

*Встановлено можливість біосорбції іонів важких металів на бактеріальних структурах консорціумів залізобактерій. Досліджено процес очищення води від іонів  $Cr^{6+}$  (до 2,0 мг/дм<sup>3</sup>),  $Zn^{2+}$  (до 50 мг/дм<sup>3</sup>),  $Cu^{2+}$  (до 16 мг/дм<sup>3</sup>),  $Ni^{2+}$  (до 1,3 мг/дм<sup>3</sup>) на різних видах оса-дів станції знезалізнення. Визначена ефективність їх застосування при вилученні іонів важких металів із природних підземних та промивних вод гальванічно-го виробництва*

*Ключові слова: біомінерали, біосорбція іонів важких металів, матрикси залізобактерій, осад станції знезалізнення*

*Установлена возможность биосорбции ионов тяжелых металлов на бактериальных структурах консорциумов железобактерий. Исследован процесс очистки воды от ионов  $Cr^{6+}$  (до 2,0 мг/дм<sup>3</sup>),  $Zn^{2+}$  (до 50 мг/дм<sup>3</sup>),  $Cu^{2+}$  (до 16 мг/дм<sup>3</sup>),  $Ni^{2+}$  (до 1,3 мг/дм<sup>3</sup>) на различных видах осадков станции обезжелезивания. Определена эффективность их использования при извлечении ионов тяжелых металлов из природных подземных и промывных вод гальванического производства*

*Ключевые слова: биоминералы, биосорбция ионов тяжелых металлов, матриксы железобактерий, осадок станции обезжелезивания*

# RESEARCH INTO THE BIOSORPTION PROCESS OF HEAVY METAL IONS BY THE SEDIMENTS FROM STATIONS OF BIOLOGICAL IRON REMOVAL

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## 1. Introduction

Most of water intakes of underground water today are, to varying degrees, under the influence of anthropogenic load [1]. Its main factors are industry, agriculture, and transport. Among industrial wastes, particular attention should be given to the infiltration of insufficiently treated industrial effluents and wastewaters from accumulators and drainage storages [1]. For example, the main sources of environmental pollution with chromium are galvanic production, textile industry, and production of special alloys. As a result, local areas of heightened concentrations of chromium may appear in underground waters. In addition, a negative impact of multicomponent metal-containing wastewaters from galvanic production [2] on the environment should be noted. Existing groundwater treatment technologies cannot effectively remove such anthropogenic pollution. Furthermore, today the most common ways to purify the reverse effluents from galvanic production are such energy-consuming technologies as chemical and electrochemical deposition, ion exchange, reverse osmosis [2, 3]. It is emphasized in paper [4] that such biological methods as biosorption and bioaccumulation can be considered as an alternative to traditional and expensive physico-chemical methods.

Therefore, research and development of new energy- and resource-saving technologies based on the processes of

microbial biosorption of ions of heavy metals (IHM) from natural waters and wastewaters is a relevant task.

## 2. Literature review and problem statement

One of the promising methods of the removal of heavy metal ions from both natural and waste waters is the use of various precipitating reagents and microbial biosorption. In paper [5], theoretical and experimental substantiations of the technology of galvanic production wastewater treatment with the use of chemically generated magnetite suspension are given. The suspension is formed as a result of the oxidation of bivalent iron with oxygen in the hot solutions of iron hydroxide (II) at a temperature of 60–70 °C and pH 10–11. The disadvantages of the described process of chemical generation of magnetite suspension are the complexity and high cost of its obtaining. Results of the studies presented in paper [6] showed a high ability for complex formation of metals with extracellular polymeric substances (EPS) by means of various mechanisms, including proton exchange. The disadvantages of the process are the need for special equipment and media for the cultivation of relevant microorganisms. In paper [7], the possibility of biosorption of IHM by inactivated and inanimate biomass is considered: *Aspergillus niger*, *Penicillium chrysogenum*, *Rhizopus nigricans*,

