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Synthesis of Magnetic Composite Based on Vermiculite

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Abstract

The aim of the study was to synthesize a magnetic composite based on vermiculite and to evaluate its physicochemical properties and adsorption capacity. An increase in the content of Fe (III) in the composition of clay and the inversion for the sign of the charge of vermiculite particles accompanies the formation of the composite. Introducing magnetite particles into the vermiculite structure is substantiated by the appearance of its diffractogram of 2θ angle values characteristic of magnetite. On the FTIR spectrum of clay after the synthesis of magnetite a new absorption band appears at a vibrational frequency of 1404 cm^{-1}, attributed to the Fe–O bond of magnetite, and the position of peaks in the interval 797–602 cm^{-1}. The adsorption capacity of the vermiculite-magnetite composite was evaluated by the adsorption of methylene blue on it. Processing of adsorption data according to Langmuir and Freundlich showed that the maximum adsorption of methylene blue on the surface of vermiculite-magnetite composite is 113.64 mg/g. The constant 1/n has a value less than 1.0, showing the high affinity of dye molecules to the composite surface. These results show that vermiculite-magnetite composite has a significant potential for use as a sorbent in the treatment of wastewater from oil, organic pollutants, as well as carriers of drugs.

1. Introduction

Modern methods for obtaining nanosized particles are promising for the synthesis of new composites with magnetic properties for various fields of production [1]. The synthesis of these composites is simple and affordable, but some limitations in the adsorption of organic and inorganic adsorbates on magnetite causes problems when using it in medicine and production. The idea of using magnetic sorbents to remove oil from the surface of water is very promising [2, 3]. However, magnetite does not have high porosity and a specific surface area. Therefore, treatment with clays or polyelectrolytes is very important for regulating the adsorption properties of magnetite [4–6]. Vermiculite can be used as a clay mineral.

Vermiculite is found in different places in the world, large reserves of this mineral are in the Kulantau deposit in Kazakhstan. It belongs to the class of hydromica, has a layered structure [7, 8]. Natural vermiculite increases sharply in volume when calcined, since the water molecules between its layers, turning into steam, push apart the silicate layers in a perpendicular direction. When cooling, this space is preserved, which gives the mineral valuable properties. This change significantly increases the adsorption capacity of vermiculite for hydrophobic organic compounds, so vermiculite is an indispensable adsorbent of organic pollutants [9–11]. The vast majority of research on the use of clays is devoted to the surface treatment of their particles with polymers, surfactants and metal ions. Meanwhile, an interlayer space in most natural aluminosilicates would make it possible to get their compositions with fine particles and get new materials based on them with specified characteristics.

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2. Experimental

2.1 Research materials and methods

The samples of vermiculite from the Kulantau deposit (South Kazakhstan) were used as a clay mineral. To activate the clay surface, it was subjected to thermal acid treatment. The natural mineral was washed with water and then heated in a 15% sulfuric acid solution in a water bath for 2 hours. After this time, the clay was washed with water and a 5% alkali solution. The dried clay was crushed and sifted through a sieve. A fraction with a particle size of < 70 µm was selected for the studies.

The treated vermiculite was kept in water for 24 h for swelling. Then, magnetite was synthesized in the suspension by successively introducing $FeSO_4$ and $FeCl_3$ solutions in the presence of ammonia water at pH = 9.5 and a temperature of 298 K.

FTIR spectra of magnetite and vermiculite were obtained in the range of 4000–440 cm^{-1} using a Spectrum 65 setup (PerkinElmer, USA).

The sizes and ζ-potential of vermiculite, magnetite, and vermiculite-magnetite composite particles were determined by light scattering using a Malvern Zetasizer Nano ZS 90 spectrometer (Malvern, UK).

The adsorption value of methylene blue was calculated using the equation:

$$A = \frac{(C_i - C_{eq}) \cdot V}{m}$$

where C_i and C_{eq} – the initial and equilibrium concentration of methylene blue, mg/L; V – the volume of the solution, L; m – the mass of the adsorbent, g. All experiments were carried out at room temperature of 298 K.

