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PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

Adsorption Kinetics of Nickel(II) and Copper(II) Ions by Modified Aluminosilicates

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Abstract—The adsorption kinetics of nickel(II) and copper(II) ions by alumosilicates modified with *N*,*N'*-bis (3-triethoxysilylpropyl) thiocarbamide (BTM-3) and HCl is studied using the kinetic pseudo-first and pseudo-second order models. It is shown that when aluminosilicates are modified the time for equilibrium establishment is reduced by factors of 1.33 for adsorption of copper(II) ions and 2 for nickel(II) ions. The rate and energy of adsorption increase. It is established that the kinetics of the adsorption of the studied ions is best described by a pseudo-second order model. At the same time, the values of the correlation coefficients are 0.997–0.998. The maximum value of the adsorption rate constant of 33.7×10^{-5} g/(mmol min) corresponds to nickel(II) ions for aluminosilicates modified with HCl. The initial adsorption rate is 8.70×10^{-3} mmol/(g min). The maximum value of the adsorption rate constant value of 2.91×10^{-5} g/(mmol min) for aluminosilicates modified with BTM-3 corresponds to Cu(II) ions.

Keywords: modified alumosilicates, adsorption kinetics, pseudo-first and pseudo-second order models, nickel (II) and copper (II) ions

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INTRODUCTION

The continuously increasing negative effect of the anthropogenic load on the environment has led to the creation of priority technologies for the rational use of natural resources and improvement of the environmental safety of manufacturing as a whole. At the same time, the use of natural materials, aluminosilicates, as inexpensive adsorbents, is very promising and ecologically justified. The effective indicators of the practical use of adsorbents include their cost, adsorption capacity, equilibrium time in the adsorbate–adsorbent system, and adsorption rate. The results of the study of the adsorption kinetics of ions of toxic metals are presented in the papers [1–3, 6–8].

The adsorption kinetics of Pb(II), Cu(II), and Zn(II) ions have been studied in [1] by natural zeolite tuff from Maramuresh Kaunti (Northern Romania) at temperatures of 25 and 50°C. As a result of studying the adsorption kinetics of the studied ions of heavy metals, various kinetic models (pseudo-first order, pseudo-second order, and Weber–Morris) were obtained. At the same time, the best results were obtained while using the pseudo-first order model.

The authors of [2] studied the competitive adsorption of Cd(II), Cu(II), Ni(II), and Pb(II) ions from industrial wastewater with the use of Iranian natural alumosilicate. The adsorption rate was studied and equilibrium was established on single and multicomponent solutions. The optimal conditions for the purification process were investigated by observing the effect of pH, the presence of competing ions, the change in the aluminosilicate mass, and a different contact time. The adsorption kinetics on alumosilicate were described by a first-order reaction showing that about 100% of the Pb(II) ions are removed within 40 min and an equilibrium state for Cd(II), Cu(II), and Ni(II) ions is reached within 24 h.

The use of kaolin and bentonite as materials for nanoscale zero-valent iron applied for the simultaneous removal of Cu(II) and Zn(II) ions from an aqueous solution was estimated in [3]. Of the three components, bentonite was most effective for the simultaneous removal of Cu(II) and Zn(II) ions, with 92.9% of Cu and 58.3% of Zn being removed from an aqueous solution containing 100 mg/dm^3 of Cu(II) and Zn(II) ions. Kinetic studies have shown that the removal of Cu(II) and Zn(II) by nanoscale material agrees closely with the pseudo-first order model.

It is well known that the adsorption capacity of natural adsorbents can be increased by using the modification of adsorbents [4, 5]. The authors of [6] used Iranian natural clinoptilolite of tuff, which was pretreated and crushed into micro and nanoparticles by the mechanical method. The micro- and nano-particles, as well as their Ni-substituted forms, were modified using dimethylglyoxime (DMG). Removal of

Ni(II) ions on modified and unmodified samples is studied by a periodic method. Modified nanoparticles (DMG) have been found to be more suitable for removing Ni(II) ions. A comparison of two kinetic models shows that kinetic adsorption can be described well by a pseudo-second order equation, which indicates that the speed limit of the process is related to the chemical reaction.

In the paper [7], the authors obtained a composite material containing calcium alginate, clinoptilolite, coal, and humic acids. The obtained samples were studied as adsorbents for the removal of cadmium, mercury, and lead. The data for each metal ion on all adsorbents showed close agreement of the kinetic model of a pseudo-second order. The equilibrium data were established using the Langmuir, Freindlich, and Dubinin–Radushkevich models, as well as the Temkin isotherm.

