Magazine of Civil Engineering. 2022. 111(3). Article No. 11110

Magazine of Civil Engineering

ISSN
2712-8172

journal homepage: http://engstroy.spbstu.ru/

Research article

UDC 628.316

DOI: 10.34910/MCE.111.10

Removal of heavy metals from wastewater with natural and modified sorbents

S.V. Stepanov , A.K. Strelkov , O.N. Panfilova ✉

Samara State Technical University, Samara, Russia

✉ *samoliasgsy@yandex.ru*

Keywords: water adsorption, heavy metals, wastewater, modified clay, montmorillonite, dolomite, kaolinite, peat

Abstract. The paper presents research results of heavy metal ions sorption from a model solution and wastewater of an electroplating enterprise under static conditions. The purpose of this work is to develop a technology of tertiary treatment of electroplating production wastewater from heavy metals to achieve MPC levels for fresh fishery water bodies using local powder sorption materials. The authors examined such sorbents as modified clay (MC) obtained by thermal modification of its natural components (montmorillonite, kaolinite, peat, dolomite), as well as certain primary components and their mixtures without thermal modification. The studies were conducted at low initial concentrations of heavy metals (from 0.002 to 2.8 mg/l) characteristic of wastewater subjected to tertiary treatment. The concentration of heavy metals in wastewater was determined by inductively coupled plasma optical emission spectrometry on Avio™ 200. The research demonstrated that the contact time required to achieve the equilibrium of the treated wastewater and the modified clay sorbent varied from 60 to 120 minutes for the investigated heavy metals. Taking into account the time required to reach the MPCs of heavy metals for fresh fishery water bodies, the estimated contact duration of 90 minutes was recommended. The calculated dose of the modified clay sorbent, sufficient for tertiary treatment of acid-base wastewater of electroplating production to the MPC, was 1 g/l. Experiments with unmodified materials conducted on a multicomponent model solution showed that montmorillonite had the best sorption properties, ensuring the achievement of MPC for all metals, except aluminum, at doses from 0.1 to 0.9 g/l. Peat was the most effective in extracting nickel to MPC with its estimated dose being 0.1 g/l. Dolomite turned out to be the only material that provided the removal of aluminum to MPC at a dose of 1 g/l. The obtained results suggest that it is possible to increase the efficiency of heavy metals removal by selecting sorbent mixture without thermal modification and with mixed sorbent dose of 1–1.6 g/l. The authors recommend a technology of tertiary treatment of acid-base wastewater of electroplating production. This technology is to carry out the sorption process under static conditions using powder sorbents based on local natural materials, followed by separation of the spent sorbent with a precoat cartridge filter.

1. *Introduction*

Contamination of water resources by heavy metals is an enormous environmental problem. For example, the quality of the Kuibyshev reservoir waters in 2009–2018 varied from "polluted" to "dirty". In 2018, compared to the period of 2008–2017, water pollution from copper compounds increased by 47 % in the area below Samara, the excess of contamination for manganese varied from 3 to 6 MPC values of heavy metals for fresh fishery water bodies, and the excess of cadmium reached up to 2 MPC values. The

---

Stepanov, S.V., Strelkov, A.K., Panfilova, O.N. Removal of heavy metals from wastewater with natural and modified sorbents. Magazine of Civil Engineering. 2022. 111(3). Article No. 11110. DOI: 10.34910/MCE.111.10

main part of heavy metal pollution is caused by discharges from electroplating enterprises. Their wastewater is characterized not only by a diverse composition of pollutants, but also by the irregularity of the incoming wastewater. Paper [1] states that the wastewater of electroplating plants contains such elements as cadmium and lead, which are highly dangerous, while aluminum, iron, manganese, copper, nickel, chromium (VI) and zinc are referred to as moderately dangerous substances. Therefore, the degree of purification at local treatment facilities of industrial enterprises should be high, and the technologies used should provide the required efficiency.

The choice of physical and chemical methods of wastewater treatment from heavy metals depends on such initial parameters, as the volume of wastewater, the concentration of metals to be removed, and the total salt content [2–4].

Chemical precipitation is considered the most common method due to its simplicity and low capital costs. This method is widely used for the treatment of highly concentrated wastewater, including industrial wastewater subjected to tertiary treatment. The most frequently used reagents are slaked and quicklime, as well as soda ash. At the same time, even though the reagent method is used everywhere, it does not allow to achieve the required quality of purified water [2]. The purification process is complicated by the fact that each metal has its own pH range, at which the maximum precipitation of insoluble hydroxide occurs. Table 1 shows data on the efficiency of heavy metals precipitation from single- and multicomponent solutions at optimum pH values.

Table 1. Efficiency of chemical precipitation of heavy metals at optimum pH values.

Metals	Initial concentrations, mg/l	Final concentrations after neutralization, mg/l	MPCs of heavy metals for fresh fishery water bodies	Reagents used	Optimum pH	References
Cr (III)	30	0.01	0.07	$Ca(OH)_2$	8.7	[2]
Cu (II)*	48.51	0.694	0.001	aeration+ $Ca(OH)_2$ or NaOH	12	
Zn (II)**	32	0.22-0.32	0.01	CaO	9–10	[2]
Cu (II), Zn (II), Cr (III), Pb (II)	100	0.14	0.001	CaO+ ash dust	7–11	[2]
		0.45	0.01			
		0.08	0.07			
		0.03	0.006			
Fe (III)**	1.6	0.928	0.1	CaO	8	[5]
Co (II)	1.8	0.11	0.01			
Ni (II)	6.5	0.05	0.01			
Cr (III)	101.6	2.12	0.07			
Cu (II)	4.5	0.079	0.001			
Zn (II)	6.9	0.102	0.01			
Cd (II)	5.3	0.014	0.001			
Pb (II)	1.7	0.1	0.006			
Al	215.9	–	0.04	NaOH	5.5–7.5	[6]

*Cuprammonium solution

**Multi-component solution

The disadvantages of this method are the large amount of precipitation generated, and, as Table 1 shows, the concentrations after treatment are more than MPCs of heavy metals for fresh fishery water bodies. Thus, an additional wastewater treatment is required afterwards.

The method of ion exchange makes it possible to achieve the MPCs of heavy metals for fresh fishery water bodies during wastewater treatment. The main disadvantages of ion exchange are the competition of metals in multicomponent solutions for active ion exchange centers, the interfering influence of H^+, K^+, Na^+, Ca^{2+}, Mg^{2+} cations contained in the source water, the need to use chemical reagents for ionite regeneration, and the complexity of spent regenerating solutions treatment [3]. Due to high operating costs, ion exchange is economically feasible only when demineralized water is required.