3. Results and discussion

To get information on the chemical composition of vermiculite before and after including magnetite particles in its structure, X-ray fluorescence analysis of clay samples and its magnetic composite was performed (Table 1). It should be noted that this method does not allow detecting elements with low atomic mass, so the table on the chemical composition does not contain information on the content of oxygen and hydrogen in the mineral. The dominant metals in the composition of vermiculite are Fe, Al and K, the content of which is 45.30, 21.68 and 3.51%, respectively. In the composition of the vermiculite-magnetite composite, the Fe content increases to 77.51%, and the content of Al and K decreases. This shows the inclusion of magnetite in the vermiculite structure. These metals are part of clays as oxides, so considering the proportion of oxygen in the mineral, it can be assumed that the specific contribution of each element can be significantly less than indicated.

Vermiculite, like many clay minerals, is a layered silicate [12–14]. Exchange cations are between the silicate layers; water molecules and adsorbed substances may also be located there. Therefore, the increase in the Fe content when moving from vermiculite to the vermiculite-magnetite composite may be because of the replacement of metal cations with iron ions, as well as the formation of magnetite particles in the interlayer space of clays. Figure 1 shows electron microscopic images of vermiculite and its composite. The images of vermiculite clearly show parallel layers and the free space between them, which determine the high swelling capacity and sorption properties of vermiculite. It should be noted that perpendicular layers were not found in the study of bentonite clays and their magnetic composites [15], they are characteristic only of vermiculite.

The magnification of the SEM images (Fig. 1b) allows us to explain the contribution of pores in the clay structure to its sorption capacity. It should be noted that when studying bentonite clays and their magnetic composites, no perpendicular layers were found [11], they are characteristic only of vermiculite. Figure 1c shows a view of a magnetic vermiculite composite, the increase of which (Fig. 1d) shows the saving of high porosity of clay in the composite. This is very important to ensure the adsorption capacity of the composite.

Table 1. Chemical composition of vermiculite and vermiculite-magnetite composite

Element	Vermiculite, %	Vermiculite-magnetite composite, %
Fe (III)	45.30	77.51
Si	19.60	9.30
K	3.51	0.92
Ca	1.52	0.50
Ti	2.90	0.73
Mn	0.15	0.13
Cr	0.04	0.05
Fe (II)	21.68	18.10
Cl	0.55	0.01
Zn	1.96	–