The possibility of using synthetic zeolite 4A to remove Cu(II) ions from aqueous solutions was studied in the study [8]. The effect of the pH and temperature on the adsorption process was studied. The optimum pH of adsorption is 8. The reaction rate was described by a pseudo-second-order model. Experiments on the adsorption of Cu(II) ions were carried out at room temperature (25°C), while the Langmuir and Freundlich equations were used to describe the isotherm. The maximum copper removal obtained from the series of studies was 99.99%.

From a brief review of the presented works, it follows that the adsorption kinetics on natural alumosilicates are most accurately described by the model of the pseudo-first order, while the modified and synthetic samples were best described mostly by the second order. The purpose of the work was to study the adsorption kinetics of Ni(II) and Cu(II) ions from aqueous solutions by modified alumosilicates.

EXPERIMENTAL

Natural alumosilicates of the Transbaical deposit were used as the object of the study. In the experiments, a fraction of 1.0 mm, which was preselected on a sieve, was used.

The X-ray phase analysis was performed on a D8 ADVANCE automated X-ray diffractometer equipped with a Goebel mirror and a VÅNTEC-1 PSD detector. The survey was carried out in a step-by-step mode in the range of 2θ angles from 5° to 70° using Cu-radiation. The X-ray diffraction was calculated using a diffractometer software. The phases were identified using the PDF-2 powder diffractogram database. The content of mineral components in the sample was calculated using the TOPAS program.

The alumosilicates were modified as follows: 10 g of alumosilicate was in contact upon stirring with 100 g of a 30% aqueous solution of *N*,*N*′-bis(3-triethoxysilylpropyl)thiocarbamide (BTM-3) in hexane [9]. The solution was stirred for 3 h at 50°C. After the specified time, the alumosilicate was separated from the solution, dried in air, and kept in a drying cabinet for 1 h at 110°C. The resulting product was cooled in a vacuum desiccator and the change in mass during the modification was determined.

Alumosilicates were modified with HCl in accordance with the following technique: 10 g of alumosilicates dried to a constant weight at 120–150°C were mixed for 24 h with 200 mL of a 12% HCl solution in water. Then the suspension was filtered and washed with distilled water until a neutral reaction. The obtained modified alumosilicates were dried to a constant weight and analyzed for the content of the main elements. The increase in the mass of the alumosilicate was 20%.

The adsorption kinetics of the modified alumosilicates were studied under static conditions. In this work, the model solutions prepared from $NiSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ of the CP qualification and distilled water were used. The content of the metal ions in the solutions was determined by the standard techniques [10, 11]. The initial concentration of Ni(II) ions was 160 mg/dm^3, and that of Cu(II) ions was 120 mg/dm^3. The mass of the studied adsorbents was 1 g. The studied solutions were prepared with a volume of 0.1 dm^3. The mass ratio of the liquid and solid phases was 1 : 100. The adsorption value (*A*, mmol/g) was calculated by the following formula:

$$A = \frac{C_0 - C_{\text{eq}}}{m} V, \tag{1}$$

where C_0 and $C_{\text{eq.}}$ are the initial and equilibrium concentrations of the metal in the solution, mmol/dm^3; V is the volume of the solution, dm^3; and m is the mass of the adsorbent, g.

RESULTS AND DISCUSSION

According to the results of the X-ray-phase research, it was established that the sample of alumosilicate rock consisted of heulandite $Ca[Al_2Si_7O_{18}] \cdot 6H_2O$, 64.3%; impure rock—sanidine $KAlSi_3O_8$—20.5%; and cristobalite SiO_2, 15.2% (Fig. 1).

The adsorption kinetics were constructed by constructing and processing the kinetic curves (Figs. 2, 3).

The adsorption equilibrium corresponding to the constancy of the concentration of metal ions in the adsorbate–alumosilicate system was 60 min for Ni(II) ions (Fig. 2) and 90 min for Cu(II) ions (Fig. 3). In the case of natural alumosilicates, the time to reach equilibrium upon the adsorption of the Ni(II) and Cu(II) ions was 120 min [12]. As can be seen from the presented data (Fig. 3), alumosilicates modified by BTM-3 adsorb Cu(II) ions much better. The high adsorption value in this case can be explained by the presence of chemically active thiocarbamide groups in the compo-

