

PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

The Mechanism of Adsorption of Zinc and Cadmium Ions onto Bentonite Clay

A. V. Kostin, L. V. Mostalygina, and O. I. Bukhtoyarov

Kurgan State University, Kurgan, Russia

e-mail: alexandr.v.kostin@gmail.com

Received March 26, 2014

Abstract—Adsorption of zinc and cadmium ions onto bentonite clays from the Zyryanskoe deposit (Kurgan region, Russia) was studied as a function of contact duration, pH, and temperature. Silanol and aluminol groups of the clay were found to participate in ion exchange and in complex formation with zinc and cadmium ions; a certain process prevails depending on pH. Adsorption of zinc and cadmium ions from equimolar binary solutions was studied. Adsorption of ions onto clay increases with temperature increasing from 293 to 333 K. Adsorption mechanisms of Zn(II) and Cd(II) ions were proposed.

DOI: 10.1134/S2070205115050172

INTRODUCTION

Copper, cadmium, lead, and zinc are the most common heavy metals (ecotoxicants). We focused on the behavior of zinc and cadmium ions in the presence of bentonite clay. Cadmium is likely to accompany zinc in natural objects. Zinc and cadmium are widely used in technology to apply galvanic coatings (cadmium and zinc plating), to manufacture galvanic cells (zinc galvanic cells) and storage batteries (nickel–cadmium batteries), to protect steel from corrosion, and to perform metallothermic reactions (extraction of metals and production of hi-tech alloys).

Since montmorillonite has a high specific surface area and cation-exchange capacity, it can ensure effective adsorption of ions of these metals. Adsorption of Zn²⁺ and Cd²⁺ ions under their copresence in the model solution were studied, and adsorption mechanisms of these ions were proposed.

EXPERIMENTAL

An average sample of coarsely ground bentonite clay was dried to constant weight at 105 ± 5°C for 3 h and passed through a sieve with 0.1-mm mesh size.

To determine the adsorption capacity of clay, a 1.0000-g sample was placed into 50.00 mL of the model zinc(II) or cadmium(II) nitrate solution with a concentration of 0.004–0.1 mmol/L at room temperature or into 50 mL of the solution containing equimolar amounts of ion metals and left for 24 h under static conditions. Metal ion concentration in the solution before and after adsorption was determined by inversion voltammetry (Voltammetric Complex STA, OOO YuMKh, and Research Laboratory of Microimpurities, Tomsk Polytechnic University).

Adsorption (*a*) was calculated using the formula

$$a = \frac{(C_0 - C_p)V \times 1000}{m_r},$$

where *a* is adsorption (mmol/g), *C*₀ is the initial concentration of metal ion (mol/L), *C*_{eq} is the equilibrium concentration of metal ion (mmol/L), *V* is the volume of metal salt solution (L), and *m*_c is weight of clay (g).

The thermodynamic and kinetic parameters of adsorption were determined in the temperature range from 293 to 333 K.

RESULTS AND DISCUSSION

Characteristics of Bentonite Clay

Previous studies have demonstrated that the phases that can be isolated in the samples of bentonite clay from the Zyryanskoe deposit are as follows: montmorillonite, low-temperature quartz, illite, kaolinite, and palygorskite (Fig. 1) [1]. Montmorillonite is the main rock-forming mineral in native clay from the Zyryanskoe deposit. According to Brindley [2], its composition corresponds to the formula Na_{0.3}(Al, Mg)₂Si₄O₁₀(OH)₂ · 8H₂O.

IR spectroscopic examination of bentonite clay as a suspension in a thin layer of mineral oil showed that the spectrum contains two broad bands at 3608 and 3368 cm⁻¹, which are likely to belong to relaxation oscillations of OH–silanol (Si–OH) and H–OH (water) groups, respectively (Fig. 2) [3]. The peak at 1628 cm⁻¹ also corresponds to bond vibrations in water molecule. The remaining peaks in the range of from 1300 to 400 cm⁻¹ correspond to vibrations of the Si–O bond and cannot be quantitatively described under these conditions.

