

REVIEW
of the dissertation
by Yu Junjie
on the topic "Materials based on silica and aluminosilicates for environmental
protection"
submitted for the degree of Doctor of Philosophy
in the field of knowledge 16 Chemical and Bioengineering
specialty 161 Chemical Technologies and Engineering

Relevance of the Dissertation Topic.

The dissertation is devoted to the development of materials based on natural and synthetic raw materials for the protection of water from contamination by various toxicants. It is expedient to design technologies utilizing adsorbents derived from affordable and inexpensive raw materials. Natural, synthetic, and technogenic silicates are considered promising candidates. By applying different methods of surface modification, sorbents with improved characteristics can be obtained. The production of so-called "low-cost" materials based on aluminosilicates in granulated form will enable rapid phase separation. An important task is to investigate the features of obtaining such materials and to study the regularities of removing heavy metals and dyes from water.

Assessment of the Validity, Reliability, and Novelty of the Dissertation's Scientific Results.

The scientific statements and conclusions formulated in the dissertation are theoretically substantiated, and the reliability of the scientific results is confirmed by the use of modern instrumental research methods. The morphology of the adsorbents was studied using electron microscopy methods. The phase composition and surface chemistry of the obtained materials were determined by X-ray diffraction analysis, X-ray photoelectron spectroscopy, and infrared spectroscopy. The specific surface area and parameters of the porous structure of the sorbents were investigated by the low-temperature nitrogen adsorption-desorption method. The thermal stability of the materials was evaluated using differential thermal analysis and thermogravimetric analysis. The initial and equilibrium concentrations of copper ions and the organic dye in solutions were determined by inductively coupled plasma atomic emission spectrometry and spectrophotometric methods, respectively.

The scientific novelty of the dissertation research lies in the following:

- For the first time, the features of obtaining adsorption materials based on dendritic silica and commercial silica gel modified with zero-valent iron particles, 3-aminopropyltriethoxysilane, and nickel oxide were established, ensuring the formation of improved structural and sorption characteristics.

- The approach to the granulation (or modification) of natural and modified saponite in the presence of sodium alginate was improved through the study of the rheological behavior of clay suspensions, which made it possible to obtain stable in aqueous media and economically affordable (“low-cost”) granulated adsorbents.

- For the first time, a mesoporous adsorption material with a deposited zeolitic layer was obtained on the basis of technogenic aluminosilicate waste (fly ash) under relatively simple synthesis conditions and with the use of readily available equipment.

- The understanding of the physicochemical features of the removal processes of copper (II) ions and methylene blue by novel adsorbents was further developed, which made it possible to substantiate the prospects of their application for the efficient purification of aquatic media from heavy metals and organic dyes.

The research was carried out by the applicant at the Department of Chemical Technology of Ceramics and Glass of National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” within the framework of the initiative project “Functional silicate materials with modified surfaces” (0124U001967, 2024–2026), under the supervision of the Head of the Department of Chemical Technology of Ceramics and Glass, PhD in Technical Sciences, Associate Professor Viktoriia Tobilko.

Thus, in the dissertation, the scientific task of obtaining adsorbents based on silicas as well as natural and synthetic aluminosilicates for the protection of aquatic environments from contamination by heavy metal ions and organic dyes has been fully accomplished, and the applicant has demonstrated complete mastery of the methodology of scientific research.

Assessment of the Dissertation’s Content, Its Completeness, and Adherence to the Principles of Academic Integrity.

In terms of its content, the dissertation of the applicant Yu Junjie fully complies with the Higher Education Standard for specialty 161 Chemical Technologies and Engineering and aligns with the research directions of the educational program Chemical Technologies and Engineering.

The dissertation is a completed scientific work and demonstrates the applicant’s personal contribution to the scientific field of obtaining new substances and materials.

Based on the similarity report obtained from the plagiarism check of the dissertation, it can be concluded that the dissertation by Yu Junjie is the result of the applicant’s independent research and does not contain elements of falsification, compilation, fabrication, plagiarism, or misappropriation. The ideas, results, and texts of other authors used in the work are properly referenced to their respective sources.

Language and Style of Presentation of the Results.

The dissertation is written in English using generally accepted terminology. The results of the scientific research are presented concisely, accurately, and convincingly, which ensures their clear perception.

