"Sorption of Cu2+ ions and Fe3+ with alkaline forms of montmorillonite containing clay"

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RESUME

Este trabalho representa os resultados da avaliação comparativa da capacidade de sorção de formas alcalinas enriquecidas e modificadas de montmorilonita contendo depósitos de argila da região de Belgorod (Rússia). O processo de ativação complexa da montmorilonita contendo argila consiste no isolamento da fração de grão fino e posterior ativação da matriz por soluções de cloretos de metais alcalinos (lítio, sódio e potássio). É mostrado que durante o tratamento com sal o diâmetro médio das partículas de argila diminui, o que é explicado pela ação dispersante de soluções de cloretos de metais alcalinos e alcalino-terrosos. Ao mesmo tempo, as características de textura dos materiais permanecem quase inalteradas. Os resultados do tratamento matemático de isotermas de sorção de íons $Cu2+$ e $Fe3+$ de soluções aquosas modelo em materiais experimentais são apresentados neste trabalho. Os coeficientes de correlação de R2 na conversão de isotermas de sorção de íons metálicos em forma linear, indicando conformidade da sorção com o modelo de Langmuir, são 0,99. A maior quantidade de adsorção marginal entre as formas alcalinas é a forma sódica da argila. A atividade de absorção relativamente baixa da forma K da argila é devido à menor mobilidade e, portanto, à possibilidade de dissociação superficial dos íons K + em soluções aquosas. Em geral, em termos de sua capacidade de absorver cátions de metais pesados ($Cu2+$ e $Fe3+$), as amostras ativadas são superiores à forma de argila enriquecida na faixa de 20 a 40%.

Palavras-chave: *Sorção, isotermas de sorção, montmorilonita contendo argila, modificação, soluções aquosas.*

ABSTRACT

This work represents the results of comparative assessment of sorption capacity of enriched and modified alkaline forms of montmorillonite containing clay deposit of Belgorod region (Russia). The process of complex activation of montmorillonite containing clay consists in isolation of fine-grained fraction and subsequent activation of matrix by solutions of alkali metal chlorides (lithium, sodium and potassium). It is shown that during salt treatment the average diameter of clay particles is decreased, which is explained by dispersing action of solutions of alkali and alkaline earth metal chlorides. At the same time, the texture characteristics of the materials remain almost unchanged. The results of mathematical treatment of isotherms of sorption of Cu^{2+} ions and Fe^{3+} from model aqueous solutions on experimental materials are given in this work. The correlation coefficients of R^2 in the conversion of isotherms of sorption of metal ions into linear form, indicating compliance of the sorption with the Langmuir model, are 0.99. The highest amount of marginal adsorption among alkaline forms is the sodium form of clay. The relatively low absorption activity of the K-form of clay is due to the lower mobility and hence the possibility of surface dissociation of K^+ ions in aqueous solutions. In general, in terms of their capacity to absorb heavy metal cations (Cu^{2+} and Fe^{3+}) the activated samples are superior to the enriched clay form on the 20 - 40%.

Keywords: Sorption, sorption isotherms, montmorillonite containing clay, modification, aqueous solutions.

1. INTRODUCTION:

A large number of different clay minerals, different in crystal lattice structure, composition and properties, are found in nature. Montmorillonite is a clay mineral belonging to the class of layered silicates of structural type 2: 1 with anintumescent crystal lattice. Theoretical formula of montmorillonite $(OH)_4Si_8Al_4O_{20} \cdot xH_2O$ (xH_2O is interlayered water). The crystal lattice of montmorillonite is electrically unbalanced (excess negative charges are created). The lack of positive charges is covered by exchange cations adsorbed on the outer and inner surfaces of the package and on its edge parts (on the sections of chips and disorders) (Grim, 1962; Bergaya, *et al.,* 2006).

The minerals of the montmorillonite group are separated among the other groups by their high sorption and ion exchange capacity, with the exchange capacity of montmorillonite being greatest than that of all other clay minerals. (Klyaev & Vlisarenko, 1967; Aripov & Agzamkhojayev, 1983). This increase in the sorption capacity of montmorillonite is due to the fact that in crystals of this mineral ion exchange occurs not only on the outer surface, but also inside the crystal lattice between atomic layers. Also, in montmorillonite within the crystal lattice, isomorphic substitutions are common, so targeted ion substitution in the crystal lattice also results in increased sorption capacity and selectivity of the mineral by the appearance of uncompensated charges in the structural cell (Dritz & Kossovskaya, 1990; Golubeva & Yu, 2016).

Various methods of modifying clay minerals by chemical (treatment with solutions of salts, alkalis, organic and mineral acids) and physical (e.g. ultrasonic) treatment exist and continue to be developed (Morrison, 1980; Baghernejad *et al*., 2015; Vengris, *et al.,* 2001). The thrust

of this process consists in "loosening" the sorbent microstructure, increasing its porosity and specific surface area, as well as changing crystal structure features, increasing ion exchange properties due to changing the composition of exchange cations and creating new active centers (Steudel, 2009; Lopes *et al.,* 2017).

