ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program «8D07113 – Nanomaterials and nanotechnology in chemistry»

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Development of a Method for Obtaining Synthetic Zeolites and Nanocomposites from Industrial Waste for Water Purification from Pollutants

The relevance of the topic. At present, pollution of water resources is one of the most acute environmental problems. Particularly hazardous are toxic and persistent pollutants (heavy metal ions, dyes, phenols, naphthalenes, etc.) contained in solid and liquid industrial wastes, which negatively affect aquatic ecosystems and human health. In this context, the development of effective and environmentally safe water purification technologies is of high scientific and practical importance.

Synthetic zeolites and nanocomposites exhibit high adsorption capacity toward organic and inorganic pollutants, which determines their widespread use in modern water treatment technologies. However, conventional methods for producing adsorbents are characterized by high energy and material consumption, increasing their cost. Therefore, the use of industrial and agro-industrial wastes as raw materials for the synthesis of zeolites and nanocomposites represents an environmentally and economically promising approach.

Given the increasing volumes of waste in industrial regions of Kazakhstan and the limited availability of water resources, this research is particularly relevant for the development of environmentally safe water treatment technologies.

The aim of the work is to develop a method for obtaining porous nanocomposites from agricultural waste and thermal power plant waste via hydrothermal synthesis and to apply them for the removal of mercury ions from water.

Research objectives. To achieve this goal, the following tasks were solved:

– production of silicon dioxide from at least two types of local agro-industrial waste and characterization of its properties (microstructure, morphology, elemental composition, thermal behavior);

– optimization of hydrothermal reaction conditions for converting agricultural waste and thermal power plant waste into nanoporous zeolites (reagent ratio, crystallization and aging time, calcination temperature, and other parameters);

– preparation of nanocomposites by introducing metal nanoparticles or metal impregnation, functionalization of zeolites, and surface modification of zeolites derived from agricultural and thermal power plant wastes for pollutant removal (using silver nitrate, sodium dodecyl sulfate (SDS), or alkylsulfonic acids);

– experimental investigation of adsorption kinetics and equilibrium adsorption of the synthesized zeolites and nanocomposites for mercury ion removal.

Research methods. Devices of modern methods of analysis were used to conduct research on the topic of the dissertation: infrared spectroscopy using a

Nicolet 6700 instrument (Thermo Scientific, USA); X-ray diffraction analysis using a SmartLab diffractometer (Rigaku Corporation, USA); scanning electron microscopy using a Quanta 3D 200i Dualsystem FEI (USA); Brunauer–Emmett–Teller (BET) method using an Autosorb-1 instrument (Quantachrome Instruments, UK); as well as statistical methods for processing experimental data.

The objects of the research are rice husk, silicon dioxide, synthetic zeolites, as well as their experimental nanocomposite samples modified with silver nanoparticles and sodium dodecyl sulfate for pollutant removal.

The subject of the research is the synthesis of modified nanocomposites.

The main provisions submitted for defense:

Chemical treatment of rice husk resulted in the formation of SiO_2 particles with sizes of 50–100 nm. The pore volume of the obtained nanostructured SiO_2 samples increased to 0.8 cm^3/g, while the average pore diameter reached 18.4 nm. The increase in pore volume and changes in pore size are explained by the formation of nanostructures.

The specific surface area of zeolites synthesized from rice husk ash and coal fly ash was 62.5 m^2/g and 112 m^2/g, respectively, with average pore diameters of 0.95 nm and 17 nm. The narrowing or widening of pore parameters is attributed to the chemical composition of the raw materials, the Si/Al ratio, and the influence of mineral impurities present in fly ash, as confirmed by analytical results.

Silver nanoparticles (AgNPs) with a mass fraction of 2% and particle sizes of 20–25 nm were deposited onto synthetic zeolites derived from rice husk and coal fly ash using ion-exchange and reduction methods. The formation of AgNPs is explained by their incorporation into the microstructure of porous zeolites.

The adsorption efficiency of synthetic zeolites and nanocomposites derived from industrial waste for mercury removal was investigated. The pristine zeolite removed 27.3% of mercury within 24 hours, whereas the nanocomposite demonstrated 76.8% removal efficiency, confirming its superior adsorption performance.

The main results of the work:

1. Amorphous silicon dioxide obtained from rice husk is a nanomaterial with particle sizes of approximately 50–100 nm. It was found that its pore volume increased to 0.5–0.8 cm^3/g, while the average pore diameter decreased from 26.4 to 18.4 nm, indicating the formation of a more developed porous structure and a significant enhancement of adsorption capacity.

2. During the transformation of SiO_2-based material into zeolite, the structure changes from an amorphous mesoporous state to a crystalline microporous form, resulting in a decrease in specific surface area from 150 to 62.5 m^2/g and a reduction in pore diameter from 18.4 to 0.95 nm. These changes confirm zeolite formation and restructuring of the pore system. In contrast, zeolites synthesized from coal fly ash exhibit an increase in specific surface area from 20 to 112 m^2/g and an increase in average pore diameter from 15 to 17 nm, explained by the formation of an ordered porous zeolite structure and new pore channels during hydrothermal synthesis.

3. Silver nanoparticles (AgNPs) with a mass fraction of 2% and particle size of 20–25 nm was successfully deposited onto synthetic zeolites obtained from rice husk

and coal fly ash. The formation and stable fixation of AgNPs within the porous microstructure confirm effective modification of the materials. Preservation of the original zeolite structure after modification was confirmed by SEM, TEM, and XRD analyses.

