PHYSICOCHEMICAL STUDIES
OF SYSTEMS AND PROCESSES

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


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

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

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Because of the wide use of adsorption technolo-
gies in the present-day development and moderni-
зation of various industries, it becomes an increas-
ingly 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 control-
ling the chemical structure of their surface layer
and thereby of widely varying the adsorption-struct-
tral characteristics of adsorbents 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 presen-
t study, the adsorption properties of minerals
were improved by activating samples with 20\% sul-
furic acid and modifying the activated samples with
a magnesium chloride solution.

EXPERIMENTAL

As objects of study served two samples of na-
tural silicates from a deposit in Lipetsk oblast, in
which the rock-forming minerals are montmoril-
onite and kaolinite. Montmorillonite is a layer-
ed 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 montmorillon-
ites, these are, as a rule, Na and Ca. The general
crystallogeochemical formula of montmorillonite is
(Ca,Na)(Mg,Al,Fe)_{2}(OH)_{2}Si_{4}O_{10} \cdot nH_{2}O [3, 4].
The montmorillonite clay used in the study con-
tained 65 wt\% rock-forming mineral, with hallo-
site (20 wt\%) and vermiculite (15 wt\%) the rest.

Kaolinite is composed of two-layered packets:
one silica-oxygen tetrahedral layer of composition
Si_{2}O_{5}^{2-} and one aluminum–oxygen–hydroxyl oc-
tahedral layer of composition Al_{2}(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, silicate 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: montmorillon-
ite (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 result-
ing 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.
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 (MN_1, KN_1), which provides an increase in the total exchange capacity, and for 6 h (MN_6, KN_6), 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 (MN_1 and KN_1) were treated with a 1 N magnesium chloride solution to obtain cation-substituted forms (MMg, KMg). 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 descator 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 sulfurous 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, KMg). 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 silicic