

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). The amount of bentonite in the concentration of iron (aluminum) was 5 mmol Me³⁺/g. It was established that the modification of natural bentonites using polyhydroxocations of iron (III) (mod. 1_Fe_5-c, mod. 2_Fe_5-c) and aluminum (III) (mod. 1_Al_5-c, mod. 2_Al_5-c) 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 ([Al₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺) and poly-hydroxyl-Fe or polyoxo-Fe were intercalated into clay layers, which led to an increase in the values of d₀₀₁ and specific surface areas compared to those of the original bentonite, from 37 to 120 m²/g for the Pogodaevoo bentonite and from 51 to 172 m²/g 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 1.5–8.0 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 aluminum (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) 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 centers 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

Nickel is often found in the flow of raw wastewater from industries, such as mining, electroplating, pigment and ceramic, and battery and accumulator manufacturing, and is used in a variety of industries, such as the chemical industry [1].

Humanity is facing a global water crisis: almost a billion people around the world do not have access to safe drinking water, and more than two billion people do not have a water treatment system, which is the main cause of diseases being transmitted via water resources.

As a result of the industrialization process, metal ions are released into the environment as waste, which, in turn, leads to the pollution of the water system. Even at the smallest level, the presence of metal ions in water can damage the ecosystem and human life since they are not biodegradable [2].

Industrial wastewater treatment is currently a critical environmental issue globally [3]. The current wastewater treatment plants are not designed for the removal of these pollutants in water. Heavy metals [4] and organic compounds [5] are the most dangerous.

Heavy metals are priority pollutants, such as nickel (II); in an aqueous solution at high concentrations, they may cause nose, bone and lung cancer [6].

Methods used to remove metal ions from aqueous media include reduction and precipitation, coagulation and flotation, adsorption, ion exchange, membrane technology and electrolysis. However, most of these methods have disadvantages such as the presence of secondary contaminants, low efficiency, as well as high operational and investment costs.

Among all known methods of wastewater treatment, adsorption is one of the most common ways to remove contaminants from water [7]. Adsorption is a simple and effective strategy for industrial wastewater treatment, as well as an important technology for environmental protection [8,9].

Adsorption is among the most efficient technologies because it relies on low-cost materials such as aluminum and iron oxides or oxyhydroxides, zeolites, clay minerals, silicates, etc. [10,11]

Adsorption is widely used to purify metal ions from aqueous solutions due to significant advantages, such as its suitability for use in periodic and continuous processes, ease of use, less sediment formation, efficiency and the possibility of regeneration [12].

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 via several mechanisms with the predominance of one. Adsorption processes carried out in montmorillonites occur mainly via three mechanisms:

1. The type of ion exchange;
2. The formation of chelate complexes with surface hydroxyl groups of the mineral;
3. 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) in water.

Currently, there is a significant increase in interest in the creation of new environmentally friendly sorbents based on natural clay materials and aluminosilicates [12]. Clays and composite materials based on them have a higher adsorption capacity than other low-cost adsorbents [13,14]. 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 [15,16]. 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 aluminum, iron (III), titanium, chromium, zirconium and other elements, known as pillar clays [17], 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 [18]. In comparison to synthetic zeolites [10,11], 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 [17,18]. The saturation of clays with Al Keggin cations followed by calcination results in strong heat-resistant pillared structures [3].

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 (Uralsk, West Kazakhstan region, Republic of Kazakhstan), natural bentonite of the Dash-Salakhli deposit (Dash-Salakhli, Azerbaijan) and purified via precipitation in combination with ultrasound treatment and centrifugation. Aluminum 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 (Millipore, Sigma-Aldrich, Supelco). 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, Kyoto, Japan) using the method of fundamental parameters. The porous structure of the samples was determined via low-temperature nitrogen adsorption on a high-speed gas sorption analyzer Quantachrome NOVA (Quantachrome, Kaliforniya, 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 $0.967-0.4 P/P_0$ is used as initial data for calculations using the BJH method. X-ray diffraction analysis was carried out on a DRON-4 diffractometer (St. Petersburg, Russia) 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 cations was determined by constructing sorption isotherms via the method of variable concentrations under statistical conditions. The model solution was a $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ salt solution. Nickel ion (II) was analyzed using atomic absorption spectroscopy (AAS, SHIMADZU-6800, Shimadzu, Kyoto, Japan).