Membrane filtration technologies with different types of membranes show great promise for heavy metals removal for their high efficiency, easy operation and space saving. When using ultrafiltration, it is necessary to bind heavy metals into compounds whose particle size exceeds the pore size of ultrafiltration membranes. Two methods of water pre-treatment are used for this purpose. The first method involves surfactant molecules able to aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The second method is based on water-soluble polymers that combine with metal ions and form macromolecules having a higher molecular weight than the molecular weight cut off of the membrane [2]. In reverse osmosis and ultrafiltration, semi-permeable membranes are used to trap hydrated heavy metals. Electrodialysis is another membrane process for the separation of ions across ion-exchange membranes from one solution to another using an electric field as the driving force. However, such disadvantages as high cost, the need for pre-treatment, the large amount of concentrates produced and the cost of their purification, mineral deposits on the surface of the membranes and frequent regeneration with reagents limit their use for the removal of heavy metals [7].

Among electrochemical methods of wastewater treatment from heavy metals, electrocoagulation and electroflotation are most well-known. Electrocoagulation involves the generation of coagulants in situ by electrolytic dissolution of aluminum or iron electrodes. The metal ion generation takes place at the anode, and hydrogen gas is released produced at the cathode. The hydrogen gas can help to float the flocculated particles out of the water. Electroflotation is a solid/liquid separation process that floats pollutants to the water surface by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. Electrochemical methods of wastewater treatment ~~from~~ are highly effective, especially at high initial concentrations of heavy metals. They are tightly controlled and require fewer chemical substances. Besides, they provide high-quality purification of wastewater with little precipitation. However, high initial investment and significant energy consumption limit the widespread use of electrochemical methods [2, 7].

Over the last years, researchers considered various sorption materials for removal of heavy metals from wastewater. They made use of such sorbents as activated carbon [8, 9], peat [10], dolomite [11], paper-and-pulp industry wastes [12, 13], natural [14–16] and synthetic zeolites [17]. Activated carbons with their high cost are characterized by low efficiency in removing heavy metals [18].

The experiments on using natural and modified clays seem most interesting [18–27]. Clay-based sorbents demonstrated high binding capacity for ions of heavy metals. Clays are widely distributed and inexpensive, and when modified, their sorption capacity increases significantly [23, 24, 27]. Montmorillonite and its modified forms have a higher sorption capacity to metals than kaolinite [24]. Adsorption of heavy metals by clay minerals is explained by ion exchange mechanism, direct binding of metal cations to the surface of the sorbents, as well as surface complexation. Many researchers note an increase in the aluminum concentration in water after its interaction with sorbents containing clay. It is explained by the the ion-exchange nature of interaction and release of aluminum contained in clay during it [26, 32]. In the study of acid-modified clays, researchers note a high rate (within 5–10 minutes) of metal adsorption and the achievement of maximum recovery rates after 30 minutes. Thus, maximum values of the exchange capacity at pH = 5.5 for metal ions were as follows: 45 mg/g for iron; 50 mg/g for copper; 48 mg/g for zinc; 89 mg/g for lead [5]. The study of sorption properties was carried out at high initial concentrations, which makes ~~it~~ impossible its application in the calculation of tertiary treatment facilities for low-concentrated wastewater.

This work continues a whole series of studies on the sorption properties of sorbents based on natural materials [29–31]. The purpose of this work is to develop a technology for tertiary treatment of pre-treated wastewater from electroplating production from heavy metals to the MPCs for fresh fishery water bodies using local sorption materials. To do this, the researchers aim to establish the contact time required to achieve the equilibrium between the treated wastewater and the sorbents used; to determine calculated doses of recommended sorbents; to find a solution for separating the suspension of the spent sorbent from the treated water; to develop a schematic diagram of treatment facilities.

2. Methods

The sorbents analyzed included a thermally modified mixture of natural materials, mainly clays. Other individual components that are part of this mixture (without thermal modification and binder) included montmorillonite, kaolinite, peat and dolomite as well as a sorbent agent consisting of a composition of these natural components. The composition of sorbents and the methods of their preparation are shown in Table 2.

Table 2. Composition of sorbents and methods of their preparation and production.

Sorbent	Production method	Composition, weight by dry mass	Symbols
Dolomite powder	Drying to a constant weight at 105 °C and grinding in a ball mill to a particle size less than 0.1 microns	–	D
Kaolinite	The same method	–	K
Montmorillonite	The same method	–	M
Peat	The same method	–	P
Modified clay	Preparation of the initial components, as indicated above, mixing with water, thermal modification at 500 °C, grinding to a particle size of less than 0.1 microns	10 parts montmorillonite, 10 parts kaolinite, 10 part of peat, 1 part of dolomite	MC
Sorbent mixture	A mixture of natural components prepared as described above without thermal modification	5 parts of montmorillonite, 4÷10 parts of dolomite, 1 part of peat	SM

When studying the sorption kinetics in each experiment, a sorbent portion of 0.50±0.03 g was added to 200 ml of wastewater (a dose of 2.5 g/l) at a temperature of 20±1 °C, the mixture was mixed with a magnetic stirrer. A water sample was taken after a specified time (5-120 min) of "sorbent-solution" contact and filtered through a paper filter with a pore size of 2-3 microns. Then the concentration of heavy metal ions was determined.

Experiments under static conditions were carried out at a temperature of 20±1 °C by contacting a sample of wastewater with sorbent doses of 0.1–1 g/l while mixing with a magnetic shaker and a contact duration of 90 minutes. Before determining the concentration of heavy metals in purified water, the sample was filtered through a paper filter with a pore size of 2-3 microns.

The effect of coagulation and flocculation on the intensification of the process of sorbent separation from the purified water was studied by the test coagulation. To do this, the suspension of the sorbent after 90 minutes of contact with the wastewater was poured into laboratory cylinders, a 1 % solution of the coagulant was injected into it with a dose of 10-50 mg/l of Al_2O_3 and rapid mixing was carried out at a speed of 500 min.$^{-1}$ for 20 seconds. Then the mixing speed was reduced to 120 min.$^{-1}$ and slow mixing was carried out for 2 minutes. If the experiment involved the use of flocculant, then after two minutes of slow mixing, a 0.05 % solution of flocculant was added with a dose of 0.4–2 mg/l and slow mixing continued for another 5 minutes. After mixing was completed, settling was carried out in the same cylinders, or the suspension was poured into a Lisenko vessel with a water layer height of 350 mm, in which the kinetics of precipitation and compaction of the suspension were observed. After 30 minutes of settling, samples of purified water were taken.

