Removal of anionic surfactants from aqueous solutions using Fe-aluminosilicate sorbents

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Abstract. Fe-aluminosilicate sorbents were obtained by modifying bentonite clay with iron polyoxyocations and heat treatment at 400°C and 500°C. The specific surface of the sorbents determined by the method of low-temperature nitrogen adsorption was 118-136 m²·g⁻¹. The iron content in sorbents was equal 7.8 %. The adsorption properties of the obtained sorbents were studied with respect to anionic surfactants (sodium dodecyl sulfate and sodium dodecylbenzenesulfonate) in aqueous solutions. It was shown that the modification of clay leads to a significant increase in anion-exchange capacity. The value of the adsorption capacity was in good agreement with the increase in the number of the basic groups of Fe − OH and the value of the specific surface of the sorbents. Adsorption isotherms of sodium dodecyl sulfate on bentonite clay and on Fe−aluminosilicate sorbents are described by the Langmuir adsorption isotherm equation which describes monolayer adsorption on a homogeneous surface with a correlation coefficient of 1.000 at initial surfactant concentrations of 10-1000 mg·l⁻¹. The adsorption capacity of Fe-aluminosilicate sorbents was more than 3 times higher than the capacity of the original clay in the adsorption of sodium dodecyl sulfate and was about 5 times higher in the adsorption of sodium dodecylbenzenesulfonate. The results of the study suggest that the Fe-aluminosilicate sorbents can be effective for removing anionic surfactants from wastewater.

1. Introduction
The widespread use of synthetic surface-active substances (surfactants) in various industries caused by their high wetting, emulsifying and washing ability. Due to these specific properties, they are used in the petroleum and chemical industries, mechanical engineering, as well as in the production of synthetic detergents, cosmetics, textile, pulp and paper, pharmaceutical and other industries. According to the classification based on the ionogenic properties of hydrophilic groups, there are five main types of surfactants: cationic, anionic, amphoteric (ampholitic), zwitterionic, non-ionic [1]. A widely used type of synthetic surfactants are anionic synthetic surfactants, which are characterized by their ability to dissociate in polar solvents with the formation of surface-active anions. These include salts of carboxylic acids (soaps), alkyl aryl sulfonates, alkyl sulfates and alkyl sulfonates. The use of surfactants in the technologies of production and use of various substances and materials is based on their ability to regulate the stability of colloidal systems and the wettability of the surface. This leads to the fact that synthetic surfactants are secondary agents in industrial wastewater accompanying those compounds, wettability, dispersibility or stability, which they must provide [2]. Surfactants in waste and surface
waters have a variety of harmful effects. The foam formed by them prevents the metabolism in the reservoir and has a toxic effect on aquatic inhabitants [3,4]. At present, various physical and chemical methods are used to purify industrial wastewater from surfactants: coagulation, flotation, ultrafiltration, adsorption on active carbon, ion exchange, oxidation with reagents (chlorine, ozone, hydrogen peroxide), catalytic oxidation, electrochemical oxidation. The application of a particular method is determined by the concentrations of pollutants in the waste water and the composition of wastewater. Several physicochemical methods can be used in combination with biochemical purification in complex technological schemes [5–7]. Sorption methods are used for purification of weakly and moderately concentrated wastewaters of surfactants. Their high efficiency is due to the high energy of the adsorption interaction of synthetic surfactants with the surface of the sorbents. Active carbons are most often used as sorbents. The high cost of active carbons and the difficulties of their regeneration lead to the need to search for alternative sorbents that can replace active carbons. The most suitable materials are dispersed natural minerals such as clays (bentonite, kaolinite), zeolites and their modified forms [8,9]. The interest of researchers working in the field of wastewater treatment to natural sorbents is due to a number of their properties, such as a developed surface, the presence of adsorption centers of different nature, as well as availability, low cost, and environmental safety.

In this work, we have studied the effect of modifying bentonite clay with iron polyoxocomplexes on the adsorption properties of clay with respect to anionic surfactants and the regularities of the adsorption of anionic surfactants on the resulting Fe-aluminosilicate sorbents from aqueous solutions.

2. Experimental

2.1. Synthesis of Fe-aluminosilicate sorbents

A fine fraction of bentonite clay from the Mukhortaly deposit (the Republic of Buryatia, Russia) was used as a raw material to obtain an iron-containing sorbent. The clay contained about ~ 80% of the montmorillonite mineral and had a chemical composition (mass%): SiO₂ ~ 65.50; Al₂O₃ ~ 14.30; Fe₂O₃ ~ 1.78; MgO ~ 1.42; CaO ~ 1.08; FeO ~ 0.22; MnO ~ 0.02; TiO₂ ~ 0.19; P₂O₅ ~ 0.03; H₂O ~ 15.16 [10]. A 0.1 M solution of NaOH was added dropwise to the solution of FeCl₃ to obtain the ratio OH / Fe = 1.5. The mixed solution containing iron polyoxocations was added to the aqueous suspension of clay with constant stirring (the ratio of solid and liquid phases was 1/10, the iron content was 3.0 mmol / g clay) and left to stand for 1 day at room temperature. The obtained iron-containing clay was separated from the liquid phase by centrifugation and washed with water until complete removal of excess chloride ions. Iron-containing clay was subjected to heat treatment at a temperature of 400°C and 500°C for 2 hours after its preliminary drying at room temperature [11]. The resulting Fe-aluminosilicate sorbents were ground and used in adsorption studies. The iron content of the sorbents was determined with o-phenanthroline after keeping the catalyst for 1 day in a concentrated HCl solution [12].

