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MATERIAL COMPOSITION AND COLLOID-CHEMICAL PROPERTIES OF NATURAL AND MODIFIED MONTMORILLONITE CLAYS

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ABSTRACT

There is determined the dependence of colloid-chemical properties of the natural and modified montmorillonite clays from "Polyana" deposit in Shebekinsky district, Belgorod Region, Russian Federation, on their material composition, i.e. on their chemical, mineral and granulometric composition. It is shown that cation-substitution in the inter-pack positions of montmorillonite results in the increase of clay's sorption capacity and its natric form can be used for the efficient water purifying from iron ions (III). It has been observed the high adsorption rate of Fe^{3+} ions within the first five minutes of purifying water solutions, which is conditioned by increase of exchange cations content, increase of sorbent's specific surface and alteration of zeta-potential towards the negative range at beneficiation and modification. It has been detected that sorption of Fe^{3+} ions by natural and modified clays is determined by processes of ion exchange and are of chemosorption nature predominantly.

Keywords: clay, montmorillonite, modification, sorption, electrokinetic potential, specific surface, particle size, iron ions (III), water purifying.

INTRODUCTION

Clays are traditionally a subject matter of colloidal chemistry. Clays are sedimentary rocks on the base of high-dispersity clay minerals with particle size less than 2 μm. Clay minerals are presented by layer silicates with layer thickness (interplanar spacing, perpendicular to basal plane) 0,73 nm for layer silicates of 1:1 structure type and 0,96 nm for layer silicates of 2:1 structure type. Clay minerals are nanostructured, often nanofilm, nanoporous materials, which can be used as nanoreactor [1, 2].

Clay minerals, due to the well-developed heterovalent isomorphous cation substitution in octahedral and tetrahedral position possess high ion exchangeability, i.e. some cations on the surface and in the inter-pack positions of crystal lattice can be replaced by cations from the solution. Such a peculiarity of clay minerals, along with their high dispersity and very developed surface, determine their high sorption capacity, i.e. ability to adsorb different substances from solutions. The cation exchange by now has received more study, than anion exchange. The main exchange cations in clays are Ca^{2+}, Mg^{2+}, H^+, Na^+.

There are distinguished several groups of clay minerals: allophanic, kaolinite, montmorillonite, illite etc. The most interesting, from a perspective of colloid chemistry, group of clay minerals, due to their adsorbability and swellability, are smectites. The most widespread mineral of this group is montmorillonite - the main source mineral of bentonite clays. Apart from clay minerals, clays can contain finely-dispersed low-temperature trigonal quartz; calcite, magnesite, limonite and other disperse minerals.

The clays from different deposits are very unlike in their material (mineralogical and chemical) composition and, as a result, in colloid-chemical properties, on which the possibility of their practical application in various spheres of human activity depends to a large extent.

The first mentions about using clays in ceramic material production date back to extreme antiquity [3]. It is known that they were used in metal industry. Since ancient times they have been used for sorption purification of wines and juices.

Due to environmental degradation in the world the search of efficient and cost-effective methods of purifying natural, domestic and industrial sewage waters from various pollutants [4, 5] becomes of great importance all over the world. The active research concerning the use of clay for sorption purification of water from radionuclides, surface acting agents (SAA), heavy metals (in the ionic form), oil-products and other organic pollutants [6, 7] is being carried out.

The sorption capacity of clay depends on its composition, structure and correlates with a number of physical and chemical properties. So, researching the material composition and properties of natural clay, as well as modifying it in order to increase the sorption activity is a very topical issue.

To improve the sorption properties of native clay there are used different methods of its modification: thermal, acidic, salt treatment (cation-substitution), electromagnetic fields action etc. [8-14].

Over the past ten years at the general chemistry department of Belgorod National Research University (NRU "BelGU") there is carried out active research of montmorillonite clays of Kiev suite, deposited at the territory of Belgorod region, and their modified forms with the purpose of designing the efficient sorption-active materials, which can be used for purifying water, developing fodder additives for livestock and veterinary drugs [15-19].

