ANNOTATION
of doctoral dissertation
(PhD)
6D060600 – Chemistry
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Sorption properties of magnetic clays

General characteristics of the work. The thesis is devoted to the production of magnetic composites based on bentonite, flask, vermiculite and the determination of their adsorption capacity. The mechanism of formation of magnetic composites of clay minerals is revealed, the inclusion of magnetite nanoparticles in the structure of aluminosilicates is shown using modern physical and chemical methods.

The obtained magnetic composites are stabilized with polyacrylic acid, and the effect of the polymer on their adsorption capacity is studied. The sorption capacity of the synthesized clay-magnetite composites was estimated by the adsorption of kazkaine, tetracycline, methylene blue, and copper (II) ions. The results of the adsorption were processed in the framework of the Langmuir and Freundlich models, and the adsorption parameters were calculated. The kinetic and thermodynamic parameters of the adsorption process are also determined.

Relevance of the research topic. Currently, methods for producing nanoscale particles make it possible to obtain new materials based on them that have the properties necessary for use in various industries and in medicine. Nanoscale sorbents also include magnetite (Fe_3O_4) nanoparticles, their dispersion and high specific area allow us to consider these substances as effective sorbents. The structure and movement of magnetite nanoparticles can be regulated by an external magnetic field, so the scope of their application is very wide. Magnetic particles can be convenient carriers of medicines, the main advantage of which is the ability to hold and direct the drug to the right place by means of a magnetic field. In this regard, they are of great interest, but for the use of such systems in medicine, a detailed study of their structure and properties is necessary.

Methods for the synthesis of magnetite are simple and accessible, so the number of studies on magnetic sorbents increases every year. But the presence of certain restrictions on the use of individual magnetites in the adsorption of organic and inorganic substances creates difficulties for their use in medicine and production. This leads to the problem of the synthesis of magnetic composites, which can be universal carriers of various substances. Since magnetite has a very high aggregation capacity in the blood circulation in the body, it is important to treat them with clay or polyelectrolytes.

An effective way to solve the problem of obtaining magnetic composite sorbents is to choose inexpensive and natural clay materials that can be used as carriers of magnetite. There are many deposits of clay minerals in Kazakhstan. As carriers of magnetite can be used bentonite clay deposits Tagan in East Kazakhstan region, flask Kunarac deposits in southern Kazakhstan and vermiculite clay

Kulantau field. These silicate minerals have high microporosity, sorption capacities, and ion exchange properties. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and H^{+} cations provide ion-exchange properties, with Na^{+}, K^{+}, and H+cations being particularly active. The main advantage of these systems, which ensure compatibility with the body, is the lyophilicity of the surface. Therefore, the actual problem is to obtain composite sorbents by synthesizing magnetic nanoparticles in the structure of clays in Kazakhstan.

The purpose of this work - preparation of magnetic composites of clay minerals, their stabilization and determination of the adsorption capacity.

To achieve this goal, you must complete the following tasks::

- synthesis of magnetite composites (α-Fe_2O_3, Fe_3O_4) by introducing nanoparticles into the space of bentonite, flask and vermiculite and determining the optimal content of magnetite in clay;
- to determine the mechanism of interaction of magnetite nanoparticles with silicate minerals in clay-magnetite composites;
- characterization of synthesized magnetic composites by chemical composition, phase state, particle size, surface charge, and magnetic properties;
- evaluation of the adsorption capacity of clay-magnetite composites and optimization of the adsorption process.

Object of study: Magnetic composites, obtained on the basis of the magnetite particles, bentonite, flask and vermiculite clay.

Subject of research. Synthesis of new composites based on magnetite, clays and adsorption processes occurring on their surface.

Method of research. X-ray diffraction analysis, X-ray fluorescence analysis, IR-spectroscopy, UV-spectrophotometry, electron microscopy (TEM, SEM), vibration magnetometry, dynamic skeleton scattering (Z-sizer), BET method.

The source base and research materials comprise 176 literature sources on the synthesis and application of magnetite and clay-magnetite composites, as well as on other areas of natural science related to this research work.

Scientific novelty.

- Magnetic nanocomposites have been synthesized in a series of silicate minerals: bentonite, flask, and vermiculite, and the dependence of the magnetite content in them on the Fe fraction in the composition of the initial clays has been established;
- It is shown that the magnetic properties of clay-magnetite nanoparticles are manifested when Fe_3O_4 minerals are saturated: 32 % in BMC and FMC, and 40 % in VMC of magnetite;
- The reduction in the size of bentonite and the growth of flask and vermiculite particles as a result of the formation of the clay-magnetite composite are due to the processes of exchange of Na^{+} and Fe^{3+} ions during the formation of composites, exfoliation of clay minerals and heterocoagulation of small magnetite particles and dispersed clay packages;
- The adsorption of medicinal substances of kazkaine, tetracycline, dye methylene blue and Cu (II) ions on the surface of magnetic composites of bentonite, flask and vermiculite proceeds along the SiO^{-} groups of clay minerals. In addition,

the adsorption of tetracycline is carried out by the mechanism of complexation on Fe^{3+} ions, and the adsorption of methylene blue is due to the formation of H-bonds with silicate groups; magnetite particles give the system magnetic properties;

- It was found that the stabilization of clay-magnetite composites with polyacrylic acid increases their adsorption capacity;

- It is shown that the adsorption processes are endothermic in magnetic composites of bentonite and flask, exothermic in composites of vermiculite, and this difference is justified by the peculiarities of the chemical composition and structure of vermiculite.

