share of particular forms of phosphorus depends on many factors, the most important of which is source of contamination.
- Source of organic phosphorus may be substances from decomposition of organic matter, mainly proteins.
- Condensed phosphates occurs as the result of wastewater inflow with surfactants containing phosphorus.
- Orthophosphates may occur as the result of leaching from soils or as the result of transformations of other phosphorus forms in water (mineralization, hydrolysis).
- The concentration of phosphates on small sections of rivers occurs in a wide range of values.
- In dissertation did not considered bottom sediments, which may be internal source of phosphates in water and may influence on concentration of phosphates among the river (Bartoszek & Koszelnik 2016).
- Municipal treatment objects have significant influence on water quality and contaminations from them may be transferred on long distances from source.
- Obtained results indicates high level of eutrophication in all analyzed rivers.

5. Conclusion

Among all the analyzed objects, the lowest concentrations of total phosphorus were noticed in the waters of Utrata – average 0.38 mg P/l, the highest in Długa – average 2.8 mg P/l. Average amount of orthophosphates was between 0.23 (Długa) and 0.45 mg P/l (Pisia Gągolina). According to conducted research, it may be concluded that all four watercourses are highly contaminated by phosphates. Identified sources of phosphates in analyzed objects were:

- Contamination from municipal wastewater treatment plants,
- Industrial wastewater from nearest industrial plants,
- Agricultural runoff,
- Organic contamination from fish ponds.

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Wpływ użytkowania zlewni na stopień zanieczyszczenia wód rzecznych formami fosforem

Streszczenie

Celem pracy było dokonanie analiza wpływu obiektów gospodarki wodno-ściekowej na jakość wody w wybranych rzekach poprzez ocenę stopnia eutrofizacji tych rzek. Zakres pracy obejmował analizę form fosforu: fosforu

ogólnego, ortofosforanów, polifosforanów oraz fosforu organicznego w wodach rzecznych. W celu realizacji zaplanowanych zadań, do badań wytypowano cztery ciek wodne, znajdujące się na terenie województwa mazowieckiego – rzeki: Długa, Pisia Gągolina i Utrata oraz struga Srebrna. Wszystkie cztery rzeki wykazują pewne cechy wspólne. Są to rzeki nizinne, przepływające w pobliżu aglomeracji warszawskiej. Długa i Srebrna mają swe źródło w pobliżu Mińska Mazowieckiego (miasto na wschód od Warszawy). Rzeki Pisia Gągolina i Utrata przepływają przez powiaty na wschód od Warszawy i obie uchodzą do Bzury w okolicach Sochaczewa. Źródła występujących zanieczyszczeń to przede wszystkim zrzuty ścieków z oczyszczalni, przecieki z nieszczelnych (uszkodzonych, bądź świadomie rozszczelnionych) zbiorników bezodpływowych, spływ powierzchniowy z terenów rolniczych oraz z dróg, odcieki ze składowisk odpadów. Stan ekologiczny wód, według monitoringu prowadzonego przez WIOŚ, dla wszystkich omawianych cieków jest zły. Przeprowadzone badania wykazały, że najmniejsze stężenia fosforu ogólnego odnotowano w wodach Utraty – średnio 0,38 mg P/l, natomiast największe w Długiej: średnio 2,8 mg P/l. Średnia zawartość ortofosforanów wynosiła od 0,23 mg P/l (rzeka Długa) do 0,45 mg P/l (rzeka Pisia-Gągolina). Na podstawie przeprowadzonej analizy można stwierdzić wysokie zanieczyszczenie fosforanami wody wszystkich czterech rzek. W trzech badanych ciekach, największy udział w odniesieniu do fosforu ogólnego stwierdzono dla ortofosforanów. W przypadku rzeki Długiej, przeważa zawartość fosforu organicznego (71%). Źródłem fosforu organicznego mogą być substancje pochodzące z rozkładu materii organicznej, głównie białek. Fosforany skondensowane występują na skutek dopływu do rzek ścieków komunalnych zawierających substancje powierzchniowo czynne, których składnikiem jest fosfor. Ortofosforany mogą pojawiać się na skutek wymywania fosforu z gleby lub na skutek zachodzących w wodach przemian związków fosforu, jak mineralizacja czy hydroliza. Stężenie fosforanów na niewielkich odcinkach rzek występuje w szerokim zakresie wartości. Ma to związek z dużym wpływem terenów rolniczych, stawów hodowlanych oraz odprowadzanych ścieków z oczyszczalni ścieków komunalnych. Obiekty gospodarki komunalnej mają znaczny wpływ na jakość wód, a zanieczyszczenia z nich pochodzące mogą być przenoszone na duże odległości od miejsca zrzutu ścieków. Ogólny stan jakości wód we wszystkich badanych rzek jest zły.

Abstract

The subject of dissertation was analysis of wastewater and sewage management on water quality in particular rivers by assessment of eutrophication level of those rivers. Scope of work concerned analysis of phosphorus forms: total phosphorus, orthophosphates, polyphosphates and organic phosphorus. To

complete the subject of dissertation, four watercourses were selected. All of them are placed in the Masovian Voivodeship: Długa, Pisia Gągolina, Utrata rivers and Srebrna stream. All of them have several common features. Those are lowland rivers, located near to Warsaw agglomeration. Długa and Srebrna have sources near to Mińsk Mazowiecki (city placed to the east from Warsaw). Pisia Gągolina and Utrata flow through districts on west from Warsaw and flows into Bzura near Sochaczew city. Sources of contamination in all river are mainly: disposal of wastewater from water treatment plants, leaks from septic tanks (damaged or intentionally leaked), surface runoff from agricultural areas and roads, landfill leachate. The ecological state of all watercourses, according to WIOŚ (Regional Inspectorate for Environmental Protection) monitoring is bad. Research showed that, the lowest concentration of total phosphorus was in the waters of Utrata (average 0.38 mg P/l), while the highest in Długa – average 2.8 mg P/l. Average concentration of orthophosphates was between 0.23 mg P/l (Długa) and 0.45 mg P/l (Pisia Gągolina). Basing on conducted analysis, it can be stated that phosphate contamination in all four watercourses is high, which leads to conclusion that eutrophication level is high. Reasons of that state can be caused by sewage disposals and agriculture. In three perennial streams (Długa, Pisia Gągolina and Srebrna), the highest share in total phosphorus concerned orthophosphates. It means, that phosphorus compounds in rivers are in some part subject to self-cleaning processes. In the case of Długa river, organic phosphorus is a main part of total phosphorus (71%). Source of organic phosphorus may be substances from decomposition of organic matter, mainly proteins. Condensed phosphates occurs as the result of wastewater inflow with surfactants containing phosphorus. Orthophosphates may occur as the result of leaching from soils or as the result of transformations of other phosphorus forms in water (mineralization, hydrolysis). Range of phosphates concentration occurs even on short segments of rivers. It is caused by strong influence of agriculture, breeding ponds and wastewater from treatment plants. Municipal treatment objects have strong influence on water quality and the contamination caused by them can be carried over long distances from place of sewage discharge. General state of water quality of all analyzed rivers, is bad.

Słowa kluczowe:

wody rzeczne, formy fosforu, eutryzacja, źródła zanieczyszczenia

Keywords:

river waters, forms of phosphorus, eutrycosis, sources of pollution



Research on Clogging of the Sand Filter

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1. Introduction

Rapid filtration with a fixed filter bed is the most commonly used process in drinking water treatment plants (Piekarski 2011, Janczukowicz 2013, Toczyłowska 2005, Skoczko 2016). One of the most commonly used types of filters are high-pressure filters. These devices are made as closed steel tanks with bottoms (Biedron 2013, Cheremisinoff & Ferrante 1995). The use of vertical pressure filters brings many benefits. Compared to rapid gravitational filters, their design helps to reduce the costs associated with pumping water after the filtration process, as they maintain the pressure given by the raw water supply pump (Spellman 2013). They also allow for higher filtration speeds compared to open filters (Piekarski 2011). However, the main disadvantage of pressure filters is that the operator cannot observe the state of the filter bed (Johnson 2009). The inconvenience can be eliminated when the filter has an automatic sensor that switches the filter off if the permissible turbidity of the purified water is exceeded. It is also difficult to assess the effectiveness of the rinsing process (Skoczko 2011, Kumar & Singh 2006). Maintenance work is also difficult.

Filter clogging has been the subject of many studies over the years. Many theories describing the technological process of filtration arose with time. Hendricks (2016) states that the formulated filtration theories were aimed at describing variables, developing mathematical models that describe the filtration process and the explanation of the mechanism of removing particles during depth filtration. Historically, the first experimental work on the filtration mechanism appeared in the

Ph.D. thesis of Eliassen completed in 1935 at MIT (Massachusetts Institute of Technology). Subsequent studies were conducted by Stein (1940), Stanley (1955) and Ives (1962). The first issues regarding the filtration theory in the aspect of mathematical modeling were formulated by Iwasaki in 1937, while in 1962 Ives based on Iwasaki's experiments used the results of research to create a mathematical model (Hsiung 1967). In 1977, the first results of the experiments of two Israeli researchers – M. E. Rebun and A. Adin were published. Adin and Rebhun (1977, 1978, 1979) describe that the intensity of total suspended solids retention during filtration process is variable per unit of time. Initially, there is an increase to the set maximum value, then there is a decrease to zero value due to clogging of the deposit. In the initial period of the filtration cycle, total suspended solids are retained in the upper layers of the filter bed, while after their saturation, penetration into the deeper layers occurs. An increase in the concentration of pollutants also causes an increase in pressure losses.

In view of the above, experimental work has been undertaken to check the efficiency of water filtration on the sand bed in a modern model filtration column at different flow rates and at different column heights on a semi-technical scale.

2. Material and methods

Tap water was used for research works. Water was prepared by preliminary de-chlorination and subsequent dosage of iron (III) sulfate (VI), aluminum sulfate (VI), aluminum chloride, and loam containing 30% clay fraction, a minimum of 40% of the total silty, sandy and quartz fraction and 30% colloidal fraction. The solution was mixed quickly, followed by slow stirring for 30 minutes until flocs were formed. Prepared total suspended solids was introduced into a 180 liter water-filled tank and then directed to the filter bed and the filtration effect was observed. Total suspended solids concentration was about 1 g/dm^3 , what let observe clogging process, water color – about 400 mg Pt/dm^3 and turbidity 65 NTU.

The tests were carried out at the CE 582 GUNT water treatment station (Figure 1 and 2).

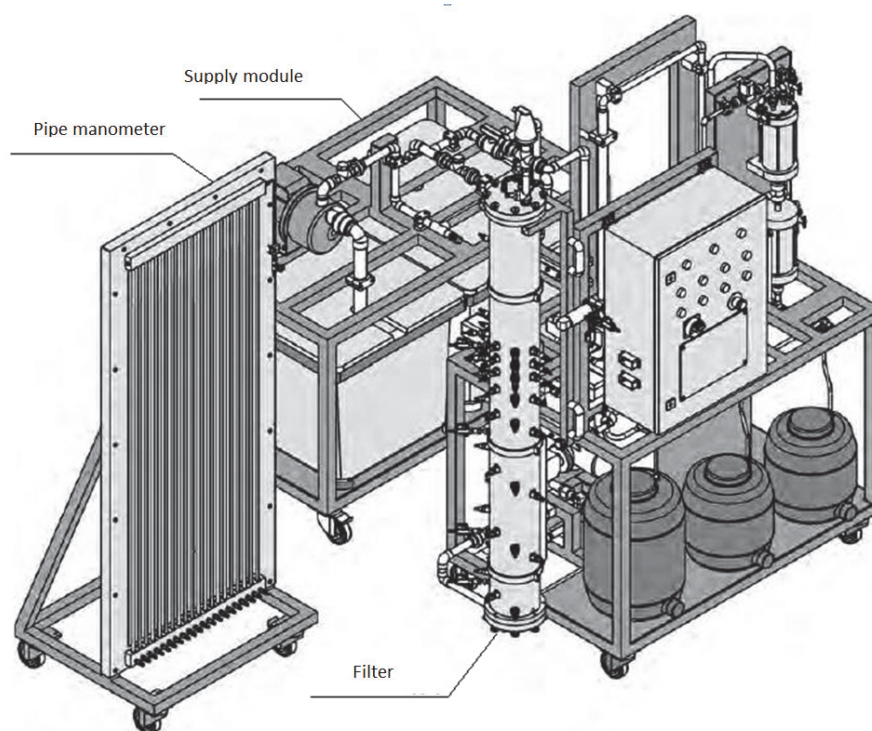


Fig. 1. Main elements of research stand CE 585

Rys. 1. Główne elementy stanowiska badawczego CE 582

The most important part of the model was a filtration column with dimensions: external diameter \varnothing : 164 mm, internal diameter \varnothing : 150 mm, height: 1610 mm.

The research involved filtration at a specific speed of the amount of prepared raw water, which allowed to observe changes in filtrate quality and sampling from various depths of the deposit (Table 1). Clogging of the filter was observed with different volume of water 1,2, and 3 m³ filtrated through the filter. During the filtration at a given speed, a series of samples were taken after filtering each subsequent cubic meter of prepared water. After each completed filtration step, the filtration bed was washed, and filtration was started at a different speed. In the samples taken, parameters were determined such as pH, conductivity, color, turbidity and total suspended solids. The test was carried out for the following filtration rates: 10, 15, 20, 25, 30 and 35 m/h.

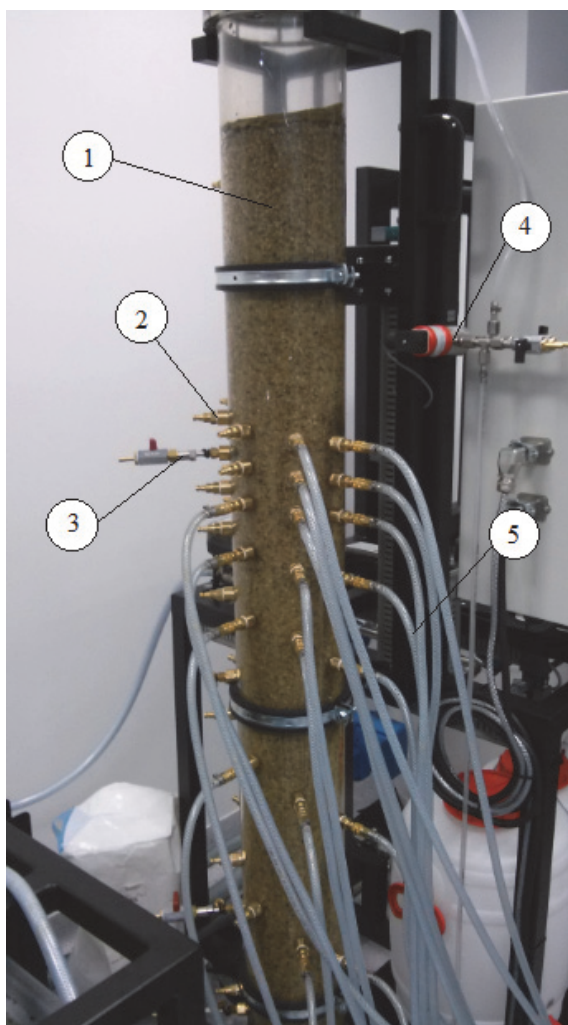


Fig. 2. Sand filter – view: 1 – filter column, 2 – pressure measurement terminal, 3 – water intake terminal, 4 – pressure sensor, 5 – flexible cable joining pipe-manometer

Rys. 2. Widok na filtr piaskowy: 1 – kolumna filtracyjna, 2 – przyłącza do pomiaru ciśnienia, 3 – przyłącze do poboru próbek, 4 – czujnik ciśnienia, 5 – przewody elastyczne łączące manometr rurkowy

Table 1. Depths where were pollution indicators measured

Tabela 1. Głębokości, na których prowadzono pomiary wskaźników zanieczyszczeń

Measurement Point	Filter depth from the surface (cm)
1	43
2	77
3	117
4	137

3. Results and discussion

As part of the research work, filtration of contaminated water was carried out on the GUNT research model with six different speeds. During the filtration at a given speed, a series of samples were taken from various depths of the bed after filtering each subsequent cubic meter of prepared water. The obtained results are shown in Figures 3, 4 and 5.

