PHYSICAL CHEMISTRY
OF SURFACE PHENOMENA

Effect of the Acidic and Alkaline Activation of Bentonite-Like Clays on Sorption Properties in Relation to Fe^{3+} Ions under Static Conditions

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Abstract—A study is performed of the effect the means of activation of bentonite-like clays (acidic, alkaline, combined) have on the adsorption characteristics of Fe^{3+} ions under static conditions. The mechanism of the acidic and alkaline activation of montmorillonite is identified and found to depend on the concentration of the activating agent. Solutions of sulfuric acid and lithium hydroxide are used as activating agents. It is shown that during combined treatment of enriched clay which includes activation with sulfuric acid and lithium hydroxide, its sorption capacity grows by 2.0–9.4 times, in relation to Fe^{3+} ions.

INTRODUCTION

Clay minerals are widely used in different fields of industry. The availability and abundance of this feedstock are complemented by its unique sorption characteristics, along with the flexibility of its structure in relation to the action of various modifiers of organic and inorganic nature [1–3]. One area of scientific and practical interest is using clays for the sorption purification of natural and waste waters where heavy metal ions are concerned. Clay rocks based on layered hydroaluminosilicates of the 2 : 1 type with an expanding crystal lattice have high sorption performance. This group of minerals includes nanostructured montmorillonite. Its elementary packet, which consists of two external silicon–oxygen tetrahedral networks and one internal alumohydroxyl–oxygen network, is 0.94 nm thick. The thickness of the interpacket distance can vary and be as high as 3 nm, depending on the concentration of water and the composition of the cation-exchange complex [4, 5].

A structural model of the crystal lattice of montmorillonite was proposed by Hofmann, Endel, and Wilm in 1933 and later improved somewhat by Marshall and Hendricks (Fig. 1).

However, we believe that cations of silicon, aluminum, iron, and magnesium play a key role in the structure of montmorillonite. We earlier proposed the model of the mineral's crystal lattice that is presented in Fig. 2.

The crystal lattice of montmorillonite is distinguished by an electrical imbalance generated by an excess of negative charges. Isomorphic substitutions that result especially in an excess of uncompensated negative charges could be one reason for the imbalance of the charges of the tetrahedral and octahedral layers of the crystal lattice of montmorillonite. For example, minor isomorphic substitutions of Al^{3+} ions for Si^{4+} are thus characteristic of the tetrahedral layer [6–8]. Also, the substitution of phosphorus for silicon is possible in the tetrahedral layer, and Al^{3+} can be replaced by Mg^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Li^{+}, and other ions in the octahedral layer. The total negative charge is compensated for by cations that are adsorbed on the surface of montmorillonite in the interlayer space and around the elementary structural packets.

The acidic and alkaline activation of montmorillonite allows more efficient exchange of the cations in its structure. They also promote the formation of acid and base sites on its surface. It is known that at the initial stage of acidic activation, exchange cations are
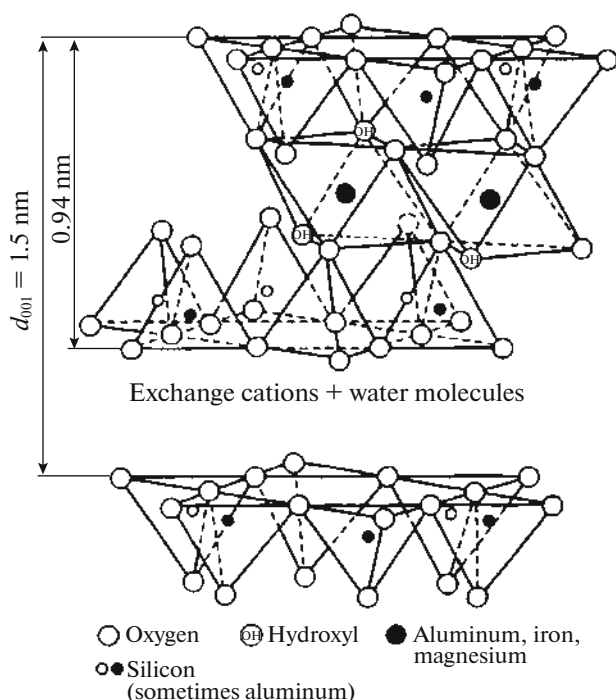
Fig. 1. Scheme of the crystal lattice of montmorillonite, according to Marshall and Hendricks [4].

