

Effective purification of natural and wastewater from heavy metals is a relevant environmental and national-economic problem. It can be solved by using plant-waste-derived biosorbents in water treatment technologies. They are formed in large quantities by agricultural and food enterprises. Taking into consideration data on the peculiarities of mechanical and thermal effects on the components of plant biomass, the techniques have been substantiated to obtain biosorbents from pea processing waste. It has been shown that the dehydration of the waste, its carbonization, and the crushing of char can produce biosorbents with different sorption properties. The nature of influence exerted by the process parameters of the Cu(II) and Fe(III) ions biosorption from model aqueous solutions on a change in the concentration of the solution, the value, and adsorption uptake has been established. In particular, the effect of the process duration, the type and initial content of metal in the solution, dosage, and a biosorbent production technique was studied. It has been shown that 38 to 98 % of heavy metals can be removed from solutions at their initial concentration between 2 and 20 mg/dm³ and a biosorbent dosage between 1 and 30 g/dm³. It was found that char is more efficient at removing heavy metals. It was also determined that the biosorbents made from pea processing waste are better at removing the Cu(II) ions from aqueous solutions than the Fe(III) ions. The generalization of the results of kinetic research is represented in the form of a multifactor regression equation. The equation makes it possible to calculate a change in the concentration of heavy metal in the solution depending on its initial concentration, the duration of the biosorption process, and the dosage of a biosorbent. For the mathematical notation of the experimental adsorption isotherms, values of the coefficients in a Langmuir equation have been determined. The derived equations could make it possible to optimize the technological parameters of the process

Keywords: aqueous solutions, heavy metals, plant waste, biosorbents, kinetics, adsorption isotherms

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THE KINETICS OF THE PROCESSES OF EXTRACTING THE CU(II) AND FE(III) IONS FROM AQUEOUS SOLUTIONS BY THE BIOSORBENTS BASED ON PEA PROCESSING WASTE

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1. Introduction

One of the modern environmental problems is the growing contamination of natural water reservoirs with heavy metals (hereinafter referred to as HMs). Drinking water with excess content of HMs is the cause of diseases in humans and animals [1, 2].

Contamination of water facilities with HMs is due primarily to the discharge of non-treated or insufficiently treated wastewater from industrial enterprises into reservoirs. The largest pollutants of water reservoirs with HMs are electroplating production, chemical and petrochemical industry, machine engineering, metallurgy, typography, mining [3, 4]. The contamination of natural waters with HMs is

contributed to by the intensive use of mineral fertilizers and plant protection products in agriculture [5]. The non-treated food production drains, albeit to a lesser extent, but are also sources of contamination of natural water facilities with HMs [6]. The source of HMs' arrival in the environment and reservoirs may be excess active sludge and sediment from biological wastewater treatment facilities. They accumulate HMs. Such waste should be disposed of by burying it in slag storage, by thermal or thermochemical treatment. However, in practice, there is still its immediate discharge to agricultural lands. The negative consequence of such activities is the contamination of soils and groundwater with HMs [1].

The technique to purify natural or wastewater from HMs is chosen depending on their amount and chemical

composition. The selected technique is influenced by the form of HMs in the aquatic environment (adsorbed by humus substances and clay minerals, in the form of dissolved and insoluble complexes with organic and inorganic ligands, in an ionic form). Important criteria are the technique's environmental safety and cost-effectiveness. After all, the technology and materials selected for use should ensure the effective removal of HMs from the aquatic environment. However, they must not become an additional source of toxic waste to the ecosystem. In addition, the cost of treated water should be acceptable to the consumer.

There are the following purification techniques of natural and wastewater from HMs: chemical precipitation, ion metabolism, membrane technologies, coagulation with flocculation, electrodialysis, electroflotation, electrocoagulation, electrical deposition, photocatalysis, adsorption. Numerous modifications of these techniques make it possible to remove HMs from aquatic environments with varying efficiency. The downside of existing techniques is the high cost of water treatment. That does not contribute to solving the issue related to the pollution of natural reservoirs with HMs. In addition, waste materials and wastewater from washing the equipment, if they are not disposed of, are an additional source of environmental pollution [7]. Therefore, it is a relevant task to improve existing techniques and to develop new ways to purify natural and wastewater from HMs.

2. Literature review and problem statement

Among the promising ways to consider for cleaning sewage and natural waters from HMs is their extraction using biosorbents [7]. The plant wastes from the agro-industrial industry are considered promising as a raw material for biosorbents. The advantages of such biosorbents are that they are derived from cheap, available, and constantly renewed raw materials [8]. The price of such biosorbents is lower compared to activated coal derived from coconut shells [9]. Depending on the technique of obtaining a biosorbent and its application modes, water can be purified from oil and petroleum products [9], heavy metals [10], dyes [11], herbicides [12]. Biosorption can be used as an additional technological process to improve the quality of natural and wastewater, particularly in water desalination technologies that employ freezing. The low-temperature separation of highly mineralized solutions makes it possible to desalinate and soften water but the degree of extraction HMs from water is insufficient [13]. The production and use of biosorbents make it possible to minimize the formation of environmentally harmful emissions (due to the disposal of large-tonnage wastes from agricultural and food industries, as well as the result of using spent biosorbents as an alternative energy source, a component of mixtures for road coatings, etc.) [8]. The development of biosorbent production techniques, studying their properties and conditions of using them in the purification of water from HMs has been addressed by a large body of modern research [14].

The enterprises in the agricultural sector and in the food industry generate a lot of different plant waste. It includes the waste from processing green peas, namely pea peels. They account for 30 % of the total mass of green peas gathered in the field. The leaders in pea processing are China and India [15]. A lot of such waste is formed at enterprises in Europe [16]. The annual production of pea peels in the UK is

54,000 tons, and in India – more than 1 million tons. Some of the fresh pea peels are used as feed for goats and cattle. However, the overwhelming amount of them is wasted, which is an ineffective solution. Note that pea peels contain some substances that can be used, after treatment, as food additives [15], raw materials to produce bioethanol [17], biosorbents for water purification [18].

The authors of work [17] proposed making bioethanol from pea peels. In their research, the authors show the prospects of using pea peels as raw materials for the production of bioethanol on a global scale and a good alternative to fossil fuels. In addition, the cited work describes the chemical composition of fresh pea peels. In particular, the content of glucose, xylose, lignin, dry substances, moisture, ash was determined. Considerable content of cellulose and lignin in raw materials allows the authors to conclude about the possibility of its use in the production of biosorbents. However, how to get them, they do not point out.

Nevertheless, this idea was advanced by the authors of study [19]. To obtain a biosorbent, they washed pea peels with bidistillate and dried at 70 °C in the furnace by hot air to a constant mass. The dried product was crushed and sifted. The size of the biosorbent particles varied from 0.106 to 0.90 mm. The cited study reports the chemical and element composition of the resulting biosorbent. The researchers also found that the biosorbent contains more acid groups than the base ones. The following functional groups were found at the surface of the biosorbent: hydroxyl groups of alcohols and phenols, carboxyl and hydroxyl groups of carbonic acids, amine groups of amine and amino acids, carbonyl groups of aldehydes, cyan groups of nitriles, aromatic compounds. The surface pH of pea peels is close to neutral. That is why the study's authors argue about the possibility of using a biosorbent from pea peels for the removal of both cationic, in particular HMs, and anionic contaminants. In addition, the authors identified the physicochemical characteristics of the biosorbent such as bulk density, particle density, the biosorbent porosity, water absorption. The surface of the biosorbent particles is irregularly shaped, rough, and porous. The biosorbent is thermally stable at temperatures below 150 °C. The value of the specific sorption surface area is low but typical of carbon biosorbents. The authors explain this by the presence of gaseous impurities in the biosorbent and the complexity of their extraction under the specified treatment technique.