MATERIALS AND METHODS

This work presents the findings of integrated research of natural clay from "Polyana" deposit in Shebekinsky district, Belgorod Region, Russian Federation, and its modified forms. The choice of this deposit is conditioned by the fact that clays of this deposit have mode of occurence suitable for commercial production. For research there were taken samples of clay from the depth 4, 5 meters.

X-ray phase analysis and X-ray structure analysis were performed with a general-purpose X-ray diffractometer DRON-3, 0 modernized by specialists in St.Petersburg and Perspective Equipment Laboratory in Moscow with powder diffraction technique in the range 2θ from 4 to 64°.

To determine the chemical composition of the clay samples' separate minerals, and to study their surface structure there was used a scanning ion microscope Quanta 200 3D (produced by FEI). The morphological and structural features of clay were researched with transmission electron microscope JEM-2100 of the company JEOL, fitted with energy-dispersive analyzer EDAX WDX/EDX. The specific surface was determined with the automatic porosity and specific surface area analyzer TriStar II 3020 by the method of nitrogen low-temperature adsorption. The granulometric composition of samples was identified by method of dynamic laser light scattering with the instrument Micro Sizer 201C. The electrokinetic potential was determined by electrophoretic method with the instrument Zetasizer Nano ZS.

To increase the sorption capacity of clay there were used beneficiation, acid and salt treatment. These methods are described in more details in the previously published works [15, 17]:

- beneficiation - method of modifying clays, aimed at spoil disposal and increasing of sorption-active minerals content by gravitational method;
- cation-substitution - method of substituting exchange cations in the clay minerals structure with other cations, carried out by treating clay 1M with NaCl solution in mass ratio 1:20 within 2 hours at boiling water bath temperature and washing sediment from traces of chloride ions.

The content of montmorillonite in the clay was determined by adsorption luminescence analysis method. It is based on the cation-exchange adsorption of luminous organic pigments by clay with formation of an organoclay coagulate complex according to RF National State Standard 28177-89.

The adsorption capacity of clay samples under research was determined beforehand by standard solution of methylene blue, which is normally used as a sorbate for identifying the sorbents' sorption properties.

The research of sorption properties of clays was carried out by using standardized test solution $FeCl_3$ with Fe^{3+} ion concentration 0, 1 mmol/l (the consumption of 1 g of clay accrues to 50 ml of standardized test solution). The choice of this very metal is conditioned by the fact that natural waters of Belgorod region, as well as many other regions, contain the excess amount of iron, due to the presence of iron ore deposits [20-23]. The technogenic sources of this metal are mining industry, ferrous metallurgy, cement production, metalworking factories etc.

It is known that iron-containing water causes skin irritation, dryness, itching, similar to allergenic reactions. It does much harm to the flora and fauna of water bodies. The uptake of excess amount of iron results in many organ dysfunctions.

The content of iron ions (III) in the filtrate after the adsorption was determined by photometric method with the instrument KFK-3.01. This method is based on the ability of iron cations to form a yellow complex compound with sulphosalicylic acid in alkaline medium.

RESULTS AND DISCUSSION

According to the data of energy-dispersive analysis (Figure-1) there was determined the chemical composition of natural, beneficiated, sodium-substituted forms of beneficiated clay and clay treated with 30% water solution of sulfuric acid which is shown in Tables 1, 2 and 3.
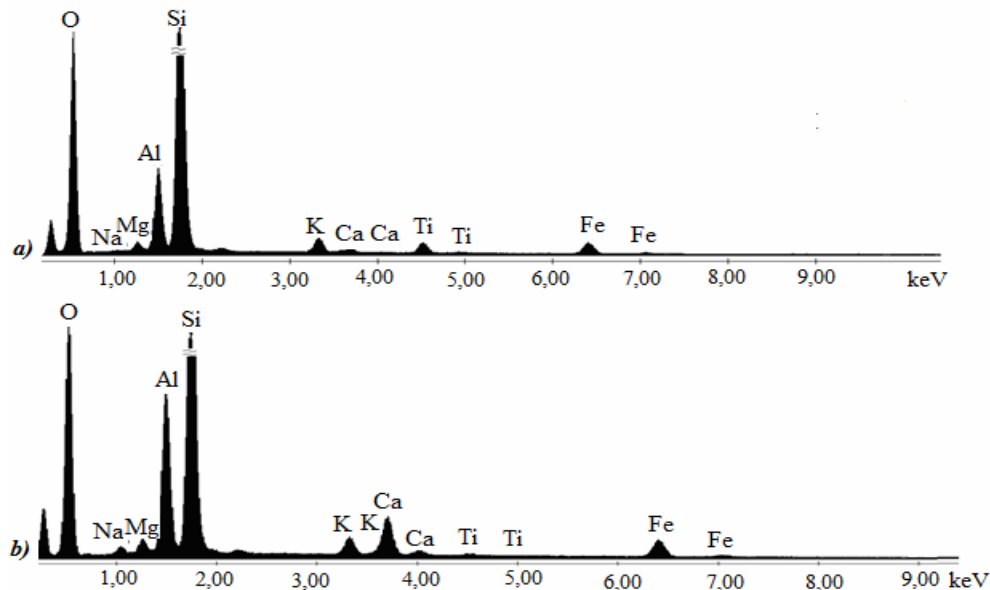
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Figure-1. The energy-dispersive spectra of native (*a*) and beneficiated (*b*) clay (particle size less than 10 μm).

