Experimental Simulation of Sorption Processes of Heavy Metals on Natural Clay Minerals

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Abstract. The sorption of iron (III) and copper (II) ions on natural clay minerals of deposits of Buryatia is investigated. The adsorption of ions of these metals depends on pH of solution, clay loading, concentration of metals ions and also on the temperature of adsorption carrying out and regularities of influence of these parameters on adsorption efficiency are determined. Kinetic regularities of adsorption of ions of Fe³⁺ and Cu²⁺ on natural clays are consistent with kinetics model of pseudo-second order. The isotherms of equilibrium adsorption of above-mentioned ions on natural clay are described by Langmuir equation with the correlation coefficient of R² equal 0.994. Results of testing of clays in the process of purification of adit wastewater of iron and copper ions testify to a possibility of effective use of natural clays of Buryatia in sewage treatment from ions of heavy metals.

1. Introduction

Wastewater pollution by heavy metals is observed in industrial waters of such enterprises as quarries for mining, metallurgical enterprises, thermal power plants, for the production of paints and pigments, for the production of glass, etc. Reagent treatment, most commonly used in these plants, does not provide a sufficient degree of treatment of water from heavy metals, because their residual content can reach up to 1-5 mg l⁻¹, while the maximum permissible concentration (MPC) in the water of sanitary water bodies and in water of fish-economic importance reservoirs, for example, copper is 0.1 and 0.001 mg l⁻¹, and iron - 0.5 and 0.1 mg l⁻¹, respectively. Although some metals are important microelements of living organisms, but their excess has a toxic effect on organisms. Heavy metals are dangerous because they have the ability to accumulate in living organisms, causing serious diseases, including oncology.

Among the physicochemical methods of wastewater treatment containing heavy metals, adsorption is the most effective and inexpensive method, characterized by ease of implementation and a high degree of purification with the optimal selection of used sorbents [1-3]. Bentonite clays can serve as sorbents in wastewater treatment from heavy metal ions, because they have high adsorption capacity, ecological safety, availability and low cost. The high exchange capacity of clay minerals is due, first, to the increase in the structural cell in contact with water and other polar liquids, and secondly, the ability of exchange cations to be replace of by cations of other metals.
The purpose of this work is to study the adsorptive properties of the bentonite clay of the Tuldon deposit (Buryatia) with respect to copper and iron ions in model aqueous solutions.

2. Experimental

The bentonite clay of the Tuldon deposit was used which as a sorbent has the following chemical composition (mass%): SiO$_2$ – 69.00; Al$_2$O$_3$ – 16.70; Fe$_2$O$_3$ – 2.60; MgO – 1.32; CaO – 1.52; K$_2$O – 2.80; Na$_2$O – 2.27; TiO$_2$ – 0.19; P$_2$O$_5$ - 0.35; other – 3.44. The cation exchange capacity (CEC) of clay, determined by the sorption of ammonium ions, was 1.03 meq g$^{-1}$. Adsorption studies were carried out by the method of limited volume with constant mixing. The clay was used which was preheated at 500 °C for 2 hours in the adsorption experiments. Adsorption of copper was carried out at pH 5.5, and iron adsorption at pH 2.9, which corresponds to the existence of ions of these metals in the form of hydrated ions Cu$^{2+}$ and Fe$^{3+}$. The amount of adsorbed metal ions was determined from the decrease in the concentration of their ions in the solution. The concentration of copper ions in the aqueous solution was determined by the photometric method with sodium diethylcarbamate in ammonia solution and the concentration of iron by the sulfosalicyl method using an Agilent UV-Vis spectrophotometer. The amount of metal ions ($q_t$, mg g$^{-1}$) sorbed on clay was calculated by the formula:

$$q_t = \frac{(C_o - C_t) \cdot V}{m},$$

where $C_o$ is the initial concentration of metal ions in solution, mg l$^{-1}$, $C_t$ is the concentration of metal ions in solution at time t, mg l$^{-1}$, $V$ is the volume of solution, l, $m$ is the mass of bentonite clay, g. The degree of purification from iron ions were calculated by the formula:

$$Degree\ of\ purification, \ % = \frac{C_o - C}{C_o} \cdot 100\%$$

3. Results and discussion

Bentonite clays of the Tuldon deposit have a grayish-green color and belong to the alkaline-earth type of clay. The content of montmorillonite in the rock is about 70%, which is confirmed by reflexes at 2θ equal to 5.7°, 17.6°, 19.9° and 36° on the diffractogram of natural clay (Figure 1). Clay also contains α-cristobalite (up to 30% of the rock volume), orthoclase and geylandite.

