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Article

Comparative Study of the Physico-Chemical Properties of Sorbents Based on Natural Bentonites Modified with Iron (III) and Aluminium (III) Polyhydroxocations

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Abstract: A comparative study of the physicochemical properties of natural bentonite clays of Pogodayevo (Republic of Kazakhstan, mod.1) and Dash-Salakhli (Republic of Azerbaijan, mod.2) deposits and modification of the bentonite clay with polyhydroxocations of iron (III) and aluminium (III). It was established that the modification of natural bentonites using polyhydroxocations of iron (III) and aluminium (III) by the method of "co-precipitation" leads to a change in their chemical composition, structural and sorption properties. The results showed that hydroxy-aluminum cations ($[Al_3O_4(OH)_{24}(H_2O)_{12}]^{7+}$) and poly-hydroxyl-Fe or polyoxo-Fe were intercalated into clay layers, which led to an increase in the values of d_{001} and specific surface areas compared to those of the original bentonite, from 37 to 120 for the Pogodaevo bentonite and from 51 to 172 respectively for bentonite from the Dash-Salakhli deposit. It is shown that modified sorbents based on natural bentonite are finely porous objects with a predominance of pores of 1.5–6.0 nm in size. As a result, there is a significant increase in the specific surface area of sorbents. Modification of bentonite with polyhydroxocations of iron (III) and aluminium (III) by the "co-precipitation" method also leads to an increase in the sorption capacity of the sorbents obtained with respect to nickel (II) cations. Modified bentonites were used for the adsorption of Ni (II) ions from the model solution. Ni (II) was absorbed in a neutral pH solution. The study of equilibrium adsorption showed that the data are in good agreement with the Langmuir isotherm model. The maximum adsorption capacity of the Ni (II) monolayer obtained from the Langmuir equation was 25.0 mg/g (mod. 1_Al_5-c), 18.2 mg/g (mod. 2_Al_5-c) for Al-bentonite and 16.7 mg/g (mod. 1_Fe_5-c), 10.1 (mod. 2_Fe_5-c) for Fe-bentonite. The kinetics of adsorption is considered. The high content of Al-OH anion exchange centres in them determines the higher sorption activity of Al-modified bentonites.

Keywords: bentonite sorbent; sorption of nickel (II) cations; specific surface area; polyhydroxocation; "co-precipitation" method

1. Introduction

Industrial wastewater treatment is currently a critical environmental issue globally [1]. The current waste water treatment plants are not designed for the removal of these pollutants in water. Heavy metals [2] and organic compounds [3] are the most dangerous.

Among all known methods of wastewater treatment, adsorption is one of the most common ways to remove contaminants from water [3]. Adsorption is a simple and effective strategy for

industrial wastewater treatment, as well as an important technology for environmental protection [4].

Currently, there is a significant increase in interest in the creation of new environmentally friendly sorbents based on natural clay materials and aluminosilicates [5]. Clays and composite materials based on them have a higher adsorption capacity than other low-cost adsorbents [6,7]. Because of their high specific surface area, chemical, and mechanical stability, variation in surface and structural characteristics, and low cost, bentonites, montmorillonites, kaolinites, illites, chlorites, and other clay minerals are widely used [8,9]. The lack of effective granulation technologies is a limiting factor in the widespread use of natural sorbents for the purification of drinking water and industrial effluents because clay minerals are susceptible to the peptization effect in aquatic environments.

The development of methods for obtaining semi-synthetic microporous sorbents based on layered natural silicates with an expanding structural cell and the main salts of aluminium, iron (III), titanium, chromium, and other elements, known as pillar clays [10], is a significant achievement in the field of creating new sorption materials. The reaction of substitution of interlayer exchange cations of the initial mineral with oligomeric polyhydroxocation cations is the basis for the production of such sorbents [11,12]. In comparison to synthetic zeolites [8], the advantage of pillar sorbents is their large open microporosity, which improves the kinetics of sorption and catalytic processes, as well as their relative cheapness, which is important for their use in water purification processes [13].

