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Obtaining of Functional Product by Mechanical Processing of Secondary Fish Raw Materials

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1. Introduction

The most competitive type of fish product that is in steady demand among the population is fresh or frozen fillets resulting from the deep cutting of raw materials. For the countries bordering the Baltic Sea, the raw materials for the production of fillets are cod, pike-perch, salmon, herring and others. Depending on the species composition of fish, the choice of cutting technology and equipment used, the output of the finished product (fillet) is 40...50%.

Remaining wastes (bones, fins, heads, scales, skin, insides) from the point of view of complex non-waste technology are rationally directed to fishmeal and hydrolysate production, however, the majority of fish processing enterprises do not have such production due to obvious economic, financial, industrial and technological difficulties. In practice, the easiest way is implemented by the enterprises: directing waste to cattle, birds, fur animals, etc. Disposal of fish waste is unacceptable for developed countries as it does not correspond to their environmental safety.

In fact, the components of fish produced by filleting are not wastes, but valuable secondary raw materials with rich biocapacity. Each of the components, individually or in combination, contains a rich spectrum of macro nutrients, minerals and vitamins, which determine the importance of their use in food, pharmacological, medical, fodder, technical purposes. One of the most modern directions of rational use of secondary fish resources is obtaining on their basis food and therapeutic and preventive additives: biologically active additives (BAA).

The problem of processing secondary fish raw materials into healthy food products is of great importance. Suyue Song et al. (2020) describes the proposed method and the corresponding validation experiments with carp fillets. The differences in Raman spectra between fish bone and fish meat were investigated, and the optimal band information was selected using a fuzzy-rough set model based on the thermal-charge algorithm. Pınar Terzioğlu et al. (2018) summarizes the literature on the production of hydroxyapatite from fish bones and discusses their potential applications in biomedical field. The effect of processing conditions on the properties of final products including Ca/P ratio, crystal structure, particle shape, particle size and biological properties are presented in the light of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetric-differential thermal analysis, bioactivity and biocompatibility investigations.

Albrektsen et al. (2018) suggests that hydrolysed compounds from fish bones may improve Ax utilization in salmon, and that they may have an impact on the functional properties of the muscle. Anindya Pal et al. (2017) presents aims at the synthesis of hydroxyapatite (HAp) from fish bone by simple heat treatment in the temperature ranging from 200 to 1200°C. The synthesized powders were characterized using X-ray diffraction and Fourier transform infrared spectroscopy to identify the phases and functional groups. Jin Zhang et al. (2016) investigates of effects of thermal treatments on breakage and calcium release of fish bone particles during high-energy wet ball milling. Heating temperature (55-130°C) showed much more obvious influences on the breakage and calcium release than heating time (20-60 min). Weeraphat Pon-On et al. (2018) fabricates composite scaffolds consisting of mineral ion-loaded hydroxyapatite derived from fish scale (mHAFS) in a poly (lactic acid) (PLA)/chitosan (Chi) matrix (mHAFS@PLA-Chi) by an *in situ* blending technique. Mineral ion loaded HAFS was successfully converted into mHAFS via the hydrothermal heating of HAFS in a SBF (simulated body fluid) solution.

We chose Baltic cod bone tissue as the object of research, which is a part of heads and fins when cutting on fillets, forms rib and ridge bones with muscle tissue incisions. Fish bone tissue is 6 to 20% of its muscle tissue. It is a source of protein and minerals. Protein is 73-95% represented by osseoalbumoids, which together with glucosaminoglycans form a glycoprotein that is more resistant to decomposition than collagen. Mineral substances are Ca, P, K, Na, Mn, Fe, Cu, Sn, Al. The contents of calcium in fish bone is 6.2 times higher than in muscle tissue, magnesium – 8 times higher, manganese – 1.1 times higher.

Substances included in the fish bone tissue have a positive effect on humans, stimulate the metabolism of proteins and carbohydrates. Complex of mineral salts and calcium has a positive effect on the treatment and prevention of caries, osteochondrosis, rickets. It is also known that the introduction of fish bone tissue in the diet leads to a decrease in the accumulation of radioactive isotopes in the human skeleton, reduces the risk of malignant tumors, prevents metastasis of already developed tumors and diseases of the hematopoietic and bone systems.

In this regard, the purpose of this study is to substantiate the developed technology of natural bone tissue supplement of hydrobionts (on the example of cod) and the development of recommendations for its use as a food and therapeutic additive in the production of dietary supplements.