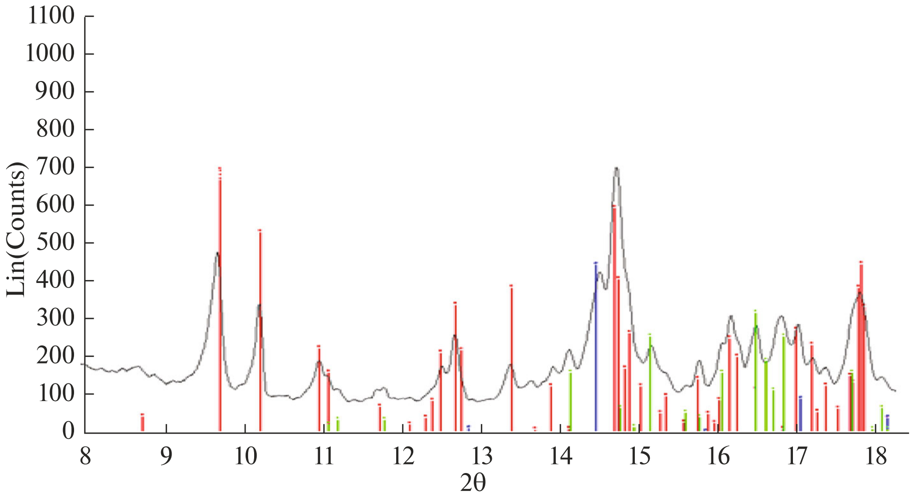

Fig. 1. Diffraction pattern of alumosilicate sample. — heulandite, — cristobalite, — sanidine.

sition of the coupling agent; and the process under study in this case is accompanied by the formation of stable coordination compounds on the surface of the material [13], which results in more efficient materials. If we compare their adsorbability with that of alumosilicates modified with HCl, the adsorption value for BTM-3 increases by a factor of 1.5; when compared with natural analogues [12], it increases by a factor of 1.7. The adsorption value of Ni(II) ions by the modified samples diverges slightly (Fig. 2, Table 1). If we compare the adsorption value for natural [12] and modified alumosilicates, its value more than doubles in the latter case.

Adsorption kinetics are usually described by the pseudo-first order equation

$$\log(A - A_\tau) = \log A - k\tau/2.303, \tag{2}$$

where A is adsorption, mmol/g; A_τ is adsorption in time τ, mmol/g; and k is the adsorption rate constant of the pseudo-first order, min^{-1}.

To determine the adsorption rate constant k and the correlation coefficient R^2, linear dependences $\log(A - A_\tau) = f(\tau)$ are used (Figs. 4, 5).

The values of the adsorption rate constant for Ni(II) and Cu(II) ions are obtained according to the slope of the presented dependences (Figs. 4, 5). The correlation coefficients are determined (Table 2).

The maximum value of the adsorption rate constant $3.18 \times 10^{-2}\ \text{min}^{-1}$ corresponds to Ni(II) ions, and the minimum of $0.72 \times 10^{-2}\ \text{min}^{-1}$ corresponds to Cu(II). The value of the correlation coefficient varies from 0.936 to 0.958. It can be concluded from this that the adsorption kinetics of Ni(II) and Cu(II) ions by the modified samples can be described by the pseudo-second order equation.

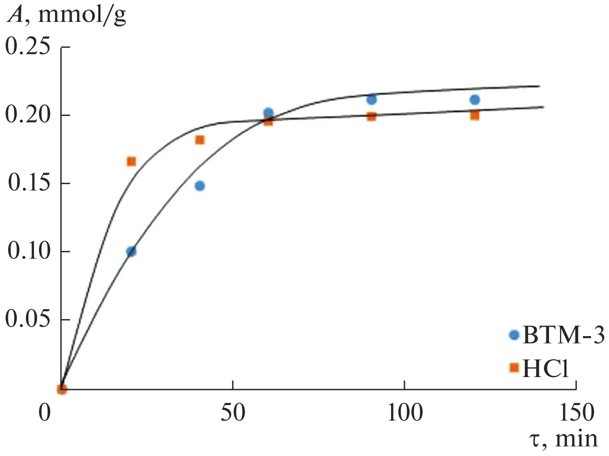

Fig. 2. Kinetic curves of adsorption of Ni(II) ions.