An ion exchange is the one way of modifying adsorption-active materials, which allows influencing specific interaction between sorbate and surface, thus increasing selectivity of adsorbent to certain groups of compounds.

2. MATERIALS AND METHODS:

2.1. Materials

In the present work, a sample of bentonite clay of the field of Belgorod region (Russia) with mass content of montmorillonite 42 - 45% was tested as the object of the study. The natural clay was subjected to complex activation. In the first step, the ground native clay was mixed with distilled water (solid: liquid ratio = 1:10) and held for 24 hours. The suspension was then muddled for one minute. The sand separation from montmorillonite was carried out by taking a clayslurry from the top 10-centimeter layer 20 minutes after stirring. The suspension having a clay particle size of less than 0.01 mm was settled, the clarified water was drained, and the precipitate was dried at a temperature of 105-130 ° C, then it was ground to a dust state. The obtained enriched clay samples with a weight content of montmorillonite of 55.0 - 60.0% were used in the further experimental work.

In the second step, the modification of the enriched clay was carried out by treating the solid material with solutions of alkali metal chlorides (lithium, potassium and sodium). The raw material previously dried to a constant mass does not need to be ground to a powder state, since the modification process is carried out in a salt solutions and in this case the dispersion of the material will occur spontaneously. The solid to liquid phase ratio was 1:10. The weight ratio clay: modifying agent (Me^{z+}) was 10: 1. The duration of the activation process was 3 hours at 95 - 97 °C and the suspension was constantly stirred. At the end of the time, the resulting product was washed from the associated anions and dried to a constant mass at a temperature of 105-130 °C. The finished modified samples were ground to a powder state with a particle size of less than 50 micron and used for further studies.

The chemical composition of the original and modified forms of montmorillonite clay was determined by electron microprobe analysis (EDAX energy-dispersive analyzer combined with Quanta 200 3D SEM-analyzer).

In the present work, the particle size distribution (dispersion) of the natural clays was determined using an «Analysette 22 NanoTec» laser particle size analyzer. The specific surface area and porosity of the materials were determined by low temperature adsorption, which was developed and theoretically justified by Brunauer, Emett and Teller (BET). The experiment was performed on an automatic unit of TriStar II 3020.

The sorption properties of the modified clay forms with respect to Cu^{2+} and Fe^{3+} ions were determined by constructing sorption isotherms by varying concentrations under static conditions. For this purpose, a series of model solutions of the iron (III) chloride and copper (II) sulfate were prepared. To prevent hydrolysis of these salts, the model solutions were acidified with a sulfuric acid solution. The solid to liquid phase ratio was 1:100. The process temperature was maintained constant - 25 °C, the exposure time was 4 hours with constant stirring. At the end of the process, the suspensions were filtered. The residual concentration of cations in the solution was determined photometrically at the appropriate wavelength using a Spekord-50 device.

2.2. Quantitative measurement of Cu2+, Fe3+sorption

sorptionSolution containing single metal salt: One hundred ml suspensioncontaining 0.2 g nanocellulose in 100 ml (CNCSLor CNCBEor phos-CNCSLor phos-CNCSL) was prepared and placed in a dialysis tube(dialysis tubing cellulose membrane, Sigma–Aldrich). The dialysistube was then placed in 400 ml Ag^+or Cu^{2+}or Fe^{3+}solution, witha concentration of 62.5 mg/L (equivalent to initial concentrationof 50 mg/L in the adsorption system, including the dialysis tube).The sorption system was kept under stirring for 42 h, as shownin Fig. 1. A dialysis bag acts as a barrier to trap the nanocellu-loses inside the dialysis tube while metal ions can pass throughthe dialysis bag freely, as represented. In order to prevent gen-eration of metal hydroxide precipitate, the metal solution pH iscontrolled in the range from 3.5 to 4.5 by addition of dilute nitricacid (ion product < Ksp). Sorption behaviors can be studied by themetal concentration variations. Solution samples with a volumeof 15 ml (outside the dialysis tube) were collected at 3 h, 8 h, 12 h,24 h and 48 h, respectively. The metal sorption experiments wereperformed at room temperature and metal concentrations of allsamples were detected by ICP-OES.Solution containing multi-metal salts: The same experimental setup as described above was performed in the case of multiple ionadsorption evaluation. 600 mg of nanocellulose in 100 ml was taken in the dialysis tube and placed in 400 ml of metal ion solution con-taining a mixture of Ag^+, $Cu^{2+}$and $Fe^{3+}$with a concentration of62.5 mg/L for each metal ion. The metal sorption experiments wereperformed at room temperature and metal concentrations of allsamples were detected by ICP-OES.