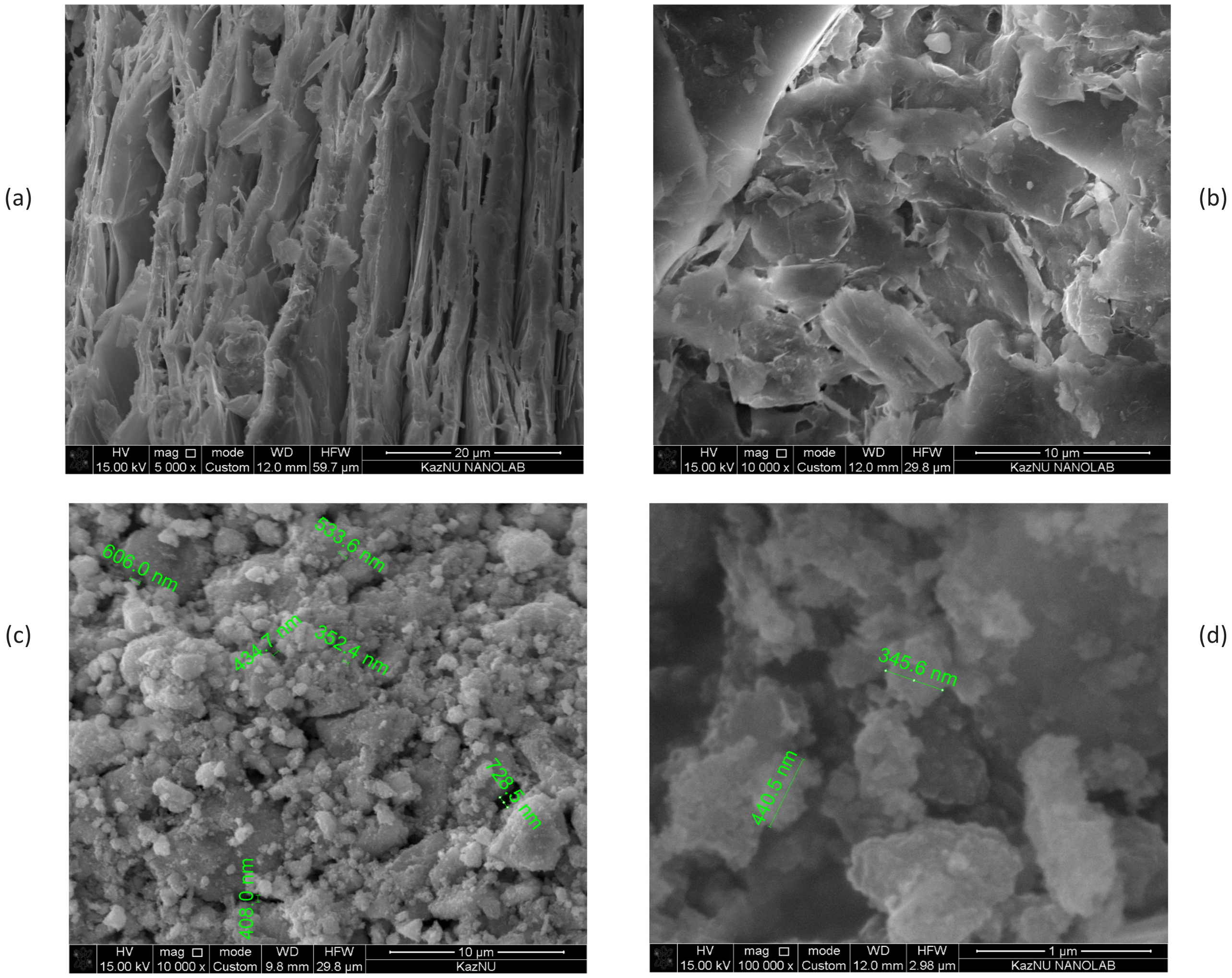

Fig. 1. SEM images of vermiculite (a, b) and vermiculite-magnetite composite (c, d).

To confirm the composition of the vermiculite composite, an FTIR spectroscopic study of vermiculite and its magnetic composite was carried out. In the FTIR spectrum of the original vermiculite (Fig. 2), peaks corresponding to O–H bonds of the water molecule and silicate groups are observed at vibration frequencies of 3436 cm^{-1} and 1634 cm^{-1} (Fig. 2, spectrum 1). Peaks at vibration frequencies of 1097 cm^{-1} and 468 cm^{-1} can be attributed to Si–O–Si bonds of silicate. The vibration peak at 797 cm^{-1} can correspond to metal oxides in vermiculite [16, 17].

In the FTIR spectrum of the vermiculite-magnetite composite (spectrum 2), the absorption bands at vibration frequencies of 3436 cm^{-1} and 1634 cm^{-1} undergo some changes but keep their general appearance. A new absorption band appears at the vibration frequency of 1404 cm^{-1}, showing the Fe–O bond of magnetite in the clay; the position of the peaks at 797 cm^{-1} and 602 cm^{-1} also change. These results show the incorporation of magnetite into the composition of vermiculite, i.e., the formation of a vermiculite-magnetite composite.

The X-ray diffraction patterns of vermiculite and its magnetic composite are shown in Fig. 3. In the vermiculite diffraction pattern, the 2θ angle values are 9.10; 18.22; 27.50; 32.70; 36.80, and 46.50°. These 2θ angle values show that the original kaolinite rock sample comprises montmorillonite (9.10°), hydromica (18.22°), as well as sepiolite (46.50°), gibbsite, palygorskite, and quartz [18].

In the magnetite diffraction pattern, the 2θ angle values are 30.09; 35.47; 43.37; 53.80; 57.60; 62.60, and 74.22. With the vermiculite-magnetite composite, the 2θ angle values of vermiculite 32.70; 36.80 and 46.50° disappeared, but peaks appeared at the 2θ angle values characteristic of magnetite: 30.07; 35.50; 43.22; 57.42 and 63.90°. The increase in the d values from 9.71 to 10.02 Å upon transition from vermiculite to its magnetic composite is probably because the interlayer space in the clay structure is expanded because of the location of small magnetite particles in it.