Theoretical significance of the work. The results obtained in this work serve as the basis for the synthesis of new composites with the specified properties. The results on the thermodynamic and kinetic parameters of the adsorption processes supplement the data on the adsorption properties of magnetic and clay minerals and their composites, so they can be used as teaching aids.

Scientific and practical significance of the study

The practical significance of the results of the work lies in the synthesis of magnetic clay composites with a high adsorption capacity, and the regulation of their properties. The possibility of practical application is based on the production and characterization of highly effective carriers of medicinal substances with an externally controlled trajectory of movement and sorbents for wastewater treatment from dyes and heavy metal ions. These sorbents can be used in chemical analysis, pharmaceuticals, food processing, and environmental protection. The economic efficiency of the production and application of magnetic clay composites lies in the low cost and availability of raw materials.

Main provisions to be submitted for defense:

- Synthesis of magnetite nanoparticles in the inter-pack space of clays leads to exfoliation of clays;

- In the formation of magnetic composites of bentonite, flask and vermiculite, the electrostatic interactions of $\equiv$SiO-groups of clay minerals and FeO^{+} groups of magnetite play a decisive role;

- The penetration of magnetite nanoparticles into the clay structure is characterized by the appearance of new peaks on their X-ray diffractograms at the values of the angle 2θ 30.09; 35.47; 57.6 and 74.22 ^{o}, in the IR spectra–the absorption band in the region of 1405 cm^{-1}, which characterizes the Fe-O bond, and a decrease in the negativity of the ζ-potential;

- The reason for the special physico-chemical and adsorption properties of the vermiculite-magnetite composites is due to the predominance of the Fe fraction in the composition of this mineral;

- Stabilization of clay-magnetite composites with polyacrylic acid increases their adsorption capacity;

- The release of adsorbed substances from the surface of magnetic clay composites by lowering the pH of the medium allows the reuse of adsorbents that have undergone regeneration.

The main results of the dissertation research are published in 14 scientific papers, including:

- 1 article in the journal with impact factor, included in the Scopus database;

- 4 articles in national publications defined by the Committee for the Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;

- 1 article in the journal registered with the Ministry of information and public development of the Republic of Kazakhstan;

- 8 abstracts of reports at international scientific conferences and symposiums.

Structure and Scope of the dissertation.

The thesis consists of an introduction, 3 chapters, conclusion, list of references and appendices. The total volume of the dissertation is 136 pages. It contains 176 references, 81 figures, and 19 tables.

The relationship of the research topic with the research work plan and various government programs.

The dissertation work was carried out within the framework of the scientific project "Development of technology for obtaining magnetic sorbents based on bentonite clays of Kazakhstan", funded by the Ministry of Education and Science of the Republic of Kazakhstan (2015-2017 y.y., № GR 0115RK00446).

According to the results of the dissertation research, the following conclusions are made:

- Using the Elmore method, magnetite particles were synthesized in the presence of bentonite, flask and vermiculite, and magnetic clay composites were obtained. The inclusion of magnetite particles in the clay structure is justified by the results of TEM on the ability of composites to diffract light. According to the results of X-ray fluorescence analysis, the share of Fe in the composition of the initial clays: bentonite, flask and vermiculite is 18.22 %, 20.53 % and 45.30 %; the share of Si is 51.40 %, 58.48 % and 9.30 %, respectively, and in the magnetic composites of these minerals, the share of Fe increases by 4-2 times, and the share of Si decreases by 5-2 times. The intensity of these changes decreases in the series: bentonite, flask, vermiculite and confirms the formation of composites;

- The IR spectroscopy method shows that the transition from bentonite, flask, and vermiculite minerals to clay-magnetite composites shows the following changes: a peak appears at 1405 cm^{-1}, attributed to the deformation vibrations of the Fe–O bond, which confirms the entry of the FeO group into the clay structure. The displacement and decrease in the intensity of the Si-O–Si bonds characteristic of silicates in the range of 1039-1100 cm^{-1}, Si-O and Al-O bonds at 698 cm^{-1} and 630 cm^{-1} indicate the interaction of silicate ions with magnetite;

- The inclusion of magnetite particles in the structure of bentonite, flask, and vermiculite is proved by the XRD method by the appearance of peaks characteristic of it on the diffractograms of composites. While in clays, the main values of the angle 2θ, characteristic of silicates, are observed at values of 19.8; 26.57 and 35.18 ^{o}, in magnetic composites, new peaks appear at values of the angle 2θ 30.09; 35.47 and 74.22 ^{o}. The decrease in basal reflexes in bentonite and their increase in flask and vermiculite is explained by the exchange of Na^{+} ions in

bentonite for smaller Fe^{3+} ions, as well as the possibility of aggregation in it along with the introduction of magnetite into the interplane space of clays;