Nitric and sulfuric acids readily oxidize organic components present in the clay. These acids are often used at the stage of purifying bentonite clays. Hydrochloric acid promotes more efficient transformation of smectites to the H-from without side processes of oxidation. Hydrochloric acid is therefore used most often for the acidic activation of clay. The conditions of the acidic treatment of bentonite-like clays from different deposits vary, so the parameters of the acidic activation of clay must be selected for each deposit. The problem of finding the optimum conditions for the acidic activation of clay while preserving the structure of its minerals is especially relevant.

A promising way of activating bentonite-like clays is alkaline activation. This technique is more versatile than acidic activation in terms of both obtaining more active sorbents and having lower requirements for the initial feedstock. Alkaline metal hydroxides and mixtures of calcium hydroxide with salts of mineral acids (e.g., $NaCl$, Na_2SO_4, Na_3PO_4, Na_2CO_3, etc.) are commonly used as alkaline agents.

The alkaline activation of natural aluminosilicates has a number of fundamental differences in comparison to acidic activation. These are associated with both the mechanism of the dissolution of clay minerals and the composition of products that form in the solution. Alkaline treatment with sodium and calcium hydroxides using the above salts in the activating solutions will transform them into oxides of aluminum, iron, magnesium, and other metals, along with silica. This can result in the formation of an aluminosilicate component, calcium and aluminum hydrosilicates, and compounds with an intrinsic developed porous structure and acidic surfaces upon subsequent precipitation of the hydroxides and the clay being activated [10].

replaced by hydrogen ions, and the so-called H-form of bentonite is obtained. Depending on the concentration of the acid, the leaching of structural cations then occurs in the order $Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+}$ [9]. It should be noted that the choice of the acid depends on the chemical composition of the native clay and the subsequent application of the activated samples.
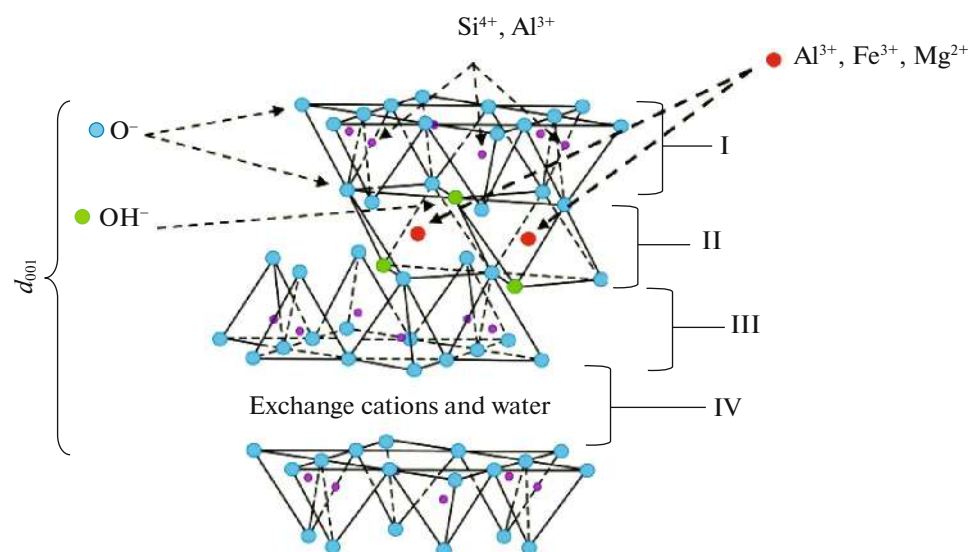

Fig. 2. Improved model of the crystal lattice of montmorillonite: (I) tetrahedral, (II) octahedral, and (III) tetrahedral layers; (IV) the interpacket space.