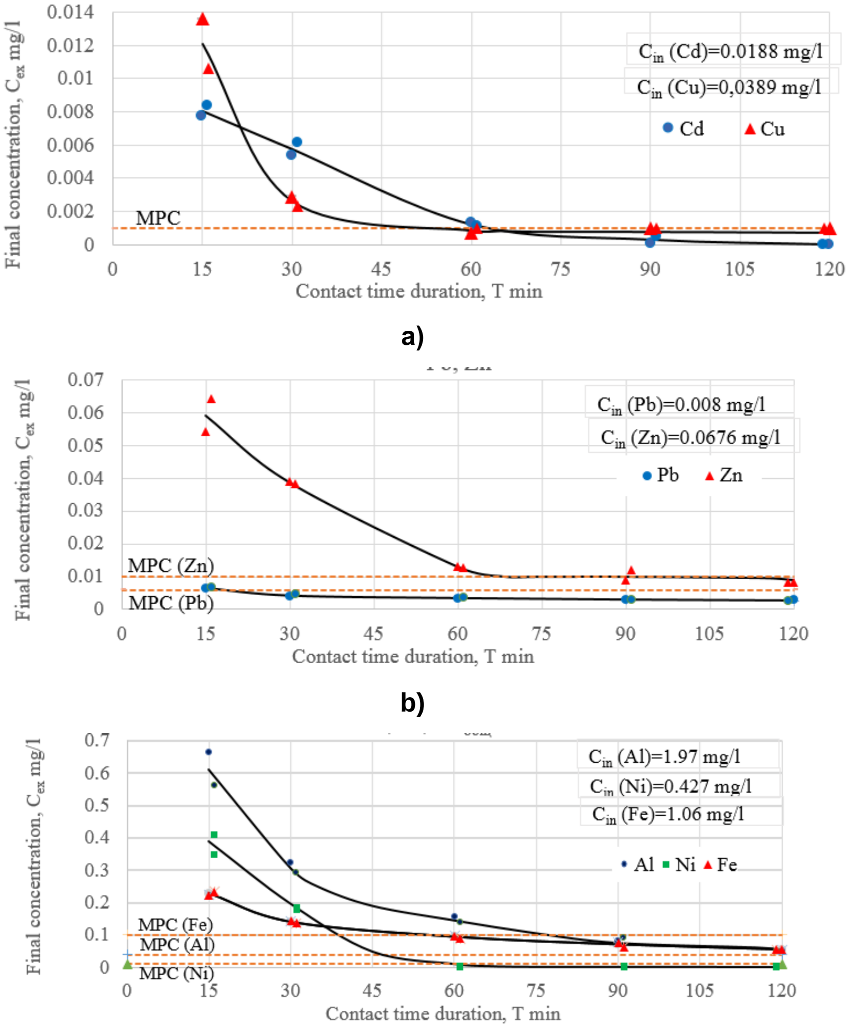
The studies were carried out on model solution and on real wastewater. A model solution was prepared by dissolving salts $CuSO_4 \cdot 5H_2O$, $Cd(CH_3COO)_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $Pb(NO_3)_2$иand$AlCl_3 \cdot 6H_2O$, chemical pure (CP) and analytically pure (AP) grades in distilled water. The concentrations of metals in the model solution with pH = 5.5 were, mg/l: copper – 0.0081; cadmium – 0.0211; iron (III) – 1.023; nickel – 0.152; zinc – 0.098; lead – 0.0512; aluminum – 0.9971.

Real wastewater of electroplating production was collected at one of the enterprises of the Samara region. At the existing treatment facilities of this enterprise, chromium (VI) is recovered with sodium sulfite in an acidic environment. After that, chromium-containing wastewater is mixed with acid-base wastewater and the mixture is alkalized with caustic soda, followed by the separation of the resulting chromium (III), copper, cadmium, iron, nickel, zinc, lead and aluminum hydroxides in the precipitation plant. The treated wastewater is disposed into the city sewer network. Since the existing treatment facilities did not always correctly fulfill wastewater neutralization, the samples of treated wastewater from electroplating production were alkalized to pH = 8 and then additionally settled for two hours. The resulting clarified water was used in experiments as the original real wastewater. The initial concentrations of metals during the experiment were (mg/l): copper 0.0036 – 0.0389; cadmium 0.0022–0.0561; iron (III) 0.154–3.31; nickel 0.011–0.529; zinc 0.059–0.121; lead 0.008–0.0521; aluminum 0.643–2.81. The total salt content of this wastewater was 834–950 mg/l.

The concentration of heavy metals in wastewater was determined at all treatment stages by Inductively coupled plasma optical emission spectrometry on Avio™ 200 according to Environmental Federative Specification Document (EFSD = [PNDF] in Russian transcription) 14.1:2:4.135-98 "Methods for measuring mass concentration of elements in drinking water and wastewater samples by inductively coupled plasma atomic emission spectrometry". The measurement errors for each element are calculated in the tables depending on the initial concentration.

3. Results and Discussion

To study the kinetics of sorption and to determine the duration of contact sufficient to achieve equilibrium in the system "sorbent modified clay–solution", two series of experiments were performed. The experiments were carried out on real wastewater from electroplating production, previously clarified and neutralized to pH = 8.0. The results of the experiments with MC are shown in Fig. 1.



a)

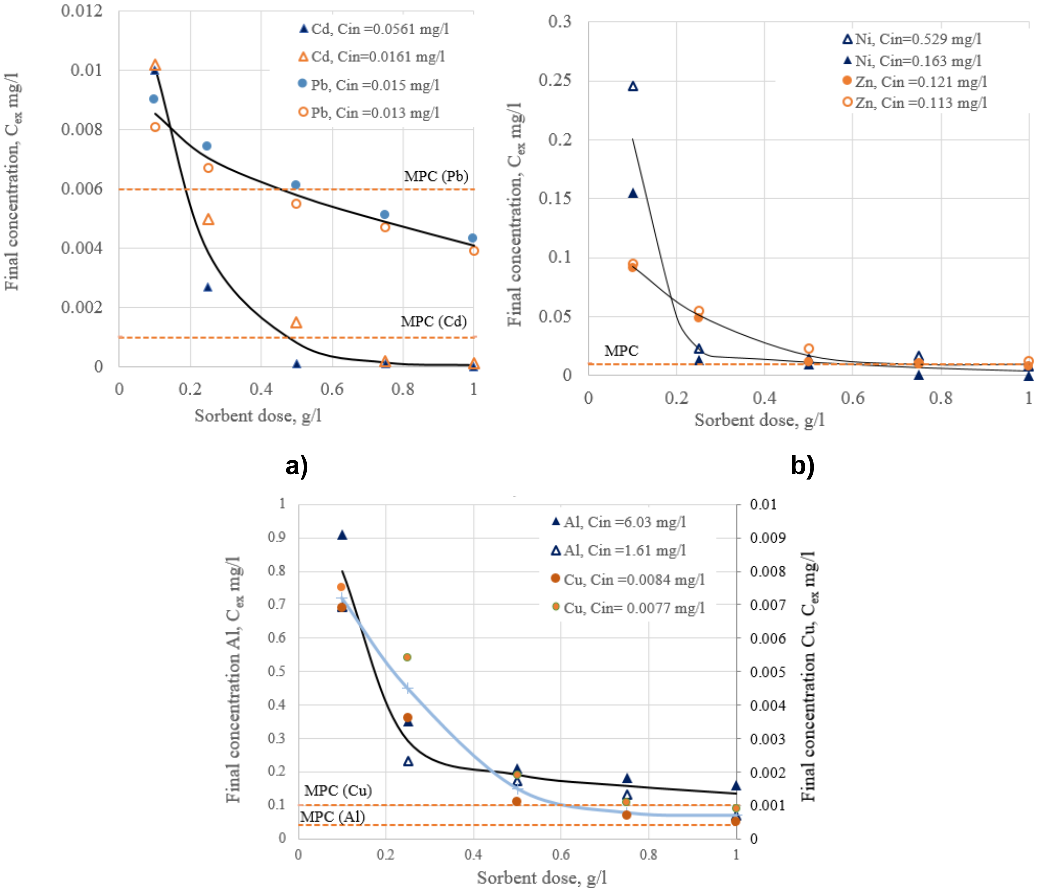
b)

c)

