

Sorption of Heavy Metal Ions by Composite Materials Based on Polycarboxylic Acids and Bentonite Clay

Sh.N. Zhumagaliyeva, R.S. Iminova*, G.Zh. Kairalapova,
B.M. Kudaybergenova, Zh.A. Abilov

Al-Farabi Kazakh National University, 71, Al-Farabi Ave., Almaty, Kazakhstan

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Abstract

The paper shows the study results of sorption capacities of composite gels based on polyacrylic and polymethacrylic acids with bentonite clay as the mineral filler concerning heavy metal ions (Pb^{+2} , Cu^{+2} , Ni^{+2} , Zn^{+2} , Fe^{+2} , Cd^{+2}). The binding of metal ions to gels occurs through the formation of electrostatic bonds between the charged surface of bentonite clay and ionogenic functional groups of polymers in the composition, as well as the coordination bonds between metal ions and unshared pairs of oxygen electrons in the functional groups of polymers. The gel swelling degree decreases in metal solutions with increasing metals concentration and the content of BC in the composite. The sorption and desorption of heavy metal ions from the polymer-clay composites from model solutions and samples of industrial wastewater from the Kazakhstani metallurgical plants were evaluated. The adjustment of the pH, the temperature of the medium and the clay content in the composite leads to increasing the degree of sorption and achieving regeneration of the used composite gels in certain media. The data obtained testify to the prospects of using these composites as effective sorbents of heavy metals from industrial wastewaters expanding the range of composite materials for wastewater treatment.

1. Introduction

The bentonite clay of the Manyrak deposit of the East Kazakhstan region is among the most demanded and rich mineral deposits. It has been actively used for many years in various areas of human life (medicine, construction, oil industry, purification facilities, etc.). The use of domestic clay as an object of research in the creation of various ion-exchange materials, composite polymer systems with high performance characteristics, for example, for group extraction of non-ferrous metal ions [1], as sorbents and carriers of surfactants, prolonged forms of drugs, remains a topical task in our days and in the country.

Bentonite is commonly referred to as clay containing at least 70% of the mineral of the montmorillonite group. Montmorillonite is a highly dispersed layered aluminosilicate of structural

type 2:1, in which, due to non-stoichiometric substitution of crystal lattice cations, an excess negative charge is established to compensate cations located in the interlayer space [2]. The features of the crystal structure of montmorillonite predetermine the specific properties of bentonite clays such as adsorptive, astringent, colloidal and other properties. These clay minerals can swell due to an increase in the space between the basal layers in which the adsorbed ions or molecules are placed. In montmorillonite, a part of silicon ions (Si^{+4}) in tetrahedral positions is replaced by aluminum ions (Al^{+3}), and some of the aluminum ions in octahedral positions are substituted by divalent ions of magnesium (Mg^{+2}) and iron (Fe^{+2}). Each elementary unit of layered silicates of structural type 2:1 has a thickness of 0.94 nm, and their specific surface area 660 m^2/g [3]. The elementary units are interconnected by weak van der Waals forces. Therefore, it is possible to place large ions between the layers forming the columns, and thus generating a system of voids, where various small molecules

*Corresponding author.
E-mail: iminova123riz@gmail.com

can be placed. The pore sizes formed as a result of the stratification process lie in the region of several tenths of a nanometer [4].

Natural bentonite is widely available and can be used directly for cleaning the polluted water from heavy metals, but it is possible to increase its sorption capacity by modifying its chemical composition. This can be achieved, for example, by reducing the content of silicon dioxide during the dissolution of free silica in an alkaline medium, the amount of aluminum, iron, alkali and alkaline earth metal oxides in the samples increases. The replacement of alkaline earth metals in the ion exchange complex with sodium ions leads to an increase in the ion exchange capacity of the clay from 75 to 120 $\mu\text{g}/100\text{ g}$ clay [5]. In recent years, some studies have been devoted to developing methods for modifying clay by polymers, to increase their adsorption capacity to remove contaminants from drinking water [6]. Thus, the authors of [7] found that layered aluminosilicate could be relatively easily modified by introducing hydrogel chains of polyacrylic acid or polyacrylamide into the clay gallery using the intercalation method. Successful intercalation was confirmed by the powder X-ray diffraction method, as well as by IR spectroscopy. This modification leads to a significant increase in the sorption capacity of the material for Fe^{+3} (III) ions, which suggests that the developed composite materials can be used as sorbents of pollutants in aqueous solutions. Although natural materials have a much lower exchange capacity than expensive synthetic polymer cation exchangers, they offer a cost-effective alternative. The availability of numerous bentonite deposits in the Republic of Kazakhstan is suitable for the uptake of heavy metal ions. Indeed, their extraction does not require large costs, so that they can be used as local, readily available, raw materials in the technology of sorbent production for wastewater treatment aimed at heavy metals removal.