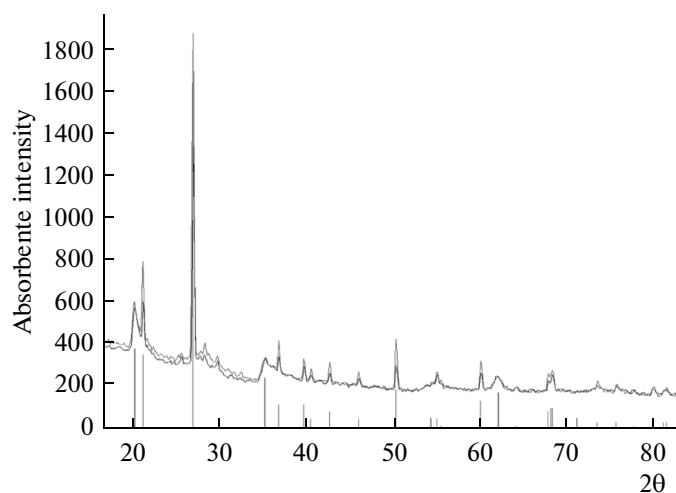


Fig. 1. X-ray diffraction pattern of bentonite clay from Zyryanskoe deposit (Kurgan region, Russia).

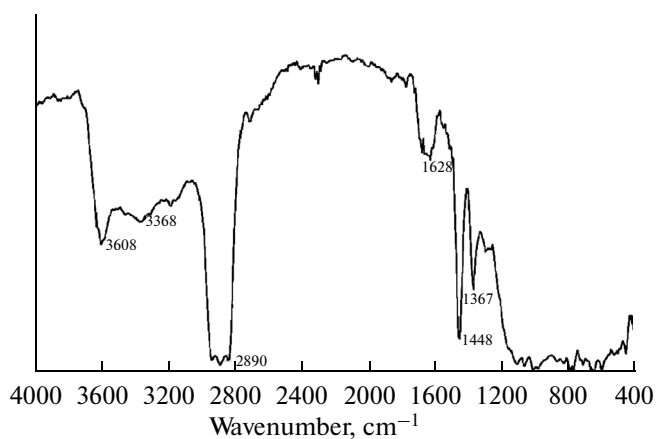


Fig. 2. IR spectrum of bentonite clay from Zyryanskoe deposit (Kurgan region, Russia).

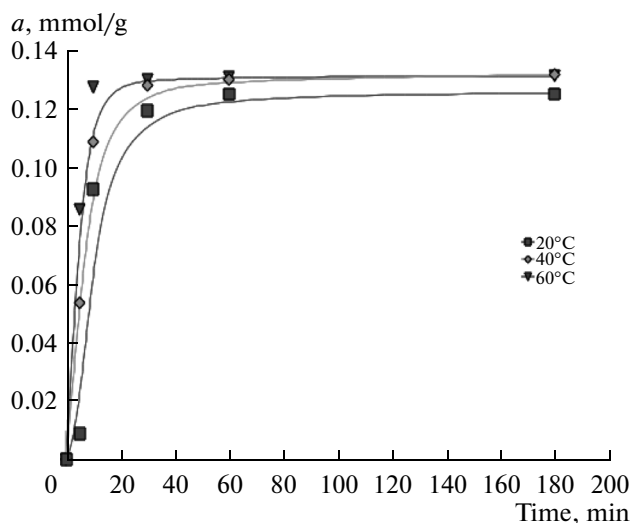


Fig. 3. Kinetic curves of adsorption of cadmium ions ($C_0 = 0.1$ mmol/L).