The energy-dispersive spectrum of natural clay has identified the presence of the following chemical elements: silicon, aluminum, potassium, iron, titanium, magnesium, calcium, sodium (the elements are listed in the order of decreasing of their content) (Figure-1.*a*). In the process of beneficiation there is observed the increase of intensity of spectrum bands for the following elements:

Al, Mg, Ca, Na, K, Fe and decrease of intensity for Si and Ti (Figure-1.*b*).

The chemical composition of natural and beneficiated clay with particle size less than 10 μm according to the results of energy-dispersive analysis is shown in Table-1.

Table-1. The chemical composition of natural and beneficiated samples of clay, mass. %.

Sample	SiO_2	Al_2O_3	K_2O	Na_2O	MgO	CaO	Fe_2O_3	TiO_2
Natural clay	66,4	18,5	1,76	1,62	2,46	4,64	3,91	0,72
Beneficiated clay	51,3	23,6	3,19	5,14	2,51	5,50	8,35	0,41

The data, presented in Table-1, show that clay beneficiation results in substantial content reduction of SiO_2 and TiO_2 in it, and, consequently, increase of Al_2O_3, K_2O, Na_2O, MgO, CaO, Fe_2O_3 content.

The chemical composition of natural and beneficiated clay was determined not only by energy-

dispersive analysis method, but also by methods of classical analytical chemistry. The findings of energy-dispersive analysis, concerning the chemical composition of samples, correlate with the chemical composition data, determined by classical analytical methods (Table-2).

Table-2. The chemical composition of natural and beneficiated samples of clay, mass. %. (method of classical analytical chemistry)

Sample	SiO_2	Al_2O_3	K_2O	Na_2O	MgO	CaO	Fe_2O_3	TiO_2
Natural clay	62,4	12,4	1,81	0,66	2,27	4,72	3,95	0,71
Beneficiated clay	52,4	16,4	3,16	4,76	2,36	5,08	7,25	0,43

The modifying of beneficiated clay with a 30 % H_2SO_4 solution with the subsequent treating it with NaCl solution, and cation-substitution of beneficiated clay with

NaCl solution results in the three-fold increase of Na_2O content (Table-3).

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Table-3. The chemical composition of modified samples of clay, mass. %.

Sample	SiO$_2$	Al$_2$O$_3$	K$_2$O	Na$_2$O	MgO	CaO	Fe$_2$O$_3$	TiO$_2$
Benef. + 30 % H$_2$SO$_4$+ NaCl	76,4	3,36	1,02	15,3	0,35	-	3,39	0,18
Benef. + NaCl	62,3	14,5	1,02	11,9	1,77	1,25	7,21	0,23

During the cation-substitution process the sodium ions expel ions of Mg^{2+}, Ca^{2+}, Fe^{3+}, Fe^{2+} from the exchange positions. The maximum content of Na^+ ions in the modified sample is conditioned by the fact that besides the expelling of exchangeable ions, the substitution of H^+ and Al^{3+} ions, which appear on the surface of montmorillonite crystal lattice in the process of modifying, can also take place.