In this regard, the present study describes an attempt to prepare polymer-clay composite gels based on bentonite clay from Manyrak field and ionic polymers – polyacrylic and polymethacrylic acids with improved sorption properties for heavy metal ions removal; the factors affecting the sorption properties of different compositions investigated have been identified.

2. Experimental part

To produce polymer-clay composite gels,

domestic bentonite clay of the Manyrak deposit (East Kazakhstan region) and monomers – acrylic and methacrylic acids, were used.

Acrylic acid (AA) from Aldrich Chemistry was subjected to a two-stage vacuum distillation under a nitrogen atmosphere, and the fraction with the boiling point of 305 K/10 mm Hg was collected. Its refraction index, $n_d^{20} = 1.4220$.

Methacrylic acid (MAA) from Aldrich Chemistry was subjected to a two-stage vacuum distillation under reduced pressure, and the fraction with the boiling point of 331 K/10 mm Hg was collected. Its refraction index, $n_d^{20} = 1.4320$.

N, N'-methylene-bis-acrylamide (MBAA) of the general formula $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$, and molecular weight of 154.2 (intended for electrophoresis), from Acros Organics, Belgium, was used as a cross-linking agent without additional purification.

Dinitrile of azo-bis-isobutyric acid (AIBN), which was recrystallized several times, was used as an initiator.

The following salts purchased from Sigma-Aldrich were used in the work: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – nickel (II) chloride hexahydrate ($M = 237.69\text{ g/mol}$), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ – zinc sulphate heptahydrate ($M = 287.5\text{ g/mol}$), $\text{Pb}(\text{NO}_3)_2$ – lead nitrate (II) ($M = 331.2\text{ g/mol}$), $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ – cadmium bromide tetrahydrate ($M = 344.2\text{ g/mol}$), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – copper (II) sulphate pentahydrate ($M = 249.55\text{ g/mol}$), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ – iron (III) chloride hexahydrate ($M = 269\text{ g/mol}$) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ iron (II) hydrogen sulfate heptahydrate ($M = 277\text{ g/mol}$).

Cleaning of bentonite clay. The bentonite clay was cleaned using the D.P. Salo method, by repeated washing with distilled water [8]. The chemical composition of the purified bentonite clay determined by the diffraction spectral analysis method (using diffractometer DFS-13) includes oxides: SiO_2 (60%), Al_2O_3 (9%), Fe_2O_3 , CaO and K_2O (0.5%), MgO (1%), Na_2O (0.8%), H_2O (7%) and corresponds to aluminosilicates.

Based on the results of the X-ray diffraction data (DRON-4-07) three phases were detected in the bentonite clay: intensive: α -quartz SiO_2 , predominant montmorillonite $\text{Al}[\text{OH}]_2\{\text{Si}_4\text{O}_{10}\}^*\text{mH}_2\text{O}$ and an amorphous phase (Table 1).

Synthesis of homopolymeric gels of polyacrylic acids (PAA G, PMAA G) and their composite gels with bentonite clay (BC-PAA, BC-PMAA). The synthesis was carried out by radical polymerization with preliminary intercalation of clay particles (the intercalation time is generally 24 h) in the monomer solution, as described previously [9, 10].

Table 1
The X-ray analysis of bentonite clay

Clay samples	Phase			
	Intensity (a.u.)		Amorphous phase	
	SiO ₂ 3.3θ (degree)	Montmorillonite 4.6θ (degree)		
Natural	62.0	92.0	3.50 θ	2.20 θ
Cleaned	35.0	130.0	3.63 θ	2.20 θ

The content of the mineral component was varied within the range of 1–5 wt.% of the amount of the monomer.

The content, physicochemical characteristics and nature of the interaction of metal ions in the various systems were determined by the equilibrium swelling and confirmed by FTIR spectroscopy, using a Fourier spectrometer “FTIR Satellite” from Mattson (USA) in KBr pellet. The morphological structure of the composite gels was examined using photographs taken with an optical microscope and topographic images on an atomic force microscope Ntegra THERMA (Russia). A more detailed discussion of the results of the investigation and the analysis of the synthesis, morphology, composition, and swelling characteristics of the obtained gels, was published in [9].