The dissertation consists of an introduction, five chapters, conclusions, and a list of references. The total volume of the dissertation is 194 pages.

The introduction provides the rationale for the relevance of the research, the connection of the work with scientific themes, programs, and plans, the aim and objectives of the study, the applied research methods, the scientific novelty and practical significance of the obtained results, the applicant's personal contribution, the approbation of the dissertation results, and its structure.

The first chapter of the dissertation presents a literature review concerning adsorbents used for water protection. Methods for obtaining sorbents based on synthetic silicates as well as natural and artificial aluminosilicate raw materials are analyzed.

The second chapter contains a description of the methodologies for obtaining adsorbents and the applied research methods, including scanning and transmission electron microscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, infrared spectroscopy, low-temperature nitrogen adsorption–desorption, differential thermal analysis and thermogravimetric analysis, the method for determining the rheological characteristics of clay suspensions, inductively coupled plasma atomic emission spectrometry, and spectrophotometry.

The third chapter is devoted to the synthesis of dendritic mesoporous silica nanoparticles (DMSN), modified with zero-valent iron (Fe^0) and 3-aminopropyltriethoxysilane, and to the investigation of their efficiency in removing Cu(II) from aqueous solutions. The effect of synthesis time on the formation of monodisperse microspheres was established. It was shown that the samples obtained after different mixing durations (1.5 h – DMSN-1.5; 3 h – DMSN-3; 5 h – DMSN-5) are monodisperse spheres with an average diameter of 200 nm. All microspheres exhibited type IV isotherms with H3 hysteresis loops. The pore size of the microspheres ranged from 5 to 50 nm, and the specific surface areas were 504, 452, and 308 m^2/g for DMSN-1.5, DMSN-3, and DMSN-5, respectively. A synthesis time of 1.5 h was determined to be optimal for achieving favorable morphology without significant pore coalescence or edge thickening.

An adsorbent ($\text{Fe}^0\text{@DMSN}$) was obtained by depositing Fe^0 nanoparticles onto the surface of DMSN-1.5. The nitrogen adsorption–desorption isotherms of the modified samples were of type IV with H3 hysteresis loops. The specific surface area of the modified sample was almost twice as low as that of the pristine DMSN. The pore size distribution showed a wide range (3–50 nm). At $\text{pH} = 5.7$, the maximum

adsorption capacity of Fe⁰@DMSN toward Cu(II) ions reached 39.8 mg·g⁻¹, which is 57 times higher than that of the unmodified DMSN-1.5 (0.7 mg·g⁻¹).

An amino-functionalized adsorbent was obtained by modifying dendritic mesoporous silica nanoparticles with 3-aminopropyltriethoxysilane (DMSN-NH₂). The nitrogen adsorption–desorption isotherms of the modified samples corresponded to type IV with H3 hysteresis loops, typical of mesoporous structures. It was found that pristine DMSN exhibited almost no adsorption capacity toward Cu(II) ions at pH 6, while DMSN-NH₂ demonstrated efficient Cu(II) removal across the entire investigated pH range.

The fourth chapter presents the results of Cu²⁺ and methylene blue removal using materials based on silica gel and nickel oxide with different mass ratios of the components (SiO₂@0.5NiO and SiO₂@NiO). The obtained nitrogen adsorption–desorption isotherms correspond to type IV. These materials exhibit a narrow mesopore range (2.5–3 nm). It was shown that in the series SiO₂ > SiO₂@0.5NiO > SiO₂@NiO, the specific surface area decreased from 411 m²/g to 186 m²/g. It was established that SiO₂ practically does not adsorb Cu²⁺ ions at pH 5.5. The maximum adsorption capacities were 0.9 mg/g and 1.7 mg/g for the SiO₂@0.5NiO and SiO₂@NiO samples, respectively. It was also demonstrated that methylene blue removal from solution by the synthesized materials occurs rather rapidly, with the maximum adsorption capacity (19.3 mg/g) observed for the sample with a SiO₂ to NiO mass ratio of 1:0.5.