The pH tests for each of the measured series at each speed showed very slight increase in the pH in relation to the value determined for the prepared raw water. The minimum parameter value was 6.38, while the maximum 6.76. The average value for all measurement series was 6.52 and the standard deviation 0.078. In general, it can be concluded that the pH of water in each series was neutral with a slight predominance of hydrogen ions. Conductivity tests showed that the minimum value of this parameter was 0.39 $\mu\text{S}/\text{cm}$, the maximum 0.57 $\mu\text{S}/\text{cm}$, average – about 0.51 $\mu\text{S}/\text{cm}$, while the standard deviation – 0.02 $\mu\text{S}/\text{cm}$. Very small dispersion of results was observed both in the case of pH and conductivity in relation to the average.

Figures 3a, 3b and 3c present a comparison of color test results for various filter bed depths and tested filtration speeds after filtration of a given volume of raw water – 1 m^3 , 2 m^3 and 3 m^3 , respectively.

At the early stage of the filtration cycle, i.e. after filtration of 1 m^3 of prepared water, the highest color removal efficiency of 77% was recorded for the lowest tested speed of 10 m/h. As the filtration speed increased, the cleaning effect decreased. It was respectively 65% for 15 m/h, 46% for 20 m/h, 29% for 25 m/h, 34% for 30 m/h and only 25% for 35 m/h. The color value of water decreased in a very even manner along the filter bed for the lowest speeds. In the case of higher speeds, e.g. 35 and 25 m/h, the low removal efficiency of the bed layers at the depth of 77-137 cm was visible. In the later stage, after filtering 2 m^3 of water, the highest color removal efficiency – 69% was noted for speeds of 15 m/h and 10 m/h. The lowest effect was noted for the highest filtration speeds in the range of 23-25%. After filtration of 3 m^3 of raw water, the highest color removal efficiency was recorded at a speed of 10 m/h, equal to 62%, while the weakest efficiency was 14% for the filtration speed of 35 m/h. Along with the increase in the volume of filtered water, the efficiency of purification decreased in the case of the vast majority

of measurement series carried out for the tested speeds. The tests after filtration successively 2 m^3 and 3 m^3 show a tendency of decreasing the efficiency of removing the water color in the upper layers of the filter bed, which has an impact on the decrease of the overall purification efficiency.

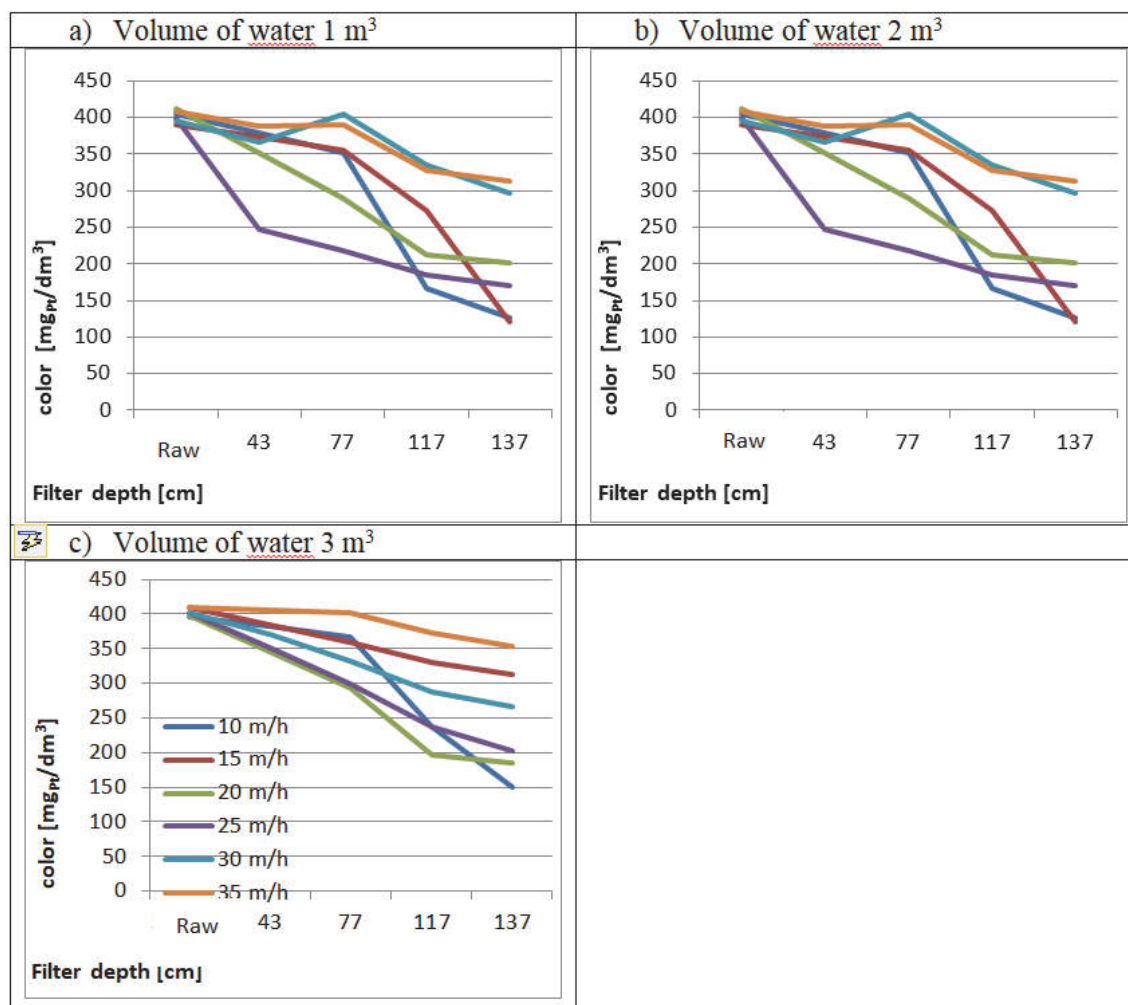


Fig. 3. Water color changes along filtration column for different filtration speeds

Rys. 3. Zmiany wartości barwy wzdłuż złoża dla poszczególnych prędkości filtracji

Figures 4a, 4b and 4c present a comparison of turbidity test results for various filter bed depths and tested filtration speeds after filtering a given volume of raw water – 1 m³, 2 m³ and 3 m³, respectively.

After filtering 1 m³ of raw water, the highest turbidity removal efficiency of approximately 82% was recorded for the lowest tested speed of 10 m/h. It can be assumed that with the increase of filtration speed, the efficiency of the parameter removal decreased. They were respectively 71% for 15 m/h, 54% for 20 m/h, 32% for 25 m/h, 47% for 30 m/h and only 29% for 35 m/h. After filtering 2 m³ of raw water, the highest cleaning efficiency of approximately 78% was obtained again for the filtration speed of 10 m/h. The lowest one was recorded for the highest filtration speeds, i.e. 26% for 30 m/h and 29% for 35 m/h. The comparable efficiency of turbidity removal in the range of 40-60% was obtained for speeds of 15 m/h, 20 m/h and 25 m/h. At the final stage of the filtration cycle, the highest turbidity removal efficiency of approximately 73% was obtained at a speed of 10 m/h. The low effect was still obtained at the highest speeds – 34% for 35 m/h and 28% for 30 m/h. It can be noticed that the removal of water color and turbidity proceeded with a similar tendency on the filter bed under test. The efficiency of turbidity removal decreased as the volume of filtered water increased. In the final stage of filtration, a decrease in the efficiency of turbidity removal in the upper bed layers was observed for the majority of tested speeds, while the largest reduction in the parameter was recorded in the 77-137 cm depth range.

Figures 5a, 5b and 5c present comparison of the results of the total suspended solids testing for various depths of the filter bed and tested filtration speeds after filtration of a given volume of raw water – 1 m³, 2 m³ and 3 m³, respectively.

The results from total suspended solids tests show that as the volume of filtered water increased, the effect of water purification did not change significantly. There was also no significant change in the efficiency of total suspended solids removal with the change of filtration speed. In the case of the vast majority of measurement series in the upper layer of the filter bed (in the range of 0-43 cm depth), the efficiency of removing the parameter equal to 50% was obtained. In the case of majority of measurement series, the effectiveness of the total suspended solids removal in the range of 75-100% was found.

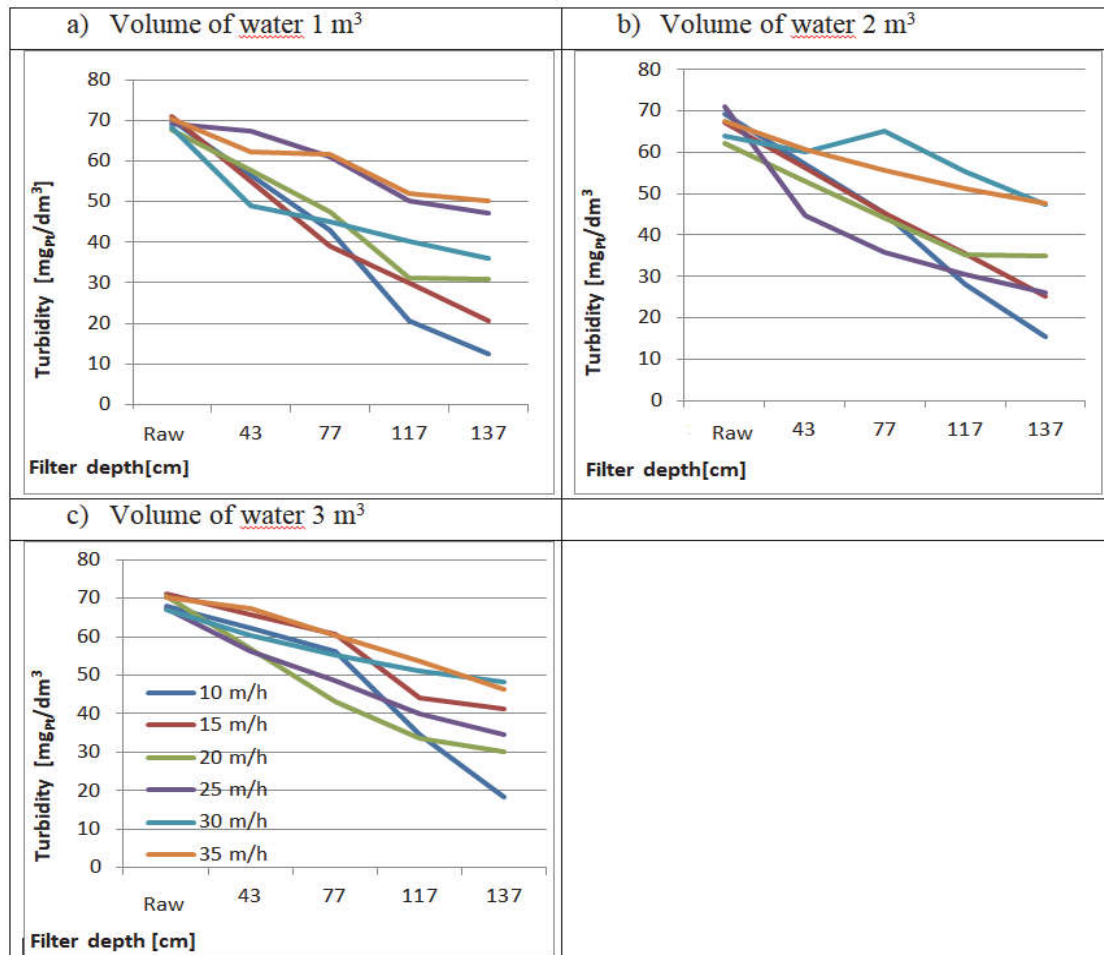


Fig. 4. Water turbidity changes along filtration column for different filtration speeds

Rys. 4. Zmiany wartości mętności wzdłuż złoża dla poszczególnych prędkości filtracji

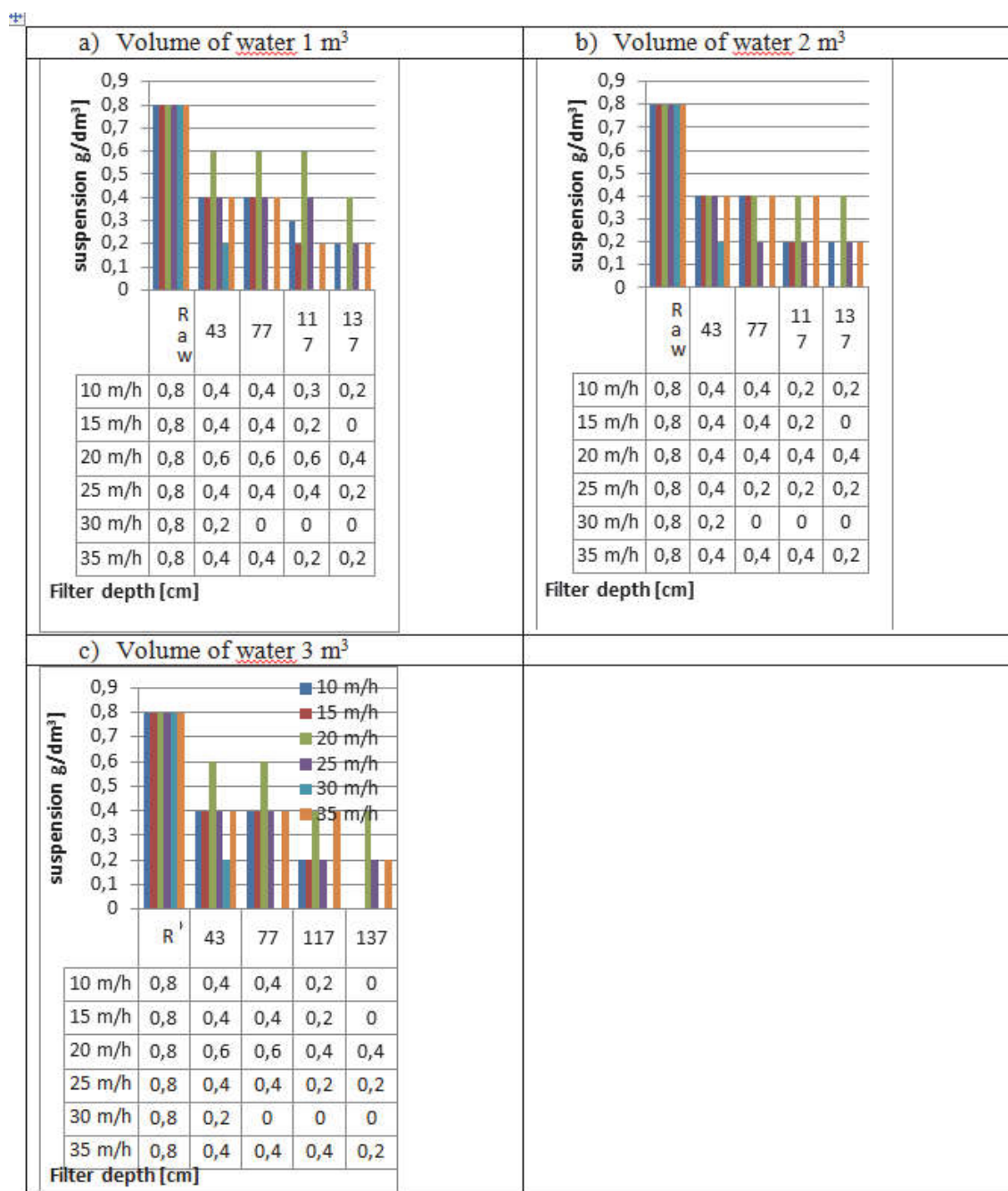


Fig. 5. Total suspended solids changes along filtration column for different filtration speed

Rys. 5. Zmiany wartości zawiesiny ogólnej wzdłuż złoża dla poszczególnych prędkości filtracji

Similar research was carried out by Eliassen (1941), who conducted filtration of prepared water on a bed of 60 cm depth and grain granulation of 0.46 mm. The filtration was performed at one constant speed of 4.88 m/h. Results of testing the total suspended solids in the time range of 9-120 h for different depths of the bed were recorded. At the earliest recorded filtration stage (after 9 hours), the filtration efficiency was 90%. With the passage of filtration time, the efficiency of removing the parameter decreased. In the final stage of filtration, after 119 hours, the efficiency decreased to 66%. Movement of the filtration front was also noticeable. In the initial stage, the largest parameter reduction took place in the top layers of the bed, while saturation of the upper layers of the bed occurred with time. In the final stage of filtration, after 119 hours at the deposit depths of the 0-10 cm, there was a saturation zone and very low efficiency of parameter reduction was noted in these layers. Research conducted within the framework of this study covered a similar time range of 12-120 h, with the efficiency of water treatment depending on the volume of filtered water and not on the working time of the bed. It should be clearly stated that the tested GUNT filtration model allowed for filtration studies on a semi-technical scale using such filtration rates that are used on real plants of the treatment station. The shifting of the clogging top was observed for all the contamination indicators measured. The conducted research allowed to notice that the clogging of the deposit for color, turbidity and total suspended solids did not occur at the same depth of the deposit. Own research coincided with the research by Eliassen when observing the clogging top only for turbidity, while in the case of color and total suspended solids, they differed significantly.