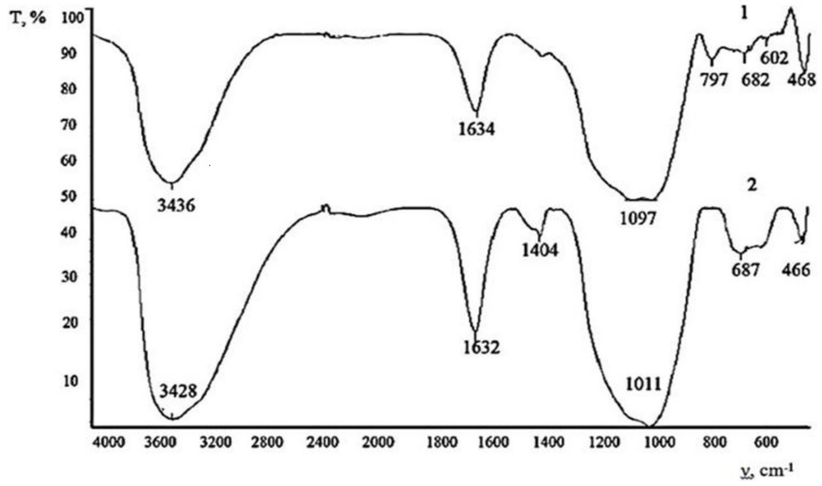

Fig. 2. FTIR spectra of vermiculite (1) and vermiculite-magnetite composite (2).

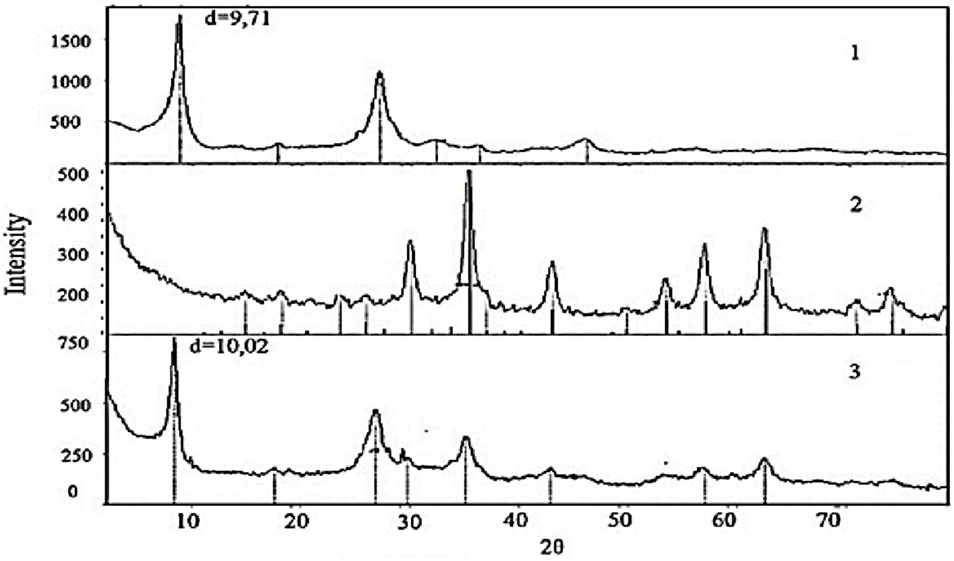

Fig. 3. Diffraction patterns of vermiculite (1), magnetite (2) and vermiculite-magnetite composite (3).