The purpose of this study is to develop sorbents based on bentonites from deposits in Pogodayevo and Dash-Salakhli that have been modified with polyhydroxocations of iron (III) and aluminium (III) cations via the "co-precipitation" method to increase their sorption capacity about metal cations.

2. Materials and Methods

Bentonite clay was obtained from the Pogodayevo deposit (West Kazakhstan region, Republic of Kazakhstan), natural bentonite of the Dash-Salakhli deposit (Azerbaijan) and purified by precipitation in combination with ultrasound treatment and centrifugation. Aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), silver nitrate (AgNO_3 , 98%), and sodium hydroxide (NaOH , 98%) were purchased from Merck. Nickel salt ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 98%) was used for the model solution.

Quantitative analysis of the elemental composition was carried using an energy-dispersive X-ray fluorescence spectrometer EDX-720 (SHIMADZU, Japan) by the method of fundamental parameters. The porous structure of the samples was determined by low-temperature nitrogen adsorption on a high-speed gas sorption analyzer Quantochrome NOVA (USA). The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface area of solid samples. The Barrett-Joyner-Halenda (BJH) method was used to measure the pore volume and determine the pore size distribution. The desorption or adsorption branch of the isotherm in the pressure range 0.967 - 0.4 P/Po is used as initial data for calculations using the BJH method. X-ray diffraction analysis was carried out on a DRON-4 diffractometer using an X-ray tube with a copper anode (Cu-K radiation). For the analysis of diffractograms, the database PCPDFWIN, v. 2.02, 1999, of the International Center for Diffraction Data was used. (JCPDS). The ability of the studied samples to absorb salt anions was determined by constructing sorption isotherms by the method of variable concentrations under statistical conditions. The model solution was a nickel (II) salt solution. Nickel ion (II) was analyzed using atomic absorption spectroscopy (AAS, SHIMADZU-6800).

2.1. Preparation of Fe-bentonite and Al-bentonite

Modification of bentonites was carried out by the method of "co-precipitation" (intercalation, or pillarization) [14]. FeCl_3 , AlCl_3 salts was added to the aqueous suspension of bentonite (the ratio of solid to the liquid phase is 1:10 and the pH of the aqueous extract of the suspension is 8) The amount in which the concentration of iron (aluminum) was bentonite of 5 mmol Me^{3+}/g . The suspension was then sonicated at 22 Hz for 3 minutes [15]. Next, 0.5 M NaOH solution was added to the prepared

suspension ($[\text{OH}^-]/[\text{Me}^{3+}] = 2.23$) and during the day the suspension was subjected to ageing at room temperature. After 24 hours, the resulting modified bentonite was separated from the liquid phase on the Buchner funnel using a vacuum pump, washed with water until a negative reaction to chloride ions, and dried at 80°C. The washed sample was stored in an airtight container and labelled.

Nomenclature

- natural bentonite of the Pogodayevo deposit – mod. 1;
- natural bentonite (mod. 1) modified with iron (III) polyhydroxocations by the "co-precipitation" method (5 mmol $[\text{Fe}^{3+}]$ /g of bentonite) – mod. 1_Fe_5-c;
- natural bentonite (mod. 1) modified with polyhydroxocations of aluminum (III) by the "co-precipitation" method (5 mmol $[\text{Al}^{3+}]$ /g of bentonite): mod. 1_Al_5-c;
- natural bentonite of the Dash-Salakhli deposit – mod. 2;
- natural bentonite (mod. 2) modified with iron (III) polyhydroxocations by the "co-precipitation" method (5 mmol $[\text{Fe}^{3+}]$ /g of bentonite) – mod. 2_Fe_5-c;
- natural bentonite (mod. 2) modified with polyhydroxocations of aluminum (III) by the "co-precipitation" method (5 mmol $[\text{Al}^{3+}]$ /g of bentonite): mod. 2_Al_5-c;

2.2. Adsorption studies

The samples of the studied sorbents weighing 1-2 g were filled with distilled water for 1 hour, then decanted and filled with 100 ml of a model solution containing the studied ion (nickel(II) cations) of various concentrations, the adsorbent was mixed with the model solution and kept for 2 hours until an equilibrium state was reached in the solution. Then samples were taken from the middle layers of the solution. Quantitative analysis of the elemental composition of the sample was performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 by the method of calibration curves. The pH of the solution was neutral 7. The adsorbent dose is 1-2 g.