At the same time, work [19] did not investigate the kinetics of HMs extraction by the obtained biosorbent and its sorption capacity for such pollutants. In addition, such a technique to obtaining a biosorbent is proposed that involves washing pea peels with bidistillate, drying raw materials to a constant mass, and grinding it. The technique is simple but its disadvantage is the additional formation of wastewater at the stage of washing the starting raw materials. The use of this technique will not contribute to the rational use of water resources and the preservation of their quality. We also believe that sulfo-groups may be present in the biosorbent, in addition to the specified functional groups. The conclusion was drawn on the basis of the analysis of the elemental composition of the biosorbent reported in the cited study. The presence of such groups would increase the sorption capacity of the biosorbent to the cationic impurities in water.

The authors of [20] studied the mechanisms of extracting the Pb (II) and Ni (II) ions from aqueous solutions using treated pea peels. They also conducted kinetic studies

into the biosorption process of these metals. The kinetic data were generalized by using known kinetic equations and the adsorption isotherm equations. The thermodynamics of the biosorption process has also been studied. To obtain a biosorbent, the following technique was used. Fresh pea peels were washed with tap water and then with distilled water. They were dried under the sun to a constant mass, crushed with a pestle in a mortar, sifted. The resulting material was soaked with distilled water and aged wet for (8-10) hours. Water was drained, the raw materials were again poured with distilled water, and aged over the above time once again. Such an operation was carried out until the decanted water became transparent. Next, the material was dried in the furnace at 100 °C to a constant mass. The kinetic studies were carried out on model solutions at an initial concentration of HMs equal to 40 mg/l. The biosorbent dosage changed from 10 to 90 g/l. The temperature in the experiments was constant, 30 °C, the pH varied between 3 and 11. Flasks containing the solution and biosorbent were stirred at a frequency of 200 rpm and additionally shaken for 60 minutes. The contents of the flasks were filtered; the content of HMs was determined in the filtrate.

The study results established that the increase in the sorbent dosage increases the biosorption of these HMs. The authors conclude that increasing the biosorbent dosage increases the number of active centers, and, therefore, the sorption of HMs grows. However, it should be noted that the dosage of the biosorbent increases by 9 times while the magnitude of adsorption increases by 1.08 times. It is obvious that a further increase in dosage makes no sense because there would be the overconsumption of the biosorbent without beneficial effect. We also believe that there should be no linear dependence between dosage and the magnitude of adsorption as far as the biosorbents are concerned. After all, the removal of HMs occurs not due to the physical adsorption but mainly due to the reactions of ionic exchange. Substitution or complexation reactions are also possible. For the ionic exchange reactions to take place, the biosorbent functional groups must be ionized in water. Earlier work [19] reported a study into the biosorbent surface chemistry. Its analysis shows that the functional groups of weak electrolytes were involved there. Therefore, the higher the concentration of these groups in the aqueous solution, the worse the conditions for dissociation. Thus, the value of the adsorption of cation impurities from aqueous solution would be lower. Most likely, there is a dosage optimum. It should be determined by extending the dosage range, in particular, toward low values.

To summarize the kinetic data, the authors of [20] applied a pseudo-second-order equation while the equilibrium state is described by the Freundlich equation. However, despite the high accuracy of calculations based on these equations, their practical application for design is still limited. After all, the kinetics of the biosorption process has been studied for only one concentration and only two types of HMs in the model solution. For practical use, both the kinetic equation and adsorption isotherm equations are required in order to summarize the results obtained for the range of values of the initial concentrations. After all, both in natural and wastewater, the HM content is different.

The authors of work [21] obtain a biosorbent from pea peels through the pyrolysis of raw materials at 800 °C for 30 minutes in the atmosphere of N₂. The material is

then activated by a 50-% solution of concentrated H₂SO₄ for 24 hours. The work reports a kinetic study into the process of biosorbent extraction of the dye “methylene blue” from the aqueous solution. The results were generalized by using known equations that describe the adsorption isotherms. The reported results show that using the pyrolysis of raw materials can produce a material with high sorption characteristics. Such a treatment of raw materials causes the transformation of biomass components, the result of which increases the carbon content in the biosorbent and the number of functional groups capable of participating in the chemisorption of impurities. The material's porosity increases. Therefore, we consider it relevant to conduct further studies into the kinetics of HM biosorption both by the carbonized and non-carbonized raw materials. This would form a theoretical basis for the development of technologies and the design of equipment to produce biosorbents from pea peels, as well as to use them to extract HMs from water.

3. The aim and objectives of the study

The aim of this study was to determine the kinetics of the process of extracting copper and iron ions from model aqueous solutions by the biosorbents obtained from pea processing waste according to various techniques. This is necessary to understand the effect of the process parameters on the patterns of HM extraction from the aqueous solution, the equilibrium state of the system. Obtaining and generalizing such data would make it possible to move to the next stage of work, namely industrial production and application of the proposed biosorbent during water treatment.

To achieve the set aim, the following tasks have been solved:

- to substantiate the choice of techniques to obtain biosorbents;
- to experimentally investigate, on model solutions, a change in the concentration of HMs in the process of biosorption depending on their type and initial concentration in the solution, the dosage of the biosorbent, the process duration, the technique of obtaining biosorbent;
- to estimate the static activity of biosorbents in terms of adsorption capacity and the adsorption uptake;
- to generalize experimental data in the form of regression equations and the equations that describe the adsorption isotherms.

4. Materials and methods to study the kinetics of the biosorption of HMs ions from model solutions

4.1. The techniques for obtaining biosorbents and the possible mechanisms of their extraction of HMs from aqueous solutions

Raw materials for biosorbents were the waste from pea processing, namely pea peels. The place where peas are cultivated is the south of the Odesa oblast (Ukraine). To obtain biosorbents, we used two techniques for treating the raw materials.

Under a first technique (technique No. 1), fresh pea peels were partially dehydrated in the environment under the following conditions: average air temperature, (20...22) °C; relative air humidity, (65...70) %; duration of the dehydration

process of the raw materials, (10...12) hours. Next, pea peels were dried in the drying chamber 2SH-0-01 at a temperature of $(120 \pm 1)^\circ\text{C}$ for (2...4) hours depending on the thickness of the loaded layer of raw materials. The dehydrated raw materials were crushed to the particle size of (2 ± 1) mm and used as a biosorbent.

