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Hydrophobization of Diatomite-Magnetite Composite Surface with Laurylpropylenediamine

S.M. Tazhibayeva*, K.N. Mamyr, Zhang Haoran, B.B. Tyussyupova, K.B. Musabekov

Al-Farabi Kazakh National University, 71 Al-Farabi ave., Almaty, Kazakhstan

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Abstract

Cleaning water from oil and oil products is one of the pressing problems of our time. One of the effective methods of water purification is sorption. In this regard, hydrophobized composite sorbents based on diatomite and magnetite were obtained; laurylpropylenediamine was used to hydrophobize their surface. The presence of magnetite and laurylpropylenediamine in the composites is substantiated based on SEM, FT-IR and X-ray fluorescence analysis data. The hydrophobization of the surface of the diatomite-magnetite composite is assessed by the change in its ζ-potential and wettability. The study of crude oil adsorption on the surface of the composite sorbents showed that when moving from the diatomite-magnetite composite to the diatomite-magnetite-laurylpropylenediamine composite, adsorption increases from 3.0 to 3.5 g/g, and the degree of oil extraction increases from 92.0 to 96.0%. The BET method showed that the specific surface area of diatomite is 67.8 m^2/g, and when forming diatomite-magnetite and diatomite-magnetite-laurylpropylenediamine composites, it decreases to 13.5 m^2/g and 10.3 m^2/g, respectively. Based on this, it was concluded that the increase in adsorption and the degree of oil extraction after coating the surface of the diatomite-magnetite composite with laurylpropylenediamine, is due to its hydrophobization.

1. Introduction

Currently, oil and oil product spills on water are of concern to researchers [1, 2]. Composite sorbents are widely used to purify water from various pollutants. A large number of composite sorbents have been obtained and characterized that are capable of purifying water from heavy metal ions, dyes, surfactants and spilled oil to a degree of purity that meets environmental requirements [3-5]. The main components of composite sorbents are solid carriers of organic and inorganic origin, modified by chemical compounds capable of binding to pollutant molecules. Highly porous materials are used as solid carriers: zeolite, clays, activated carbon [6-8]. In most cases, the modifiers of such porous carriers are polymers; however, along with water-soluble polymers, nanoparticles of solid materials are sometimes used to impart special properties to solid sorbents [9, 10]. For example, dispersed magnetite particles were used to impart magnetic sensitivity to particles of montmorillonite, bentonite and activated carbon [11-13]. Such adsorbents are effective in extracting heavy metal ions from water, the degree of water purification reaches 99.8–99.9%. At the same time, hydrophobization of the surfaces of sorbents and other materials with silane agents – such as membranes – plays a crucial role in the removal of organic pollutants and oil from water [14-17]. For instance, cellulose membranes coated with silane agents such as hexadecyltrimethoxysilane and triethoxy(octyl)silane have demonstrated water contact angles in the range of 140–150°, offering high efficiency in oil–water separation [16-17]. Moreover, the hydrophobization of kaolin using similar silane agents, like dimethyldichlorosilane, has been shown to increase its water contact angle from

*Corresponding author.
E-mail address: sagdattazhibayeva2018@gmail.com

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93° to 144°, further enhancing its water-repellent properties [18]. Since clay is an accessible natural material, the hydrophobization of their surface is of great interest to researchers [18-21]. Traditional cationic surfactants – quaternary ammonium salts – are used as a hydrophobizing agent. Hydrophobization of the bentonite surface using hexadecethyltrimethylammonium bromide significantly increases the adsorption of non-ionic surfactant – Triton X-100, which is evidence of the success of the modification [22]. The increase in the adsorption capacity of bentonite is explained by the interaction of hydrocarbon chains of both surfactants, but the modification leads to a decrease in the specific surface area of the clay from 35.7 to 7.1 m^2/g. Bentonite clays modified with cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, and dodecyltrimethylammonium chloride were tested for adsorption of atrazine [23]. The maximum Langmuir adsorption value on the original clay was 108 mg/g, and on the modified clay – 285.7 mg/g. The modification is also accompanied by a decrease in the specific surface area of bentonite and an expansion of its interlayer space. The authors [15, 24] note the possibility of modifying layered silicates through their intercalation with various quaternary ammonium salts and the effectiveness of modified clays in the adsorption of oil and oil products.