3. Results and Discussion

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

3.1. Characterization of the adsorbent

3.1.1. Elemental composition of the studied sorbents

Chemical and mineral composition of modified bentonite-based sorbents. Table 1 shows data on the elemental composition of the studied samples of sorbents modified with polyhydroxocations of iron (III) and aluminium (III) by the "co-precipitation" method. Quantitative analysis of the elemental composition was performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 by the method of fundamental parameters.

Table 1. Elemental composition of the studied bentonite-based sorbents.

Samples of sorbents	The content of the element, wt. %						
	Al	Fe	Si	Ca	K	Ni	Ti
mod. 1	7	47	14	2	13	20	2.5
mod. 1_Fe_5-c	7	71	8	0.6	4	14	0.7
mod. 1_Al_5-c	15	46	11	1	8	16	2
mod. 2	8	23	44	17	5	-	2
mod. 2_Fe_5-c	6	57	31	2	2	-	1
mod. 2_Al_5-c	16	17	47	12	5	-	2

The data in Table 1 confirm that sorbents based on natural bentonite are aluminosilicates. An increase in the concentration of the modifying component leads to an increase in the concentration of the corresponding element in the bentonite sample. This increase in concentration occurs as a result of the substitution of exchange cations of bentonites. Figure 1(a, b) show X-ray diffractograms of the initial bentonites and modified sorbents based on them. XRD analysis was carried out on a DRON-4 diffractometer using an X-ray tube with a cobalt anode (Co-K α radiation).