The mineralogical composition of natural and beneficiated clay was determined by method of X-ray phase analysis. Montmorillonite in the natural clay was identified by reflections 1.497, 1.319, 1.236, 0.454, 0.258, 0.167 nm. Reflection $d_{001}=1.236$ nm characterizes the natric form of montmorillonite. Apart from the essential mineral - montmorillonite there are ancillary minerals: illite (1.010, 0.907, 0.454, 0.258 nm), kaolinite (0.728, 0.258 nm), quartz (0.428, 0.335, 0.228, 0.224, 0.199 nm), clinoptilolite (0.897, 0.398, 0.298 nm), calcite (0.228 nm).

The electron diffraction and electron microscopy research, performed with a transmission electron microscope, showed that natural clay is represented by the association of montmorillonite and its structurally imperfect forms - smectite, muscovite, quartz and kaolin, with impurities of rutile. Electron micrographs and microdiffraction patterns of the first three minerals are presented in Figures 2-4.
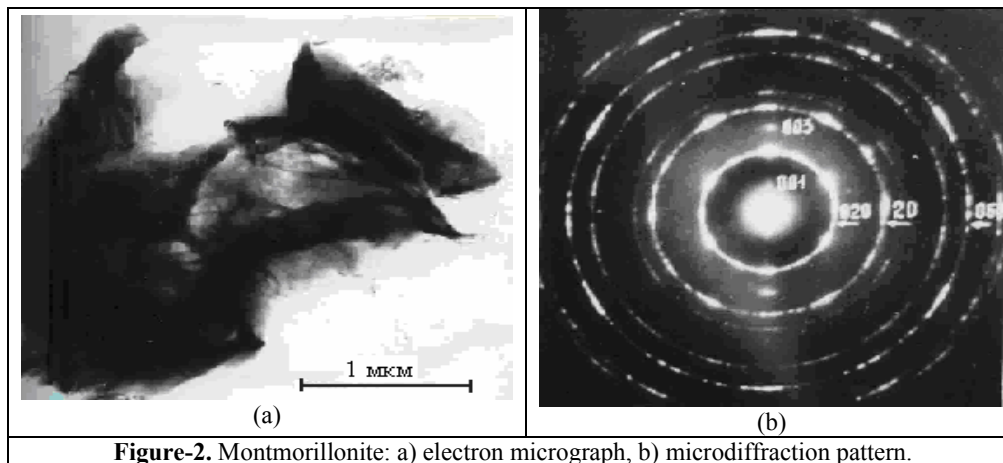
Figure-2. Montmorillonite: a) electron micrograph, b) microdiffraction pattern.
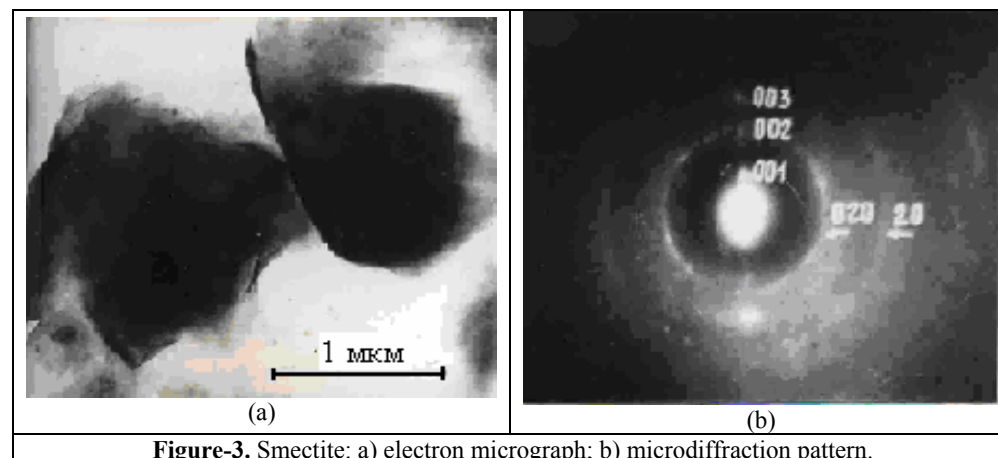
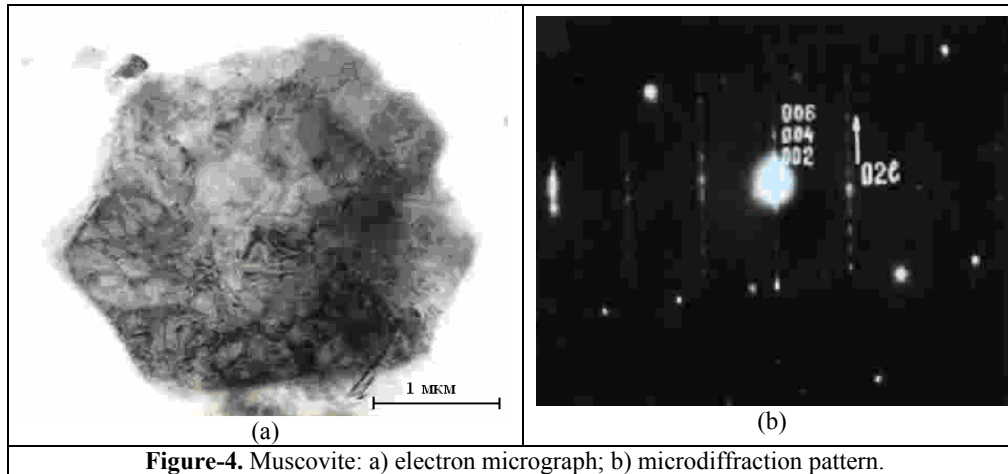**Figure-3.** Smectite: a) electron micrograph; b) microdiffraction pattern.

