Modified Layered Alumosilicate Nanosorbents For Water Treating

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Annotation

An author's method of modification of natural layered alumo-silicate nanostructured mineral montmorillonite is presented. The ability of the modified alumosilicate nanosorbent to adsorb iron (III) and copper (II) ions from model aqueous solutions has been investigated. The maximum sorption activity is established and the comparative assessment of absorbing ability of the modified product and native montmorillonit bentonite clay is given.

**Key words:** sorption technology, water treatment, ions of heavy metals, layered alumosilicates, modification

Introduction

In sorption methods of industrial sewage water's treating the increasing application is found by natural mineral sorbents: special clays, gaizes, zeolites, etc. The advantage of such materials compared to other sorbents is in the first place their law cost, availability of mining and enrichment, a unique set of colloidal and chemical properties – sorption, ion exchange, molecular-sieve properties, as well as the possibility of their modification, regeneration and utilization. However, in some cases it is irrational to use the natural sorbents themselves for purification of water bodies because of their increased consumption. So when using natural materials there is need to improve their efficiency by using different technological approaches.

It is known that natural montmorillonite, which is an argillaceous mineral, class of layered alumosilicate structure type 2 :1, with swelling of the crystal lattice [1], has high saturation characteristics. Its structure is shown in Figure 1.

The interlayer space of montmorillonite is 1.25 -1.50 nm. It isn't rigid and can strongly change. Depending on the water content in the mineral and the composition of exchangeable cations this distance can vary from 0.96 nm dry to 14 nm at the introduction of large molecules in the interlayer space. By heterovalent substitution of

cations in the octahedral and tetrahedral layers the crystal lattice of montmorillonite is electrically unbalanced (an excess of negative charges is created). Lack of positive charges is covered by the exchangeable cations absorbed on the external and internal surfaces of the elementary structural layer and on its edge parts (at sites of spallings and breaches).
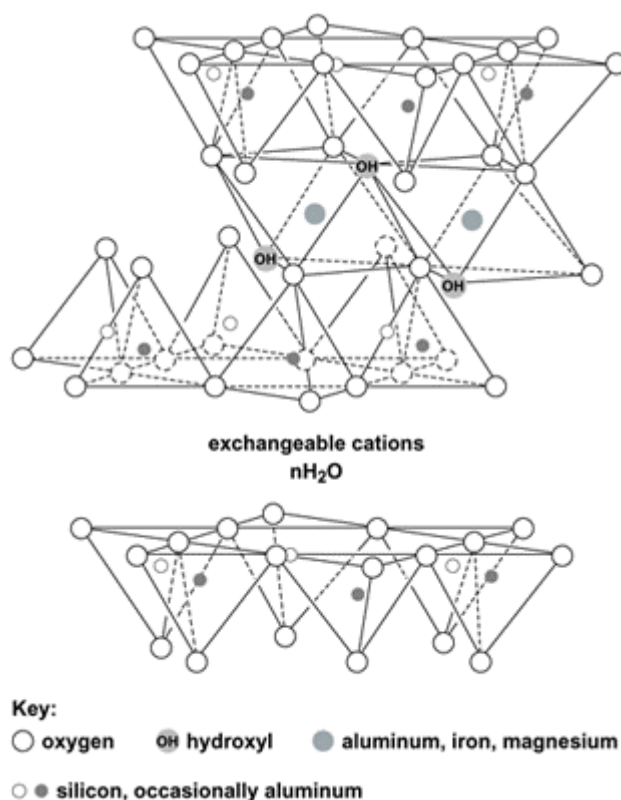
Figure 1: Structure of montmorillonite [1]

An important feature of montmorillonite is the possibility of its activation and modification by using different processing methods (heat, acid, salt, etc.). The focus of this process is "undermining" of the crystalline grid of mineral, increasing its porosity and specific surface area, as well as change in crystal structure features, increasing ion-exchange properties due to changes in the composition of exchangeable cations and the creation of new active centers [2-4]. It enhances the range of natural aluminosilicate sorbents due to a sharp increase in sorption capacity and competitiveness in comparison with artificial sorption materials.

