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Hydrophobic Sorbent of Silica Clay

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Abstract: The paper presents the results of a study of the physicochemical and sorption characteristics of the modified silica clay. It is established that the modification of the silica clay provides an increase in the hydrophobicity, specific surface, and porosity of the sorbent, and also increases its capacity in petroleum absorption. It was found out that the modified silica clay is a highly effective sorbent with respect to emulsified petroleum products. The sorption activity of the modified silica clay on petroleum products was estimated using sorption isotherms.

Introduction

The problem of pollution of the environment with petroleum products is an acute problem all over the world at present. To purify such wastewater, mechanical, physicochemical and biological methods are used [1]. Sorption is one of the physico-chemical methods of wastewater treatment, which enjoys wide practical application. This is due to its effectiveness, providing for adequate sanitary-hygienic indicators of residual content of petroleum products; environmental safety, eliminating formation of secondary pollution; and ease of process control.

However, despite the merits of this method, its use is limited by insufficient sorption capacity of natural materials and the high cost of efficient carbon sorbents.

Literature data analysis has shown that the search and development of new effective cheap and affordable sorption materials for extraction of emulsified petroleum products from wastewater is a pressing issue [2-7].

One of the promising directions is the creation of more effective adsorbents by modifying the surface of materials of natural origin: aluminosilicates, clays, silica clays. At the same time, it is rational to use for modification the materials that are locally available in raw form.

The objective of this study has been the obtaining of the hydrophobic sorbents based on natural silica clays by modifying their surface, and studying their physical and chemical characteristics.

Theoretical background and experimental studies

Sedimentary fine porous rocks (silica clay) have proven themselves as good sorbents in cleaning soil from oil and petroleum products in spills [8]. This is due to their porous structure with the predominance of micro- and mesopores. Silica clays are formed, mainly, by finest (less than 0,005 mm) silica particles, the mass content of which varies from 75 to 92% depending on the source deposit. Clay minerals are a steady component of the flasks. The average density of silica clays is 1100-1600 kg/m³, the porosity reaches 55%. Silica clays are lightweight, with rough surface of flinty or flat-rugged fracture.

Of the silica clays' flaws one can mention their high hygroscopicity, which reduces the effectiveness of their use in cleaning oily wastewater.

A promising method of modifying natural materials in order to increase the selectivity and sorption capacity with respect to petroleum products is the hydrophobization of their surfaces [9-12].



Specific methods of modifying silica clays are determined by the peculiarities of their chemical composition, namely, the presence of silanol groups [13], capable of forming hydrogen bonds. Silanol groups bind water, the presence of which has a significant negative effect on capacity and selectivity with respect to petroleum products. The water adsorbed on the surface of material can be removed by heating to a temperature of 150-200 °C. After this, the interaction of the "freed" silanol groups with substances containing electron-donating functional groups is possible. Such substances include a low polarity compound - ethyl acetate, whose carbonyl oxygen exhibits proton acceptor properties. This determines the possibility of adsorption of ethyl acetate molecules on polar adsorption centers, those are silanol groups. In this case, these centers become inaccessible to water molecules, so the surface of the material acquires hydrophobic properties.

The object of the study was the silica clays of the Astrakhan deposit (Figure 1).



Figure 1. Silica clays of Kamennyarskoe Deposit of Astrakhan region

Silica clays were modified by treating the ground raw material with hydrophobizing agent, namely ethyl acetate. The prepared clay was mixed with a hydrophobizer at a certain ratio, placed in a muffle furnace, and held there for 3 hours at a temperature of 200 °C. Crushed silica clays and silica clays held in a muffle furnace at the same temperature and for the same time without a hydrophobizer were used as comparative samples.

The following characteristics were studied for all samples: moisture, total intergranular volume for water, maximum limit of sorption space for benzene vapor, specific surface area for methylene blue, and oil capacity.

Humidity was determined in accordance with GOST 12597-67 [14] (Russian state standards), total intergranular volume for water - in accordance with GOST 17219-71 [15], specific surface area for methylene blue (MB) – in accordance with GOST 13144-79 [16], oil capacity – in accordance with [17]. Maximum limit of sorption space (W_s) was determined under static conditions by the desiccator method for benzene vapor [18]. The results are listed in Table 1.