2. Materials and methods

Determination of mass and chemical composition of the object of study was carried out in accordance with GOST of Russian Federation.

The mineral composition was determined by atomic-absorption spectroscopy on the device AA280Z of VARIAN company with graphite cell, sources of resonance radiation of the elements to be determined, prefix for generation of hydrates VARIAN VGA77. The method is based on the measurement of the absorption (optical density) of the atomic pair of a certain element, obtained by electrothermal atomization of the sample in the graphite cell of the spectrometer. To determine the contents of phosphorus, a two-beam spectrophotometer Hitachi 220A was used.

In the course of microbiological control in accordance with Russian Sanitary and Epidemiological Rules and Regulations, fish bone samples were examined by standard methods for the presence of: mesophilic aerobic and facultative anaerobic bacteria, the presence of Escherichia coli bacteria, Staphylococcus aureus, and the presence of pathogenic microflora, including the genus Salmonella.

Experimental studies of the fish bone drying process were carried out on a specially designed unit designed for vacuum drying of various moisture-containing food materials. Experiments were carried out at the temperature of heating plates on which the dried material was located, 70°C; 80°C; 90°C and absolute pressure inside the vacuum chamber of 1.6 kPa; 2.0 kPa; 2.4 kPa.

3. The results of the study

Hygiene assessment of radionuclide contents in fish raw materials is an integral part of a set of measures aimed at ensuring radiation safety of the population. Among the radioisotopes polluting water bodies the most important are 90Sr strontium and 137Cs cesium. For strontium, the critical organ is the bone tissue, and for cesium – muscle tissue and internal organs. According to the data of the laboratory of radioecological researches of Atlant-NIRO in the bone tissue of cod extracted in the waters of the Baltic Sea, Curonian and Kaliningrad (Vistula) bays, strontium radioisotopes have not been found, which allows classifying such raw materials as safe in the radio-hygienic aspect.

The technological sequence of obtaining a food additive from fish bone tissue provides for cooking of the backbone with cuts in muscle tissue, upper and lower fins and tail fins (in this form, the raw material comes after filleting). In this process, the bone is cleaned, and after additional centrifugation is released from foreign inclusions and excessive moisture. Mass and chemical composition of cod bone before and after cooking is given in Table 1.

Table 1. Chemical composition of pike-perch and cod bone before and after cooking

	Factors												
	Mass fraction, %				Contents, %				Contents, mg/kg				
	Fat	Pr.*	Mo.*	Ash	K	P	Ca	Na	Mn	Fe	Cu	Al	Sn
Before boiling	0,3	13,0	71,0	15,6	0,10	1,90	2,40	0,10	5,7	8,0	1,5	< 0,1	< 0,01
After boiling	0,3	12,9	56,6	30,1	0,08	5,60	4,40	0,21	21,7	4,	3,8	< 0,1	< 0,01

* Pr. – Protein; Mo. – Moistur

Analysis of the data presented in Table 1 shows that the implementation of the thermal calculation of the boiling process does not lead to a reduction in the number of microelements in the bone tissue of fish and their content (in terms of dry matter) remains high.

As a parameter of process rationalize the rate of product dehydration (V) is chosen, it characterizes the rate of moisture removal per process:

$$V = (W_0^c - W_K^c)/\tau, \tag{1}$$

where:
W_0^c, W_K^c – Initial and final moisture content of the product, in relation to dry matter, %;
τ – Drying time, min.

It is important at what rational parameters of the drying process of the object of study will be provided the minimum duration and maximum performance of the plant for the finished product. The limitation is the moisture-containing of the final product and its quality, which determines the duration of storage.

In the process of vacuum drying of raw materials the influencing factors of the process are the temperature (T) of heating plates (heat exchangers) of the drying plant and the absolute pressure (P) inside the chamber of the device.

Implementation of experiments using the method of experiment planning allowed to obtain the following regression equations adequately describing the influence of factors on the rate of vacuum drying of cod bone (multiple determination factor R^2 = 0,95).

In the coded values of the factors:

$$y = 0{,}8019 + 0{,}0365x_1 + 0{,}115x_2 - 0{,}031x_1 \cdot x_2 - 1{,}583 \cdot 10^{-2}x_1^2 - 0{,}093x_2^2. \quad (2)$$

In the natural values of the factors:

$$V = -7{,}9098 + 1{,}1071T + 0{,}1763P - 7{,}750 \cdot 10^{-3}TP - 9{,}8958 \cdot 10^{-2}T^2 - 9{,}3333P^2. \quad (3)$$

The obtained regression equation allows not only to predict the value of the response function for the given conditions of implementation of the process of vacuum drying of the fish bone, but alsoprovide information on the shape of the response surface, which is presented in Fig. 1.