The aim of this work was a comparative assessment of the sorption activity of bentonite-like clay subjected to acidic, alkaline, and combined activation, in relation to iron(III) ions. Sulfuric acid and lithium hydroxide at different concentrations were used as the activating agents.

EXPERIMENTAL

Enriched clay from the Polyana deposit (Shebekinsky district, Belgorod oblast) with concentrations of montmorillonite up to 65 wt % was our material of study. Acidic treatment was performed according to the experimental procedure described by Batalova in [11]. A 10% solution of sulfuric acid was poured over the clay after it was ground and sieved through a screen with a mesh size of 80.0 μm. The clay : acid solution weight ratio was 1 : 4. The solution was heated for 6 h on a boiling water bath with constant stirring. When the process was complete, the material was thoroughly rinsed with distilled water until all sulfate ions were removed, as was determined from the negative reaction with Ba^{2+}. Alkaline activation was performed using solutions of lithium hydroxide with concentrations of 2.5, 5.0, and 10.0 wt %. The clay : modifying agent weight ratio was 1 : 0.09–0.36. The mixtures were stirred and heated for 6 h at 80–100°C. When the process was complete, the resulting products were rinsed until excess lithium hydroxide was removed, with pH being kept at 8.5–9.5. A series of samples was obtained: enriched clay (EC), clay modified with sulfuric acid (AcMC), enriched clay treated with solutions of lithium hydroxide at corresponding weight ratios of 1 : 0.09–0.36 (AlkMC), and acid-activated clay treated with solutions of lithium hydroxide at corresponding weight ratios of 1 : 0.09–0.36 (AcAlkC).

The chemical composition of the experimental samples was determined via classical analytical chemistry and energy dispersive X-ray analysis (EDAX) combined with a Quanta 200 3 D scanning electron microscope. A bright-field electron microscopic study of the clay in combination with electron microdiffraction and EDAX determination of the chemical composition was performed using a JEM-2100 transmission electron microscope equipped with a 200-kV electron gun and EDAX accessory that allowed local determination of the chemical composition of a sample, including the distribution of the elements along a fixed segment or inside a fixed region. Powder X-ray diffraction analysis was performed on an Ultima IV XRD-320 X-ray diffractometer in the 2θ range of 4°–64° in the automated mode.

The specific surfaces of the samples were determined on a TriStar II 3020 automated specific surface area and porosity analyzer. The true densities of the samples were found via pycnometry.

The electrokinetic potentials of the samples in the state of suspension (with distilled water as the dispersion phase) was determined on a Zetasizer Nano ZS analyzer.

The Fe^{3+} sorption capacity was determined under static conditions using model aqueous solutions of variable concentrations at a constant clay : solution weight ratio of 1 : 100. The solutions were thermostatted for 60 min at 295 K. Model aqueous solutions were prepared using ferric chloride. Several drops of sulfuric acid diluted with distilled water in a ratio of 1 : 5 were added to each solution to prevent hydrolysis of the relevant salt. The suspensions were filtered after exposure was complete. The residual concentrations of the Fe^{3+} ions in the filtrate were determined spectrophotometrically at a wavelength of 425 nm. This analysis method is based on the formation of a yellow iron disulfosalicylate complex in alkaline media (pH 9–11.5); the pH was adjusted with ammonia solution. The detection limit was 0.2 mg/L.

The Fe^{3+} sorption capacities of the samples (A, mmol/g) was calculated on the basis of the obtained results:

$$A = \frac{(C_{in} - C_{eq})}{m} V, \qquad (1)$$

where C_{in} is the initial concentration of Fe^{3+} cations in the solution; mmol/g; C_{eq} is the equilibrium concentration of Fe^{3+} cations in the filtrate; mmol/L; m is the weighed amount of the sorbent, g; and V is the volume of the contacting model solution, mL.