AAS Shimadzu 6200 atomic-adsorption spectrometer (National Nanotechnological Laboratory of the Open Type, al-Farabi KazNU, Almaty, Kazakhstan) was used for the quantitative determination of metal ions in solution. The concentration of metal salts was varied within 10–100 µg/ml.

The possibility of extracting heavy metals from wastewater and natural waters by the synthesized composite materials was studied using individual and mixed model aqueous solutions of salts of the corresponding metals. The sorption of ions Ni²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Cu²⁺, Fe²⁺ was studied in batch conditions. The degree of sorption, A%, was calculated using the equation:

$$A = (C_{\text{initial}} - C_{\text{final}}) \cdot 100 / C_{\text{initial}},$$

where C_{initial} is the initial concentration of metal ions and C_{final} is the residual concentration of metal ions after sorption in the aqueous phase.

To verify the possibility of regenerating the used sorbent, the desorption parameters of the obtained compositions were investigated. The degree of desorption, W% was calculated using the equation:

$$W = (n_0/n) \cdot 100\%,$$

where W is the yield of Me²⁺ from the gel, n_0 is the concentration of Me²⁺ in the solution at time t, and n is the initial concentration of Me²⁺ in the gel.

The following samples of wastewater from plants in Kazakhstan were used: No. 1 (pH = 9–11), No. 2 (pH = 11) and No. 3 (pH = 4–5).

3. Result and discussion

The results relative to the investigation on the influence of various factors [9, 10] on the swelling capacities, as well as IR spectra data of the composites, allow us to conclude that the formation of composite gels is due to hydrogen bonds between hydroxyl groups on the surface of bentonite clay and undissociated carboxyl groups of polyacids. In the stabilization of BC-polymer composites, hydrophobic interactions of hydrocarbon chains play an important role, which is more pronounced in the case of composites based on a more hydrophobic PMAA [10].

In the sorption process for the immobilization of heavy metal ions, as a rule, the surface of the sorbent undergoes some deformation and changes in its morphological structure. This is due to the simultaneous swelling of the gels in the metal salt solution and the sorption of the corresponding metal ions from the solution and their subsequent drying. In this regard, with the help of an atomic force microscope, the samples of the gels and their complexes with metal ions (Pb²⁺, Ni²⁺, Zn²⁺, Fe²⁺) were studied. Surface investigations in 2D and 3D formats as well as roughness spectra show that the morphological structure of the composite depends on the nature of the original components (Fig. 1). The composites with metal ions immobilized by sorption have a certain smoothing of the polymer surface and a decrease in the intensity of the peaks characteristic of bentonite clay particles. The gel samples swollen in solutions of metal salts were studied using an optical microscope by removing the gel surface and passing a beam of light through the entire volume of the gel sample (Fig. 2).

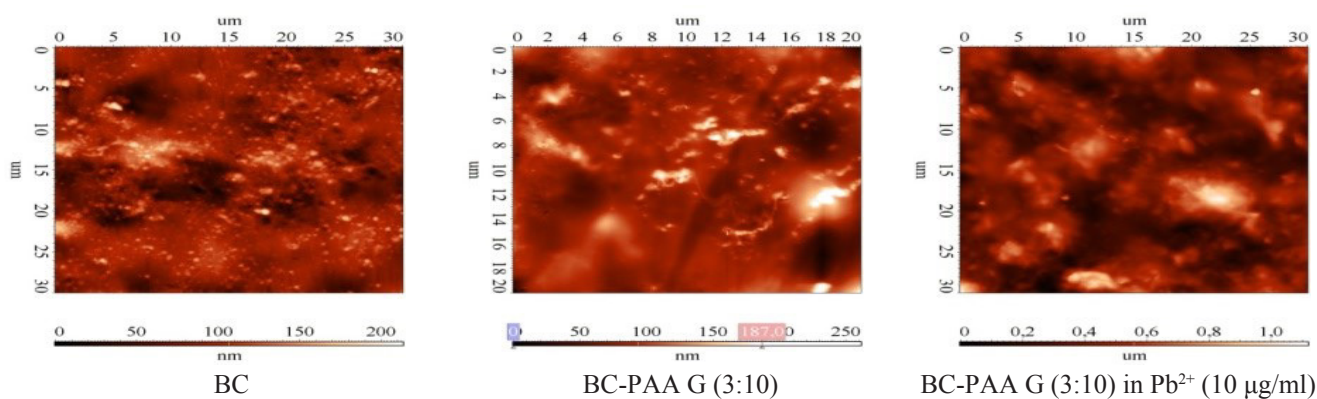


Fig. 1. The atomic force microscopic images in 2D Image format.

