ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the speciality «6D074000 – Nanomaterials and nanotechnologies»

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«Development of nanostructured sorbents based on diatomite for water purification»

General characteristics of the work. This dissertation examines the adsorption properties of natural diatomite from the Mugalzhar deposit and the development of nanostructured sorbents based on it for the purification of aqueous solutions from heavy metals and organic dyes.

It has been experimentally established that unmodified diatomite effectively removes Pb^{2+} ions , while the adsorption process is spontaneous and endothermic in nature and is described by a pseudo-second-order kinetic model and Langmuir and Freundlich isotherms.

Natural diatomite has been shown to possess a developed porous structure and high chemical and thermal stability, making it a promising matrix for the creation of functional sorption materials. Modification of diatomite with hydrophilic carbon nanoparticles (2-5 wt%) increases the specific surface area, pore volume, and the number of active sites without disrupting the structure.

It has been established that the adsorption of methylene blue occurs predominantly by the chemisorption mechanism and is described by the Elovich model and the Freundlich isotherm.

Modification of diatomite with iron-containing compounds made it possible to obtain magnetic nanocomposites with a particle size of about 30-38 nm and saturation magnetization of up to 10.9 emu/g, providing fast magnetic separation.

Relevance of the research topic. Water pollution with heavy metals and organic compounds remains a serious environmental problem. The growth of industrial production, the development of mining, metallurgy, and the chemical industry are accompanied by increasing emissions of toxic substances into the environment. Among these, heavy metals, including lead, pose a particular threat, as they are highly stable, toxic, and can accumulate in living organisms. The increasing anthropogenic load on aquatic ecosystems necessitates the search for new water treatment solutions.

In this regard, one of the priority tasks is the development of effective sorption materials that ensure the removal of hazardous pollutants at minimal cost and in compliance with environmental requirements.

The rational use of natural resources adds additional significance to the study. Kazakhstan possesses significant diatomite reserves, which are currently under limited use. However, this material is widely used internationally in filtration and water purification technologies, as well as in the chemical and construction industries. Incorporating such resources into economic circulation not only expands the raw material base but also helps address pressing environmental issues.

Thus, the development of nanostructured sorbents using Kazakh diatomite is a significant scientific and practical challenge. Its relevance stems from the need to produce effective and affordable materials that purify water and reduce environmental risks associated with water pollution.

The aim of the work is to develop nanostructured sorbents based on Mugalzhar diatomite with adsorption properties that ensure effective purification of water from pollutants.

Objectives of the work. To achieve the goal of this dissertation, the following objectives were set:

1. To determine the sorption properties of Mugalzhar diatomite in relation to heavy metal ions, in particular lead ions, based on the analysis of the structural, textural and physicochemical characteristics of the material.
2. To obtain hybrid materials based on diatomite and hydrophilic carbon nanoparticles and to identify the effect of this modification on the properties of the material.
3. To determine the adsorption characteristics of the obtained hybrid materials in relation to cationic organic dyes (adsorption kinetics and isotherms, maximum adsorption capacity).
4. To establish the effect of modification of natural diatomite from the Mugalzhar deposit using iron sulfate and to determine the optimal ratio for obtaining magnetic composite sorbents.

The main provisions submitted for defense:

1. The established dependence of the adsorption capacity of Pb^{2+} (61.5-74.9 mg/g) of natural Mugalzhar diatomite on temperature in the range of 25-45 ºC demonstrates the potential of its use in processes of adsorption removal of lead ions from aqueous solutions .
2. The method of structural activation of natural diatomite using hydrophilic carbon nanoparticles (5 wt.%) with particle sizes of about 15-20 nm provides a targeted change in textural characteristics, an increase in the specific surface area from 38 to 50 m^2/g and the total pore volume to 0.148 cm^3/g while maintaining the integrity of the structure of the mineral matrix.
3. A hybrid sorbent based on diatomite and hydrophilic carbon nanoparticles (5 wt.%) has an adsorption capacity for methylene blue of up to 464.9 mg/g (pure diatomite – 457.2 mg/g) ; the sorbent is stable over a wide pH range of 2–9, which is confirmed by the results of the ζ-potential.
4. A method has been developed for producing a composite magnetic sorbent based on natural diatomite from the Mugalzhar deposit using iron (II) sulfate to form magnetite nanoparticles (Fe_3O_4) with a size of approximately 30-38 nm; the resulting material is characterized by a specific surface area of 55 m^2/g and a magnetization of 10.9 emu/g.

The object of the study is Kazakh diatomite mined in the Mugalzhar district of the Aktobe region, as well as nanocomposites obtained on its basis (magnetic and hybrid nanocomposites).

The subject of the study is the processes of diatomite modification, the formation of nanocomposites based on it and their structural and adsorption properties.