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Figure-4. Muscovite: a) electron micrograph; b) microdiffraction pattern.

By method of natural clay washing there were obtained samples of beneficiated clay with particle size less than 50, 10, 5 and 1 μm. The X-ray powder diffractograms of beneficiated clay samples demonstrate the increase of intensity of montmorillonite reflections (1.349, 1.253, 0.257, 0.173 nm) by 2-4 times and decrease of intensity of the low-temperature trigonal quartz reflections (0.428, 0, 182, 0.154 nm). This gives evidence of the increase of montmorillonite, illite and clinoptilolite content due to reduction of content of the low-temperature trigonal quartz.

Table-4 shows the content of sorption-active mineral montmorillonite in the natural clay and in the samples of beneficiated clay with various particle sizes.

Table-4. Content of montmorillonite in clay, mass. %.

Natural	Beneficiated			
	Particle size, μm			
	less than 50	less than 10	less than 5	less than 1
49,8-50,1	53,2-54,3	59,8-60,2	61,3-62,3	94,5 - 95,2

It follows from the data, presented in Table-4, that in the beneficiated samples, in comparison with native clays, the content of montmorillonite is increased and its maximum content is observed in fractions with particle size less than 1 μm, which is caused by the removal of draw rock - quartz and part of illite as the less sorption-active clay mineral. As a consequence of beneficiation there increases the content of oxides, the cations of which are included into the tetrahedral and octahedral packs of montmorillonite crystal lattice.

The increase of content of sorption-active mineral - montmorillonite, in theory must result in the increase of the clay's sorption capacity, which will be shown below.

At carrying out the experimental studies, apart from the material composition, there was determined a number of colloid-chemical properties of natural, beneficiated and modified forms of clays.

In Table-5 there are presented values of electrokinetic potential, specific surface (Ssp) and true density (d) of clay samples under study.

It is known that electrokinetic potential of the natural clays surface is negative. The natural clay under research has ξ = -32, 1 mV. The beneficiation process results in the increase of [zeta]-potential in absolute magnitude to -45, 5 mV. With the reduction of particle size the [zeta]- potential acquires the more negative value.

Table-5. Values of ξ-potential, specific surface and density.