2.1. Preparation of Fe-Bentonite and Al-Bentonite

Modification of bentonites was carried out using the method of “co-precipitation” (intercalation, or pillarization) [19]. FeCl_3 and AlCl_3 salts were 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 of bentonite in the concentration of iron (aluminum) was 5 mmol Me^{3+} /g. The suspension was then sonicated at 22 Hz for 3 min [20]. 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 aging at room temperature. After 24 h, 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.

2.2. Adsorption Studies

The samples of the studied sorbents weighing 1–2 g were filled with distilled water for 1 h, 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 h 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 using the method of calibration curves. The pH of the solution was neutral 7. The adsorbent dose is 1–2 g.

3. Results and Discussion

3.1. Characterization of the Adsorbent

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 aluminum (III) using the “co-precipitation” method. Quantitative analysis of the elemental composition was performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 using 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 occurs as a result of the substitution of exchange bentonite cations, particularly calcium cations. It was not possible to determine the presence of sodium and magnesium elements in bentonite and sorbent samples modified on its basis. This is due to the measurement range of the energy dispersion. The X-ray fluorescence spectrometer EDX-720 is in the range from Na to U; therefore, a small content of light metals in the samples can be taken using the device as a background and not diagnose them. Figure 1a,b shows 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 copper anode (Cu-K α radiation, 1.5418 Å).

As follows from the obtained diffractograms, the additional introduction of aluminum (III) and iron (III) polyhydroxocations into bentonite via 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).