Ives (1962) also performed filtration tests for the removal of total suspended solids. It carried out filtration of prepared raw water on a 60 cm deep bed and granulation of 0.54 mm grains. The filtration was conducted at 4.88 m/h. Samples were taken from various depths of the bed. The tests were carried out for a period of 24 hours. In the earliest recorded stage, after 20 minutes of filtration process, the efficiency of removing the total suspended solids close to 100% was obtained already at a depth of 30 cm. In the early stages of the filtration process, from 20 min to 4 hours, the efficiency of removing the total suspended solids in the upper bed layers was recorded, while after about 5 hours, gradual saturation of the upper bed layers associated with deterioration of the total suspended solids re-

removal efficiency in these layers, was noted. After 24 hours, in the final stage of testing, the saturation zone reached a depth of 20 cm. Like Eliassen, Ives conducted filtration at low speeds and low bed heights that deviated significantly from real conditions. In addition, Ives' studies included a short period of time compared to the studies described in this paper. The obtained results of the total suspended solids as well as in the case of studies by Eliassen and Ives indicate that 50% reduction in the parameter in the case of majority of measurement series was obtained in the top layers of the deposit. However, there was no significant change in the effectiveness of total suspended solids removal over time. Deterioration of removal efficiency was noticeable in the final stages of testing for parameters such as color and turbidity, which may indicate saturation of these layers due to the accumulation of contaminants.

Based on our own research, it can be assumed that the most satisfactory results of all tested parameters were obtained for the lowest filtration speed of 10 m/h. Regarding the results of the studies by Eliassen and Ives and the conclusions formulated by Ives regarding the grain diameter, it can be assumed that an improvement in filtration efficiency could be obtained by using a bed with smaller grain diameter. However, in real conditions, during the filtration process, due to the accumulation of impurities in the bed and the increase in the concentration of suspended matter on the grain surface, there is a gradual increase in the equivalent diameter and at the same time, reduction in porosity and change in the specific surface area (Grabarczyk 2010). Over the years, attempts have been made to define methods for describing the course of filtration process, and no comprehensive answer has been provided so far, which would explain the method of filtration media clogging. In the case of commonly used filtration rates, phenomena such as dispersion and changes in the concentration of suspended matter inside the pores are negligible. Modern filtration models (like GUNT used in own research) contradict this. In the case of grains with larger diameter, a lower filtration coefficient is obtained, and thus a lower efficiency of contamination reduction. The efficiency of removing the contaminants is directly related to the flow rate. It follows that the smaller the granulation of deposit, the faster the clogging, while the time of the filtration cycle is shortened.

4. Conclusions

- The highest efficiency of total suspended solids, turbidity and color removal was obtained for the lowest tested filtration speed of 10 m/h, while the lowest efficiency was recorded for higher speeds of 30 m/h and 35 m/h.
- Along with the increase in the volume of water filtered through the bed, there was a decrease in the efficiency of color and turbidity removal in the upper filtration layers in the range of 0-43 cm depth, which may indicate their saturation with impurities. The decrease in the efficiency of removal in these layers had an effect on reducing the overall efficiency of color and turbidity removal.
- The breakthrough of the tested deposit occurred after 30 hours of prepared water filtration. The drop in the efficiency of purification on the filter bed was around 50%.

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Badania kolmatacji złoża piaskowego

Streszczenie

Jednym z podstawowych i powszechnie stosowanych procesów uzdatniania wody jest proces filtracji. Rozwój wiedzy na temat tego procesu ma swoje korzenie na przełomie lat trzydziestych oraz czterdziestych ubiegłego wieku. Do dnia dzisiejszego prowadzone są wciąż badania w zakresie filtracji przez wielu naukowców na całym świecie. Obecnie projektowanie filtrów do uzdatniania wody odbywa się na podstawie niezmiennego zbioru wytycznych. W związku z tym zasadne wydają się badania nad kolmatacją procesu filtracji, gdyż mają one wpływ na bardziej racjonalne projektowanie filtrów.

Celem niniejszej pracy było zbadanie kinetyki kolmatacji procesu filtracji wybranego złoża piaskowego. Realizowane eksperymenty polegały na filtracji przygotowanej wody ze zmiennymi prędkościami: 10, 15, 20, 25, 30, 35 m/h. Na podstawie przeprowadzonych obserwacji stwierdzono, iż efektywność usuwania zanieczyszczeń jest bezpośrednio związana z szybkością filtracji i ilością przefiltrowanej wody. Wraz ze wzrostem objętości przefiltrowanej wody przez złożo odnotowano spadek efektywności usuwania barwy oraz mętności w wierzchnich warstwach filtracyjnych w zakresie głębokości 0-43 cm. Spadek efektywności oczyszczania w tych warstwach miał wpływ na obniżenie ogólnej efektywności usuwania barwy oraz mętności. Wynika z tego, iż im mniejsza granulacja złoża w górnej warstwie, tym szybsza kolmatacja i krótszy czas cyklu filtracyjnego.

Abstract

Filtration is one of the basic and commonly used process of water treatment filtration process. The development of knowledge about this process has its roots at the turn of the thirties and forties of the last century. To this day, there are still conducted research in the field of filtration by many scientists around the world. Currently, the design of water treatment filters is based on a set of guidelines. Therefore, studies on the clogging of the filtration process, seem to be important, as they affect the more rational filter design.

The aim of this work was to investigate the kinetics of the clogging of the filtration process for the selected sand bed. Carried out experiments consisted in filtration of the prepared water with variable speeds: 10, 15, 20, 25, 30, 35 m/h. Based on the observations, it was found that the efficiency of impurities removing is directly related to the rate of filtration and the amount of filtered water. With the increase of the filtered water volume of through the bed, there was a decrease in the efficiency of color and turbidity removing in the upper filter layers in the depth range of 0-43 cm. The decrease in the efficiency of purification in these layers resulted in efficiency of removing color and turbidity. It follows that the smaller the granulation of the bed in the upper layer, the faster the clogging and the shorter filtration cycle time.

Słowa kluczowe:

filtracja, kolmatacja, oczyszczanie wody

Keywords:

filtration, clogging, water treatment



The Organization of Municipal Waste Collection: the Decision Model

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1. Introduction

The organization of municipal waste collection is defined as designating the routes of vehicles which collect the waste. The vehicle routing problem referring to the municipal plants is an issue widely discussed in the literature (Jacyna-Gołda et al. 2017a, Izdebski 2014, Beliën et al. 2014). Solving the routing vehicle problem in the municipal plant one should take into account various aspects, including network structure (e.g. location of municipal plant, location of the points generated the waste) and form of relationships of objects in the network (e.g. constraints of waste collection). The vehicle routing problem is a key step in transport network design. The network is defined as a set of elements: inhabitants, plants linked to each other by the flow of the waste. Depending on the number of intermediaries in the way of movement of the waste, the network structure can be single-level (e.g. levels: a municipal plant – single loading points e.g. a hospital – a municipal plant) or multi-level (levels: a municipal plant – inhabitants – a municipal plant), so-called hierarchical. In the single-level network a vehicle collects the waste from one place and goes to the municipal plant, in the multi-level network a vehicle collects the waste from many places, e.g. inhabitants and goes to the municipal plant.

The municipal waste collection may be considered from two basic viewpoints, i.e. the single or multi-criteria decision making problem. The municipal waste collection in the single-decision making problem was solved by an ant algorithm (Bautista et al. 2014, Izdebski 2014), a genetic

algorithm (Izdebski 2014, Jacyna-Gołda et al. 2017b). In this case the main criterion is a transportation cost.

In this paper the organization of municipal waste collection was presented in the context of the multi-criteria decision making problem (Jacyna 1999). In the literature the multi-criteria municipal waste collection problem was solved by Technique for Order Preference by Similarity to Ideal Solution (TOPSIS), Preference Ranking Organization Method for Enrichment Evaluations (PROMETHEE) I and PROMETHEE II (Coban et al. 2018, Soltani et al. 2015, Mardania et al. 2015, Rousis et al. 2008), ELECTRE III (Perkoulidis et al. 2010, Banar et al. 2010, Soltani et al. 2015), a modified fuzzy TOPSIS methodology (Ekmekcioglu et al. 2010, Soltani et al. 2015), a TOPISIS method (Mir et al. 2016, Soltani et al. 2015). In this case the main criteria are transportation cost, operation cost, environmental risks, emissions to environment, infrastructure requirements. The decision model in these publication refers to the multi-criteria assessment. Among many variants the one variant is selected according to the adapted weight for each criterion.

In this paper the decision model of the organization of municipal waste collection bases on multi-criteria optimization. In this case the optimization algorithm was an ant algorithm. This algorithm was specially modified in order to solve multi-criteria decision making problem. The authors of this publication did not find the application of this approach and this algorithm in the literature to designate the organization of municipal waste collection.

The organization of municipal waste collection is a complex decision making problem and refers to the salesman problem (Izdebski 2014). The salesman problem belongs to NP-hard problems. In order to solve the salesman problem the heuristic algorithm must be used (Abdoun 2011, Nagata et al. 2013, Szczepański et al. 2014, Jacyna-Gołda 2015, Jacyna-Gołda et al. 2016). Fast time of generating the result by the ant algorithm is its main feature, what is desired in the process of designating the organization of municipal waste collection. This process depends on many factors, e.g. capacity of vehicles, the size of the tasks. The algorithm for designating this type of problem must be adapted to frequent changes of these factors and generate the solutions in a quick way. In municipal companies the time of generating the solution by the algorithm plays the most important role. The ant algorithm generates the results in

a quick way and therefore this algorithm was selected in this problem. The presented decision model refers to the waste collection from individual inhabitants. The vehicle visits loading points (inhabitants) and collects the waste. The main aim is to designate this route. This fact additionally highlights the use of heuristic algorithm in this problem.

2. The decision model

The transportation network of municipal plants consists of the following elements: the municipal plant and the junctions. The places where the waste are generated are located between these junctions, on both sides of the road. The main task of the vehicle is to collect the waste from points located next to the road on a given route. When the vehicle is loaded and full, it goes to the municipal plant. On the Figure 1 the transportation network was presented, additionally the route of collection was presented (red arrows), waste (blue rectangles).

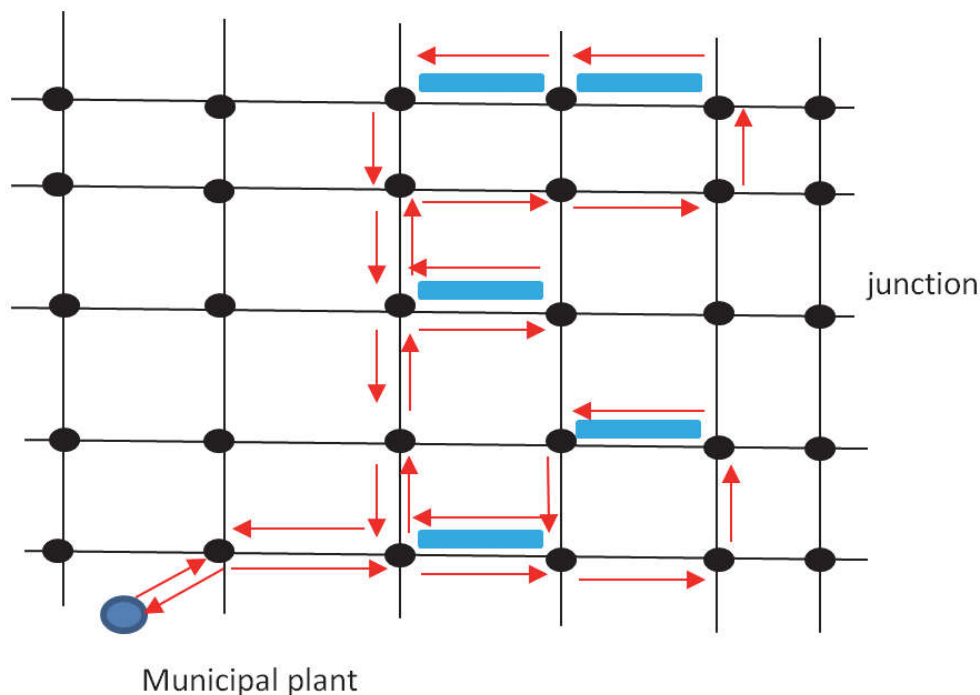


Fig. 1. The transportation network of municipal plant
Rys. 1. Sieć transportowa zakładu komunalnego

Source: own study

In order to describe the mathematical model the following variables were introduced:

- $V = \{v : v = 1, 2, \dots, v', \dots, V\}$ – the set of point elements of the transport network, i.e. municipal plants, junctions,
- $J = \{v : \alpha(v) = 1 \text{ for } v \in V\}$ – the set of junctions,
- $MP = \{v : \alpha(v) = 2 \text{ for } v \in V\}$ – the set of potential municipal plants,
- $VEH = \{1, \dots, veh, \dots, VEH\}$ – the set of numbers of vehicles,
- $Tr = \{1, \dots, tr, \dots, TR\}$ – the set of numbers of routes,
- $D1 = [d1(v, v') : d1(v, v') \in \mathbf{R}^+, v \in MP, v' \in J]$ – distance matrices in relations: municipal plants - junctions,
- $D2 = [d2(v, v') : d2(v, v') \in \mathbf{R}^+, v \in J, v' \in J]$ – distance matrices in relations: junctions - junctions,
- $D3 = [d3(v, v') : d3(v, v') \in \mathbf{R}^+, v \in J, v' \in MP]$ – distance matrices in relations: junctions - municipal plants,
- $T = [t(v) : t(v) \in \mathbf{R}^+, v \in J]$ – transition time via the junction,
- $T1 = [t1(v, v') : t1(v, v') \in \mathbf{R}^+, v \in MP, v' \in J]$ – time matrices in relations: municipal plants – junctions,
- $T2 = [t2(v, v') : t2(v, v') \in \mathbf{R}^+, v \in J, v' \in J]$ – time matrices in relations: junctions - junctions,
- $T3 = [t3(v, v') : t3(v, v') \in \mathbf{R}^+, v \in J, v' \in MP]$ – time matrices in relations: junctions - municipal plants,
- $T4 = [t4(v) : t4(v) \in \mathbf{R}^+, v \in MP]$ – unloading time in municipal plants,
- $T5 = [t5(v, v') : t5(v, v') \in \mathbf{R}^+, v \in J, v' \in J]$ – loading time in relations: junctions - junctions,
- $A = [a(v, v') : a(v, v') \in \{0, 1\}, v \in J, v' \in J]$ – 1 – there are the waste on a given connection, 0 – there are not the waste,
- $Q = [q(v, v') : q(v, v') \in \mathbf{R}^+, v \in J, v' \in J]$ – the volume of waste between junctions,
- ΔT – working time of the vehicle,
- $C = [c(veh) : c(veh) \in \mathbf{R}^+, veh \in VEH]$ – the cost of fuel consumption,
- $QV = [qv(veh) : qv(veh) \in \mathbf{R}^+, veh \in VEH]$ – capacity of the vehicle.

