Full Articles

On the adsorption mechanism of copper ions on bentonite clay

A. I. Vezentsev,[a] N. M. Gorbunova,[a] P. V. Sokolovskiy,[b]★ S. G. Mar´inskikh,[c,d] A. V. Chub,[e]
Nguyen Hoai Chau,[f] and A. A. Greish [b]

[a]Belgorod State National Research University,
85 ul. Pobedy, 308015 Belgorod, Russian Federation.
E-mail: vesentsev@bsu.edu.ru, natrase@mail.ru
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prospect, 119991 Moscow, Russian Federation.
E-mail: levap90@list.ru, agreish@yandex.ru
[c]LLC "Company BENTONIT,"
Build. 1, 12 ul. Tverskaya, 125009 Moscow, Russian Federation
[d]Tyumen Industrial University,
38 ul. Volodarskogo, 625000 Tyumen, Russian Federation.
E-mail: marinskih@bentonit.ru
[e]LLC "Leading,"
1a ul. Lermontova, Bol´shoe Polpino, 241903 Bryansk, Russian Federation.
E-mail: chub@bentonit.ru
[f]Vietnam Academy of Science and Technology, Institute of Environmental Technology,
650000 Hanoi, Vietnam.
E-mail: nhchau.iet@gmail.com

The adsorption of copper ions on bentonite clay was studied as a function of the pH of the medium, contact time, and temperature. A comparative study of the applicability of the Langmuir and Freindlich adsorption models for the description of the experimental adsorption isotherms of Cu^{2+} was carried out. The constants and parameters of the equations describing the adsorption equilibrium were determined. The correlation coefficients (R^2) indicate that both models satisfactorily outline the sorption process. However, the Langmuir adsorption isotherm is more preferable for describing adsorption of Cu^{2+} ions on bentonite clay, since it allows one to determine the limiting adsorption capacity. The adsorption of Cu^{2+} ions on bentonite clay increases as the temperature increases from 293 to 333 K. At the same time, the shape of the adsorption isotherms remains unchanged.

Key words: kinetics, adsorption mechanism, montmorillonite, bentonite clay, copper ions, water purification.

Heavy metals are dangerous pollutants of hydrosphere. Among them copper is the most abundant source of contamination. Various methods, such as electrolytic deposition, complexation, and adsorption, are applied for water purification from copper ions. The following ion-exchange materials are used as adsorbents of copper ions: mineral, carbon, and composite adsorbents, ion-exchange resins, and zeolites. Natural bentonite clays are the most available and cheap adsorbents in industrial purification processes.[1] The main rock-forming mineral of bentonite clays is montmorillonite (>60 wt.%). Bentonite clays contain as foreign components quartz, feldspars, calcite, a number of organic substances, other clay minerals: kaolinite, illite, mixed layered minerals, and more rarely chlorite and vermiculite.

Montmorillonite and, correspondingly, bentonite clays have interesting sorption and ion-exchange properties. Montmorillonite contains in the interpackage positions metal cations acting as exchange cations. The most abundant exchange cation in bentonites is Ca^{2+}. However, bentonites bearing Na^+ and H^+ as exchange cations are characterized by a significantly higher activity. The earlier studies showed a high efficiency of water purification using adsorbents based on bentonite clays.[2—9] The data on high efficiency of clays in radionuclide removal were published.[10,11]

Montmorillonite is efficiently applied as a sorbent of heavy metals.[12—16] Pillaration[17] makes it possible to considerably enhance the adsorption capacity of montmorillonite clay toward Cd^{2+} ions and organic dyes.[18]

Montmorillonite clay is of most interest for the purification of sewage from copper (Cu^{2+}) and nickel ions.[19—24] Hydrogels of montmorillonite are characterized by high adsorption capacity toward Cu^{2+} and Pb^{2+} ions.[25,26]

