

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 development of effective and economically feasible technologies for the purification of water from heavy metal ions and dyes is one of the most important issues in environmental protection. Among the existing methods for removing inorganic and organic toxicants from water, adsorption methods occupy a special place, as they allow pollutants to be eliminated to levels below the maximum permissible concentrations (MPC). To date, a wide variety of adsorptive materials have been developed, both from natural and synthetic raw materials. The advantages of synthetic sorbents, such as mesoporous silicas, include their high sorption capacity and selectivity, which can be achieved by chemically modifying their surface. This makes it possible to obtain materials with a stable composition and predetermined properties. On the other hand, when selecting materials for the treatment of large volumes of water from metal cations and dyes, sorbents based on inexpensive natural raw materials (such as clay minerals) or technogenic silicates (such as fly ash) are promising. The advantages of layered silicates include their mechanical strength, thermal and chemical stability, high dispersity, ion-exchange capacity, availability, and low cost. The synthesis of mesoporous materials based on synthetic and natural silicates — in particular, silica, saponite, and fly ash — through surface modification with zero-valent iron particles, metal oxides and oxyhydroxides, or organosilicon compounds leads to sorbents with sufficiently high structural-sorption characteristics and enhanced adsorption capacity toward pollutants of various natures. An important aspect is the study of the regularities of obtaining mesoporous materials both in powder and granular forms, as well as the investigation of the physicochemical features of removing heavy metals and cationic dyes using these sorbents. Thus, the relevance of the dissertation is determined by the necessity to develop efficient adsorbents for the purification of water from metal ions and synthetic organic dyes.

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 sorption

materials was examined using electron microscopy methods. The phase composition and surface chemistry of the samples were determined by means of X-ray diffraction analysis, X-ray photoelectron spectroscopy, and infrared spectroscopy. The specific surface area and pore structure parameters of the sorbents were studied using low-temperature nitrogen adsorption–desorption. The thermal stability of the materials was assessed through 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 the spectrophotometric method, respectively.

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

- the features of obtaining adsorption materials based on dendritic silica and commercial silica gel with improved structural and sorption characteristics have been studied by modifying their surfaces with zero-valent iron particles, 3-aminopropyltriethoxysilane, and nickel oxide;
- based on the study of the rheological behavior of suspensions of natural and modified saponite with sodium alginate, the necessary conditions were identified for producing low-cost granulated adsorbents that are stable in aqueous media;
- a mesoporous material with a deposited zeolitic layer was obtained from technogenic aluminosilicate waste (fly ash) under relatively simple synthesis conditions and using readily available equipment;
- the physicochemical features of the removal of copper compounds and methylene blue by the obtained adsorbents were studied, and the potential of their application for efficient water purification from such pollutants was demonstrated.

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, the scientific task of obtaining sorption materials based on modified silicas and aluminosilicates for the protection of the aquatic environment from pollution by heavy metals and organic dyes has been fully accomplished in the dissertation, and the applicant has completely mastered 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 a justification of the relevance of the research, the connection of the work with scientific topics, programs, and plans, the aim and objectives of the research, the methods applied, the scientific novelty and practical significance of the obtained results, the personal contribution of the applicant, the approbation of the dissertation results, and its structure.

The first chapter of the dissertation presents an analytical review of the literature, including a critical analysis, systematization, and evaluation of scientific studies on modern adsorptive materials developed for the purification of water from heavy metal ions and organic dyes. Particular attention is paid to the methods of obtaining mesoporous adsorbents based on silicas and aluminosilicate raw materials. A deep understanding of the research topic is demonstrated, and its relevance is assessed.

The second chapter contains a description of the methods for obtaining adsorption materials and the research methods applied in this dissertation.

The third chapter is devoted to the synthesis of dendritic mesoporous silica nanoparticles (DMSN), modified with zero-valent iron and 3-aminopropyltriethoxysilane, and to the study of their efficiency in removing copper ions from aqueous solutions. It has been established that the synthesis time (1.5, 3, and 5 hours) affects the morphology of the obtained silica microspheres (DMSN-1.5, DMSN-3, DMSN-5). It was shown that the monodisperse spheres possess a mesoporous structure, with specific surface areas of 504, 452, and 308 m²/g for DMSN-1.5, DMSN-3, and DMSN-5, respectively.