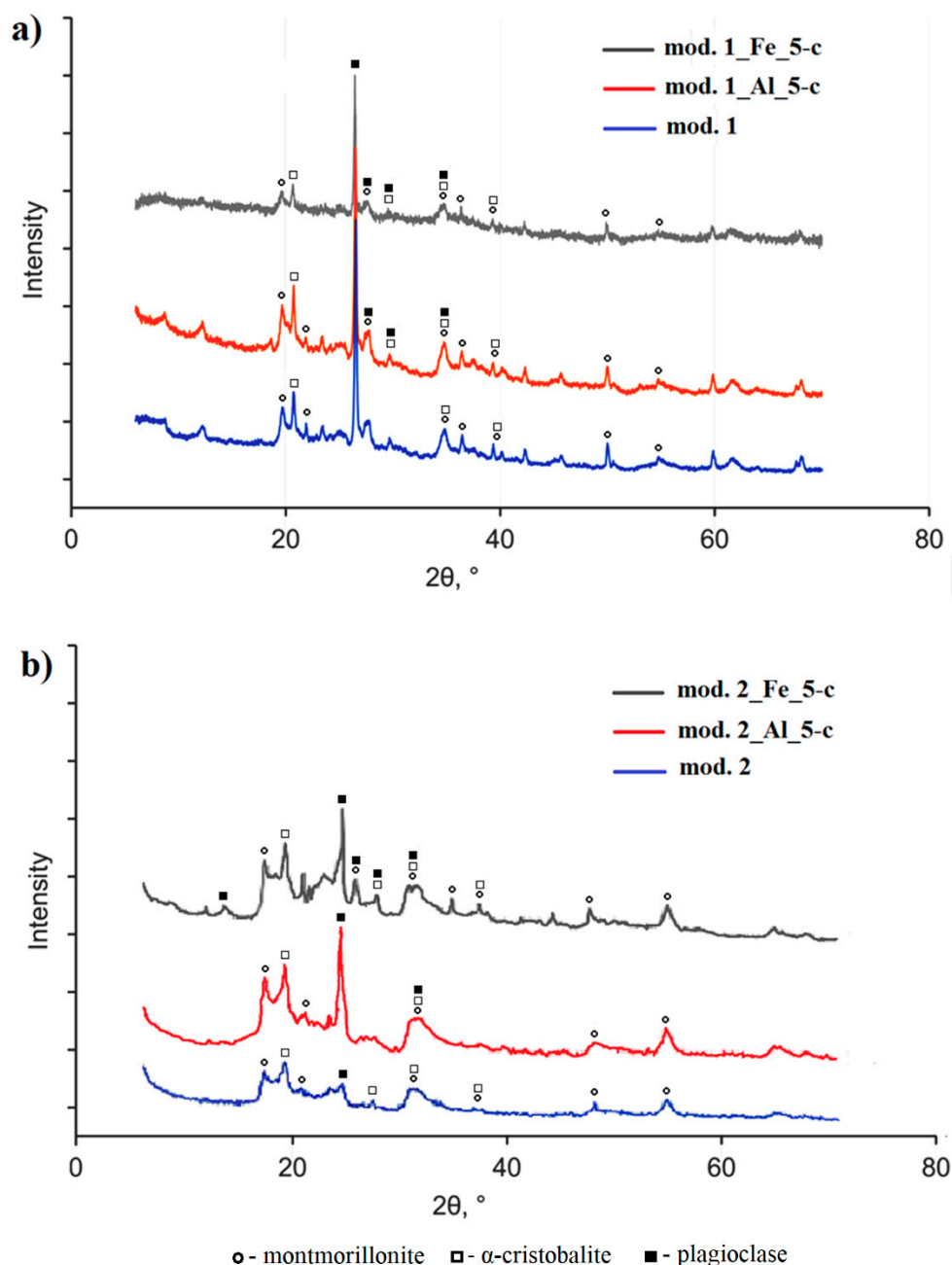


Figure 1. XRD spectra of the sorbents.

As follows from the obtained diffractograms, the additional introduction of aluminium (III) and iron (III) polyhydroxocations into bentonite by the "co-precipitation" method does not lead to a change in the mineral and phase composition of bentonite (in all the cases considered, minerals are observed: montmorillonite, α - cristobalite, plagioclase). The porous structure of the studied sorbents. The structural characteristics (specific surface area, porous structure, pore distribution by radius) of the studied samples were determined by low-temperature nitrogen adsorption on a high-speed gas sorption analyzer Quantachrome NOVA. The results of the study of the porous structure of natural

bentonites and sorbents based on them modified with polyhydroxocations of iron (III) and aluminium (III) by the "co-precipitation" method are presented in Table 2. It can be seen from the table data that the modification of bentonites leads to an increase in the number of micro- and mesopores and to a decrease in the number of macropores in comparison with the original bentonites. A large proportion of the pores of all modified samples account for pores with a size of 1.5-8.0 nm.

Table 2. The main characteristics of the porous structure of the studied sorbents based on bentonite modified with polyhydroxocations of iron (III) and aluminium (III) by the "co-precipitation" method.

Sample	Specific surface area, m ² /g	Pore volume, cm ³ /g	Distribution of pores by radius, %			
			1.5 – 2.0 nm	2.0 – 4.0 nm	4.0 – 8.0 nm	more than 8.0 nm
mod. 1	37	0.054	8	15	20	56
mod. 1_Fe_5-c	91	0.101	13	27	17	43
mod. 1_Al_5-c	120	0.073	16	38	14	32
mod. 2	51	0.061	9	21	21	49
mod. 2_Fe_5-c	86	0.125	22	46	19	13
mod. 2_Al_5-c	172	0,122	23	47	18	12

Such a redistribution in pore sizes also led to a significant increase in the specific surface area of the modified sorbents. It should also be noted that aluminum-modified sorbents have a slightly smaller specific surface area compared to iron-modified samples, which, is determined by a greater proportion of macropores in them.