It was shown that modification of clays with cetylpyridinium chloride and hexadecyltrimethylammonium bromide was accompanied by an increase in basal spacing of clay from 12.7 Å to 21.08 and 26.0 Å [25]. It should be noted that modification of clays with quaternary ammonium salts helps prevent phase separation and agglomeration of clay particles [26]. This property of modified clays can be considered a significant advantage over other hydrophobic sorbents when used to extract oil from water surfaces. However, despite such a positive effect of hydro-phobization on the properties of clay sorbents, it is accompanied by a reduction in their specific surface area. In this connection, the question arises about the influence of hydrophobization of clay sorbents on the amount of oil adsorption on their surface. Taking into account the above, the production and study of hydrophobized magnetic sorbents based on clays is of particular interest. The most convenient carrier for obtaining such composite sorbents is diatomite, which, unlike typical clays, has large pores [26], capable of holding both magnetite and adsorbate. The aim of the work is to obtain hydrophobic composite sorbents based on diatomite, magnetite and to determine their sorption capacity in relation to oil.

2. Experimental

Diatomite from the Mugodzhar deposit (Kazakhstan) was used as the basis of composite sorbents. The original diatomite was washed three times with distilled water, filtered and dried at a temperature of 80–90 °C for 2 hours. Then the sample of purified diatomite was treated with a solution of 15% H_2SO_4 at a temperature of 90 °C for 3 hours. To neutralize the acidity of the mineral sample, 10% NH_4OH was used.

To obtain magnetic diatomite composites, Fe(III) and Fe(II) salts ($FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$) with a concentration of 0.1 mol/L were used. The clay–magnetite composite was synthesized as follows: 20 ml of 0.1 mol/L $FeCl_3$ solution were added to a 10% suspension of diatomite under continuous stirring, and the mixture was maintained for 1 hour. Subsequently, 10 mL of 0.1 mol/L $FeSO_4$ solution were introduced into the mixture in the presence of 15% NH_4OH with stirring. The suspension was kept for another 1 h, after which the precipitate was washed three times with deionized water, filtered, and dried.

Hydrophobization of the surface of the diatomite-magnetite composite was carried out using the cationic surfactant laurylpropylenediamine (Sigma Aldrich). Lauryl propylene diamine was prepared at a concentration of 0.1 mol/L, using 90% ethyl alcohol as a solvent. 150 ml of the surfactant solution was mixed with 7 g of the diatomite-magnetite composite, and the mixture was stirred for 4 h at a temperature of 30–40 °C. Then the composite was washed with 90% ethyl alcohol, filtered and dried (Fig. 1).

Scanning electron microscopy. Electron microscopic images of the surface of the original diatomite, diatomite-magnetite and diatomite-magnetite-amine composites were taken on a JSM-6490LA scanning electron microscope. For the studies, the diatomite and its composites were dried, crushed and sifted through a sieve with a mesh size of 1 mm.

FT-IR spectroscopy. FT-IR spectra of diatomite samples and its composites were recorded on an FT-IR spectroscope (Shimadzu, Japan). A potassium bromide pellets were fabricated with a powder of samples. FT-IR spectra were recorded in the ranges from 4000 to 400 cm^{-1}.

Determination of ζ-potential of particles. The ζ-potential values of diatomite particles and its composites were determined using a Zetasizer Nano ZS (Malvern Instruments, UK). Aqueous suspensions of diatomite, diatomite-magnetite and diatomite-magnetite-laurylpropylenediamine composites with a concentration of 0.05% were used for the study. Particle mobility was measured at 25 °C.