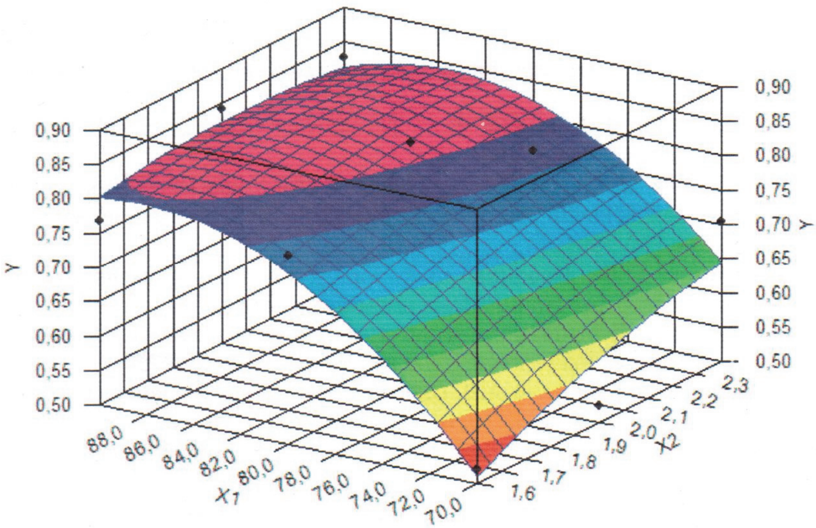

Fig. 1. Surfaces of the response function in the selected area of the factor space for cod bone

Rational parameters of the vacuum drying process of cod bone are:

$$P = 2{,}0 \text{ kPa};\ T = 80°C;\ \tau = 155 \text{ min};\ W_K^c = 3{,}09\% \quad (4)$$

After drying, the fish bone becomes brittle and changes colouration from white to light beige. In order to obtain a product in the form of a powder, it is subjected to fine grinding, and the rational process is when the final moisture content of the bone after drying corresponds to 3-5%. The finely grinded bone mass can be obtained with a hammer-type mill. The final product is an air-dry polydisperse substance consisting of 0.6 to 0.08 mm particles.

The shredded bone mass should be packaged in containers, which should have the least moisture and light permeability to ensure maximum preservation of the valuable properties of the finished product during storage. The best variant of packing containers: paper multilayered, jute or craft bags of different sizes.

The condition of storage of finely grinded fish bone is determined by its hygroscopic properties. The equilibrium moisture content of the bone mass (flour) W_p depends on the relative moisture content of the surrounding air (y), and within the range of 60-100% this dependence looks like:

$$W_p = 10^{(a+by)}, \quad (5)$$

where: a and b – constants depending on the properties of flour (for crumbly flour a = 0.072, b = 1.345).

Storage of flour in conditions of increasing moisture content and temperature contributes to the active absorption of moisture by the product, the breakdown of proteins, hydrolysis and oxidation of lipids, the destruction of vitamins, the development of residual microflora. Oxidative processes in the flour can lead to its self-heating and spontaneous combustion. The rational conditions for storing fishmeal are the air temperature 15…20°C at a relative moisture content of not more than 75%.

At determining the shelf life of the shredded fish bone in the specified rational conditions the actual moisture content of the product corresponds to the equilibrium moisture content and is 10-12%. The guaranteed minimum shelf life is 1 year from the date of manufacture.

Organoleptic evaluation of the product at the end of its shelf life. Appearance – finely grinded, finely dispersed and easily scattered powder. Colour – white. Smell – odorless. Taste – typical for this product. The presence of signs of oxidation – there are no signs of oxidation.

Lipid indicators of cod bone tissue are as follows. The acid number changed insignificantly from 1.2 to 1.5 mg KOH/g, which indicates that the degree of fat hydrolysis is insignificant. The peroxide number changed from 0.08

to 0.12%I during the same period, which shows that there is practically no oxidative process of fat.

It is interesting to compare the acceptability of the described technology for other fish species with high fat content in bone tissue. Despite the significant difference between this indicator for cod and pike-perch, the whole technological sequence of treatment is preserved and the parameters recommended in formula (4) are similar. However, during the storage of finely grinded pike-perch bone, the peroxide number increases significantly faster, which indicates a more intensive oxidation of fat, although it also does not reduce the final quality of the product. For fish bone raw materials with high fat content, storing the powder in vacuum packaging, which is known to slow down the oxidation process, is a recommended option.