3.2. Adsorption study

Study of sorption characteristics of modified bentonite-based sorbents. An important characteristic in the study of the adsorption process is the kinetics of adsorption, which is necessary to determine the time of the establishment of adsorption equilibrium when removing adsorption isotherms. Nickel (II) cations were selected as testing metal cations in the study of the adsorption process by modified sorbents based on the studied bentonites obtained by the "co-precipitation" method. The sorption experiment technique was as follows: the samples of sorbents weighing 1-2 g were filled with distilled water for 1 hour, then the water was decanted and 100 ml of a model solution of nickel (II) sulfate of a certain concentration was poured, and the adsorbent was mixed with the model solution. Then samples were taken from the middle layers of the solution through 5, 10, 15, 20, 30, 60, 120, and 180 minutes. Quantitative analysis of the sample for the content of nickel cations was performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 by the method of calibration curves. Data on the kinetics of adsorption of nickel (II) cations on the studied sorbents, obtained based on bentonite from the Dash-Salakhli deposit, are shown in Figure 2. Analysis of kinetic data on the sorption of nickel (II) cations on the studied sorbents indicates that the saturation of sorbents with cations under these conditions has been occurring for 2 hours. Therefore, in the future, when removing the sorption isotherms, the time for establishing the adsorption equilibrium was 2 hours.

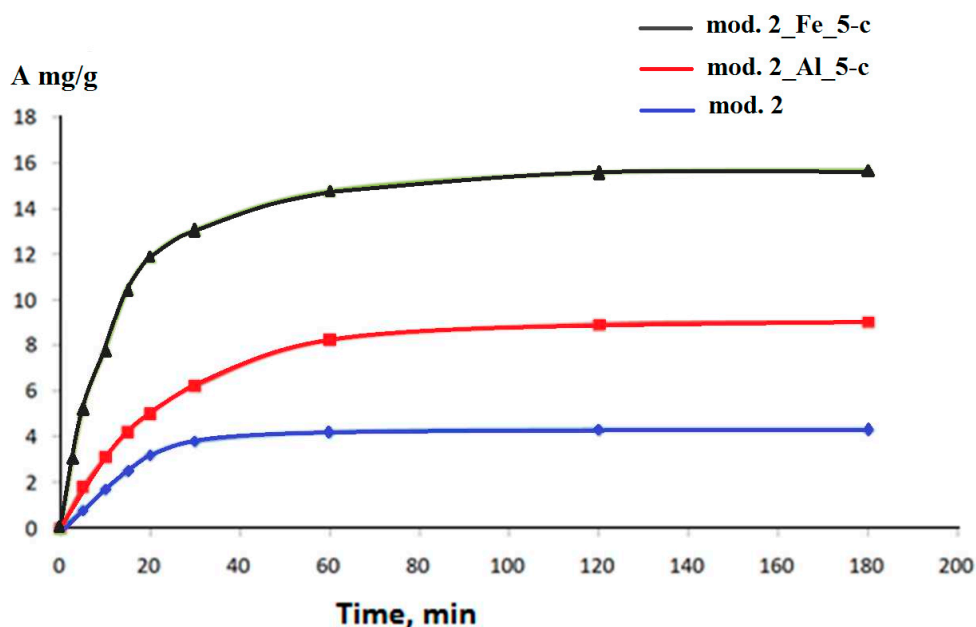


Figure 2. Kinetic curves of adsorption of nickel (II) cations in a neutral medium.

The method of removing the adsorption isotherms of nickel cations on the studied sorbents was as follows: as in kinetic experiments, the samples of the studied sorbents weighing 1-2 g were filled with distilled water for 1 hour, then the water was decanted, and filled with 100 ml of a model solution of nickel sulfate of various concentrations (100, 200, 300, 400 and 500 mg / l), were kept for 2 hours until the equilibrium concentration in the solution was reached. The samples were taken from the middle layers of the solution. Quantitative analysis of the elemental composition of the sample was also performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 using calibration curves.

According to the average values of equilibrium concentrations (at least two parallel measurements), the adsorption value was calculated using the following formula (1):

$$A = (C_i - C_e) \cdot V/m \quad (1)$$

A – adsorption capacity of the sorbent, mg/g;

C_i – initial concentration of the studied ions in solution, mg/l;

C_e – equilibrium concentration of the studied ions in solution, mg/l;

V – volume of the test solution, l;

m – the mass of the sorbent taken for analysis, g.