During the synthesis of magnetic composites, changes in the composition and structure of clay also affect the particle size. Studies were conducted to determine the particle sizes of clay and its magnetic composites (Fig. 4). From the curves of the distribution of mineral particles by size, the most probable particle size of magnetite is 195 nm, vermiculite – 345 nm, and magnetite-vermiculite composite – 359 nm. In addition, iron oxide particles precipitate on the outer surfaces of vermiculite. If we assume that each clay particle contains magnetite particles, then we would expect a corresponding change in its size. However, it should be taken into account that the smallest particles of magnetite can be in the interlayer space of clays. Therefore, the increase in particle size upon transition from vermiculite to the composite is insignificant, from 345 to 359 nm. With placing larger particles of magnetite in the interlayer space of clay one would expect destruction of its structure, the process of intercalation of clay could be replaced by its exfoliation.

One of the important characteristics of dispersed particles is their electrokinetic potential. The surface of the particles of the original clay has a ζ-potential equal to -13.2 mV, which is quite expected for clays since their charge is determined by ≡SiO$^-$ groups (Table 2). A gradual increase in the mass fraction of magnetite in the composition of the vermiculite-magnetite composite (VMC 1, VMC 2) leads to a decrease in the negative values of the ζ-potential, and at 45.0% magnetite content (VMC 3) the charge becomes positive, the value of the ζ-potential is equal to +5.7 mV. Note that the value of the ζ-potential of magnetite particles is +19.1 mV. This change in the sign of the vermiculite charge is explained by the neutralization of the negative charge of ≡SiO$^-$ groups by the positive charge of magnetite FeO$^+$ groups. The electrostatic attraction

Table 2. Effect of mass fraction of magnetite on ζ-potential of vermiculite-magnetite composite particles

System	Mass fraction of magnetite, %	ζ-potential, mV
Vermiculite	–	-13.2±0.3
VMC 1	32.0	-6.9±0.3
VMC 2	40.0	-1.5±0.1
VMC 3	45.0	5.7±0.2
Magnetite	–	19.1±01

between these ions determines the stability of the composite. Here, the smallest fraction of magnetite particles can be in the interlayer space of the clay, and larger particles can be attracted to the surface of the clay particles.

Since the prospects for the practical application of the vermiculite-magnetite composite are associated with its use as an adsorbent, the study of its sorption activity was of particular value. To assess the sorption capacity of the obtained magnetic vermiculite composite, the adsorption of methylene blue dye on its surface was studied. The adsorption isotherm of the dye on the composite gives an S-shaped curve (Fig. 5), which is typical for non-porous adsorbents [19]. This may be due to the saturation of the interlayer space with magnetite particles.

Increased adsorption at high dye concentrations shows the occurrence of polymolecular adsorption caused by the formation of several dye layers, the molecules of which are linked to each other because of hydrophobic interactions between their non-polar regions. The attachment of the first layer of dye molecules to the surface of vermiculite and its magnetic composite can be caused by the electrostatic attraction of dye cations to silicate groups of the composite surface. Subsequent layers of dye molecules are then attached to the adsorbed dye molecules because of hydrophobic interactions between the non-polar regions of the dye molecules.

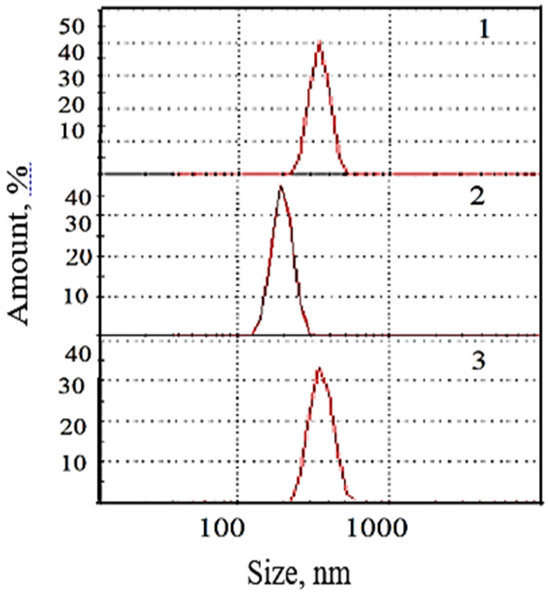

Fig. 4. Particle size distribution curves of vermiculite (1), magnetite (2) and vermiculite-magnetite composite (3).