Figure 1. Kinetics of heavy metals sorption with MC sorbent at a temperature of 20±1°C: a) cadmium, copper; b) lead, zinc; c) aluminum, nickel, iron; C_{in} is initial heavy metals concentrations

As the graphs in Fig. 1 show, MPC requirements were met in the "sorbent-solution" system after 60–90 minutes of contact. MPC for lead was reached after 20–30 minutes, and it was the fastest time. It took 60 minutes for iron, nickel, copper and cadmium and 90 minutes for zinc to meet MPC requirements. The MPC values for aluminum were not reached; its final concentration after 120 minutes of stirring was 0.051 mg/l. It turned out that the required duration of contact slightly exceeds the time given in Paper [5]. During the time period under study the equilibrium in the "sorbent – solution" system was reached for cadmium, zinc, copper, aluminum and nickel, and it was not reached for lead and iron. According to the results of the experiment, a contact time of 90 minutes was adopted for further experiments on wastewater from electroplating enterprises tertiary treatment.

In order to determine the sorption capacity and the calculated dose of the modified clay sorbent, which under static conditions ensure the achievement of an equilibrium concentration of heavy metals at the level of MPCs for fresh fishery water bodies, a series of experiments was conducted on real wastewater in accordance with the above methodology. For this purpose, a mixture of chromium-containing and acid-base wastewater pre-treated under production conditions was neutralized to pH = 8 and then additionally settled. The results of experiments with different doses of the sorbent are shown in Fig. 2 and Table 3.



a) b)

c)

Figure 2. Dependence of the equilibrium concentration of heavy metals on the modified clay sorbent at a temperature of 20±1 °C: a) cadmium, lead; b) zinc, nickel; c) copper, aluminum; C_{in} is initial heavy metals concentrations

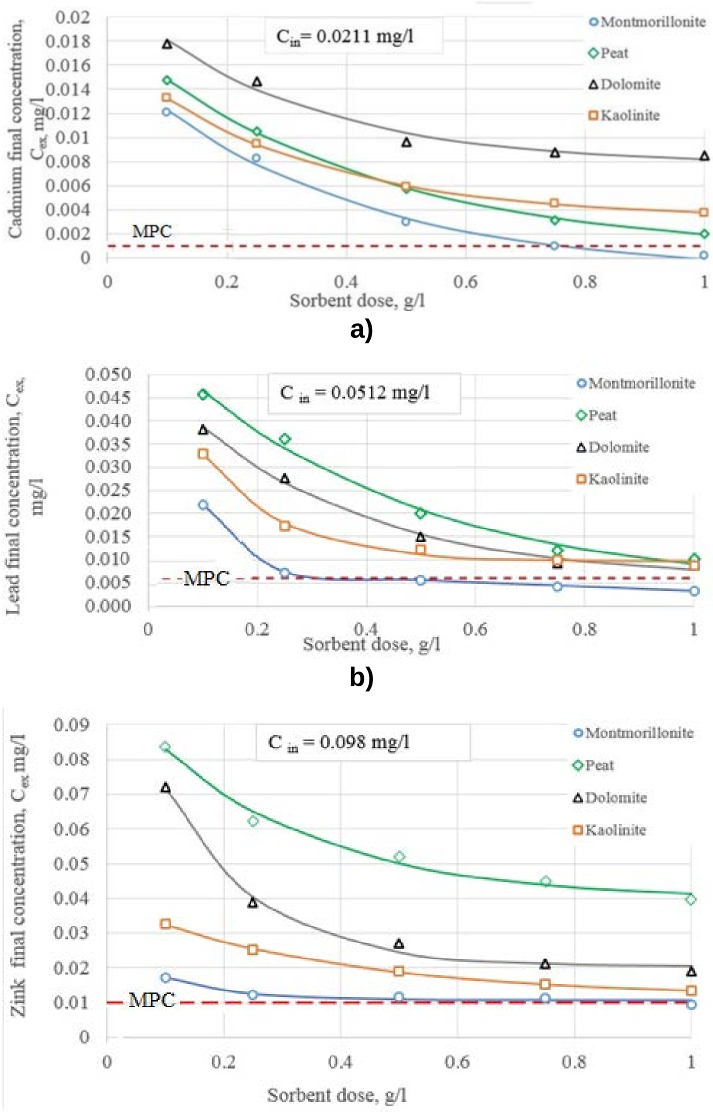
Table 3. The values of the sorption capacity and the calculated dose of MC sorbent, which ensure the achievement of an equilibrium concentration of heavy metals at the level of the MPCs for fresh fishery water bodies under static conditions during tertiary treatment of wastewater from electroplating production, T = 20 °C.

Metal	Series 1				Series 2			
	C_{in}, mcg/l	D_{MPC}, g/l	C_{in}, mcg/l	D_{MPC}, g/l	C_{in}, mcg/l	D_{MPC}, g/l	C_{in}, mcg/l	D_{MPC}, g/l
Cd	56.1±13.5	0.5	56.1±13.5	0.5	56.1±13.5	0.5	56.1±13.5	0.5
Pb	15.0±6.3	0.5	15.0±6.3	0.5	15.0±6.3	0.5	15.0±6.3	0.5
Zn	121.0±29.0	0.75	121.0±29.0	0.75	121.0±29.0	0.75	121.0±29.0	0.75
Cu	8.4±3.53	0.75	8.4±3.53	0.75	8.4±3.53	0.75	8.4±3.53	0.75
Fe_{total}	3310.0±496.5	0.25	3310.0±496	0.25	3310.0±496.5	0.25	3310.0±496.5	0.25
Al	6030.0±964.8	1.0	6030.0±964	1.0	6030.0±964.8	1.0	6030.0±964.8	1.0
Ni	529±84.6	0.5	529±84.6	0.5	529±84.6	0.5	529±84.6	0.5

Note: S_{in} is initial concentrations of heavy metals; D_{MPC} is the sorbent dose required to achieve MPC; C_{ex} is heavy metals equilibrium concentrations in purified water; a is sorption capacity

Most researchers who studied sorption properties of clays and clay-based sorbents, determined sorption capacity at high initial and equilibrium concentrations of heavy metals [19, 24, 26, 28]. Therefore, it is difficult to compare the results obtained in the experiments described with other research data. Still, a meaningful comparison can be made with the data obtained in Paper [18] when studying the sorption of heavy metals from biologically treated wastewater in Khabarovsk using natural zeolite as a sorbent. At close initial concentrations, the researchers obtained such sorption capacities that correspond to the achievement of the MPCs of heavy metals for fresh fishery water bodies, which are: 0.45 mg/g for aluminum; 0.1 mg/g for zinc and iron; 0.025 mg/g for manganese. We also note that the modified clay sorbent sorption capacity for aluminum and iron was significantly higher than that of zeolite; similar values were obtained for zinc.