Presently, montmorillonite can serve as an enteroadsorbent for removal from organisms of human and agricultural animals of toxins, heavy metal ions, radionuclides, and other harmful substances. The animal and human organisms absorb copper ions with food products, since the copper-based preparations are used to suppress the development of negative fungal microflora. However, when using bentonite clays as food additives, one should take into account specific features of adsorption of diverse compounds, in particular, equilibrium and kinetic characteristics of the adsorption process. The limiting adsorption capacity and adsorption mechanism are significant. The equilibrium in the adsorption system depends on the nature of interaction of the adsorbent with adsorbate, pH of the medium, and adsorbate concentrations in a solution.[27] As known, the Henty equation is used at low concentrations of the adsorbed substance for the description of the sorption process and interpretation of experimental data, whereas the Freundlich or Langmuir equation is used as medium adsorbate concentrations depending on the character of interaction of the adsorbate with adsorb-

ent.[28,29] The known models for the Langmuir and Freundlich adsorption describe this interaction in different ways. The Langmuir isotherm is known to characterize coverage of the uniform surface, whereas the Freundlich isotherm equation is applicable to adsorption processes that occur on heterogeneous surfaces[31] and have the exponential distribution of active sites over the adsorption energy.[32]

An analysis of published data[27,30—38] show that the mechanism of sorption of Cu^{2+} ions from aqueous media on bentonite clay is a matter of discussion. Therefore, it was of interest to reveal the applicability of the indicated equations to interpret experimental data on Cu^{2+} adsorption on bentonite clay and to choose a model that would describe the process most precisely.

Experimental

Commercial samples of bentonite clay presented by the "Company BENTONIT" (Taganskoe deposit, Republic of Kazakhstan) were used as objects of the study. The substantial composition of the studied sample of montmorillonite clay was studied in detail.[37,38] The adsorption capacity of bentonite clay toward Cu^{2+} ions was determined spectrophotometrically by a standard procedure using a KFK-3-01 photocolorimeter and a Specord 50 spectrophotometer. Copper ions were sorbed on bentonite clay under static conditions at a constant temperature (20 °C) from a model solution of copper sulfate pentahydrate with a concentration of Cu^{2+} ions of 5 mg L^{-1}. A clay sample was taken in an amount of 3 g per 50 mL of solution. A model aqueous solution of copper sulfate with a Cu^{2+} content of 2 mg mL^{-1} was used to determine the maximum adsorption capacity of clay. To obtain the calibration curve, a number of reference standard solutions of copper sulfate containing from 10 to 20 mg of copper(II) were prepared and placed in 50-mL volumetric flasks. A concentrated ammonia solution (5 mL) was added to each flask, the volume of the solution was brought to 50 mL by pouring distilled water, and the absorbance was measured. A solution containing concentrated ammonia (5 mL) in distilled water (45 mL) served as the reference solution. The thickness of the spectrophotometer cell was 1 cm. The concentration of copper ions was measured on a spectrophotometer at the wavelength 610 nm. The adsorption efficiency was calculated by the equation

$$\alpha = (C_0 - C_1)/C_0 \cdot 100\%, \qquad (1)$$

where C_0 is the initial concentration of copper ions in the solution (mmol L^{-1}), and C_t is the concentration of copper ions in the solutions after sorption (mmol L^{-1}).