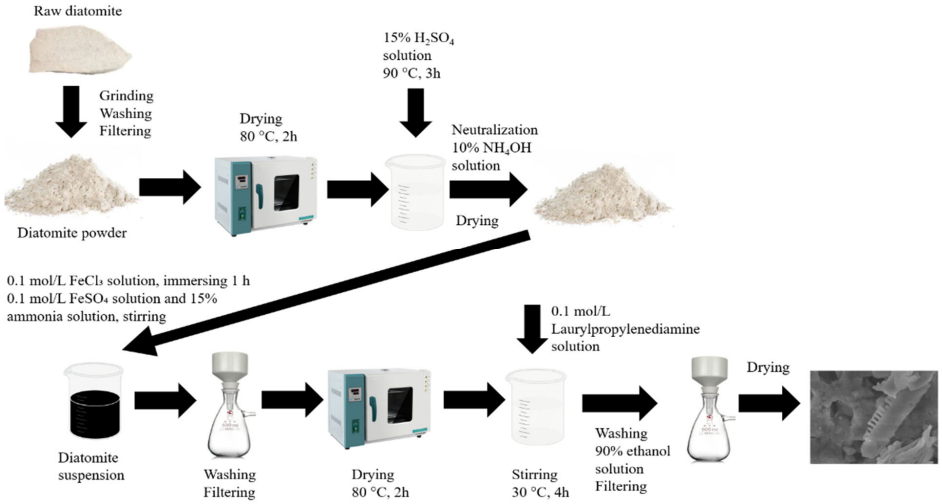

Fig. 1. Scheme of the diatomite-magnetite-laurylpropylenediamine composite preparation.

BET analysis of specific surface area. Determination of specific surface area and pore sizes of adsorbents was carried out on an automated specific surface area analyzer BST – 660S (China). The mass of samples for analysis was 300–350 mg.

Adsorption of oil. To determine the adsorption of oil on diatomite and its composites, 1 g of the adsorbent was mixed with various amounts of oil/water mixture, then the resulting mixtures were thoroughly mixed and left for 1 h at a temperature of 25 °C. After this, the non adsorbed oil was separated from the adsorbent to determine its mass. Oil adsorption (A) is calculated as the ratio of the masses of non adsorbed oil and adsorbent using the formula:

$$A = (m_1 - m_2)/m_{ad},$$

here, m_1 and m_2 – are the mass of oil before and after adsorption, g; m_{ad} – is the mass of the adsorbent, g.

The degree of oil recovery is calculated as the ratio of the mass of extracted oil to the initial mass of oil.

3. Results and Discussion

Diatomite is a very interesting silicate mineral which, unlike typical clays, has a wide range of pore sizes. This is the basis for obtaining composites from it by adsorption or synthesis of the necessary compounds in its pores, in this case magnetite. Figure 2 shows SEM images of diatomite, diatomite-magnetite composites, and diatomite-magnetite-laurylpropylenediamine composites. The image of the original diatomite that underwent thermal acid treatment clearly shows pores with sizes in the range of 1.0–1.3 μm. When moving to the diatomite-magnetite composite, magnetite particles of different sizes are visible on the surface and in the pores of the diatomite. After treating the diatomite-magnetite composite particles with a laurylpropylenediamine solution, their surface is covered with a thin layer of surfactant, which in some places looks like threads.

It should be noted that the use of a polymer as a modifier can lead to clay aggregation [19]. Apparently, polymers, due to their high molecular weight, can combine particles into large floccules, which causes aggregation. From this point of view, low-molecular surfactants are more preferable as clay surface modifiers, since the adsorption layers formed by them will protect the particles from sticking together.

