Development of organobentonite based on bentonite clay for the purpose of disposing of oil spills on water bodies

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Abstract. Today, oil spill response is an urgent problem for oil-producing countries. This paper researches the elimination of oil pollution using organomineral sorbents. The authors present a scheme for obtaining sorbents based on natural bentonite clays by modifying with a quaternary ammonium salt. Two variants of modification of natural bentonites have been studied: with preliminary Na₂CO₃ treatment to convert the main component of bentonite into the sodium form and without preliminary treatment. The obtained organobentonites have high sorption and hydrophilic properties. The sorbent obtained from natural bentonite with preliminary treatment with Na₂CO₃ has better properties in comparison with the sorbent without preliminary treatment. The authors also demonstrated the ability of the obtained organobentonites for oil sorption. Organobentonites upon contact with oil films on the water surface form dense agglomerates that can be easily removed mechanically.

Spills of oil and oil products on the water surface are a very serious environmental problem, the consequences of which can be extremely destructive for aquatic ecosystems. Both flora and fauna of these natural objects suffer from such spills [1]. Oil and its refined products quickly cover the surface of the water with a dense film, which hinders the access of air and light.

To eliminate these consequences, it is necessary to promptly localize and collect the products of leakage of hazardous substances. For these purposes, various methods and means are traditionally used: mechanical, thermal, physicochemical, biological methods and the use of various sorbents [2].

The development of effective sorbents capable of completely absorbing and binding oil and oil products and preventing the transfer of pollutant components into bottom sediments is an urgent task [3,4].

It is known that sorbents of natural origin exhibit hydrophilic properties and, without special treatment, are ineffective for the adsorption of hydrophobic pollutants. At the same time, the manufacture of synthetic sorbents is an energy-consuming process, and the resulting product has a high cost price. Modification of natural sorbents by imparting hydrophobic properties to them will make it possible to resolve the issue of economic feasibility and efficiency of the obtained adsorption materials for cleaning the surface of water bodies from oil and oil products spills.

Among the known natural mineral sorbents, clayey rocks have a dominant content of layered aluminosilicates, which have a high cation exchange capacity. This characteristic of minerals is important when modifying natural raw materials. It demonstrates the exchange capacity of the material and the ability to substitute for cations of a different type. One of these layered silicates are minerals of
the montmorillonite group, which have a cation exchange capacity of up to 90-120 mg equivalent per 100 g of dry clay [5].

In this regard, the minerals of the montmorillonite group have high sorption and exchange properties. Representatives of this group of layered silicates tend not only to surface sorption, but also to interpacket sorption of both cations and organic compounds [6-8]. The chemical composition and structure make it possible to use minerals of the montmorillonite group in the synthesis of materials with desired properties by means of chemical transformation, including the preparation of organomineral composites [5].

Data in the literature indicate that the synthesis and application of organomodified clays has been studied since the 80s of the 20th century. Bentonite and bentonite-like clays with a montmorillonite content of more than 50% may be the most suitable material for modifying natural clays [9-11].

Thus, the study of the properties of smectites, their interaction with organic substances and their application, in particular in solving environmental problems associated with the elimination of technogenic consequences arising from the transportation of oil and oil products, is an urgent issue in modern science.

As the object of research, as well as the basis for the synthesis of organobentonite sorbents, bentonite clay was chosen. Mineral and chemical compositions, as well as thermal properties are presented in tables 1-3.

The mineral composition of the sample (table 1) was determined by the powder method on a Rigaku SmartLab diffractometer using CuKα radiation in a step scan mode (step - 0.02 ° 2θ, exposure time at a point - 1 sec.). X-ray tube operating mode - 40 kV, 200 mA.

| Mineral content, mass % | smectite | zeolite | quartz | feldspar | plagioclase | mica | kaolinite | cristobalite |
|-------------------------|----------|---------|--------|----------|-------------|------|-----------|-------------|
| 69,6                    | 5,1      | 18,3    | 2,0    | 4,7      | <1          | <1   | <1        |             |

The chemical composition of the sample (table 2) was determined using various methods: the determination of the elemental and cationic composition was carried out by the method of atomic emission spectrometry with inductively coupled plasma; loss on ignition (LOI) - by the method of gravimetry; the capacity of the exchange complex - by the calculation method.