4. Adsorption experiments demonstrated that unmodified zeolite derived from rice husk removed 27.3% of Hg^{2+} ions, while zeolite derived from coal fly ash removed 43.8%. In contrast, the corresponding nanocomposites exhibited significantly higher efficiencies: 76.8% and 90.1%, respectively. According to the Langmuir model, adsorption capacities were 136.98 mg/g (rice husk zeolite) and 7.65 mg/g (coal fly ash zeolite), increasing to 285.71 mg/g and 21.94 mg/g for the respective nanocomposites. These results confirm that the introduction of AgNPs enhances adsorption capacity by up to twofold.

Scientific novelty of the obtained results.

For the first time, a scientifically grounded method has been developed for synthesizing synthetic zeolites and nanocomposites using industrial and agricultural wastes rich in silica and aluminosilicates as raw materials.

For the first time, it was experimentally demonstrated that the adsorption properties of zeolites derived from rice husk ash and coal fly ash can be purposefully controlled by modifying pore structure, surface area, and functional centers, thereby enabling control of material properties through the choice of raw materials and synthesis conditions.

For the first time, silver nanoparticles were introduced into zeolites obtained from technogenic waste via ion-exchange and reduction methods, resulting in stable AgNP–zeolite nanocomposites with preserved structure.

For the first time, the adsorption performance of the obtained nanocomposites toward Hg^{2+} ions was comprehensively investigated and shown to be significantly higher than that of pristine zeolites, supporting their potential as highly efficient universal adsorbents for heavy metal removal.

The theoretical significance of the work lies in the development of scientific foundations for the application of nanocomposites to improve the functional properties of synthetic zeolites and to design new adsorption materials. The results deepen the understanding of nanocomposite–pollutant interaction mechanisms in aqueous environments, provide a scientific basis for enhancing adsorption efficiency, and expand the possibilities of utilizing natural and technogenic raw materials in environmentally safe and innovative technologies.

The practical significance of the work. From a practical point of view, the significance of the work lies in the development of an effective method for water purification through the creation of modified nanocomposites. The results can be used in lectures and practical classes within the educational programs “Ecology and Environmental Protection” and “8D074000 – Nanotechnology and Nanomaterials”.

Compliance with scientific development directions or government programs. The dissertation work was carried out within the framework of the grant project: AP14869646 “Development of a Method for Obtaining Synthetic Zeolites and Nanocomposites for Water Purification from Mercury and Cationic Dyes” (2022–2024).

Publications. As a result of the research conducted on the dissertation topic, 7 scientific papers were published, including: 2 articles in journals indexed in the Web of Science database, 1 article in journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Republic of Kazakhstan, 4 publications in the proceedings of international symposia and national conferences.

Publications in Journals Indexed in Scopus and Web of Science

1. Suleimenova M., Zharylkan S., Mekenova M., Mutushev A., Azat S., Tolepova A., Baimenov A., Satayeva A., Tauanov Z. Fusion-assisted Hydrothermal Synthesis of Technogenic Waste Derived Zeolites and Nanocomposites: Synthesis, Characterization, and Mercury (II) Adsorption. *International Journal of Molecular Sciences*, 24(14), 11317. https://doi.org/10.3390/ijms241411317
2. Zharylkan S., Sultakhan S., Suleimenova M., Azat S., Sailaukhanuly Y., Tulepov M., Tauanov Z. Enhanced Adsorption of Mercury and Methylene Blue Using Silver and Surface Modified Zeolite-NaX Derived from Rice Husk. *Engineered Science*, 2024, 31, 1241. https://doi.org/10.30919/es1241

Publication in a Journal Recommended by the Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan

Suleimenova M., Zharylkan S., Mekenova M., Tolepova A., Mutushev A., Azat S., Tauanov Z. Synthesis of synthetic zeolite and nanocomposite from rice husk for the removal of mercury ions from water. *Chemical Bulletin. Bulletin of KazNU*, recommended by the Committee for Quality Assurance in Science and Higher Education, 2023, No. 2–3, Vol. 109. https://doi.org/10.15328/cb1323

The main results of the dissertation were presented and discussed at international and national conferences:

1. Suleimenova M., Tauanov Z. Development of a method for obtaining synthetic zeolites and nanocomposites from industrial waste to purify water from pollutants. INTERNATIONAL WINTER SCHOOL – 2023, "Kazakh-Chinese round table 'Energy intensive systems – prospects for cooperation'", December 26, 2023, Almaty, Kazakhstan.
2. Suleimenova M., Tauanov Z. Synthesis of synthetic zeolite and nanocomposite from rice husk for the removal of mercury ions from wastewater. VIII Kazakhstan Student Scientific and Practical Conference "Chemical Physics and Nanomaterials", March 15, 2024, Almaty, Kazakhstan.
3. Suleimenova M., Tauanov Z. Synthetic zeolites and nanocomposites for removal of mercury and methylene blue. "Sustainable Future 2024: Biotech, Ecology, Energy", November 20–21, 2024, Almaty, Kazakhstan.
4. Suleimenova M., Tauanov Z. Synthetic zeolites and nanocomposites for removal of mercury and methylene blue. XVI International Symposium on "Combustion and Plasma Chemistry. Physics and Chemistry of Carbon and Nanoenergetic Materials", October 1–3, 2025, Almaty, Kazakhstan.

The structure and scope of the dissertation. The dissertation consists of an introduction, three chapters, and a conclusion. The work is presented on 105 pages and contains 17 tables and 19 figures. The list of references includes 200 sources.