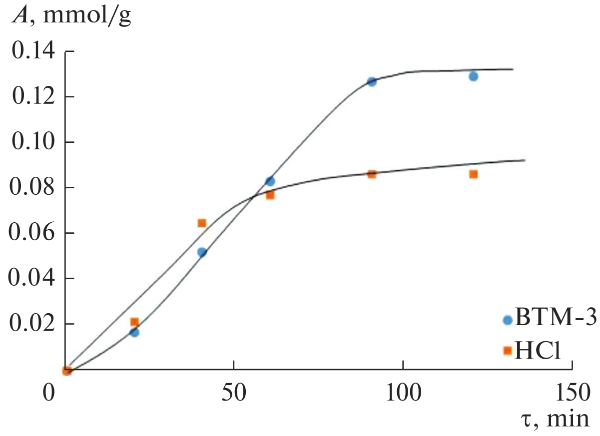

Fig. 3. Kinetic curves of adsorption of Cu(II) ions.

Table 1. Adsorption values of modified alumosilicates

Ions	Modified with BTM-3		Modified with HCl	
	A, mmol/g	A, mg/g	A, mmol/g	A, mg/g
Ni(II)	0.214	12.6	0.197	11.6
Cu(II)	0.128	8.1	0.085	5.4

Table 2. Rate constants of pseudo-first order equation

Ions	Modified with BTM-3		Modified with HCl	
	$k \times 10^2$, min^{-1}	R^2	$k \times 10^2$, min^{-1}	R^2
Ni(II)	1.85	0.947	3.18	0.950
Cu(II)	2.28	0.958	0.72	0.936

The pseudo-second order adsorption equation is

$$\tau/A_\tau = 1/h + \tau/A, \qquad (3)$$

where A is adsorption, mmol/g; A_τ is adsorption in time τ, mmol/g; h is the initial adsorption rate at $\tau \to 0$ $h = kA^2$, mmol/(g min); and k is the pseudo-second order adsorption rate constant, g/(mmol min).

The values of the initial adsorption rate and the pseudo-second order rate constant for Ni(II) and Cu(II) ions are determined from the size of the segments obtained at the intersection of the straight lines with the ordinate axis (Figs. 6, 7). The correlation coefficients are obtained (Table 3).

The initial adsorption rate of Ni(II) ions was 8.70×10^{-3} mmol/(g min) with alumosilicates modified with HCl and 5.26×10^{-3} mmol/(g min) for the samples modified with BTM-3. The maximum value of the adsorption rate constant 33.7×10^{-5} g/(mmol min) corresponds to Ni(II) ions, the minimum value of 1.40×10^{-5} g/(mmol min) corresponds to Cu(II) for HCl modifications. The value of the correlation coefficient is 0.997–0.998. From this we can conclude that the adsorption of Ni(II) and Cu(II) ions by modified alumosilicates can be described by the pseudo-second-order equation. It was previously established that the adsorption of Ni(II) and Cu(II) ions on alumosilicates

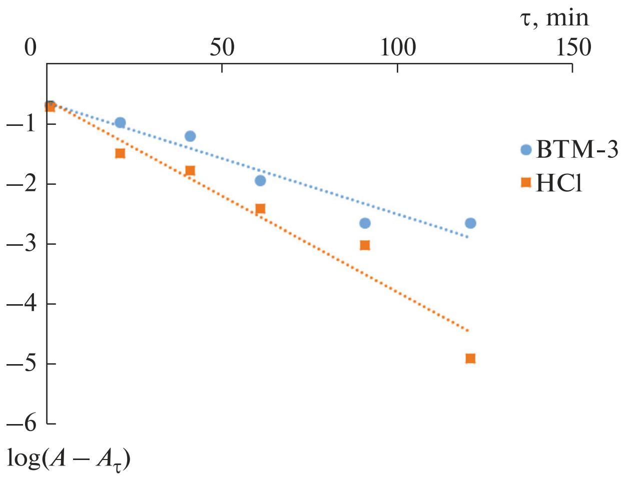

Fig. 4. Kinetic curves of adsorption of Ni(II) ions of the pseudo-first order.

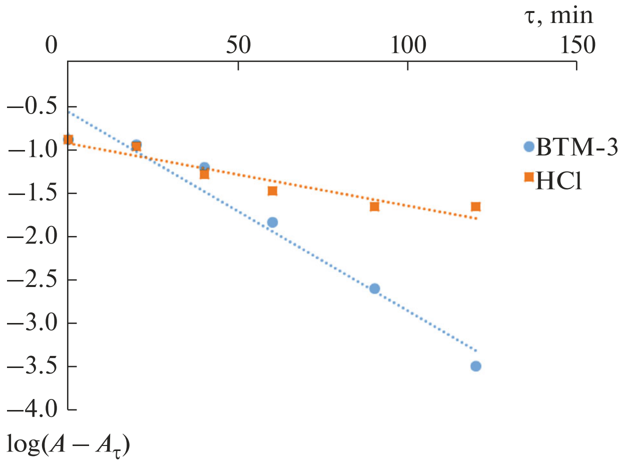

Fig. 5. Kinetic curves of adsorption of Cu(II) ions of the pseudo-first order.