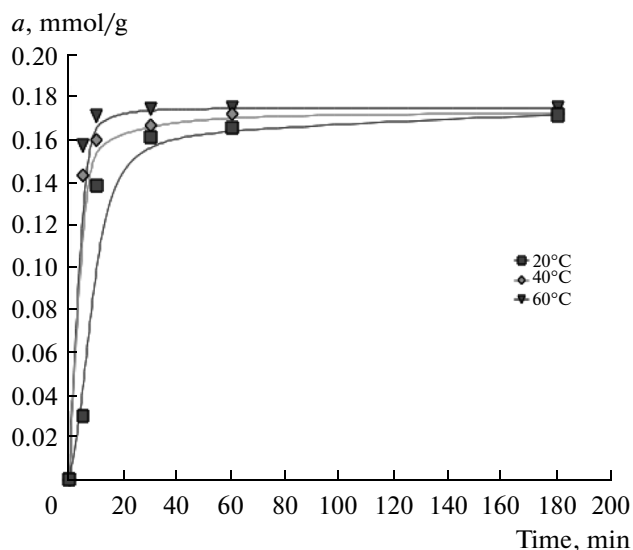


Fig. 4. Kinetic curves of adsorption of zinc ions ($C_0 = 0.1$ mmol/L).

Investigation of Adsorption Rate

Investigation of the kinetic parameters of adsorption of Cd^{2+} and Zn^{2+} ions onto preswollen bentonite clay in the temperature range from 273 to 333 K demonstrated that the time required to reach equilibrium ($T = 293$ K) is less than 1 h (Figs. 3 and 4). The adsorption rate of the ions under study is maximum ($v_{\text{Zn}} = 2.3 \times 10^{-3}$, $v_{\text{Cd}} = 1.5 \times 10^{-3}$) during the first 20 min.

The empirical equations (diffusion model [3]) show the equilibrium concentration of metal ions as a function of their contact time with clay at different temperatures: $C_{\text{eq}} = kt^n$, where C_{eq} is the equilibrium concentration of metal ion (mmol/L), t is contact

time (min), and k and n are the constants of the diffusion equation and are shown in Table 1.

Analysis of these dependences demonstrates that the constant k increases in a regular manner with increasing temperature, while n decreases in all cases. It indicates that the rate of ion transfer to clay surface increases, which favorably affects the adsorption process [3].

Effect of pH of Medium on Adsorption of Cd^{2+} and Zn^{2+} Ions

The effect of pH of the medium on adsorption of cadmium and zinc ions onto bentonite clay was studied in the pH range of 1–13 (Figs. 5 and 6). Molar

concentrations of metal ions were 0.025 mmol/L and 0.1 mmol/L. 1 M solutions of nitric acid and sodium hydroxide were used to control pH.

A number of researchers [4] distinguish three portions in the curves having a similar shape. According to our data, ~40% of cadmium ions are adsorbed on the first portion in the pH range of 1–4; adsorption of cadmium ions in the pH range of 4–6 increases to 90%, and at pH 6–12 it is more than 90%. For zinc ions, the adsorption curve has a similar shape: 40% of zinc ions are adsorbed at pH 1–5; up to 90%, at pH 5–6; and over 90%, at pH 6–12.

The pH value at which complex formation on the clay surface starts was determined using the pH versus $\ln a$ curve: 4.93 for cadmium and 5.27 for zinc (Figs. 7 and 8). In the pH range above the kink points in metals, the formation of outer-sphere complexes competes with deposition of $\text{Me}(\text{OH})_2$ on the clay surface; the ion exchange process predominates in the range of low pH values, while formation of outer-sphere complexes occurs to a lesser extent.

Adsorption of heavy metal ions onto clays is known to include two main mechanisms: the ion exchange mechanism and formation of chelate complexes with surface hydroxyl groups of the mineral [5]. If ion exchange takes place under conditions of hydrogen ion desorption for diluted solutions of metal ions, equation of the reaction is as follows:

$2\text{RH} + \text{Me}^{2+} \leftrightarrow \text{MeR}_2 + 2\text{H}^+$, the conditional rate constant (K') of this process is

$$K' = \frac{[\text{M}^{n+}]_c [\text{H}^+]_p}{[\text{M}^{n+}]_p};$$

the conditional distribution constant (K_D) is

Table 1. Parameters of the empirical kinetic equation $C_p = kt^n$ at different adsorption temperatures