| Content of components for a completely dry sample, mass % | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO | TiO₂ | CaO | MgO | MnO | Na₂O | K₂O | P₂O₅ | LOI | Total |
|---------------------------------------------------------|------|-------|-------|-----|------|-----|-----|-----|------|-----|------|-----|-------|
| 67,93                                                   | 14,83| 5,12  | 0,33  | 0,42| 1,78 | 0,89| 0,10| 0,58| 1,55 | 0,18| 6,18 |     | 99,89 |

| Cationic composition, mg equivalent per 100 g of dry clay | Ca²⁺ | Mg²⁺ | Na⁺ | K⁺ | Exchange complex capacity |
|----------------------------------------------------------|------|------|-----|----|---------------------------|
| 37,92                                                    | 6,58 | 2,18 | 1,53|    | 48,21                     |

The results of chemical analysis show that the predominant cation of the exchange complex is Ca²⁺, which indicates an alkaline earth type of bentonite clay.

It is known that, depending on the content of calcium, magnesium and/or sodium in the composition of the exchange complex, there are alkaline earth (calcium, magnesium, magnesium-calcium) and alkaline (sodium and calcium-sodium) bentonites. Alkaline bentonites have the highest ion exchange and sorption capacity, in contrast to alkaline earth ones [12]. In addition, it should be noted that the alkaline earth type of bentonite is the most widespread in nature. Therefore, in order to increase
the sorption properties of the studied natural bentonite clay and obtain an organobentonite sorbent, it is necessary to modify the alkaline-earth type of raw material into an alkaline type. The method for modifying natural raw materials into a sodium form (alkaline) is described in the section - "Synthesis of organobentonite".

Thermal studies of the sample (table 3, figure 1) were carried out on a synchronous thermal analyzer STA 6000. Measurement conditions: temperature range 30-700 ºC; heating rate - 10 K / min, environment - air, platinum crucible.

Table 3. Thermal properties of the original bentonite sample

| Temperature ranges (maximum effect, ºC) | Weight loss, mass % | Total weight loss in the range 30-700 ºC, mass % |
|--------------------------------------|---------------------|-------------------------------------------------|
| 30-220 (100)                         | -7.98               | 11.28                                           |
| 220-370 (-)                          | +0.02               |                                                 |
| 370-570 (470)                        | -0.94               |                                                 |
| 570-700 (666)                        | -2.38               |                                                 |

The method of differential scanning calorimetry (DSC) and differential thermogravimetry (TG-DTG), in accordance with the amount of weight loss when removing weakly bound (interlayer) water, allows you to determine the content of the montmorillonite component and the type of bentonite.

In the low-temperature range (30-220 ºC), according to DSC curves, there is a pronounced endothermic effect of the removal of weakly bound water, which is characteristic of clay minerals. The weight loss in this range is 7.98% of the mass.

Structural water is removed in the temperature range 370-700 ºC. The weight loss in this range is 3.32%. By the nature of the removal of structural water, the studied sample can be attributed to clays with a mixed type of dehydration.

The synthesis of organobentonite took place on bentonite clay in two stages. At the first stage, natural alkaline earth bentonite (sample AEB) was modified to convert it into an alkaline bentonite (sample AB). For this, a 10% aqueous suspension was prepared based on bentonite powder with a fraction of less than 100 μm, and Na₂CO₃ was added thereto in an amount of 3% of the clay weight. The resulting suspension was poured into a mixer and stirred while maintaining a temperature of 70 ºC with a stirrer speed of 2700 rpm. Stirring lasted 20 minutes.

At the second stage, a suspension of clay powder with a quaternary ammonium salt (QAS) was prepared in a ratio of 1:0.2. This procedure was carried out as follows, to the previously prepared clay suspension, QAS was added in portions and the resulting mixture was stirred at 2700 rpm for 30 min at a temperature of 60 ºC. In the event of a significant increase in the level of foam in the mixer, the stirring frequency was lowered to 1800 rpm. In the intervals between the addition and stirring of portions of QAS, the suspension was allowed to stand for at least 30 min while maintaining a temperature of 60 ºC. After the completion of the stirring process, the suspension was allowed to stand for 24 hours to
complete the exchange reaction. Then, the suspension was washed with hot distilled water, dried, and shredded to a fine powder.

The obtained organomineral powder was investigated by the methods of chemical analysis, X-ray quantitative phase analysis (with consideration of the structural characteristics of the crystal lattice of the main mineral and interplanar distances), gravimetric analysis (with the determination of the amount of the organic component in the structure of the material), and the study of the microstructure of the obtained products by the method of scanning electron microscopy. To identify the technological characteristics of the product, the dispersed composition was studied by the method of laser diffraction, and the characteristics of the porosity were calculated. The adsorption capacity of the resulting product relative to oil was also evaluated.