The Langmuir model in linear coordinates was used to determine sorption parameters:

$$\frac{C_{eq}}{A} = \frac{1}{A_{max} K} + \frac{C_{eq}}{A_{max}}, \qquad (2)$$

where C_{eq} is the equilibrium concentration of Fe^{3+} cations in the filtrate, mmol/L; A_{max} is the maximum adsorption of Fe^{3+} cations, mmol/g; and K is the Langmuir constant.

RESULTS AND DISCUSSION

The chemical compositions of the experimental samples were studied after the acidic, alkaline, and combined activation of the bentonite-like clay. Results are presented in Table 1.

A trend toward a drop in the concentration of oxides SiO_2 and Al_2O_3 was observed after alkaline treatment of both enriched and acid-treated forms of clay. This is apparently explained by the destruction of tetrahedral silicon–oxygen and octahedral aluminum–oxygen layers, followed by silicate and aluminate ions migrating into the solution in the strongly alkaline medium. Raising the concentration of lithium hydroxide in the modifying solution increased the concentration of Li_2O in the experimental samples.

Table 1. Chemical composition of clay samples, wt % (LOI denotes losses on ignition)

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	Li_2O	LOI
EC	63.23	16.73	3.36	0.60	2.20	3.20	1.95	2.06	—	6.80
AcMC	73.25	14.43	2.51	0.52	1.94	0.65	1.06	0.29	—	5.35
AlkMC 1 : 0.09	60.12	15.63	4.73	0.60	3.43	4.31	2.08	1.85	1.04	6.21
AlkMC 1 : 0.18	60.16	15.60	4.70	0.41	3.42	4.23	1.97	1.48	1.23	6.80
AlkMC 1 : 0.36	58.87	15.61	4.74	0.50	3.92	4.80	2.05	1.47	1.30	6.74
AcAlkC 1 : 0.09	70.30	14.27	2.33	0.60	2.71	1.85	1.08	0.23	1.07	5.56
AcAlkC 1 : 0.18	70.23	13.85	2.18	0.55	2.52	1.89	1.07	0.33	1.51	5.87
AcAlkC 1 : 0.36	70.26	13.54	2.40	0.55	2.49	1.83	1.04	0.35	1.71	5.83

Preliminary acidic treatment increased the number of vacant positions in the structure of montmorillonite, as was confirmed by a drop in the concentration of each oxide, except for silica. The concentrations of Ca^{2+} and Na^+ cations fell considerably. The treatment with alkaline solutions on oxidized montmorillonite allowed us to intercalate Li^+ cations into its structure, as was observed when studying the chemical compositions of the resulting samples.

The mineralogical composition of the obtained samples contained phases of montmorillonite (calcium and sodium forms), low-temperature trigonal quartz, illite, kaolinite, muscovite, calcite, and feldspars. The phase compositions of the materials did not change appreciably during either acidic or alkaline treatment.

Fundamental structural changes in particles of montmorillonite after alkaline activation were observed by analyzing their electron micrographs and microdiffraction patterns (Fig. 3).

Bright-field electron microscopy of the enriched form of clay in combination with electron microdiffraction showed that montmorillonite was present in the form of thin nanosized films with crystalline structure (Fig. 3a).

The characteristic multiple bends at the edges of montmorillonite crystals are due to the layered structure of the mineral. The size of particles varies from tenths of a micrometer to 3–5 μm. The polycrystalline nature of the particles affects the microdiffraction patterns, which are often circular. Particles identified as low-temperature trigonal quartz, muscovite, and illite were present in the samples of clay, in addition to montmorillonite.