Figure 3 (a, b) show the adsorption isotherms of nickel (II) cations on the studied sorbents obtained on the basis of natural bentonites of the mod.1 and mod.2 deposits. Ranges of different concentrations show the true picture of the surface [16]. All the obtained isotherms belong to Langmuir-type (L-type) isotherms [17]. The Langmuir adsorption isotherm equation, derived based on molecular kinetic theory and ideas about the monomolecular nature of the adsorption process, when applied to solutions has the form of equation (2):

$$A = A_{\infty} \cdot \frac{K \cdot C}{(1 + K \cdot C)} \quad (2)$$

Where, K is the adsorption equilibrium constant characterizing the adsorption energy;

C – equilibrium concentration, mg/l;

A_{∞} – the maximum adsorption value, (monolayer capacity), mg/g.

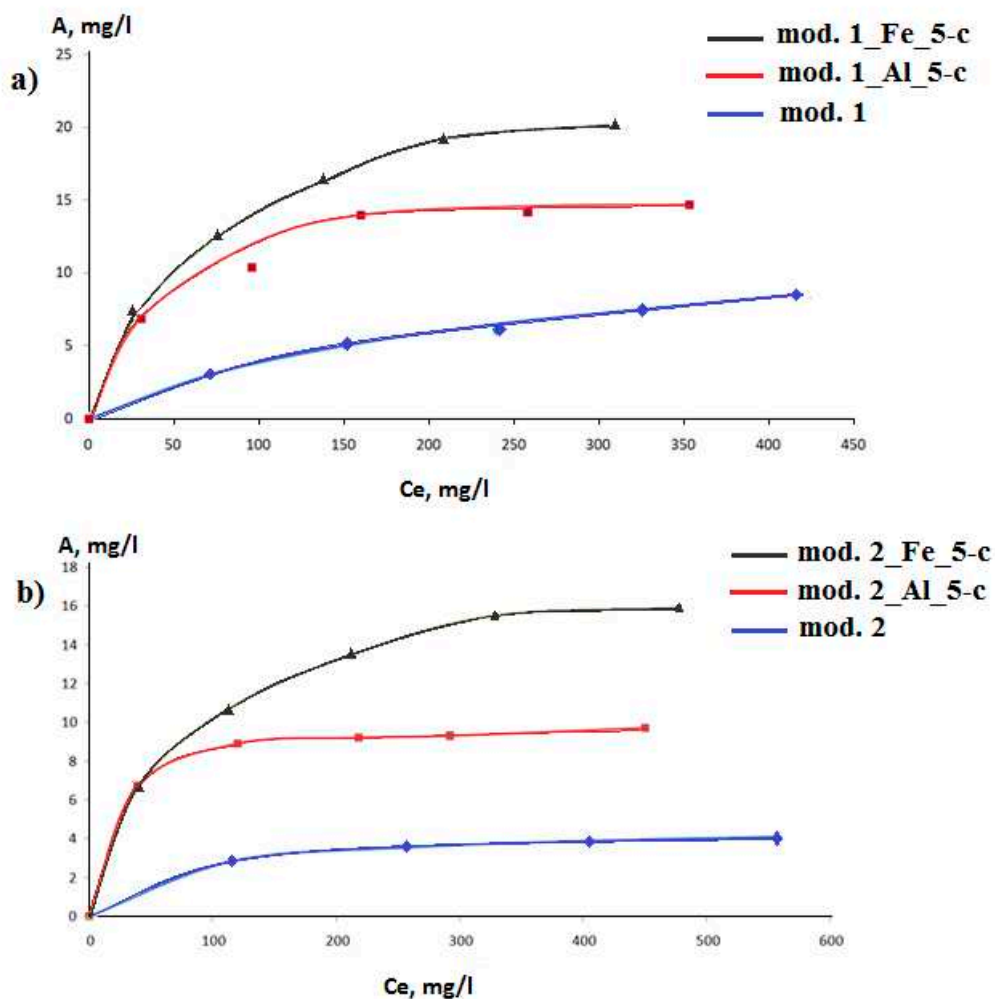


Figure 3. (a, b) Adsorption isotherms in a neutral medium of nickel (II) ions on the obtained sorbents.