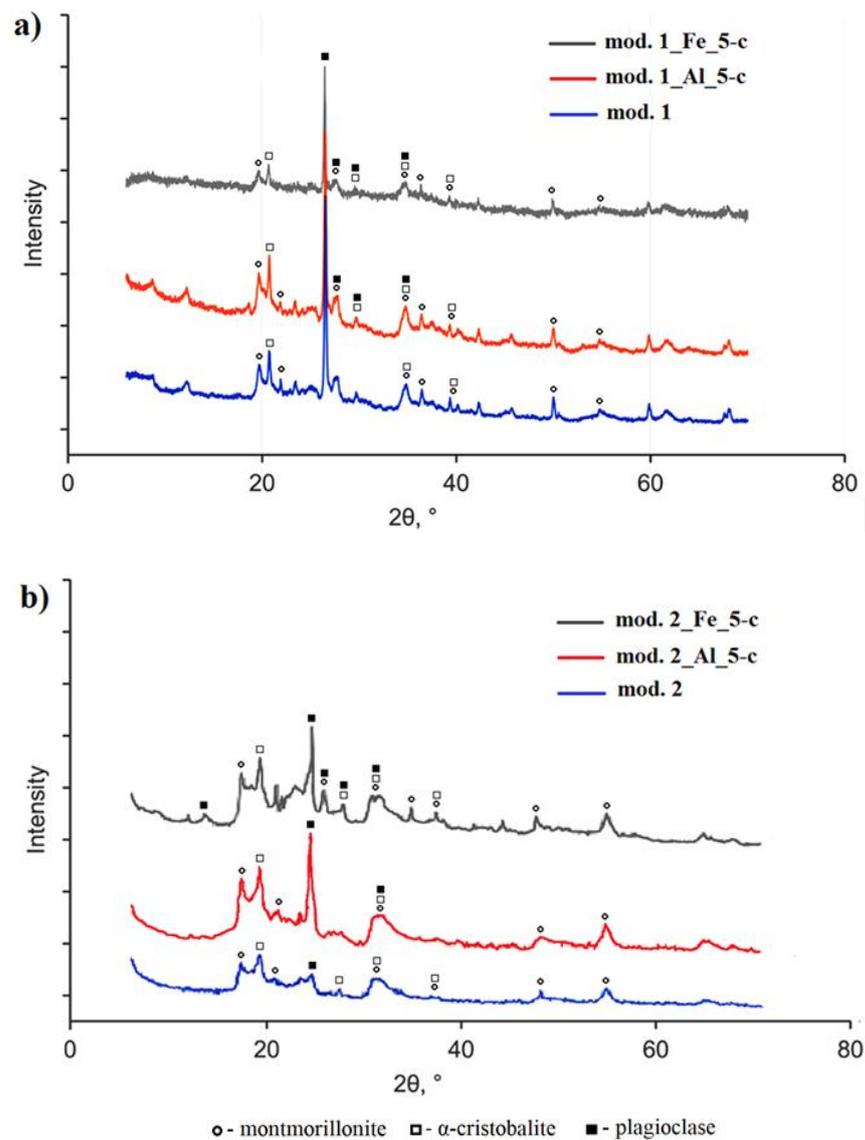


Figure 1. XRD spectra of the sorbents. (a) Pogodayevo deposit, (b) Dash-Salakhli deposit.

3.2. The Porous Structure of the Studied Sorbents

The results of the study of the porous structure of natural bentonites and sorbents based on them modified with polyhydroxocations of iron (III) and aluminum (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.

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 iron-modified sorbents have a slightly smaller specific surface area compared to aluminum -modified samples, which, is determined by a greater proportion of macropores in them.

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) using the “co-precipitation” method [21].

| 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 |

3.3. Study of the Sorption Kinetics

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 in 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 h, 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 at 5, 10, 15, 20, 30, 60, 120, and 180 min. Quantitative analysis of the sample for the content of nickel cations was performed on an energy-dispersive X-ray fluorescence spectrometer EDX-720 using 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 and Pogodayevo deposit, are shown in Figure 2a,b. The 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 h. Consequently, in the future, when taking off the sorption isotherms, the time for establishing the adsorption equilibrium was 2 h.

The method of taking 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 h, 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 h 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.

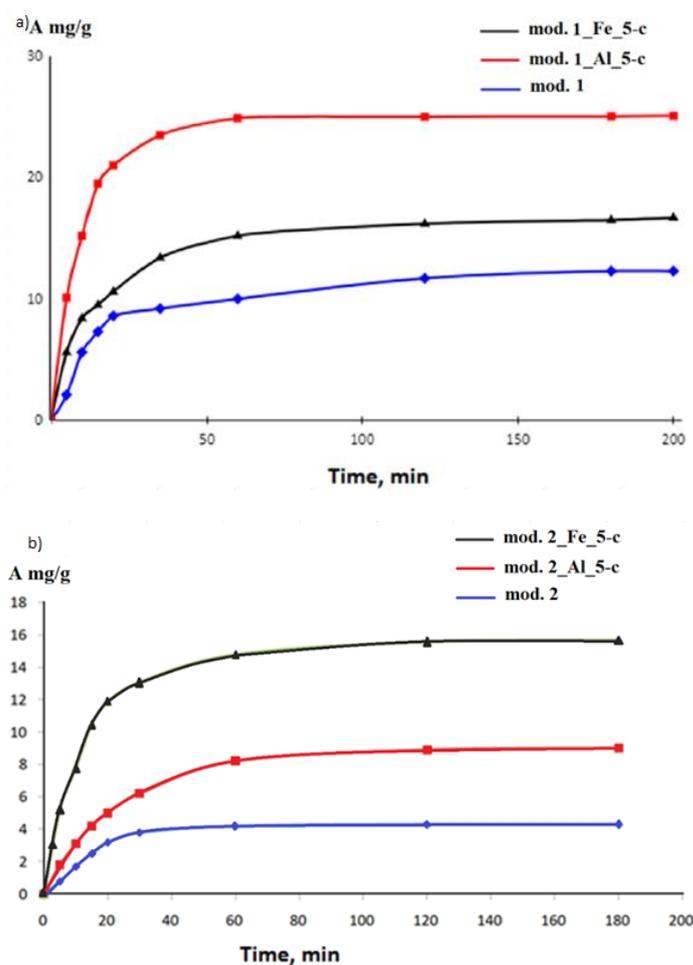


Figure 2. (a,b) Kinetic curves of adsorption of nickel (II) cations in a neutral medium.