2.3. ICP-OES

An inductively coupled plasma-optical emission spectrometer,ICP-OES, Optima 2000 DV, PerkinElmer, (USA) with a radial torchwas used to measure the Cu^{2+} or Fe^{3+} concentration. The fil-trate of each single sample was collected at different times andused to calculate the metal sorption capacities after different incu-bation times, as shown in Fig. 1. (See Supporting information forthe detailed equations used for the calculation).

2.4. Performance in industrial effluent

The industrial effluent used for metal sorption testing is fromthe mirror industry and was provided by Acondaqua Water Engi-neering S.L., Valencia, Spain. The effluent is enriched with Cu^{2+} and Fe^{3+}(pH 7). The effluent water and 0.05 g nanocellulose were mixedin a 25 ml volumetric flask. All samples were sealed and kept understirring for 42 h to complete the adsorption process. The disper-sions were subjected to vacuum filtration with a membrane poresize of 0.45 _m (Nylaflo, Pall) to separate the nanocellulose fromthe effluent.The iron and copper concentrations of both industrial effluentand filtrate were detected using inductively coupled plasma opti-cal emission spectrometry. Sorption capacity (mg/g) and removalrate were calculated from the variation of metal ion concentrationsbefore and after the sorption.

3. RESULTS AND DISCUSSION

The chemical composition of the original and modified forms of montmorillonite clay is shown in Table 1:

Table 1: *Chemical composition of montmorillonite containing clay*

Name of a sample	Containing, mass %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	Li_2O
Enriched clay form	49.70	21.35	7.55	0.87	2.66	14.73	3.14	-	-
Li-form	45.65	22.33	7.92	0.91	2.65	15.37	3.61	-	1.56
Na-form	45.72	21.34	7.06	0.72	2.76	14.95	3.46	3.98	-
K-form	46.53	22.23	6.37	1.35	2.49	14.74	6.28	-	-

It has been found that during the treatment of clay material with solutions of alkali metal chlorides, the amorphous SiO_2 is partially dissolved and removed from the system during subsequent washing of the product. During the salt modification of montmorillonite containing clays, an ion exchange reactions occur between the inter-compact montmorillonitecations and cations represent in the aqueous salt solution. At the same time, no immediate changes in the structure of the mineral have been detected.

Characterizing the sorption properties of materials, an important aspect is a research aimed at studying their textural characteristics, such as particle size, as well as specific surface and porosity values. The results of the experimental studies are shown in the Table 2.

Table 2: *Textural characteristics of test sorbents*

Material	Average particle size, μm	Specific surface area, m^2/g (BET method)	Pore volume, sm^3/g (BJH method)
Enriched clay form	12.72	42	0.057
Li-form	4.96	48	0.060
Na-form	6.97	47	0.054
K-form	7.77	43	0.051

It has been found that during the modification process, the resulting activated materials show a decrease in the average particle size compared to the original matrix. This is due to the additional dispersion of montmorillonite particles in hydrothermal treatment of clay with the salt solutions. The average particle size of the alkaline forms of the clay materials increases in the order of Li-form < Na-form < K-form. This may

be due to the increase in the radius of alkali metal ions intercalated by an ion exchange into the inter-pack space of montmorillonite in a given row. In a comparative analysis of the specific surface the area and porosity of the alkaline and enriched forms of clay, it has been found that during the salt treatment the texture characteristics of the materials remain virtually unchanged. Thus, it can be said that the geometric parameters of the clay materials are maintained here.

