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Modification of Natural Clays for Use in the Processes of Sewage Treatment

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ABSTRACT

The paper deals with the modification of clay sorbents in order to improve the efficiency of of copper ions extraction from wastewater. The study examined the elemental, mineralogical and phase composition of kaolin and montmorillonite clays. The authors analyzed the sorption capacity of natural sorbents under static conditions before and after modification with hydrochloric acid, sodium chloride and sodium hydroxide. The work also determines the change in the physical and chemical properties of the sorbent after modification. The most optimal modification conditions for the purification of wastewater from copper ions are distinguished.

Keywords: efficient waste treatment, clay adsobent, copper ions; adsorption isotherms

INTRODUCTION

The Tyumen region is an intensively developing region with a high anthropogenic load. The rates of industrial growth affect the increase in the level of pollution of water bodies in the South of the Tyumen Region. The total volume of wastewater discharged by the 80 largest enterprises in the region is about 350 million m^3 annually, out of which 237.62 million m^3 are treated as standard, which is less than 68%. As a result, the total amount of pollutants entering the water bodies exceeds 20 thousand tons per year [Government of the Tyumen region, 2018]. The composition of pollution entering the water bodies in the region is summarized in Figure 1.

Among the heavy metal ions found in water bodies of the Tyumen region, lead, cadmium, copper, zinc, mercury, nickel and titanium [Petukhov 2017, Guzeeva 2014] prevail in the concentrations exceeding the sanitary-hygienic standards [Chief state sanitary doctor of the russian federation, 2017] (Fig. 2.)

On the basis of these data, it can be argued that the treatment of waste water from heavy metals is an important task at present. Natural inorganic adsorbents have found wide application in water purification. The adsorption properties of such materials are not well-studied. Layered aluminosilicates with a developed adsorption surface are of particular interest [Pimneva 2017, 2018].

The purpose of this work was to study the adsorption properties of modified forms of natural clay minerals of the Tyumen region in relation to copper ions.

MATARIAL AND METHODS

Natural clay minerals of the Tyumen region: kaolin adsorbent and clay adsorbent containing montmorillonite were used in the work. The analysis of the chemical composition of clays was performed by a scanning electron microscope (SEM). According to the data obtained, its main components are oxides in the amounts shown in Table 1.

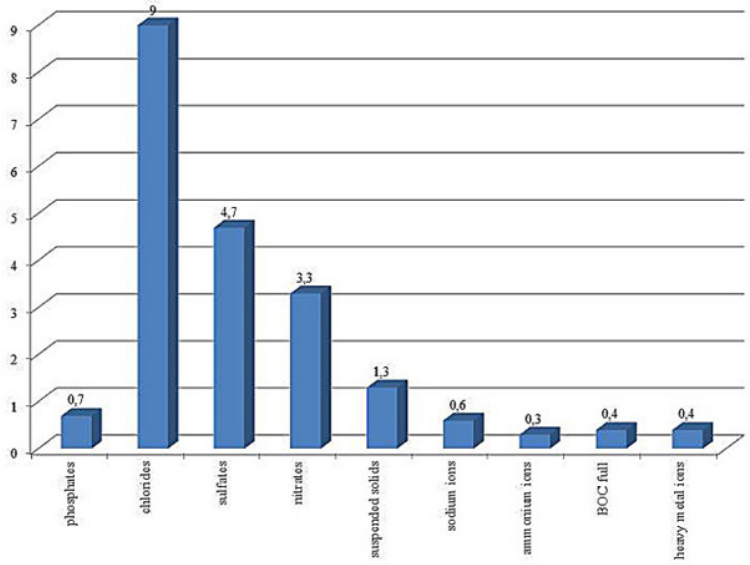

Figure 1. Discharge of pollutants into water bodies of the South of the Tyumen Region, tons/year

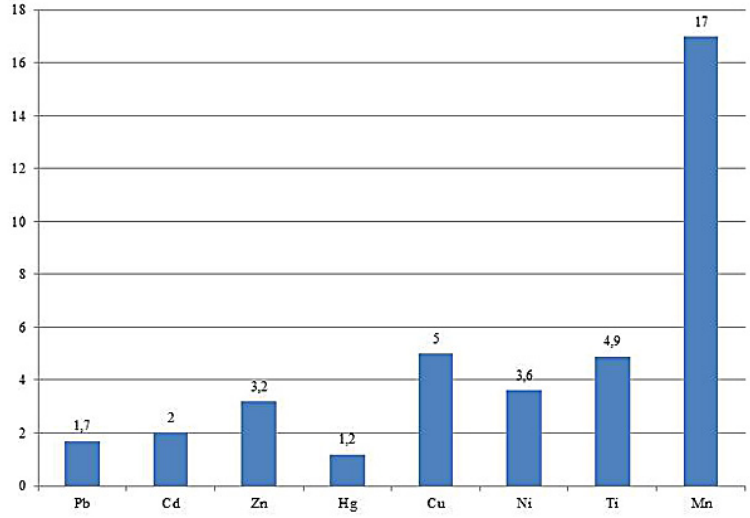

Figure 2. The content of metal ions in the waters of the South of the Tyumen region, in fractions of the MPC

The mineralogical and phase composition of natural clays was determined through X-ray phase analysis using a DRON diffractometer with a copper anode (λ=1.5406 Å). Figure 3 shows the phase composition. Figure 4 presents that the particles of natural clays have sizes lesser than 1 micron, in the form of thin leaves with irregular outlines.