Results and Discussion

The adsorption kinetics of Cu^{2+} ions on bentonite clay was studied at 20, 40, and 60 °C. Figure 1, *a* shows the copper ion concentration in the solution as a function of the contact time with bentonite clay obtained at three temperatures. The corresponding adsorption isotherms of Cu^{2+} ions on bentonite clay are shown in Fig. 1, *b*.
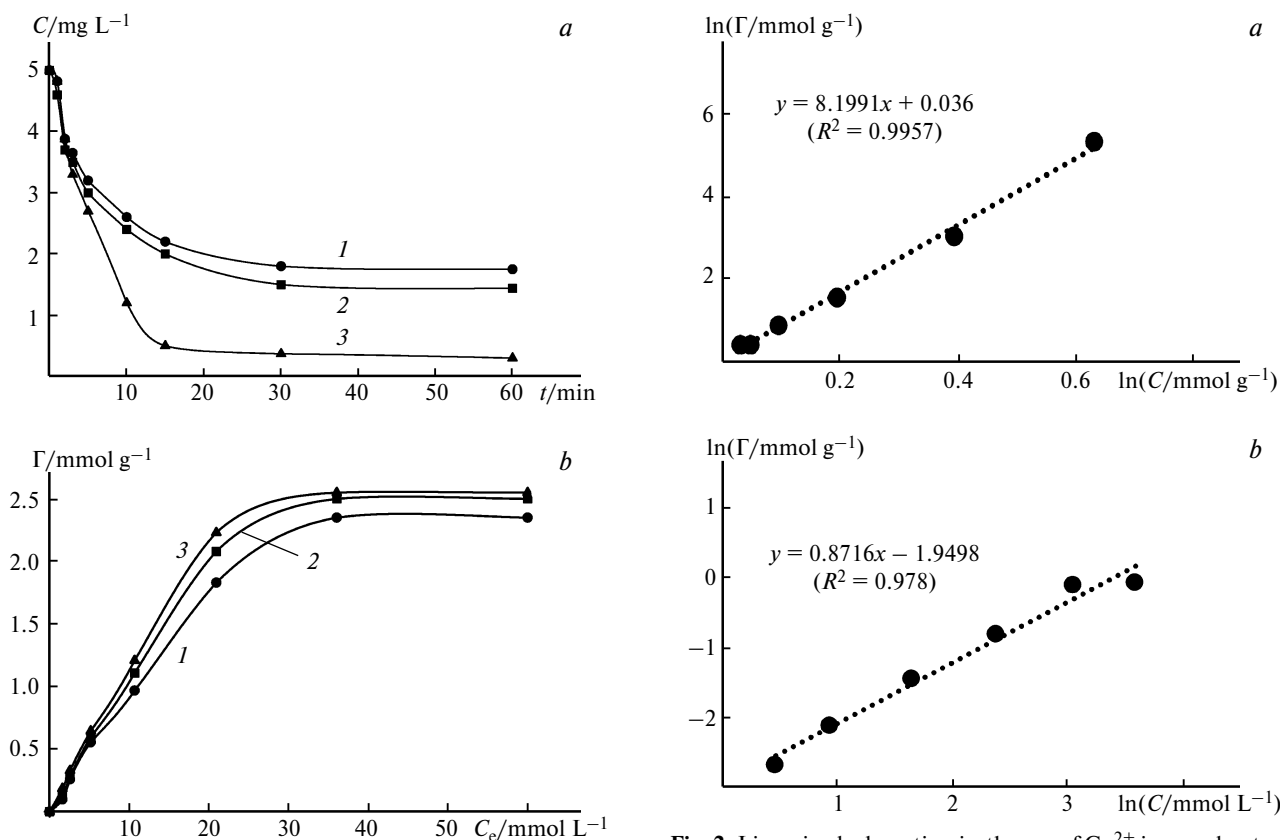
Fig. 1. (*a*) Kinetic curves of sorption of copper ions on bentonite clay and (*b*) adsorption isotherms of Cu^{2+} ions on bentonite clay at 20 (*1*), 40 (*2*), and 60 °C (*3*); $C_0 = 5$ mg L^{-1}; C_e is the equilibrium concentration.

Fig. 2. Linearized adsorption isotherms of Cu^{2+} ions on bentonite clay at 20 °C according to the Langmuir model (*a*) and Freundlich model (*b*).

The adsorption isotherms were found to have a shape of the classical Langmuir isotherm. The kinetic curves indicate a fast uptake within the first 15 min with the adsorption equilibrium achieved in 20 min. A stronger adsorption of Cu^{2+} ions from an aqueous solution on bentonite clay is observed with increasing temperature. The adsorption isotherm of Cu^{2+} ions on bentonite clay at 20 °C was used for the calculation of the quantitative parameters of the adsorption process and presented in the linearized form corresponding to the Langmuir and Freundlich models (Fig. 2).

The results show that the experimental data are well consistent with the theoretical curve. The adsorption parameters of Cu^{2+} ions on bentonite clay are given in Table 1.