An adsorbent (Fe⁰@DMSN) was obtained by depositing zero-valent iron particles onto the surface of DMSN-1.5. The mesoporous structure of the resulting

material was confirmed. It was demonstrated that the specific surface area of the modified sample was nearly two times smaller than that of the synthesized DMSN. It was further established that at $\text{pH} = 5.7$, the maximum adsorption capacity of FeO@DMSN toward copper ions reached $39.8 \text{ mg}\cdot\text{g}^{-1}$, which is significantly higher than that of the unmodified DMSN-1.5 material ($0.7 \text{ mg}\cdot\text{g}^{-1}$).

An adsorbent was also obtained through chemical modification of dendritic mesoporous silica nanoparticles with 3-aminopropyltriethoxysilane (DMSN- NH_2). It was shown that this material retained a mesoporous structure and could rapidly and efficiently remove copper ions from aqueous solutions within the studied pH range. The formation of coordination bonds between Cu^{2+} ions and the amino groups present on the silica surface was confirmed. Based on sorption–desorption experiments, the possibility of regeneration and reuse of the obtained material was demonstrated.

The fourth chapter presents experimental data on the adsorption removal of copper ions and methylene blue by adsorbents based on commercial silica gel modified with nickel oxide at different mass ratios of the components ($\text{SiO}_2@0.5\text{NiO}$ and $\text{SiO}_2@\text{NiO}$). It was established that the obtained materials exhibited mesoporous structures. It was determined that the greater the amount of nickel oxide deposited on the silica gel surface, the smaller the specific surface area of the samples. For the modified samples, the degree of Cu^{2+} removal increased with increasing pH. It was shown that maximum sorption values were observed at pH 5.5, amounting to $0.9 \text{ mg}\cdot\text{g}^{-1}$ and $1.7 \text{ mg}\cdot\text{g}^{-1}$ for $\text{SiO}_2@0.5\text{NiO}$ and $\text{SiO}_2@\text{NiO}$, respectively. It was also found that methylene blue was rapidly removed by the obtained materials, with the maximum adsorption capacity ($19.3 \text{ mg}\cdot\text{g}^{-1}$) recorded for the sample with a SiO_2 -to- NiO mass ratio of 1:0.5.

The fifth chapter investigates the efficiency of copper ion removal from aqueous solutions using sorbents based on saponite and fly ash. It was demonstrated that granules obtained from ferrihydrite-modified saponite combined with a biopolymer (sodium alginate), as well as a powdered adsorbent derived from fly ash with a deposited zeolitic layer, exhibited adsorption capacity toward copper ions. Based on the study of the rheological behavior of suspensions containing saponite and biopolymer in various mass ratios, it was established that these systems are thixotropic. It was determined that their viscosity is influenced by the solid-phase content when the same amount of sodium alginate is introduced. The necessary conditions for the granulation process were identified to produce granules stable in aqueous media. The thermal properties of the obtained granulated adsorbents were studied. The morphology, phase composition, and chemical structure of sorbents based on aluminosilicate microspheres were examined. It was found that the deposition of a zeolitic phase on the surface of fly ash increased the copper adsorption capacity from $4.94 \text{ mg}\cdot\text{g}^{-1}$ to $6.53 \text{ mg}\cdot\text{g}^{-1}$. The obtained materials

demonstrated promising potential for application in the purification of water contaminated with heavy metal ions.

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.

1. The dissertation lacks data on the efficiency of the obtained sorption materials for the removal of copper compounds from water in an alkaline medium. The information presented refers only to a narrow pH range of 3 to 6 (p. 83, Fig. 3.1).

2. The efficiency of the obtained sorption materials was evaluated only on model waters (for example, the sorption material DMSN-NH₂ demonstrates the highest sorption capacity toward copper compounds at 37.5 mg/g (Table 3.6, p. 103)). However, there are no data on the effectiveness of purification of real wastewater, which, apart from copper compounds, would also contain other contaminants.

3. The efficient removal of copper compounds by the sorption material DMSN-NH₂ occurs within 10 minutes (Fig. 3.18, p. 101). Therefore, it would be advisable to study the kinetics of the process precisely within this range and, in particular, calculate the rate constant.

4. The shape of the kinetic curves of copper compound sorption on the NiO-modified sorption material (Fig. 4.4, p. 116) indicates a change in the sorption mechanism with increasing NiO content in the modified material. It would be advisable to calculate the rate constants for all Ni-containing materials for the duration of the process from 0 to 10 minutes and from 10 to 40 minutes, which

correspond to the changes in the slope of the curve observed on the graphs within these ranges.

5. The dissertation does not provide a methodology for separating the spent sorption materials or methods for their further disposal.

6. It would be advisable for the dissertation to propose a conceptual scheme of water purification from copper compounds using one of the obtained sorption materials, or at least to outline the mandatory stages of the technology.

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, on the topic “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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