Materials and research methods.
Method of modification of montmorillonite.
As a natural alumosilicate material natural clay from the "Polyana" deposits of the Belgorod region, Russia, has been used. By X-ray diffraction (diffractometer Rigaku

Ultima IV XRD-320) and electron microscopic analysis (TEM JEM-2100) it has been found that the main rock-forming mineral in the clay is montmorillonite. The content of montmorillonite in the clay is 60 – 65 mass. % [5, 6].

Modification of natural montmorillonite clay was carried out with a LiOH solution both directly and with a pretreatment with a 10 % H_2SO_4 solution. The resulting modified product was washed until the pH = 7.5 – 8 (which corresponds to the pH of the natural clay) [7].

Characterazation of colloidal and chemical properties of natural and modified montmorillonites.

Chemical composition of natural and modified montmorillonites was determined by energy-dispersive method (EDX analyzer EDAX combined with REM Quanta 200 3D) and by the methods of classical analytical chemistry. It has been found that during the treatment of both natural and acid activated alumosilicate material with a lithium hydroxide solution the SiO_2 and Al_2O_3 content decreases due to the destruction of octahedral aluminum-oxygen and tetrahedral silico-oxygen layers in a strongly alkaline medium with subsequent release into the solution of silicate and aluminate ions. With the direct treatment of the native clay with a solution of lithium hydroxide the Li_2O content in the resulting material is 1.23 mass. %. With pretreatment with sulfuric acid an increase in the vacant positions in the structure of montmorillonite occurs. In this case, the content of lithium oxide in the models during the subsequent modification is higher (1.51 mass. %), compared to the direct activation of the natural clay with LiOH.

An important point in understanding and regulating the sorption processes occurring with the participation of solid-phase products of modification is to study the characteristics of their surface. Table 1 shows the results of the study of colloid-chemical properties of natural and modified alumosilicates.

**Table 1. Colloidal and chemical properties of native and modified alumosilicates**

Material	ξ-potential, mV	Specific surface area, m^2/g (BET method)	Pore volume, sm^3/g (BJH method)
Native montmorillonite clay	-19.5 ± 0.2	118	0.20
MM 1*	-35.7 ± 0.2	80	0.18
MM 2**	-34.9 ± 0.2	96	0.20

Montmorillonite, modified with LiOH (1 : 0,18, mass ratio solid alumosilicate : LiOH).
**Montmorillonite, pretreated with 10% H_2SO_4 solution, modified with LiOH (1 : 0,18)*

The experimental results show that treatment of clay with alkaline solutions leads to an increase of ξ- potential in absolute value. It may be associated with the

following processes. Firstly, the transition of weakly dissociated surface elements of the structure ≡Si−OH into more dissociated surface elements of the structure ≡Si−OLi will take place:

$$\equiv Si-OH + LiOH \rightarrow \equiv SiO^- Li^+ + H_2O.$$
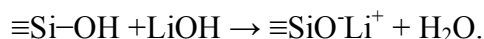
Secondly, the adsorption of OH⁻-groups on the edges of layered crystals is possible. These groups also bring their contribution to a negative value of the charge of the mineral.

In the process of alkaline activation, a decrease of specific surface of modified clays can be observed. This is probably due to epitaxial-destructive deposition on the surface of aluminosilicate matrix of hardly soluble silicates formed during the treatment of the material with alkaline solutions [8]. It should be noted that the modified model where there was a pretreatment with sulfuric acid, had a specific surface area on average 17 % higher than that of the model without pretreatment. Thus, the positive effect of sulfuric acid pre-activation on the textural characteristics of the developed sorbent has been experimentally confirmed.