Table 1. Sorption characteristics of materials

silica clay	Humidity, %	Total intergranular volume for water e , cm^3/g	specific surface area for MB, m^2/g	Maximum limit of sorption space (W_s) for benzene vapor, cm^3/g	Oil capacity, g/g
Natural silica clay	4.51 ± 0.3	0.26 ± 0.4	122 ± 10	0.24 ± 0.04	1.54 ± 0.1
Thermally processed silica clay	2.81 ± 0.2	0.44 ± 0.3	136 ± 12	0.27 ± 0.03	1.83 ± 0.1
Modified silica clay	1.43 ± 0.2	0.52 ± 0.3	163 ± 10	0.64 ± 0.04	3.68 ± 0.1

To assess the hydrophobicity of the silica clay surface we used non-destructive analysis according to

Karsten method [19]. The essence of the method is determining of the exact amount of water penetrating per unit of time through a unit of surface area of the material [19]. During the Karsten test, the graduated tube was fixed on the vertical surface of the test material. Then the tube was filled with water to the required height, and then the volume of water sorbed at certain intervals was determined.

The results of the study are presented in Table 2.

Table 2. Hygroscopicity (Karsten method)

Silica clay	Hygroscopicity, ml/2hr
Natural silica clay	4.8
Thermally processed silica clay	2.3
Modified silica clay	0.2

A visual assessment of the spreading of water drop on the surface of silicate clays was carried out (Figure 2).

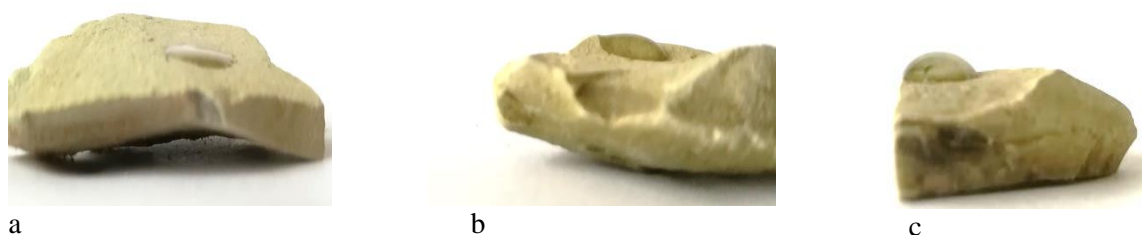


Figure 2 – Spreading a drop of water (0.1 ml) on the surface of the silica clay (0.1 ml) (triple magnification)

a – Natural silica clay, *b* – Thermally processed silica clay, *c* – Modified silica clay

Sorption ability with respect to emulsified petroleum products was studied in static conditions on model emulsions of different concentrations prepared from emulsion of Universal Oil-1 coolant PS, which is a balanced mixture of oil, emulsifiers, metal corrosion inhibitors, lubricants, biocides and other additives. The sorption material was added to the model emulsion at a sorbent-emulsion ratio of 1:50, then the mixture was stirred until equilibrium was reached. After that, the adsorbent was separated and the residual concentration of emulsol in the model system was determined by the calibration schedule. The calibration curve was made from the results of determining the optical density of emulsions with different concentrations of emulsol at a wavelength of 670 nm. The results of sorption capacity study of the materials in question are presented in Figure 3, 4.

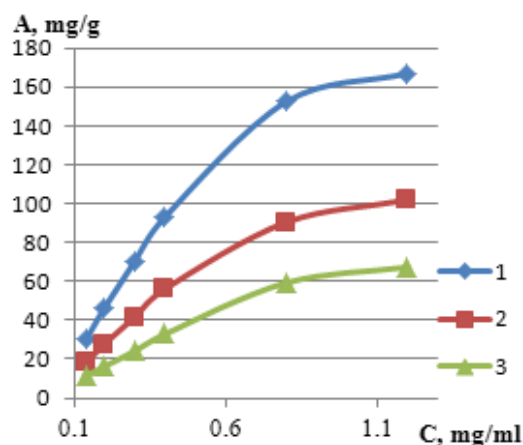


Figure 3 - Isotherms of adsorption of petroleum-containing cutting fluid "Unverisal-1 PS" by silica clays.