The fifth chapter presents data on the removal of copper ions using materials based on natural and technogenic silicates. Granules were obtained from modified saponite and sodium alginate, as well as an adsorbent derived from fly ash. To obtain water-stable granules, the rheological behavior of clay suspensions was investigated, and the necessary conditions for granulation were identified. The properties and thermal characteristics of the obtained adsorbents were examined. The morphology, phase, and chemical composition of sorbents based on fly ash with a deposited zeolitic layer were studied. It was established that the deposition of the zeolitic phase onto the surface of fly ash increased the copper adsorption capacity from 4.94 mg/g to 6.53 mg/g.

The dissertation is formatted in accordance with the requirements of the Order of the Ministry of Education and Science of Ukraine No. 40 dated January 12, 2017, “On the Approval of Requirements for Dissertation Formatting.”

Dissemination of the Dissertation Research Results.

The scientific results of the dissertation are presented in nine scientific publications authored by the applicant, including: four articles in scientific journals included, at the time of publication, in the list of specialized scientific journals of Ukraine; and two articles in peer-reviewed scientific journals indexed in the Web of

Science Core Collection and/or Scopus databases, of which one article was published in a journal ranked in the first to third quartiles (Q1–Q3) according to the SCImago Journal and Country Rank or Journal Citation Reports classification.

In addition, the results of the dissertation were presented at three scientific conferences.

The applicant's publications are written at a high scientific level in full compliance with the principles of academic integrity. The results presented in the published articles and conference abstracts fully reflect the content of the dissertation, correspond to its objectives and research tasks, and confirm the applicant's personal contribution to obtaining new scientific and practically significant results.

The scientific results described in the dissertation are fully reflected in the scientific publications, with strict adherence to the principles of academic integrity.

Shortcomings and Comments on the Dissertation.

In the first point of scientific novelty, the author experimentally investigates, rather than “for the first time establishes,” the features of obtaining adsorption materials based on dendritic silica and commercial silica gel modified with zero-valent iron particles, 3-aminopropyltriethoxysilane, and nickel oxide, which ensured the formation of improved structural and sorption characteristics. I believe this point of scientific novelty should be revised.

The conclusions include a recommendation regarding longer synthesis at higher temperatures, but no evidence is provided that such conditions would indeed significantly improve the material's characteristics, as the increase in sorption capacity from 4.94 mg/g to 6.53 mg/g is relatively small and requires a more detailed analysis of potential energy and economic costs.

The dissertation does not provide data on the ecological or economic efficiency of the proposed technology for wastewater treatment from copper ions and methylene blue, nor does it contain a comparative table of efficiency in relation to other sorbents.

The presented experimental data were obtained only on model solutions of Cu^{2+} ions and methylene blue. However, the dissertation lacks results of testing on real industrial wastewater, which contains a multicomponent composition of pollutants. This is essential for protecting aquatic environments from various toxicants in enterprises of the chemical, food, and mining industries.

The dissertation should have included results of multiple reuse cycles of the sorbents to assess their durability and service life, as well as developed recommendations for the disposal or reuse of spent materials.

These comments are not considered critical and do not diminish the overall scientific novelty or the practical significance of the results, nor do they affect the positive evaluation of the dissertation.

Conclusion on the Dissertation.

I consider that the dissertation submitted by the applicant for the degree of Doctor of Philosophy, Yu Junjie, entitled “Materials based on silica and aluminosilicates for environmental protection” has been carried out at a high scientific level, does not violate the principles of academic integrity, and represents a completed scientific study. The set of theoretical and practical results obtained in the dissertation solves a scientific problem of significant importance in the field of knowledge 16 Chemical and Bioengineering. By its relevance, practical value, and scientific novelty, the dissertation fully meets the requirements of the current legislation of Ukraine, as stipulated in paragraphs 6–9 of the “Procedure for Awarding the Degree of Doctor of Philosophy and Revoking the Decision of a One-Time Specialized Academic Council of a Higher Education Institution or Research Institution on Awarding the Degree of Doctor of Philosophy,” approved by the Resolution of the Cabinet of Ministers of Ukraine No. 44 dated January 12, 2022.

The applicant Yu Junjie fully deserves to be awarded the degree of Doctor of Philosophy in the field of knowledge 16 Chemical and Bioengineering, specialty 161 Chemical Technologies and Engineering.

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