Results and discussion.
Prototypes of modified alumosilicate nanosorbents have been tested in the treatment process of model aqueous solutions, containing Cu^{2+} and Fe^{3+} ions.

The dependence of purification efficiency on the duration of contact of solid-phase material with a model aqueous solution containing heavy metals ions has been investigated. The experiment was performed for 15 minutes at the temperature of 25 °C. The mass ratio of sorbent to the model solution was constant and amounted to 1 : 100. As shown in Figure 2, the use of modified clays as adsorbents for only three minutes can achieve purification efficiency of 90 – 95 %. 5 minutes are enough for almost complete extraction of both Cu^{2+}, and Fe^{3+} ions. The efficiency of native montmorillonite as a sorbent during this time is 70 – 75 % when purifying an aqueous solution of Cu^{2+} and Fe^{3+} ions respectively.
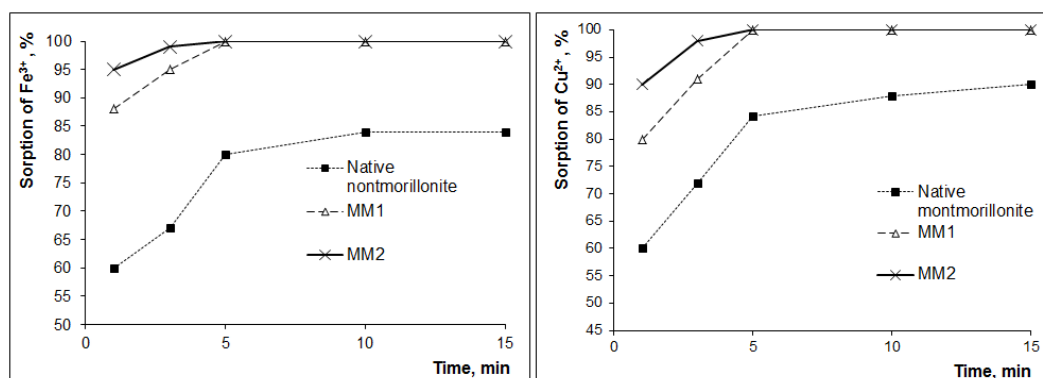
Figure 2: Effect of contact time on the sorption of metal ions (at initial concentration of metal ions = 0,1 mmol/l and temperature = 25 °C)

Dependence of the efficiency of the extraction of heavy metals ions on pH of the medium (Fig. 3) has shown that the optimal value of this index during sorption purification of Fe^{3+} and Cu^{2+} ions ranges from 2 to 5 units. When above pH = 5, the formation and precipitation of metal hydroxides occur, which in its turn contributes to the reduction of the concentration of copper (II) and iron (III) in an aqueous medium. It has been also found that the contribution of pH-factor in the purification process is 5 – 10 %.
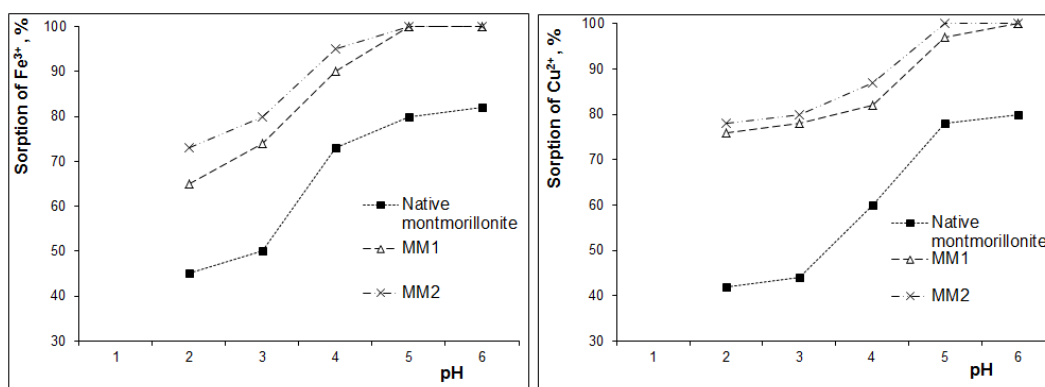
Figure 3: Effect of pH-factor on the sorption of metal ions (at initial concentration of metal ions = 0,1 mmol/l and temperature = 25 °C)

