The use of Al₂O₃ - pillared clay in cleaning of aqueous solutions from surfactants

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Abstract. The paper describes the Al₂O₃ -pillared clays synthesized by modifying the natural montmorillonite clay with aluminum polyhydroxy complexes and subsequent heat treatment of the modified samples at temperatures of 400°C and 500°C. The textural characteristics of natural and Al₂O₃ -pillared clays were determined by the method of low-temperature nitrogen adsorption. The results showed that the obtained materials had a specific surface area, which was 1.7 times larger than the surface of the original clay, and the total pore volume, which was 1.2 more, than the pore volume of the original clay. Anionic surfactants (sodium dodecyl sulfate C₁₂H₂₅OSO₃Na and sulfonol C₁₂H₂₅C₆H₄SO₃Na) adsorption results have shown that the clay modifying by polyhydroxocomplexes of aluminum leads to a significant increase in their aniono-exchange capacity. Al₂O₃ -pillared clay exceeds the adsorption capacity of natural clay more than 2 times in the adsorption of sodium dodecylsulfate and sulfonol. It is established that the adsorption isotherms of sodium dodecylsulfate and sulfonol on Al₂O₃ -pillared clays well obey the Freundlich adsorption isotherm equation, which describes multilayer adsorption on a heterogeneous surface of sorbents. Al₂O₃ -pillared clays may be of interest for use in wastewater treatment from anionic surfactants.

1. Introduction
Currently, synthetic surfactants are widely used in various industries. The main consumers of synthetic surfactants are enterprises that produce synthetic detergents, fabrics and products based on natural, artificial and synthetic fibers. Also major consumers of synthetic detergents are the petroleum and chemical industries, the building materials industry, metallurgy, mechanical engineering, automotive and aviation, leather, pulp and paper, pharmaceutical and other industries. The surfactants contained in the untreated effluents of these enterprises enter the surface waters and have a harmful effect on the sanitary state of natural water bodies. The foam formed by them has a toxic effect on hydrobionts, interferes with the metabolism in water bodies and reduces the ability of water bodies to self-purify. Many representatives of synthetic surfactants, which contain radicals of saturated and aromatic hydrocarbons in their molecules, are very resistant to biochemical oxidation and can accumulate in natural water bodies for a long time. Therefore, wastewater discharged into reservoirs should be treated to the maximum permissible concentrations of synthetic surfactants, which, depending on the class of compounds, are 0.1-0.5 mg · l⁻¹ [1].
Various methods such as reagent treatment, flotation [2-4], electrochemical oxidation and adsorption [5-7] are used to purify wastewater from synthetic surfactants and related pollutants. The most widely used in the practice of water treatment are adsorption methods that allow to achieve a high degree of water purification at the level of modern requirements. The efficiency of adsorption treatment depends on the nature of the used sorbents, the composition of wastewater the optimal conditions for the adsorption process. Active carbons and synthetic ion exchangers, which are quite expensive materials, are most often used as sorbents. The use of active carbons for these purposes almost completely removes all types of synthetic surfactants from wastewater however the specific consumption of active carbon per unit mass of adsorbed synthetic surfactants is significant due to the inaccessibility of micropores for large molecules or ions of synthetic surfactants [8]. In this connection, along with active carbons and synthetic ion exchangers, natural minerals are increasingly used, the high adsorption capacity of which is due to both physical adsorption on the developed porous surface of the adsorbent and ion exchange. The availability, low cost and ease of disposal of natural sorbents significantly reduce the cost of wastewater treatment. These sorbents can be effectively used in the technology of wastewater treatment from synthetic surfactants, which are often found in water together with other pollutants [9].