The decision variable take the following form:

- $\mathbf{X1} = [x1(v, v', veh, tr) : x1(v, v', veh, tr) \in \{0,1\}, v \in \mathbf{MP}, v' \in \mathbf{J}, veh \in \mathbf{VEH}, tr \in \mathbf{TR}]$ – 1 – there is connection between the municipal plant and the junction realized by the vehicle in the route, 0 – there is no connection,
- $\mathbf{X2} = [x2(v, v', veh, tr) : x2(v, v', veh, tr) \in \{0,1\}, v \in \mathbf{J}, v' \in \mathbf{J}, veh \in \mathbf{VEH}, tr \in \mathbf{TR}]$ – 1 – there is connection between junctions realized by the vehicle in the route, 0 – there is no connection,
- $\mathbf{X3} = [x3(v, v', veh, tr) : x3(v, v', veh, tr) \in \{0,1\}, v \in \mathbf{J}, v' \in \mathbf{MP}, veh \in \mathbf{VEH}, tr \in \mathbf{TR}]$ – 1 – there is connection between the junction and the municipal plant realized by the vehicle in the route, 0 – there is no connection.

The constraints of the mathematical model take the following form:

- working time of the vehicle must be less than allowable time of work:

$$\begin{aligned} & \forall veh \in \mathbf{VEH} \\ & \sum_{v \in \mathbf{MP}} \sum_{v' \in \mathbf{J}} \sum_{tr \in \mathbf{TR}} x1(v, v', veh, tr) \cdot [t1(v, v') + t(v')] + \\ & \sum_{v \in \mathbf{J}} \sum_{v' \in \mathbf{J}} \sum_{tr \in \mathbf{TR}} x2(v, v', veh, tr) \cdot [t2(v, v') + t(v') + a(v, v') \cdot t5(v, v')] + \\ & \sum_{v \in \mathbf{J}} \sum_{v' \in \mathbf{MP}} \sum_{tr \in \mathbf{TR}} x3(v, v', veh, tr) \cdot [t3(v, v') + t4(v')] \leq \Delta T \end{aligned} \tag{1}$$

- capacity of vehicle must be met:

$$\begin{aligned} & \forall veh \in \mathbf{VEH}, tr \in \mathbf{TR} \\ & \sum_{v \in \mathbf{J}} \sum_{v' \in \mathbf{J}} x2(v, v', veh, tr) \cdot q(v, v') \leq qv(veh) \end{aligned} \tag{2}$$

The criteria functions minimalize the total time of realization of the routes and the cost of fuel consumption:

- the total time of realization of the routes:

$$\begin{aligned}
F1(X1, X2, X3) = & \sum_{v \in MP} \sum_{v' \in J} \sum_{tr \in TR} \sum_{veh \in VEH} x1(v, v', veh, tr) \cdot [t1(v, v') + t(v')] + \\
& \sum_{v \in J} \sum_{v' \in J} \sum_{tr \in TR} \sum_{veh \in VEH} x2(v, v', veh, tr) \cdot [t2(v, v') + t(v') + a(v, v') \cdot t5(v, v')] + \\
& \sum_{v \in J} \sum_{v' \in MP} \sum_{tr \in TR} \sum_{veh \in VEH} x3(v, v', veh, tr) \cdot [t3(v, v') + t4(v')] \longrightarrow \min
\end{aligned} \tag{3}$$

– the cost of fuel consumption:

$$\begin{aligned}
F2(X1, X2, X3) = & \sum_{v \in MP} \sum_{v' \in J} \sum_{tr \in TR} \sum_{veh \in VEH} x1(v, v', veh, tr) \cdot d1(v, v') \cdot c(veh) + \\
& \sum_{v \in J} \sum_{v' \in J} \sum_{tr \in TR} \sum_{veh \in VEH} x2(v, v', veh, tr) \cdot d2(v, v') \cdot c(veh) + \\
& \sum_{v \in J} \sum_{v' \in MP} \sum_{tr \in TR} \sum_{veh \in VEH} x3(v, v', veh, tr) \cdot d3(v, v') \cdot c(veh) \longrightarrow \min
\end{aligned} \tag{4}$$

3. The modified ant algorithm

In order to solve the multi-criteria routing vehicle problem of municipal plants, the method based on the ant algorithm was developed. Theory of this algorithms introduces the concept of artificial ants (Dorigo et al. 2004). The main task of ants is to determine the loading route consisting of all loading points. The value of the ant must be interpreted as the length of routes which are realized by the vehicles or one vehicle in the collection process. Each ant builds its own route till the moment when all loading points are visited. The ant goes to the municipal plant in the case when the realization time of the collection (1) is not met or all loading points were visited or capacity of vehicle is not met (2). Each ant has own capacity which equals the capacity of a given vehicle. At first the data input needs to be determined: the set of ants was defined as **MR**, the number of iterations of the algorithm **I**. The starting and ending point of each route is in the municipal plant. In the ant algorithm the following steps were distinguished:

- Step 1. The choice of the municipal plant in a random way in the case when there are many plants. The first ant and the first iteration of the algorithm is set in this step.
- Step 2. The ant goes to the junctions with a certain probability:

$$PR^{mr}_{zz'}(t) = \left\{ \frac{[\tau_{zz'}(t)]^\alpha \cdot [\eta_{zz'}(t)]^\beta}{\sum_{z' \in Z} [\tau_{zz'}(t)]^\alpha \cdot [\eta_{zz'}(t)]^\beta} \right. \quad (5)$$

where:

$\tau_{zz'}(t)$ – the intensity of pheromone trail between the z – the a z' – the point in t – the iteration,

α, β – parameters determining the effect of pheromones and the heuristic information on the behavior of ants,

Z – the set of junctions which are connected with analyzed junction (z), this set is different for each junction (z),

$\eta_{zz'}(t)$ – the heuristic information, in this case in order to take into account the multi – criteria aspect of the problem, the heuristic information takes the following form:

$$n_{zz'}(t) = \frac{1}{\frac{t(z') + tmr(z, z')}{Const1} + \frac{d(z, z') \cdot c(mr)}{Const2}} \quad (6)$$

where:

$t(z')$ – in the mathematical model the variable $t(v)$,

$tmr(z, z')$ – in the mathematical model the variable $t1(v, v'), t2(v, v'), t3(v, v'), t5(v, v')$

$d(z, z')$ – in the mathematical model the variable $d1(v, v'), d2(v, v'), d3(v, v')$

$c(mr)$ – in the mathematical model the variable $c(veh)$

$Const1$ – the value greater than the numerator of the first quotient, the value is established at the beginning of working the algorithm,

$Const2$ – the value greater than the numerator of the second quotient, the value is established at the beginning of working the algorithm

The probability of selection of a given connection between points increases when the heuristic information increases. This situation takes place when the denominator of the equation (6) approaches the minimum value. The smaller value of the criteria function, the larger the value of the probability of selection of a given connection (5).

Random choice of the route between the point z and points z' begins from calculating the probability of the transition to the junctions. The first point in the route (z) is determined as the municipal plant, the another points are defined as junctions.

The next step is to calculate the distribution for each transition path (z, z') and draw the number r from the range $[0,1]$. The route tro about the value of the distribution q_{tr} which fulfills the condition $q_{tro-1} < r \leq q_{tro}$ is selected, where tro is the number of the route between z – the point and z' – the points.

- Step 3. The constraints of the model must be checked: working time of the vehicle must be less than allowable time of work and capacity of vehicle must be met. If the ant is full, it goes to the municipal plant. There are junctions in the network that are connected with the municipal plant. The ant seeks the junctions that are connected with the municipal plant. Additionally the ant goes to the municipal plant, when working time is finished or all the loading points are realized. This step is repeated until all the loading points will be collected.
- Step 4. Steps 1-3 are repeated for the next ant from the population.
- Step 5. In this step the pheromone update is actualized. Three types of the pheromone update can be distinguished: ant – density, ant – quantity, ant – cycle. In order to update the pheromone the ant – cycle was used as the most efficient version of the ant algorithm (Dorigo et al. 2004). At the beginning, it is assumed that the trail on the links between the points is equally strong. In subsequent iterations, the pheromone trail is calculated according to the formula:

$$\tau_{zz'}(t+1) = (1 - \rho)\tau_{zz'}(t) + \sum_{mr=1}^{MR} \Delta\tau_{zz'}^{mr}(t) \quad (7)$$

where:

mr – another ant $mr \in MR$ $mr \in MR$, ρ – a factor pheromone ($0 < \rho \leq 1$), $\tau_{zz'}(t+1)$ – the strengthening of the pheromone, for the first iteration this strengthening takes the value τ_0 for each connections.

$$\Delta \tau_{zz'}^{mr}(t) = \begin{cases} \frac{1}{L^{mr}(t)} & \text{when the route } (z,z') \text{ was used by} \\ & mr - \text{this ant otherwise} \\ 0 & \end{cases} \quad (8)$$

where:

$L^{mr}(t)$ – the heuristic information of the route in t iteration realized by mr – this ant, if the segment of routes (z,z') was realized by mr – this ant then $\Delta \tau_{yz}^{mr}(t)$ equals $1/L^{mr}(t)$, otherwise 0.

- Step 6. The steps 1-5 are repeated determined the number of iterations.
- Step 7. The stop of algorithm. Of all routes which were generated by ants, the route with maximum value of the heuristic information is selected.

4. Results

The algorithm was implemented by the use of the real input data in the C++ programming language. Distance between junctions [km], the driving time between junctions [h], the assignment of the waste to the links [1 or 0] take the following values [km, h, 0 or 1]: link (1,2): [3;0,06;0], link (2,3): [5;01;1], link (2,5): [7;0,14;1], link (2,6): [5;0,2;1], link (3,4): [10;0,2;0], link (4,5): [4;0,08;0], link (4,8): [10;0,2;1], link (4,9): [11;0,22;0], link (5,6): [3;0,12;1], link (5,7): [4;0,08;0], link (5,8): [5;0,1;1], link (6,7): [5;0,2;1], link (7,8): [3;0,12;0], link (8,10): [10;0,2;1], link (9,10): [7;0,14;0], link (9,11): [4;0,2;0], link (10,12): [4;0,13;1], link (11,12): [3;0,12;0].

Additional input data: the capacity of vehicle: 2500 m³, the cost of fuel consumption – 4,5 zł (32l/100 km), working time of the vehicle – 4h, the volume of waste between junctions for each links – 250 m³, unloading time in municipal plants – 0,05 h, transition time via the junctions [h] (junction: 1 – 0,08, 2 – 0,07, 3 – 0,05, 4 – 0,09, 5 – 0,03, 6 – 0,02, 7 – 0,01, 8 – 0,04, 9 – 0,05, 10 – 0,02, 11 – 0,03, 12 – 0,02).

The first step of implementation of the ant algorithm was to find the set of the best parameters which characterizes this algorithm (i.e. $\alpha = 1$, $\beta = 0,5$, $\rho = 0,6$). The number of iterations was set to 200. The size of population (ants) was set to 600.

In order to verify the correctness of the ant algorithm (AA), its results were compared with random values (RA). The ant algorithm in each case generated a better solution than the random algorithm. The results are shown in Tab. 1. The heuristic information (for a total route of the ant) in the case of the ant algorithm is greater than the random algorithm. On the basis on the route of the ant one can designate the number of vehicles which realizes the given route. In the case , when the ant goes to the municipal plant because of working time, another vehicle starts the realization of routes.

Table 1. Comparison of algorithms

Tabela 1. Porównanie algorytmów

No.	The number of vehicle [AA]	η [AA]	The number of vehicle [RA]	η [RA]
1	2	7,62	6	2,4
2	3	8,01	5	1,4
3	2	7,99	7	3,0
4	3	8,0	8	4
5	4	9,01	5	1,9
6	3	7,89	7	3,4
7	2	7,98	6	2,7
8	3	8,90	7	3,4
9	4	9,0	5	1,8
10	2	7,98	8	4
11	3	8,98	6	2,8
12	4	9,0	7	3,2

Source: own development

5. Conclusion

The aim of the paper is to present the decision model of the organization of municipal waste collection. This model bases on multi-criteria optimization. The optimization algorithm in this case is the ant algorithm.

It should be emphasized that ant belongs to heuristic algorithms. The solution generated by these algorithms for complex decision problems is a sub-optimal solution. However, considering the complexity of the organization of municipal waste collection, the solution is accepted from a practical point of view. The further step is to use Anti-colonial systems in the organization of municipal waste collection. The early

convergence to the sub-optimal solution is blocked by the use of the update pheromone ant – cycle in the ant algorithm.

The optimal results generated by the algorithm depend on many factors, e.g.: parameters of the algorithm, the number of iterations or ants in population.

It should be underlined that results of the ant algorithm depend on the type of the data input which are taken into account in the mathematical model. This algorithm was implemented by the use of the fixed data input, e.g. the average driving time. The presented model does not take into account the random values of the input data. Further research in the context of the presented problem will be conducted taking into account random character of transport process.

The developed algorithm can be used in municipal companies to develop, e.g. the driver's working schedules. The main advantage of this algorithm is that the results are generated in a quick way, what is very important for this companies.

The processes occurring in the municipal companies are the dynamic processes. For this reason, the algorithm must be started a few times depending on the volume of waste, vehicle capacities. In this case, the calculation speed plays the huge role what underlines utility of this algorithm in the municipal companies.

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Organizacja zbiórki odpadów komunalnych: Model decyzyjny

Streszczenie

W pracy przedstawiono problem organizacji zbiórki odpadów komunalnych od indywidualnych mieszkańców. Organizacja zbiórki odpadów jest zdefiniowana jako wyznaczenie tras jazdy pojazdów realizujących daną zbiórkę. W celu rozwiązania tego problemu zaproponowano model decyzyjny wyznaczania tras jazdy pojazdów.

Organizacja zbiórki odpadów komunalnych może być rozpatrywany w ujęciu jedno lub wielokryterialnym. W niniejszym opracowaniu przedstawiono zbiórkę odpadów komunalnych w kontekście wielokryterialnego problemu decyzyjnego. W niniejszej pracy model decyzyjny organizacji zbiórki odpadów komunalnych opiera się na optymalizacji wielokryterialnej. W tym przypadku algorytm optymalizacji był algorytmem mrówkowym. Algorytm ten został specjalnie zmodyfikowany w celu rozwiązania problemu podejmowania decyzji w oparciu o wiele kryteriów. Autorzy tej publikacji nie znaleźli zastosowania tego podejścia i tego algorytmu w literaturze do wyznaczenia organizacji zbiórki odpadów komunalnych.

Organizacja zbiórki odpadów komunalnych jest złożonym problemem decyzyjnym i odnosi się do problemu komiwojażera. Problem ten należy do problemów NP-trudnych. Aby rozwiązać problem komiwojażera, należy zastosować algorytm heurystycznych. Szybki czas generowania wyniku przez algorytm mrówkowy jest jego główną cechą, co jest pożądane w procesie wyznaczania organizacji zbiórki odpadów komunalnych. Proces ten zależy od wielu czynników, np. pojemność pojazdów, wielkość zadań. Algorytm wyznaczania tego typu problemu musi być dostosowany do częstych zmian tych czynników i szybkiego generowania rozwiązań. W firmach komunalnych najważniejszą rolę odgrywa czas generowania rozwiązania. Algorytm mrówkowy generuje

wyniki w szybki sposób i dlatego ten algorytm został wybrany w tym problemie. Przedstawiony model decyzyjny dotyczy zbiórki odpadów od poszczególnych mieszkańców. Samochód odwiedza punkty załadunku (mieszkańców) i zbiera odpady. Głównym celem jest wyznaczenie tej trasy. Fakt ten dodatkowo podkreśla zastosowanie algorytmu heurystycznego w tym problemie.