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.

The rate of heterogeneous reaction (sorption of metal ions from a solid phase solution) is determined using many factors. The study of sorption kinetics allows one to identify the aspects that influence the dynamics and limit the process pace. The sorption rate is an important feature that determines whether or not the examined substance may be used as a sorbent. In general, the interaction of a sorbate with a sorbent has a high rate in the early minutes of contact and thereafter settles to a consistent level. To reduce the sorption cycle time in a technological or laboratory process, it is preferable to attain sorption equilibrium soon [22,23].

Diffusion in pores or migration along the pore surface or internal diffusion or particle interaction are two methods of controlling the mass transfer of solutes inside porous sorbents, which, in turn, control the rate of adsorption. The Morris–Weber intraparticle diffusion model, pseudo-first-order, pseudo-second-order and Elovich models were used to model the kinetics of nickel (II) ion sorption on initial and modified bentonites. Kinetic diagrams for the tested models are shown in Figures 3 and 4a–d.

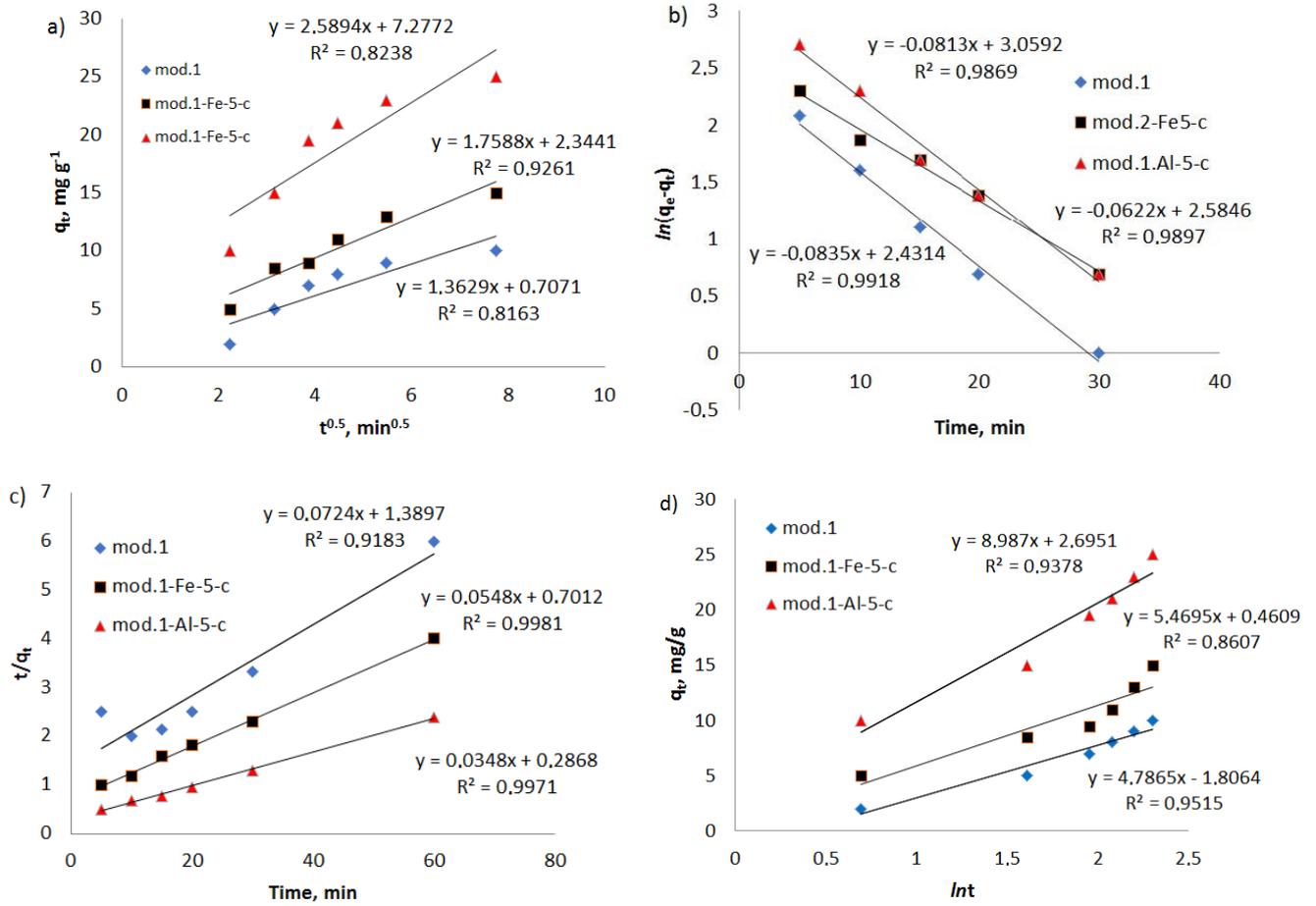


Figure 3. Kinetic model plots of Morris–Weber intra-particle diffusion model (a), pseudo-first-order (b), pseudo-second-order (c) and Elovich model (d) for Pogodaev deposit.

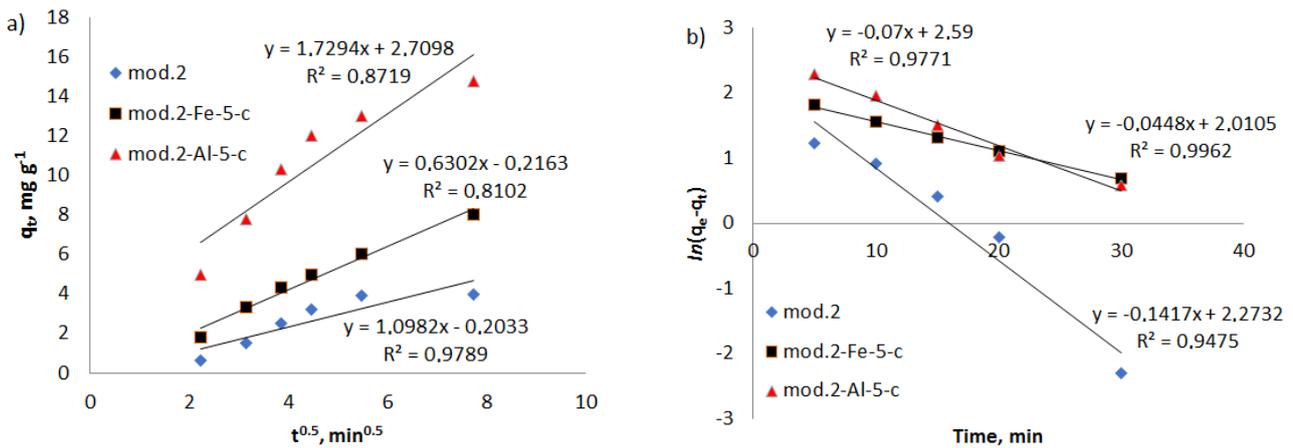


Figure 4. Cont.