Considering high biological value of a final product – fine-grained fish bone mass in the form of a flour or a powder is possible to use in industrial scales in following directions:

1. When preparing food for fish, birds and animals as an additive enriched with minerals and vitamin-enzymatic complex.
2. When added to wheat flour and meat products, sugar, confectionery and other products as a prophylactic component with easily assimilable protein and minerals of osteo-tropic and chondroprotective action. This practice exists in the USA, England and Canada.
3. As a component of biologically active substances containing easily digestible calcium, and recommended in medical practice as a general strengthening agent that helps reduce blood sugar levels, as well as with increased mental stress (powders "Tian Shan", "Calcium magnesium chelate", etc.).
4. As the main component of the dietary supplement, designed to improve the musculoskeletal system. In Russia, 44% are domestically produced dietary supplements, while the rest are imported dietary supplements (BAA "Calcimax", "Glucosamine", "Joint Flex" (USA), "Wise Dragon" (Vietnam), "Doholodan" (China),"Ortoosteo" (Germany) and etc.).
5. As an additive recommended for the prevention and treatment of radioactive threats to the human body.

Depending on the physiological needs of different population groups, a certain amount of fish powder supplement is calculated. Its application can be both in bulk form and in the form of bars, granules, tablets, capsules, etc. At the same time, the use of fish bone supplements to obtain the products recommended by us can be carried out on the basis of known traditional technologies.

4. Conclusion

1. Fish bone waste is a valuable secondary resource enriched with macro- and microelements and vitamins.
2. The technology of fish bone processing for obtaining mineralized food additive has been developed.
3. Rational mode of vacuum drying of fish bone with minimum moisture content is developed.
4. Conditions and guaranteed shelf life of the mineralized food additive are determined.
5. The recommendations on industrial use of the food mineralized additive are offered.

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Abstract

The most competitive fish product is fresh or frozen fillets. The yield of the finished product is 40...50%. Waste from production is sent to livestock, birds for feeding and other purposes, as well as disposed of, which does not correspond to environmental safety. The bone components of fish are valuable secondary raw materials containing a wide range of macro nutrients and minerals. Their most rational use is to obtain biologically active additives on their basis. The object of research is cod bone tissue. The technology of obtaining a natural mineral additive from bone tissue is substantiated. After boiling, the bone tissue is cleared of muscle tissue, while the content of minerals remains high. Vacuum drying of the grinded product allows it to be stored for a long time without compromising its quality. The rational values for vacuum drying of bone waste are given. The conditions of storage of finely grinded mineral bone additive are considered. The ways of its rational industrial use as a biologically active additive are determined.

Keywords:
cod, bone tissue, secondary raw materials, minerals, biologically active additive

Produkcja produktu funkcjonalnego przez obróbkę mechaniczną wtórnych surowców ryb

Streszczenie

Najbardziej konkurencyjnym rodzajem produktu rybnego jest świeży lub mrożony filet. W takim przypadku wydajność produktu końcowego wynosi 40...50%. Odpady z produkcji są kierowane na paszę dla zwierząt gospodarskich, ptaków i innych celów, a także są usuwane, co nie odpowiada bezpieczeństwu środowiska. Składniki kostne ryb są cennym surowcem wtórnym zawierającym bogate spektrum makroskładników i minerałów. Najbardziej racjonalnym zastosowaniem jest uzyskanie biologicznie aktywnych dodatków na ich bazie. Jako przedmiot badań wybrano tkankę kostną dorsza. Technologia uzyskiwania naturalnego suplementu mineralnego z tkanki kostnej jest uzasadniona. Po ugotowaniu tkanka kostna uwalnia się od tkanki mięśniowej, a zawartość minerałów pozostaje wysoka. Suszenie próżniowe pokruszonego produktu pozwala przechowywać go przez długi czas bez pogorszenia wskaźników jakości. Podano racjonalne wartości parametrów suszenia próżniowego odpadów kostnych. Uwzględniono warunki przechowywania drobno zmielonych mineralnych suplementów kostnych. Określono sposoby jego racjonalnego zastosowania przemysłowego jako biologicznie aktywnego dodatku.

Słowa kluczowe:
dorsz, tkanka kostna, surowce wtórne, minerały, suplement diety