*Ascophyllum nodosum*, *Sargassum natans*, *Chlorella fusca*, *Oscillatoria angustissima*, *Bacillus firmus*. It highlights its high adsorption capacity (from 5 to 641 mg g<sup>-1</sup>) for the Zn, Cd, Cr, Cu, Ni ions. However, it should be noted that obtaining the required biomass is possible as a by-product of the enzymatic process only, and this factor complicates the application of the proposed method considerably. In paper [8], the possibility of sorption of IHM by biogenic Mn oxides with negative charge has been investigated. According to the authors, this charge is compensated for by irreversible binding to the Na, Ca, Zn, Co, Ni cations. The sorption efficiency of the biogenic Mn oxides is ten times higher than the sorption efficiency of chemically synthesized oxides. The complexity of the method's implementation is in the need to develop special oxidizing manganese bacteria *Bacillus sp.*, *Leptothrix discophora*, *Spores of Bacillus sp.*, which grow in appropriate media containing manganese compounds. In paper [9], results of studies on the removal of As (V), Pb (II) and Cd (II) ions on the loading of the filters of biological iron-removal stations of underground waters are presented. The optimal pH values (within 5.5) for their extraction have been determined. It is indicated that the special capacity of reaction and adsorption activity of these biogenic matrices makes it possible to use it for the cost-effective removal of the indicated IHMs from water. According to results of the research at the underground water iron-removal station, Muko, Kyoto Prefecture, Japan, the possibility of extracting arsenic, iron and manganese ions was also confirmed [10]. However, in both studies there is no research into the possibility of removing the Cr<sup>6+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> ions by biogenic matrices, which are most commonly found during purification of effluents of galvanic production.

Relevant interest exists in the use of sediments from biological iron-removal stations, which have consortia of iron bacteria as precipitating reagents. Among the components of their cellular wall are chitin and chitosan, as well as negatively charged groups of anions (PO<sub>4</sub><sup>3-</sup>; COO<sup>-</sup>; OH<sup>-</sup>) that act as sorbents of heavy metals [11]. It is known that in the process of iron-removal stations operation, from 5 to 10 % of purified water is spent on the washing of filters. A considerable amount of iron oxide effluents is accumulated at such stations in the facilities for the retreatment of flushing waters [12], but there are no ways provided for its disposal. Pilot laboratory studies, which have been carried out in paper [13], showed the possibility of using waste products from biological iron-removal stations as secondary material resources in wastewater treatment technologies for galvanic production. The research was based on differences in sediments formed by biological and traditional methods of iron removal. The sediment, which is formed by the biological method, contains: crystalline structure biominerals with varying degrees of mineralization, various types of bacteria at different stages of development, bacterial organic and inorganic structures, iron hydroxide [14]. In comparison with this, the sediment from the traditional iron-removal stations has a more amorphous structure with a large number of "captured" water molecules. However, the report provides only brief data on the use of biogenic iron oxides activated in a magnetic field and a one-step injection of sediment. There is no theoretical substantiation of the process, the use of different types of sediments and the possibility of their introduction into the technological scheme in several stages have not been investigated.

In the course of analysis of *existing purification methods of natural waters and effluents* from IHM, the prospects of the application of precipitating reagents on the basis of matrices of biominerals were found with the need for their further study confirmed.

### 3. Research goal and objectives

The conducted studies aimed to investigate the possibility of adsorption of heavy metal ions on the matrices of bacterial structures from the consortia of iron bacteria and to determine the optimal parameters for the course of this process.

To achieve these objectives, the following tasks were set:

- research into the possibility of removing the Cr<sup>6+</sup> ions from natural groundwaters in bioreactors and filters of iron-removal stations using the matrix structures of consortia of iron bacteria;
- research into the process of removing the Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> ions from the washing waters of galvanic production by adsorption on the matrix structures of the iron oxides of sediments of biological iron-removal stations;
- study of the effectiveness of the process of biosorption of IHM on different types of sediments of biological iron-removal stations.

### 4. Materials and methods of examining the process of biosorption of ions of heavy metal by sediments of stations of biological iron-removal

#### 4.1. Materials and equipment used in the experiment

As a carrier of the matrix structure from biominerals, a sediment of washing waters of the station of biological iron-removal of underground waters located in the town of Berezhne, Rivne region, Ukraine was used. As a research medium, technical artesian water from the underground horizons of the Poltava region (Table 1) and washing waters from galvanic production of LLC "High Voltage Union-RZVA" (Rivne Plant of High-Voltage Equipment) (Table 2), where studies were conducted during the period from 2010 to 2011, were used.