W pracy zdefiniowano model matematyczny problemu zbiórki odpadów komunalnych, podano dane wejściowe wprowadzane do modelu np. zdefiniowano odległości pomiędzy obiektami sieci transportowej, podano czasy jazdy pomiędzy tymi obiektami, czasy załadunku, wyładunku odpadów, czas przejazdu przez skrzyżowania. Zmienna decyzyjna określa połączenie pomiędzy poszczególnymi obiektami sieci realizowane przez pojazd w danej trasie. Zmienne decyzyjne są typu binarnego. Wprowadzono ograniczenia na czas pracy oraz na pojemność pojazdów realizujących zbiórkę odpadów. Funkcje kryteriów dotyczą minimalizacji czasu realizacji wszystkich tras oraz kosztów zużycia paliwa.

W pracy szczegółowo scharakteryzowano algorytm mrówkowy rozwiązujący wielokryterialny problem decyzyjny zbiórki odpadów komunalnych.

W celu sprawdzenia poprawności algorytmu mrówkowego jego wyniki porównano z wartościami losowymi. Algorytm mrówkowy w każdym przypadku generował lepsze rozwiązanie niż losowy algorytm.

Należy podkreślić, że algorytm mrówkowy należy do algorytmów heurystycznych. Rozwiązanie wygenerowane przez te algorytmy dla złożonych problemów decyzyjnych jest rozwiązaniem nieoptymalnym. Biorąc jednak pod uwagę złożoność organizacji zbiórki odpadów komunalnych, rozwiązanie jest akceptowane z praktycznego punktu widzenia.

Abstract

The paper presents the problem of organizing municipal waste collection from individual residents. A waste collection organization is defined as the designation of vehicle routes for a given collection. In order to solve this problem, a decision model for determining driving routes has been proposed. The organization of municipal waste collection may be considered in a single or multi-criteria approach. This study presents a collection of municipal waste in the context of a multi-criteria decision problem. In this work, the decision model of the municipal waste collection organization is based on multi-criteria optimization. In this case, the optimization algorithm was an ant algorithm. This algorithm has been specially modified to solve the problem of making decisions based on many criteria. The authors of this publication have not found application of this approach and this algorithm in the literature to designate the municipal waste collection organization.

The municipal waste collection organization is a complex decision problem and refers to the traveling salesman problem. This problem belongs to NP-hard problems. To solve the problem of the traveling salesman, a heuristic algorithm should be applied. Fast time of generating the result by the ant algorithm is its main feature, which is desirable in the process of designating the municipal waste collection organization. This process depends on many factors, e.g. vehicle capacity, size of tasks. The algorithm for determining this type of problem must be adapted to frequent changes of these factors and quick generation of solutions. The time of solution generation plays the most important role in municipal companies. The ant algorithm generates results in a quick way and therefore this algorithm was chosen in this problem. The presented decision model concerns the collection of waste from individual residents. The car visits the loading points (inhabitants) and collects waste. The main goal is to designate this route. This fact additionally emphasizes the use of the heuristic algorithm in this problem.

The work defines the mathematical model of the problem of municipal waste collection, the input data entered into the model are given, e.g. distances between objects of the transport network have been defined, driving times between these objects are given, loading times, unloading of waste, crossing time. The decision variable defines the connection between individual network objects implemented by the vehicle in a given route. Decision variables are binary type. Limitations have been introduced for working time and for the capacity of vehicles that collect waste. The criteria functions concern the minimization of the time of completion of all routes and the costs of fuel consumption.

In order to check the correctness of the ant algorithm, its results were compared with random values. The ant algorithm in each case generated a better solution than a random algorithm.

It should be emphasized that the form algorithm belongs to heuristic algorithms. The solution generated by these algorithms for complex decision problems is a suboptimal solution. However, taking into account the complexity of the municipal waste collection organization, the solution is accepted from a practical point of view.

Słowa kluczowe:

organizacja zbiórki odpadów komunalnych, optymalizacja wielokryterialna, algorytm mrówkowy

Keywords:

organization of municipal waste collection, multi-criteria optimization, ant algorithm



Icing Effect on Steel Bar Structures

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1. Introduction

Ice action is a kind of load that in many cases is not included by designers, since it concerns a small number of objects. The structures vulnerable to icing effect are i.e. masts, towers, electrical overhead lines, chimneys, tie rods as well as any type of unprotected steel truss structures. They are usually located in open areas and icing is one of important determinants for their dimensioning. Icing is defined as an atmospheric phenomenon that occurs as a result of cooling and condensation. It may arise due to two processes: hoarfrost or precipitation icing, and takes various forms i.e.: soft rime, hard rime, wet snow or glaze. Its density is differentiated and varies from 200 kg/m^3 to 900 kg/m^3 . Undoubtedly, the key factors in formation of ice include ambient temperature, air humidity, wind velocity and direction as well as atmospheric pressure.

The literature can find references on the effect of ice action on structures, however, there is an insignificant number of works that relate to research in the area of Poland.

In the Polish technical literature there are not too many publications that refer solely to the issues pertaining to ice action. Appropriate adoption of all loads acting on structures as well as determination of load combinations acting on them is of great importance in the design process. Improper determination of loads acting on structures or not taking into consideration some of load types in the design process (i.e. ice action) may lead to failures or construction disasters. The most spectacular construction disasters are the destructions of power systems, since they in-

volve depriving consumers of energy. Such blackouts occurred in recent years in Szczecin (in 2008) and in Kielce (in 2010) (Rawska-Skotniczny 2014). The literature has provided the issue of icing effect on overhead power line cables with a substantially serious concern. Undoubtedly, the effect of icing on design and safety of use of overhead power networks is particularly vital (Qimao et al. 2011). In order to investigate this effect, appropriate calculation models and environmental source data should be adopted (Farzaneh 2008). One of the methods of measuring the icing of power line cables, also under uneven icing distribution, is to determine the ice action based on the final stresses caused by this type of load (McComber et al. 1987). Overhead traction networks, both rail and tram ones are another types of structures exposed to the negative effect of icing. In order to avoid failures caused by ice accumulation on cables, some technical solutions should be applied to monitor traction networks that allow for their continuous and reliable work in long-term operation (Maciołek & Szelağ 2016). It is particularly important to take into account ice action and to adopt this load in load combinations for steel bars as examples of building structures sensitive to this type of action (El-Reedy 2010). Correct value assumption of icing action – as well as its type, methods for measuring and collecting data to determine the effect of icing – is a technique incorporated by many scientists from such countries as: Austria, Bulgaria, Czech Republic, Finland, Germany, Hungary, Norway, Slovakia, Spain, Sweden, Switzerland and the United Kingdom (including data from Russia and Canada). On the basis of this extensive research and interpretation of national standards, the European guidelines have been created. (Fikke et al. 2007).

For many years in Poland there have been a great interest in a fund collecting campaign to treat children and seniors, known as the Great Orchestra of Christmas Charity (Wielka Orkiestra Świątecznej Pomocy). It takes place during winter and numerous steel structures need to be installed in order to perform charity concerts and shows. As this type of construction is particularly exposed to ice action, attention should be paid to the correct design and safety of use of these facilities (Czaplińska 2016).

2. Determination of ice load

For the time being there is no separate European standard – Eurocode on ice action. However, there are standards that designers apply selectively, depending on their requirements. In order to present the issue, the subject of ice action is presented on the basis of the following standards: PN-EN 1993-3-1:2008 Eurocode 3: Design of steel structures Part 3-1: Towers, masts and chimneys – towers and masts, PN-EN 1993-3-2:2008 Eurocode 3: Design of steel structures Part 3-2: Towers, masts and chimneys – chimneys, ISO 12494:2017 Atmospheric Icing of Structures, PN-87/B-02013 Actions on structures. Variable environmental loads. Ice load and Minimum design loads for buildings and other structures and ASCE Standards ASCEISEI 7-05, 2006.

Currently, the most appropriate to use is Annex C to PN-EN 1993-3-1:2008 (PN-EN 1993-3-1:2008 Eurocode 3: Design of steel structures Part 3-1: Towers, masts and chimneys – towers and masts) since it provides rules for determining ice load as well as ice and wind load combined. The code PN-EN 1993-3-2:2008 (PN-EN 1993-3-2:2008 Eurocode 3: Design of steel structures Part 3-2: Towers, masts and chimneys – chimneys) refers to the same annex, although it additionally refers to ISO 12494:2017 (ISO 12494:2017 Atmospheric Icing of Structures), which is an English international standard not planned to be used directly by designers but by standardisation committees. The Polish annex for those two codes PN-EN 1993-3-1:2008 and PN-EN 1993-3-2:2008 allows for applying the standard PN-87/B-02013 (PN-87/B-02013 Actions on structures. Variable environmental loads. Ice load and Minimum design loads for buildings and other structures), which restores the necessity of using PN standards, previously withdrawn as the consequence of adopting Eurocodes.

According to the code PN-EN 1993-3-1:2008 the constant thickness of ice for design purposes is adopted around the periphery of elements, which allows computation of both weight and aerodynamic drag. The method is justified for calculating elements subject to icing in the form of glaze or wet snow. The below Fig. 1 demonstrates the constant (symmetrical) thickness of ice.

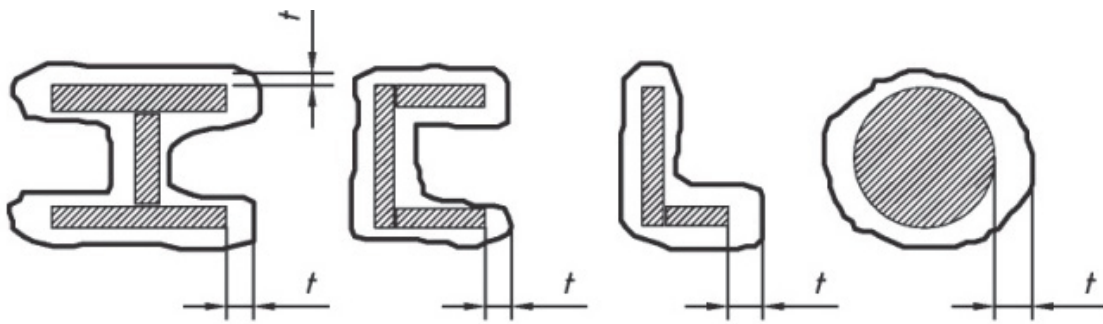


Fig. 1. Glaze thickness on structural elements according to ISO 12494:2017 (ISO 12494:2017 Atmospheric Icing of Structures), where:
 t – ice thickness (depending on the location of the object)

Rys. 1. Grubość oblodzenia szklivem elementów konstrukcyjnych wg normy ISO 12494:2017 (ISO 12494:2017 Atmospheric Icing of Structures), gdzie:
 t – grubość warstwy oblodzenia (w zależności od lokalizacji obiektu)

The icing in the form of rime is deposited on structural elements in a completely different way; it is uneven. Consequently, when designing, the same constant ice thickness is assumed, however this value is appropriately overstated as much as the largest thickness of rime.

Fig. 2 shows the model of glaze growth on structural elements, with its asymmetrical location. It should be added that the models shown in Figure 2 are adequate for profiles with a height of $w \leq 300$ mm.

It should be examined individually, which form of ice load, symmetrical or asymmetrical, is the most unfavourable for a designed structural element.

Ice thickness for structures located in Poland can be calculated on the basis of PN-87/B-02013. Characteristic values for ice load should be calculated per unit length of a given structural element. Load acting on the element with a circular cross-section e.g. a pipe, rope or rod can be calculated with the use of the following formula:

$$g_k = \pi \cdot \gamma \cdot s \cdot (d + s) \quad (1)$$

where:

g_k – characteristic value for icing [kN/m],

γ – ice density [kN/m³],

s – effective thickness of ice [m],

d – diameter of element with a circular cross-section [m].

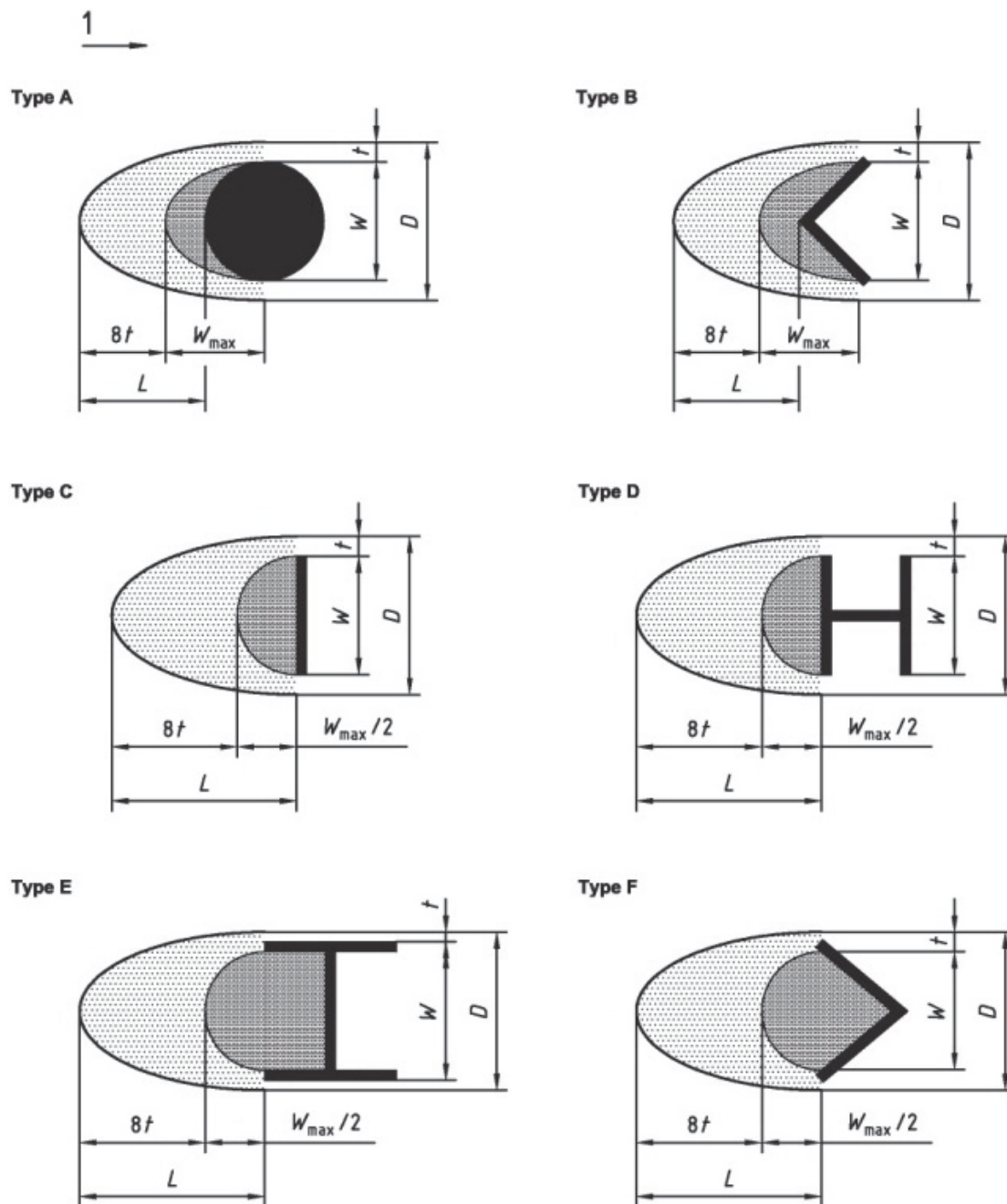


Fig. 2. Glaze thickness on structural elements according to ISO 12494:2017 (ISO 12494:2017 Atmospheric Icing of Structures)

Rys. 2. Grubość oblodzenia sadyż elementów konstrukcyjnych wg normy ISO 12494:2017 (ISO 12494:2017 Atmospheric Icing of Structures)

where:

A, B, C, D, E, F – different types of rime icing depending on shapes and dimensions of profiles and their position relative to the wind direction,

l – wind direction,
 t – ice thickness (depending on the location of the object),
 w – width of object (excluding ice) perpendicular to wind direction,
 L – length of ice vane measured in windward direction,
 D – diameter of accreted ice or total width of object including ice.

gdzie:

A, B, C, D, E, F – różne typy oblodzenia sadzią w zależności od kształtu i wymiarów profili oraz ułożenia względem kierunku wiatru,

l – kierunek wiatru,

t – grubość lodu (w zależności od lokalizacji obiektu),

w – szerokość kształtownika (bez lodu) prostopadle do kierunku wiatru,

L – długość nawisu lodowego mierzona po stronie nawietrznej,

D – średnica oblodzonego kształtownika lub jego szerokość (w tym lodu).

