ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
on specialty «6D060600 – Chemistry»
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«Sorbents based on aluminosilicate raw materials for heavy metal ions, bisphenol-A and propranolol extraction from aqueous solutions»

General description of the work

This study focuses on developing efficient sorbents derived from aluminosilicate materials, specifically zeolite (Z) and chamotte clay (C), through modification with two surfactant types – anionic sodium laureth sulfate (SLES) and cationic didodecyl dimethyl lammonium bromide (DDAB) – and their application in the extraction of heavy metal ions, bisphenol-A (BPA), and propranolol (PRO) from aqueous solutions. The investigation of the physicochemical and sorption properties of the synthesized sorbents has led to the proposal of a mechanism for their interaction with the chosen contaminants. Optimal conditions are created for the most successful sorbents examined in this study, and the thermodynamic and kinetic characteristics of the adsorption processes are investigated.

The Significance of This Work

Modern water bodies are contaminated with various pollutants, including heavy metals, organic compounds, dyes, petroleum residues, and pharmaceuticals. Sorption remains the most effective method for removing heavy metal ions from wastewater, highlighting the need for affordable, efficient, and eco-friendly sorbents.

Natural aluminosilicates like zeolites and clays exhibit good sorption capacity for metal cations and can be enhanced through chemical modifications such as ion exchange, acid treatment, or altering the Si/Al ratio. However, they are ineffective against negatively charged species like chromates, nitrates, and organic pollutants.

To overcome this, aluminosilicates are modified with cationic surfactants to form surfactant-modified zeolites (SMZs) or clays (SMCs), enabling adsorption of anions and organic pollutants. These multifunctional organo-aluminosilicates serve as amphiphilic adsorbents for removing both inorganic anions and hydrophobic organic compounds from water.

The Purpose of This Work

Obtaining novel efficient adsorbents based on natural aluminosilicate raw materials, in particular zeolite and Chamotte clay, and establishing the physicochemical regularities of heavy metal ions, bisphenol-A, and propranolol adsorption from aqueous solutions.

Key Research Tasks of the Thesis

- To obtain sorbents based on natural zeolite and Chamotte clay modified with an anionic surfactant – SLES or a cationic surfactant – DDAB;
- To evaluate the effect of modification on the physicochemical and sorption characteristics of the original zeolite and Chamotte clay;

- To apply the obtained adsorbents for extraction of heavy metal ions, bisphenol-A and propranolol from aqueous solutions and determine the most effective forms of sorbents for each studied pollutant;

- To analyze the kinetic and thermodynamic characteristics of the adsorption processes, as well as to establish the effect of various external parameters for Chamotte clay-Pb systems;

- To establish the interaction mechanisms of the reagents for Chamotte clay-Pb systems;

- To suggest ways of practical application of the results obtained.

Research methods

The following analysis methods were used in the study: X-ray diffraction, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller (BET) surface area analysis, atomic absorption spectroscopy (AAS), UV-Vis spectroscopy, and pendant drop tensiometry,

Object of the Study

Sorbents based on zeolite and chamotte clay, modified with anionic surfactant – SLES or cationic surfactant – DDAB; aqueous solutions containing ions of various TM, bisphenol-A and propranolol.

Subject of the Study

Physicochemical, structural, textural, sorption characteristics of the obtained sorbents based on zeolite and chamotte clay, as well as kinetic and thermodynamic patterns of the processes of adsorption of heavy metal ions, bisphenol-A and propranolol ions from aqueous solutions.

Main Provisions for the Defense

1. Treatment with Na^+-ions increases the cation exchange capacity (CEC) of zeolite (from 616 to 624 meq/100 g) and chamotte clay (from 234 to 286 meq/100 g), whereas acid treatment decreases their CEC (to 129 and 104 meq/100 g, respectively) but enhances their specific surface area (from 4 to 39 m^2/g for zeolite and from 8 to 15 m^2/g for clay).

2. Modification with the anionic surfactant SLES increases the sorption activity of zeolite and chamotte clay (from 73% to 97% for Cd^{2+} cations and from 50% to 92% for Sr^{2+} cations om zeolite and from 68% to 97% for Cd^{2+} cations and from 41% to 64% for Sr^{2+} cations on chamotte clay) due to surface functionalization; modification with the cationic surfactant DDAB enables effective sorption of inorganic anions such as $Cr_2O_7^{2-}$ (from 5% to 80% on zeolite and from 7% to 82% on clay) and MnO_4^- (from 9% to 75% on zeolite and from 10% to 79% on clay) due to the formation of a positive surface charge.