Table 1

Characteristics of parameters of technical artesian water

pH	Fe, mg/dm <sup>3</sup>	Alkalinity, mmol/dm <sup>3</sup>	PO, mgO <sub>2</sub> /dm <sup>3</sup>	Cr <sup>6+</sup> , mg/dm <sup>3</sup>
7.35	0.48–1.15	8.5	2.3	0.83–1.5

Table 2

Characteristics of the parameters of the quality of reverse water of galvanic production of LLC "VS-RZVA", Rivne, Ukraine

Stage of experiment	Type of precipitant reagent	Water quality parameters			
		pH	Zn <sup>2+</sup> , mg/dm <sup>3</sup>	Cu <sup>2+</sup> , mg/dm <sup>3</sup>	Ni <sup>2+</sup> , mg/dm <sup>3</sup>
I	dried at t=50 °C	7.2	29.2	2.5	–
II	calcined at t=600 °C	8.25	44	18.5	1.3
	"fresh" sediment				
III	"fresh" sediment	6.25	51.05	15.50	1.03

Research into the process of removing the  $\text{Cr}^{6+}$  ions from technical groundwater was carried out at a pilot laboratory facility (Fig. 1, *a*).

The facility included: capacity  $W=1.0 \text{ dm}^3$  of the source water; reactor tank  $W=0,5 \text{ dm}^3$ ; capacity for filtrate collecting  $W=0.300 \text{ dm}^3$  with replaceable paper filter "blue ribbon"; magnetic mixer MM-5; Kamovsky pump.

Research into the removal of the  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{+}$  ions was carried out at a pilot laboratory facility (Fig. 1, *b*). The facility included: a tank with the solution of washing water from galvanic production ( $W=10 \text{ dm}^3$ ); a column – a structuring device with a diameter of 50 mm, a height of 800 mm. Part of the column with a height of 500 mm was located in the area of the constant magnetic field (CMF).

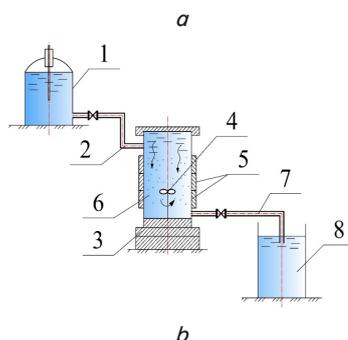


Fig. 1. Schematics of pilot installations for the removal of IHM: *a* – from technical groundwater: 1 – capacity of the source water; 2 – reactor tank; 3 – magnetic mixer; 4 – filter; 5 – capacity for filtrate collecting; 6 – Kamovsky pump; *b* – from flushing waters from galvanic production: 1 – a tank with the solution of flushing water; 2 – water supply to the column; 3, 4 – magnetic mixer; 5 – blocks of constant magnets; 6 – column structurizer; 7 – water drainage; 8 – mixer

The installation (Fig. 1, *b*) is equipped with a sampler located in its lower part. For the constant agitation of the solution with the precipitating reagent, a magnetic mixer was used. pH value was determined by the potentiometric method. Determination of the concentrations of ions of heavy metals (zinc and nickel) was carried out by photocolometric method: copper – by extraction-photometric method with lead diethyl cytochrome, chromium – by extraction photocolometric method with diphenylcarbazide. Bacteria were identified by light microscopy using

the Nikon Eclipse E200 microscope (Japan). Investigation of sediment structure, its quantitative and qualitative composition – by spectral analysis on the raster electron microscope FEI Quanta (USA), equipped with an X-ray spectrometer for microanalysis (EDAX). The agitation was carried out using the magnetic mixer MM-5 (Ukraine). The strength of the magnetic field in the magnetic structure was measured using the teslameter of the universal type 43205 (RF).

#### 4. 2. Methods of examining the process of biosorption of ions of heavy metal on sediments of stations of biological iron removal

Investigation of the process of purification of underground waters from the  $\text{Cr}^{6+}$  ions was carried out in two stages. At the first stage, effectiveness of removal of the  $\text{Cr}^{6+}$  ions was investigated on the "sealed" sediment of the washing waters of the iron-removal station in the town of Berezne. The sediment, contained 6.4 % of dry matter, was in a closed container without access to "fresh" portions of washing water and soluble oxygen for two months. At the second stage, the research was carried out on "fresh" sediment accumulated on open sludge sites as a result of the daily cleaning of the filters of the station of disinfection with 3.4 % of dry matter. The initial water from the reservoir (1) in the volume of  $0.50 \text{ dm}^3$  under the influence of vacuum, which was created with the help of the Kamovsky pump (6), arrived to the tank of the reactor (2), in which a certain amount of fresh sediment was placed in advance ( $2.0; 5.0; 10.0 \text{ cm}^3$ ). The agitation was carried out using a magnetic mixer (3). At the appropriate intervals (10, 30, 45, 60 minutes), with the help of the Kamovsky pump, a sampling from the reactor was carried out, with the samples filtered through a blue ribbon paper filter (4), followed by determining residual concentrations of the  $\text{Cr}^{6+}$  ions.