Bentonite clays belonging to highly dispersed minerals are effective cation exchangers and are widely used in the practice of wastewater treatment from inorganic and organic cations. The low efficiency of clays in adsorption of anions is due to the small number of anion-exchange centers in their structure. To increase the adsorption capacity of clays with respect to organic anions, various methods of their modification are used. One of such methods is the intercalation process, which is based on the ion exchange of cations located in the interlayer space of clays with large polyhydroxocations of metals. When the material obtained as a result of such replacement is heat treated, polymer complexes immobilized between aluminosilicate layers transform into oxides, forming supports (pillars), and fix the position of aluminosilicate layers at a distance of 1-2 nm from each other [10,11]. As a result of such modification, both the increase in the specific surface area of clays and the creation of new adsorption and catalytic centers occur.

The purpose of this work is to obtain Al$_2$O$_3$-pillared clay from natural clay and to study its adsorption properties with respect to anionic surfactants.

2. Experimental

2.1. Synthesis of Al$_2$O$_3$-pillared clay

To obtain sorbents, clay from the Mukhor-Taly deposit (the content of montmorillonite ~ 80%) was used, which has a chemical composition (mass%): SiO$_2$ – 65.50; Al$_2$O$_3$ – 14.30; Fe$_2$O$_3$ – 1.78; MgO – 1.42; CaO – 1.08; K$_2$O – 0.20; Na$_2$O – 0.10; FeO – 0.22; MnO – 0.02; TiO$_2$ – 0.19; P$_2$O$_5$ – 0.03; H$_2$O – 15.16 [12]. The clay structure was modified by exchanging interlayer cations (Ca$^{2+}$,Mg$^{2+}$) for polyhydroxocations (PHC) of aluminum. For the synthesis of PHC the hydrolysis of the AlCl$_3$ salt in aqueous solution was carried out by adding a solution of NaOH (ratio [OH$^-$]/[Al$^{3+}$] = 2.0). The pH of the hydrolyzed aluminum salt solution was 4.3-4.5. The resulting solution of aluminum PHC was kept for 24 hours at 50°C and then added to the clay suspension with constant stirring. Then the suspension of clay and aluminum PHC was kept for 24 hours at room temperature. The aluminum-containing clay was washed off excess chloride ions and dried at room temperature, then subjected to heat treatment at 400°C and 500°C for 2 hours [13]. The thus prepared Al$_2$O$_3$-pillared clays were ground and used as sorbents.

2.2. Methods

The textural characteristics of the materials were determined by low-temperature nitrogen adsorption at 77 K using the ASAP-2400 Micromeritics equipment according to the standard procedure [14]. The
study of the adsorption properties of natural and Al₂O₃-pillared clays was carried out in aqueous solutions of sodium dodecyl sulfate (C₁₂H₂₅OSO₃Na), sulfonol (sodium dodecylbenzenesulfonate - C₁₂H₂₅C₆H₄SO₃Na) at 20°C. Characteristics of surfactants are shown in Table 1. Adsorption studies were carried out at initial surfactants solution concentrations of 10-250 mg·l⁻¹ (for sodium dodecyl sulfate) and 10-200 mg·l⁻¹ (for sulfonol), a clay content of 10 g·l⁻¹, pH 5.8-6.2. Initial concentrations of synthetic surfactants are close to their values in wastewater. When determining the equilibrium adsorption, an aqueous solution of surfactant with a preset initial concentration was added to a calculated weighed portion of clay, and the mixture was stirred at 200 rpm for 24 h (equilibration time). Then the sorbent was separated from the liquid phase by centrifugation at 8000 rpm. The total determination of anionic surfactants was carried out by spectrophotometric method, which is based on the formation of a colored compound during the interaction of anionic surfactants with methylene blue, extractable with chloroform [15]. The optical density of the solutions was recorded on a Specord UV-VIS Agilent instrument at a wavelength of 670 nm. The specific adsorption value was calculated by the formula (1):

\[ q_t = \frac{(C_0 - C_t) \cdot V}{m}, \]

where \( q_t \) is the amount of the surfactant adsorbed by 1 g of the sorbent at time \( t \) (mg·g⁻¹), \( C_0 \) is the initial concentration of the surfactant in the solution (mg·l⁻¹), \( C_t \) is the concentration of the surfactant in the solution at time \( t \) (mg·l⁻¹), \( m \) is the mass of the sorbent (g), and \( V \) is volume of the surfactant solution.