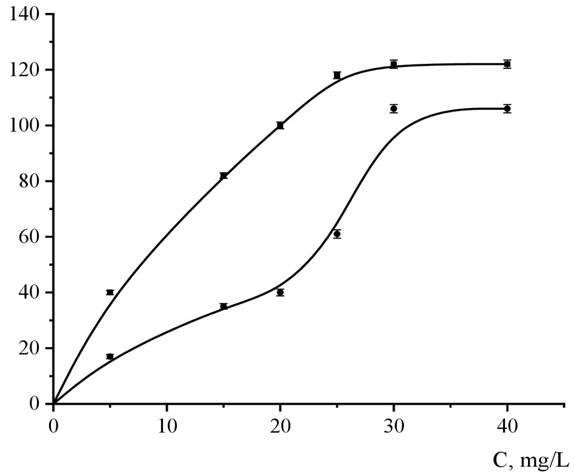

Fig. 5. Adsorption isotherm of methylene blue on the surface of vermiculite (1) and vermiculite-magnetite composite (2). T = 298 K.

The data on the adsorption of methylene blue on the surface of vermiculite were processed within the framework of the Langmuir and Freundlich adsorption models. As seen from Table 3, the values of the maximum adsorption of the dye on the surface of vermiculite and vermiculite-magnetite composite are 142.86 mg/g and 113.64 mg/g, respectively. For comparison, it should be noted that the adsorption values of the medicinal substance kazcaine during the transition from bentonite to its magnetic composite also decrease and amount to 80.65 mg/g and 74.65 mg/g, respectively [15]. According to [20], modification of the bentonite surface with magnetite leads to a decrease in the total pore volume from 0.100 cm^3/g to 0.044 cm^3/g and a decrease in the specific surface area of aluminosilicate from 58.00 to 11.46 m^2/g. Here, a slight decrease in the adsorption capacity of the initial clay because of filling its interlayer space with magnetite is quite expected. According to the data of [18], after intercalation of iron oxide in bentonite, its specific surface area increases. Anyway, a comparison of data on the adsorption of methylene blue on the surface of vermiculite-magnetite with data on the adsorption of this dye on the surface of magnetic composites of other aluminosilicates (Table 4), for example, kaolinite, diatomite, silicate, shows that the adsorption

Table 3. Parameters of methylene blue adsorption in the terms of Langmuir and Freundlich models

Adsorbent	T, K	Langmuir model			Freundlich model		
		K_L, L mg^{-1}	A_{max}, mg g^{-1}	R^2	1/n	K_F, mg g^{-1}	R^2
Vermiculite	298	0.14	142.86	0.92	0.58	16.67	0.96
Vermiculite-magnetite		0.03	113.64	0.90	0.73	5.10	0.96

Table 4. Methylene blue maximal adsorption values of different clay-based composite adsorbents

Adsorbent	A_{max}, mg g^{-1}	pH	T, K	Initial conc. MB, mg L^{-1}	t, min	References
Zeolite-magnetite composite	32.258	9	298	5-40	60	[21]
Kaolinite-magnetite composite	111	11.9	291	150	120	[22]
Diatomite-magnetite composite	101.94	12	303	20-100	120	[23]
Silica/iron oxide-composite	96.5	10	298	80.8-841.6	40	[24]
Activated carbon	80.65	6.8	298	100-350	30	[25]
Vermiculite-magnetite composite	113.64	9.5	298	5-40	120	This study

data are close and have a value of the maximal adsorption 96.5–111.0 mg/g [21–24]. The adsorption of methylene blue on the surface of a traditional adsorbent-activated carbon was 80.65 mg/g [25].

In the Freundlich model, the constant 1/n values for both adsorbents were less than 1.0, indicating a strong affinity between the adsorbate and the adsorbents [26]. The value of 1/n for the adsorption of methylene blue on the surface of the Fe_3O_4-kaolin adsorbent was also lower than 1.0 and equal to 0.934, which was explained by strong interactions between the adsorbate and adsorbent [27]. According to [28], values of 1/n above one suggest cooperative adsorption involving multi-mechanistic adsorption sequences.