Investigation of the water purification process from the  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  ions was also carried out in several stages using several technological schemes (Fig. 2) using precipitating reagents of various types (Fig. 3).

At the first stage, technological scheme (Fig. 2, *a*), the source water was mixed with the sediment pre-dried at  $T=50 \text{ }^\circ\text{C}$  (Fig. 3, *a*) and it underwent 30 minutes of treatment in the mixer followed by the filtration through a blue ribbon paper filter. According to the technological scheme (Fig. 2, *c*), the washing water, together with the sediment dried at  $T=50 \text{ }^\circ\text{C}$  (Fig. 3, *a*), was exposed to treatment in a magnetic structurizer under the action of CMF with a strength of 20–60 mTl with an exposure time of 10 minutes and subsequent 20-minute stirring. At the second stage of research, flushing water was subjected to a two-stage treatment according to the scheme (Fig. 2, *c*), using the sediments calcined at  $T=600 \text{ }^\circ\text{C}$  (Fig. 3, *b*) and the "fresh" sediment after the filters washing (Fig. 3, *c*, *d*). CMF exposure time and treatment time in the mixer are similar to that of stage one.

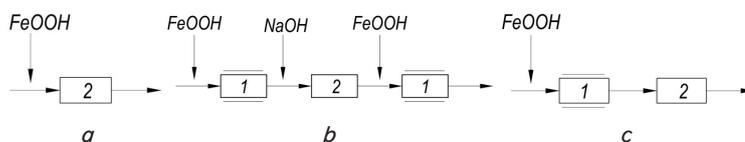


Fig. 2. Pilot technological schemes for the purification of washing waters of galvanic production: *a* – one-stage scheme: 2 – mixer; *b* – three-stage scheme: 1 – magnetic structurizer; 2 – mixer; *c* – two-stage scheme: 1 – magnetic structurizer, 2 – mixer

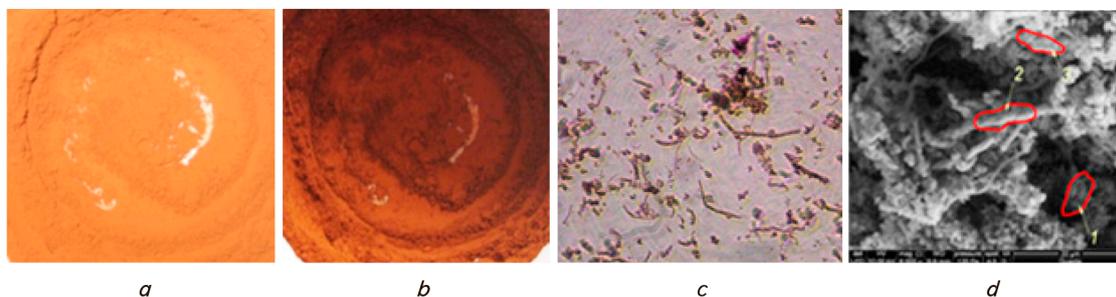


Fig. 3. Images of various types of the activated sediment: *a* – dried at  $t=50\text{ }^{\circ}\text{C}$ ; *b* – calcined at  $t=600\text{ }^{\circ}\text{C}$ ; "fresh" sediment from matrices of iron bacteria; *c* – light microscope  $\times 400$ ; *d* – SEM  $\times 6000$ : 1 – accumulation of sediment between filamentous *Gallionella* structures; 2 – case of *Gallionella* bacteria; 3 – agglomeration of bacterial consortia

At the third stage, the study was conducted according to a three-stage scheme (Fig. 2, *b*). The time of exposure in magnetic structurizers was 20 minutes, between which the alkalization with a NaOH solution was performed, and a two-minute contact in the mixer. Concentrations of precipitating reagent, before each degree of magnetic structurizers, varied depending on a series of experiments and amounted to 100, 200, 300, 400 mg/dm<sup>3</sup>.