The isotherm of low-temperature nitrogen adsorption / desorption is of the IV type according to the classification of BDDT [4], which is characterized by a pronounced capillary-condensation hysteresis (Figure 2), indicating the existence of a structure with transient porosity. The shape of the hysteresis loop is of type B according to de Boer classification, which indicates the presence of sliced pores. On the isotherm at P/P$_o$ close to 1, there is a sharp rise in the sorption curve, indicating the presence of large pores in the samples. The specific surface of the Tuldon clay, determined from the isotherm of low-temperature adsorption of nitrogen, is 60.8 m$^2$ g$^{-1}$, the pore volume is 0.142 cm$^3$ g$^{-1}$, the average pore diameter is 95Å.
The adsorption properties of the Tuldon clay were investigated in the adsorption of copper and iron ions from model aqueous solutions. The figure 3 shows the kinetic curves of adsorption of Cu\textsuperscript{2+} and Fe\textsuperscript{3+} ions on natural clay at initial concentrations of 39.7 mg l\textsuperscript{-1} (Cu\textsuperscript{2+}) ions and 40.7 mg l\textsuperscript{-1} (Fe\textsuperscript{3+}) ions. The adsorption of copper ions proceeds at a high rate in the first 15 minutes and achieves an adsorption value of 16.5 mg g\textsuperscript{-1}, then the adsorption slows down (the adsorption value increased by only 1 mg g\textsuperscript{-1} in 4 hours), and reaches equilibrium in 24 hours, adsorption is 20.6 mg g\textsuperscript{-1}. A slightly different form of the curve is observed in adsorption of Fe\textsuperscript{3+} ions. Rapid growth of adsorption is observed in the first 5 minutes (q\textsubscript{i} = 23.5 mg g\textsuperscript{-1}), then ion adsorption proceeds at a slower rate (q\textsubscript{e} = 36.3 mg g\textsuperscript{-1} in 120 minutes). The adsorption equilibrium occurs after 24 hours, while the adsorption amount is 40.6 mg g\textsuperscript{-1}. The degree of removal of Cu\textsuperscript{2+} and Fe\textsuperscript{3+} ions from these aqueous solutions is 41.5% and 99.9%, respectively (Figure 3). The high rate of adsorption in the initial period is due to the presence of a large number of free adsorption centers on the clay surface. As adsorption centers fill, the rate of adsorption of metal ions decreases. The greater sorption of iron ions (40.6 mg g\textsuperscript{-1}), compared to the adsorption of copper ions (20.6 mg g\textsuperscript{-1}), may be due to the lower effective radius of Fe\textsuperscript{3+} ions (0.067 nm), compared to the radius of Cu\textsuperscript{2+} (0.080 nm).
To understand metal adsorption mechanism and evaluating adsorbent performance for the removal of heavy metals the kinetic adsorption curves were analyzed using kinetic models of the kinetics of pseudo-first (1), the pseudo-second-order (2), and the intraparticle diffusion (3), which are often used to adsorption of substances from aqueous solutions [5].

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1); \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2); \quad q_t = k_i t^{1/2}
\]

where \(q_t\) and \(q_e\) are the amount of metal ions sorbed at time \(t\) and at equilibrium, respectively; \(k_1\) is the pseudo-first order rate constant, \(k_2\) is the pseudo-second order rate constant, \(k_i\) is the intraparticle diffusion rate constant. Figure 4 shows the experimental kinetic data on the adsorption of \(\text{Cu}^{2+}\) ions and \(\text{Fe}^{3+}\) on the bentonite clay in the coordinates of the linear forms of pseudo-first equations, the pseudo-second-order and intraparticle diffusion as dependencies \{\ln (q_e - q_t)\} and \{t ∙ q_t\} on time \(t\), and also \{q_t\} on time \(t^{1/2}\).

![Figure 4. Kinetics adsorption of ions from liquid solution](image)

The discrepancy between the experimental and calculated by the equation (1) \((q_{e,\text{exp}} \text{ and } q_{e,\text{cal}})\), reached 55%, while the difference between \(q_{e,\text{exp}} \text{ and } q_{e,\text{cal}}\), calculated from the pseudo-second order model, is 7-15%. The kinetic regularities of the adsorption of copper and iron ions are in good agreement with the pseudo-second order adsorption kinetics model, which is confirmed by the correlation coefficient \(R^2\) for copper and iron adsorption equal to 0.999 and 0.993 (figure 4 a, b), while the correlation coefficient \(R^2\) for the pseudo-first-order model is 0.912 and 0.964 (table 1), and for the intraparticle diffusion \(R^2\) model is 0.400 and 0.9375 (table 1), respectively. The pseudo-second-order model assumes that the chemical exchange reaction is the limiting stage of the sorption process [5].

| Me  | \(q_e, \text{mg g}^{-1}\) | \(k_1, \text{mg g}^{-1} \text{min}^{-1}\) | \(R^2\) | \(q_{e,\text{cal}}, \text{mg g}^{-1}\) | \(k_2, \text{g mg}^{-1} \text{min}^{-1}\) | \(R^2\) | Intraparticle diffusion |
|-----|----------------|----------------|-----|----------------|----------------|-----|----------------|
| \(\text{Cu}^{2+}\) | 20.6 | 11.22 | 1.16 | 0.912 | 17.31 | 0.0156 | 0.999 | 4.358 | 0.400 |
| \(\text{Fe}^{3+}\) | 40.6 | 18.41 | 1.05 | 0.964 | 37.71 | 0.00119 | 0.993 | 6.492 | 0.937 |

