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Adsorption of Nickel (II) Ions by Aluminosilicates Modified by Poly-1-Vinyl Imidazole and Poly-4-Vinyl Pyridine

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Abstract—Data on the synthesis and sorption properties of natural calcium aluminosilicates modified by poly-1-vinyl imidazole (PVIm) and poly-4-vinyl pyridine (PVP) are presented. The fullest recovery of nickel (II) ions from low-concentration solutions is observed for PVP-modified aluminosilicates. Adsorption of nickel (II) ions by PVIm-modified aluminosilicates is best described by the Freundlich adsorption model. In the case of PVP-modified aluminosilicates, the Langmuir model is more adequate. The free adsorption energy values indicate that the interaction between nickel (II) ions and modified aluminosilicates is of a chemical nature.

Keywords: adsorption, modified aluminosilicates, poly-1-vinyl imidazole, poly-4-vinyl pyridine, nickel (II) ions

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INTRODUCTION

The reasons for using adsorption technologies for degreasing of industrial solutions and wastewaters are cleaning efficiency, the recovery rate of valuable components, the possibility of their use, and the availability of the adsorbent and its price. Thus, it appears to be of interest to look for new efficient adsorbents satisfying the above requirements. Such adsorbents include natural aluminosilicates [1–3].

Crystalline aqueous aluminosilicates contain elements of groups I and II of the Periodic System as mobile cations: sodium, potassium, magnesium, calcium, strontium, and barium. Aluminosilicates of this composition are of both natural and synthetic origin. They belong to the group of framework zeolites that form an infinite aluminosilicate framework by connection through common apices of AlO_4 and SiO_4 tetraheda [4].

The sorption capacity of aluminosilicates is one of the main parameters characterizing their adsorption and technological properties. The value of aluminosilicate adsorption can be considerably enhanced by modification of their surface with inorganic and organic compounds [5–10].

The aim of this work is modification of natural aluminosilicates of Eastern Transbaikal by high molecular vinyl derivatives of N-heterocyclic compounds and study of adsorption of nickel (II) ions on their surface.

EXPERIMENTAL

The objects of study were natural aluminosilicates of Eastern Transbaikal. A presieved fraction with a size of 1.0 mm was used in experiments. Table 1 provides the chemical composition of the studied aluminosilicates.

The Si/Al ratio (zeolite framework) was 3.5, which confirms that aluminosilicate belongs to the class of calcium heulandite according to the classification of J. Boles: the final member of the heulandite series has an Si/Al ratio of 2.9–3.0 and clinoptilolite is characterized by the ratio of 5.0–5.1. The ratio of 4.0 can be used to divide the series: 4.0 or more corresponds to clinoptilolite, while 4.0 or less corresponds to heulandite. Minerals with a ratio of >3.5 and <4.0 are considered silicon-rich heulandite and those with the ratio of >4.0 and <4.5 correspond to silicon-poor heulandite [3].

To modify natural aluminosilicates, the polymers poly-1-vinyl imidazole (PVIm) and poly-4-vinyl pyridine (PVP) obtained by binary radical polymerization of the corresponding monomers were used according to the technique from [11]. The functional groups of these polymers contain pyridine atoms of nitrogen capable of formation of ion-coordination complexes with nickel (II) ions. Modification of natural aluminosilicates by such polymers results in the appearance of additional reaction centers providing chemical adsorption of the metal.

Polymers were immobilized on the aluminosilicate surface as follows: a solution of 1 g of the polymer in 18 mL of ethanol was added to 1 g of aluminosilicate.

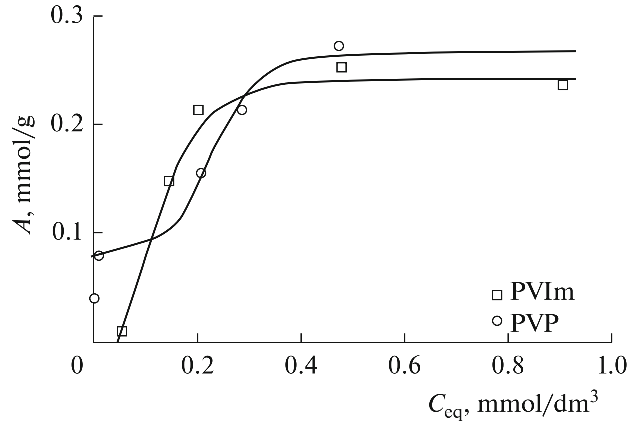

Fig. 1. Adsorption isotherms of nickel (II).