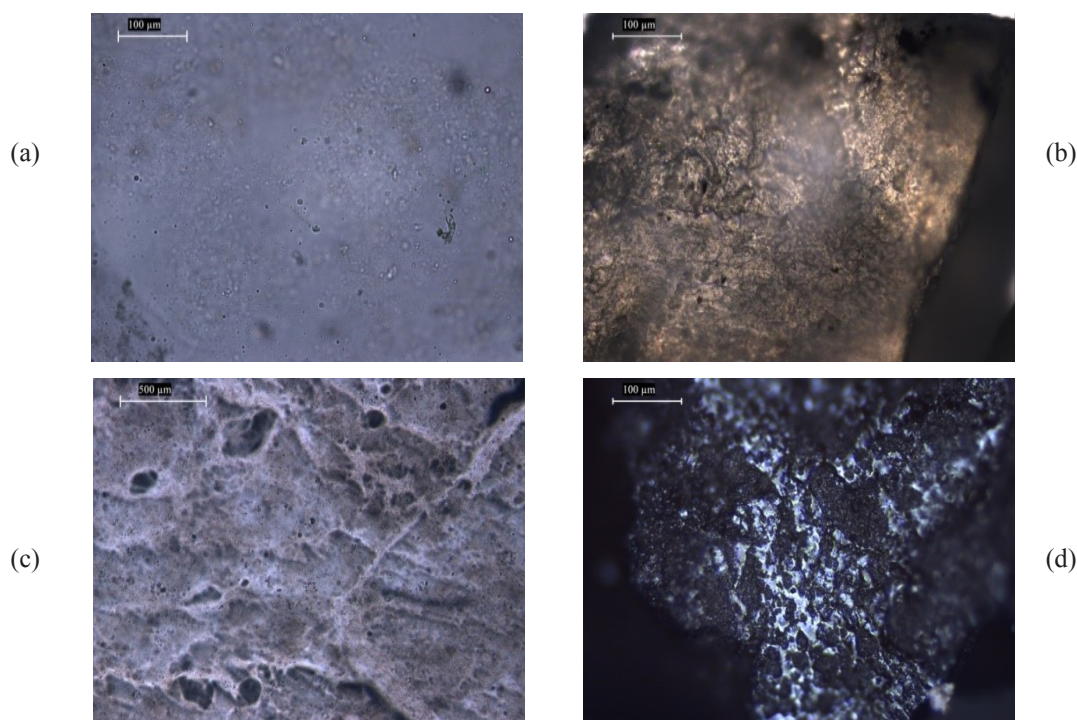


Fig. 2. Optical micrographs of BC-PAA gel (5:10) in 100 µg/ml solutions of metal ions: (a) – Ni²⁺; (b) – Fe²⁺; (c) – Pb²⁺; (d) – Zn²⁺.

As shown in these photographs, in the samples of gels swollen in solutions of metals, the characteristic fluorescence of metal ions originated under the influence of the external light beam, appeared on the gel surface, which differs markedly in comparison with the samples swollen in water.

A comparative analysis of the gel swelling kinetics curves in water and metal solutions (Fig. 3) confirms the presence of electrostatic bonding of metal ions with a negatively charged polymer-clay matrix in the composites by the presence of active sites, containing -COOH, -OH, and -SiO₃ groups. In metal solutions, there is significant compression of the gels and a decrease in the swelling degree as compared to swelling in water. The study results of the sorption capacity of composite gels for heavy

metal ions obtained with an atomic-adsorption microscope showed that the equilibrium sorption values are established after two days. In addition, depending on various factors, the numerical value of sorption capacity is near 70–94% (expressed in moles, the sorption values are in the range of 20–45·10⁻⁴ mol/g) (Fig. 4). For all the metals studied, sorption increases with the increasing pH of the medium. The observation of the coloring of the sorbent layer by different colors depending on the metal ion, shows blue (Cu²⁺), pink (Co²⁺), or greenish (Ni²⁺) as described in [10], which indirectly confirms the sorption of metals by the mechanism of complexation with the functional groups of the composition. The color of the sorbent layer becomes more intense as the pH rises.