Under a second technique (technique No. 2), the raw materials, dried under the above conditions but not shredded, densely filled the container. It was covered with a lid, which was then screwed. Thus, the container with the raw materials was sealed. The container and lid were made of stainless steel. The structural dimensions of the container and lid are as follows: height, 100 mm; outer diameter, 43 mm; the thickness of the wall of the container and lid, 4.5 mm. The container with the raw materials was placed in the muffle furnace, the brand ESZTERGOM (the country-manufacturer is Hungary), for the thermal carbonation of the raw materials in an oxygen-scarce environment. Carbonization was carried out at a temperature mode of the muffle furnace equal to 600°C . The process duration was 30 minutes (excluding the time it took for the furnace to enter the specified temperature regime). The choice of temperature was justified by previous experimental studies. During them, pea peels were carbonized at 350°C , 500°C , 600°C , and 800°C . The duration of the carbonation process varied from 15 minutes to 1 hour. The obtained biosorbents were used to purify an aqueous solution from HMs. The study results showed that at a temperature of 600°C and the carbonization duration equal to 30 minutes, the received material demonstrated the highest mass and sorption capacity among others.

Upon carbonization, the containers with char were left in the muffle furnace until it was completely cooled. The thermally-treated raw materials were crushed in a porcelain mortar in order to increase the biosorbent's contact surface with the biosorbents that contaminate water. The prevailing fraction of the crushed material (70–80 % of the total amount) consisted of particles the size of (1...2) mm. The described techniques for obtaining biosorbents have already been pre-tested [22, 23].

4. 2. The procedure for preparing model solutions for studying

Model solutions with the concentrations of copper and iron ions equal to 2 mg/dm^3 , 10 mg/dm^3 , and 20 mg/dm^3 were prepared for the experimental study. [24] When preparing them, we followed the recommendations given in [24]. In particular, the model solutions with Cu(II) ions were prepared by dissolving the exact batch of pentahydrate copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a small amount of acidified distilled water, (40–50) ml. The water was acidified by the addition of 1 cm^3 of a solution of concentrated sulfuric acid (H_2SO_4), diluted by 5 times [25]. The model solutions with Fe(III) ions were prepared by dissolving in distilled water an exact batch of iron ammonium alum ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) [25]. The degree of reagent purity is "clean for analysis". The solutions of copper and iron salts were chosen for our study because these metals are the most typical representatives of HMs in natural and sewage waters.

To perform the experiment, we initially prepared starting solutions with a concentration of HMs equal to 100 mg/dm^3 . The starting solutions were used, by diluting them with distilled water, to receive working solutions with the required

lower concentration. We obtained model solutions with the required pH value by adding 0.1 M HCl or 0.1 M NaOH to them.

4. 3. The equipment and procedures for determining the concentration of HMs in the solutions; the solutions' pH and temperature

The initial and current concentration of HMs in the model solutions was measured using the multi-parametric Photometer 7500, Palintest (the country-manufacturer is the UK). The HM concentration was measured according to the procedure outlined by the manufacturer of the device.

To determine the concentration of HMs in model solutions, we used complex reagents in the form of tablets. The reagents were added to the solution; Photometer 7500 measured the concentration of HMs in it. The accuracy of measuring the concentration of HMs by this device is $\pm 0.5\%$.

The initial pH values of the model solutions were controlled by a pH-meter (pH – 150 MI, the country-manufacturer is Russia) with a glass electrode. The measurements were carried out according to the procedure given in [26]. The error of pH-meter measurement is ± 0.05 pH units.

The solution's initial temperature was measured by the thermometer TL–6M. The measurement error by the thermometer is \pm to 0.5°C .

4. 4. The procedure for studying the kinetics of the biosorption of ions of the examined HMs from model solutions

Before conducting the kinetic study, we prepared for one experiment a series of flasks with 50 ml of the model solution in each. In all flasks, the concentration of HMs (C_0 , mg/dm^3), hydrogen index (pH_0 , pH units), and the solution temperature (t_0 , $^\circ\text{C}$) at the initial moment of the process were the same, namely, $\text{pH}=4$, $t_0=22 \pm 1^\circ\text{C}$. We added to these flasks the same batch of a biosorbent obtained by using one of the above techniques.

The process of HM extraction was carried out in static conditions with a periodic agitation of the model solution containing the biosorbent. Mechanical agitation was carried out for 30 s every 30 minutes of the process. After every hour from the beginning of the process, the content of one of the flasks was filtered through the filter paper "white ribbon" with $D=110$ mm. We determined the current concentration of HM ions (C_τ , mg/dm^3) in the filtered solution.

Next, according to the same procedure, we performed a kinetic study of the model solutions that had a different initial concentration of HM ions and with other dosages of the biosorbents (DS , g/dm^3).

To establish patterns of changes in the concentration of HM ions in the solution depending on the technique of obtaining the biosorbent and the conditions of the biosorption process, we built graphical dependences based on the experimental data. Dependences had the form of the function $C_\tau=f(\tau, DS)$ at C_0 , biosorbent production method and ion type = const, where τ is the process duration, h. The C_τ resulting value was the average value of the repeated measurements.

The effectiveness of the process of extraction of HMs ions from the solutions depending on various factors was evaluated on the basis of graphical dependences of the following form:

- $C_{\tau}/C_0=f(\tau, DS, C_0)$ at biosorbent production method and ion type=const;
- $C_{\tau}/C_0=f(DS, \tau)$ at C_0 , at C_0 , biosorbent production method and ion type=const;
- $C_{\tau}/C_0=f(DS, C_0)$ at τ , at τ , biosorbent production method and ion type=const.

The C_{τ}/C_0 indicator is numerically the ratio of the current concentration of the solution to the initial one and is measured in shares from unity. That is, it reflects the proportion of HM ions, which has not yet been removed from the solution at the current point in time. Unlike the actual current concentration of the solution C_{τ} , the relative indicator C_{τ}/C_0 is more convenient for analyzing and generalizing an array of the experimental data.

To evaluate the static activity of the biosorbents, we calculated the following indicators based on the experimental data: the quantity of adsorption (A , mg/g) and the adsorption uptake (A' , %):

$$A = \frac{C_0 - C_{eq}}{m} \cdot V = \frac{C_0 - C_{eq}}{DS}, \quad (1)$$

$$A' = \frac{C_0 - C_{eq}}{C_0} \cdot 100, \quad (2)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of HM ions in a model solution, mg/dm³. In the calculations, the equilibrium concentration was accepted to be the minimum concentration of HMs ions in a model solution, which was achieved as a result of its treatment with a biosorbent; V is the volume of a model solution, dm³; m is the weight of a biosorbent added to the solution, g.

The quantity of adsorption reflects the amount (in mg) of HM ions adsorbed by the unit of mass (in g) of a biosorbent under certain conditions of the process. And the adsorption uptake shows how many HM ions were removed from a solution under these conditions as a percentage relative to its initial content in it.

Based on the calculation results, we built graphical dependences in the form $A=f(\tau, DS)$ at C_0 , biosorbent production method=const, and diagrams that reflected the effect of various process factors on the percentage of the adsorption of metals' ions A' .

5. Results of the experimental study into the kinetics of the biosorption of heavy metals from aqueous solutions

5.1. Justification for choosing the techniques to obtain biosorbents

As stated in chapter 4. 1, under the first technique of processing the starting raw materials, fresh pea peels were dehydrated and crushed. We dried the raw materials in order to dehydrate them and to partially decompose the organic and inorganic substances available in small amounts in the cellular juice of plant waste (sugars, organic acids, proteins, lipids, mineral salts). The purpose of grinding the dried raw materials was to obtain the small fragments of the raw materials and increase the accessibility of the functional groups of plant polymers for HMs, namely cellulose and lignin. It was believed that the biosorbent obtained in this way would more intensively remove HMs from aqueous solutions.