1- modified silica clay, 2- thermally processed clay, 3- natural clay.

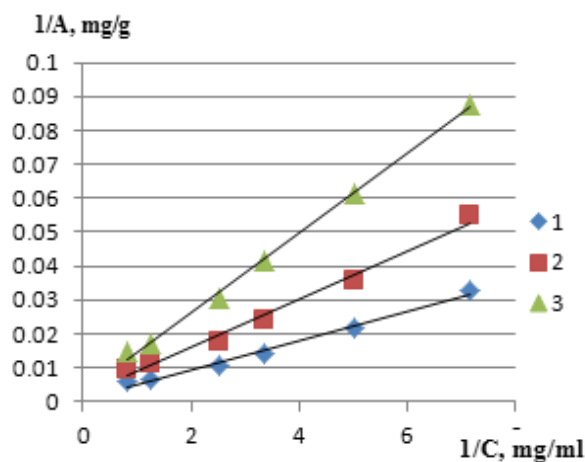


Figure 4 - Isotherms of adsorption of petroleum-containing cutting fluid "Unverisal-1 PS" by silica clays in the coordinates of linear form of the Langmuir equation.

1 - modified silica clay, 2- thermally processed clay, 3- natural clay

The sorption under dynamic conditions was studied on modeled gasoline emulsions prepared under ultrasonic dispersion. The samples were passed through a bulk adsorption filter consisting of various silica clay. Crushed samples of silica clay (0.5-2.0 mm) were placed in a column of 50 mm diameter. The height of the silica clay layer was 250 mm. The movement of test samples was carried out from the top down with the speed of the transmission of 30 ml/min. The filtrate was collected in a conical bulb, while the first portion of the filtrate (50 ml) was discarded. The total of 1000 ml of the filtrate was taken from each sample. The efficiency of the adsorption process was evaluated by the value of its Permanganate Demand (PD) [20]. The results are shown in Figure 5.

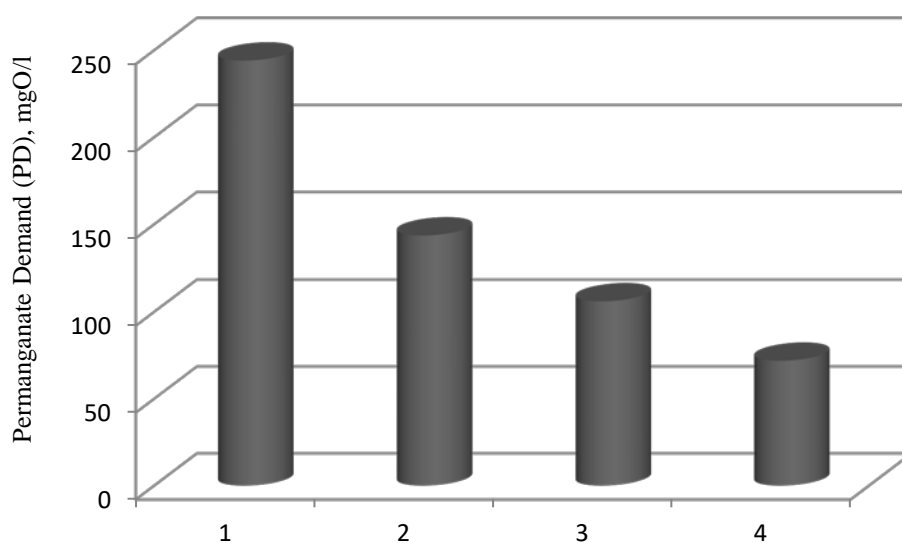


Figure 5 – Permanganate Demand (PD) of gasoline model samples

1– before cleaning; after filtration through samples: 2 - natural silica clay, 3 - thermally processed silica clay, 4 - modified silica clay

Calculations and graphical presentation of the results were carried out in Microsoft Office 2010 with MS Word 2010 and MS Excel 2010. Calculation in the framework of statistical processing was carried out according to [21].