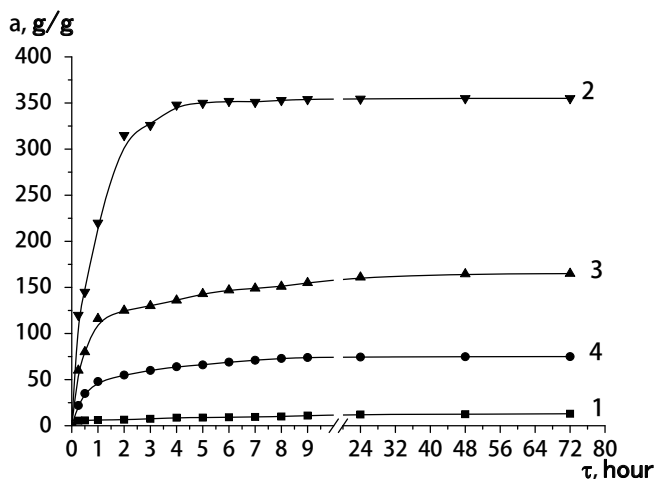


Fig. 3. Kinetics of swelling of composite gels and their individual components: $t = 23\text{ }^{\circ}\text{C}$; $[\text{MBAA}] = 0.5\%$; $[\text{ABIN}] = 0.5\%$; BC (1), PAA G (2), BC-PAA G (3:10) (3, 4) (1, 2, 3) – in water, (4) – in 10 mcg/ml of solution Pb^{2+} .

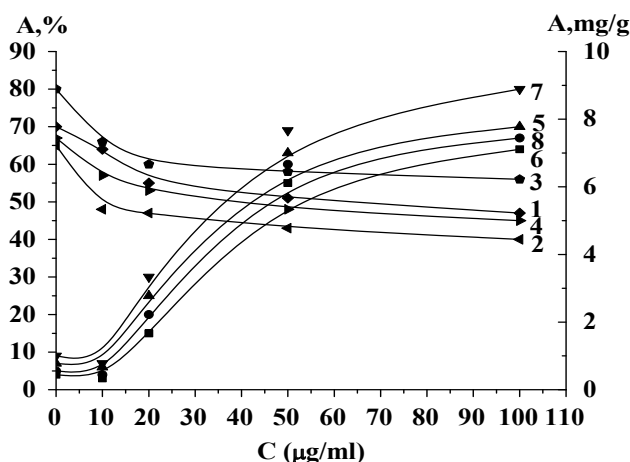


Fig. 4. Sorption capacity of composite BC-polymer gels (3:10) in metal ion solutions of different concentrations: $\tau = 6\text{ h}$; $[\text{MBAA}] = 0.5\%$; $[\text{AIBN}] = 0.5\%$; 1–4%; 5–8 mcg/g; BC-PAA G – (1, 3, 5, 7); BC-PMAA G – (2, 4, 6, 8); 1, 2, 5, 6 – solution $[\text{Cd}^{2+}]$; 3, 4, 7, 8 – solution $[\text{Zn}^{2+}]$.

The maximum sorption of the sorbent occurs in such a pH range when the functional groups pass into a coordinately active form, and precipitation of hydroxides and basic metal salts is still impossible. In the case of Cu^{2+} and Pb^{2+} ions, the maximum recovery occurs at pH 7–8, and for Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} is reached even at pH 4–5 [11]. In the case of BC-PAA compositions likely, the complexation with oxygen-containing groups in the polyacrylate-clay matrix of the sorbent contributes to the total sorption capacity for these ions.

The radius, coordination number and electro-negativity of the metal ions also significantly influence the sorption degree. With the same charge and

coordination number, metal sorption corresponds to the following series in terms of the radius size and the atomic mass: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{2+}$. The decrease in sorption capacity in a neutral medium (pH = 4–6) corresponds to the following series: $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ [12, 13] The sorption capacity of PMAA-based gels are lower, which is attributed to their lower swelling capacity of PMAA [14] and a higher degree of ionization of the PAA, therefore the ability of the latter to electrostatically bind the metal ions is higher. Polycarboxylic acids make a significant contribution to the sorption capacity of composites, and the presence of BC in the composite additionally increases the degree of metal ions sorption. Montmorillonite can adsorb heavy metals using two different mechanisms, which include cation exchange in the interlayer as a result of interaction between ions and a negative constant charge, and, secondly, the formation of the inner sphere of complexes with the help of the system Si-O- and -Al-O- groups on edge clay particles [5]. With an increase in the concentration of metal ions in solution (Fig. 4), the equilibrium degree of swelling and the percentage degree of sorption reduces. Hence, the degree of swelling and sorption capacity of the composite gel is in a directly proportional relationship.