3. Lead ions sorption on chamotte clay occurs mainly through ion exchange, with some contribution from physical adsorption in pores; for bisphenol-A and propranolol, enhanced adsorption on DDAB-modified zeolite is associated with surface recharging and strengthened hydrophobic interactions, the adsorption mechanism involves chemisorption and electrostatic attraction for both BPA and PRO, as well as physisorption in the case of PRO.

The main results of the study

1. Three series of sorbents based on zeolite and clay were synthesized and modified with surfactants. The first series included the initial sorbents treated with varying concentrations of cationic surfactant (didodecyl dimethyl ammonium bromide, DDAB) or anionic surfactant (sodium laureth sulfate, SLES). The second series comprised sorbents that underwent pre-treatment with 1 M NaCl before surfactant modification, which enhanced their cation exchange capacity (CEC) and improved their ion-exchange properties. The third series was subjected to acid activation using HCl at concentrations of 1, 3, and 6 M, resulting in an increase in the specific surface area of the sorbents but a decrease in their CEC. It was established that high acid concentrations (6 M HCl) led to the degradation of the zeolite framework, whereas clay remained stable under these conditions. The optimal acid concentration for activation was determined to be 3 M HCl, as it provided the best balance between increased surface area and structural integrity.

2. Physicochemical characterization confirmed the effectiveness of surfactant modification, as evidenced by IR and Raman spectroscopy, as well as BET analysis. The surface properties of the sorbents varied depending on the type of pre-treatment: NaCl-treated samples exhibited enhanced ion-exchange interactions, while acid-activated samples demonstrated increased physisorption capacity. Structural alterations induced by salt or acid pre-treatment influenced the interaction of the sorbents with the surfactant modifiers, thereby affecting their adsorption behavior and selectivity toward different pollutants.

3. The adsorption experiments revealed that the initial zeolite and clay materials effectively removed Pb^{2+} ions without requiring pre-treatment, achieving nearly 100% extraction efficiency. Modification with anionic surfactant (SLES) enhanced the adsorption of Cd^{2+} and Sr^{2+} cations, while cationic surfactant (DDAB) significantly improved the removal of $Cr_2O_7^{2-}$ and MnO_4^- anions. The most effective sorbents for Bisphenol-A (BPA) were those pre-treated with 3 M HCl and subsequently modified with 1 mmol/L DDAB. For Propranolol (PRO), the highest adsorption efficiency was observed in sorbents pre-treated with 1 M NaCl and modified with 0.1 mmol/L DDAB, as well as in clay-based sorbents pre-treated with NaCl and modified with 0.5 mmol/L SLES.

4. The adsorption mechanism of heavy metal ions was primarily governed by ion exchange with Na, K, Ca, and Mg cations present in the zeolite channels, as well as by physical adsorption within the internal layers of AlO_6 octahedra, driven by van der Waals interactions. Analysis of IR and Raman spectra confirmed that Pb^{2+} ions interacted with both the surface layers of SiO_4 tetrahedra and the internal structures of AlO_6 octahedra. In the case of organic pollutants, adsorption was predominantly controlled by hydrophobic interactions and electrostatic forces between the BPA/PRO molecules and the surfactant-modified zeolite. The adsorption mechanism of BPA and PRO involved chemisorption, electrostatic attraction, and hydrophobic interactions, and physisorption for PRO.

5. The practical significance of this study lies in the potential for targeted application of the developed sorbents for the removal of specific pollutants. The different modification strategies enable the fine-tuning of sorbent selectivity,

making them suitable for use in complex water purification systems for the simultaneous removal of heavy metals and organic contaminants. Furthermore, the sequential application of the examined sorbents for the remediation of multi-component pollution was identified as a promising approach, necessitating further investigation.

Substantiation of the novelty and importance of the results obtained For the first time, sorbents based on natural zeolite from the Shankanai deposit and chamotte clay were modified with anionic (SLES) and cationic (DDAB) surfactants. The effects of acid and Na^+ pre-treatment on their physicochemical and sorption properties were studied. Optimal conditions for lead ion sorption on chamotte clay were identified, and ion exchange was found to be the dominant mechanism. A new method was developed to evaluate the contributions of physisorption in pores and ion exchange to the overall sorption mechanism, and was applied to the zeolite–DDAB–BPA and zeolite–DDAB–PRO systems. Additionally, for the first time, interaction mechanisms between surfactants, aluminosilicates, and pollutants were described. Models of electrostatic, hydrophobic, and donor–acceptor interactions were proposed, which are relevant to pollutant removal processes.