To calculate load acting on structural elements with different cross-sections, the following formula should be used:

$$g_k = \gamma \cdot s \cdot u \quad (2)$$

where:

u – circumference of the outer element contour that is measured in half of the effective ice thickness [m].

The effective thickness of ice is presented with the formula below:

$$s = b \cdot \mu \cdot \xi \quad (3)$$

where:

b – characteristic value for ice thickness [m],

μ – shape coefficient,

ξ – height above terrain coefficient.

The calculated value of load is determined from the correlation:

$$g = g_k \cdot \gamma_f \quad (4)$$

where:

γ_f – load coefficient, for icing $\gamma_f = 1.5$.

Comparing the code PN-87/B-02013 to ISO 12494:2017 and ASCEISEI 7-05, 2006 (ASCE Standards ASCEISEI 7-05, 2006), results in noticing the following differences and similarities. According to PN-87/B-02013, the density of ice should be 700 kg/m^3 , while ISO 12494:2017 and ASCEISEI 7-05, 2006 designate that value as 900 kg/m^3 . Characteristic values for ice thickness b should be adopted for particular areas in Poland separately. The map of Poland with division into load zones is included in the code PN-87/B-02013. There is no possibility of using a different standard in this matter, since the codes ISO 12494:2017 and ASCEISEI 7-05, 2006 do not cover the area of Poland. ISO 12494:2017 contains a division into ice classes for both rime and glaze, but it does not relate this data to the location of objects. On the other hand, the code ASCEISEI 7-05, 2006 provides design guidance for all actions affecting structures, yet it covers only the territory of the United States of America.

The shape coefficient μ is precisely provided in the code PN-87/B-02013. Its value depends on a cross-section shape, i.e. there are given values for sections ($\mu = 0,5$), closed profiles, box profiles ($\mu = 0,7$) and profiles with a circular cross-section according to their diameter (when $d \leq 0,007 \text{ m}$ then $\mu = 1,1$, when $0,007 \text{ m} < d \leq 0,16 \text{ m}$ then $\mu = \frac{1}{\sqrt[4]{100 \cdot d}}$ and when $d > 0,16 \text{ m}$ then $\mu = 0,5$). The code PN-87/B-02013 designates the height above terrain coefficient as ξ , the code ISO 12494:2017 as K_h , while the code ASCEISEI 7-05, 2006 as f_z .

The code PN-87/B-02013 determines the coefficient ξ with the use of the following formula:

$$\xi = \left(\frac{h}{10}\right)^{0.3} \quad (5)$$

where:

h – height above terrain of a structural element.

Principles included in the code ASCEISEI 7-05, 2006 describe the height above terrain coefficient with the following formula:

$$f_z = \left(\frac{z}{10}\right)^{0.1} \quad (6)$$

where:

z – height above terrain of a structural element within $0 \text{ m} < z \leq 275 \text{ m}$.

The code ISO 12494:2017 describes the height above terrain coefficient with the following formula:

$$K_h = e^{0.01H} \quad (7)$$

where:

H – height above terrain of a structural element.

The comparison of height above terrain coefficient values on the basis of the referred formulas is included in the calculation example set out in the following part of the article.

Scientific expertise proves that a structure is never subject to just one load. In case of ice load what might be of crucial importance is a combination of various loads, including wind action. The maximum load may cause an increase in the aerodynamic drag due to icing of an element, even at a lower wind velocity value than the maximum one. The code PN-EN 1993-3-1:2008 presents a calculation algorithm for the aerodynamic drag of a structure subject to icing, taking into account an increase in the width of elements at glazed icing. The code PN-EN 1993-3-1:2008 provides combinations of ice load and wind load, which should be followed, taking into consideration the class of icing i.e. whether it is symmetrical or asymmetrical. There are two combinations to be considered:

- ice load is dominant, while wind load is accompanying, which is presented as the following correlation:

$$\gamma_G \cdot G_k + \gamma_{ice} \cdot Q_{k,ice} + \gamma_w \cdot \Psi_w \cdot k \cdot Q_{k,w} \quad (8)$$

where:

γ_G – partial coefficient for constant loads,

γ_{ice} – partial coefficient for ice load,

γ_w – partial coefficient for wind load,

G_k – characteristic value for constant loads,

$Q_{k,ice}$ – characteristic value for ice load,

$Q_{k,w}$ – characteristic value for wind load,

Ψ_w – factor of combination for wind load,

k – factor for velocity pressure from wind action.

- wind load is dominant, while ice load is an accompanying phenomena, which is presented as the following correlation:

$$\gamma_G \cdot G_k + \gamma_w \cdot k \cdot Q_{k,w} + \gamma_{ice} \cdot \Psi_{ice} \cdot Q_{k,ice} \quad (9)$$

where:

Ψ_{ice} – combination factor for ice load.

The given formulas also include the coefficient k described in the code PN-EN 1993-3-1:2008. It concerns a characteristic wind pressure and is used to decrease a wind pressure value. Its value depends on the class of icing, which – in line with the recommendation contained in PN-EN 1993-3-1:2008 – should be determined according to the code ISO 12494:2017. However, the recommendation is completely unworkable for Polish designers, since the code ISO 12494:2017 does not include Poland within its territorial scope. Another incoherence is the value of a combination factor, as the code PN-87/B-02013 determines ice load on structures but does not specify the value of a combination factor. In such a case, it is recommended to refer to the code PN-EN 1993-3-1:2008 where there are given combination values adopted for the Polish territory. These are $\Psi_w = 0.5$ and $\Psi_{ice} = 0.5$, respectively. Summing up the above overview of standards, the current legal status in respect of ice action considerations can be regarded as unsatisfactory and ambiguous for designers.

3. Calculation example

To demonstrate the effect of ice load there were carried out calculations for a steel bar with the diameter of 25 mm. It is a bracing element of the platform in the object directly exposed to atmospheric conditions, located 20 m above terrain in Poznań.

- weight of bar \varnothing 25 mm is $m = 3.85$ kg/m,
- ice thickness according to PN-87/B-02013 is $b = 0.012$ m,
- shape coefficient for elements with a circular cross-section, if 0.007 m $\leq d \leq 0.16$ m, acc. to PN-87/B-02013 is:

$$\mu = \frac{1}{\sqrt[4]{100 \cdot d}} = \frac{1}{\sqrt[4]{100 \cdot 0.025}} = 0.795$$

The height over terrain coefficient calculated according to the referred formulas (5-7) is summarized in a tabular form. Table 1 additionally presents the value of effective ice thickness according to the code PN-87/B-02013 taking into consideration various height over terrain coefficients. There are also summarized the values of characteristic load per unit length having regard to the fact that according to the code PN-87/B-02013 the density of ice is 700 kg/m^3 , while according to the codes ISO 12494:2017 and ASCEISEI 7-05, 2006 the value adopted is 900 kg/m^3 . To summarise calculations, Table 1 presents ice mass for particular calculations as well as there is given a percentage increase in weight of the bar including the ratio of self-weight of ice to self-weight of the bar.

Table 1. Comparison of values according to: ISO 12494:2017, PN-87/B-02013 and ASCEISEI 7-05, 2006

Tabela 1. Porównanie wartości wg norm: ISO 12494:2017, PN-87/B-02013 i ASCEISEI 7-05, 2006

standards applied for calculations	height above terrain coefficient	effective ice thickness [m]	characteristic load per unit length [kN/m]	ice mass [kg/m]	percentage increase in weight of the bar due to icing [%]
ISO 12494:2017	1.22	0.012	0.0123	1.23	32
PN-87/B-02013	1.23	0.012	0.0096	0.96	25
ASCEISEI 7-05, 2006	1.07	0.010	0.0097	0.97	25

4. Conclusion

On the basis of theoretical considerations and the above calculation example it can be determined that ice load has a significant effect on structural elements. It should be added that it concerns a small number of structures, primarily closed profiles with small cross sections for which additional weight of ice constitute a large percentage of weight relative to their self-weight. However, this is not the reason for the ambiguity of standards. By analysing Table 1, it can be stated that Polish designers should design structures taking into account ice action on structures ac-

ording to ISO 12494:2017. Subsequently, there is obtained the most unfavourable ice load for a given element for calculation purposes in which the most important is to know the ice class that depends on location. Unfortunately, the codes ISO 12494:2017 and ASCEISEI 7-05, 2006 are excluded from being applied in Poland, since they do not include data in regard to the Polish territory. Undoubtedly, it is very important to take into account ice load together with other loads acting on structures, with the most important ones i.e. wind action and temperature load. For the reason that currently there is no separate standard relating to calculation of ice load, designers find it difficult and confusing to include this action in their calculations. As a consequence, it often leads to adopting underestimated values, as exemplified in the Table 1.

Evidently, the normalisation of ice load can benefit from the experience of the electricity industry, for it is an economy branch with great potential that uses global standards for design, construction and operation of overhead lines.

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Oddziaływanie oblodzeniem na stalowe konstrukcje prętowe

Streszczenie

Postępujące zmiany klimatyczne przyczyniają się do występowania ponad normatywnych obciążeń środowiskowych działających na konstrukcje budowlane. Obciążenia te są często przyczyną występujących na świecie katastrof budowlanych. Dlatego bardzo ważne jest właściwe określanie działających na obiekt budowlany obciążeń jak również przyjęcia najbardziej niekorzystnej kombinacji działających oddziaływań. Oddziaływanie oblodzeniem jest zaliczane do obciążeń zmiennych środowiskowych. Jest ono nie precyzyjnie określone w polskich przepisach normowych dotyczących projektowania konstrukcji. W pracy odniesiono się do norm polskich: PN-87/B-02013 Obciążenie budowli. Obciążenia zmienne środowiskowe. Obciążenie oblodzeniem, PN-EN 1993-3-1:2008 Eurokod 3: Projektowanie konstrukcji stalowych Część 1-1: Wieże, maszty i kominy. Wieże i maszty, PN-EN 1993-3-2:2008 Eurokod 3: Projektowanie konstrukcji stalowych Część 3-2: Wieże, maszty i kominy – kominy oraz norm międzynarodowych: ISO 12494:2017 Atmospheric Icing of Structures i Minimum design loads for buildings and other structures, ASCE Standards ASCEISEI 7-05, 2006. Ponieważ na dzień dzisiejszy nie istnieje oddzielny Eurokod dotyczący oddziaływania oblodzeniem, zaproponowano zasady określania tego oddziaływania podczas projektowania konstrukcji stosując wymienione normy. Trudność stosowania norm międzynarodowych wiąże się z barierą językową projektantów lub po prostu brakiem szczegółowych danych dla Polski. Ustawa z dnia 12 września 2002 r. o normalizacji zniosła obligato-

ryjność stosowania norm przy projektowaniu obiektów budowlanych, przyczyniając się do dobrowolności ich stosowania. Zatem decyzji projektanta pozostawiono, według których norm wykonuje projekt lub czy w ogóle z nich skorzysta. Konstrukcje stalowe, szczególnie prętowe i o niewielkich polach przekroju, narażone na wpływy atmosferyczne podlegają oddziaływaniu oblodzeniem. Również stalowe konstrukcje hydrotechniczne narażone są na szereg oddziaływań, w tym także na obciążenie oblodzeniem. Oddziaływaniem towarzyszącym oblodzeniu jest oddziaływanie wiatrem. W pracy pokazano kombinacje oddziaływań atmosferycznych dotyczące obciążeń wiatrem i oblodzeniem. Wskazano, że dla konstrukcji wrażliwych na oblodzenie warto korzystać z doświadczeń przemysłu elektroenergetycznego. W napowietrznych liniach elektroenergetycznych jak również sieciach trakcyjnych można stosować pewne rozwiązania techniczne umożliwiające monitoring ich stanu w niekorzystnych warunkach atmosferycznych. W artykule zamieszczono przykład obliczeniowy obrazujący wpływ oddziaływania oblodzeniem dla stalowego elementu prętowego. Porównano między innymi procentowy przyrost ciężaru pręta z oblodzeniem w stosunku do ciężaru własnego pręta. Analizę wykonano dla następujących norm: ISO 12494:2017, PN-87/B-02013 i ASCEISEI 7-05, 2006.

Praca stanowi wstęp do dalszych szerszych rozważań nad uwzględnieniem oddziaływania oblodzeniem dla konstrukcji szczególnie narażonych takich jak kratownice wiat, słupy elektroenergetyczne, prętowe konstrukcje stężeń i inne konstrukcje obiektów nieosłoniętych, które podczas użytkowania narażone są na bezpośredni wpływ warunków atmosferycznych. W pracy zwrócono uwagę na problem niejednoznaczności przepisów prawnych dotyczących oddziaływania oblodzeniem podczas projektowania konstrukcji.

Abstract

Progressive changes in climate have been substantially contributing to the occurrence of abnormal environmental loads acting on building structures. These loads are often the cause of construction disasters occurring in the world. Therefore, it is of crucial importance to properly determine loads acting on the exposed structures and to include the most unfavourable combination of actions. Ice load is classified as an environmental variable. It is imprecisely defined in the Polish standards for structural design. The paper refers to the Polish standards: PN-87/B-02013 Loads on structures. Variable environmental loads. Ice load, PN-EN 1993-3-1:2008 Eurocode 3: Design of steel structures Part 1-1: Towers, masts and chimneys. Towers and masts, PN-EN 1993-3-2:2008 Eurocode 3: Design of steel structures 3-2: Towers, masts and chimneys – chimneys as well as international standards: ISO 12494:2017 Atmospheric Icing of Structures and Minimum design loads for buildings and other structures, ASCE

Standards ASCEISEI 7-05, 2006. Since there is no separate Eurocode for ice action at present, it has been proposed to follow the rules for determining the action when designing a structure compliant with the standards listed above. The general difficulty in applying international regulations lies in the language barrier affecting some of designers or simply in the lack of detailed data for Poland. The Act of 12 September 2002 on normalisation abolished the obligatory application of standards in building design, contributing to their voluntary use. Therefore, it is the designer who decides whether or not to implement a given standard. Steel structures, particularly bars and structures with small cross-sections exposed to atmospheric conditions are affected by icing. Hydraulic steel structures are also exposed to a number of actions, including icing. Ice load is dominant, while wind load is an accompanying phenomena. The paper presents the combinations of atmospheric interactions describing wind and ice loads. It also points out that for structures sensitive to ice action, it is highly recommended to learn from the experience of the electricity industry. Overhead power lines, as well as traction lines, may use certain technical solutions to monitor their operation under adverse atmospheric conditions. In support of the arguments put forward, the article contains a calculation example illustrating the effect of icing on a steel bar element. The authors compared a percentage increase in weight of the bar with icing in the ratio to self-weight of the bar. The analysis was conducted in compliance with the following standards: ISO 12494, N-87/B-02013 and ASCEISEI 7-05, 2006.

The paper is an introduction to further broader reflections on the effect of icing on particularly vulnerable structures such as truss systems, power poles, steel bracings and other unprotected engineering elements, which during use are exposed to direct impact of weather conditions. Additionally, it draws attention to the problem of ambiguity of legal provisions regarding the icing effect that are to be applied in structural design.

Słowa kluczowe:

oddziaływanie oblodzeniem, kombinacje obciążeń, stalowy element prętowy, zasuwka płaska, norma polska, norma europejska

Keywords:

ice action, load combinations, steel bar, flat valve, Polish Standard, European Standard



Analysis of the Electric Energy Consumption in Teaching Centers and the Issue of the Environment Protection

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1. General information

The most important elements of higher schools/universities infrastructure are IT resources and related to them tele-information and electric installations. They are of strategic meaning if the profile of schools/universities is technical. In such cases computers and specialized software are used during most of classes, practical exercises and in laboratories. A didactic plan of a school / university requires using computer classrooms but they are also used to teach students how to work with applications and hardware.