System	T, K	k	n
Cd^{2+} (0.05 mmol/L)	293	0.0162	0.2069
Cd^{2+} (0.05 mmol/L)	313	0.0250	0.1146
Cd^{2+} (0.05 mmol/L)	333	0.0325	0.0554
Zn^{2+} (0.05 mmol/L)	293	0.0032	0.5224
Zn^{2+} (0.05 mmol/L)	313	0.0247	0.0531
Zn^{2+} (0.05 mmol/L)	333	0.0283	0.0279

$$K'_D = \frac{[\text{M}^{n+}]_c}{[\text{M}^{n+}]_p},$$

then,

$$K' = K'_D [\text{H}^+]^n,$$

$$\log K' = \log K'_D + n \log [\text{H}^+],$$

$$\begin{aligned} \log K'_D &= \log K' - n \log [\text{H}^+] = \log K' + np\text{H} \\ &= \text{const} + np\text{H}, \end{aligned}$$

where $[\text{M}^{n+}]_p$ is the equilibrium concentration of metal ion in the solution, $[\text{M}^{n+}]_c$ is the equilibrium concentration of metal ion on sorbent surface, and $[\text{H}^+]_p$ is the equilibrium concentration of hydrogen ions in the solution.

If the adsorption mechanism includes only ion exchange, the slope ratio of the curve ($\tan \alpha$) plotted in coordinates $\log K_D - \text{pH}$ will be equal to 2 for double

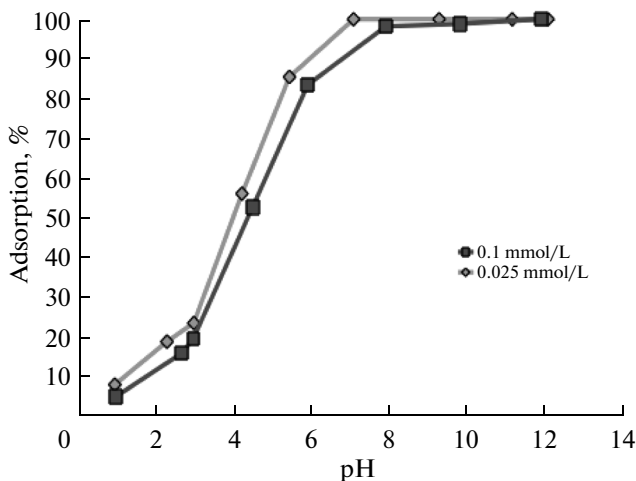


Fig. 5. Curve of adsorption of Cd^{2+} ions in the pH range 1.0–12.0 ($C_{in} = 0.025 \text{ mmol/L}$).

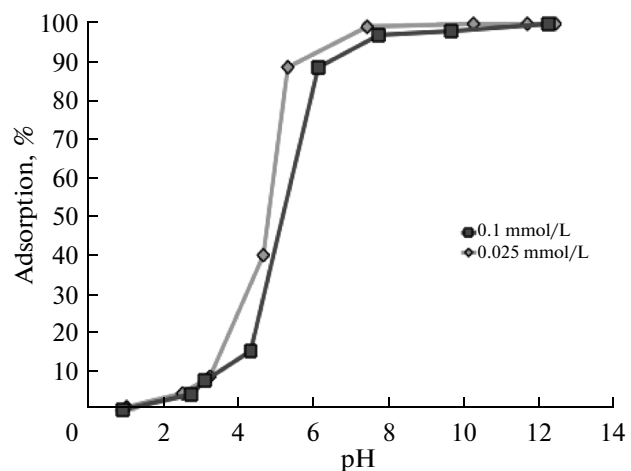


Fig. 6. Curve of adsorption of Zn^{2+} ions in the pH range 1.0–12.0 ($C_{in} = 0.025 \text{ mmol/L}$).