### 5. Results of examining the process of biosorption of ions of heavy metals on the sediments of stations of biological iron removal

Results of the comparative survey conducted (Fig. 4, *a, b*) show that the effectiveness of purification of technical natural water from the Cr<sup>6+</sup> ions is much higher when using "fresh" sediment than the "compacted" one. Thus, for example, at concentrations of the Cr<sup>6+</sup> ions up to 1.0 mg/dm<sup>3</sup>, the efficiency of adsorption on the "fresh" sediment is 100 % (Fig. 4, *a*, curve 1), while when using the "compacted" sediment – 67–80 % (Fig. 4, *b*, curve 1). At concentrations of the Cr<sup>6+</sup> ions from 1.0 to 2.5 mg/dm<sup>3</sup> and a reagent dose of 300 mg/dm<sup>3</sup>, the efficiency of the adsorption was 80–90 % for the "fresh" sediment (Fig. 4, *a*,

curve 2), and 64–73 % for the "compacted" (Fig. 4, *b*, curve 2). With an increase in the dose of "fresh" sediment by dry matter up to 400 mg/dm<sup>3</sup>, the efficiency of extracting the Cr<sup>6+</sup> ions from the solutions reached 81–90 % (Fig. 4, *a*, curve 3), which corresponded to the standards of their discharge into the surface reservoirs within the city area. While using similar doses of "compacted" sediment, the efficiency was 67–82 % (Fig. 4, *b*, curve 3). An increase in the concentration of "fresh" sediment up to 500 mg/dm<sup>3</sup> leads to complete purification of technical natural water (Fig. 4, *a*, curve 4).

Results of the studies into extraction of the Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> ions from the galvanic washing waters were split into several stages. At stage I, in the study of a one-stage scheme (Fig. 2, *a*), precipitation efficiency of heavy metal ions was 56 % for copper and 38 % for zinc, respectively. Using a two-stage scheme (Fig. 2, *c*), the purification efficiency increased to 60 % for copper ions and up to 40 % for zinc ions. The next series of experiments was conducted using a solution of iron chloride coagulant at a dose of 50 mg/dm<sup>3</sup>. The efficiency of removing IHM was 62 % for copper, 45 % for zinc. The addition of a coagulant solution facilitated the coagulation of small suspended particles with the sorbed heavy metal ions.

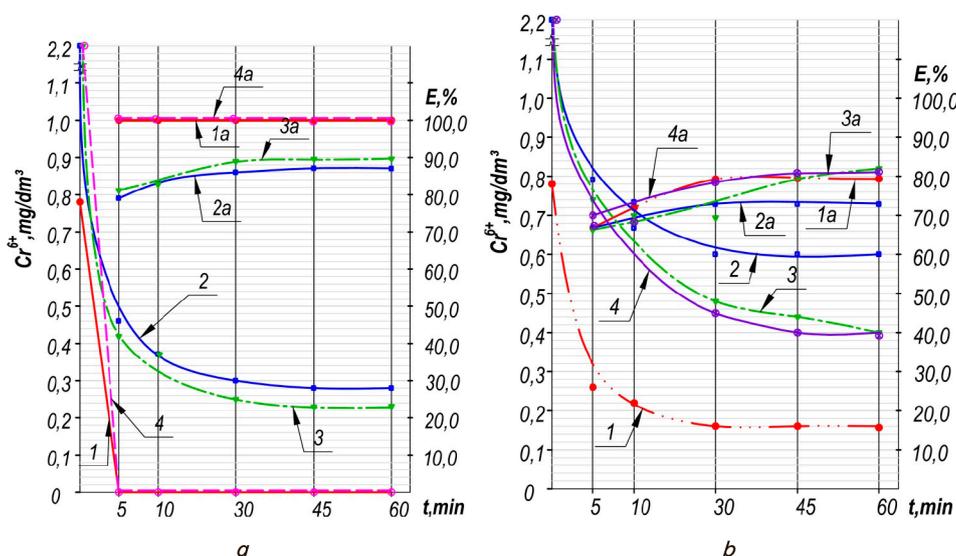


Fig. 4. Kinetics and efficiency of the Cr<sup>6+</sup> ion extraction from natural waters at concentrations: *a* – "fresh" sediment: 1 – 300 mg/dm<sup>3</sup>, Cr<sup>6+</sup> up to 1.0 mg/dm<sup>3</sup>; 1a – cleaning efficiency; 2 – 300 mg/dm<sup>3</sup>, Cr<sup>6+</sup> 1.0 – 2.5 mg/dm<sup>3</sup>; 2a – cleaning efficiency; 3 – to 400 mg/dm<sup>3</sup>; 3a – cleaning efficiency; 4 – 500 mg/dm<sup>3</sup>; 4a – cleaning efficiency; *b* – "compacted" sediment: 1 – 300 mg/dm<sup>3</sup>, Cr<sup>6+</sup> up to 1.0 mg/dm<sup>3</sup>; 1a – cleaning efficiency; 2 – 300 mg/dm<sup>3</sup>, Cr<sup>6+</sup> 1.0 – 2.5 mg/dm<sup>3</sup>; 2a – cleaning efficiency; 3 – 400 mg/dm<sup>3</sup>; 3a – cleaning efficiency; 4 – 500 mg/dm<sup>3</sup>; 4a – cleaning efficiency