The results and considerations

Analysis of the results of the study of silica clays' sorption properties (Table 1) showed that the differences in indicator values are statistically significant.

Comparison of the humidity of studied silica clay samples reveals that the natural silica clay has the highest moisture content. This is due to its hydrophilic nature. The moisture content of thermally treated silica clay decreases 1.6 times, which is explained by the removal of adsorbed water from the material and the formation of siloxane groups. Silica clay modified with ethyl acetate has the lowest moisture content, which is due to the presence of a hydrophobic film on its surface, which prevents adsorption of moisture from the air.

Total pore volume of the samples indicate that thermal treatment of silica clay increases material porosity. Thermal activation removes adsorbed moisture, and, as a consequence, increases cavities. The total pore volume of modified silica clay is slightly higher than that of thermally treated flask. It can be assumed that this is due to chemical processes caused by ethyl acetate hydrolysis in the presence of water vapor to form ethanol reacting with silanol groups, and acetic acid reacting with metal cations. As is the case, metal cations are removed from the samples, so the number of pores increases [22].

Analysis of the specific surface area of silica clays for methylene blue reveals a similar pattern. In view of the fact that the MC molecule is a marker for organic substances sized 2 nm to 10 nm, the obtained results indicate increased mesopores in the structure of the modified clays.

Maximum limit of sorption space for benzene vapor (W_s) indicate the ability of the material to adsorb non-polar compounds, that is, its hydrophobic properties. An analysis of the results obtained suggests that the thermal treatment of silica clays does not lead to increased selectivity for nonpolar compounds. Modification of silica clay with ethyl acetate provides an increase of the parameter in question by more than 2.5 times, which corresponds to "BAU" active carbon [23]. This indicates an increased hydrophobicity of the samples.

Oil capacity increases in silica clays as follows: natural - thermally processed - modified with ethyl acetate. This shows the same tendency as above.

Comparison of the experimentally obtained water absorption values determined by the Karsten method revealed the highest values for the natural silica clay. The smallest value of this indicator is characterized by a modified silica clay. Thermally processed silica clay has water absorption values silica clay are close to the natural silica clay. The results indicate a decrease in water wettability of the surface of the modified silica clay, that is, its hydrophobization. This is indirectly confirmed by the nature of the water droplets on the surface of the silica clay. In the series of silica clay: natural - thermally processed - modified the height of droplets increases (Figure 2), and the diameter decreases, indicating an increase in surface tension at the interface between the surface of water and the flask, which prevents the spreading of the droplet.

Study of sorption processes of emulsified petroleum products from model systems (Figure 3) revealed that the isotherms are described by the Langmuir equation. It was found that sorption capacity in the row of silica clays "natural - thermally treated - modified with ethyl acetate" increases significantly. The Langmuir equation was linearized to numerically determine the limiting adsorption corresponding to complete filling of surface with a monomolecular layer of the adsorbent (Figure 4). On the basis of the data, the limiting adsorption of petroleum products from "Universal-1 PS" emulsol emulsions coolant were calculated. For natural silica clay the value is 370 mg/g, 588 mg/g for thermally treated, and 1111 mg/g for treated with ethyl acetate.

Comparison of the experimentally obtained water absorption values determined by the Karsten method revealed the highest values for the natural silica clay. The smallest value of this indicator is discovered of the modified silica clay. Heat-treated silica clay has water absorption values that are close the natural silica clay. The results indicate a decrease in water wettability of the surface of the modified

silica clay, that is, its hydrophobization. This is indirectly confirmed by the nature of the water droplets on the surface of the silica clay. In the series of silica clay: natural - thermally treated - modified silica clay the height of droplets increases (Figure 2), and the diameter decreases, indicating an increase in surface tension at the interface between the surface of water and the silica clay, which prevents the spreading of the droplet.

Thus, the conducted studies reveals that thermal treatment of silica clays leads to increased porosity and specific area of sorbent, but does not change their hydrophilicity. Treatment of silica clays with ethyl acetate gives them hydrophobic properties and increases the selectivity for non-polar compounds. Modified silica clay is not inferior to active carbon by maximum limit of sorption space for benzene and by oil capacity. It also demonstrates high sorption ability.

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