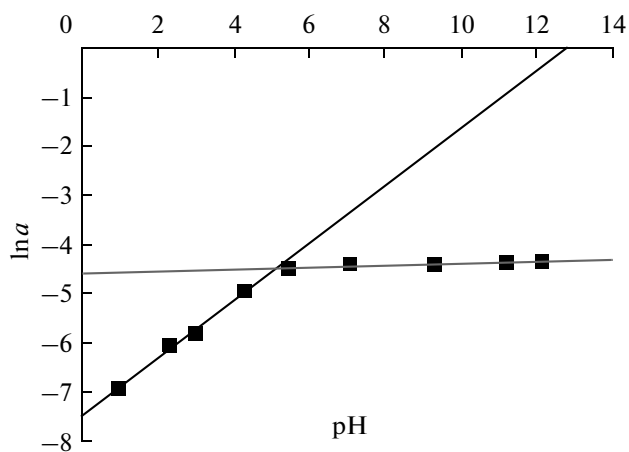


Fig. 7. Curve of adsorption of Cd^{2+} ions in the pH range 1.0–12.0 on a logarithmic scale ($C_{\text{in}} = 0.025$ mmol/L).

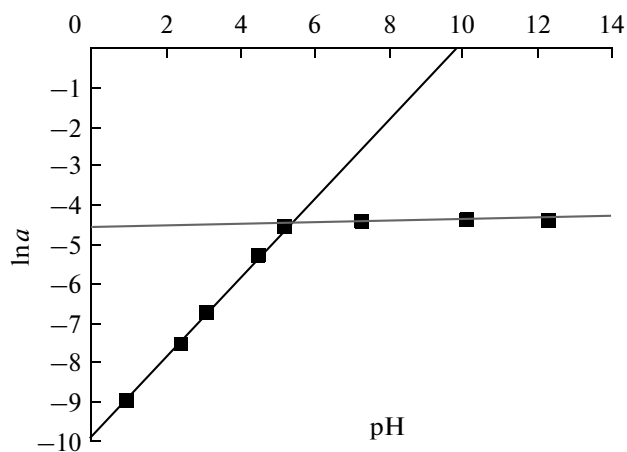


Fig. 8. Curve of adsorption of Zn^{2+} ions in the pH range 1.0–12.0 on a logarithmic scale ($C_{\text{in}} = 0.025$ mmol/L).

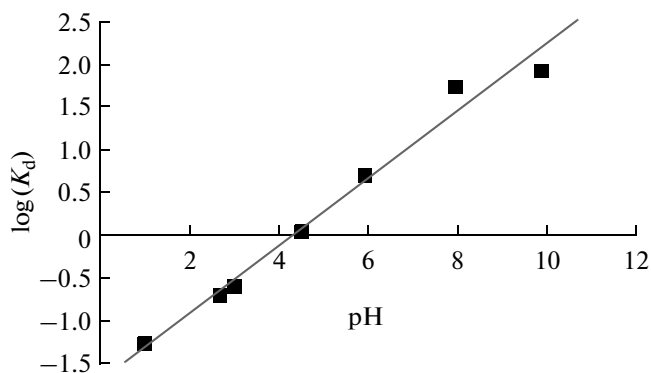


Fig. 9. $\log K'_D$ as a function of pH for cadmium ions ($C_{\text{in}} = 0.025$ mmol/L).

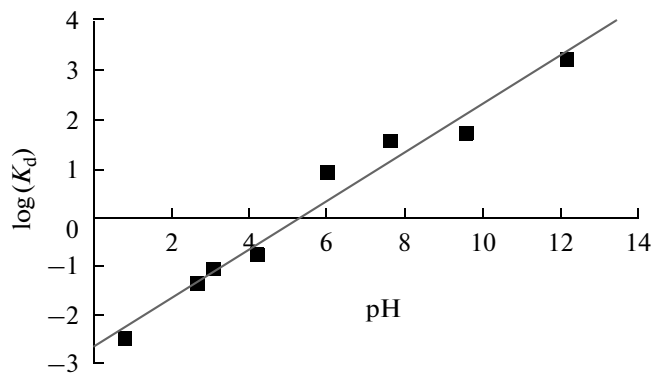


Fig. 10. $\log K'_D$ as a function of pH for zinc ions ($C_{\text{in}} = 0.025$ mmol/L).