Analysis of electron micrographs of the sample of clay activated with lithium hydroxide (Fig. 3b) showed that the morphology of montmorillonite particles did not change. Acidic activation did not degrade the structure of montmorillonite. Structural and morphological changes that occurred in the material during
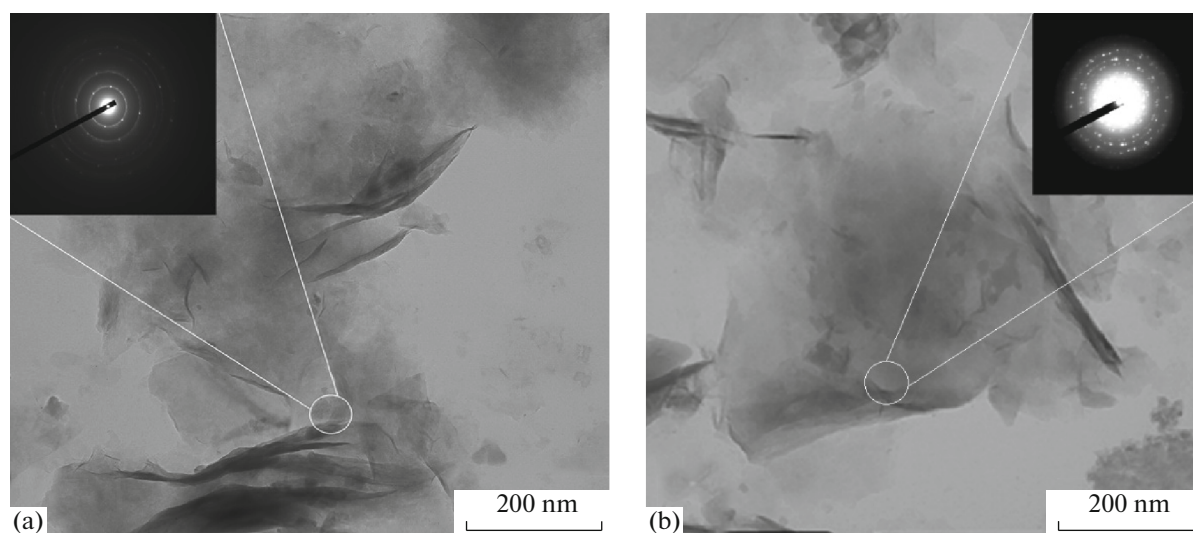
Fig. 3. Electron micrographs and microdiffraction patterns of the particles of montmorillonite: (a) enriched form of the clay; (b) clay subjected to treatment with a 10% solution of LiOH.

chemical activation were reflected in the textural characteristics of the experimental samples (Table 2).

A rise in the specific surface (from 118 to 164 m^2/g) and porosity (from 0.20 to 0.24 cm^3/g) of the sample was observed during acid treatment, due to the partial dealuminization of the crystal lattice of montmorillonite and the removal of exchangeable cations from the interpacket positions [11]. This was accompanied by a drop in the true density of the sample (from 2.20 to 1.70 g/cm^3). A trend toward a reduction in the specific surfaces and porosities of the resulting products was observed when treating the clay substrate with the solutions of lithium hydroxide. This could be explained by epitaxial destruction [12] induced by the deposition of poorly soluble lithium silicates on the surfaces of the materials and the possible shielding of pore spaces. Raising the concentration of the alkali in the solution shifted the equilibrium toward an increase in the solubility of the silicates and the ease of removing them during the rinsing of the product. This reduced the shielding effect and increased the specific surfaces, porosities, and true densities of the materials.

Figure 4 presents adsorption isotherms for the Fe^{3+} ions on our experimental samples of the clays.

The sample of clay treated with a 10% solution of sulfuric acid displayed the lowest Fe^{3+} sorption capacity, as was determined by the interaction between a number of factors: a drop in the fraction of the ion-exchange cations (Na^+, Ca^{2+}) in the interpacket positions of montmorillonite, and the compensating effect of exchangeable protons on broken bonds. There was thus a transition of $\equiv SiO^-$ to $\equiv SiOH$ groups, which reduced the absolute magnitudes of the electrokinetic potentials of the clay particles (-27.3 and -15.3 mV for the samples of enriched and acid-treated clays, respectively). It is noteworthy that the samples subjected to