Under the second technique, the dried raw materials were first subjected to thermal carbonization in an ox-

xygen-deficient environment and then crushed. Carbonization was carried out for the purpose of the thermal destruction of cellulose and lignin. The thermal destruction of plant polymers is known to be accompanied by the formation of new high-molecular compounds with higher carbon content, as well as water and other substances, including volatile ones. The high-molecular compounds are formed mainly by splitting the side benzol rings of lignin and binding them to other macromolecules in places of unsaturated bonds. The "stitching" of lignin macromolecules via benzol rings, as well as with carbohydrate fragments and aldehyde groups of other polymers, forms a material of the graphite-like structure. In the resulting char, the number of functional groups able to react with HMs is also increasing. In addition, the thermal carbonization of plant raw materials yields ash. It adsorbs anions but can also adsorb the high-charged cations, such as Fe³⁺ or Al³⁺, related to hydroxyl groups.

Both the first and second techniques of processing pea peels make it possible to obtain biosorbents to extract HMs from aqueous solutions. However, their sorption ability will be different. The biosorbents obtained from carbonization will be more effective at extracting HMs from solutions. However, the biosorbents obtained only by drying and shredding the raw materials will be cheaper. After all, the number of energy-intensive processes involved in this technique will be less. Based on the results of our kinetic studies, we shall choose one technique out of two that would be more appropriate for industrial technology. To this end, the processes must be optimized. The optimization criterion is an integrated indicator, which will take into consideration both the sorption characteristics of the biosorbent and the costs of its production.

5.2. The use of model solutions to experimentally study a change in the concentration of HMs in the process of biosorption, depending on their type and initial concentration in the solution, the biosorbent dosage, the process duration, and the technique for obtaining a biosorbent

Fig. 1–6 show the results of our experimental study into the effect exerted by the technique of biosorbent production and the conditions of the biosorption process on a change in the concentration of Cu(II) and Fe(III) ions in model solutions. The array of the experimental values was generalized in the form of equation (3), given below in chapter 5. 4.

An analysis of the resulting curves (Fig. 1–3) allows us to note the following:

1. The process of contact between the biosorbent obtained by technique No. 1 or No. 2 and a model aqueous solution can be divided into three periods: intensive biosorption; the time the system is in a state of the dynamic equilibrium; and desorption. They fundamentally differ in the nature of changes in the concentration of Cu(II) and Fe(III) ions over time.

During the first period, there is a rapid decrease in the content of HM ions in the solution. The duration of the first period of the process does not change significantly when the initial concentration of the solution and the dosage of the biosorbent change. However, it depends on the properties of the material formed as a result of treating the raw materials by any technique. The period of intensive biosorption lasts two to three hours in case of using the dehydrated raw materials as a biosorbent, and an hour or an hour and a half – in case of using char. In addition, the duration of the first peri-

od is influenced by the chemical composition of the solution. Under the same process conditions, the extraction of Fe(III) ions from the solution by the biosorbent occurs slower than the ions of Cu(II).

During the second period, the concentration of HM ions in the solution does not change significantly. The duration of this period is from two to eight hours. It does not depend on the dosage of the biosorbent but depends on the initial concentration of the solution. The higher the initial concentration of the solution, the longer the second period of the process. In addition, its duration is influenced by the chemical composition of the solution. It is longer for solutions containing the ions of Cu(II). Since the concentration of impurities in the solution does not change significantly during the second period, one can argue about entering the state close to equilibrium and the exhaustion of the sorption capacity of the material.

During the third period of the process, there is the desorption of HM ions into the solution, that is, a reverse process. The concentration of HM ions in the solution increases and reaches the initial value within two to six hours depend-

ing on the initial concentration of HM ions in the solution and their types. Longer desorption is typical of solutions with a higher initial concentration of HM ions. Slower is the desorption of Fe(III) ions to the solution.

2. The effectiveness of extracting the Cu(II) and Fe(III) ions from an aqueous solution is influenced by the initial concentration, the biosorbent dosage, and the duration of contact between the biosorbent and solution. The following patterns have been established:

- at the same dosage of a biosorbent and the same process duration, the biosorption process is more effective in solutions with a higher initial concentration of HMs (Fig. 4, curves 3 and 9, Fig. 5);
- the higher the initial concentration of HM ions in the solution, the greater the dosage of a biosorbent should be (Fig. 5, a);
- the effectiveness of extracting the HMs ions from the solution using the biosorbents first increases and then decreases. A minimum of this function is clearly visible. For example, for $C_0=20 \text{ mg/dm}^3$, it is observed at $\tau=4 \text{ h}$ (Fig. 4, 5, b).

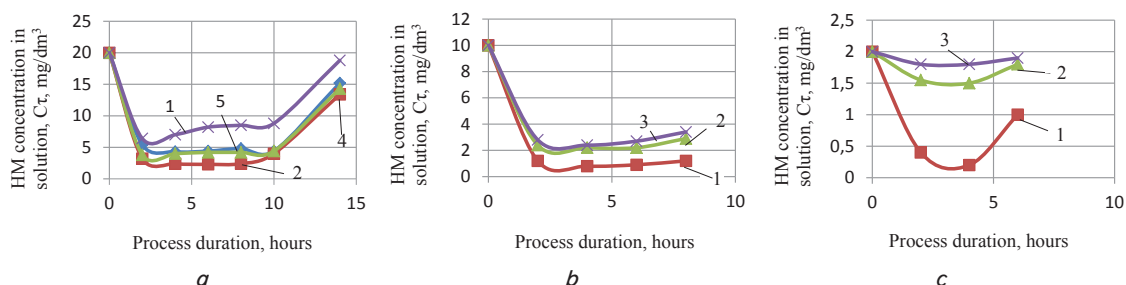


Fig. 1. Change in concentration of Cu(II) ions in model solutions when treating them with the biosorbents obtained by technique No. 1: a - $C_0=20 \text{ mg/dm}^3$; b - $C_0=10 \text{ mg/dm}^3$; c - $C_0=2 \text{ mg/dm}^3$ (1 - $DS=2 \text{ g/dm}^3$; 2 - $DS=10 \text{ g/dm}^3$; 3 - $DS=15 \text{ g/dm}^3$; 4 - $DS=20 \text{ g/dm}^3$; 5 - $DS=30 \text{ g/dm}^3$)

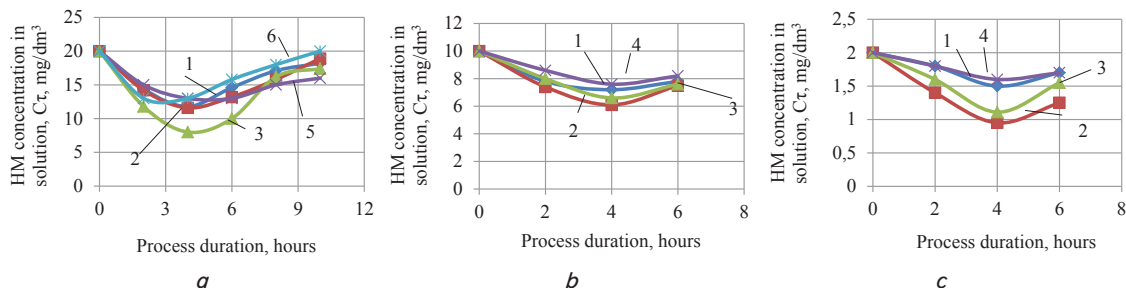


Fig. 2. Change in the concentration of Fe(III) ions in model solutions when treating them with the biosorbents obtained by technique No. 1: a - $C_0=20 \text{ mg/dm}^3$; b - $C_0=10 \text{ mg/dm}^3$; c - $C_0=2 \text{ mg/dm}^3$ (1 - $DS=1 \text{ g/dm}^3$; 2 - $DS=2 \text{ g/dm}^3$; 3 - $DS=10 \text{ g/dm}^3$; 4 - $DS=15 \text{ g/dm}^3$; 5 - $DS=20 \text{ g/dm}^3$; 6 - $DS=30 \text{ g/dm}^3$)