It follows from the calculation results that the Langmuir model (correlation coefficient 0.9957) is the most appropriate for the description of the adsorption of Cu^{2+} ions on bentonite clay. Therefore, the monomolecular mechanism of adsorption seems to be preferred.

It is established that the maximum efficiency of Cu^{2+} ions on bentonite clay is 85%, which corresponds to a limiting adsorption capacity of 2.55 mmol g^{-1}. It is known that the efficiency of sorption depends significantly on the acidity of the medium.[27] To evaluate the influence of the pH of the medium on the efficiency of extraction of Cu^{2+} ions from model aqueous solutions, the experiments were carried out within the pH range from 2 to 8. The results are presented in Fig. 3.

As shown by the data obtained, at pH <4 the efficiency of adsorption of Cu^{2+} cations on bentonite clay is low and

Table 1. Adsorption parameters of Cu^{2+} ions on bentonite clay corresponding to the Langmuir and Freundlich equations

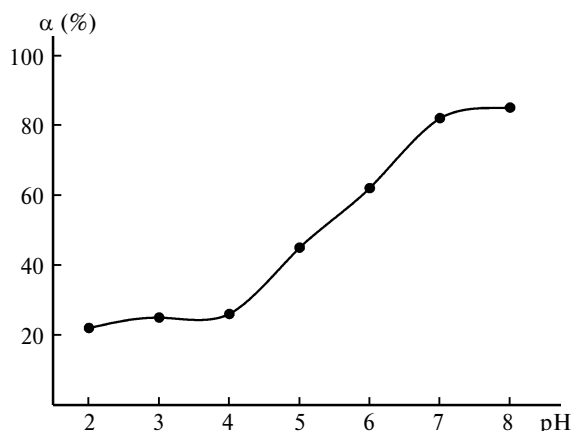| Langmuir model			Freundlich model			Efficiency
Γ_{max}/mmol g^{-1}	K_L/L mol^{-1}	R^2	K_F/mmol L g^{-1}	n	R^2	of adsorption (%)
2.5	0.1219	0.9957	0.1423	7.03	0.9783	85

Fig. 3. Adsorption curve of Cu^{2+} ions on bentonite clay at pH 2—8 ($C_0 = 5$ mg L^{-1}); α is the efficiency of sorption.

increases sharply at pH 5—8. This can probably be related to the adsorption mechanism. At low pH, the adsorption of Cu^{2+} cations proceeds *via* the ion-exchange mechanism. An increase in the pH results in the formation of $M(OH)^+$ complexes and chelate hydroxo complexes on the sorbent surface with copper ions. In addition, the surface of montmorillonite as the bentonite clay component is deprotonated in a range of high pH. As a result, the montmorillonite surface is charged negatively, which favors the electrostatic interaction of positive copper ions with the negatively charged surface of the clay.[27]

To conclude, the adsorption of Cu^{2+} ions on bentonite clay proceeds *via* the ion-exchange mechanism by the formation of chelate complexes with surface hydroxo groups of montmorillonite. It is shown that the most appropriate kinetic model for the description of the adsorption of Cu^{2+} ions on bentonite clay is the Langmuir model (correlation coefficient 0.9957), which makes it possible to calculate the limiting adsorption capacity equal to 2.55 mmol g^{-1}. It is found that the adsorption of Cu^{2+} ions on bentonite clay increases as the temperature increases from 20 to 60 °C, but the pattern of adsorption isotherms is temperature-independent in the chosen range. It is revealed that at low pH of the solution copper is adsorbed slowly, which is probably related to the interference of ion exchange. An increase in the pH of the medium results in a significant increase in the adsorption capacity of bentonite clay toward Cu^{2+} ions, which can be due to the formation of $M(OH)^+$ complexes and chelate hydroxo complexes on the sorbent surface covered with copper ions. It was assumed that the montrmorilonite surface composing the basis of bentonite clay is deprotonated at high pH values.

No human or animal subjects were used in this research. The authors declare no competing interests.

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