The objects of investigation of the adsorption properties of natural clays were model copper sulfate aqueous solutions. The dilution methods were prepared from copper sulphate solutions with solutions with different concentrations of copper ions. The adsorption process was studied under static conditions. The concentration of copper ions was determined before and after the adsorption process with the standard trilonometric method [Schwarzenbach, 1970].

RESULTS

Modification of natural clays with hydrochloric acid, sodium chloride and sodium hydroxide led to a change in the physicochemical properties of clays. While using sodium hydroxide for modification, it contributed to an increase in the negative electrokinetic potential of clay particles. This can be explained by the fact that the OH^- ions were introduced into the structure of the adsorbent.

The changes in the physicochemical properties of modified clay adsorbents are manifested in

Table 1. The chemical composition of natural clays and in modified forms, mass. %

Elemental composition	Mass fraction, %			
	Native	H – form	OH – form	Na – form
Clay adsorbent containing montmorillonite (MMT)				
SiO_2	53.62	49.69	52.52	51.51
Al_2O_3	20.29	19.73	22.90	20.99
Na_2O	0.41	0.26	0.41	0.31
K_2O	3.88	3.86	3.49	3.74
CaO	1.53	0.48	0.31	0.40
Fe_2O_3	13.13	19.52	14.94	16.94
TiO_2	1.71	1.95	1.67	1.83
MgO	1.63	1.35	1.63	1.42
Kaolin adsorbent				
SiO_2	49.22	49.31	49.58	50.14
Al_2O_3	46.87	47.02	46.75	45.31
Na_2O	0.13	0.09	0.09	0.21
K_2O	0.37	0.38	0.41	0.52
CaO	0.86	0.42	0.44	0.88
Fe_2O_3	1.12	1.21	1.20	1.30
TiO_2	0.94	0.95	0.93	0.98

the efficiency of the adsorption of copper ions on the surface of the adsorbents. Figure 5 shows the dependences of the effect of pH on the adsorption value. The value of adsorption increases along with the pH of solutions.

As a result of the study on the adsorption properties, adsorption isotherms of copper ions were obtained (Fig. 6). It was established that the adsorption isotherms are described by the Langmuir adsorption equation. This allowed us to determine the maximum adsorption and the adsorption equilibrium constant from the adsorption isotherms from the linear form of the Langmuir equation:

$$\frac{C_P}{A} = \frac{C_P}{A_\infty} + \frac{1}{A_\infty \cdot k_L} \qquad (1)$$

where: A is the amount of sorbed copper and
A_∞ is the value of the limiting sorption (mg/g),
C_p – equilibrium concentration of copper ions in solution (mg/g),
k_L – concentration constant of sorption equilibrium, characterizing the intensity of the process of sorption, l/mg.

Adsorption isotherms have a convex appearance, which is evidenced by the high affinity of copper ions to natural kaolin and clay adsorbent containing montmorillonite. There are no kinks on the adsorption isotherms of Cu^{2+}, which confirms the complete dissociation of copper sulfate molecules in water.

Modification of the used adsorbents clearly shows that salt and alkaline treatment leads to an increase in the adsorption of copper ions. When processing adsorbents with hydrochloric acid, the active centers are blocked; thus, there is a sharp decrease in the amount of copper adsorption.