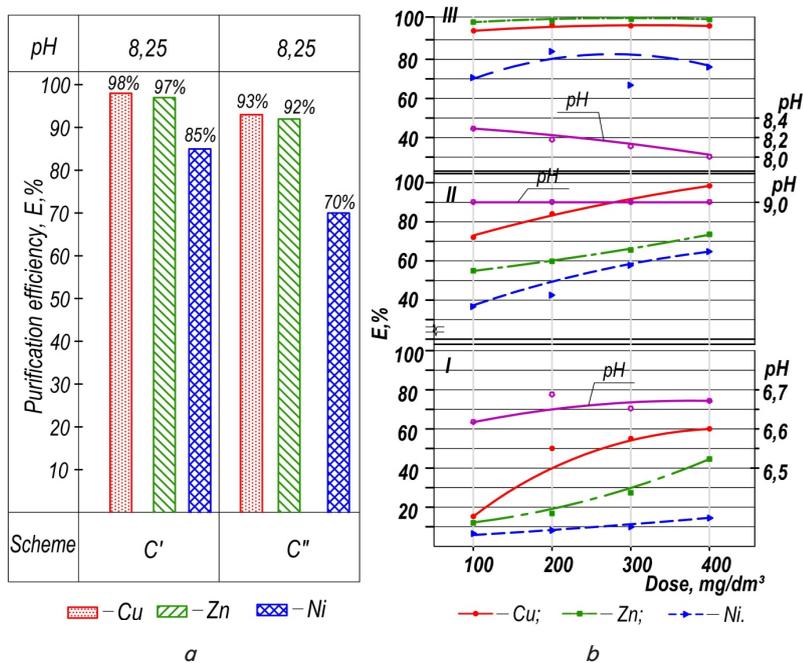


Fig. 5. Dependences of the efficiency of cleaning the washing waters of galvanic production: *a* – on the technological scheme and type of reagent-precipitant (column C' – using a calcined sediment; column C'' – using a "fresh" sediment); *b* – on the dose of the precipitating reagent and pH of the solution at successive treatment of washing waters from the baths of zinc coating: I, III – magnetic structurizers; II – hydromechanical mixer

At stage II of the research, a two-stage scheme (Fig. 2, *c*) was used with different types of precipitating reagents. The most qualitative process of removing of IHM occurred according to the scheme (Fig. 2, *c*) using a sediment calcined at  $t=600^{\circ}\text{C}$  (Fig. 5, *a*, column C'). The need for special equipment and high energy consumption associated with the preparation of calcined sediment make it more attractive to use another type of the precipitating reagent – the untreated sediment from the stations of biological groundwater iron removal (Fig. 5, *a*, column C'').

At stage III comparative studies were carried out according to the three-stage purification scheme (Fig. 2, *b*) to make the residual concentrations of the  $\text{Zn}^{2+}$  ions to conform to the norms of sewage system discharge. The purpose of the research was to determine the optimal concentration of the precipitating reagent, which was gradually introduced to the reverse waters. Considering the results of experiments (Fig. 5, *b*), it is clear that the optimal precipitant dose introduced before each stage was  $300\text{ mg/dm}^3$ .

It is also evident from graphs (Fig. 5, *b*, II) that with an increase in the pH level up to 9.0 there is a rapid decrease in the concentrations of heavy metal ions (Cu, Ni, Zn) at the second stage of purification to  $0.31\text{ mg/dm}^3$ ;  $0.15\text{ mg/dm}^3$ ;  $0.48\text{ mg/dm}^3$ , respectively.

## 6. Discussion of results of examining the process of biosorption of ions of heavy metals

As noted above, the speed of removal of the  $\text{Cr}^{6+}$  ions using a «compacted» sediment is less than the speed when using the «fresh» one. This, first of all, can be explained by the

storage conditions of the sediment. In the first case, the precipitate was in a compacted state. In this case, there was a destruction of the matrix of iron bacteria and a reduction of the saturated surface of the contact. In the second case, the sludge sites on a daily basis received fresh volumes of washing water with sediment, viable matrices of iron bacteria and soluble oxygen absorbed from the atmosphere when washing the filters. Conditions for the life activities of iron bacteria consortia and the initial structure of biominerals were maintained in the sediment. When using such a sediment in the reaction flask (Fig. 1, *a*), the iron bacteria continued to function, oxidizing the  $\text{Fe}^{2+}$  ions. In this case, there is an increase in the number of active cells and externally cell exopolymers as additional centers of adsorption of the  $\text{Cr}^{6+}$  ions. Until the appropriate moment, an increase in the number of microbial cells in the medium intensified the process of binding the  $\text{Cr}^{6+}$  ions to cellular metabolites, but over time the sorption efficiency began to gradually decline and eventually plateaued (Fig. 4, *a*, curves 2a, 3a) at the point of exhaustion of the adsorption capacity of the biomass. Having analyzed kinetics of the  $\text{Cr}^{6+}$  ions extraction (Fig. 4, *a*, *b*), it is possible to conclude that the efficiency of