Wastewater can contain more than one type of metal ions [15]. In Table 2 the results of the study of metal ions sorption from individual solutions and a mixture of various metal ions at the maximum allowable concentration (MAC) are shown. On average, the quantitative values of sorption are located between 40–99%, depending on the method of obtaining the composite and its ratios. To determine the selectivity of metal ions sorption by composites it was prepared a complex solution of Zn^{2+} , Ni^{2+} , Fe^{2+} , and Pb^{2+} ions (model solution). A rather high recovery (on average 80–89%) of all metal ions occurs on the gels from this complex solution.

The results suggest that fairly homogeneous organo-inorganic composite materials with a high yield of gel fraction swelling ability have a good sorption capacity, especially when using a sorbent BC-PCA G (5:10) with intercalation. In general, the experimental data on the sorption-desorption characteristics of the proposed sorbents for Ni^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} show that the use of the intercalation process increases the sorption capacity of composite gels. The degree of sorption of metal ions is represented by the following series: $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

Table 2
Degree of sorption of metal ions on composite gels in a solution with the maximum allowable concentration (MAC) of metal

Metal ions		Pb ²⁺ , %		Zn ²⁺ , %		Ni ²⁺ , %		Fe ²⁺ , %	
		Individual	Mixture	Individual	Mixture	Individual	Mixture	Individual	Mixture
BC-PAA G(5:10)	Intercalated	99	58	76	52	81	40	38	42
	Without intercalation	98	54	67	40	57	42	40	43
BC-PMAAG(5:10)	Intercalated	93	55	85	44	77	40	52	44
	Without intercalation	91	50	63	47	53	38	51	37

[MBAA] = 0.5 %; [AIBN] = 0.5%; t = 24 h; T = 23 °C; Me²⁺ = MAC, mg/dm³
Composition of the metal mixture: Ni²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Cu²⁺, Fe³⁺, Fe²⁺

The degree of sorption increases with the content of BC in the composite. The composites obtained without intercalation showed a higher sorption capacity compared to the intercalated composites due to the better swelling ability of the former. Comparing BC-PAA and BC-PMAA, better swelling and sorbing ability of the PAA-based composite should be noted versus the more hydrophobic BC-PMAA composite, which is related to the greater ability of PAA to ionize and bind metal ions. In addition, the radius, coordination number and atomic mass of metals affect the degree of sorption.

The desorption results (Table 3) indicate the possibility of subsequent regeneration of the proposed sorbents for their reuse. The effective desorption of metal ions from gels is favored by certain environmental conditions such as the creation of a weakly alkaline medium and heating.

In order to use the obtained composites as sorbents for purification of industrial wastewater from heavy metal ions, sorption-desorption characteristics of composites with respect to heavy metal ions were investigated with samples of sewage water from several industrial plants in Kazakhstan (e.g.

in cities Zhezkazgan, Aktau and Pavlodar). Each industrial wastewater sample contained a mixture of heavy and non-ferrous metal ions, had a certain pH environment, color and mechanical impurities. The mechanical impurities were removed by filtration and centrifugation of the sample. The chemical composition of wastewater samples is shown in Table 4. The sewage of Plant No. 1 has an alkaline medium with pH 9–11. The parameters of ion sorption by gels were high, due to their good swelling ability. In addition to the metal ions listed in the table, there were also small amounts of other metal ions of Al, Mg, Ca, K, and Na in this water. Sewage No. 3 has an acidic medium with pH = 5. Gels collapsed in this water, so there was a low degree of swelling of the gels and a low degree of sorption. In addition to the metal ions listed in the table, metal ions of Al, Mo, Sr, Ca, and Cr were also present in small amounts in the sewage water of the metallurgical plant. The sewage of plant No. 2 has an alkaline medium with pH = 11. In addition to the metals listed in the table, there are no other metals in its composition. There were a large swelling and sorbing ability of gels in this sample.

Table 3
Desorption of metal ions from composite gels

Composite	BC-PAA G		BC-PMAA G		
	Metal ion	n _g , µg/ml	W, %	n _g , µg/ml	W, %
	Ni ²⁺	0.125	60	0.116	82
	Fe ²⁺	0.108	42	0.151	55
	Pb ²⁺	0.118	30	0.115	28
	Zn ²⁺	0.135	26	0.121	53
	Cd ²⁺	0.114	28	0.106	31

BC-PCA G (5:10), [MBAA] = 0.5 %; [AIBN] = 0.5 %; Time of desorption 6 h; temperature 60 °C; pH = 8;
n_g – the number of metal ions in the composition, µg/ml; W – the desorption percentage, %

Table 4
Chemical composition of sewage water of different plants in Kazakhstan

Me ²⁺ , mg/l	Pb ²⁺	Cu ²⁺	Ni ²⁺	Fe ²⁺	Zn ²⁺	Mn ²⁺	Cd ²⁺
%, Plant #1	1.89	1.69	1.12	2.12	2.47	3.15	1.02
%, Plant #2	1.35	0.98	1.26	1.05	1.13	7.08	1.38
%, Plant #3	0.86	1.22	0.5	0.68	2.21	1.41	2.36

Composite gels based on BC and PAA (5:10) according to the results of the studies have the best sorption and swelling characteristics. Sorption was carried out in a batch mode, with periodical mixing of the system, and selecting a sample for analysis with atomic adsorption spectroscopy.