# Sample	Sorbent	ξ, mV	Ssp, m^2/kg	d, kg/m^3
1	Natural clay	-32,1	79968	2508
2	Beneficiated clay:			
	Fraction less than 50 μm	-39,7	86406	2566
	Fraction less than 10 μm	-43,5	93259	2632
	Fraction less than 5 μm	-45,5	98121	2713
3	Benef. + 30 % H_2SO_4+ NaCl	-32,4	160380	2395
4	Benef. + NaCl	-45,5	88818	2724

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The treating of beneficiated clay with the 30% H_2SO_4 solution within 6 hours results in the decrease of electrokinetic potential value in absolute magnitude to - 28,8 mV. The treating of beneficiated clay with sodium chloride results in the increase of [zeta] - potential in absolute magnitude (Table-5).

With the reduction of the particle size the specific surface of beneficiated clay increases from 79968 m^2/kg to 98121 m^2/kg.

The introduction of Na^+ cations into the exchange positions of montmorillonite-containing clay, pretreated with acid, doesn't have any substantial influence on the specific surface area. For comparison we give the values of specific surface and density of clay, treated only with acid (without the subsequent introduction of Na^+ ions): they amount respectively to 161510 m^2/kg and 2320 kg/m^3.

The slight alteration of samples' specific surface at introducing Na^+ is conditioned by the fact that aqueous solutions of salt don't cause any noticeable destruction of montmorillonite structure, as it is observed at the influence of strong acid.

The observed tendency to the increase of clay's true density as a result of its beneficiation gives evidence of the strengthening of packing of highly dispersed particles, which make up the certain fractions. The increase of sodium-substituted samples' density, in comparison with beneficiated and acid-modified ones, results from the intrusion of Na^+ cations into the inter-pack positions of montmorillonite crystal lattice.

The preliminary estimate of the sorption activity of the clay samples under study is performed with methylene blue standard solution and is presented in Figure-5.
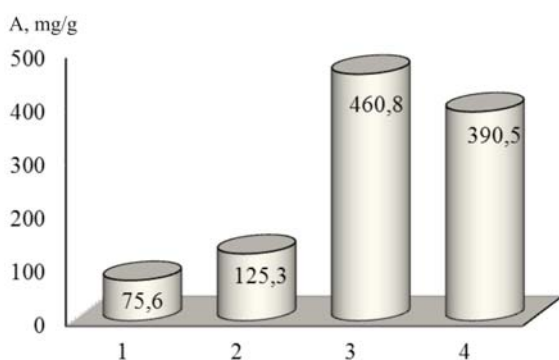

Figure-5. Adsorption capacity (A) of clays according to methylene.
blue (C_0= 1500 mg/l): 1 - natural clay; 2- beneficiated clay; 3 - beneficiated clay + 30% H_2SO_4 + NaCl; 4 - beneficiated clay + NaCl.

Experiments proved that beneficiation raises the adsorption capacity, working on methylene blue, by 66 % for samples with particle size less than 10 μm, which can be explained in the following way. The decrease of

particle size and increase of specific surface of beneficiated clays make meso - (2-50 nm) and macropores (> 50 nm) available for sorbing molecules of methylene blue, the size of which is large enough (1, 97 nm^2). Besides, the stronger attraction of methylene blue molecules to the negatively charged surface of beneficiated clays is promoted by the increase of [zeta] - potential in absolute magnitude (Table-5).

The adsorption capacity of cation-substituted forms of clay is higher than that of beneficiated clay by 3, 7 and 3, 1 times for samples # 3 and # 4 respectively. The maximum adsorption of methylene blue is shown by sample # 3, due to its larger specific surface (Table-5).

The increase of natric forms of clay adsorption capacity results from the accretion of active sites, which appear in beneficiated clay after saturating it with Na^+ ions. The lesser adsorption capacity of sample # 4 compared with sample # 3 is conditioned by the lesser specific surface area of the first one (Table-5). The high adsorption capacity towards methylene blue is conditioned also by the fact that this pigment can be adsorbed not only on the surface of montmorillonite, but in its interlayer space as well.