charged metal ions [6]. For adsorption of cadmium and zinc ions, the slope angles are 0.33° and 0.5° , respectively (Figs. 9 and 10). This means that the interaction of cadmium and zinc ions with bentonite clay includes other mechanisms than the purely ion exchange mechanism. The linear dependence of $\log K'_D$ on pH indicates that the conditional distribution constant of the adsorption process depends on the acidity of the medium (the correlation coefficient (r) for cadmium and zinc ions is 0.970 and 0.986, respectively). The acidity in the half-adsorption point ($\text{pH}_{50\%}$, in the coordinates $\ln \alpha - \text{pH}$) coincides with the onset of formation of $\text{Me}(\text{OH})^+$ complexes in the solution, which is clearly seen in diagrams of hydroxo complexes [7]. Thus, the surface hydroxyl groups participate both in ion exchange and in formation of hydroxo complexes with heavy metal ions. The formation of chelate hydroxo complexes with heavy metal ions on the sorbent surface probably takes place at pH above $\text{pH}_{50\%}$. In addition, deprotonation of the mineral surface takes place at high pH values. As a result, montmoril-

lonite surface becomes negatively charged, which contributes to electrostatic interaction between the positively charged ions of heavy metals and the negatively charged clay surface [4].

Isotherms of Cd^{2+} and Zn^{2+} Adsorption onto Bentonite Clay

The isotherms of Zn^{2+} and Cd^{2+} adsorption onto bentonite clay were recorded in the range of initial concentrations from 0.004 to 0.1 mmol/L (Fig. 11). Analysis of the experimental adsorption isotherms of zinc and cadmium ions demonstrated that they coincide to the greatest extent with the model of the classical Freundlich isotherm (the correlation coefficient for zinc and cadmium is 0.949 and 0.906, respectively). In the $\text{Zn}(\text{NO}_3)_2\text{-Cd}(\text{NO}_3)_2\text{-clay}$ system, they are best fitted by the model of Langmuir monomolecular adsorption ($r = 0.978$ and 0.967, respectively). When adsorption in this system is fitted by the

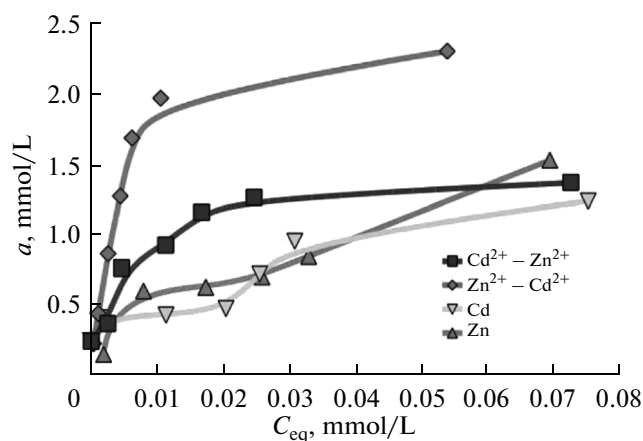


Fig. 11. Adsorption isotherms of cadmium(II) and zinc(II) ions.

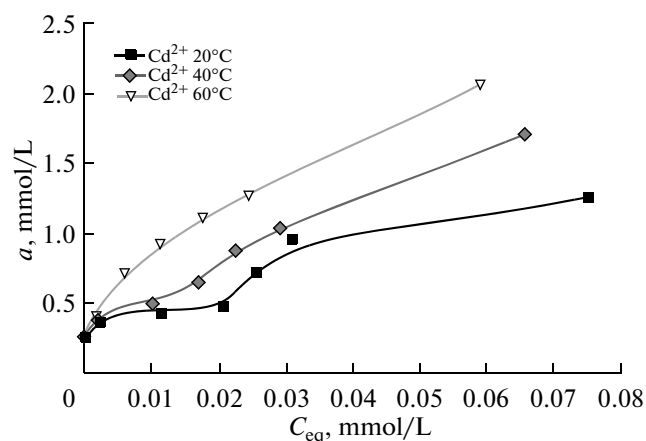


Fig. 12. Adsorption isotherms of cadmium(II) ions at different temperatures.