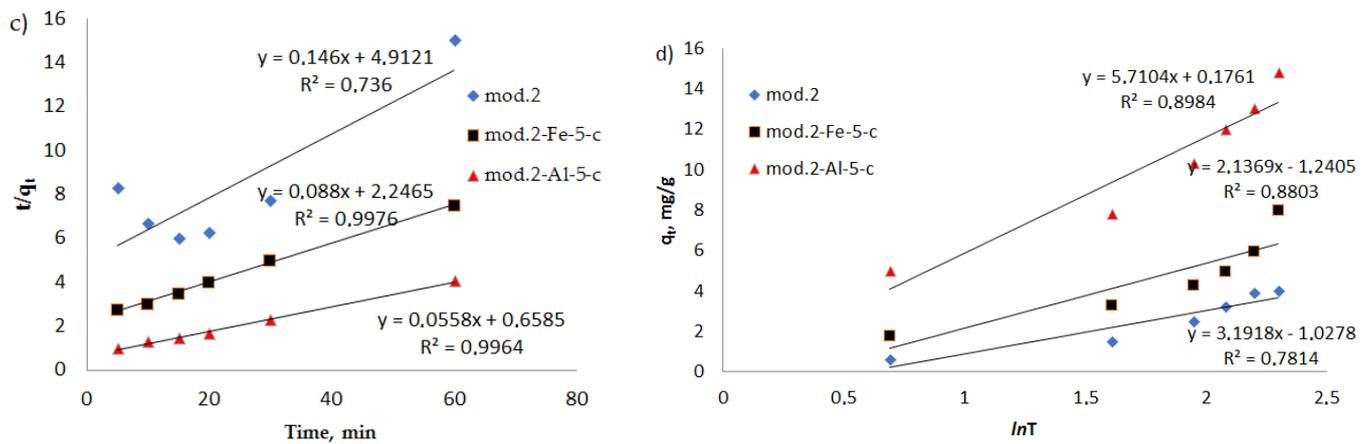


Figure 4. Kinetic model plots of Morris–Weber intra-particle diffusion model (a), pseudo-first-order (b), pseudo-second-order (c) and Elovich model (d) for Dash-Salakhli deposit.

The analysis of the diffusion models on the sorption of nickel (II) ions on the studied sorbents, including unmodified ones, showed that they work only at the initial stage of sorption (sometimes less than 20–30 min). At the end of this time interval, a mixed diffusion sorption model is observed.

To clarify the contribution of chemical stages to the rate of adsorption of nickel (II) ions via the sorbents under study, kinetic curves were processed using chemical kinetics equations (models: Morris–Weber intraparticle diffusion (2), pseudo-first-order (3), pseudo-second-order (4) and Elovich (5)):

$$q_t = K_p t^{0.5} + C \quad (2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = \frac{1}{\beta} (\ln \alpha \beta) + \frac{1}{\beta} \ln t \quad (5)$$

where q_t is the adsorbed amount at time t , mg g^{-1} ; q_e is the adsorbed amount at equilibrium, mg g^{-1} ; k_1 is the rate constant of pseudo-first-order adsorption, min^{-1} ; k_2 is the rate constant of pseudo-second-order adsorption, $\text{g} (\text{mg}^{-1} \text{h}^{-1})$; the parameter α is the initial adsorption rate, $\text{mg/g} \cdot \text{min}$ and β is related to the extent of the surface coverage and activation energy for chemisorptions, mg/min ; k_p is the intraparticle diffusion rate constant, $\text{mg} (\text{g}^{-1} \text{h}^{-0.5})$.

When the rate determination stage is based on the mass transfer of the adsorbate to the surface of a solid, the Morris–Water diffusion model inside the particles can be used [23]. If the graph is linear and passes through the origin, then, according to this model, the limiting state is intraparticle diffusion.

Figures 3a and 4a shows that the plots are linear but do not pass through the origin, which may be attributable to the difference in the mass transfer rate between the start and final stages of adsorption. There also appears to be a layer barrier. Resistance is there at the outset, and intra-particle diffusion is not the only rate-controlling step. However, different kinetic models may simultaneously influence the adsorption rate.