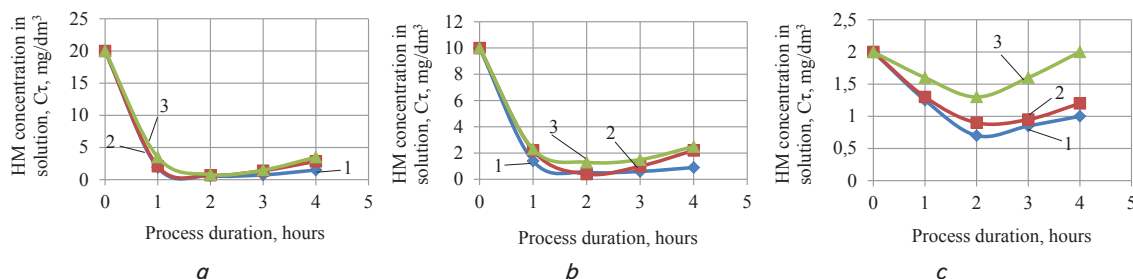


Fig. 3. Change in the concentration of Fe(III) ions in model solutions treated with the biosorbents obtained by technique No. 2: a - $C_0=20 \text{ mg/dm}^3$; b - $C_0=10 \text{ mg/dm}^3$; c - $C_0=2 \text{ mg/dm}^3$ (1 - $DS=2 \text{ g/dm}^3$; 2 - $DS=10 \text{ g/dm}^3$; 3 - $DS=20 \text{ g/dm}^3$)

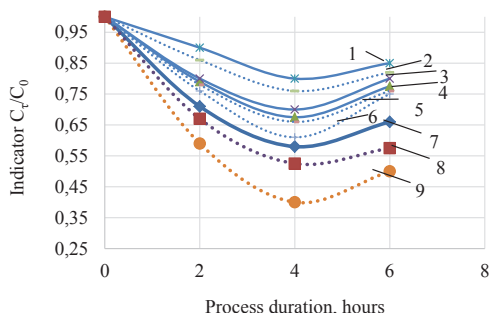


Fig. 4. Effect of the process duration, the solution initial concentration, and the biosorbent dosage (production technique No. 1) on the effectiveness of extracting the Fe(III) ions: 1 – $DS=15 \text{ g/dm}^3$, $C_0=2 \text{ mg/dm}^3$; 2 – $DS=15 \text{ g/dm}^3$, $C_0=10 \text{ mg/dm}^3$; 3 – $DS=10 \text{ g/dm}^3$, $C_0=2 \text{ mg/dm}^3$; 4 – $DS=2 \text{ g/dm}^3$, $C_0=2 \text{ mg/dm}^3$; 5 – $DS=10 \text{ g/dm}^3$, $C_0=10 \text{ mg/dm}^3$; 6 – $DS=2 \text{ g/dm}^3$, $C_0=10 \text{ mg/dm}^3$; 7 – $DS=2 \text{ g/dm}^3$, $C_0=20 \text{ mg/dm}^3$; 8 – $DS=15 \text{ g/dm}^3$, $C_0=20 \text{ mg/dm}^3$; 9 – $DS=10 \text{ g/dm}^3$, $C_0=20 \text{ mg/dm}^3$

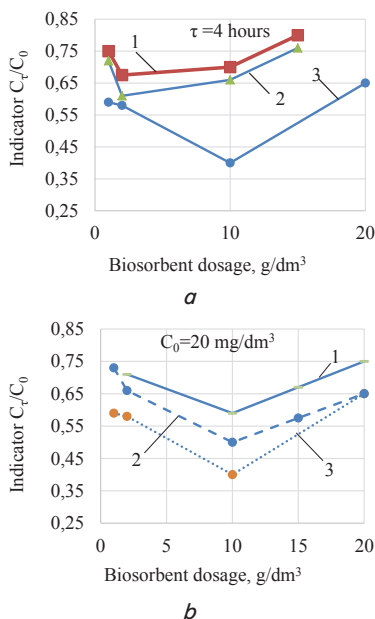


Fig. 5. Effect exerted on the effectiveness of extracting the Fe(III) ions by: *a* – biosorbent dosage (production technique No. 1) and the solution initial concentration (1 – $C_0=2 \text{ mg/dm}^3$; 2 – $C_0=10 \text{ mg/dm}^3$; 3 – $C_0=20 \text{ mg/dm}^3$); *b* – biosorbent dosage (production technique No. 1) and the duration of contact between the solution and biosorbent (1 – $\tau=2 \text{ hours}$; 2 – $\tau=6 \text{ hours}$; 3 – $\tau=4 \text{ hours}$)

5.3. Estimating the static activity of biosorbents in terms of adsorption capacity and the adsorption uptake

The calculation results, based on equations 1 and 2, of the sorption characteristics of biosorbents, namely, the adsorption capacity (A , mg/g) and the adsorption uptake (A' , %), are represented in the form of curves in Fig. 6, *a-c*, and a diagram in Fig. 7. An analysis of the curves in Fig. 6, *a* has shown that the amount of HMs (in mg) that can be extracted by one gram of a biosorbent is from 0.23 mg/g to 9.6 mg/g. The best values of the adsorption rate were obtained from the experiments where the HM ions extraction involved the biosorbent obtained by the thermal carboniza-

tion of pre-dried raw materials in an oxygen-deficient environment at $600 \text{ }^\circ\text{C}$ for 30 minutes. For comparison, the quantity of the adsorption of Cu(II) ions from model solutions for the biosorbents, obtained by washing and drying rice husks at $180 \text{ }^\circ\text{C}$, is 6.76 mg/g . A for the biosorbents obtained by the sequential thermal carbonization of rice husks in the presence of oxygen at 300 and $600 \text{ }^\circ\text{C}$, it is 9.11 mg/g [27].