Freundlich equation, the correlation coefficients are lower ($r = 0.884$ and 0.925 , respectively).

In the concentration range under study, zinc and cadmium hydroxo complexes start to be formed in the alkaline region at $\text{pH} \sim 8$ and higher; the poorly soluble complex $\text{Me}(\text{OH})_2$ is formed at $\text{pH} \sim 9$ in addition to complexes of $\text{Me}(\text{OH})^+$ type [7]. A number of researchers have found that the adsorptive capacity of montmorillonite with respect to positively charged hydroxo complexes of heavy metals $\text{Me}(\text{OH})_x^{n-x}$ is higher than with respect to Me^{n+} ions [5, 8]. Outer-sphere complexes (including polynuclear ones) can also be formed on the clay surface [9, 10]; the bond may emerge between different ligands on the surface and water molecules in the coordination sphere of the Me^{n+} complex. Outer-sphere complexes are characterized by low stability, and they are formed in diluted solutions. These complexes can be converted into more stable inner-sphere complexes accompanied by the release of water molecules as the temperature or metal concentration increase [7, 10].

Stability of the bond between metal cation and clay surface is affected by stability of the $(\text{Me}(\text{OH})_x^{n-x})$ hydroxo complex [5, 8]. The stability constants (β_1) of $\text{Zn}(\text{OH})^+$ and $\text{Cd}(\text{OH})^+$ are 1.1×10^6 and 4.7×10^3 , respectively, which explains why adsorption of zinc is higher compared to cadmium (Fig. 11).

Adsorption of Zn^{2+} ions in the presence of Cd^{2+} and adsorption of Cd^{2+} ions in the presence of Zn^{2+} (equimolar amounts) were studied (Fig. 11). Adsorption of zinc is almost twice as high as that of cadmium.

The adsorption isotherms of metal ions are similar at different temperatures, indicating that they are characterized by the same adsorption mechanism (Figs. 12 and 13).

The Gibbs free energies were calculated for the adsorption of Cd^{2+} and Zn^{2+} at 293, 313, and 333 K

(Table 3). The resulting negative values indicate that this process is spontaneous.

ΔG increases with temperature, implying that the strength of the sorbent–sorbate bond also increases reliably, although slightly. The increase in adsorption with temperature may be due to the following processes:

- (1) pore size in the montmorillonite structure changes and the number of active sites of adsorption increases because some internal bonds on the montmorillonite surface are disrupted [4];
- (2) the percentage and activity of heavy metal ions in the solution, affinity of ions to the surface, and potential of the montmorillonite surface charge increase; and
- (3) the rate of ion diffusion into montmorillonite pores increases [4].

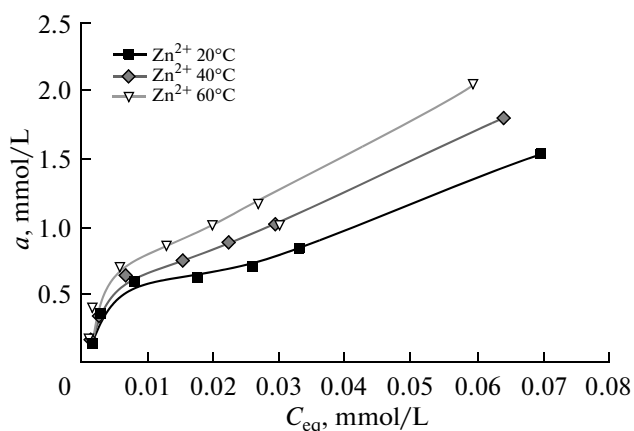


Fig. 13. Adsorption isotherms of zinc(II) ions at different temperatures.