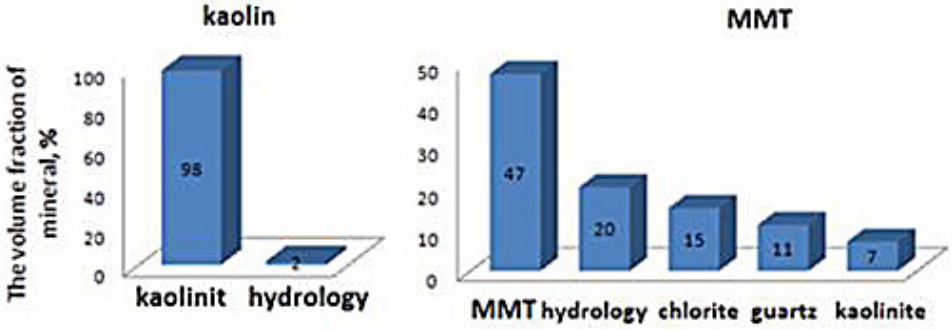

Figure 3. Phase composition of natural clays

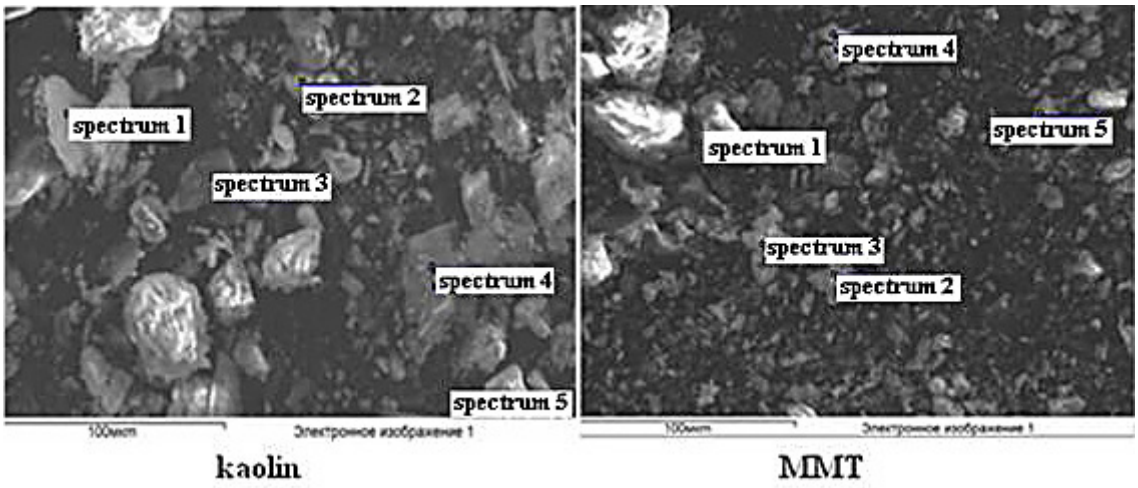

Figure 4. SEM photomicrograph

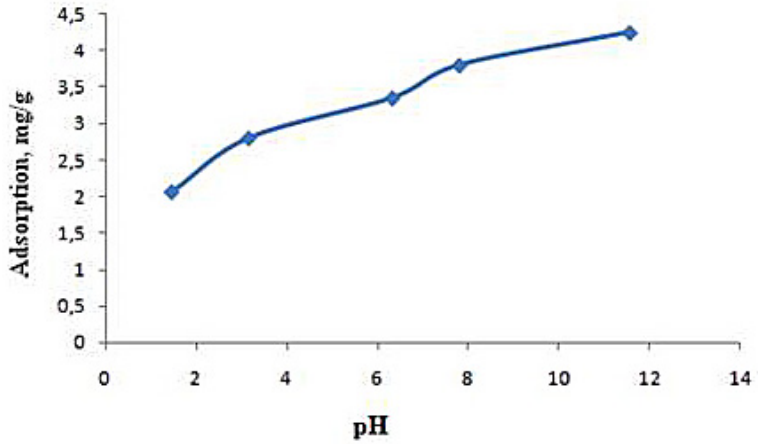

Figure 5. Dependence of adsorption of copper ions on the pH of solutions on modified forms of natural adsorbents

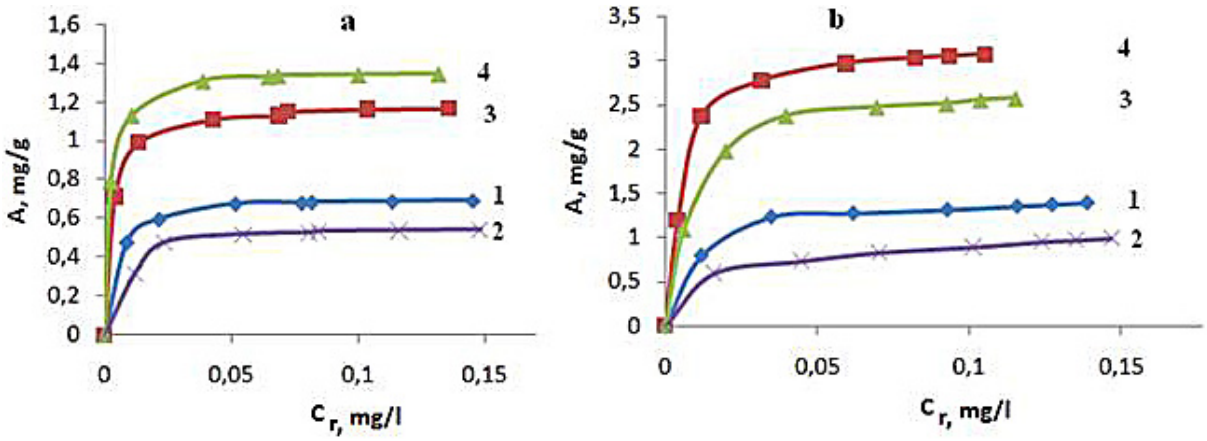

Figure 6. Adsorption isotherms of copper ions in various forms: kaolin (a) and MMT: 1 – native form; 2 – H-form; 3 – OH-orm; 4 – Na-form

According to the results of the experiment, the value of the limiting adsorption and the adsorption equilibrium constants according to the Langmuir equation are presented in Table 2.