In order to determine the effect of the salt activation process on the absorption characteristics of clay materials, an experimental work was carried out to determine the sorption properties of modified clay forms with respect to Cu^{2+} and Fe^{3+} ions. The ability of the tested samples to absorb cations of heavy metals is shown in the figure 1.
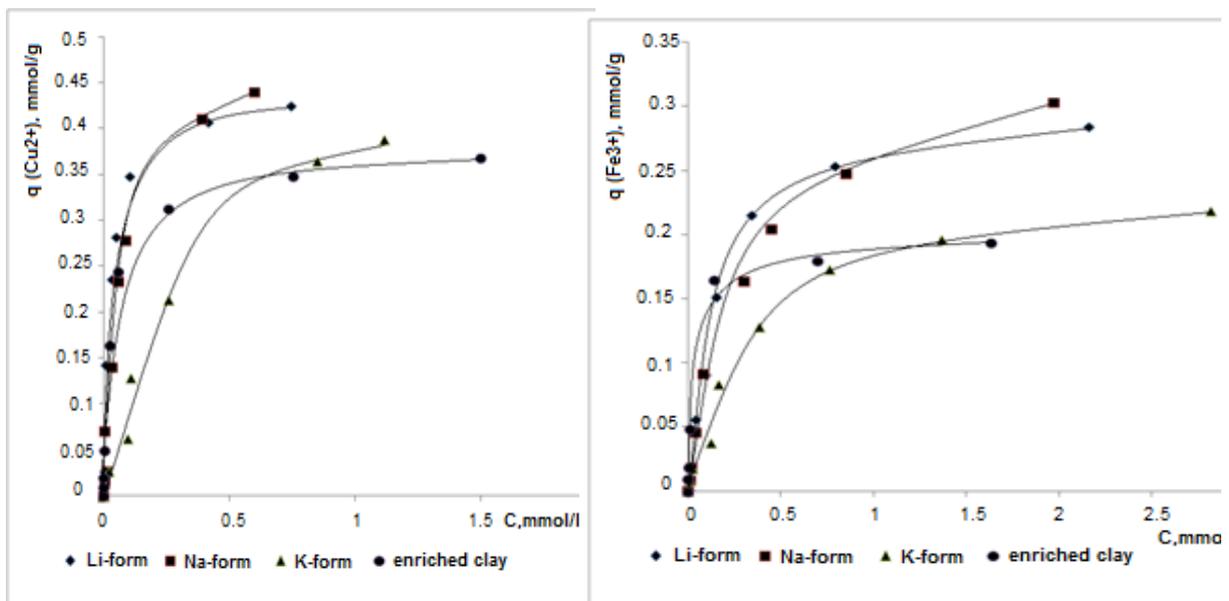

Figure 1. Sorption isotherms of Fe^{3+} and Cu^{2+} ions on enriched and modified forms of montmorillonite containg clay as a function of equilibrium metal ion concentration
at temperature 25 °C

The analysis of the figure revealed thedifferent absorbency of the experimental sorbents.

Thus, it has been found that the ability to sorb the copper (II) ions for all tested samples is higher, compared to ferric ions. This explains that the enriched clay, which was the matrix upon the modification, initially showed an increased affinity to the Cu^{2+} ions.

It is worth noting that the potassium form is inferior to Li- and Na-samples in its ability to sorb iron and copper ions. This may be due to the fact that the exchange cations K^+ are strongly bound to the surface of the clay minerals, this probably complicates the ion exchange process between the sorbate and the sorbtive.

For the mathematical treatment of the obtained sorption curves, we used the Langmuir model. A graphical solution of the Langmuir equation (by converting it into a straight equation) allowed to determine the maximum value of sorption q_m, as well as the adsorption equilibrium constant b, which are important parameters of the sorption process (Eq.1).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}, \qquad \text{(Eq.1).}$$

Where C_e corresponds to the equilibrium concentration, q_m is an adsorption limit value, q_e is an adsorption at this equilibrium concentration, b is an empirical constant. In addition, R^2 correlation coefficients were calculated when converting isoterms of sorption of metal ions into linear form, which indicate compliance of Lengmuir model sorption (Volovicheva *et al.,* 2015; Önal, *et al.,* 2006). The results of mathematical processing of experimental data are represented in Table 3.

Table 3: Mathematical parameters of the Langmuir equation for 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
Enriched clay form	0.9992	0.189	29.41	0.9993	0.358	40.00
L-form	0.9894	0.316	5.05	0.9997	0.437	41.67
Na-form	0.9934	0.323	4.12	0.9964	0.480	16.67
K-form	0.9990	0.244	3.05	0.9978	0.471	4.00

When assessing the limit value of the sorption capacity for the activated samples, it is shown that sodium form of montmorillonite containing clay has the greatest absorption capacity among alkaline forms. The relatively low sorption capacity of the K-form of clay is due to the lower mobility and hence the possibility of dissociating cations of said metal from the surface of the clay materials in aqueous solutions. At the same time, these samples outperform enriched clay by an average of 20 - 40% by its absorptive power.

4. CONCLUSIONS:

Thus, in the process of experimental work it is shown that the complex treatment of a natural clay of the deposit of the Belgorod region (Russia), including the stages of enrichment and hydrothermal activation with solutions of alkali metal chlorides allows to preserve the phase composition and geometric parameters of clay materials. The process of enrichment by the method of extraction of the fine fraction allows to increase the proportion of montmorillonite in the obtained product. Due to the salt activation, the sodium oxide content in the obtained Na-form was 3.98 wt%, and the lithium oxide in Li-form of clay was 1.56 wt%. There was also a 2-fold increase in the proportion of K_2O in the corresponding sample.

A complex activation of montmorillonite containing clays results in the increased sorption activity of the obtained solid-phase

samples with respect to Cu^{2+} and Fe^{3+} ions. Herewith the most effective sorbent is the sodium form. By treating the enriched sample with a sodium chloride solution, it was possible to increase the sorption capacity of the material with respect to copper (II) ions by 1.3 times, and with respect to iron (III) ions by 1.7 times.

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