### Table 1. Characteristics of surfactants.

| Surfactants         | The structural formula of the surfactants | Molecular mass (g·mole⁻¹) |
|---------------------|------------------------------------------|--------------------------|
| Sodium dodecyl sulfate | ![Sodium dodecyl sulfate](image)              | 288.4                    |
| Sulfonol            | ![Sulfonol](image)                           | 348.5                    |

### 3. Results and discussion

Layered aluminosilicates, which include montmorillonite clays, have the ability to adsorb both cations and anions due to their structure features. The cation-exchange ability of clays is mainly due to heterovalent isomorphic substitution in their structure: \( \text{Al}^{3+} \rightarrow \text{Si}^{4+} \) in tetrahedral and \( \text{Mg}^{2+} \rightarrow \text{Al}^{3+} \) in octahedral networks. The resulting negative charge of the layers is compensated by the exchangeable cations \( \text{Na}^+ \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) [16]. The charges that occur on the surfaces of clay particles due to heterovalent isomorphism are fixed and do not depend on the properties of the solution [17]. Another exchange centers are the weakly acidic hydroxyl groups of SiOH on the side faces and edges of the clay particles. Their protons at pH > 2.0 - 2.5 can be exchanged for metal cations. The number of such protons in contrast to interlayer cations is not constant for a particular sample and depends on the pH of the medium. The basic hydroxyl groups of Al–OH, Mg–OH, Fe–OH are located on the side faces and edges of the lamellar clay particles. At pH values less than the pH of surface zero charge (pHₚzc) of the corresponding clay hydroxides, they can adsorb anions. For Al and Fe(III)
hydroxides the pHZ values are 7-9. The most basic are OH groups associated with the octahedral cations Mg\(^{2+}\). For MgO, the pH\(_Z\) value is 12.4 [17]. The number of basic hydroxyl groups in the structure of montmorillonite clays is significantly less than the number of cation-exchange centers; therefore, montmorillonite clay has a low ability to anions adsorption [18].

To increase the number of basic groups, we introduced aluminum polyhydroxocations in the interlayer space of natural clay. When Al\(-\)intercalated clay is heated at 400\(^{\circ}\)C, aluminum polyhydroxo cations are destroyed to form Al\(_2\)O\(_3\) - oxide particles, which prevent the aluminosilicate clay layers from closing, leading to the appearance of stable slit-like micropores [19]. The increase in the volume of micropores leads to an increase in the specific surface area and total pore volume, as shown by the results of studying the textural properties of natural and Al\(_2\)O\(_3\) -pillared clays, shown in Table 2.

Table 2. The textural characteristics of natural clay and Al\(_2\)O\(_3\) - pillared clay.

| Sorbents                  | \(S_{\text{BET}}\)\(^a\) (m\(^2\) · g\(^{-1}\)) | \(\sum V_{\text{pore}}\)\(^b\) (cm\(^3\) · g\(^{-1}\)) | \(D_{\text{pore}}\)\(^c\) (nm) | \(\sum V_{\mu}\)\(^d\) (cm\(^3\) · g\(^{-1}\)) |
|---------------------------|-----------------------------------------------|-----------------------------------------------|-------------------------------|-----------------------------------------------|
| Natural clay 400\(^{\circ}\)C | 113                                           | 0.268                                         | 9.7                           | < 0.003                                      |
| Natural clay 500\(^{\circ}\)C | 109                                           | 0.249                                         | 9.3                           | < 0.003                                      |
| Al\(_2\)O\(_3\) -pillared clay 400\(^{\circ}\)C | 203                                           | 0.316                                         | 6.5                           | 0.031                                        |