Figure 3 shows the FT-IR spectra of diatomite and its composites. The FT-IR spectrum of the original diatomite shows a sharp peak at 1009 cm^{-1}, corresponding to the deformation vibrations of Si-O-Si bonds [12]. The absorption bands at 1637 cm^{-1} and 3620 cm^{-1} can be attributed to the deformation vibrations of the O-H groups of the adsorbed water molecules and the SiOH groups of the diatomite. The peaks at 789 cm^{-1} and 693 cm^{-1} are also visible in the right part of the spectrum, which can be due to Si-O and Al-O bonds. In the case of the diatomite-magnetite composite, the peak at 3620 cm^{-1} broadens and deepens, which may be due to the superposition of the vibrations of the Fe-O bonds of magnetite on the deformation vibrations of the O-H groups of water molecules and the SiOH groups of diatomite. In addition, the peak at the vibration frequency of 1009 cm^{-1}, corresponding to vibrations of Si-O-Si bonds, shifts to 1018 cm^{-1}. This may be evidence of the interaction of magnetite particles with the silanol groups of the mineral. New peaks also appear at 1408 cm^{-1} and 524 cm^{-1}, the intensity of the peak at 789 cm^{-1} increases, which can be explained by vibrations of Fe-O bonds of magnetite [12].

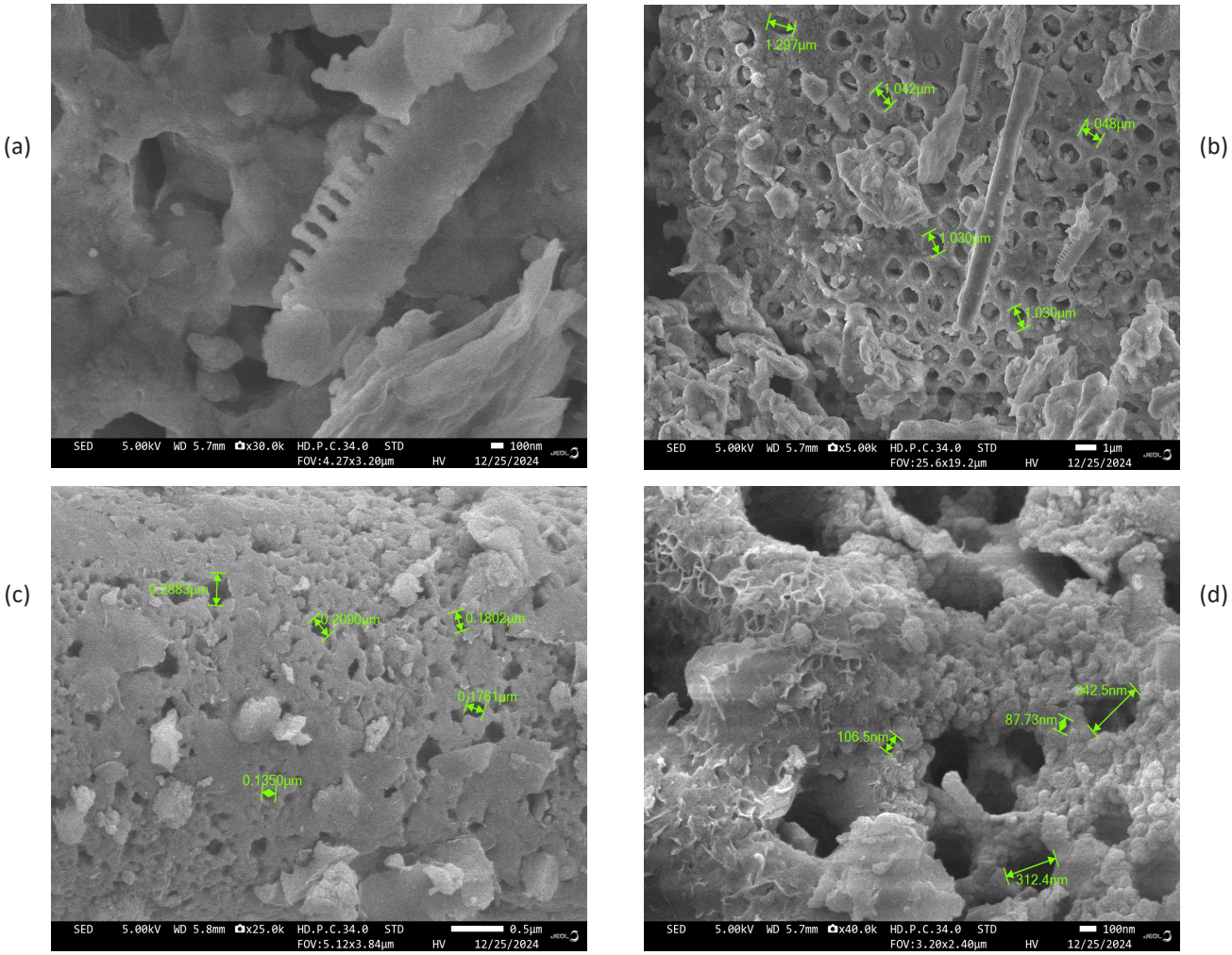

Fig. 2. Electron microscopic images of native (a) and thermal acid-treated diatomite (b), diatomite-magnetite composite (c), diatomite-magnetite-laurylpropylenediamine composite (d).

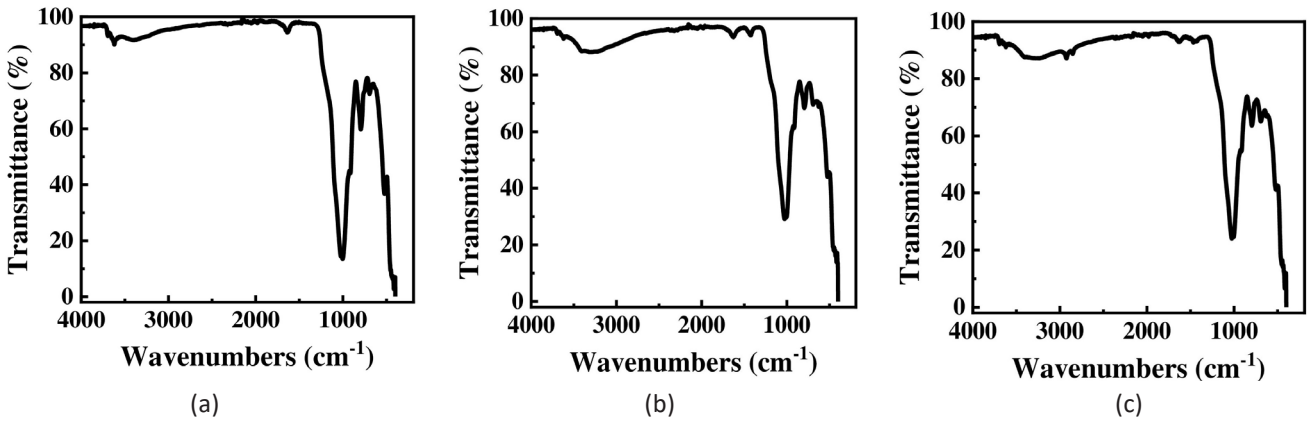

Fig. 3. FT-IR spectra of diatomite (a) and diatomite-magnetite (b), diatomite-magnetite-laurylpropylenediamine (c) composites.

In the IR spectra of the diatomite-magnetite-laurylpropylenediamine composite, a small peak appears at 2800 cm^{-1}, which may be due to the stretching vibrations of the N-H and C-H groups of the fatty amine molecules.