The obtained mixture was stirred for 6 h at the temperature of 20°C on an electromagnetic stirrer. At the end of this time, aluminosilicate was separated from the solution by filtration, washed by water and ethanol, and dried in a drying box at 100°C for 2 h. The obtained product was weighed. The calculated weight gain was 28–30%. Such modification results in polymer fixation on the aluminosilicate surface.

The presence of structural groups characteristic for natural aluminosilicates and modifier polymers in modified aluminosilicates was confirmed using IR spectroscopy. IR spectra were obtained using a Specord 75IR spectrophotometer.

IR spectra of the modified aluminosilicates manifest high-intensity absorption bands in the range of 794 and 727 cm^{-1} characterized by valence vibrations of the Al–O bond. A high-intensity absorption band at 1040 cm^{-1} corresponds to asymmetric valence vibrations of the Si–O–Si bond. The absorption band at 3441 cm^{-1} confirms the presence of the O–H bond. The absorption bands in the range of 1590–1600 cm^{-1} characterize the valence vibrations of the pyridine PVP nitrogen atom, while those at 1500–1510 cm^{-1} are typical for the PVIm azole cycle.

Table 1. Composition of zeolite-containing tuff of Eastern Transbaikal

Component	Content, %	Component	Content, %
SiO_2	63.72–68.09	FeO	0.17–0.73
Al_2O_3	16.52–17.18	TiO_2	0.07–0.23
K_2O	3.19–4.59	SO_3	0.13
Na_2O	1.7–2.97	SO	0.07
CaO	1.17–1.89	MnO	0.05–0.18
Fe_2O_3	0.44–1.97	P_2O_5	0.04–0.054
MgO	0.25–0.62	Rb_2O	0.045

Studies of adsorption properties of aluminosilicates with respect to heavy metal ions were carried out using model solutions prepared from $NiSO_4 \cdot 7H_2O$ (chemically pure grade) and distilled water. The choice of the initial concentration of model solutions was based on the actual composition of industrial electroplating wastewater containing nickel ions [12]. The content of nickel (II) ions in the solutions was determined using standard techniques [13].

The adsorption ability of the chosen aluminosilicates was studied using the statistic method. The method of constant-weight samples (1 g) and variable concentrations (5–200 mg/L) was used in the work. The volume of the studied solutions was 100 mL. The mass ratio of the liquid and solid phases was 1 : 100. Adsorption A, mmol/g, was calculated according to the formula

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

where C_0 and C_{eq} are the initial and equilibrium metal concentrations in the solution, mmol/L; V is the solution volume, L; and m is the sorbent mass, g.

RESULTS AND DISCUSSION

The adsorption ability of the modified aluminosilicates with respect to nickel (II) ions was estimated on the basis of an analysis of adsorption isotherms. The time in which adsorption equilibrium corresponding to the constant nickel (II) concentration in the solution was established was determined to be 2 h. The obtained isotherms are shown in Fig. 1.

The highest adsorption value in the low-concentration range is manifested by PVP-modified aluminosilicates (Fig. 1). The average adsorption value triples as a result of modification as compared to the initial aluminosilicates [14–17] and reaches 17 mg/g.

It is known that equilibrium in the adsorption system depends on the mature of the adsorbent–adsorbate interaction [18]. The adsorption models of Langmuir, Freundlich, BET, Dubinin–Radushkevich, etc., describe these interactions in different ways [19]. Therefore, it was advisable to study the possibility of applying the above models for interpretation of the obtained experimental data.

Thus, the Langmuir-isotherm equation takes the form of

$$A = A_\infty \frac{KC_{eq}}{1 + KC_{eq}}, \quad (1)$$

where A is the current adsorption value, mmol/g; A_∞ is the limiting adsorption value, mmol/g; K is the adsorption equilibrium constant; and C_{eq} is the equilibrium concentration of metal ions, $mmol/dm^3$.