- Using the Z-sizer, it was found that the formation of composites neutralizes the negative charge of the clay surface. If, as a result of the interaction of bentonite and flask with iron oxide, the negativity of the values of their electrokinetic potentials decreases, then in the case of vermiculite, the sign of the surface ζ-potential changes from negative to positive. Such changes are caused by the initial chemical composition of the clay: in vermiculite, a high proportion of Fe and, consequently, a low value of the initial ζ-potential, equal to -13.2 mV. The interaction of silicate ions in the composite with FeO^{+} ions increases the ζ-potential to +5.7 mV;

- The method of dynamic light scattering shows that the formation of composites is accompanied by a decrease in the size of bentonite and an increase in the size of flask and vermiculite particles. These changes indicate that the processes of ion exchange, exfoliation of clay minerals, and heterocoagulation of small particles of magnetite and dispersed clay occur during the formation of composites. The increase in the size of the composite particles in the presence of polyacrylic acid by 20-70 nm is due to the fact that a thin polymer layer is formed on their surfaces;

- A study of the magnetic properties of clay-magnetite composites has shown that permanent magnetization exists only in composites saturated with magnetite: in BMC and FMC, the proportion of magnetite is 32 %, and in VMC, the proportion of magnetite is 40 %. When the fraction of Fe_3O_4 decreases, the magnetic properties are observed only in the magnetic field set from the outside;

- The adsorption capacity of magnetic composites was estimated by the adsorption of methylene blue, the medicinal substances of cocaine and tetracycline, and Cu^{2+} ions. The adsorption data were processed using the Langmuir and Freundlich models. Comparison of the composites by A_∞ values showed that the sorption capacity of the bentonite-magnetite composite is significantly higher than that of other composites. It was found that the maximum adsorption is for MK - 129.9 mg / g, for kazkaine - 74.7 mg / g, for tetracycline - 93.5 mg / g and for Cu (II) ions 10.2 mg / g. The difference in the values of A_∞ for Cu (II) ions and organic substances is justified by the fact that H-bonds, hydrophobic interactions, and donor-acceptor bonds participate in the adsorption of drugs and dyes along with electrostatic interactions;

- Thermodynamics and kinetics of adsorption processes on the surface of composites are studied. According to the changes in the Gibbs energy (ΔG), enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption, it is shown that in bentonite and flask this process is endothermic, and in vermiculite - exothermic, and this difference is justified by the chemical composition and features in the structure of clays. Kinetic studies have shown that the process of adsorption on the surface of clay-magnetite composites belongs to the second order, in this process both the amount of the composite and the adsorbate play an important role;

- To regulate the desorption of adsorbed substances from the surface of composites, it is proposed to change the pH of the medium. The release of molecules of adsorbed methylene blue and medicinal substances with a decrease in the pH value is associated with the transition of SiOH groups on the surface of clays to $SiOH_2^+$ under the action of H^+ ions in the medium, i.e., the competition of hydrogen ions with adsorbates. The possibility of repeated application of the reduced composites for the separation of the MB from water is shown.

Assessment of the completeness of the implementation of the set goals.

The set goals and objectives are fully met. Magnetic composites have been synthesized on the basis of bentonite, flask, and vermiculite minerals. The optimal content of magnetite in clay composites was determined, and the composite suspensions were stabilized with polyacrylic acid. The obtained composites were studied by modern physical and chemical methods (electron microscopy - transmission and scanning, X-ray phase analysis, X-ray fluorescence analysis, vibration magnetometry, infrared spectroscopy, dynamic light scattering, BET) and the entry of magnetite into the clay structure was justified. The magnetic properties of clay-magnetite composites are determined. Their adsorption capacity was estimated from methylene blue, the drugs kazkaine and tetracycline, and Cu^{2+} ions, and the adsorption data were processed in the framework of the Langmuir and Freundlich models. The kinetic and thermodynamic parameters of the adsorption process are determined. Degree of implementation.

The possibility of implementation in practice. The results obtained can be used in medicine and pharmaceuticals to create carriers of medicines, the trajectory of which is regulated by a magnetic field from the outside. The use of magnetic composites as adsorbents for the treatment of industrial wastewater from heavy metal ions and other organic and inorganic pollutants is also promising. It is possible to use clay-magnetite composites to collect spilled oil from the surface of reservoirs.

Evaluation of the technical and economic efficiency of the proposed solution in the dissertation work. The possibility of using the obtained results as sorbents of heavy metal ions, oil residues, adsorbents of other organic and inorganic pollutants, as well as carriers of medicinal substances in medicine is justified. The resulting composites will reduce the impact of pollutants on the environment. It is possible to use clay-magnetite composites as water purifiers, to collect oil from the surface of reservoirs. The economic efficiency of their use lies in the low cost and availability of starting materials – iron salts and clays.