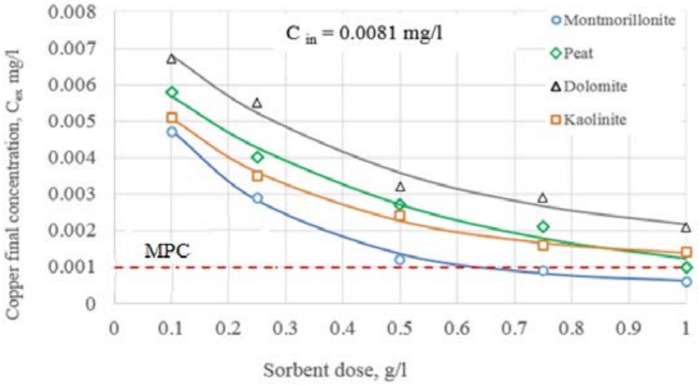
To find a more economical option for sorption tertiary treatment of wastewater from electroplating production, the following series of experiments was conducted. The sorption capacity and the calculated dose were determined for the initial unmodified components of sorbents such as montmorillonite, kaolinite, dolomite and peat without their thermal processing. The preliminary preparation of these materials is shown in Table 2. A model solution prepared by dissolving salts of seven heavy metals in distilled water was used as the source water, as indicated in the "Methods" section. In other respects, the method of the experiment was similar to the previous series. The dependences of heavy metals equilibrium concentrations on the sorbent dose are shown in Fig. 3.



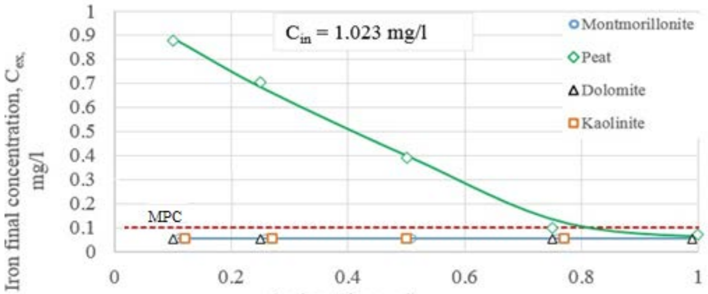
a)

b)

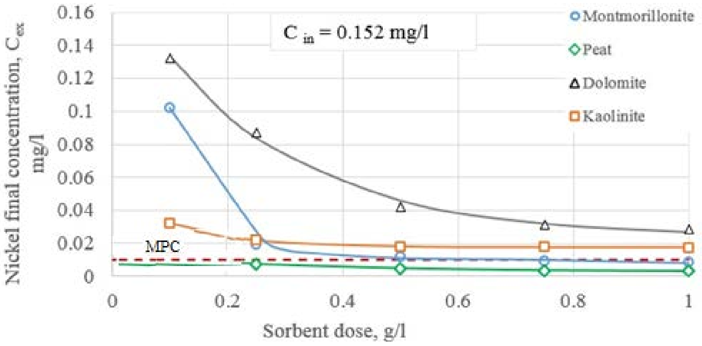
c)



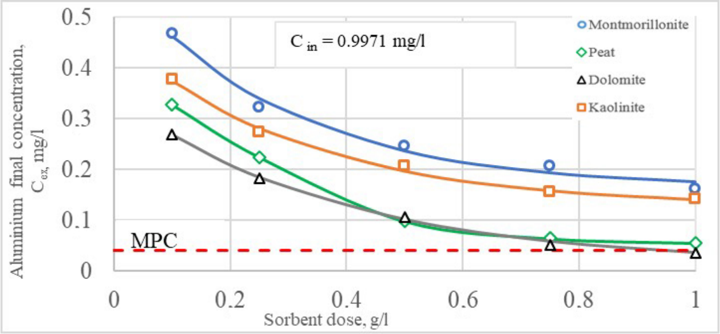
d)



e)



f)



g)

Figure 3. The dependences of heavy metals equilibrium concentrations on the sorbent dose for the model solution at a temperature of 20±1 °C: a) cadmium; b) lead; c) zinc; d) copper; d) iron; e) nickel; g) aluminum; C_{in} is initial heavy metals concentrations

The results of research in static conditions, presented in the form of graphs in Fig. 3, are summarized in Table 4. It specifies the doses of four sorbents sufficient to reduce heavy metals concentration from the initial to the MPCs.

Table 4. Doses of the initial non-modified sorption materials that ensure the achievement of the equilibrium concentration of heavy metals under static conditions at the level of the MPCs for fresh fishery water bodies during tertiary treatment of wastewater of electroplating production (on a model solution, T = 20 °C)

Metal	Initial concentration, mg/l	The sorbent dose, g/l, required to achieve MPC			
		montmorillonite	kaolinite	peat	dolomite
Cd	0.0211±0.0068	0.75	not registered	not registered	not registered
Pb	0.0512±0.0164	0.4	not registered	not registered	not registered
Fe_{total}	1.023±0.153	0.1	0.1	0.75	0.1
Zn	0.098±0.024	0.9	not registered	not registered	not registered
Ni	0.152±0.040	0.75	not registered	0.1	not registered
Al	0.9971±0.1595	not registered	not registered	not registered	1
Cu	0.0081±0.003	0.65	not registered	1	not registered

Table 4 shows that montmorillonite has the best sorption properties among all local materials, ensuring the achievement of the MPCs for all metals, except aluminum, at doses varying from 0.1 to 0.9 g/l. These doses turned to be the lowest for cadmium, lead, zinc and copper as compared to other sorbents. The montmorillonite dose of 0.1 g/l needed to remove iron was the same as the doses of kaolinite and dolomite. Peat was most effective in extracting nickel with its estimated dose being 0.1 g/l. Dolomite was the only material that provided aluminum removal at a dose of 1 g/l. The use of kaolinite did not give any advantages for any of the examined heavy metals, which confirmed the data [24, 26] about the significantly higher sorption capacity of montmorillonite compared to kaolinite.

