

## REVIEW

by the official opponent 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 adsorption materials based on synthetic mesoporous silicas and natural or artificial mineral raw materials (aluminosilicates) represents a promising area of research both in the field of inorganic materials science and environmental water protection. This is due not only to the availability as well as the mechanical, thermal, chemical, radiation, and biological stability of silicate carriers, but also to the possibility of tailoring the structural and sorption characteristics of composite materials based on them. Through chemical surface modification of synthetic dendritic mesoporous silicas and aluminosilicates of natural (saponite) and technogenic (fly ash) origin, it is possible to purposefully alter the physicochemical properties of silicate sorbents, thus obtaining composite materials with unique surface structure and morphology.

Effective modifiers in this context may include zero-valent iron particles, metal oxides and oxyhydroxides (such as nickel oxide and ferrihydrite), as well as organosilicon compounds (such as 3-aminopropyltriethoxysilane). To enable continuous technological processes, it is advisable to granulate dispersed materials. The production of low-cost granulated adsorbents based on saponite and sodium alginate significantly improves the processability of adsorption-based water treatment due to the ease of separating solid and liquid phases after the sorption process.

Thus, the topic of this dissertation is highly relevant, and the study of the features of obtaining modified dendritic mesoporous silicas and powdered or granulated aluminosilicates is important for evaluating their potential effectiveness in technologies for sorption removal of hazardous inorganic and organic toxicants from contaminated 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 sorption materials obtained was studied using scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, as well as transmission electron microscopy. The phase composition of the starting materials and composites, as well as the surface chemistry of the samples, were determined using X-ray diffraction analysis, X-ray photoelectron spectroscopy, and infrared spectroscopy. The porous structure parameters of the sorbents were investigated by low-temperature nitrogen adsorption-desorption analysis. Differential thermal and gravimetric analyses were used to determine the thermal stability of the materials. The initial and equilibrium



concentrations of copper ions and the organic dye in the solutions were determined using inductively coupled plasma atomic emission spectrometry and spectrophotometric methods, 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.

Thus, the applicant has fully accomplished the scientific objectives set to achieve the aim of the study, which indicates that he has fully 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 the rationale for the relevance of the research, states its connection to scientific topics, programs, and plans, outlines the aim and objectives of the research, describes the instrumental methods used, emphasizes the scientific novelty and practical significance of the obtained results, presents the



applicant's personal contribution, and summarizes the approbation of the dissertation results and its structure.

The first chapter presents an analytical review of the literature on the development of modern adsorption materials for removing heavy metal ions and organic dyes from aquatic environments. Particular attention is paid to methods of obtaining mesoporous adsorbents based on synthetic silicates (silicas) and natural or artificial aluminosilicate raw materials.

The second chapter describes the methods used to obtain synthetic silica coated with zero-valent iron, amino-functionalized silica, commercial silica gel modified with nickel oxide, granulated samples based on saponite and sodium alginate, and mesoporous adsorbents derived from fly ash, as well as the research methods employed in this dissertation.

The third chapter is devoted to the synthesis and characterization of dendritic mesoporous silica nanoparticles (DMSN) modified with zero-valent iron and 3-aminopropyltriethoxysilane, and to studying their efficiency in removing copper ions from aqueous solutions. Optimal parameters were established, in particular the effect of synthesis time (1.5, 3, and 5 hours) on obtaining monodisperse silica microspheres with controlled structural and physicochemical characteristics (DMSN-1.5; DMSN-3; DMSN-5). Infrared spectroscopy confirmed the presence of all characteristic Si–OH, O–Si–O, and Si–O–Si vibrational bands typical of amorphous SiO<sub>2</sub>. It was found that silica microspheres synthesized with different mixing durations are monodisperse spheres approximately 200 nm in diameter, possessing a mesoporous structure with pore sizes from 5 to 50 nm, and with specific surface areas of 504, 452, and 308 m<sup>2</sup>/g for DMSN-1.5, DMSN-3, and DMSN-5, respectively. It was established that a synthesis time of 1.5 hours is optimal for achieving a high specific surface area and well-defined morphology without significant pore coalescence or edge thickening.

A sorbent material (Fe<sup>0</sup>@DMSN) was obtained by depositing zero-valent iron particles onto the surface of DMSN-1.5. Successful modification was confirmed by scanning and transmission electron microscopy, X-ray diffraction analysis, and infrared spectroscopy. The mesoporous structure of the obtained materials, with pore sizes ranging from 3 to 50 nm, was confirmed by low-temperature nitrogen adsorption–desorption analysis. It was shown that the specific surface area of the modified sample was almost twice lower than that of the synthesized DMSN, which may be due to Fe<sup>0</sup> occupying or partially blocking the pore channels of DMSN. It was established that at pH 5.7, the maximum adsorption capacity of Fe<sup>0</sup>@DMSN toward copper ions was 39.8 mg·g<sup>-1</sup>, which is about 57 times higher than that of the original DMSN-1.5 material (0.7 mg·g<sup>-1</sup>).