\(^{a}\) \(S_{\text{BET}}\) – total surface area;  
\(^{b}\) \(V_{\text{pore}}\) – total pore volume;  
\(^{c}\) \(D_{\text{pore}}\) – the average pore diameter  
\(^{d}\) \(V_{\mu}\) – micropore volume

Figure 1 shows the equilibrium isotherms of sodium dodecyl sulfate adsorption on natural clay and Al\(_2\)O\(_3\) -pillared clay obtained at initial surfactant concentrations of 10-500 mg · l\(^{-1}\). It can be seen that Al\(_2\)O\(_3\) -pillared clay exceeds natural clay by more than 2 times in adsorption capacity. The increase in the adsorption capacity of Al\(_2\)O\(_3\) -pillared clay is due to an increase in the total specific surface area, as well as an increase in the number of Al – OH groups.

Figure 2 shows the equilibrium isotherms of sulfonol adsorption on natural clay and Al\(_2\)O\(_3\) -pillared clay with initial surfactant concentrations equal to 10-200 mg · l\(^{-1}\). An increase in the adsorption capacity for Al\(_2\)O\(_3\) -pillared clay is also more than 2 times higher than that of the natural clay from the Mukhortalny deposit in experiments on sulfonol adsorption, which indicates a good correlation between the value of anion-exchange capacity of clays and their total specific surface area. A comparison of the adsorption capacity of Al\(_2\)O\(_3\) -pillared clay with the results of sulfonol adsorption on clay from the Chernigovsky field [8] shows that Al\(_2\)O\(_3\) -pillared clay exceeds this clay by the adsorption capacity more than 5 times.
The obtained experimental isotherms were analyzed in terms of the models that are used to describe the adsorption of solutes, i.e., the Langmuir isotherms, which describe the monolayer adsorption on homogeneous surfaces, and the Freundlich isotherm, which reflects the multilayer adsorption on heterogeneous surfaces [20]. The linear form of the Langmuir isotherm is expressed by the equation (2):

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}}$$

where $Q_{max}$ is a theoretical constant corresponding to the maximum adsorption (mg·g$^{-1}$) and $K_L$ is the Langmuir constant, which depends on the adsorption energy and temperature (1·g$^{-1}$).

The linear form of the Freundlich isotherm is expressed via the following equation (3):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e,$$

where $K_F$ is the Freundlich adsorption constant (1·g$^{-1}$) and $n$ is the experimental Freundlich constant describing the adsorption intensity.

Figures 3 and 4 show the obtained experimental data on the adsorption of sodium dodecyl sulfate and sulfonol on natural clay and Al$_2$O$_3$-pillared clay in the coordinates of linear forms of equations describing the Langmuir and Freundlich isotherms. The adsorption of sodium dodecyl sulfate on natural clay is well described by both the Langmuir and Freundlich isotherms with the correlation coefficient $R^2=0.9938$. The experimental data on the adsorption of sodium dodecyl sulfate on Al$_2$O$_3$-pillared clay correspond better to the Freundlich model (Figure 3, B) than to the Langmuir model (Figure 3, A), judging by the values of the correlation coefficients. The adsorption of sulfonol on both natural and Al$_2$O$_3$-pillared clay is well described by the Freundlich adsorption isotherm equation with correlation coefficients of 0.9906 and 0.9951, respectively (Figure 4, A, B). This indicates the heterogeneity of the surface and the multilayer coating of the surface of sorbents with sulfonol.
The results of the adsorption of anionic surfactants indicate that the modification of bentonite clay with aluminum polyhydroxocations leads to a significant increase in anion-exchange capacity. $\text{Al}_2\text{O}_3$-pillared clay exceeds the adsorption capacity of natural clay more than 2 times in adsorption of sodium dodecyl sulfate and sulfonol. $\text{Al}_2\text{O}_3$-pillared clays may be of interest for use in wastewater treatment from anionic surfactants.

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