From the data presented in Figures 3b and 4b, it follows that the adsorption of nickel (II) ions at the initial stage is best described using the pseudo-first-order model ($R^2 > 0.9$), regardless of which sorbent the sorption of nickel (II) ions occurs on the pure or modified

bentonite. This indicates that “sorbent-sorbate” interactions prevail at this stage. The analysis of kinetic curves in accordance with the pseudo-second-order adsorption model (Figures 3c and 4c shows that for modified sorbents, this model works over the entire time interval ($R^2 > 0.9$), while for pure bentonites, it practically does not work. This allows us to conclude that the “sorbate-sorbate” interactions during the sorption of nickel (II) ions largely contribute to the overall rate of the sorption process.

Based on the high value of the correlation coefficient for the Elovich model ($R^2 > 0.9$) Figures 3d and 4d show for almost all studied sorbents, it can be concluded that there are structural disorders in the porous system of sorbents, and their surface can be considered as a heterogeneous system. Therefore, the Elovich equation is used exclusively when describing the kinetics of adsorption of substances in heterogeneous systems, taking into account the adsorption capacity.

Considering that heterogeneous processes take place on the surface of the sorbent, it is natural that all surface properties (structure, chemical composition of the surface layer, etc.) will play an important role in the adsorption process [24].

3.4. Study of the Sorption Mechanism

Heavy metal ion sorption is a complex process regulated by a number of factors. Possible processes include chemisorption, complexation, and adsorption on the sorbent surface and in its pores, as well as complexation, ion exchange, microprecipitation, and precipitation of heavy metal hydroxides [25].

The study of isotherms is the primary method for investigating the adsorption mechanism. Sorption isotherms depict the distribution of metal ions in equilibrium between the adsorbent and the liquid phase as a function of concentration. The investigation of these isotherms helps us to reach conclusions about the nature of the sorbent surface and the sorbate–sorbent interactions. Langmuir model was used to conduct the research.

Figure 5a,b shows 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 [24]. All the obtained isotherms belong to Langmuir-type (L-type) isotherms [25]. 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 (6):

$$A = A_{\infty} \cdot \frac{K \cdot C}{1 + K \cdot C} \quad (6)$$

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.

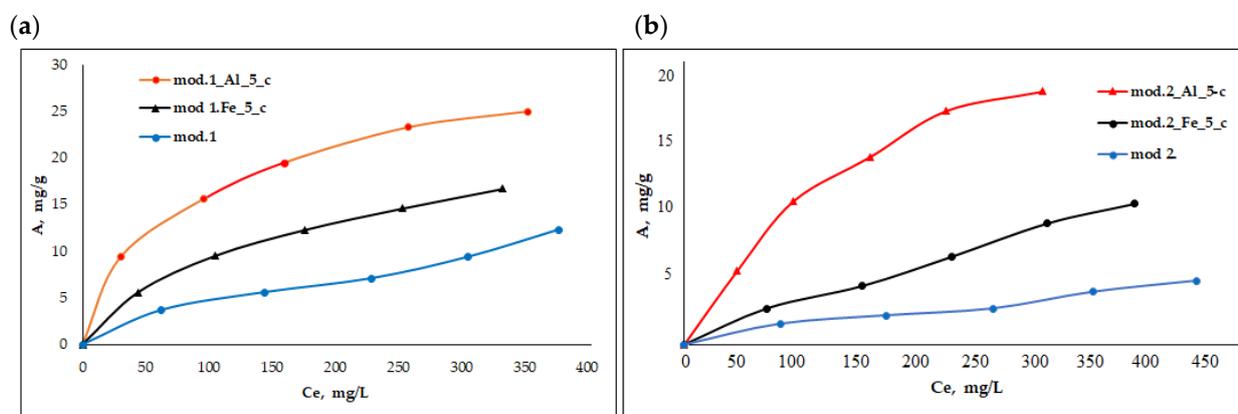


Figure 5. (a,b) Adsorption isotherms in a neutral medium of nickel (II) ions on the obtained sorbents.