The sorption capacity of natural, beneficiated and modified forms of clay working on heavy metal ions was researched on iron salts (III). The dependence of Fe^{3+} ions mass, absorbed by clays under research, on the time is shown in Figure-6. The research was carried out within the time interval from 5 to 90 minutes. The initial mass of Fe^{3+} ions in 50 ml of $FeCl_3$ standard solution amounted to 0, 28 mg.
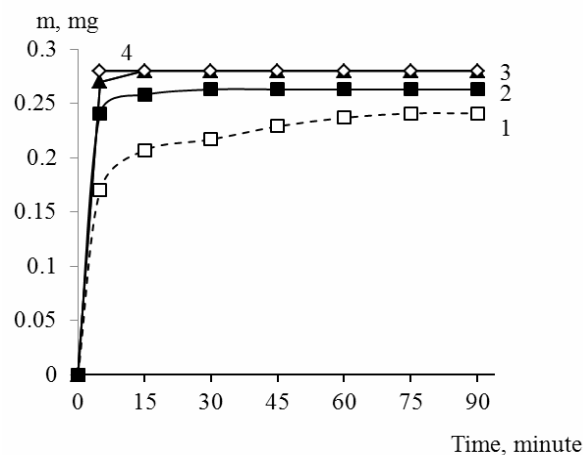

Figure-6. The kinetic dependence of Fe^{3+} ions mass adsorbed by 1 g of natural and modified forms of clays: 1- natural clay; 2 - beneficiated clay (fraction less than 10 μm); 3 - beneficiated clay + 30% H_2SO_4 + NaCl; 4 - beneficiated clay + NaCl.

Kinetic curves, presented in Figure-6, demonstrate that beneficiated clay at the indicated concentration of Fe^{3+} ions and at the indicated proportion sorbate:sorbent adsorb over 85 mass. % of Fe^{3+} ions within

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the first five minutes, while the natural clay during the indicated period of time adsorb only 61 mass. %. The maximum absorption of Fe^{3+} ions by the beneficiated clay amounted to 93 mass. %.

The sulphuric-acid treatment of beneficiated clay and the subsequent saturating it with sodium ions resulted in its sorption capacity increase. In 15 minutes the 99 % sorption of Fe^{3+} ions was achieved.

The optimal sorption capacity towards iron ions was shown by clay sample # 4: in this case the 99 % sorption of ions was achieved within 5 minutes.

The analysis of the kinetic curves has shown that the maximum adsorption rate of Fe^{3+} ions for all the samples is observed within the first five minutes. The high ion adsorption rate at the initial stage of sorption is explained by a number of factors, mentioned above. Firstly, the content of sorption-active mineral montmorillonite in clay is raised in the process of its beneficiation (Table-1), which is conditioned by the increase of exchange cations content and increase of the sorbent's specific surface. Secondly, in the process of beneficiation and cation-substitution the zeta-potential alters towards the negative range (Table-4), which causes the stronger attraction of polyvalent iron cation to the negatively charged surface of clay. As ions of iron are high-charged, they can be sometimes adsorbed in even larger amounts, than is required for neutralization of the surface charge.

The comparative assessment of adsorption capacity of sorbents under research was also performed by isotherms of Fe^{3+} ions adsorption. There was prepared a set of standardized test solutions of $FeCl_3$ with different concentration of Fe^{3+} ions, the highest of which amounted to 2 mmol/l. The sorption process was carried out within 24 hours. The graphs of adsorption isotherms were plotted in the following coordinates: adsorption A, mmol/g - equilibrium concentration of Fe^{3+} ions in solution C, mmol /l (Figure-7).

The analysis of adsorption isotherms confirms the dependence, which was detected by kinetic curves. Beneficiation increases the sorption capacity of clay (sample 2), the acid treatment with subsequent cation-substitution almost doesn't change the character of isotherm (sample 3), and cation-substitution with sodium ions raises the sorption capacity of clay considerably (sample 4).
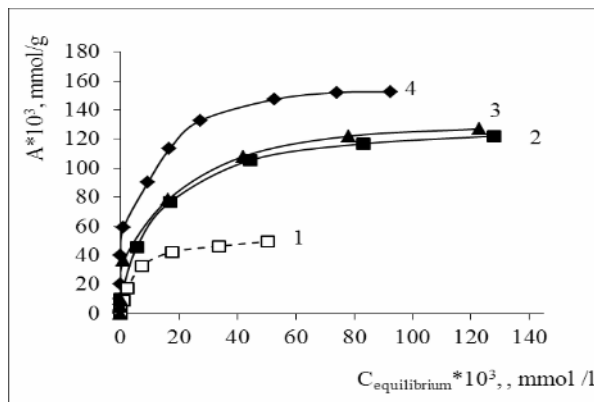