The results obtained suggest that it is possible to increase the efficiency of heavy metals removal by selecting the mixture of natural sorbents. In this case, montmorillonite should make up the bulk of the composition. If there is nickel and aluminum in the composition it is advisable to add peat and dolomite, respectively. The verification of this assumption was carried out on treated wastewater from electroplating production, which was additionally neutralized and clarified, as indicated in the "Methods" section.

Since the addition of sorbent mixture to the treated water formed a suspension, poorly separated by settling, the selection of doses of coagulant and flocculant was further performed to intensify this process. Considering the content of nickel (being 6.3 of MPC) and aluminum (93.3 of MPC) in the source water (see Table 5), a dose of sorbent mixture of 1 g/l was taken with the ratio of the components by weight being montmorillonite: dolomite: peat = 5:4:1. The corresponding sorbent sample was added to a 1.25l of wastewater sample. After 90 minutes of the wastewater and the sorbent mixing, the suspension was poured into five cylinders with a volume of 250 ml each and a trial coagulation was performed at doses of aluminum polyoxychloride 10; 20; 30; 40 and 50 mg/l for Al_2O_3 in accordance with the procedure presented in the "Methods" section. According to the minimum turbidity of the clarified water, the optimal dose of the coagulant was determined as 40 mg/l for Al_2O_3. Then the experiment was repeated under the same conditions, but with the same dose of aluminum polyoxychloride – 40 mg/l for Al_2O_3. Additionally, the flocculant Magnafloc*LT20* with doses of 0.4; 0.8; 1.2; 1.6 and 2 mg/l were introduced. According to the minimum turbidity of the clarified water, the optimal dose of the flocculant was determined as 0.4 mg/l.

The main experiment of this series was carried out in a glass cup with a volume of 1000 ml, a dose of sorbent mixture (SM) being 1 g/l, with the following ratio of components by weight – montmorillonite: dolomite: peat = 5:4:1. The final suspension was mixed with a magnetic stirrer at a temperature of 20 °C. After 90 minutes of contact, in accordance with the above-mentioned procedure, a coagulant – aluminum polyoxychloride with a dose of 40 mg/l for Al_2O_3 and a flocculant Magnafloc*LT200* with a dose of 4 mg/l were successively introduced into the glass. After mixing was completed, the suspension was poured into a Lisenko vessel, in which the kinetics of precipitation and compaction of the suspension were observed. After 30 minutes of settling, the sediment settled down to 8.1 ml/l. The efficiency of heavy metals removal in this experiment was determined twice: after settling and after filtering the clarified water through a paper filter with pores of 2-3 microns.

The experiment results are shown in Table 5.

Table 5. Efficiency of tertiary treatment of wastewater from electroplating production with sorbent mixture (sorbent dose – 1 g/l, aluminum polyoxychloride dose – 40 mg/l for Al_2O_3, flocculant Magnafloc LT20 dose – 0.4 mg/l, temperature 20 °C).

Metal	Concentration in wastewater, mg/l			Efficiency, %		Adsorption capacity, mg/g
	source	purified		the degree of sorption-sedimentation	general	
		unfiltered	filtered			
Cd	0.0014±0.0005	0.0007±0.0003	0.00048±0.0002	51.4	66.7	0.0010
Pb	0.0064±0.0027	0.0018±0.0008	0.0008±0.0003	71.9	87.5	0.0056
Fe_{total}	0.123±0.032	0.073±0.018	0.058±0.014	40.7	52.8	0.0650
Zn	0.0326±0.014	0.0142±0.005	0.0101±0.003	56.4	69.0	0.0225
Ni	0.0631±0.016	0.0075±0.003	0.0057±0.002	88.1	91.0	0.0574
Cu	0.0028±0.0012	0.0017±0.0007	0.0016±0.0007	39.3	42.9	0.0012
Al	3.73±0.597	0.643±0.103	0.313±0.075	82.8	91.6	3.4170

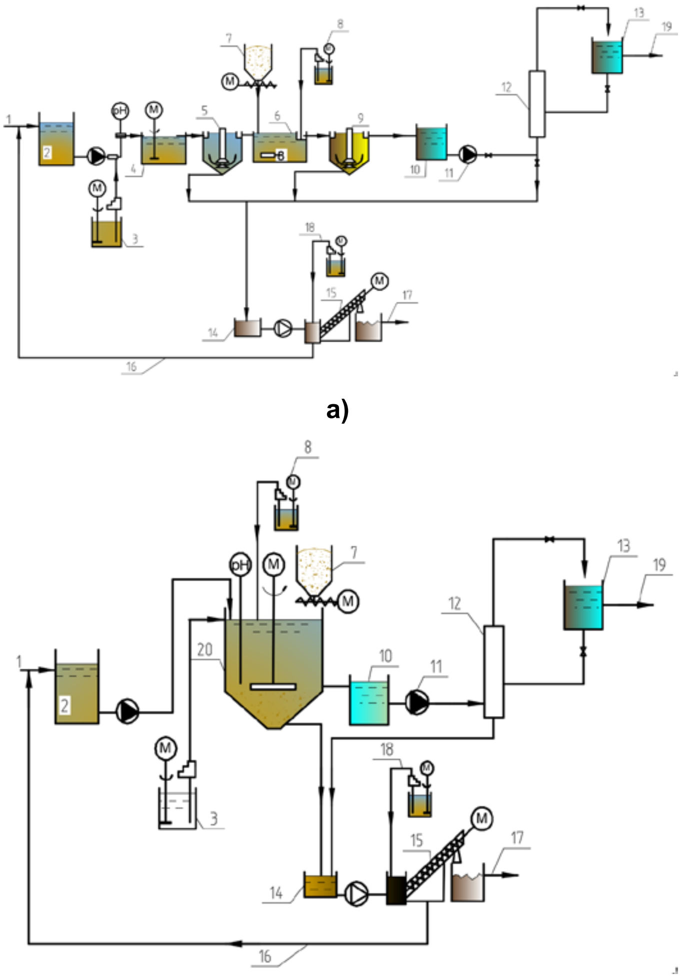
The data given in Table 5 show that the assigned task of reducing the concentration of heavy metals to MPC was almost completed. Only copper and aluminum exceeded the permitted concentrations. At the same time, the efficiency of aluminum removal as well as its sorption capacity were both high (91.6 % and 3.417 mg/g, respectively). The data given in Fig. 3d and 3g indicate that to meet the standards for copper and aluminum for a given concentration of heavy metals in the source wastewater, it is sufficient to increase the proportion of dolomite in sorbent mixture to the ratio of components being montmorillonite: dolomite: peat = 5:10:1 and take a 1.6 g/l dose of sorbent mixture. It is also important to note that the main part of heavy metals is removed from the treated wastewater at the settling stage, with the share of filtration in the overall cleaning effect varying from 3 to 15 %.

The research results make it possible to recommend the described technology for the treatment of wastewater containing heavy metals as well as acid-base wastewater from electroplating production. This technology includes correction of the pH of water to the range corresponding to the lowest solubility of heavy metal hydroxides, depending on the composition of the initial wastewater in each specific case (see Table 1) and sorption tertiary treatment with the use of sorbents based on local natural materials.