To obtain organobentonites and identify the best method for their production on the bentonite clay, the following compositions were prepared:
Composition №1 - AEB + QAS (sample C1);
Composition №2 - AB + QAS (sample C2).

Comparative analyzes of organobentonite were carried out with the original unmodified bentonite (sample AEB) and bentonite modified with Na₂CO₃ (sample AB).

To assess the quality of the obtained organobentonite, a particle size analysis was carried out. The particle size distribution of the original bentonite, as well as the variants of organobentonites obtained on its basis, were investigated on a laser scattering particle size distribution analyzer Horiba La-950V2 according to ISO 13320, the results are shown in table 4.

| Sample | Amount of particles (% vol.) in fraction (μm) | Mean size, μm | <10 μm, (% vol.) | S.P. area, cm²/cm³ |
|--------|---------------------------------------------|---------------|-----------------|-------------------|
|        | ≤1  | 1-10 | 10-20 | 20-40 | 40-63 | >63 | '<10 μm, (% vol.) | |
| AEB    | 20.53 | 31.68 | 9.57 | 18.23 | 8.15 | 11.78 | 25.77 | 52.27 | 32035 |
| C1     | 37.76 | 45.77 | 9.62 | 3.59 | 1.31 | 1.95 | 7.65 | 83.53 | 87651 |
| AB     | 0.00  | 13.89 | 27.85 | 18.79 | 17.6 | 21.87 | 40.36 | 13.89 | 3169  |
| C2     | 0.00  | 24.67 | 48.06 | 18.79 | 5.17 | 3.30 | 19.57 | 24.67 | 4741  |

The results of the study of particle size distribution showed that the modification of clay by the QAS without preliminary adding of Na₂CO₃ to the (sample C1) increased the opening of mineral aggregates relative to the sample AEB. Thus, the surface area also increased from 32035 cm²/cm³ to 87651 cm²/cm³, while the number of particles <10 μm increased from 52.57% vol. to 83.53% vol.

As for the samples modified into the sodium form (samples AB and C2), according to the results, a significant decrease in the surface area of the obtained organobentonites is observed in comparison with the AEB and C1. This is probably caused by the formation of larger agglomerates from dispersed particles.

This assumption is confirmed by the study of the microstructure of organobentonites. The study was carried out on JAMP-9510F auger electron spectrometer at a primary beam energy of 10 kV, a primary beam current of 1 nA and 0.1 nA, a primary beam diameter of less than 0.01 μm/ The research results are shown in figure 2.
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Figure 2. Structure of the obtained organobentonite: C1 (a, b) and C2 (c, d)

The obtained micrographs of organobentonites (figure 2) confirm the effect of the formation of larger agglomerates after the addition of Na₂CO₃.

Successful intercalation of QAS into the structure of natural and sodium smectite is confirmed by the results of X-ray structural analysis.

Table 5 and figure 3 show that the interplanar distance upon organomodification of the sample AEB increases from 13.53 Å to 15.30 Å (sample C1), and upon saturation of the sodium form of clay with the QAS, the interplanar distance increases from 9.80 Å (sample AB) to 15.34 Å (sample C2). It indicates that the modification of bentonite with a quaternary ammonium salt affects the change in the interplanar space, and the sorption of QAS by the sodium form of bentonite is higher than that of the original natural form. This fact is confirmed by a large expansion of the interplanar space (1.77 Å for sample AEB versus 5.54 Å for sample AB).

Table 5. Determination of interplanar space and LOI of the bentonites and organobentonites

| Sample | Interplanar spacing d₀₀₁ of smectite, Å | Increase in interplanar spacing d₀₀₁ of smectite, ΔÅ | LOI, % |
|--------|----------------------------------------|--------------------------------------------------|-------|
| AEB    | 13.53                                  | -                                                | 6.18  |
| AB     | 9.80                                   | -                                                | 5.96  |
| C1     | 15.30                                  | 1.77                                             | 18.90 |
| C2     | 15.34                                  | 5.54                                             | 23.48 |

*Note: an increase in interplanar spacings d001 of smectite in calcium and sodium forms of organobentonites*
To clarify these data, a gravimetric assessment of the organic matter of the original and modified samples was carried out. From the obtained organobentonites, weighed portions were selected to determine the LOI. The samples were calcined under the same conditions at a temperature of 1000 °C. The results are also presented in table 5.