Research methods

To achieve the goal and solve the set tasks, the following research methods were used: thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy, Brunauer-Emmel-Tedder analysis (BET), energy-dispersive X-ray analysis (EDS), Raman spectroscopy (Raman spectroscopy), infrared spectroscopy (IR), X-ray diffraction analysis (XRD), ultraviolet-visible spectroscopy (UV-VIS), atomic absorption spectroscopy (AAS), determination of granulometric composition and particle size (by laser granulometry), measurement of ζ-potential, elemental analysis: (CNH-analysis), SQUID-superconducting quantum interference magnetometry, the method of mechanochemical processing and ultrasonic processing.

Scientific novelty of the work

The following results were obtained for the first time in this work:

1. For the first time, the sorption properties of unmodified diatomite from the Mugalzhar deposit were determined, with the maximum adsorption capacity for Pb^{2+} being 74.9 mg/g, which indicates the high efficiency of the material for purifying aqueous solutions from lead.
2. For the first time, hybrid materials based on diatomite and hydrophilic carbon nanoparticles (5 wt.%) were obtained, and it was established that their modification leads to a synergistic effect: the specific surface area increases by 12 m^2/g and the total pore volume, which indicates the structural activation of the diatomite mineral matrix.
3. The adsorption characteristics of the obtained hybrid materials confirm the chemisorption mechanism of methylene blue adsorption on Kazakh diatomite and its hybrid forms, which corresponds to the Elovich kinetic model ($R^2 = 0.9848$), the proximity of the calculated and experimental values.
4. It has been established that modification of natural diatomite from the Mugalzhar deposit by precipitation followed by thermal decomposition of iron sulfate at an optimal ratio of diatomite to iron of 1:1.7 leads to the formation of magnetite nanoparticles and an increase in the specific surface area by 15 m^2/g.

Theoretical significance.

The results obtained in this study expand our fundamental understanding of the physicochemical mechanisms underlying the modification of natural silica-containing minerals with carbon and magnetic nanoparticles. Relationships have been established between the structural and textural characteristics of diatomite (specific surface area, pore volume, and pore size distribution), surface charge (ζ-potential), and the mechanisms of adsorption interaction with cationic pollutants.

The synergistic effect of structural activation of diatomite with low-concentration carbon nanoparticles is demonstrated, leading to targeted changes in textural parameters without disrupting the mineral matrix. The role of surface charge and the chemical nature of active sites in the formation of the multilayer chemisorption mechanism of methylene blue is demonstrated.

The developed scientific principles contribute to the development of the theory of adsorption processes on hybrid silica-carbon systems and can serve as a basis for the further design of functional sorbents with adjustable properties.

Practical significance.

The practical significance of this work lies in the potential application of the developed nanostructured sorbents based on Kazakh diatomite in water purification technologies for removing pollutants. The results obtained can be used in the development of cost-effective and environmentally friendly water purification systems, as well as in educational programs under program 6D074000 – Nanotechnology and Nanomaterials.

The connection of this work with other research works.

The dissertation was completed within the framework of the grant funding project “Obtaining composite materials based on diatomite” (2025-2027) under the Zhas Galym program, implemented with the support of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan.

Publications.

The main results of the dissertation have been published in 18 printed works, including: 6 articles included in the Scopus database; 1 patent for an invention; 3 articles published in journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Higher Education of the Republic of Kazakhstan; 7 abstracts in proceedings of international and regional scientific and practical conferences; 1 publication in a book.

The doctoral student's personal contribution to the preparation of publications included the analysis of literary data, participation in setting up and conducting experiments, obtaining and processing experimental results, their interpretation, and preparing materials for publication.

The following works have been published on the topic of the dissertation:

1. “The use of diatomite as a catalyst carrier for the synthesis of carbon nanotubes,” – Nanomaterials.
2. “Carbon nanoparticles and diatomaceous earth hybrids: a synergistic approach for methylene blue uptake,” – Environmental science and pollution research.
3. “Efficient Pb(II) adsorption by natural mugaldzhar diatomite: isotherm, kinetic and thermodynamic analysis” – Journal of composites science.
4. “Raman characteristics of multiwall carbon nanotubes on diatomite” – Eurasian Chemico-Technological Journal.
5. "Use of pure diatomite for the sorption of heavy metal ions" – Combustion and Plasma Chemistry.
6. “Acid modification of diatomite-based sorbents” – Eurasian Chemico-Technological Journal.
7. “Tabigi diatomite negizinde sorbender alu” - KazҰTZU Khabarshysy.
8. “Al/diatomite based composite materials” – News of the national academy of sciences of the Republic of Kazakhstan . Series Chemi stry and Technolog y .

9. “Carbon nanotubes synthesized by CCVD method using diatomite and shungite minerals” – Eurasian Chemico-Technological Journal.

10. “Diatomite a naturally occurring bioinspired Nanomaterial with complex shape and its application in synthesis of MWCNTs as a substrate” – White Paper on Nanotechnology.

11. Patent "Method for manufacturing membranes based on natural diatomite" (patent No. 6794 dated December 31, 2021).

12. Proceedings of scientific conferences and symposia.

Volume and structure of the dissertation.

The dissertation is presented on 111 pages of printed text and contains 56 figures and 15 tables. It consists of an introduction, literature review, description of the objects and methods of the study, results and their discussion, conclusion, a list of 152 references, and one Appendix A patent.