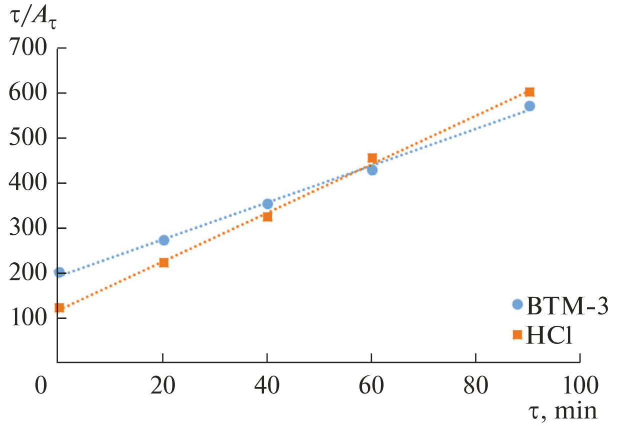

Fig. 6. Kinetic curves of adsorption of Ni(II) ions of the pseudo-second order.

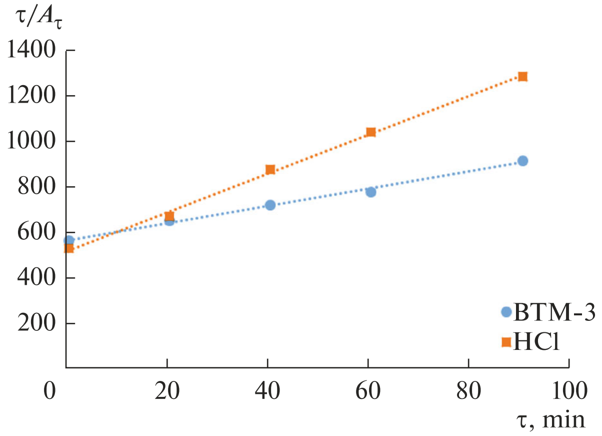

Fig. 7. Kinetic curves of adsorption of Cu(II) ions of the pseudo-second order.

modified with BTM-3 is most adequately described by the model of Langmuir and Freundlich adsorption [9]. When modifying HCl, the Langmuir adsorption model is most applicable [14].

Thus, it has been established that upon the modification of alumosilicates, the time required to establish the adsorption equilibrium is reduced by a factor of 1.33 during the adsorption of Cu(II) ions and by a factor of 2 for Ni(II) ions. The rate and energy of adsorption increase. Thus, the value of the free energy of the adsorption of Ni(II) ions of 17.74 and 12.50 kJ/mol for Cu(II) points to the ion-exchange mechanism [9, 15], and the fixation of heavy metal ions has a chemical nature.

CONCLUSIONS

1. The adsorption kinetics of Ni(II) and Cu(II) ions by alumosilicates modified with BTM-3 and HCl are studied using the kinetic models of the pseudo-first and pseudo-second orders.

2. It is shown that when modifying aluminosilicates, the time required to establish equilibrium is reduced by a factor of 1.33 during the adsorption of Cu(II) ions and by a factor of 2 for Ni(II) ions. The rate and energy of adsorption increase.

3. It has been established that the adsorption kinetics of the studied ions by modified alumosilicates was best described by the pseudo-second order model. The values of the correlation coefficients were 0.997–0.998.

4. The maximum value of the adsorption rate constant of 33.7 × 10^{-5} g/(mmol min) corresponds to Ni(II) ions for alumosilicates modified with HCl. The initial adsorption rate was 8.70 × 10^{-3} mmol/(g min).

5. The maximum value of the adsorption rate constant of 2.91 × 10^{-5} g/(mmol min) for aluminosilicates modified with BTM-3 corresponds to Cu(II) ions. At the same time, the initial adsorption rate was 1.78 × 10^{-3} mmol/(g min).

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Table 3. Rate constants of pseudo-second order equation

Ions	Modified with BTM-3				Modified with HCl			
	1/*h*	*h* × 10^3, mmol/(g min)	*k* × 10^5, g/(mmol min)	R^2	1/*h*	*h* × 10^3, mmol/(g min)	*k* × 10^5, g/(mmol min)	R^2
Ni(II)	190	5.26	24.1	0.998	115	8.70	33.7	0.998
Cu(II)	563	1.78	2.91	0.997	517	1.93	1.40	0.998

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