Protection of correct, safe and reliable computers' operation at a school/university is a challenge for the IT team. The most important identified problems in this area are the following:

1. Administrators of the IT infrastructure must manage large groups of computers. This situation enforces automation of tasks in order to accelerate their execution and prevent human errors when carrying out arduous and repetitive operations.
2. Computers at the university are used by students intensively. Hence, it means frequent maintenance operations. Computers are also used by lecturers/teachers expecting that software used during classes is available at the computers.

3. Type of tasks carried out by students affects work quality of the operating systems which requires their frequent refreshing or changes of configuration. At the same time, these operations require great authorizations assigned to the administrator team.
4. Computers are generally used by a large group of persons, who frequently do not shut down the machine making extensive consumption of energy.

Except security of computer rooms, it is also significant to control and to reduce operation costs. Main costs of a school/university are generated by lecturers/teachers and the hardware used by students. In case of IT classes, a computer is a main tool and it consists of a monitor and a central (processing) unit. Both devices demand great quantity of power. Taking into consideration variety of IT classes, varied range of specialized software applied: graphics, programming, analysis and similar it's possible to say that computers in a computer room are used very intensively and they consume serious quantity of the electric energy.

The paper was developed on the ground of experiences' analysis and needs of an administrator team working and offering general classes at the IT university (Intel). Despite these analyses and consequent conclusions regard a higher school, they can be translated into reality of every single teaching center (Hłobił 2010, Schelly et al. 2010), where IT equipment is used during classes. Because of a wide range of applications, problem of habits' modification among students in IT class rooms may substantially affect decrease the cost of the electric energy (Attari et al. 2010). The next important reason to write this paper was that decision as for equipment acquisition must be based on knowledge of new technologies, not necessarily related to the daily use equipment, but permitting also to increase safety and efficiency of the equipment. It is also important that purchase decisions in the IT field may substantially decrease expenses concerning consumption of the electric energy.

2. Analysis of students' behavior in a computer room

Recently the successive change of personal computer has been taking place. Starting from 80's and first 20 years of the twenty first century a personal computer was built as a module system comprising the central processing unit and a monitor as well as peripheral devices such

as a mouse and a keyboard. The computer of this shape was the most frequently stored in rooms, houses, offices and schools. Modular structure computer was considered to be a static unit and it did not move along with a user as it takes place nowadays. What is important, every user had to face such a configuration. It made that behaviors in terms of use were the same, among others, it concerned the startup procedure and shut down one. Every user remembered to shut down the computer when operation had been completed and any deviations were rather rare.

Since approx. 10 years new computer types have been appearing: laptops, netbooks, tablets or smart phones. Computers converted themselves into mobile ones and they became a significant part of our life. Apart from the operating system, also the way of use of computers has changed. The most frequently they use batteries and they do not require constant connection to a socket. They are designed and carried out in order to assure quick and simple access, hence, frequently they are not shut down but hibernated instead. It takes place after the cover has been closed or automatically, after expiration of a particular time. New possibilities made that users of mobile computers stopped paying attention whether or not their computers were on and they consumed energy – it is natural and universal. Since these are relatively energy saving electric devices they use a few dozen Watts only and compared to previous solutions these are small values. Moreover their users do not care whether they operate even if this operation is pointless.

The situation is different in case of modular computers still dominating in IT classrooms. Average computer set is equipped with a central unit with a power supply unit 350 W (average) and 50 W monitor. Even in the standby mode both, the unit and the monitor consume electric energy. It is not so much – approx. 5 W, but when number of computers in IT classrooms is serious, this value in question becomes serious as well (Gawłowski et al. 2010).

In order to determine behaviors regarding use of computers in a typical computer room, there was conducted a questionnaire survey among 57 students, who were divided into four lab groups attending classes: programming, computer graphics, databases and numerical computations. Despite the classes were very varied in the field of content, they required intensive work with the computer.

In the survey in question students answered questions included in the Table 1. We imposed a one question - one answer rule. From prelimi-

nary analysis of the questionnaires it results that all of them were filled out correctly and they could be used.

Table 1. Question and answers in the questionnaires

Tabela 1. Pytanie i odpowiedzi udzielone w badaniu ankietowym

Question	Number of answers	%
1. After you have come into a computer classroom and taken your seat you start up the computer:	57	100
<i>per request of a lecturer / teacher</i>	46	81
<i>I chose the time</i>	11	19
2. During scheduled classes you use a computer in a classroom:	57	100
<i>only to perform scheduled exercises</i>	44	77
<i>to perform scheduled exercises, but in a free time I use a computer for personal needs</i>	9	16
<i>I do not perform exercises, I use computer at university in order to spend time of the class</i>	1	2
<i>other: e.g. for personal job</i>	3	5
3. at the time of classes, in the computer room, free electric sockets:	57	100
<i>are used by me for private needs such as: mobile charging, charging of private computer, power bank</i>	13	23
<i>I do not use it for private goals</i>	44	77
4. When classes in the computer room are ended:	57	100
<i>I shut down the computer instinctively, without request of the lecturer / teacher</i>	24	42
<i>I shut down the computer per request of the lecturer / teacher</i>	16	28
<i>I do not shut down the computer even in case of a request of the lecturer / teacher</i>	7	12
<i>I shut down the central unit only</i>	2	4
<i>I shut down the monitor only</i>	8	14

Source: own work.

On the basic analysis of the questionnaires it can be concluded that more and more loosening concerning the use of computers has been observed. It was proved by answers to the point 1 and subsequent ones. Students frequently start their computers without a clear command, they bring own computers into the computer room and at the end of class they do not shut down a computer despite a command of the teacher.

From the first point of the questionnaire one can conclude that as many as 19% students want to use a computer when they can see it. It can be a result of the fact they use private computers daily for different goals. This is also confirmed by answers to the second question since 23% of students during IT classes use the university's computer for private or professional purposes at their free time.

At desks at computer rooms there are frequently available power strips with free electric sockets. As the results of the questionnaires prove, the sockets in question are used by students for varied goals. It concerns approx. 23% of answers and means connection of private computers, charging of mobiles and tablets or power banks (Panasiuk & Panasiuk 2015).

In the light of the energy saving habit, the most crucial answers are the ones to the last question. Answers to this question show that less than 50% students normally shut down their computers. The main role is assigned to the lecturer/teacher. In case he/she asks for it, additionally 28% students shut down computers. It is unquestionably effect of certain weakening of behaviors. It is disturbing that more than 30% of students do not shut down the entire computer set or its particular elements. Such a behavior may be a result of a casual contrariness (Gizowski et al. 2016), but it also could be a habit arising from use of mobiles, which are rarely shut down normally (Sikora 2012).

Such survey is an argument to develop a system, which could autonomously shut down computers after the end of classes and play additional functions such as: protect them from theft, inform on failures or non-authorized intervention into parts of a computer.

3. Introduction of Intel AMT

Recent years we have been observing giving up classic solutions that is maintenance of IT infrastructure in organizations. There appeared

revolutionary technologies which enabled making the infrastructure and software available in form of services (e.g. PaaS, SaaS, DbaaS). AMT is one of many technologies, which enables automation of work with the computer infrastructure. Technology Intel® Active Management (Intel® AMT) enables to manage the computer infrastructure via TCP/IP when the machine connected to the power grid and the network is shut off. It is *firmware* manufactured by Intel and installed at main boards equipped with chipsets (PCH) and processors *Core vPro* and *Xeon for workstation*.

Solution offered by Intel operates at a low level – it assures management of power supply and the hardware, it also enables configuration of BIOS and UEFI settings, that is operations which are unavailable and barely available from the operating system level.

The most important and the largest area where AMT is applied is final user support. Access to KVM (*Keyboard Video Mouse*) enables remote procedures and provision of the help desk type services which are much more extensive compared to RDP (*Remote Desktop Protocol*) or VNC (*Virtual Network Computing*) (Tan et al. 2007, Kumar 2009).

This technology is not hardware only, but also varied software. The technology comprises inbuilt systems, controllers for the operating system, web applications, BIOS or UEFI or tool packs for programmers.

At the market a few programs are available enabling application of the Intel AMT technology. Exemplary programs are: *Intel® vPro™ Platform Solution Manager*, *Intel Open Manageability Developer Tool Kit*, *Microsoft System Center*, IPMI and *SuperMicro IPMI View*. In the following part of the paper the most important attributes of the applications are described. On the basis of their capabilities and own experiences certain functional requirements were defined for the suggested interface TUI (*Text User Interface*).

First described program is *Intel® vPro™ Platform Solution Manager*. It enables to manage power supply simply, as well as to re-direct, read events from a platform or a configuration. It also enables to download entire list of platforms from XML (Tan et al. 2007).

The second of the mentioned programs assures the same functionality as the first one, but extends it to a great extent. Additional functions in the *Intel Open Manageability Developer Tool Kit*, are dozens of options and information on connected computers and AMT Discovery, which is scanning of set range of IP addresses in order to look for computers with

active AMT service. Other interesting functionality is capability to carry out operations from many computers at the same time (Tan et al. 2007).

Microsoft System Center is not the Intel software and it is designed mainly to manage configuration and licenses in large grids based on solutions of the Microsoft company. One of functionalities of the application is provision of basic services by Intel AMT limited to certain versions of the Intel AMT (Tan et al. 2007).

IPMI is a different solution from the AMT and it is designed for server machines, but it also has the common functionality which is reading of physical parameters from sensors installed at a platform. It enables to manage the power supply. It directs the managing console which enables to commence BIOS remotely and to configure it. Additionally, it is capable to manage users (Tan et al. 2007).

Software, which is designed to manage remotely is e.g. *SuperMicro IPMI View*. The application operates also on Windows and Linux systems (developed in Java). It provides many information from physical sensors, rpm of fans, temp. in varied regions of a server, levels of voltages, valid consumption of the electric energy by particular power supply units. Information is helpful in case of operation with server machines. It enables to estimate load of the electric installation or quantity of produced warmth, as well as needs in the field of cooling e.g. increase in power of air conditioning units or other placement of servers in order to distribute warmth evenly (Tan et al. 2007).

The most important conclusion from the analysis of the aforementioned program is that these are frequently too extensive systems which require complicated configuration and usually they are developed for Windows. Additionally, migration of this software into other platform is impossible. One of reasons to develop the application in a version with the TUI interface there was a chance to use this technology from the Linux level or OS X and to increase its productivity.

4. Architecture of the system and interfaces

Assumption of the system was to embed the application in an operating system, and to assure access to it from the Linux system or the Windows console in a computer network. Giving considerations to the requirements stipulated above, users are proposed the TUI type interface in form of a user text interface.

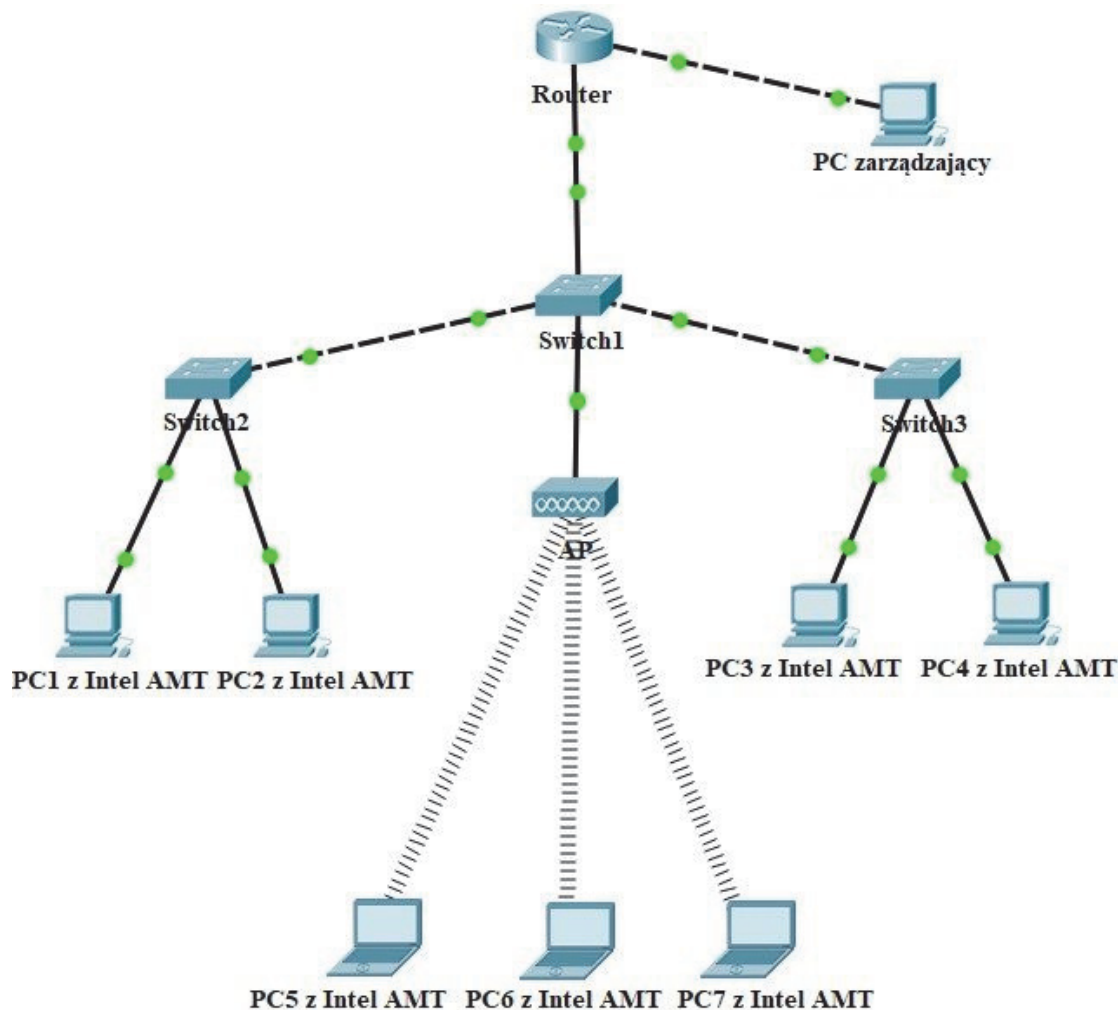


Fig. 1. Architecture of the computer network where there operates a system based on Intel AMT, and where: managing PC – computer, from which it is possible to manage other computers remotely, equipped with Intel AMT, marked accordingly: PC1-PC7

Rys. 1. Architektura sieci komputerowej, w której działa system oparty technologię Intel AMT, gdzie: PC zarządzający – komputer, z poziomu którego można zdalnie zarządzać pozostałymi komputerami wyposażonymi w Intel AMT oznaczonymi odpowiednio: PC1-PC7

Parts of the system are demonstrated in the Fig. 2. The application was developed in Java technology with application of object designing technologies. The most important libraries are supplied by the Intel company. These were two libraries, which simplified communication with the WS-Management and SOAP: *Intel WS-Management Library* and *Intel RDK-SOAP*. Other libraries supporting development of the application were libraries in the Mavena repository: Google Guice, Log4j, TestNG, XStream.