An adsorption isotherm is a good tool for understanding the nature of the sorbent surface. The Langmuir adsorption isotherm (2) is linearized in coordinates $1/A = f(1/C)$, which allows graphoanalytically determining the values of the coefficients K and A_{∞} . The obtained adsorption isotherms were processed in accordance with the Langmuir equation in inverse coordinates according to equation (3):

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} \cdot \frac{1}{C} \quad (3)$$

Figure 4 (a, b) show the adsorption isotherms of nickel (II) cations for the studied sorbents in inverse coordinates in accordance with equation (3).

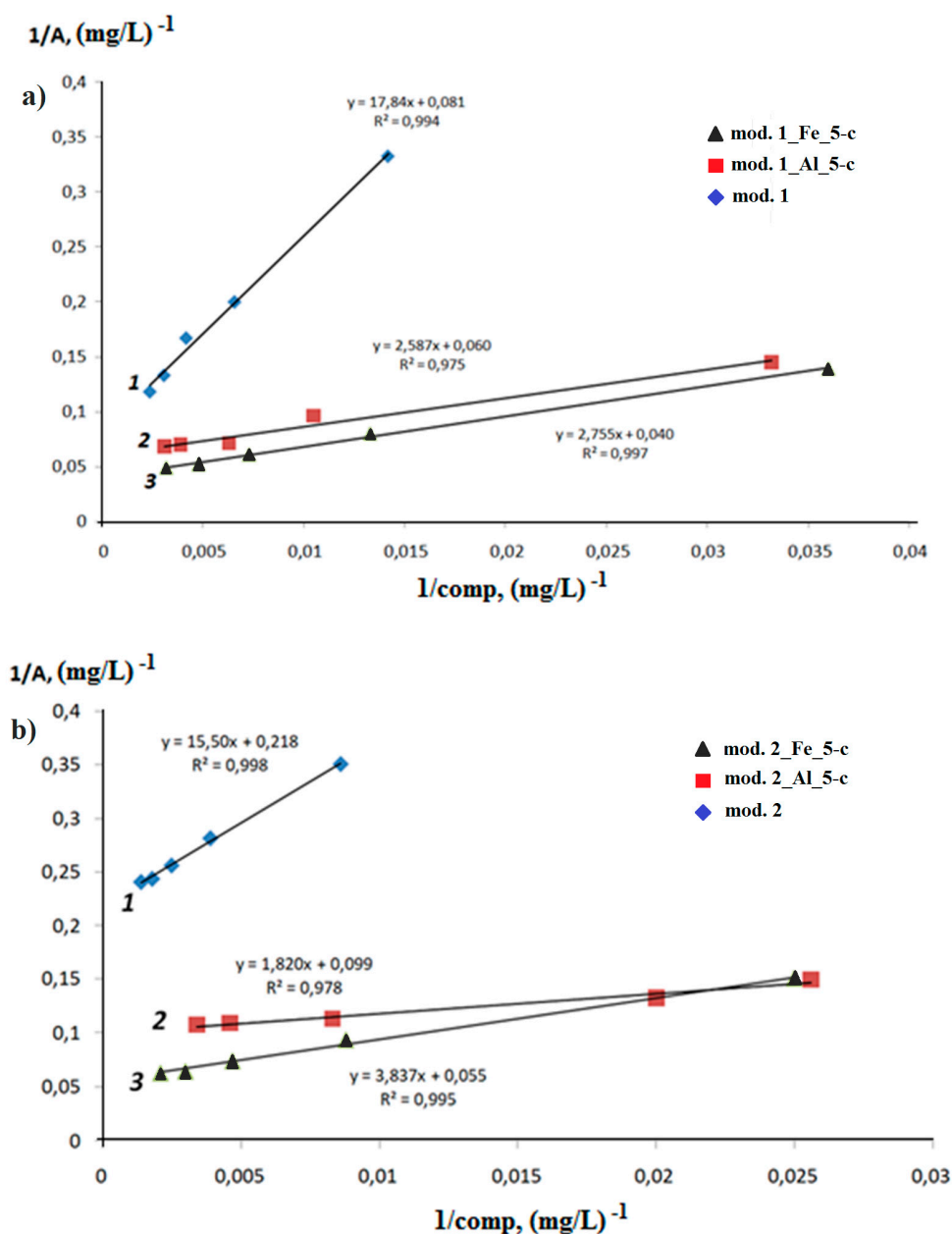


Figure 3. (a, b) Isotherms of adsorption of nickel (II) cations in a neutral medium.