From the results of determining the LOI, a significant increase in the organic part in the structure of the obtained organobentonites is seen. It is also worth noting that organomodification of the sodium form of bentonites (sample C2) gives a higher result than a similar modification of the original calcium form of bentonites (sample C1). This indicates that the sodium form of bentonites adsorbs more QAS.

To research the adsorption properties of the obtained organobentonites, some physical and adsorption parameters, such as mass fraction of moisture, bulk density, real density and maximum adsorption volume for water vapor (table 6), were determined.

Table 6. Physical and adsorption characteristics of the bentonites and organobentonites

| Sample | Mass fraction of moisture, mass. % | Bulk density, g/cm³ | Real density, g/cm³ | Maximum adsorption volume for water vapor, cm³/g, at P/P₀=0.98 |
|--------|-----------------------------------|---------------------|---------------------|-------------------------------------------------|
| AEB    | 8.2                               | 1.2203              | 2.7368              | 0.1622                                          |
| AB     | 7.7                               | 1.2951              | 2.7967              | 0.2010                                          |
| C1     | 1.8                               | 0.3972              | 2.1065              | 0.0319                                          |
| C2     | 1.6                               | 0.2667              | 2.1180              | 0.0411                                          |

According to the physical characteristics, the values of the real density of the original bentonite samples lie within 2.7368-2.7967 g/cm³, while the obtained organobentonites are characterized by lower values (2.1065-2.1180 g/cm³). There is a significant difference between the true and bulk density of the obtained organobentonites. Having considered the values of the real and bulk densities of organobentonites, the amount of pore space for samples C1 and C2 was determined, which is 81.14% and 87.41%, respectively. With such a high porosity, the mass fraction of water is only 1.6-1.8%, which indicates the hydrophobic properties of the materials obtained.

The low maximum adsorption volume for water vapor for organobentonites, confirms the hydrophobization properties of the obtained material.

At the next step the oil capacity of the obtained organobentonites was determined. The best adsorption properties are possessed by sample C2, its oil capacity was 104 g of oil per 100 g of sorbent, in contrast to sample C1, the oil capacity of which was 61 g per 100 g of sorbent. This indicates the expediency of converting calcium bentonites into the sodium form when obtaining organophilic clays.
and the effectiveness of using organobentonites as a sorbent for cleaning oil contaminants from the water surface.

To consider the possibility of water purification from oil by organobentonites, the pollution of the water surface with oil was modeled under laboratory conditions. Oil was added to a glass with clean tap water, which was distributed over the water surface in a layer (1-2 mm).

An oil film obtained in this way in a glass of water was sprinkled with 20 g of organobentonites C1 and C2. The binding of oil on the water surface by the obtained organobentonites can be observed in figure 4.

![Figure 4. Binding of oil on the water surface by organoclays, where: a) oil on the water surface; b) Agglomerate formed by sample C1; c) Agglomerate formed by sample C2](image)

Figure 4 clearly shows the efficiency of the binding capacity of organobentonites. It should be noted that the agglomerate formed by C2 organobentonite (figure 4c) is characterized by more distinct boundaries, the oil film is collected in a single dense lump, concentrated in the central part on the surface of the water. Tactilely, the structure of the lump formed on the surface is not sticky and can be easily removed from the water by mechanical means.

Sample C1 (figure 4b) formed an oily agglomerate on the water surface with implicit boundaries distributed over the entire surface, which is confirmed by the lower oil capacity of this composition. Tactilely, the structure of the lump formed on the surface is sticky.

Thus, regarding the purification of the water surface from oil, the best adsorption properties of sample C2 are confirmed due to their higher oil capacity, described earlier, and as a consequence of the economy of use. To achieve a similar binding of oil with sample C1, a larger amount of this sorbent is required.

As a result of the study, an optimal scheme for obtaining organobentonites with hydrophobic and high sorption properties has been developed.

When assessing the quality of the obtained organobentonites, it was found that sorbents based on the sodium form of bentonites have better properties in comparison with organobentonites based on natural raw materials. More quaternary ammonium salt penetrates into the interplanar space of the sodium form of smectite than into the space of the calcium form. The greater increase in the interplanar spacing of smectites and the greater value of the LOI confirm this. Sodium-based organobentonites have higher hydrophobicity and sorption properties, which is confirmed by the physical and adsorption parameters of the obtained sorbent.

When assessing the possibility of using organobentonite in water purification from oil pollution, it was found that organobentonite based on the sodium form of smectite is capable of forming an agglomerate with oil spots floating on the water surface, which is subsequently mechanically removed and does not fall into the muddy part of the bottom sediments of the reservoir, preventing the application damage to the ecosystem.
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