the biosorption depends on the concentration of the matrix structures introduced into the solution with the sediment, and on the contact period. An important factor affecting the sorption kinetics is the concentration of metal ions, with an increase in which above the critical one – the intensity of sorption begins to decrease.

Insignificant characteristics of efficiency of the purification of washing waters of galvanic production from IHM, at stage I of the research, are linked to the insufficient magnitude of  $\text{pH}=7.2$ . As is known [2], the estimated pH values for the IHM deposition in the form of hydroxides are, respectively, for copper 7.2–10.0; for zinc 8.0–8.5. For the solutions with a simultaneous presence of these metals, optimal pH values are 10.0–10.5. When considering results of the studies by the two-stage scheme (Fig. 2, *c*), it is evident that the influence of CMF on this type of sediment is negligible. This is due to the fact that the sediment, dried at  $T=50^{\circ}\text{C}$ , consists mainly of the Fe compounds, insufficiently freed from physically and chemically bound water, insufficiently active in the magnetic field. The percentage of removed metals can be attributed to the sorption process on the surface of micro-particles, which form the sediment.

The relatively high percentage of IHM extraction using calcined sediment at the second stage of the study is due to the exoeffect that occurs at a wide temperature range of  $200\text{--}400^{\circ}\text{C}$ . In this case, there is a smooth decrease in the mass of the sediment, indicating the combustion of the amorphous component and the crystallization of the amorphous phase. As a result, goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ) are converted into hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\gamma\text{-Fe}_2\text{O}_3$ ), which have magnetic properties. When using a fresh sediment as a reagent, active

involvement in the process of adsorption of heavy metal ions is carried by biominerals, cells and polymer matrices of iron bacteria that have a crystalline structure and a large saturated surface. Analysis of the microflora of flush waters sediment from bioreactors performed when using the Nikon Eclipse E200 microscopes and the FEI *Quanta* raster electron microscope showed the domination of *Gallionella* and *Leptothrix* genera of iron bacteria. The size of the *Leptothrix* filament forms, shown in Fig. 3, *d*, was – 10 nm. Analysis of the formed bio-oxides of iron was achieved by the diffraction of X-rays, light and scanning electron microscopy (SEM). The sediment for electron microscopy was taken by a pipette from the thickest substance, dried in a vacuum chamber, and placed on a microscope stand. Scanning of the sediment in the sample taken was selected in three regions (Fig. 3, *d*): 1 – spectral analysis of the sediment accumulated between the *Leptothrix* filamentous structures; 2 – spectral analysis of the *Leptothrix* case; 3 – spectral analysis of agglomeration of bacterial consortia. Quantitative results of spectral analysis of the «fresh» sediment from filter washing are given in Table 3.

Considering data on the spectral analysis, it can be seen that the sediment formed between filamentous struc-

tures, in its qualitative and quantitative characteristics, is significantly different from other types of the examined structures. First of all, by the content of light metal ions, silicon and iron. It is seen that the bulk of iron is accumulated in bacterial structures (positions 2, 3 of Table 3), which are characterized simultaneously by the presence of carbon, nitrogen and phosphorus. This indicates the organic component of both the cells themselves and their organic matrices. The high concentration of oxygen is due to the entry of this element to the component of the cell wall, among which are the negatively charged groups ( $PO_4^3-$ ;  $COO^-$ ;  $OH^-$ ). As a result of external cellular activity of polysaccharides with Fe (II) ions,  $\alpha$ -FeOOH nanocrystals are formed. From the point of view of the adsorption process of ions of metals with variable valence ions, the presence of aluminum ions in all examined samples is of interest. Metals are electrostatically bound both with the anionic surface of the cell wall, and with organic polymers, which are isolated by cells from the outside, accumulating on their developed surface. Fig. 6 shows an X-ray spectral microanalysis of the sediment of the surface of the case of the *Leptothrix* bacterium, where it is seen that adsorption of Fe, Al, and Si ions occurs on its surface.