The results of adsorption studies are presented in Table 3.

Table 3. Values of the maximum adsorption capacity of nickel (II) cations for the studied bentonite-based sorbents.

Sorbentsample	Maximum adsorption, mg/g
mod. 1	12,3±0,6
mod. 1_Fe_5-c	16,7±0,9
mod. 1_Al_5-c	25,0±0,9
mod. 2	4,6±0,2
mod. 2_Fe_5-c	10,1±0,5
mod. 2_Al_5-c	18,2±0,8

The obtained values of the maximum adsorption capacity with respect to nickel cations are generally consistent with the data on the total specific surface area of these sorbents. For samples with a high specific surface area, the absorption of the studied cations from model solutions is greater than for samples with a low specific surface area. The observed increase in the adsorption of nickel cations on Fe- and Al-modified sorbents compared to natural bentonites can also be explained by the fact that, along with the formation of a layered-columnar structure leading to an increase in the specific surface area, modification also leads to an increase in the number of Al-OH and Fe-OH anion exchange centers [14,18].

Establishing the mechanism of the adsorption process on natural bentonite and sorbents based on it is difficult to describe, because the adsorption process on bentonite clays can be carried out simultaneously by several mechanisms with the predominance of one. Adsorption processes carried out by montmorillonites occur mainly by three mechanisms:

- a) by the type of ion exchange.
- b) by the formation of chelate complexes with surface hydroxogroups of the mineral.
- c) with the help of valence "broken" bonds at the edges and corners, at the shear growth stages of montmorillonite crystals.

The most well-known mechanism is ion exchange. Ion exchange has a fundamental and practical application for all bentonite clays. It is known that the source of bentonite cation exchange ability is interlayer cations of sodium, lithium, calcium, potassium, and magnesium, which compensate for the negative charge of montmorillonite layers. As a result of this mechanism, interlayer cations are exchanged for adsorbent cations (heavy metals) that are in water.

In addition, heavy metal ions can be deposited on the surface in the form of (hydr)oxides, hydroxocarbonates or other basic salts.

Most authors interpret the mechanism of adsorption on natural clay minerals of aluminosilicate composition as ion exchange [18,19]. But based on the data we have obtained; it follows that the mechanism of adsorption on bentonite clays is complex. The main process is ion exchange, which can be either cation exchange or anion exchange. The higher sorption activity of the studied Al-modified bentonites in comparison with Fe-modified ones is determined by the high content of Al-OH anion exchange centres in them, which can also take part in the processes of complexation.

5. Conclusions

A method for obtaining effective sorbents based on bentonites of various deposits modified with polyhydroxocations of iron (III) and aluminium (III) by the "co-precipitation" method has been developed; their physicochemical and adsorption properties with respect to nickel (II) cations have been studied. X-ray phase analysis has established that the additional introduction of aluminium and iron (III) polyhydroxocations into bentonite by the "co-precipitation" method does not lead to a change in the mineral and phase composition of bentonite (in all the cases considered, minerals are observed: montmorillonite, α - cristobalite, plagioclase). It was found that the modification of bentonite with polyhydroxocations of iron (III) and aluminium(III) leads to an increase in the total specific surface area (up to 180 m²/g). It is shown that modified bentonite-based sorbents are microporous materials; most of the pores of all modified samples are pores with a size of 1.5-6.0 nm. The mechanism of the adsorption of nickel(II) cations from model solutions is complex, and is described simultaneously by several processes. The main mechanism is ion exchange, which is accompanied by complexation, in which the more active groups are Al-OH.

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Conflicts of Interest: The authors declare no conflict of interest.

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