To obtain information about the chemical composition of the obtained composites, X-ray fluorescence analysis of their samples was carried out. As seen from Table 1, the synthesis of magnetite in the pores of diatomite leads to an increase in its Fe

Table 1. Chemical composition of diatomite and its composites

№	Basic elements	Fe	Cu	Se	Si	K	Ti	Cr
1	Diatomite, %	31.76	3.02	1.79	1.79	3.90	1.74	0
2	Diatomite-magnetite composite, %	55.96	0.08	0.19	0.19	2.10	0.80	0.13
3	Diatomite-magnetite-laurylpropylenediamine composite, %	43.25	0.11	0.02	0.02	3.04	0.89	0.10

composition from 31.76% to 55.96%, which may be evidence of the formation of a diatomite-magnetite composite. However, after treating the surface of the diatomite-magnetite composite with a laurylpropylenediamine solution, the Fe content in it decreases slightly and the Si content increases. Unfortunately, this method does not allow determining the content of H, N and O atoms in the analyzed sample. These results suggest competition between Fe and N atoms for binding to the diatomite surface.

The fact is that magnetite particles have a positive charge due to the positive charge of $Fe\text{-}O^+$ [27, 28]. Amino groups of surfactants in an aqueous environment are capable of being protonated by H^+ ions of water molecules, whereby tertiary nitrogen atoms become quaternary and acquire a positive charge. In this case, the formation of the diatomite-magnetite composite is due to the electrostatic attraction of positively charged magnetite particles to the negatively charged $Si\text{-}O^-$ groups of the diatomite particle surface. The modification of the diatomite-magnetite composite surface can also be due to the electrostatic interaction of amine groups with silicate groups of diatomite. Therefore, the decrease in the amount of Fe in the composition of the diatomite-magnetite-laurylpropylenediamine composite (Table 1) can be explained by the displacement of some of the magnetite from the diatomite surface by surfactant molecules. In this case, the surfactant molecules will be directed with their cationic polar parts toward the diatomite surface, and their hydrocarbon radicals will be directed outward. It is precisely this orientation of the amphiphilic surfactant molecules that will ensure effective hydrophobization of the surface of the diatomite-magnetite composite.

Determination of the charge sign and the value of the ζ-potential of the surface of the original diatomite and its composites showed that the diatomite particles have a high negative charge, ζ = -39.92 mV (Table 2). In the diatomite-magnetite composite, the mineral surface changes the charge sign, the ζ-potential becomes equal to +0.20 mV. This change in surface charge is due to the positive charge of FeO^+ groups of magnetite particles.

Table 2. Effect of magnetite and laurylpropylenediamine on the ζ-potential of diatomite particles

№	System	ζ, mV
1	Diatomite	-39.92
2	Diatomite-magnetite composite	+0.20
3	Diatomite-magnetite- laurylpropylenediamine composite	-0.76

After modifying the surface of the diatomite-magnetite composite with laurylpropylenediamine solution, the surface of the diatomite becomes negative, but the ζ-potential value is not as high as that of the original diatomite, and it is -0.76 mV. This change in the ζ-potential confirms the assumption of competition between magnetite particles and laurylpropylendiamine cations for binding to the $\equiv SiO^-$ groups of the diatomite surface.

To assess the degree of hydrophobization of the surface of the diatomite-magnetite composite, a study was conducted on the wettability of the surface of diatomite and its composite with magnetite with water before and after treatment with laurylpropylenediamine. As seen from Table 3, the surface of the diatomite-magnetite composite is less hydrophilic than the surface of the diatomite, and after coating with a layer of laurylpropylenediamine, the surface of the diatomite-magnetite composite becomes hydrophobic, the water contact angle (WCA) is 117 °.

Table 3. Changes in the WCA of diatomite during the formation of composites

System	WCA, degree	cos θ
Diatomite	18.0	0.95
Diatomite-magnetite composite	61.0	0.48
Composite diatomite-magnetite-laurylpropylenediamine (0.05 mol/L)	78	0.21
Composite diatomite-magnetite-laurylpropylenediamine (0.1 mol/L)	117	-0.45