According to the data obtained, the copper ions are extracted from aqueous solutions more on the Na-form and OH-form using natural adsorbents. Figure 7 shows the dependence of the extraction of copper ions on the initial concentration of solutions. On the kaolin adsorbent in the OH form, 92% is extracted at an ion concentration of 0.02 mg/ml. In turn, the degree of montmorillonite clay extraction from concentration does not have a linear relationship, but passes through a maximum corresponding to 67% at a concentration of 0.06 mg/ml. With increasing concentration of ions, the degree of extraction decreases.

On the Na-form, the change in the degree of extraction from the kaolinite adsorbent passes through an extremum of 84% at a concentration of copper ions in the solution of 0.065 mg/ml, in montmorillonite, the adsorbent has a linear relationship, with a maximum of 86% at a concentration of 0.03 mg/ml.

CONCLUSION

The results obtained confirm that the natural clays in a modified state exhibit a high adsorption capacity with respect to copper ions. The degree of adsorption is influenced by the initial concentration of the copper solution. For the studied adsorbents, the value of adsorption increases along with the concentration of copper ions in solution, while the degree of extraction decreases.

The obtained data correspond to the average degree of contamination of wastewater with

Table 2. Calculated values of the maximum adsorption and the adsorption equilibrium constant of the Langmuir equation

Adsorbent form	A∞, mg/l	K_1	Correlation coefficient R^2
Kaolin			
Native	1.5	0.44	0.999
H – form	1.0	0.33	0.994
OH – form	1.9	0.79	0.997
Na – form	2.5	0.32	0.998
MMT			
Native	166.7	0.0088	0.999
H – form	58.8	0.0187	0.997
OH – form	1000.0	0.0033	0.999
Na – form	500.0	0.0055	0.999

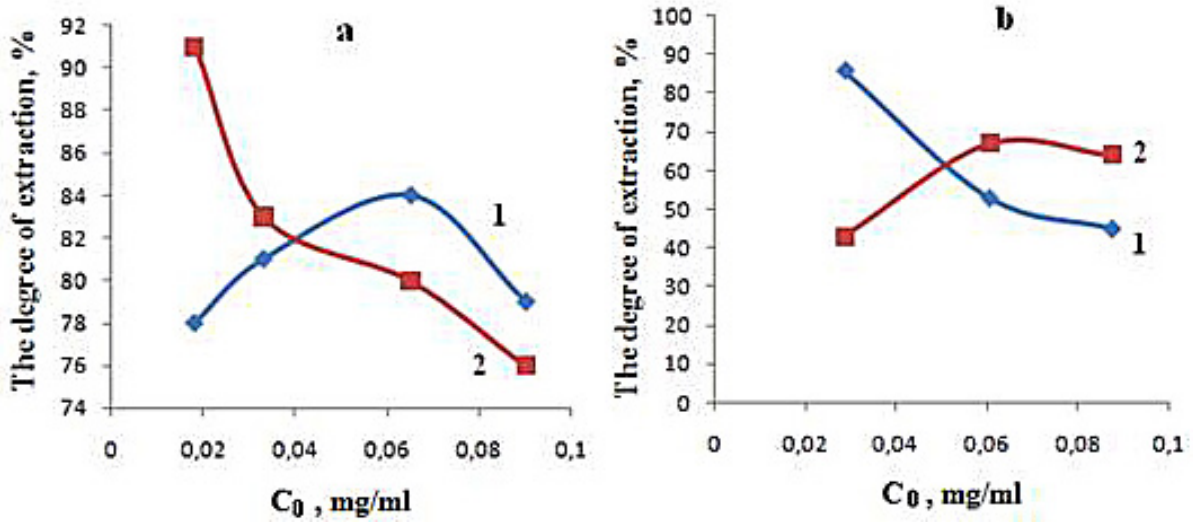

Figure 7. The degree of extraction of nickel ions on natural kaolin (a) and montmorillonite clay (b) in the Na-orm (1), OH-form (2)

copper ions – from 20 to 100 mg/dm^3 – and confirm the possibility of using natural sorbents for wastewater treatment.

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