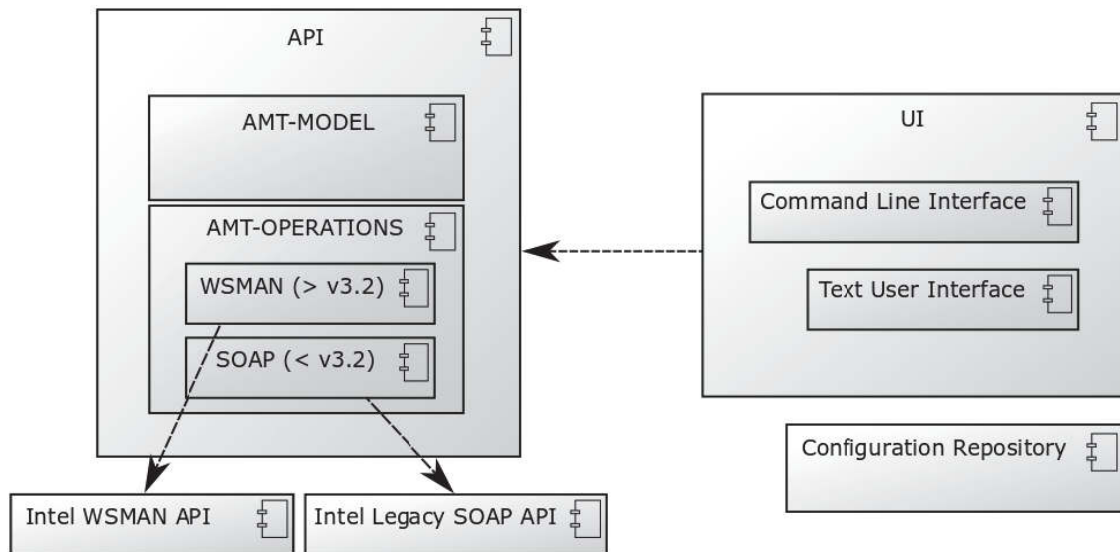


Fig. 2. Division of the system into individual parts (Saint-Hilaire & Ylian 2008), where: UI – comprises two user’s interfaces Configuration Repository – responsible for configuration of modules in the system, AMT-Model – abstractive model of data used to carry out the operations, AMT-Operations – a pack including set of functions assuring relations between platforms, Intel WSMAN API – a pack comprising set of functions to communicate with AMT up to 2.9.X, IntelSOAP – a pack comprising set of functions AMT after 2.9.X

Rys. 2. Podział systemu na elementy składowe (Saint-Hilaire & Ylian 2008), gdzie: UI – zawiera dwa interfejsy użytkownika, Configuration Repository – odpowiada za konfigurację modułów w systemie, AMT-Model – abstrakcyjny model danych wykorzystywany do prowadzenia operacji, AMT-Operations – pakiet zawierający zestaw funkcji zapewniający połączenie z platformami, Intel WSMAN API – pakiet zawiera zestaw funkcji do komunikacji z AMT do wydania 2.9.X, IntelSOAP – pakiet zawiera zestaw funkcji do komunikacji z AMT powyżej 2.9.X

TUI interface is based on the CHARVA library which derives from the Java. It is used to present graphically the user’s interface in traditional system terminals (*Character Cell Terminals*). Its operation consists in emulation of components of the AWT library and SWING into the form of terminal windows.

The application enables to perform essential functionalities in the area of management at a single computer or a group of them. User of the application can:

- manage the power supply that is to download information on the power supply and a present status of the computer and to change it,
- monitor computer configuration that is to read information on equipment configuration of an individual unit.

TUI interface enables to scan selected extents of network addresses in order to find computers with active AMT module. TUI interface is read by means of a reflection mechanism. It assures that the application can be extended easily since it does not require changes in the module logics during further development of application.

The application has been divided into modules. To erect them and to manage them the Apache Maven was applied. Modules were designed in such a way to follow assumptions of so called *loose coupling*. Loose coupling means that modules are much more independent on each other. They communicate with each other by means of interfaces or abstraction classes. Such structure of the system was guaranteed by use of a design sample under the name *dependency injection* (Panasiuk & Panasiuk 2015).

Text User Interface because of its specificity – the users do not have to know the commands and the interface is equipped with advices mechanism, is designed for users with less quantity of the experience in the area of Intel AMT. TUI interface window comprises a panel which makes system functionalities available. In the bottom part of the application window there is a console with results of made operations. TUI provides also guidelines enabling navigation within the interface.

There also available key shortcuts which enhance ergonomics and quickness of use of the system functions. In the Fig. 3 there has been presented a basic screen of the TUI interface. Functionality included there enables to catalog the equipment remotely and to manage power supplies for the platforms.

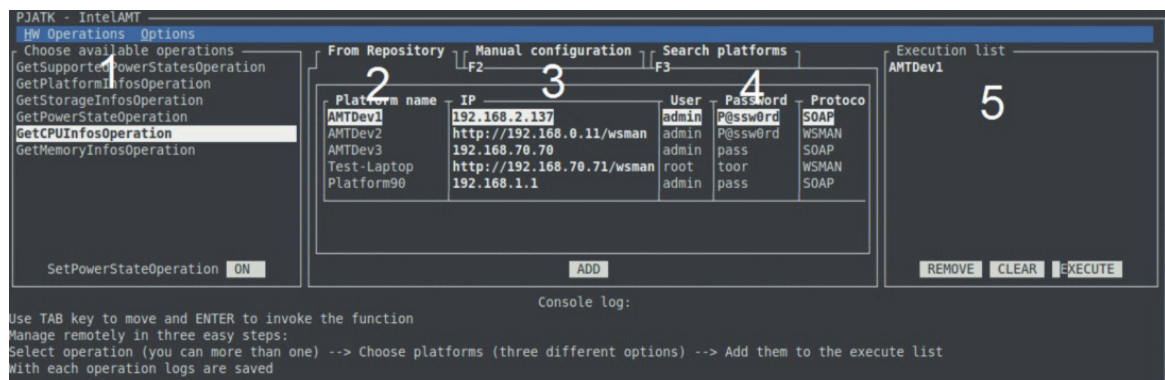


Fig. 3. Preliminary TUI interface window, where: 1 – choice of operations, 2 – display of all computers from the repository, 3 – manual configuration of computers' parameters, 4 – browser of computers in a network, 5 – list with selected computers. To adjust the list no. 5 the following buttons are designed: REMOVE (removes ticked item) and CLEAR (it clears the list). EXECUTE button performs certain operations at selected computers, informing a user on progress of operations in the console of the window

Rys. 3. Początkowe okno interfejsu TUI, gdzie: 1 – wybór operacji, 2 – wyświetlanie wszystkich komputerów z repozytorium, 3 – ręczne skonfigurowanie parametrów komputerów, 4 – wyszukiwarka komputerów w sieci, 5 – lista z wybranymi komputerami. Do korekty listy 5 służą przyciski: REMOVE (usuwa zaznaczoną pozycję) i CLEAR (czyści listę). Przycisk EXECUTE wykonuje wskazane operacje na wybranych komputerach, na bieżąco informując użytkownika o postępie prac w konsoli okna

5. Simulation test and measurement of the electric energy consumption in a computer classroom

In order to picture quantity changes of the electric energy consumption in a typical computer classroom certain simulations and measurements of the electric energy took place.

Simulations and the measurements were made for the computer classroom equipped with 16 stationary computers, IBM class, equipped with a central unit with a 400 W power supply unit and 50 W monitor. Also a multimedia projector was used in the room, 230 W and 600 W total lighting.

In the winter season 2017 during a week, that is from Monday to Sunday approx. 50 (45 minute) lessons took place. In particular, these were programming, computer graphics, software engineering, databases,

engineering computations. Such diversity results in situation that computers in the classroom were loaded in different manner.

During simulation tests average electric energy consumption was accepted equal 225 W. In the Table 2 there is also comparison of results of the simulation test for a full week, where 16 computers are shut down after the end of classes that is just after 50 (45 minute) lessons, or after 38 full hours, and comparing this situation to situation where one, two, three and half of the computers are not shut down. As it was evidenced by analysis of the results in the Table 1, case of failure to shut down 8 of the computers is impossible in practice, but it was included since it was supposed to be used as the upper asymptote for carried out analysis.

Table 2. Analysis of consumption of the energy in a computer room during a week, for 16 computers shut down after classes

Tabela 2. Analiza zużycia energii w pracowni komputerowej przez okres tygodnia dla 16 komputerów wyłączonych po zajęciach

Number of computers not shut down after the class	Energy consumptions [MWh/month]	%
0	0,54	—
1	$0,54 + 0,05 = 0,59$	10
2	$0,54 + 0,09 = 0,63$	15
3	$0,54 + 0,11 = 0,65$	18
8	$0,54 + 0,47 = 1,01$	47

Source: own work.

Analysis of the results presented in the Table 1 proves that failure to shut down the computer after the class in a computer classroom during the week causes increase in consumption of the electric energy. That increase comprises additional 10% of the electric energy in relation to total consumption by all of the 16 computers operating only during classes at the time of the tested week. Increasing number of not shut down computers during the week in question up to 2 or 3 makes an increase in the energy accordingly by 15% and 18%.

In the Fig. 4 there is demonstrated distribution of the electric energy consumption for two months (October, November). The measurement was carried out by an energy meter and the reading took place after

each week. Results of the measurement demonstrated in the Fig. 4 were placed at the background of results entered into the Table 2.

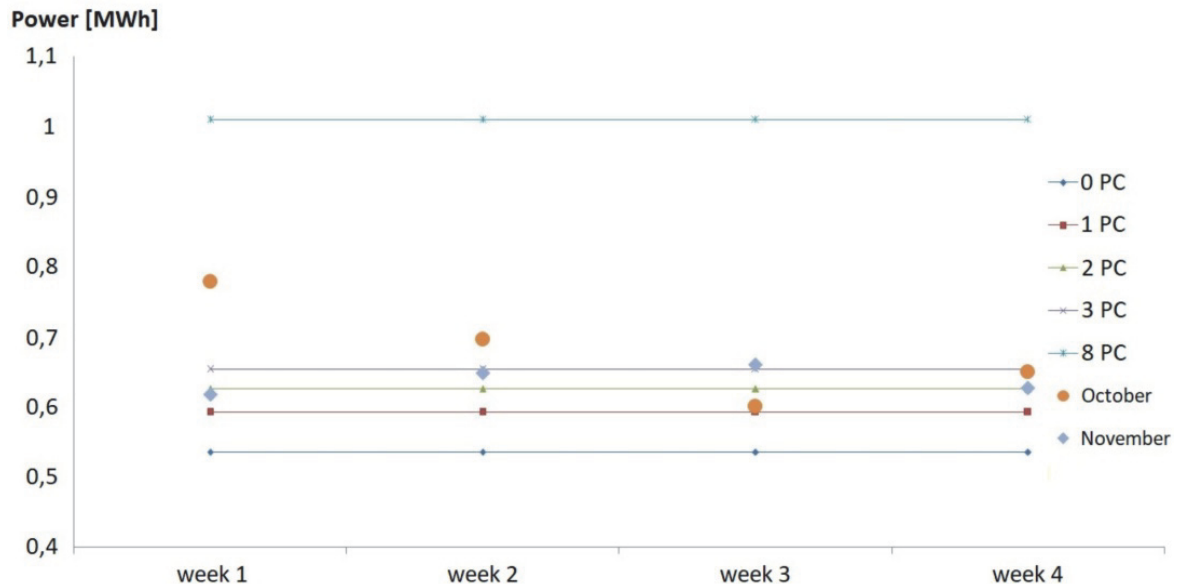


Fig. 4. Recorded consumption of the electric energy by 16 computers during 2 month period in the background of results from Table 2

Rys. 4. Zarejestrowane zużycie energii elektrycznej przez 16 komputerów przez okres dwóch miesięcy na tle wyników z tabeli 2

Presented distribution of the energy consumption shows decreasing tendency and then controlled smoothing of it. According to the Fig. 4 it results that the largest consumption of the energy was noted in October, and much lower was observed in November. At every higher school this is time, when students start attending labs and relatively frequently attend them. Large consumption of the electric energy after the first week, and then its successive drop can be explained by the fact that students were taught on how to deal (shut down) with the computer equipment. After some time for most of them it has become something normal. It confirms the results acquired in the questionnaire survey, according to which it results that, if admonished, 28% students shut down the computers while 18% of them shut down only certain parts of computers. Comparing results of the measurements and simulation tests one can conclude that the bottom asymptote of consumption of the energy may arise from the fact, that averagely one or two computers are not shut down although students have been asked to do so.

6. Conclusions

IT system developed for a higher school enables simple and effective management of its computer infrastructure. The most substantial added value arising from developed software is automation of IT administrators' duties from level of any system and possibility to control and to monitor condition and operation of the computer infrastructure. Due to high level of automation the product must enable more effective management of the electric energy and quicker reaction in case of a failure. The system can be also applied in order to make periodic cataloging of the computer equipment or other reports on IT infrastructure of a university. Proposed solution has been adjusted to the environment where it was to function and it met requirements of the final user. Even if the proposed system cannot be implemented, still the conclusion is that at the time of planning the technical infrastructure one needs to invest into new technologies since they enable improvement of the work quality and they also enable reduction of the energy consumption contributing consequently to promotion of the environment protection.

A substantial conclusion arising from conducted questionnaire survey and measurements of the electric energy consumption is that, to the some extent, it is possible to promote pro-eco approach among youths in terms of use of electric devices. Cultural changes in this field are significant and hence, trends must be controlled and watched.

When planning the IT infrastructure in an organization, especially a large one such as higher school/university, technologies similar to Intel AMT are worth of attention since due to them management and maintenance of proper technical condition of computers is much more simple and effective. At the technological process one should take into account all operations regarding ecology and environment protection. The issues refereed herein are of significant meaning for the ecological awareness growth.

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Analiza zużycia energii elektrycznej w ośrodkach dydaktycznych a ochrona środowiska

Streszczenie

Nowoczesne programy studiów prowadzone w szczególności na kierunkach technicznych, obejmują przedmioty, które w części praktycznej realizowane są w pracowniach komputerowych. Takich przedmiotów jest szczególnie dużo na uczelniach technicznych, a kierunkiem, który wiedzie prym w tym zakresie jest informatyka. W pracy przedstawiono czynniki, które mają istotny wpływ na zużycie energii elektrycznej w pracowni komputerowej. Analiza ta pokazuje, że zmiana nawyków zachowania studentów korzystających z pracowni komputerowych jest istotna ze względu na relatywnie duże oszczędności w zużyciu energii elektrycznej i w obniżeniu kosztów utrzymania pracowni. Przeprowadzono badanie ankietowe, w którym rozpoznano nawyki użytkowników pracowni komputerowych. Następnie przedstawiono oprogramowanie, które umożliwia zdalne i efektywne zarządzanie stanem platform komputerowych. System ten oparty został na technologii sprzętowej „Intel Active Management Technology”, która również została scharakteryzowana w pracy. Funkcjonalność systemu opracowano na podstawie doświadczenia i wymagań zespołu administratorów sieci komputerowej i prowadzących zajęcia informatyczne. Do najważniejszych funkcjonalności systemu należy pobieranie informacji o stanie zasilania platform i zmienianie go, pobieranie informacji o podzespołach komputera, skanowanie adresów IP maszyn i archiwizowanie ich. Powstałe oprogramowanie wyposażone zostało w dwa typy interfejsów. W stosunku do znanych rozwiązań komercyjnych stworzone interfejsy wpłynęły na poprawienie wydajności systemu oraz zwiększyły jego ergonomie w zarządzaniu platformami. Jako podsumowanie przedstawiono analizę zużycia energii elektrycznej w pracowni komputerowej bez zastosowania systemu i po jego implementacji. W artykule pokazano występującą problematykę ochrony środowiska, którą obejmuje przeprowadzona analiza zużycia energii elektrycznej w ośrodkach dydaktycznych.

Abstract

Modern programs of studies, in particular for technical majors, include classes which take place in computer rooms. Such subjects are numerous in particular at technical schools / universities and the major which is leading one is the IT. In the paper authors presented factors which have a significant impact on consumption of the electric energy in a computer room. The analysis in question shows that change of habits of students using computer rooms is important

because of relatively large savings in consumption of the electric energy and lower costs of maintenance of computer rooms. Survey was carried out in order to learn habits of users of computer rooms. Then software was demonstrated enabling remote and effective management of computer platforms. The system was based on equipment technology “Intel Active Management Technology” which also is characterized in the paper. The system functionality was developed on the basis of experience and administrators’ requirements of the computer network and IT class teachers. The most important functionalities of the system comprise collection of information on power supply of the platforms, as well as changing this state, collection of information on sub assemblies of a computer, scanning of machines IPs and archiving them. Elaborated software was equipped with two types of interfaces. In relation to known commercial solutions, developed interfaces improved efficiency of the system and enhanced ergonomics of platforms management. As a conclusion the analysis of the electric energy consumption in a computer room has been presented - the consumption without application of the system and after it has been implemented. Also the environment protection is part of this paper since it is a part of made analysis of the electric energy consumption in teaching centers.

Słowa kluczowe:

oszczędzanie energii, energia elektryczna, sieć komputerowa, technologia Intel AMT, oprogramowanie

Keywords:

energy saving, electric energy, computer network, Intel AMT technology, software