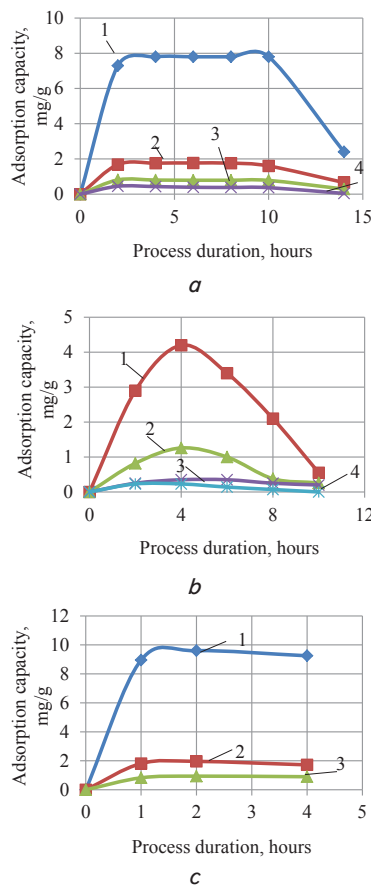


Fig. 6. Change in the HM ions adsorption capacity when treating the aqueous solutions with biosorbents: *a* – solution with Cu(II) ions, $C_0=20 \text{ mg/dm}^3$, biosorbent production technique No. 1; *b* – solution with Fe(III) ions, $C_0=20 \text{ mg/dm}^3$, biosorbent production technique No. 1; *c* – solution with Fe(III) ions, $C_0=20 \text{ mg/dm}^3$, biosorbent production technique No. 2; (1 – $DS=2 \text{ g/dm}^3$; 2 – $DS=10 \text{ g/dm}^3$; 3 – $DS=20 \text{ g/dm}^3$; 4 – $DS=30 \text{ g/dm}^3$)

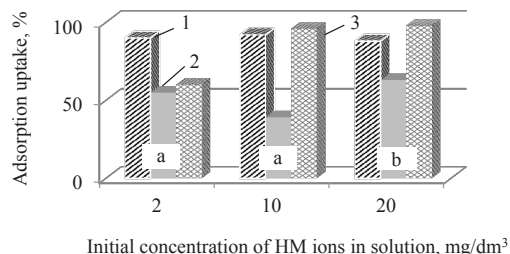


Fig. 7. The adsorption uptake of HM ions from aqueous solutions under different process conditions: solution with Cu(II) ions, biosorbent production technique No. 1, $\tau=4 \text{ hours}$; 2 – solution with Fe(III) ions, biosorbent production technique No. 1, $\tau=4 \text{ hours}$; 3 – solution with Fe(III) ions, biosorbent production technique No. 2, $\tau=2 \text{ hours}$; *a* – $DS=2 \text{ g/dm}^3$; *b* – $DS=10 \text{ g/dm}^3$

The calculated data on the adsorption uptake (Fig. 7) indicate that using the biosorbent made from pea processing waste enables the extraction from 38 to 98 % of copper and iron ions from aqueous solutions.

5. 4. Generalizing the experimental data in the form of regression equations and the equations that describe the adsorption isotherms

To generalize the results of our experiment, the data obtained were mathematically treated. The results of the mathematical treatment were the regression and kinetic equations. The following is the procedure of generalizing the experimental data, as well as the resulting mathematical equations for a single group of experiments. This is the study of the biosorption of Fe(III) ions from solutions with a concentration of 2 to 20 mg/dm³ at a dosage of the biosorbent obtained by using technique No. 1 in the range of 1 to 30 mg/dm³ (Fig. 2).

For convenience, the generalization of the data employed not the actual value of the concentration C_τ but relative, that is, C₀/C_τ (Fig. 4). The kinetic curves, in this case, are described by the functional dependence in the form C₀/C_τ=f(τ, C₀, DS). The process duration, which was taken into consideration when generalizing the data, was the first six hours of the process. It was during this period that there was an intense biosorption with the occurrence of dynamic equilibrium. For mathematical treatment, we used 27 experimental data values and the applied mathematical software for solving statistical problems *MS Excel*. A multi-factor regression equation was derived, which generalizes an array of the experimental data and takes the following form:

$$\begin{aligned} \frac{C_0}{C_\tau} = & 1.096 + 2.026 \cdot 10^{-3} \cdot DS - 1.033 \cdot 10^{-4} \cdot DS^2 - \\ & - 3.057 \cdot 10^{-3} \cdot C_0 + 4.217 \cdot 10^{-4} \cdot C_0^2 - 0.1826 \cdot \tau + \\ & + 2.241 \cdot 10^{-2} \cdot \tau^2 + 3.511 \cdot 10^{-3} \cdot DS \cdot C_0 - \\ & - 2.695 \cdot 10^{-4} \cdot DS \cdot C_0^2 - 1.531 \cdot 10^{-4} \cdot DS^2 \cdot C_0 + \\ & + 1.156 \cdot 10^{-5} \cdot DS^2 \cdot C_0^2 - 1.176 \cdot 10^{-2} \cdot DS \cdot \tau + \\ & + 1.527 \cdot 10^{-3} \cdot DS \cdot \tau^2 + 9.671 \cdot 10^{-4} \cdot DS^2 \cdot \tau - \\ & - 1.294 \cdot 10^{-4} \cdot DS^2 \cdot \tau^2 - 5.906 \cdot 10^{-3} \cdot C_0 \cdot \tau + \\ & + 8.42 \cdot 10^{-4} \cdot C_0 \cdot \tau^2 + 1.233 \cdot 10^{-4} \cdot C_0^2 \cdot \tau - \\ & - 2.59 \cdot 10^{-5} \cdot C_0^2 \cdot \tau^2. \end{aligned} \tag{3}$$

The maximum error of the generalization of experimental data based on equation (3) does not exceed 3 %.

Next, by setting a series of C₀ and DS values from the above range, equation (3) was used to calculate the indicator (C₀/C_τ)_{min}, the latter was applied to determine C_{τmin} by recalculation. This value was taken for the value of the equilibrium concentration of HM ions in the solution (C_{eq}, mg/dm³). Next, taking into consideration the refined value of C_{eq}, equation (1) was used to determine the adsorption capacity A. The calculation results are shown in Fig. 8 in the form of adsorption isotherms.

For the mathematical notation of the experimental adsorption isotherms (Fig. 8), we used, in accordance with the theory of adsorption, the equation of an adsorption isotherm by Langmuir. It is applied under the following assumptions: adsorbed particles are arranged at the surface in a single layer; the interaction between adsorbent and adsorbate on any part of the surface is of the same nature,

that is, the surface is homogeneous. In addition, it is known that the equation of an adsorption isotherm by Langmuir agrees well with the experiment if the adsorption is due to forces close in nature to chemical forces [32]. In practice, to generalize experimental data, the Langmuir equation is used in the following form:

$$\frac{1}{A} = \frac{1}{A_\infty \cdot K_L} \cdot \frac{1}{C_{eq}} + \frac{1}{A_\infty}, \tag{4}$$

where A is the adsorption capacity of HMs, mg/g; C_{eq} is the equilibrium concentration of HMs in solution, mg/dm³; A_∞ is the maximum value of the adsorption capacity of HMs, mg/g; 1/A_∞ and K_L are the constants of Langmuir equation, which are determined by the approximation of data represented as a dependence in the form 1/A=f(1/C_{eq}).