Figure-7. Isotherms of Fe^{3+} ions sorption natural clay; 2 - beneficiated clay (fraction less than 10 µm); 3 - beneficiated clay + 30% H_2SO_4 + NaCl; 4 - beneficiated clay + NaCl

The character of isotherms allows judging about affinity of sorbate and sorbent. Configuration of isotherms of Fe^{3+} ions adsorption by sodium-substituted forms of beneficiated and acid-treated samples of clay in the range of low concentration marks the high adsorption energy. Isotherms in this range are parallel to the ordinate axis and virtually merge with it, which indicates the chemical character of sorption.

The statistical processing of isotherms in accordance with Freundlich equation in logarithmical form:

$$ln\Gamma = \ln a + \frac{1}{n} * \ln c$$

has allowed determining the constants of this equation graphically (Table-6). Constant *a* in the Freundlich equation characterizes the affinity of sorbate and sorbent, and constant *n* - the curvature of adsorption isotherm.

Table-6. Constants of Freundlich equation.

Sorbent	Fe^{3+}	
	$a \cdot 10^3$	n
Natural clay	6,08	3,50
Beneficiated clay	20,9	3,84
Benef. + 30 % H_2SO_4+ NaCl	25,3	4,01
Benef. + NaCl	35,3	4,38

Constant *a* is the highest for natric forms of sorbents, which can be explained by the fact, that Na^+ ions in exchange positions are easier, than other ions, substituted with metal ions from solutions.

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CONCLUSIONS

So, the research of material composition and colloid-chemical properties of natural montmorillonite clay, as well as of the alterations caused by beneficiation, acid and salt treatment with sodium chloride, allowed obtaining an efficient sorbent for purifying water from iron ions (III).

It was determined that after beneficiation and modification there occurs the increase of exchange cations content, increase of the sorbent's specific surface and increase of the zeta-potential negative value in absolute magnitude, which provides the high adsorption rate.

a) It has been demonstrated that the basic sorption-active mineral of clay from "Polyana" deposit in Shebekinsky district, Belgorod Region, Russian Federation, is montmorillonite; as a result of beneficiating the clay under study its content raises from 49,8 mass.% to 95,2 mass.% in fraction with particle size less than 1 μm.

b) It has been found out that beneficiation of clay results in substantial content reduction of SiO_2 and TiO_2 in it and increase of Al_2O_3, K_2O, Na_2O, MgO, CaO, Fe_2O_3 content, and cation-substitution in the inter-pack positions of montmorillonite results in increase of Na_2O content from 5,14 mass.% to 15,3 mass.%.

c) It has been determined that electrokinetic potential of the surface of natural clay under study amounts to -32, 1 mV. Beneficiation of clay and modifying it with sodium chloride causes the increase of ξ-potential in absolute magnitude. With the reduction of particle size of beneficiated clay the ξ-potential reaches the value -45, 5 mV (for fraction less than 5 μm).

d) The slight alteration of samples' specific surface at introducing Na^+ ions is conditioned by the fact that aqueous solutions of salt don't cause any noticeable destruction of montmorillonite structure, as it is observed at the influence of sulphuric acid.

e) It has been proved that maximum efficiency of purifying the water solutions from iron ions at concentration of Fe^{3+} 0,1 mmol/l and at mass ratio sorbate:sorbent = 0,00028:1 with natural clay amounts to 86 mass.%, with beneficiated clay - 93 mass.%, and with cation-substituted forms - 99 mass.%.

f) It has been observed the high adsorption rate of Fe^{3+} ions within the first five minutes of purifying water solutions, which is conditioned by increase of exchange cations content, increase of sorbent's specific surface and alteration of zeta-potential towards the negative range at beneficiation and modification.

g) It has been detected that sorption of Fe^{3+} ions by natural and modified clays is determined by processes of ion exchange and are of chemosorption nature predominantly.

h) It has been demonstrated that sodium-substituted form of montmorillonite clay can be used for the efficient purifying water from Fe^{3+} ions.

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