Table 2. Parameters of the Langmuir and Freundlich equations for adsorption of Zn²⁺ and Cd²⁺ onto bentonite clay from the Zyryanskoe deposit

The adsorption isotherm is fitted by the Langmuir equation $a = a^{\infty} (C/(K + C))$			
System	a^{∞}	K	r
Zn ²⁺ –clay	1.7859	0.0243	0.841
Zn ²⁺ (Cd ²⁺)–clay	2.5152	0.0046	0.978
Cd ²⁺ –clay	1.3560	0.0159	0.682
Cd ²⁺ (Zn ²⁺)–clay	1.4495	0.0045	0.967
The adsorption isotherm is fitted by the Freundlich equation $a = k \cdot C^n$			
System	k	n	r
Zn ²⁺ –clay	5.2733	0.5081	0.949
Zn ²⁺ (Cd ²⁺)–clay	17.4375	0.5316	0.884
Cd ²⁺ –clay	1.3080	0.1691	0.906
Cd ²⁺ (Zn ²⁺)–clay	3.6763	0.3210	0.925

Table 3. Gibbs free energy of adsorption of Cd²⁺ and Zn²⁺ ions onto bentonite clay at different temperatures

System	T, K	$\Delta G, kJ/mol$
Cd ²⁺ –bentonite clay	293	-13.23 ± 0.04
	313	-14.52 ± 0.02
	333	-15.76 ± 0.07
Zn ²⁺ –bentonite clay	293	-2.61 ± 0.05
	313	-3.37 ± 0.04
	333	-4.15 ± 0.07

CONCLUSIONS

The results of the study have demonstrated that

(1) surface silanol and aluminol groups of clay are involved both in ion exchange and complex formation with heavy metal ions;

(2) the mineral surface is deprotonated at high pH and becomes negatively charged, thus facilitating electrostatic interaction between heavy metal ions and the surface;

(3) adsorption isotherms of Zn²⁺ and Cd²⁺ ions in the range of initial concentrations from 0.004 to 0.1 mmol/L when clay contacts with the individual and binary solutions of metal salts are fitted well by the Freundlich equation with high values of correlation coefficients;

(4) studies of the adsorption from individual solutions of metal ions in the specified concentration range show that zinc ions are adsorbed more effectively than cadmium ones;

(5) for equimolar binary solutions, the effectiveness of adsorption of zinc ions in the presence of cadmium is much higher than cadmium ions in the presence of zinc; and

(6) the isotherms of adsorption of metal ions onto bentonite clay are similar at different temperatures, which indicates that the adsorption mechanism is the same; the time required to reach equilibrium is less than 1 h; and increased temperature has a favorable effect on adsorption.

REFERENCES

- Mostalygina, L., Elizarova, S., and Kostin, A., *Bentoni-tovoye gliny: sorbtionnye protsessy v prirodookhranitel'nykh tekhnologiyakh* (Bentonite Clays: Implementation of Sorption in Environmental Technologies), Saarbrücken: LAP LAMBERT Acad., 2011.
- Brindley, G., *ICDD Grant-in-Aid*, University Park, PA: Penn State Univ., 1977.
- Wu, X.L., Zhao, D., and Yang, S.T., *Desalination*, 2011, vol. 269, p. 84.
- Yan, L., Shan, X., Wen, B., and Owens, G., *J. Hazard. Mater.*, 2008, vol. 156, nos. 1–3, p. 499.
- Bhattacharyya, K.G. and Gupta, S.S., *Adv. Colloid Interface Sci.*, 2008, vol. 140, no. 2, p. 114.
- Appel, C. and Ma, L., *J. Environ. Qual.*, 2002, vol. 31, p. 581.
- Charles, F., et al., *The Hydrolysis of Cations*, New York: Wiley, 1976.
- Zhu J. et al., *Chemosphere*, 2011, vol. 84, p. 484.
- Jolive, J.P., *Metal Oxide Chemistry and Synthesis – From Solution to Solid State*, New York: Wiley, 2000.
- Kopylovich, M.N., et al., *J. Mol. Catal. A: Chem.*, 2003, vol. 206, p. 163.

Translated by D. Terpilovskaya