To establish the maximum absorption capacity of the sorbents with respect to heavy metal ions, by the method of variable concentrations the isotherms of the sorption of Cu^{2+} and Fe^{3+} on natural and modified alumosilicates have been constructed. The process was carried out in static conditions, phase relation solid : liquid was 1 : 100, the pH of the model solutions was set at 4.5, temperature 25 °C.
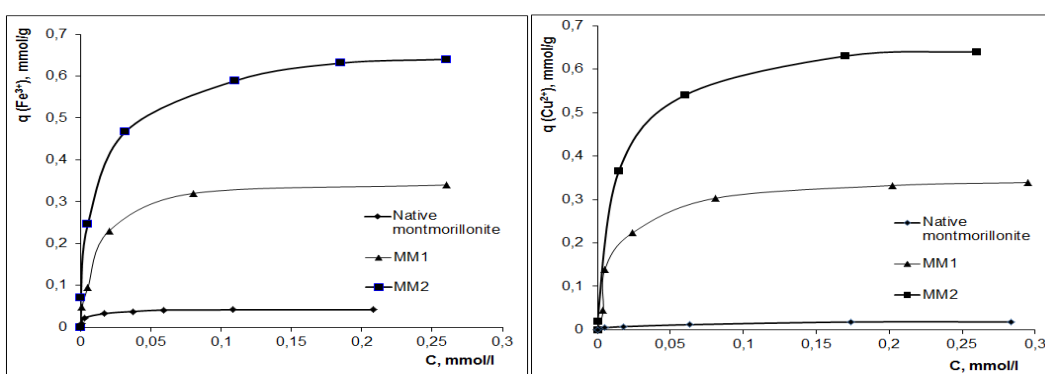
Figure 4: Sorption isotherm of Fe^{3+} and Cu^{2+} ion on native and modified forms of montmorillonite as a function of equilibrium metal ion concentration at pH 4.5 and temperature 25°C

The obtained sorption isotherms are processed as to their compliance with the Langmuir equation. The graphical decision of the Langmuir equation (by converting it into the equation of a straight line) allowed us to determine the maximum amount of sorption q_m and adsorption equilibrium constant b, which are important parameters of the sorption process:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} \cdot \frac{C_e}{q_m},$$

where C_e corresponds to the equilibrium concentration, q_m – is the limit value of adsorption, q_e – adsorption at a given equilibrium concentration, b – the empirical constant. Additionally, we calculated the correlation coefficients R^2 of the transformation of sorption isotherms of metal ions in a linear form which indicate compliance with the Langmuir adsorption model [9,10]. The calculated mathematical parameters of the Langmuir equation are presented in Table 2.

Table 2. Lengmuir constants and correlation coefficients of sorption isotherms

Material	Fe^{3+} sorption parameters			Cu^{2+} sorption parameters		
	R^2	q_m, mmol/g	b	R^2	q_m, mmol/g	b
Native montmorillonite	0.9997	0.043	351.40	0.9898	0.019	73.10
MM1	0.9994	0.360	76.00	0.9982	0.365	49.00
MM2	0.9995	0.670	85.70	0.9998	0.670	77.00

It has been established that the maximum adsorption capacity of the alumosilicate material modified directly with a solution of lithium hydroxide (model sample MM1), is: with respect to Fe^{3+} ions - 0,36 mmol/g (20, 2 mg/g) and 0,365 mmol/g (23,4 mg/g) to Cu^{2+} ions. Pretreatment of natural montmorillonite with a solution of sulfuric acid and subsequent activation of the material with LiOH (model sample MM2) can further improve the sorption capacity of the alumosilicate. The absorption capacity of the modified nano-sorbent MM2 is 36, 5 mg Fe^{3+} per 1 g of material, 43,0 mg Cu^{2+} per 1 g of material. Thus, during the two-stage modification of layered alumosilicate material we have managed to increase its absorptive capacity with respect to Fe^{3+} and Cu^{2+} ions in 15 and 35 times respectively, compared to native montmorillonite.