Table 3

Quantitative results of spectral analysis of "fresh" sediment after flushing of the iron-removal station filters Rokytno town

No.	Element composition	C	N	O	Al	Si	P	Ca	Fe
	Weight %	Wt	Wt	Wt	Wt	Wt	Wt	Wt	Wt
	Atomic %	At	At	At	At	At	At	At	At
1	Sediment between the filamentous <i>Leptothrix</i> structures	4.65	0.77	33.13	20.30	25.74	0.15	0.22	6.38
		8.56	1.22	45.73	16.61	20.24	0.11	0.12	2.52
2	Case of <i>Leptothrix</i> bacteria	5.56	1.33	28.7	4.48	4.21	0.07	0.73	54.55
		12.58	2.58	48.88	4.51	4.08	0.06	0.49	26.55
3	Agglomerate of bacteria consortia	6.95	1.17	23.29	5.65	3.40	0.14	1.25	57.95
		16.39	2.36	41.27	5.93	3.43	0.12	0.89	29.41

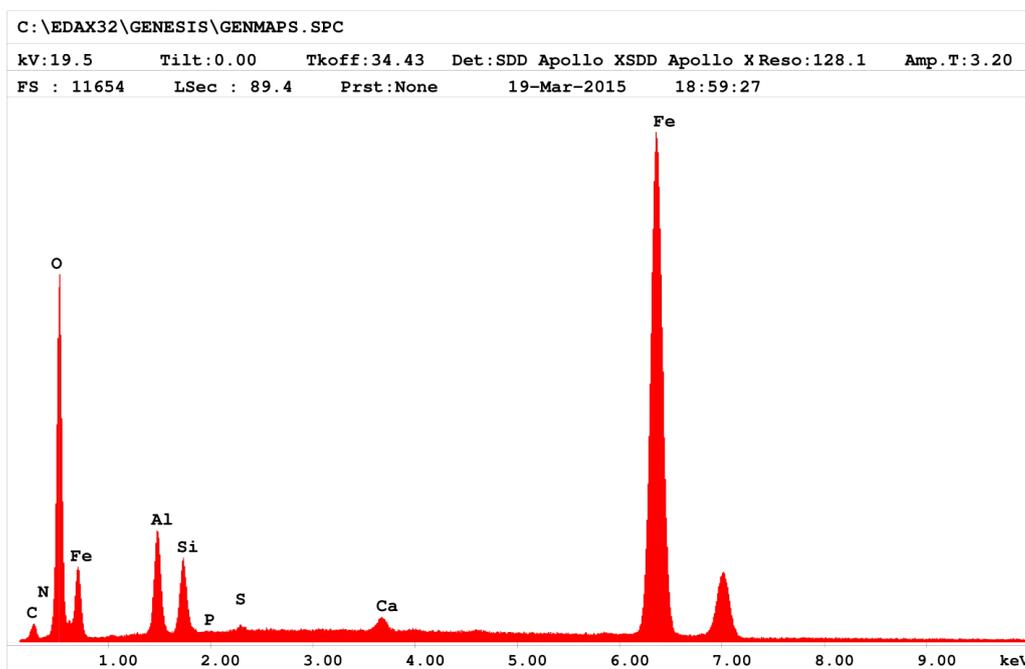


Fig. 6. X-ray spectral microanalysis of the sediment of the surface of the bacterium *Leptothrix* case

## 7. Conclusions

1. It has been established that the matrix structures of iron bacteria consortia are capable of adsorbing up to 2.0 mg/dm<sup>3</sup> of the Cr<sup>6+</sup> ions from natural groundwaters. The optimum concentrations of "fresh" sediment (400–500 mg/dm<sup>3</sup>) for the removal of Cr<sup>6+</sup> ions from ground technical waters have been determined.

2. We determined dependences of the purification efficiency of washing waters of galvanic production on IHM (Cu<sup>2+</sup> up to 16 mg/dm<sup>3</sup>, Zn<sup>2+</sup> up to 50 mg/dm<sup>3</sup>, Ni<sup>2+</sup> up

to 1.3 mg/dm<sup>3</sup>) as a result of their adsorption on matrix structures of iron bacteria on the type of the technological scheme, on the type of sediment and on its doses.

3. It has been determined that the use of "fresh" sediment is the most effective and cost-effective for removing IHM from washing and natural waters. Moreover, in order to remove IHM from the washing water from the galvanic production, a gradual introduction of a precipitant reagent with a dose of 300 mg/dm<sup>3</sup> at each of the stages should be used.

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