Theoretical significance. The theoretical significance of the results presented in the dissertation consists in establishing and analyzing the kinetic and thermodynamic parameters of the processes of adsorption of HM, BPA and PRO ions by sorbents based on Z and C modified by surfactants; describing the chemistry of aluminosilicate-surfactant interactions, as well as sorbent-sorptive; developing a new method for assessing the contribution of physical adsorption in pores and ion exchange to the mechanism of sorption of TM ions, as well as organic pollutants from aqueous solutions on aluminosilicate sorbents.

The practical significance of the study lies in the development of highly efficient surfactant-modified zeolite and clay sorbents capable of removing up to 99% of heavy metal cations and significantly enhancing the extraction of anionic pollutants, making them promising for water purification applications.

Relation of the thesis with research and government programs

The dissertation was carried out within the framework of program-targeted funding of the Ministry of Education and Science of the Republic of Kazakhstan (BR05236420) and scientific projects of the Ministry of Education and Science of the Republic of Kazakhstan (AP08957166 and AP09260116). Also, certain research results were obtained thanks to the Lulea University of Technology (Lulea, Sweden), Babes-Bolyai University (Cluj-Napoca, Romania) and Bar-Ilan University (Ramat-Gan, Israel).

The personal contribution of the author consists of the analysis of literature on the research topic, design and performance of the experiments on the synthesis of the surfactant modified aluminosilicate adsorbents, and adsorption of HM ions, BPA and PRO onto the obtained adsorbents, and processing of the obtained results.

Contribution to scientific publications writing:

1. G. Seilkhanova, A. Rakhym, A. Csavdari Preliminary assessment of modified Kazakh natural zeolites as possible sorbents for MnO_4^- removal from

aqueous solutions // Studia UBB Chemia, LXIII, 4, 2018, pp. 181-192 https://doi.org/10.24193/subbchem.2018.4.15 (Conceptualization, Investigation, Writing - original draft)

2. A.B. Rakhym, G.A. Seilkhanova, A. Csavdari Adsorption of dichromate and permanganate anions by organo-zeolite from the Shankanai deposit // Eurasian Journal of Ecology. №4 (57). 2018. – p. 58-68. (Conceptualization, Investigation, Writing - original draft)

3. M.S. Telkhozhayeva, G.A. Seilkhanova, A.B. Rakhym, A.N. Imangaliyeva, D.N. Akbayeva Sorption of lead and cadmium ions from aqueous solutions by modified zeolite // Chemical Bulletin of KazNU. №4 (91). 2018. – c. 16-22. https://doi.org/10.15328/cb980 (Formal analysis, Writing -Editing)

4. A.B. Rakhym, U.Zh. Bekturganova, G.A. Seilkhanova, A. Csavdari Chamotte clay sorbent for the extraction of lead and cadmium ions from aqueous solutions // International Journal of Biology and Chemistry. №2 (12). 2019. pp. 129-134. https://doi.org/10.26577/ijbch-2019-i2-17 (Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft)

5. G. E. Mendigaliyeva, A. B. Rakhym, G.A. Seilkhanova Composite material based on zeolite modified with polyethylene glycol for purification of aqueous solutions from Pb^{2+} and Cd^{2+} ions // Herald of Kazakh-British technical university– №4(16). 2019. – c. 63-71. (Methodology, Investigation, Formal analysis, Writing - Editing)

6. A.B. Rakhym, G.A. Seilkhanova, T.S. Kurmanbayeva_Adsorption of lead (II) ions from water solutions with natural zeolite and chamotte clay // Materials Today: Proceedings. – 2020. https://doi.org/10.1016/j.matpr.2020.05.672 (Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft)

7. Rakhym A.B., Seilkhanova G.A., Mastai Y. Physicochemical evaluation of the effect of natural zeolite modification with didodecyldimethylammonium bromide on the adsorption of Bisphenol-A and Propranolol Hydrochloride // Microporous and Mesoporous Materials. - 2021. - Vol. 318. - P. 111020 https://doi.org/10.1016/j.micromeso.2021.111020 (Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization.)

8. Abstracts at international conferences - investigation, validation, data curation, methodology, writing – original draft.

Volume and the structure of the thesis

The thesis consists of an introduction, three sections, conclusions, and a list of references, and two appendices. The work is presented on 170 pages, and contains 52 figures, 30 tables, and 289 bibliographical references.