The investigated wastewater samples contained mainly a mixture of different non-ferrous and heavy metals exceeding the MAC (Table 5) and, depending on the operating conditions of industrial plants, they had aggressive acidic or alkaline media. The prevalence of the degree of sorption of metal, as was established earlier for model solutions of a mixture of metal ions, de-

pends on the radius and coordination number of the individual metal. The sorption capacity of sorbents with respect to equally charged metal ions depends on their ionic radius [16, 17]. Ions with a large radius are sorbed in larger amounts since they are less prone to the formation of a hydrated shell reducing the force of electrostatic attraction. Table 6 shows the atomic characteristics of metal cations. Since lead has a larger ionic radius (0.132 nm) than a nickel (0.069 nm), it should be sorbed better on more polar sorbents, which agrees well with the experimental data. The obtained data of quantitative values of sorption correspond with the swelling data.

Table 5
Atomic characteristics of metals and MAC of heavy metal ions in industrial wastewater

Metal	Atomic mass	Atomic radius, nm	Ionic radius, nm	Coordination number	MAC, mg/l
Lead	207.190	0.174	0.132	4	0.03
Copper	63.546	0.128	0.098	4 and 6	0.001
Nickel	58.690	0.124	0.069	4	0.01
Iron (II)	55.847	0.126	0.080	4 and 6	0.1
Iron (III)	55.847	0.126	0.067	4 and 6	0.1
Zinc	65.390	0.139	0.060	4	0.01
Cadmium	112.410	0.146	0.092	4	0.005

Table 6
Desorption of metal ions from composite gels

Sewage samples of plants	Ions of metals	Cu ²⁺	Mn ²⁺	Pb ²⁺	Fe ²⁺	Ni ²⁺	Cd ²⁺	Zn ²⁺	
#1	n _g , µg/ml	BC-PAA G	0.108	0.135	0.105	0.145	0.129	0.130	0.103
	W, %	BC-PMAA G	46	53	42	56	50	48	41
#2	n _g , µg/ml	BC-PAA G	0.105	0.124	0.108	0.118	0.169	0.145	0.172
	W, %	BC-PMAA G	46	51	49	37	52	48	38
#3	n _g , µg/ml	BC-PAA G	0.116	0.138	0.145	0.196	0.125	0.148	0.157
	W, %	BC-PMAA G	49	38	43	48	54	48	55

BC-PCAG (5:10), [MBAA] = 0.5 %; [AIBN] = 0.5 %; t = 6 h; T = 60 °C; pH = 8;
n_g – the amount of metal ions in the composite gel, µg/ml; W – desorption degree, %

The difference in sorption between metals depends on their coordination number, ionic radius, atomic mass and electronegativity. That is, with decreasing ionic radius, metals can be arranged in the following order: $Pb^{+2} > Cu^{+2} > Cd^{+2} > Fe^{+2} > Ni^{+2} > Zn^{+2} > Fe^{+3}$. In our case, the amount of sorption by the composite gel decreases in the order $Pb^{+2} > Zn^{+2} > Cd^{+2} > Ni^{+2} > Mn^{+2} > Fe^{+2} > Fe^{+3} > Cu^{+2}$. In [18], experimental results showed that the order of the sorption capacity of the composite for metal ions follows the order: $Hg^{+2} > Pb^{+2} > Cd^{+2}$. It was also established in [19, 20] that the sorption of metals with increasing ionic radius increases, which also confirms the results we have obtained.

The swelling capacity of the investigated composites strongly depends on the pH and the ionic strength of the medium: the influence of ionic strength and acidic environment significantly reduces swelling of gels, and an alkaline environment, it increases greatly. Therefore, the swelling behavior of BC-polymer gel sorbents studied in industrial wastewater samples gives a prerequisite for a certain degree of sorption. Therefore, the immersing of BC-polymer sorbents in samples of sewage No. 3, led to a significant gel contraction, which prevented the sorption of ions. In the other two cases, the alkaline water environment promoted good swelling and, accordingly, the recovery of metals from it.