To optimize the conditions of the sorption processes, we investigated the influence of various parameters such as the loading of the sorbent, the metal iron concentration, and the temperature of the process on the sorption of metals (for example, copper ions).
Figure 5 shows the dependence of the equilibrium adsorption ($q_e$) on the clay content. With an increase in clay loading from 1 to 20 g l$^{-1}$, the amount of adsorbed copper ions per gram of clay decreases from 20.6 to 2.0 mg g$^{-1}$. The specific adsorption of copper ions is greater at small sorbent content due to the more complete use of adsorption centers, as the sorbent content increases, the number of unoccupied adsorption centers increases. The efficiency of removal of copper ions from the aqueous solution reaches 100% already at a clay content of 5 g l$^{-1}$. A study of the effect of temperature showed that, sorption increases to 25.56 mg g$^{-1}$ (by 9%) with an increase in temperature from 25°C to 40°C and up to 39.11 mg g$^{-1}$ (by 40.5%) with an increase in temperature to 50°C. Increasing the amount of sorption with increasing temperature indicates the chemical nature of adsorption.

Figure 6 shows the dependence of the amount of sorbed copper ions ($q_t$) on the equilibrium concentration of ions in solution at 25°C. The value of $q_t$ increases with an increase in the equilibrium concentration of Cu$^{2+}$ in the solution to a maximum value of 23.3 mg g$^{-1}$ (0.73 meq g$^{-1}$) with an initial copper ion concentration of 71.7 mg l$^{-1}$. This value is less than the CEC value, which is equal to 1.03 meq g$^{-1}$. It indicates that the exchange cations of bentonite clay undergo partial replacement by Cu$^{2+}$ ions. The precipitation of copper ions from the solution was observed with an increase in the initial concentration above 71.7 mg l$^{-1}$. The shape of the isotherm of adsorption of copper ions on the clay surface according to the Gils classification is of the L type, which indicates a high chemical affinity of the adsorbent to copper ions, which is due to the ability of exchange clay cations to be replaced by cations of other metals from the aqueous solution. As the concentration of copper ions in the solution increases, the adsorption centers become increasingly filled by cooper ions, which leads to a decrease in the number of free centers, and accordingly the amount of adsorbed copper ions decreases.
The natural Tuldon clay was tested in experiments on the adsorption of heavy metals (Cu, Fe, Zn, Mn) contained in real adit wastewater. The table shows the concentrations of ions of these metals in the purified water before and after adsorption.

Table 2. Results the adsorption of heavy metals from real adit wastewater.

| Me  | MPC | Initial water, mg g⁻¹ | Time of adsorption | Residual content in solution, mg g⁻¹ | qₑ, mg·g⁻¹ | Degree of purification, % |
|-----|-----|------------------------|-------------------|------------------------------------|------------|--------------------------|
| Cu  | 0.001 | 0.0113 | 1 h | 0.0026 | 0.0087 | 76.99 |
|     |       |          | 6 h | 0.0020 | 0.0093 | 82.30 |
| Fe  | 0.10   | 1.038 | 1 h | 0.0159 | 1.0226 | 98.47 |
|     |        |          | 6 h | 0.0087 | 1.0298 | 99.16 |
| Zn  | 0.01   | 3.198 | 1 h | 2.5235 | 0.6745 | 21.09 |
|     |        |          | 6 h | 1.7639 | 1.4341 | 44.84 |
| Mn  | 0.01   | 0.367 | 1 h | 0.3186 | 0.0481 | 13.12 |
|     |        |          | 6 h | 0.3158 | 0.0509 | 13.88 |

On cleaning of real adit wastewater at a clay content of 1 g l⁻¹ the largest value of adsorption is observed for zinc and iron ions. The degree of water purification from copper ions was 82.3%; from ions Fe³⁺ - 99.2%, from Zn²⁺ - 44.8%.

4. Conclusions
The natural clay of the Tuldon deposit is an effective sorbent of copper and iron ions from aqueous solutions. The sorption efficiency of ions copper is 41.5% and of ions iron is 99.9%. The sorption of metals increases with an increase in the metal concentration to 71.7 mg g⁻¹, loading sorbent to 5 g l⁻¹ and a temperature of solution up to 50 °C was established. Kinetic regularities of adsorption of ions of Fe³⁺ and Cu²⁺ on natural clays are consistent with kinetics model of pseudo-second order. The isotherms of equilibrium adsorption of above-mentioned ions on natural clay are described by Langmuir equation with the correlation coefficient of R² equal 0.994. Results of testing of clays in the process of purification of adit wastewater of iron and copper ions testify to a possibility of effective use of natural clays of Buryatia in sewage treatment from ions of heavy metals.

5. References
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