2.2. Methods

The specific surface area of the original clay and the Fe-aluminosilicate sorbents was determined by the low-temperature isotherm nitrogen adsorption at 77 K, which was taken on the ASAP-2400 Micromeritics equipment using the BET equation [13]. Adsorption studies were carried out in aqueous solutions of anionic surfactants - sodium dodecyl sulfate (C₁₂H₂₅SO₄Na) and sulfonol (sodium dodecylbenzenesulfonate - C₁₂H₂₅C₆H₄SO₃Na) at 20°C, pH 5.8-6.0. The critical micelle concentration (CMC) for sodium dodecyl sulfate is 2.38 g ∙ l⁻¹ (8.25 mM) and CMC is 0.38 g ∙ l⁻¹ (1.1 mM) for sulfonol [9, 14]. 0.1 g of sorbent was poured into the flask with a volume of 50 ml, then 10 ml of surfactant solutions with different concentrations was poured into the flask. The values of surfactant concentrations were less than the critical micelle concentrations. The initial surfactants solution concentrations were 10-1000 mg ∙ l⁻¹ (for sodium dodecyl sulfate) and 10-200 mg ∙ l⁻¹ (for sulfonol). Suspensions of the sorbent and surfactant solutions were mixed for 24 h, then the liquid phase was separated from the sorbent and the residual concentration of surfactant was determined by a
spectrophotometric method using calibration graphs. Concentrated solutions were diluted to the appropriate concentrations of the calibration graphs. The concentrations of anionic surfactants in aqueous solutions were determined by the method based on the formation in association of anionic surfactants with methylene blue in an alkaline medium and the extraction of these associates with chloroform and determining the concentration of surfactants by optical density of the obtained extract [15]. Optical densities of solutions were measured on a Specord UV-VIS Agilent instrument. The specific adsorption value was calculated by the formula (1):

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

where \( q_t \) (mg \( \cdot \) g\(^{-1}\)) is the amount of the surfactant adsorbed by 1 g of the sorbent at time \( t \) (24 h), \( C_0 \) is the initial concentration of the surfactant in the solution (mg \( \cdot \) l\(^{-1}\)), \( C_t \) is the concentration of the surfactant in the solution at time \( t \) (mg \( \cdot \) l\(^{-1}\)), \( m \) is the mass of the sorbent (g), and \( V \) is volume of the surfactant solution (l).

3. Results and discussion

Layered aluminosilicates, which include clay minerals, possess, along with cation-exchange capacity and some anion-exchange capacity [16]. Although the number of anion-exchange centers of clays is much less than that of cation-exchange, nevertheless, the adsorption of acetate, phosphate and other anions occurs precisely on these centers [17]. Anion-exchange centers in bentonite clay are hydroxyl groups Al – OH, Mg – OH, Fe – OH, which are located on the side faces and edges of the clay particles. At pH values of the medium that are less than the zero charge points of Al, Fe, and Mg hydroxides, the clay is able to sorb anions by the ion exchange mechanism:

\[ SK - OH + A^- + H^+ \rightleftharpoons SK - A + H_2O, \]

where SK is the surface cation of clay.

According to the literature, the adsorption of anionic surfactants occurs on the anion-exchange centers of clay minerals [17].

**Figure 1.** Adsorption isotherm of sodium dodecyl sulfate on bentonite clay (400 °C).

**Figure 2.** Adsorption isotherm of sodium dodecyl sulfate on sorbents: 1 - Fe – sorbent I, 2 - Fe – sorbent II.

Figure 1 shows the equilibrium values of the specific adsorption values of sodium dodecyl sulfate (SDS) on the bentonite clay, depending on the equilibrium surfactant concentration in the solution. The maximum value of SDS adsorption was 9.7 mg \( \cdot \) g\(^{-1}\) at an initial concentration of surfactant equal to 700 mg \( \cdot \) g\(^{-1}\). The obtained value of adsorption is consistent with a small number of anion-exchange centers in the original clay. Apparently, the main mechanism of sorption of anionic surfactants on clay minerals is the interaction of negatively charged anions of surfactants with positively charged parts of the clay surface, although when considering the mechanism it is also necessary to take into account the possibility of van der Waals interaction of the hydrocarbon chains of surfactants with the
clay surface [14]. To increase the anion-exchange capacity of clay, we carried out the modification of clay by introducing iron polyoxocations and subsequent calcination, which led to the fixation of iron ions in the form of oxides in the structure of clay. The analysis of Fe-aluminosilicate sorbent for iron content showed that the amount of iron introduced was 78 mg per 1 g of clay.