Table 2. Textural characteristics of the experimental samples

Sample	S, m^2/g	V, cm^3/g	ρ, g/cm^3
EC	118	0.20	2.20
AcMC	164	0.24	1.70
AlkMC 1 : 0.09	77	0.16	2.25
AlkMC 1 : 0.18	80	0.18	2.20
AlkMC 1 : 0.36	97	0.18	2.20
AcAlkC 1 : 0.09	87	0.18	2.40
AcAlkC 1 : 0.18	96	0.20	2.35
AcAlkC 1 : 0.36	106	0.28	2.15
EC	118	0.20	2.20
AcMC	164	0.24	1.70
AlkMC 1 : 0.09	77	0.16	2.25
AlkMC 1 : 0.18	80	0.18	2.20
AlkMC 1 : 0.36	97	0.18	2.20
AcAlkC 1 : 0.09	87	0.18	2.40
AcAlkC 1 : 0.18	96	0.20	2.35
AcAlkC 1 : 0.36	106	0.28	2.15

S is the BET specific surface, V is the BJH total pore volume, and ρ is the true density.

two-stage successive acidic−alkaline activation had the highest Fe^{3+} sorption capacity. The positive effect of preliminarily treating the enriched clay with a 10% solution of sulfuric acid was to increase the specific surface of the material.

Table 3 presents the parameters of Langmuir adsorption isotherms for the sorption of Fe^{3+} ions by the studied sorbents.
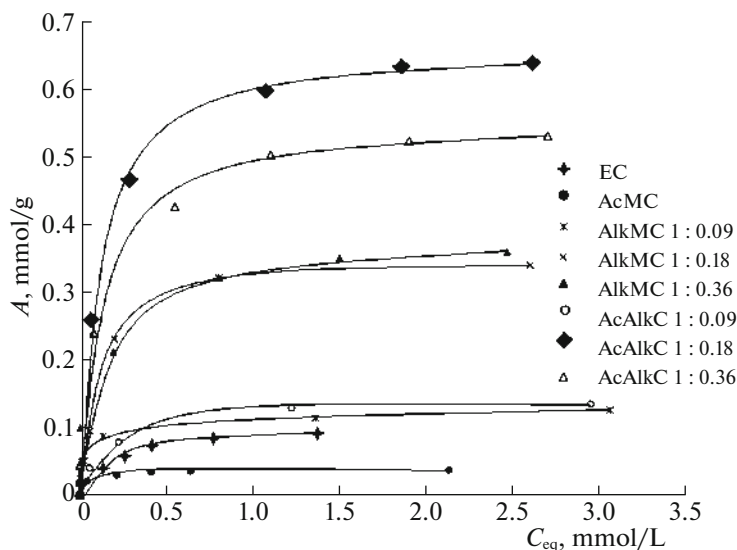

Fig. 4. Isotherms of the sorption of Fe^{3+} ions by the experimental sorbents.

Table 3. Parameters of Langmuir adsorption isotherms

Sample	A_{max}, mmol/g	K, L/mmol	R^2
EC	0.071	9.61	0.991
AcMC	0.041	12.20	0.988
AlkMC 1 : 0.09	0.138	9.35	0.993
AlkMC 1 : 0.18	0.356	8.72	0.979
AlkMC 1 : 0.36	0.387	6.90	0.995
AcAlkC 1 : 0.09	0.142	8.10	0.987
AcAlkC 1 : 0.18	0.668	6.29	0.994
AcAlkC 1 : 0.36	0.563	6.37	0.975

CONCLUSIONS

Combined modification of an enriched form of clay involving treatment with sulfuric acid and activation with lithium hydroxide leads to an increase in Fe^{3+} sorption capacity of the prepared material by 2.0−9.4 times. We may assume the sorption of iron cations by montmorillonite was due to the combined action of several processes, especially the exchange of cation in interpacket positions and processes caused by the considerable number of hydroxyl groups present on the external surface of the mineral upon alkaline treatment. Sorption also occurs on the end part of layered crystals which provide an exit for active sites that are valent bonds not compensated for (covalently unbound electrons). It was also shown experimentally that the sorption of iron(III) ions is irreversible, due to processes of epitaxial destruction that consist of the formation of poorly soluble silicates on surfaces of montmorillonite.

FUNDING

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Translated by E. Boltukhina