The authors elaborated two schemes of treatment plants that can be used to remove heavy metals from wastewater. The continuous operation scheme (see Fig. 4a) provides equalization of the source wastewater (1) in the equalization basin (2). Wastewater neutralization takes place in a flow reactor (4) equipped with a mixing device. The supply of the alkaline reagent solution is carried out from the alkali dosing unit (3) in accordance with the pH-meter signals. The resulting suspension of heavy metal hydroxides sediments in the settler (5). Clarified wastewater enters a flow sorption reactor with a mixing device (6). The sorbent is dosed into the adsorber in a dry form using a sorbent dispenser (7). At the exit from the reactor to the channel equipped with a mixing device, a coagulant solution is introduced into it from the coagulant dosing unit (8). The spent sorbent is separated in the tertiary settler (9), and the clarified water enters the transfer tank (10). The water supply for filtration is carried out by the feed pump (11). For final purification of wastewater from the residual amount of suspension, which is a spent sorbent, the installation with a precoat cartridge filter (12) is used. Treated wastewater (19) enters the clean water tank (13). A mixture of sediments containing heavy metal hydroxides and spent sorbent with removed heavy metals is collected in the sludge tank (14). To improve the dewatering process, a flocculant (18) is introduced before the mechanical dewatering unit (15). The drainage (16) obtained after dewatering is returned to the equalization basin, and the dewatered sludge (17) is taken to landfill sites for deposit.

In the batch treatment plant (see Fig. 4b), the same processes are carried out, but the wastewater neutralization, settling and removing of metal hydroxides, contact with the sorbent and its settling are carried out in the batch reactor (20), alternating in time. Wastewater treated at these stages is collected in the transfer tank (10). The operation of the precoat filter and mechanical dewatering units is similar to the operation of the corresponding units of the continuous operation scheme.

It is obvious that with an increase in capacity, the technical and economic advantages of continuous-acting plants increase in comparison with batch treatment plants. The choice of the treatment scheme is recommended to be carried out on the basis of a technical and economic calculation.



a)

b)

Figure 4. Wastewater treatment plant from heavy metal ions: a) continuous operation; b) batch operation; 1 – source wastewater; 2 – equalization basin; 3 –alkali dosing unit; 4 – reactor-neutralizer; 5 – settler; 6 – adsorber with mixer; 7 – sorbent dispenser; 8 – coagulant dosing unit; 9 – tertiary settler ; 10 – transfer tank; 11 – feed pump of filtration unit; 12 – precoat filtration unit; 13 – treated water tank; 14 – sludge tank; 15 – mechanical dewatering unit; 16 – drainage; 17 – dewatered sludge; 18 – flocculant dosing unit; 19 – treated wastewater; 20 – batch reactor

4. Conclusions

This paper considers using sorbents based on natural materials for post-treatment of wastewater from electroplating production. The experiments were carried out on a model solution containing a mixture of cadmium, lead, iron, zinc, nickel, copper and aluminum salts, as well as on wastewater from Samara electroplating plant treated at existing facilities by neutralization and sedimentation methods. The authors used local natural materials (that it montmorillonite, kaolinite, dolomite, peat and their mixtures obtained by thermal modification and without thermal modification) as sorbents. The research yielded the following conclusions:

1. Heavy metals initial concentrations in acid-base wastewater of electroplating production subjected to tertiary treatment after its neutralization to pH values corresponding to the minimum solubility of metal hydroxides, with account of the discrepancy between the optimal pH intervals, are 0.002–2.8 mg/l.

2. The contact time required to achieve the equilibrium of the treated wastewater and the modified clay sorbent (MC) varied from 60 to 120 minutes for the investigated heavy metals. Considering the time required to reach the MPCs of heavy metals for fresh fishery water bodies, the estimated contact duration of 90 minutes is recommended.

3. The calculated dose of the modified clay sorbent (MC), sufficient for tertiary treatment of pre-neutralized and clarified acid-base wastewater of electroplating production to the MPCs of heavy metals for fresh fishery water bodies, is 1 g/l.

4. The experiments demonstrated that montmorillonite had the best sorption properties among the studied natural materials, non-modified with temperature exposure, ensuring the achievement of MPC for all metals, except aluminum, at doses varying from 0.1 to 0.9 g/l. Peat was most effective in extracting nickel with its estimated dose being 0.1 g/l. Dolomite was the only material that provided aluminum removal at a dose of 1 g/l. For additional treatment of wastewater of electroplating plants from heavy metals, it is proposed to use a sorbent mixture made up of an unmodified mixture of components by the following ratio: montmorillonite: dolomite: peat = 5:4÷10:1 with its dose being 1–1.6 g/l.

5. The researchers put forward two schemes of tertiary treatment of pre-neutralized and clarified acid-base wastewater of electroplating production. The first scheme is based on a continuous treatment process and the second is based on a batch treatment process. They consist in carrying out the sorption process under static conditions using powder sorbents based on local natural materials, followed by separation of the spent sorbent suspension by coagulation, tertiary sedimentation and filtering it with a precoat cartridge filter.