As is known [29] the presence of roughness and pores enhances the hydrophilicity of hydrophilic materials and increases the hydrophobicity of hydrophobic materials. Therefore, such a small WCA of the diatomite surface can be explained both by the presence of well-hydrated groups on its surface and by the presence of pores of significant sizes. When moving from diatomite to a diatomite-magnetite composite, some of the pores are filled with particles of a less hydrophilic material, so the hydrophilicity of the surface decreases, and the water contact angle accordingly increases to 61°. After coating surface of the diatomite-magnetite composite with an amine layer, the value of WCA increases to 117°, the sign of cos WCA, which means wetting, becomes negative, the surface has become hydrophobic. In order to avoid competition between laurylpropylenediamine molecules and magnetite particles for binding with the silanol groups of diatomite, an attempt was made to reduce the concentration of surfactant from 0.1 to 0.05 mol/l. In this case, the water contact angle was acute and equal to 78° the surface remained hydrophilic. It follows from this for hydrophobization of the surface of the diatomite-magnetite composite, it is necessary to use laurylpropylenediamine concentration sufficient to cover the entire surface of the composite.

Figure 4 shows the adsorption isotherms of oil on the surface of diatomite and composites: diatomite-magnetite and diatomite-magnetite-surfactant. General view of the oil adsorption curve on the surface of the original diatomite is noteworthy, it represents an adsorption isotherm characteristic of macroporous adsorbents [30]. In the case of diatomite-magnetite and diatomite-magnetite- surfactant composites, the type of isotherms changes. Indeed, diatomite as a mineral that retains the structure of algae that served as a skeleton for its formation over a long period can have a large number of large pores, which is confirmed by SEM data (Fig. 2). In the case of diatomite composites, its pores are filled with magnetite particles, and after hydrophobization, they are covered with a layer of surfactant molecules. Therefore, the treatment of the surface of the diatomite-magnetite composite with laurylpropylenediamine solution, despite hydrophobization, did not lead to a significant increase in the amount of oil adsorption.

The adsorption of oil on the surface of diatomite and diatomite-magnetite composite may be due to the retention of oil particles in the pores of diatomite due to physical forces. In the case of a hydrophobized diatomite-magnetite-surfactant composite,

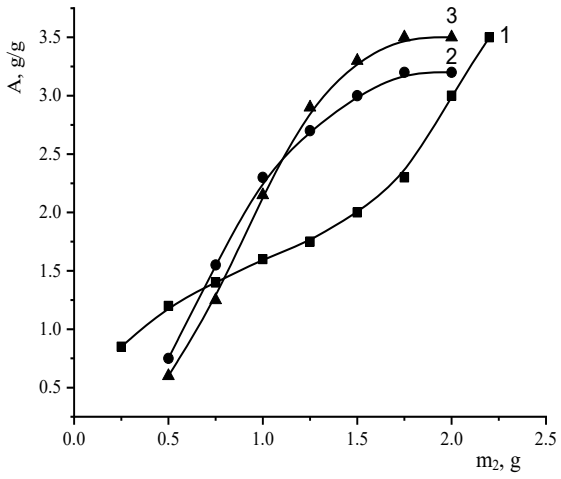

Fig. 4. Oil adsorption isotherms on the surface of diatomite (1) and diatomite-magnetite (2) and diatomite-magnetite-laurylpropylenediamine (3) composites. T = 25 °C.

hydrophobic interactions between hydrocarbon molecules in the oil and hydrocarbon radicals of the surfactant may be responsible for adsorption.

The difference in the adsorption capacity of diatomite and its composites can be explained based on the analysis of their surface by the BET method (Table 4). The specific surface area of diatomite is 67.8 m^2/g, the proportion of macropores with a size of 50–200 nm turned out to be very insignificant and equal to 13.10%, and the proportion of mesopores, i.e. particles with a size of 10–50 nm – 57.05% and with a size of 2–10 nm – 26.41%. In the case of the diatomite-magnetite composite, the specific surface area decreases to 13.5 m^2/g, while the proportion of macropores increases to 37.04%. This may be evidence of the synthesis of magnetite particles in the pores of diatomite, on the one hand, and the formation of pores between the surface of diatomite and magnetite particles, on the other hand.

