PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

Effect of Salt Modification on Adsorption Properties
of Acid-Activated Montmorillonite and Kaolinite


Voronezh State Forestry Academy, Voronezh, Russia
Lipetsk State Technical University, Lipetsk, Russia
Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

Received July 9, 2007

Abstract—Effect of modification of a layered aluminosilicate, montmorillonite, and rigid-structure kaolinitic activated by sulfuric acid with solutions of magnesium chloride was studied in order to obtain sorbents for wastewater treatment to remove organic compounds.

DOI: 10.1134/S1070427208060074

Because of the wide use of adsorption technologies in the present-day development and modernization of various industries, it becomes an increasingly urgent task to create inexpensive and readily available sorbents. A problem that remains topical for extending the application range of sorption materials is the possibility of purposefully controlling the chemical structure of their surface layer and thereby of widely varying the adsorption-structural characteristics of sorbents and improving their selectivity and multifunctionality.

The set of physicochemical properties of natural mineral sorbents is improved by their activation and modification. By the activation is commonly understood [1] the improvement of the sorption activity under any treatment of a material, and by modification, changes in the properties of sorbents, with their original structure preserved. In the present study, the adsorption properties of minerals were improved by activating samples with 20% sulfuric acid and modifying the activated samples with a magnesium chloride solution.

EXPERIMENTAL

As objects of study served two samples of natural silicates from a deposit in Lipetsk oblast, in which the rock-forming minerals are montmorillonite and kaolinite. Montmorillonite is a layered silicate material with an expanding structural unit. In montmorillonite, silicon in the tetrahedral layer is substituted by aluminum, and aluminum in octahedral positions is partly substituted by magnesium [2]. As a result, there appears charge deficiency compensated by interlayer ions having an exchange capacity. In natural montmorillonites, these are, as a rule, Na and Ca. The general crystallochemical formula of montmorillonite is (Ca,Na)(Mg,Al,Fe)2(OH)2[Si,Al4O10].nH2O [3, 4]. The montmorillonite clay used in the study contained 65 wt% rock-forming mineral, with halloysite (20 wt%) and vermiculite (15 wt%) the rest.

Kaolinite is composed of two-layered packets: one silica-oxygen tetrahedral layer of composition [Si2O5]2n and one aluminum–oxygen–hydroxyl octahedral layer of composition [Al2(OH)4]2+. Both layers are combined into a packet by a hydrogen bond formed by oxygen ions of the silicon–oxygen layer and OH groups of the octahedral layer [3, 4]. The structural unit is “rigid,” incapable of swelling. The composition of the sample under study was as follows (wt%): kaolinite 75, siliicate 10, illite 5, and goethite 10 (with a trace amount of montmorillonite).

The acid treatment of the natural samples was performed by the following scheme: montmorillonite (kaolinite) with a grain size less than 0.5 mm was dried at a temperature of 130°C for 2 h. The dried material was mixed with 2.33 M sulfuric acid in a mass ratio of 1 : 3 and activated under permanent agitation and heating on a water bath. The resulting slurry was filtered with a vacuum pump through a filter made of synthetic fibers. The filter cake was washed with distilled water to pH 4 and dried...
Table 1. Chemical composition of natural minerals

<table>
<thead>
<tr>
<th>Component</th>
<th>Natural (native) mineral, wt %</th>
<th>Samples activated with 20% H₂SO₄, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>montmorillonite</td>
<td>kaolinite</td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.2</td>
<td>49.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.3</td>
<td>20.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.21</td>
<td>3.18</td>
</tr>
<tr>
<td>MgO</td>
<td>0.49</td>
<td>0.55</td>
</tr>
<tr>
<td>CaO</td>
<td>1.4</td>
<td>0.87</td>
</tr>
<tr>
<td>Calcination loss +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>unanalyzable components</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Time of treatment with sulfuric acid (h): MN₁ and KN₁, 1; MN₆ and KN₆, 6.

to constant mass. As is known [5, 6], the duration of acid treatment is of key importance for the formation of adsorption properties and composition of the surface layer. Therefore, the samples used in the study were produced by treatment for 1 h (MN₁, KN₁), which provides an increase in the total exchange capacity, and for 6 h (MN₆, KN₆), which leads to a deeper structural transformation of the minerals and to an increase in the specific surface area and porosity of the material.

Samples subjected to the acid activation (MN₁ and KN₁) were treated with a 1 N magnesium chloride solution to obtain cation-substituted forms (MMg, K_Mg). The cation-substitution was performed at 55°C for 2 h, the filter cake was washed to trace amounts of CF in the filtrate in terms of AgCl, with the Mg-form of the clayey mineral accordingly obtained.

The chemical composition was determined by X-ray fluorescence analysis on an SRM-25 multichannel X-ray spectrometer. The content of the exchange cations in the structure of the silicates was found using procedures described in [7, 8].

The adsorption-structural parameters of the minerals in the native and cation-substituted states were determined by the pycnometric [9, 10] and desiccator methods [9]; the capacity of the monolayer was measured using the procedure described in [9–11] and calculated by formulas reported in [9, 10].

The sulfuric acid treatment is a widely known method for activation of natural aluminosilicates. In numerous publications [1, 2, 5, 12], results obtained in a study of the influence exerted by the sulfuric acid concentration and treatment conditions on the surface adjustment of the minerals were reported. In the present study, the sulfuric acid activation of montmorillonite and kaolinite is only the first stage of preliminary treatment of the minerals to reach the total exchange capacity and obtain the homo-ion H-form. The modification process is the second stage, in which the unstable H-form obtained as a result of activation (for 1 h) is treated with a magnesium chloride solution to give a Mg-modified mineral (MMg, K_Mg). The adsorption-structural parameters of the Mg-forms of kaolinite and montmorillonite were compared with those of the minerals upon an activation for 6 h, which is the optimal duration for raising the adsorption activity of layered silicates [2, 12].

The kinetic dependence of the total exchange capacity of montmorillonite treated with a 2.33 M sulfuric acid solution is shown in Fig. 1. According to the data obtained, the optimal duration of the sulfuric acid treatment of the mineral is 1 h, in which case the TEC increases from 0.64 to 0.98 mg-equiv g⁻¹. A more prolonged treatment of the mineral with sulfuric acid leads to a slight decrease in TEC, by 0.03 mg-equiv in 6 h, which may be due to a certain instability of the H-form of aluminosilicates [5, 13]. Consequently, 1 h is the optimal time for activation of montmorillonite and synthesis of the homo-ion H-form.

The chemical composition of the minerals under study strongly changed on making longer the acid activation (Table 1). The content of free silicie