Sorption of heavy metal ions from three samples of industrial sewage plants by BC-PAA sorbent with the ratio (5:10) is presented in the form of a diagram in Fig. 5. A comparative analysis of the data shows that, on average, the total sorption of metals by the BC-PAA G composite (5:10) from the plant sample No. 1 per day was 43–66%, plant #2 – 46–58%, plant #3 – 34–55%. The BC-PMAA composites with the same composition show a lower sorption capacity. Given that the three samples of wastewater are a mixture of different metal ions with different concentrations, it is difficult to follow a certain pattern and compare the degree of sorption of metals separately. In general, the sorption of metals includes a complex mechanism of ion exchange, chelation of metals with various anionic functional groups, the adsorption of physical forces and the capture of ions in the internal spaces of the structural network of the adsorbent [5].

Desorption characteristics of the compositions for the metal ions have been investigated by atomic absorption spectroscopy. In Fig. 6 and Table 6 the data of desorption of metal ions from the BC-PCA compositions (5:10) are shown; they agree

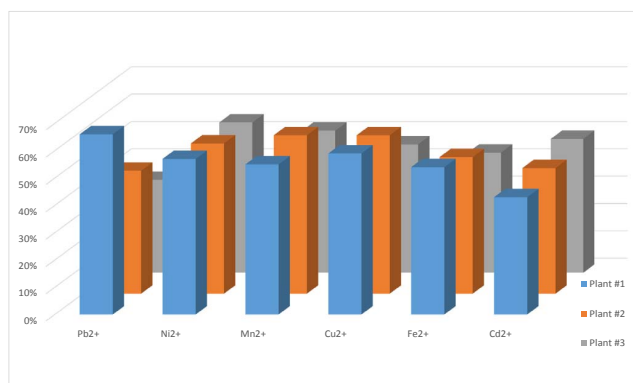


Fig. 5. Sorption of metal ions from wastewater by BC-PAA composite (5:10).

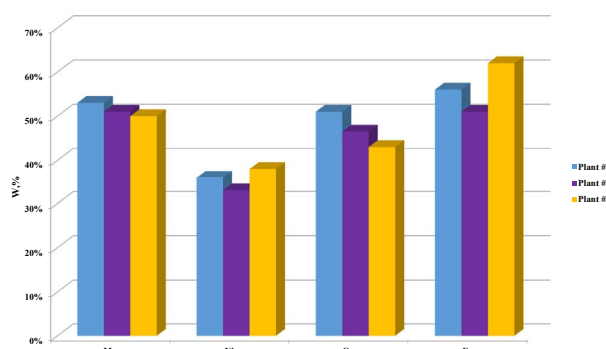


Fig. 6. Diagram of the degree of desorption of metal ions from the BC-PAA gel (5:10) containing a mixture of metal ions sorbed from sewage plants.

with the sorption data. The results of the desorption studies from gels in water under normal conditions show the degree of release of Me^{+2} reaching 4–12%. Therefore, it was expedient to study the degree of extraction of metal ions from gels by changing the conditions of the release medium. In some studies, the most optimal condition has been established, in which maximum desorption of metal ions from the sorbents under study was: $t = 60\text{ }^{\circ}\text{C}$ and $\text{pH} = 8$ ($W \sim 45\text{--}70\%$) (in a highly acidic medium, complete desorption of metal ions is possible).

4. Conclusions

The regularities of binding of polymer-clay composite gels BC-PCA with ions of heavy metals (Pb^{+2} , Cu^{+2} , Ni^{+2} , Zn^{+2} , Fe^{+2} , Cd^{+2}) are established. The binding of metal ions to gels occurs due to the formation of electrostatic bonds between the charged surface of bentonite clay and the coordination bonds between metal ions and unshared pairs of oxygen electrons in the functional groups of polymers. The degree of swelling decreases with increasing the concentration of metals and the content of BC in the composite.

The sorption ability of the obtained polymer-clay composites with respect to heavy metal ions from model solutions and from industrial sewage samples of Kazakhstan metallurgical plants have been estimated. By adjusting the pH, the temperature of the medium and the clay content in the composite, it is possible to increase the degree of sorption and achieve a higher degree of regeneration of the used composite gels in certain media. The obtained data testify to the prospects of using these composites as effective sorbents of metals. Thus, the resulting composite gels based on polymers and BC expand the range of composite materials and are able to use sorbents for wastewater treatment.

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