An adsorption isotherm is a good tool for understanding the nature of the sorbent surface. The Langmuir adsorption isotherm (6) 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 (7):

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} \cdot \frac{1}{C} \quad (7)$$

Figure 6a,b shows the adsorption isotherms of nickel (II) cations for the studied sorbents in inverse coordinates in accordance with Equation (7).

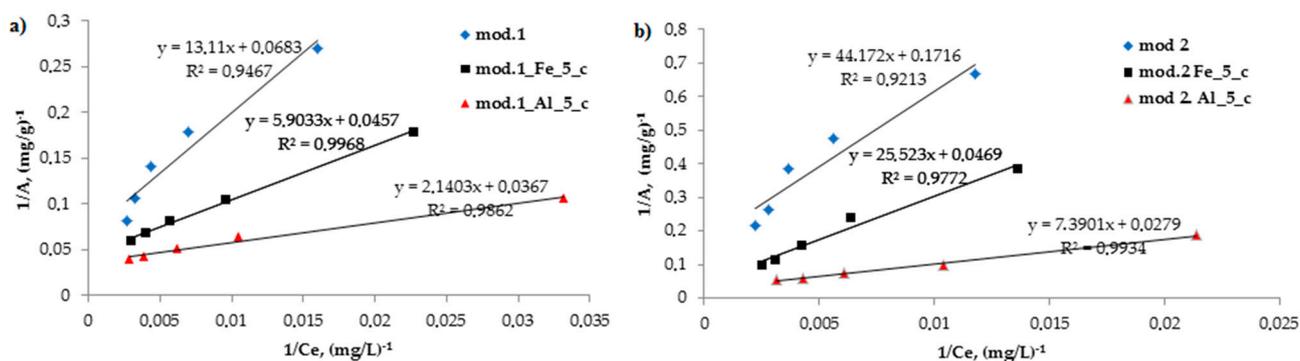


Figure 6. (a,b) Isotherms of adsorption of nickel (II) cations in a neutral medium.

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.

| Sorbent Sample | 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 [24,25].

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

Most authors interpret the mechanism of adsorption on natural clay minerals of aluminosilicate composition as ion exchange [26]. 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 centers in them, which can also take part in the processes of complexation.

4. Conclusions

A method for obtaining effective sorbents based on bentonites of various deposits modified with polyhydroxocations of iron (III) and aluminium (III) using 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 aluminum and iron (III) polyhydroxocations into bentonite using 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 -crystalite, plagioclase). It was found that the modification of bentonite with polyhydroxocations of iron (III) and aluminum (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 1.5–8.0 nm. The mechanism of the adsorption of nickel (II) cations from model solutions is complex, and is described simultaneously using several models: external and internal diffusion, pseudo-first-order, pseudo-second-order and Elovich. The main mechanism is ion exchange, which is accompanied by “sorbent-sorbate” and “sorbate-sorbate” interactions, in which the more active groups are Al-OH and Fe-OH.

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Nomenclature

| | |
|---------------|--|
| mod. 1 | Natural bentonite of the Pogodayevo deposit |
| mod. 1_Fe_5-c | Natural bentonite (mod. 1) modified with iron (III) polyhydroxocations by the “co-precipitation” method (5 mmol [Fe ³⁺]/g of bentonite) |
| mod. 1_Al_5-c | Natural bentonite (mod. 1) modified with polyhydroxocations of aluminum (III) by the “co-precipitation” method (5 mmol [Al ³⁺]/g of bentonite) |
| mod. 2 | Natural bentonite of the Dash-Salakhli deposit |
| mod. 2_Fe_5-c | Natural bentonite (mod. 2) modified with iron (III) polyhydroxocations by the “co-precipitation” method (5 mmol [Fe ³⁺]/g of bentonite) |
| mod. 2_Al_5-c | Natural bentonite (mod. 2) modified with polyhydroxocations of aluminum (III) by the “co-precipitation” method (5 mmol [Al ³⁺]/g of bentonite) |

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