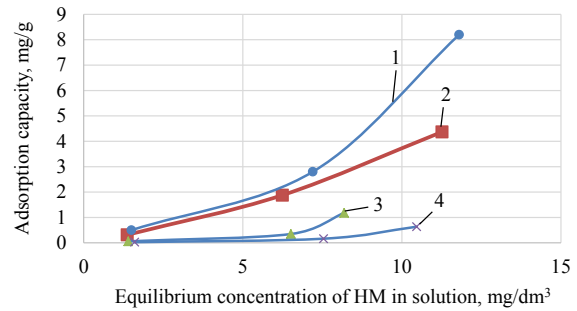


Fig. 8. The adsorption isotherms of Fe(III) ions: biosorbent production technique No. 1 (1 – DS=1 g/dm³; 2 – DS=2 g/dm³; 3 – DS=10 g/dm³; 4 – DS=15 g/dm³)

The results of the mathematical treatment of the experimental adsorption isotherms, obtained for certain biosorbent dosage values and the initial concentrations of solutions, are shown in Fig. 9, a–c. Fig. 9, d illustrates the generalization, according to the Langmuir equation, of the entire array of our experimental data. Table 1 gives the values of the resulting coefficients for the Langmuir equation.

Table 1

Coefficients to the equations that describe adsorption isotherms

No.	DS, g/dm ³	C ₀ , mg/dm ³	1/(A _∞ ·K _L)	1/A _∞	K _L	R ²
1	2	2...20	4.5775	-0.1886	-0.04119	0.999
2	10	2...20	26.003	-1.743	-0.06705	0.995
3	15	2...20	66.973	-3.846	-0.05742	0.997
4	1...30	2...20	27.149	-0.7413	-0.0273	0.387

The resulting equations (Table 1, No. 1–3) accurately describe the experimental adsorption isotherms obtained for individual biosorbent dosage values (Fig. 8). If the entire array of experimental data is used for generalization, the accuracy of such an equation is lower (Table 1, No. 4).

All the above equations are a generalization of data from a single group of experimental studies. This is the biosorption of Fe(III) ions from solutions with a concentration of 2 to 20 mg/dm³ at a dosage of the biosorbent, obtained by technique No. 1, between 1 and 30 mg/dm³. Therefore, it is advisable to apply the above equations for such conditions.

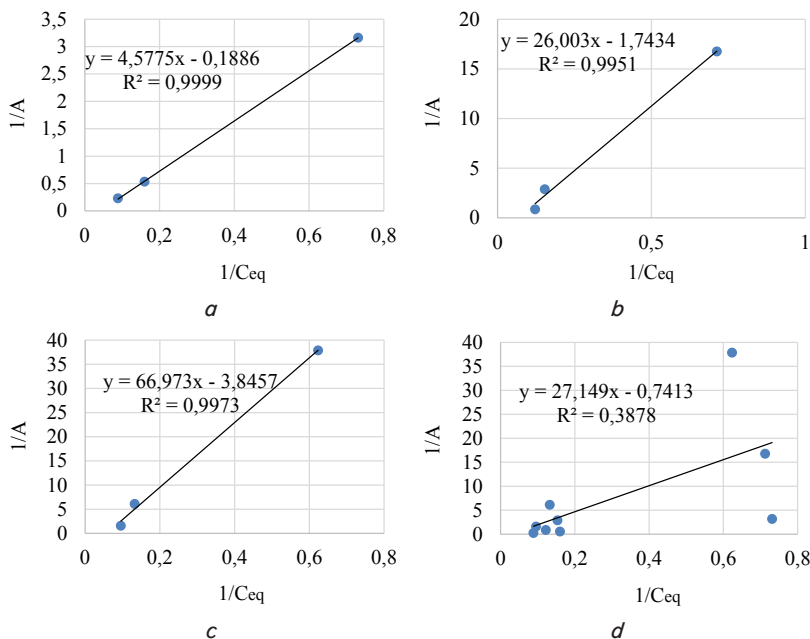


Fig. 9. Equations that describe the adsorption isotherms from Fig. 8:
 a – $DS=2 \text{ g/dm}^3$, $C_0=(2...20) \text{ mg/dm}^3$; b – $DS=10 \text{ g/dm}^3$,
 $C_0=(2...20) \text{ mg/dm}^3$; c – $DS=15 \text{ g/dm}^3$, $C_0=(2...20) \text{ mg/dm}^3$;
 d – $DS=(2...15) \text{ g/dm}^3$, $C_0=(2...20) \text{ mg/dm}^3$

6. Discussion of results of studying the kinetics of the biosorption of heavy metals from aqueous solutions

Our experimental study has made it possible to identify a series of characteristic features in the process of HM extraction from aqueous solutions using the biosorbents derived from pea processing waste. First, this is the existence of three periods in the process of contact between the biosorbent and solution, which differ in the direction of change in the concentration of the solution, as well as duration (Fig. 1–3). The duration of these periods is largely affected by the properties of the biosorbent, predetermined by the technique of its production, as well as the type of HM in the solution. A lesser effect is exerted by the initial concentration of the solution. And there is almost no effect from the dosage of the biosorbent. As regards the data acquired, of the greatest value is the information about the first and second periods of the process. After all, from a technological point of view, it is important to carry out the process to prevent the occurrence of the third period, that is, desorption.

It should be noted that the presence of three periods (intensive biosorption, dynamic equilibrium, and desorption) is typical of physical adsorption. When justifying the techniques of obtaining biosorbents and the possible mechanisms of their interaction with HMs in the solution, we were inclined to believe that we would deal with the ion-exchange adsorption. It is the reverse process. In addition, we assumed the progress of complexation processes. The dissociation of a complex compound into a metal ion and a ligand is possible if the complex formed is unstable. Probably, such complexes were formed at the surface of the biosorbents in their contact with aqueous solutions. Additional studies, both theoretical and experimental, are needed to elucidate this issue.

Second, the effectiveness of the extraction of HM ions from an aqueous solution is influenced by the initial con-

centration and type of HM, the technique of obtaining, and the biosorbent dosage, as well as the duration of biosorption (Fig. 4–6). The nature of these influences is described above. It is still important to note that for a solution with a certain initial concentration and type of HM there is a certain value of the biosorbent dosage and the process duration at which the maximum extraction of HM ions is achieved. Thus, for a solution with an initial concentration of Fe(III) ions equal to $C_0=2 \text{ mg/dm}^3$, the maximum extraction of impurities occurred during a biosorbent dosage equal to $DS=2 \text{ mg/dm}^3$. And for a solution with $C_0=20 \text{ mg/dm}^3$, the best effect was achieved at $DS=10 \text{ mg/dm}^3$ (Fig. 5, a). As regards the process duration, the greatest effect for these same solutions was achieved at $\tau=4$ hours (Fig. 4, 5, b). Therefore, at the stage of the development of technology for the purification of natural or wastewater using the biosorbents, it is desirable to optimize such parameters of the process as the dosage of a biosorbent and the duration of the process of contact between the biosorbent

and solution. This would make it possible to achieve the maximum effect of extracting the HM ions from the aqueous solution at minimal energy consumption per process.

According to the theory of ion-exchange adsorption, among the ions of Fe(III) and Cu(II), a higher adsorption capacity must demonstrate the ions of iron. This is due to the fact that they carry a higher charge. However, our study has shown that the biosorbents made from pea peels are better at removing copper ions (Fig. 7). We believe that, in this case, this is due to the prevailing share, among the functional groups of the examined biosorbent, of the amino groups of $-NH_2$. With them, copper is better, compared to iron, at forming the chelate complex compounds. And there are fewer carboxyl groups of $-COOH$, from which, in aqueous solutions, an iron ion easily displaces a hydrogen ion, in the biosorbent made from pea waste. Copper ions do not participate in the reaction of ion exchange with hydrogen ions as copper is after hydrogen in a series of metals voltage. It is known that copper can form chelate complex compounds with carboxyl groups.