After coating the surface of the diatomite-magnetite composite with a surfactant layer, its specific surface area decreases slightly, and the proportion of macropores increases from 37.04% to 45.33%. In the case of coating the surface of the original diatomite with an amine layer, the specific surface area decreases from 67.2 to 42.7 m^2/g, while the increase in the proportion of macropores is also not as significant as in the case of composites. It is likely that it is the close values of the specific surface area, total volume and pore diameter that determine the insignificant difference in the adsorption capacity of the diatomite-magnetite and diatomite-magnetite-laurylpropylenediamine composites.

Table 4. Results of BET analysis of the surface of diatomite and its composites

System	Specific surface area, m^2/g	Total pore volume, cm^3/g	Average hole diameter, nm	Part of pore with d = 50-200 nm	Part of pore with d = 0-50 nm	Part of pore with d = 2-10 nm
Diatomite	67.8	0.16	9.7	13.10	57.05	26.41
Diatomite-magnetite composite	13.5	0.15	15.2	37.04	42.78	20.18
Diatomite-surfactant composite	42.7	0.15	14.1	24.43	50.84	24.73
Diatomite-magnetite-surfactant composite	10.3	0.05	18.9	45.33	41.48	13.19

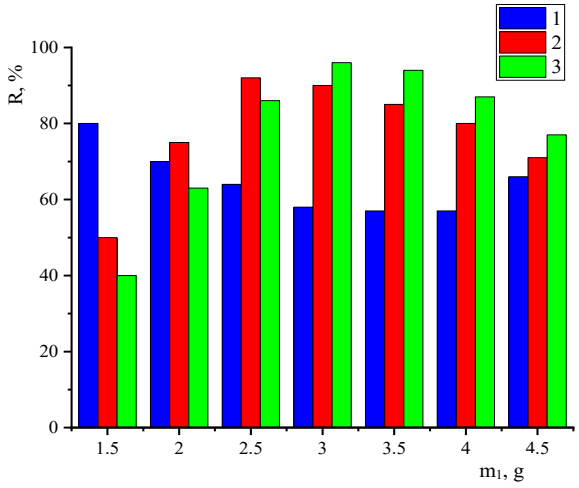

Fig. 5. Diagram for comparison of oil recovery using different adsorbents: diatomite (1), diatomite-magnetite composites (2) and diatomite-magnetite-laurylpropylenediamine (3).

Comparison of the degree of oil recovery using diatomite, diatomite-magnetite and diatomite-magnetite-amine composites (Fig. 5) shows that in the case of diatomite, the maximum degree of recovery (80%) is achieved with a low oil content in the water. For diatomite-magnetite and diatomite-magnetite-surfactant composites, with an increase in oil content, the degree of its recovery first increases to 92% and 96%, respectively, and then decreases. This is probably due to the saturation of the adsorbent surface, which is also noticeable on the adsorption curves. On the other hand, based on the diagram of oil recovery by different sorbents, it can be assumed that in the case of oil extraction by diatomite, the determining factor is the specific surface area, and in the case of composites, the hydrophobicity of the surface. Thus, coating the surface of the diatomite-magnetite composite with a layer of laurylpropylenediamine, although it promotes surface hydrophobization, cannot provide the expected increase in oil adsorption, which is associated with the closure of part of the pores and a corresponding decrease in the specific surface area of the adsorbent.

4. Conclusion

Diatomite and magnetite composites have been obtained, hydrophobized with the cationic surfactant – laurylpropylenediamine. Hydrophobization of the surface of the diatomite-magnetite composite is substantiated by the change in the values of the water contact angle of its surface and oil adsorption. During hydrophobization of the surface of the diatomite-magnetite composite, its surface WCA changes from 61° to 117°, but the increase in adsorption is not so significant, which is explained by a decrease in the specific surface of the adsorbent due to the filling of the diatomite pores with magnetite particles. Further development of research will be aimed at reducing the amount of hydrophobic agent and searching for amines with a short hydrocarbon radical.

Acknowledgments

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