The process of desorption of heavy metals has been studied. It has been established that the desorption of both Fe^{3+} cations and Cu^{2+} cations is less than 0.5%, which demonstrates the irreversible nature of the sorption (chemisorption). At the same time it has been revealed that the migration of lithium ions from the structure of the mineral in solution in the sorption process does not occur. This may be due to epitaxial-destruction processes, residing in the formation of hardly soluble silicates on the surface of montmorillonite. In connection with this it is recommended not to

remove the waste sludge to the site for waste storage, and to use it as a plastic raw material component in the manufacture of coarse pottery.

The developed experimental sorbents have been tested under production conditions in the treatment of waste water contaminated with iron ions (III) (the content of 1.46 – 3.62 mg/l), surfactants (the content of 0,684 – 1,743 mg/l), oil products (0.228 – 0.611 mg/l). It has been revealed that the efficiency of waste water treatment with modified alumosilicate nanosorbents reaches 95 – 98 %, in material consumption of 50 g/ m^3 of waste water. At the same time the effectiveness of using native montmorillonite with similar expenses of the sorbent is only 75 %.

Conclusions.
The alumosilicate material MM2 produced by the activation of natural montmorillonite with 10% H_2SO_4 and subsequent treatment with lithium hydroxide is an effective sorbent of iron (III) and copper (II) ions. The maximum absorption capacity of the modified sorbent MM2 with respect to Fe^{3+} ions is 36.5 mg/g, to Cu^{2+} ions is 43 mg/g (at a temperature of 25°C and the pH of model solutions = 4.5). The increase in the sorption capacity of the model sample MM2 can be explained by the fact that the treatment of montmorillonite with a 10% solution of sulfuric acid helps to increase the specific surface area of the material. The subsequent activation of acid-treated clays with a solution of lithium hydroxide promotes the substitution of cation exchange complexe of clays for the Li^+ ions and an increase in ζ-potential in absolute value which in turn leads to increased speed and efficiency of purification of aqueous solutions of Fe^{3+} and Cu^{2+} ions. It has been found that the sorption of heavy metal ions is irreversible. This is due to epitaxial-destruction processes, residing in the formation of hardly soluble silicates on the surface of montmorillonite.

Inferences.

1.   The method is the treatment of montmorillonite with a 10% solution of sulfuric acid and subsequent activation with lithium hydroxide at a mass ratio solid alumosilicate : LiOH equaling 1 : 0.18.
2.   The ability of the modified alumosilicate nanosorbent to adsorb iron (III) and copper (II) ions from model aqueous solutions has been investigated. It has been revealed that the optimal pH value of the aqueous solution during sorptive removal of Fe^{3+} Cu^{2+} ions is in the range from 2 to 5 units. Above pH = 5 there is a formation and precipitation of metal hydroxides, which in turn also reduces the concentration of copper (II) and iron (III) in the aqueous medium.
3.   By the method of variable concentrations the sorption isotherms of the ions of these heavy metals on natural and modified forms of montmorillonite have been obtained. The obtained isotherms have been processed for compliance with the Langmuir equation. It has been found that the maximum sorption activity of the modified product is 36. 5 mg of Fe^{3+} per 1 g of material, 43.0

mg of Cu^{2+} per 1 g of material. It is 15 times and 35 times respectively higher, compared to the native montmorillonite clay.

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