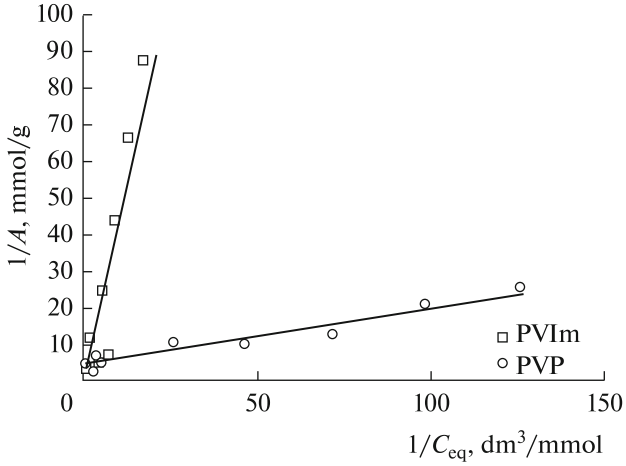

Fig. 2. Adsorption isotherm of nickel (II) in coordinates of linear form of the Langmuir equation.

Experimental data were processed using the Langmuir equation in the linear form:

$$\frac{1}{A}=\frac{1}{A_{\infty}}+\frac{1}{A_{\infty}K}\frac{1}{C_{\text{eq}}},\tag{2}$$

Plotted linear dependences (Fig. 2) were used to determine on the basis of y-intercept limiting adsorption nA_{∞}, and adsorption equilibrium constant K was found from the slope. The values are provided in Table 2.

The higher limiting adsorption value is characteristic for PVIm-modified aluminosilicates (Table 2). The values of correlation coefficients R^2 indicate that the Langmuir model most adequately describes adsorption of nickel (II) by PVP-modified aluminosilicate (Table 2).

It is known that the empirical Freundlich equation is widely used in the range of intermediate coverages of the nonuniform adsorbent surface:

$$A = K_{\text{F}}C_{\text{eq}}^{\frac{1}{n}},\tag{3}$$

where A is the adsorption value, mmol/g; C_{eq} is the equilibrium concentration of metal ions, mmol/dm^3; and K_{F} and n are constants. The Freundlich equation is most often used in a logarithmic form:

$$\log A = \log K_{\text{F}} + 1/n \log C_{\text{eq.}}.\tag{4}$$

Linear dependences of the logarithmic form of the Freundlich equation are plotted for the studied modified aluminosilicates (Fig. 3). They are used to determine constants K_{F} and n (Table 3).

Adsorption centers, according to the Freundlich models, are characterized by different energy values. Active adsorption centers with the maximum energy are the first to be filled. Constants K_{F} and n allowed comparing the adsorption ability of modified aluminosilicates. In 1 M solution of nickel (II) ions, the adsorption value of these ions is equal to constant K_{F} and parameter n characterizes the adsorbent–adsorbate interaction intensity.

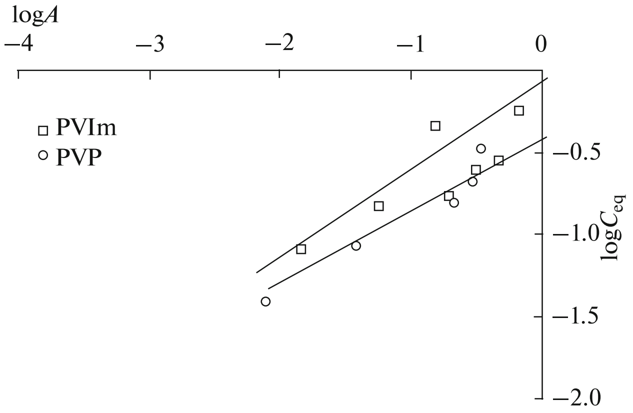

Fig. 3. Adsorption isotherm in coordinates of linear form of the Freundlich equation.

Adsorption of nickel (II) ions on PVIm-modified aluminosilicate is faster in the initial period of time. In the case of a PVP-modified adsorbent, a more intense interaction occurs between the adsorbent and nickel (II) ions (Fig. 3, Table 3).