Carbonic acids are weak acids, so their salts quite easily undergo reverse hydrolysis. This can explain the shorter duration taken by the system to be in an equilibrium state in the biosorption of Fe(III) ions from aqueous solutions (Fig. 2). Copper ions, as noted above, form with existing functional biosorbent groups mainly complex compounds. Their dissociation into a metal ion and a ligand is slower. Therefore, the duration when the system is in an equilibrium state during the biosorption of copper ions is longer (Fig. 1). This should be taken into consideration in the development of technological modes of water treatment with the help of biosorbents.

In addition, the lower effectiveness of biosorbents in relation to Fe(III) ions in the experiment may be due to the fact that double salt was used for the preparation of model solutions with Fe(III) ions. In accordance with the dissociation equation of such salt



the model aqueous solution, in addition to iron (III) cations, contained a similar number of ammonium cations. In the process of biosorption, the latter could compete with iron cations for the biosorbent's functional groups, particularly for the strong-acid sulfo-group $-\text{HSO}_3$. The presence of such groups in the biosorbent was assumed on the basis of the results from studying their elemental composition. Another reason for the lower efficacy of biosorbents to extract the Fe(III) ions may have been the formation, due to the hydration, of iron hydroxide $\text{Fe}(\text{OH})_3$ in the form of an insoluble finely dispersed suspended substance. Of course, it is advisable to perform additional experimental studies to confirm such assumptions.

As regards the techniques of obtaining biosorbents from pea processing waste, the greater efficiency of extracting the ions of Cu(II) and Fe(III) is demonstrated by the biosorbents obtained by the thermal carbonization of raw materials in an oxygen-scarce environment. This is evidenced by the calculated values of the adsorption capacity (Fig. 6) and the adsorption uptake (Fig. 7). For example, the adsorption uptake of Fe(III) ions with crushed char is 2.5 times higher than the same rate for the biosorbent obtained by drying and shredding the raw materials (at $C_0=10 \text{ mg/dm}^3$ and $DS=2 \text{ mg/dm}^3$). We believe that the main reason for this is a much larger number of functional groups in char, which are able to interact with HM ions according to the mechanisms of ion exchange or complexation.

At the same time, the technique of obtaining a biosorbent without the use of the carbonization process is less energy-consuming. Therefore, the next step should be to optimize not only the parameters of the process of extracting HMs using a biosorbent but also determining the optimal technique for obtaining a biosorbent. To this end, we need to develop an integrated optimization criterion. This criterion should take into consideration both the sorption characteristics of biosorbent and all costs for its production.

To optimize the technological parameters of the biosorption process, in particular Fe(III) ions, it is advisable to use regression equation (3). This equation accurately describes experimental data and can be applied to predict process parameters at other source data within the above limits. By differentiating equation (3) for the parameter τ or the parameter DS , and by equating the derivative to zero, one can determine the minimum time or minimum dosage of the biosorbent required for maximum HM extraction. For example, for a solution containing the Fe(III) ions at $C_0=2 \text{ mg/dm}^3$ and a biosorbent dosage (obtained by technique No. 1) equal to 2 mg/dm^3 , the determined optimal duration of the process is 4.5 hours.

To implement the biosorbents industrially in water treatment technology, a series of other studies are needed in addition to the kinetic studies of the biosorption process. In particular, it is necessary to determine the resource of biosorbents, to investigate their effectiveness in the extraction of HMs from actual natural and wastewater, to substantiate the technique for disposing of spent biosorbents, etc.

7. Conclusions

1. We have substantiated the choice of techniques to obtain biosorbents from pea processing waste in order to

extract HM ions from aqueous solutions. A first technique includes the following technological operations: partial dehydration, drying and grinding of the raw materials. A second technique involves the partial dehydration, drying, carbonization, and grinding of raw materials. It has been experimentally confirmed that using the processes of dehydration, grinding, and (or without) thermal carbonization, can produce the biosorbents from pea peels that effectively remove HM from aqueous solutions. The biosorbents obtained by the thermal carbonization of the dehydrated raw materials ($t=600 \text{ }^\circ\text{C}$, $\tau=30 \text{ min}$) without oxygen access demonstrate a higher efficiency in the extraction of Cu(II) and Fe(III) ions. Thus, the adsorption uptake of Fe(III) ions with crushed char is 2.5 times higher than the same rate for the noncarbonized biosorbent (at $C_0=10 \text{ mg/dm}^3$ and $DS=2 \text{ mg/dm}^3$).

2. The model aqueous solutions were used to examine the kinetics of the processes of the extraction of Cu(II) and Fe(III) ions applying the biosorbents obtained by the proposed techniques. We have examined a time-dependent change in the HM concentration in the solution depending on the type of HM and its initial concentration, dosage, and the technique of biosorbent production. It is shown that in the process of biosorption, three periods can be conditionally identified: intensive biosorption, dynamic equilibrium, and desorption. The duration of the periods is influenced by the technique of obtaining a biosorbent and the type of HM. In terms of organizing the water purification process, the first and second periods of the process are of interest. The period of intensive biosorption lasts (2) to (3) hours in case of using, as a biosorbent, the dehydrated raw materials, and (1–1.5) hours in case of applying char. Under the same process conditions, the extraction of Fe(III) ions from the solution using a biosorbent is slower than the ions of Cu(II). The duration of the second period is from 2 to 8 hours. The higher the initial concentration of the solution, the longer the second period of the process. It is longer for solutions containing the ions of Cu(II). It was established that the degree of extraction of the ions of Cu(II) and Fe(III) from solutions by the biosorbents depends on the initial concentration of the solution, dosage, and the biosorbent properties, as well as the duration of contact between the biosorbent and solution. Thus, for a solution with an initial concentration of Fe(III) ions equal to $C_0=2 \text{ mg/dm}^3$, maximum impurities extraction occurred at $\tau=4 \text{ h}$ and a biosorbent dosage equal to $DS=2 \text{ mg/dm}^3$. However, for a solution with $C_0=20 \text{ mg/dm}^3$, the same effect was achieved in 4 hours, only with an increase in the biosorbent dosage by 5 times.

3. Based on the calculated indicators of the adsorption capacity and adsorption uptake, we estimated the static activity of the obtained biosorbents. It is shown that using them makes it possible to remove from 38 to 98 % of copper and iron ions from aqueous solutions. Higher efficiency in the extraction of HMs is demonstrated by the biosorbents whose obtaining involved the carbonization process. It is also shown that the biosorbents made from pea processing waste are better at removing copper ions than the ions of iron.

4. Our experimental data were mathematically treated and generalized. The mathematical notation of adsorption isotherms was based on the Langmuir equation. The corresponding coefficients of the equations have been calculated. The resulting equations describe well the individual adsorp-

tion isotherms ($R^2=0.995...0.999$). However, the accuracy of the calculations based on the equation that generalizes the entire array of our experimental data is not sufficient ($R^2=0.387$). The array of the experimental data is well generalized by the derived multifactor regression equation. The maximum error of calculations based on the equation

does not exceed 3 %. The equation makes it possible to calculate a change in the concentration of HMs in the solution in the process of biosorption depending on their initial concentration, process duration, and biosorbent dosage. In the future, it will be used to optimize the technological parameters of the biosorption process.

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