References

1. Sorme, L., Lagerkvist, R. Sources of heavy metals in urban wastewater in Stockholm. Sci. Total Environ. 2002. 298. Pp. 131–145.
2. Fu, F., Wang, Q. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management. 2011. 3(92). Pp. 407–418.
3. Bobade, V., Eshtiagi, N. Heavy Metals Removal from Wastewater by Adsorption Process: A Review. APCChE 2015 Congress Incorporating Chemeca. 2015. 6(6). Pp. 312–317.
4. Kurniawan, T.A. 2003. Physico–chemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering Journal. 118. 2006. Pp. 83–98. DOI: 10.1016/j.cej.2006.01.015
5. Ramazanov, A.Sh., Qasim, E.G. Heavy metals removal from waste water in electroplating industry with the use of montmorillonite clay. Ecology and Industry of Russia. 2015. Vol. 19. Iss. 12. Pp. 11–15. DOI: 10.18412/1816-0395-2015-12-11-15
6. Le, V.G., Vo, T.D.H., Nguyen, B.S., Vu, C.T. Recovery of iron(II) and aluminum(III) from acid mine drainage by sequential selective precipitation and fluidized bed homogeneous crystallization (FBHC). Journal of the Taiwan Institute of Chemical Engineers. 115. 2020. Pp. 135–143. doi.org/10.1016/j.jtice.2020.10.007
7. Barakat, M.A. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011. № 4 (4). Pp. 361–377.
8. Sheng-Fong Lo, Song-Yung Wang, Ming-Jer Tsai, Lang-Dong Lin. Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. Chemical Engineering Research and Design. 2012. 90. Iss. 9. Pp. 1397–1406.
9. Tounsadi, H., Khalidi, A., Farnane, M., Abdennouri, M., Barka, N. Experimental design for the optimization of preparation conditions of highly efficient activated carbon from Glebionis coronaria L. and heavy metals removal ability. Process Safety and Environmental Protection. 2016. 102. Pp. 710–723.
10. Gogoi, H., Leiviskä, T, Heiderscheidt, E, Postila, H., Tanskanen, J. Removal of Metals from Mining Wastewaters by Utilization of Natural and Modified Peat as Sorbent Materials. Mine Water and Circular Economy IMWA. 2017. Pp. 218–225.
11. Kocaoba, S. Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals. Journal of Hazardous Materials. 2007. Vol.147. Pp. 488–496. DOI: 10.1016/j.jhazmat.2007.01.037
12. Shan-Shan Li, Yi-Li Song, Hua-Rong Yang, Qing-Da An., Zuo-Yi Xiao, Shang-Ru Zhai, Carboxymethyl cellulose-based cryogels for efficient heavy metal capture. Aluminum-mediated assembly process and sorption mechanism. International Journal of Biological Macromolecules. 2020. 164. Pp. 3275–3286.
13. O'Connell, D.W., Birkinshaw, C., O'Dwyer, T.F. Heavy metal adsorbents prepared from the modification of cellulose: a review. Bioresource Technology. 2008. 99 (15). Pp. 6709–6724. https://doi.org/10.1016/j.biortech.2008.01.036
14. Vatin, N.I., Chechevichkin, V.N., Chechevichkin, A.V., Shilova, E.S. Application of clinoptilolite zeolites for natural water purification. Civil Engineering. 2013. No. 2. Pp. 81–88.
15. Aziz, H.A., Adlan, M.N., Ariffin, K.S. Heavy metals [Cd, Pb, Zn, Ni, Cu and Cr (III)] removal from water in Malaysia: Post treatment by high quality limestone. Bioresource Technology. 2008. 99(6). Pp. 1578–1583. DOI: 10.1016/j.biortech.2007.04.007
16. Erdem, E., Karapinar, N., Donat, R. The removal of heavy metal cations by natural zeolites. Journal of Colloid and Interface Science. 2004. 280. Pp. 309–314. DOI: 10.1016/j.jcis.2004.08.028
17. Chen, M., Nong, S., Zhao, Y., Sohail Riaz, M., Xiao, Y., Molokeev, M. S., Huang, F. Renewable P-type zeolite for superior absorption of heavy metals: Isotherms, kinetics, and mechanism. Science of The Total Environment. 2020.726. Pp. 138535. DOI: 10.1016/j.scitotenv.2020.138535
18. Shvetsov, V.N., Morozova, K.M. Extraction of heavy metal ions from biologically treated municipal wastewater. Water Supply and Sanitary Engineering. 2012. 7. Pp. 59–63.
19. Kashifuddin, M. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal. 2017. 308. Pp. 438–462. https://doi.org/10.1016/j.ce j.2016.09.029
20. Zacaroni, L.M., Magriotis, Z.M., Cardoso, Md-G., Santiago, W.D. et al. Natural clay and commercial activated charcoal: properties and application for the removal of copper from cachaça. Food Control. 2015. 47. Pp. 536–544. https://doi.org/10.1016/j.foodcont.2014.07.035
21. Bentahar, Y., Hurel, C, Draoui, K., Khairoun, S., Marmier, N. Adsorptive properties of Moroccan clays for the removal of arsenic(V) from aqueous solution. Applied Clay Science. 2016. 119. Pp. 385–392. https://doi.org/10.1016/j.clay.2015.11.008
22. Alemayehu, D.D., Singh, S.K., Tessema, D.A. Assessment of the adsorption capacities of fired clay soils from JIMMA (Ethiopia) for the removal of Cr (VI) from aqueous solution. Universal Journal of Environmental Research and Technology. 2012. 2 (5). Pp. 411–420.
23. Abollinoa, O., Acetob, M., Malandrinoa, M., Sarzaninia, C., Mentastia, E. Adsorption of heavy metals on Na-montmorillonite. Effect of ph and organic substances. Water Research. 2003. 37. Pp 1619–1627. DOI: 10.1016/S0043-1354(02)00524-9

24. Bhattacharyya, K.G., Gupta, S.S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Advances in Colloid and Interface Science. 2008. 140 (2). Pp. 114–131. DOI: 10.1016/j.cis.2007.12.008
25. Churchman, G.J., Gates, W.P., Theng, B.K.G., Yuan, G., Bergaya, F., Theng, B.K.G. Lagaly, G. (Eds.). Clays and Clay Minerals for Pollution Control. Development in Clay Science. Vol. 1. Elsevier Press. 2006.
26. Srinivasan, R. Advances in Application of Natural Clay and Its Composites in Removal of Biological, Organic, and Inorganic Contaminants from drinkingwater. Hindawi Publishing Corporation Advances in Materials Science and Engineering. 2011. Article ID 872531, 17 p. DOI: 10.1155/2011/872531
27. Abdugaffarova, K.K., Dorogov, M.V., Vikarchuk, A. A. New sorption materials on the basis of aluminosilicates for wastewater treatment. Nano Hybrids and Composites. 2017. 13. Pp. 190–196.
28. El-Maghrabi, H.H., Mikhail S. Removal of heavy metals via adsorption using natural clay material. Journal of Environment and Earth Science. 2014. 4 (19).
29. Stepanov, S.V., Panfilova, O.N., Abdugaffarova K.K. Post-treatment of wastewater from heavy metal ions with a new sorbent based on modified clays. Water Supply and Sanitary Engineering. 2018. 1. Pp. 46–50.
30. Stepanov, S., Panfilova, O.N. Removal of heavy metal ions with clay-based sorbent. IOP Conference Series: Earth and Environmental Science. 2019. 272. DOI: 10.1088/1755-1315/272/2/022248
31. Stepanov, S.V., Panfilova, O.N., Abdugaffarova, K.K. Physico-chemical properties of the new sorbent on the basis of sand. Urban Construction and Architecture. 2019. No. 1. Pp. 52–56. DOI: 10.17673/Vestnik.2019.01.9
32. Li X., Li H., Yang G. Electric fields within clay materials: How to affect the adsorption of metal ions. Journal of Colloid and Interface Science. 2017. (501). Pp. 54–59. DOI: 10.1016/j.jcis.2017.04.040

Information about authors:

Sergey Stepanov, *Sc.D. in Technical Science*
ORCID: https://orcid.org/0000-0002-9139-680X
E-mail: stepanovsv3@yandex.ru

Alexander Strelkov, *Sc.D. in Technical Science*
ORCID: https://orcid.org/0000-0002-0419-4231
E-mail: a19400209@yandex.ru

Olga Panfilova,
ORCID: https://orcid.org/0000-0002-1383-1271
E-mail: samoliasgsy@yandex.ru

Received 23.12.2020. Approved after reviewing 12.07.2021. Accepted 13.07.2021.