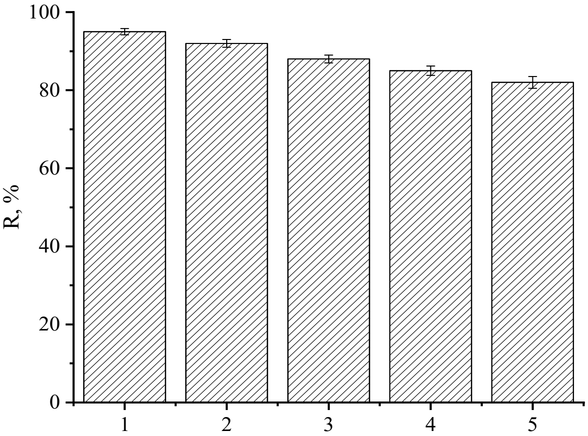

Fig. 6. The reusability of the vermiculite-magnetite composite for methylene blue removing.

An important indicator for evaluating the potential use of the synthesized vermiculite-magnetite composite is its reusability. To test the repeatability of the adsorption/desorption process of methylene blue on the composite particles, the sorbents were washed with a hydrochloric acid solution after each adsorption cycle and then reused for subsequent adsorption. As shown in Fig. 6, even after five cycles, methylene blue removal remained relatively high, decreasing from 95.0% to 82.0%. Therefore, the prepared composite shows stability and reusability as an effective adsorbent for removing methylene blue from water.

Thus, magnetic vermiculite composites were obtained by synthesizing magnetite particles in a vermiculite suspension. The stability of the composite particles is due to the forces of electrostatic attraction between the $\equiv SiO^-$ groups of vermiculite and the FeO^+ groups of magnetite. The adsorption of methylene blue estimated the sorption properties of the composite.

Based on the results of the study of the adsorption properties of the vermiculite-magnetite composite, it can be concluded that it can be used as a sorbent in wastewater treatment from oil, organic pollutants, as well as drug carriers.

4. Conclusion

Based on the results of elemental analysis, SEM, FTIR spectroscopy, X-ray phase analysis, and determination of the ζ potential of particles, the possibility of forming a composite based on vermiculite and magnetite is substantiated. It is shown that with an increase in the mass content of magnetite in the composition of vermiculite, the inversion of the charge sign of vermiculite occurs from -13.2 mV to +5.7 mV due to the neutralization of the negative charge of ≡SiO-FeO$^+$ groups by magnetite groups. The most probable particle size of vermiculite increases from 345 to 359 nm.

Introducing magnetite particles into the interlayer space of vermiculite is justified by the appearance of angle values on its diffractogram 2θ 30.07; 35.50; 43.22; 57.42; 63.90 characteristics of magnetite.

After the synthesis of magnetite, a new absorption band appears on the FTIR spectrum of vermiculite at an oscillation frequency of 1404 cm^{-1}, attributed to the Fe –O bond of magnetite, and the position of peaks at 797 cm^{-1} and 602 cm^{-1}, characteristic of iron compounds, also changes. These results show the introduction of magnetite into the composition of vermiculite, the formation of a vermiculite-magnetite composite.

The adsorption capacity of the synthesized composite was estimated by the adsorption of methylene blue. The adsorption data were processed within the framework of the Langmuir and Freundlich adsorption models. The value of the maximum adsorption of methylene blue on the surface of the composite was 113.64 mg/g, which is quite comparable with the values of the adsorption of dyes on the surface of known adsorbents, such as activated carbon, diatomite, and bentonite. The value of the constant 1/n according to the Freundlich model for the vermiculite-magnetite composite is 0.73, which shows a high affinity of methylene blue to the surface of the composite.

The most valuable for practical use are the results on the effect of the amount of magnetite on the surface charge of the vermiculite-magnetite composite, since by varying the concentration of magnetite in the composite, the surface charge can be adjusted, which makes it possible to get magnetic composites of varying degrees of hydrophilicity. This determines the prospects for the use of magnetic vermiculite composite as adsorbents for wastewater treatment from oils and organic pollutants (dyes, detergents), as well as fertilizers and metal ions.

The results got in this work can be used for the synthesis of new magnetic adsorbents and catalysts based on clays and iron compounds.

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