Figure 2 shows the equilibrium values of the specific adsorption values of sodium dodecyl sulfate on samples of Fe-aluminosilicate sorbent - Fe-sorbent I (heated at 400°C) and Fe-sorbent II (heated at 500 °C). The amount of SDS adsorption was 15.1 mg · g⁻¹ on the Fe-sorbent I, the adsorption was 27.5 mg · g⁻¹ on the Fe-sorbent II. The adsorption isotherms of Na-dodecyl sulfate on Fe-sorbent I and II have a form that is characteristic of the adsorption of anionic surfactants on positively charged oxides at concentrations much lower than CMC. According to the literature [18], the plateau at the initial part of the isotherm corresponds to a monolayer saturation of the surface with horizontally oriented surfactant molecules. The adsorbate-adsorbate interaction increases with increasing surfactant concentration at subsequent stages of adsorption. There is a strong attraction between the hydroxyl group and the surface when adsorbing on polar adsorbents like silicates and oxides, then the alkyl chain is displaced from the surface. As the concentration of anionic surfactants in the solution approaches the critical micelle concentration, there is a tendency to aggregate the chains of adsorbed molecules. This leads to a vertical orientation of the molecules, as a result of which the adsorption increases dramatically. Usually, a second plateau is observed on the isotherm of anionic surfactants on oxide sorbents at concentrations close to the CMC value, which corresponds to the complete surface coating with vertically oriented surfactant molecules. The absence of the second plateau in our case is explained by the fact that the concentration of Na–dodecyl sulfate is much lower than the CMC. The choice of the range of surfactant concentrations was made taking into account their concentrations in real wastewater. The adsorption capacity of Fe-sorbent I and Fe-sorbent II adsorption increased 1.6 and 2.9 times, respectively, compared to the original clay. The data obtained show that the modification of clay leads to an increase in anion-exchange capacity, which is consistent with an increase in the number of Fe – OH groups, which are anion-exchange centers. There is also a good correlation with the total specific surface area of the sorbents (Table 1).

| Sorbent         | S (m² · g⁻¹) |
|-----------------|-------------|
| Bentonite clay 400°C | 113         |
| Bentonite clay 500°C | 109         |
| Fe−sorbent I    | 118         |
| Fe−sorbent II   | 136         |

The adsorption properties of Fe-sorbent I have also been tested in the adsorption of sulfonol from aqueous solutions. The adsorption of sulfonol on the bentonite clay and Fe-sorbent I was studied at 20°C and initial surfactant concentrations of 10-200 mg · l⁻¹. The results are shown in Figure 3.
The value of the adsorption capacity is 5 times more for Fe$^-$sorbent I compared to natural clay as in the case of SDS adsorption. Thus, the obtained data on the adsorption of anionic surfactants indicate that the clay modification with Fe polyoxocations leads to a significant increase in their anion-exchange capacity.

The experimental isotherms adsorption of sodium dodecyl sulfate were analyzed in terms of the models that describe the adsorption of solutes. Most commonly, Langmuir and Freundlich equations are used to describe the adsorption of solutes. The Langmuir isotherm is used to describe the monolayer adsorption on homogeneous surfaces, and the Freundlich isotherm reflects the multilayer adsorption on heterogeneous surfaces [19, 20]. The linear form of the Langmuir isotherm is expressed by the equation (2):

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

where $Q_{\text{max}}$ is a theoretical constant corresponding to the maximum adsorption (mg $\cdot$ g$^{-1}$) and $K_L$ is the Langmuir constant, which depends on the adsorption energy and temperature (l $\cdot$ 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 (l $\cdot$ g$^{-1}$) and $n$ is the experimental Freundlich constant describing the adsorption intensity.

Figure 4 shows the obtained experimental data on the adsorption of sodium dodecyl sulfate on bentonite clay and Fe-sorbents in the coordinates of linear forms of equations describing the Langmuir and Freundlich isotherms. The adsorption of sodium dodecyl sulfate on bentonite clay, Fe-sorbent I and Fe-sorbent II both is better described by the Langmuir isotherm than Freundlich isotherm. Correlation coefficient $R^2$ is 1.0000 for Langmuir model while for Freundlich model correlation coefficients are 0.9455 – 0.9923. This indicates that monolayer adsorption of sodium dodecyl sulfate on bentonite clay and on its iron-modified forms occurs in the studied surfactant concentration range. The surface of bentonite clay and Fe$^-$sorbents is homogeneous for sodium dodecyl sulfate adsorption.

The results of the study showed that the modification of bentonite clay with iron polyoxocomplexes lead to a significant increase in anion-exchange capacity. Iron-containing clays exceed the adsorption capacity of original clay about 3 times in adsorption of sodium dodecyl sulfate. Fe-sorbent is about 5
times superior to the initial clay in adsorption capacity of sulfonol. This suggests that the resulting sorbents can be effective for removing anionic surfactants from wastewater.

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