The equilibrium data of the adsorption process were processed using the Dubinin–Radushkevich model isotherm:

$$A = A_{\text{m}}\exp(-k\,\varepsilon^2),\tag{5}$$

where k is a constant (mol^2/kJ^2) related to adsorption energy and ε is the Polanyi potential (kJ/mol) characterizing the isothermal work of transferring 1 mol of nickel (II) ions from the equilibrium solution bulk to the adsorbent surface determined from the expression

$$\varepsilon = RT\ln(1 + 1/C),\tag{6}$$

where R is the universal gas constant, kJ/mol K, and T is the absolute temperature, K.

Dubinin–Radushkevich Eq. (7) in logarithmic form is

$$\ln A = \ln A_{\text{m}} - \text{k}\,\varepsilon^2.\tag{7}$$

The dependences of $\ln A = f(\varepsilon^2)$ are plotted using Dubinin–Radushkevich adsorption Eq. (7) (Fig. 4).

Table 2. Parameters of the Langmuir model

Modifiers	A_{∞}, mmol/g	A_{∞}, mg/g	K	R^2
PVIm	0.289	17.023	8.693	0.689
PVP	0.251	14.820	25.165	0.956

Table 3. Parameters of the Freundlich model

Modifiers	K_F	n	R
PVIm	0.915	0.692	0.945
PVP	0.398	2.270	0.906

Table 4. Parameters of the Dubinin–Radushkevich model

Modifiers	A_m, mmol/g	k, mol^2/kJ^2	E, kJ/mol	R
PVIm	0.475	0.0045	10.54	0.874
PVP	0.248	0.0019	16.22	0.936

The slopes and y-intercept of the lines were used to determine constants k and A_m. The Dubinin–Radushkevich model indicates the nature of adsorption of the adsorbate on the adsorbent and can be used for calculation of the free adsorption energy:

$$E = (-2k)^{-0.5}. \quad (8)$$

The obtained results are presented in Table 4.

It is known that, if the value of E is within the range of 8 and 16 kJ/mol, the adsorption process occurs according to the chemosorption mechanism. If E is lower than 8 kJ/mol, the adsorption process is physical. In our case, the values of free adsorption energy for modified aluminosilicates indicate that the recovery of nickel (II) ions is of chemical nature.

CONCLUSIONS

(1) Immobilization of poly-1-vinylmidazole and poly-4-vinyl pyridine on the surface of natural aluminosilicates is used to obtain modified adsorbents for recovery of nickel (II) ions. The highest value of adsorption of nickel (II) ions in the low-concentration range is characteristic for aluminosilicates modified by poly-4-vinyl pyridine (PVP).

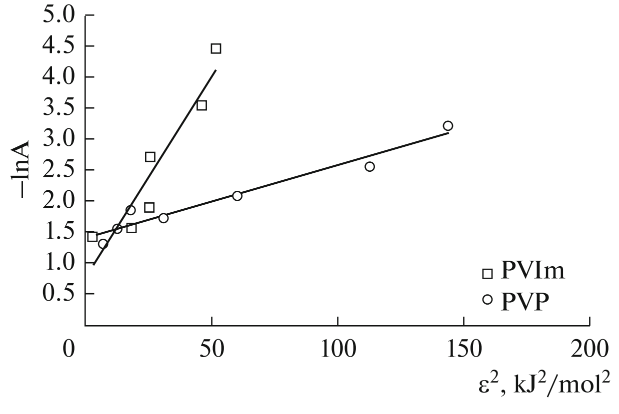

Fig. 4. Adsorption isotherm in coordinates of linear form of the Dubinin–Radushkevich equation.

(2) The adsorption process of Ni(OO) ions is studied, and adsorption isotherms are plotted. The experimental data were processed using the models of Langmuir, Freundlich, and Dubinin–Radushkevich. The constants of these equations are determined. It is shown that adsorption on PVIm-modified aluminosilicates is best described by the Freundlich adsorption model, while adsorption on PVP-modified aluminosilicates is best described by the Langmuir model.

(3) The free adsorption energy values calculated using the Dubinin–Radushkevich model point to the chemosorption mechanism of recovery of nickel (II) ions. This is possible both due to ion-exchange groups of the natural aluminosilicate and functional groups of the organic-modifier polymer.

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