An amino-functionalized adsorbent (DMSN-NH<sub>2</sub>) was obtained by chemically modifying dendritic mesoporous silica nanoparticles with 3-aminopropyltriethoxysilane. The successful attachment of amino groups to the surface of the silica particles was confirmed, and their content was determined. It was shown that this material possesses a mesoporous structure and can rapidly and efficiently remove copper ions from aqueous media across the studied pH range. X-ray photoelectron spectroscopy results indicated the formation of coordination bonds between Cu<sup>2+</sup> ions and amino groups. Regeneration studies of the spent material showed that it can be reused.



In the fourth chapter, the results of adsorption removal of copper ions and methylene blue using adsorbents based on commercial silica gel and nickel oxide with different mass ratios of components ( $\text{SiO}_2@0.5\text{NiO}$  and  $\text{SiO}_2@\text{NiO}$ ) are presented. The successful deposition of nickel oxide on the surface of silica and the mesoporous structure of the materials, which have a narrow pore size distribution (about 2.5–3 nm), were confirmed. It was shown that in the series  $\text{SiO}_2 > \text{SiO}_2@0.5\text{NiO} > \text{SiO}_2@\text{NiO}$ , the specific surface area of the adsorbents decreased from 411  $\text{m}^2/\text{g}$  to 186  $\text{m}^2/\text{g}$ . It was established that for the modified samples, the degree of  $\text{Cu}^{2+}$  removal increased with increasing pH, and the maximum sorption values were observed at pH 5.5, amounting to 0.9 mg/g and 1.7 mg/g for the  $\text{SiO}_2@0.5\text{NiO}$  and  $\text{SiO}_2@\text{NiO}$  samples, respectively. It was shown that methylene blue removal occurred fairly rapidly, with the maximum adsorption capacity (19.3 mg/g) observed for the sample with a mass ratio of  $\text{SiO}_2$  to NiO of 1:0.5.

In the fifth chapter, experimental data are presented on the removal of copper ions using materials based on aluminosilicates of natural and technogenic origin. Granules were obtained using saponite modified with ferrihydrite and sodium alginate, as well as a mesoporous adsorbent based on fly ash coated with a zeolite layer. The rheological behavior of clay suspensions based on saponite and biopolymer with different mass ratios of components was studied. It was established that these systems are thixotropic, and their viscosity, when the same amount of sodium alginate is added, depends on the solid phase content. The necessary conditions for granulation were determined. It was found that the stability of the granules in an aqueous environment is significantly influenced by the amount of sodium alginate added to the suspension. The thermal properties of the obtained granulated adsorbents were studied, and the prospects of their use in the purification of water contaminated with heavy metal ions were demonstrated. The morphology, phase composition, and chemical composition of sorbents based on aluminosilicate microspheres coated with a zeolite layer were examined. It was shown that during the synthesis process, fly ash serves as a source of silicon, while the aluminate solution provides sodium and aluminum. It was established that the deposition of a zeolite phase on the surface of fly ash increases the copper sorption capacity from 4.94 mg/g to 6.53 mg/g, although achieving higher efficiency requires longer synthesis at higher temperatures.

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 published works of the applicant are written at a high scientific level and use generally accepted scientific and technical terminology. 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. What is the production cost of the obtained sorbents, and can they compete with the widely used commercial sorbents currently applied for the removal of heavy metal ions?

2. In Chapter 2 (p. 66), a method for modifying silica gel is described, which included treating its surface with a solution containing nickel nitrate and sucrose. What was the purpose of adding sucrose?

3. Chapter 3 (Fig. 3.9) — why does the number of pores significantly decrease as the synthesis time increases?

4. Table 3.2 presents data on the main characteristics of the porous structure of the samples modified with zero-valent iron. How do you explain the increase in the micropore volume of the modified sample despite the significant (twofold) decrease in the total pore volume?

5. Figure 3.10 shows the dependence of copper ion removal efficiency on solution pH. At  $\text{pH} \approx 6$ , the formation of copper hydroxide is already possible — does this contribute to the increased removal efficiency?

6. In your opinion, what plays the key role in the increase of copper ion sorption capacity in samples modified with amino groups?

7. What is the mechanism of cation sorption on the studied sorbents? How does modification with nickel oxide affect the adsorption mechanism?

8. In the conclusions to Chapter 4, it is stated that the capacity of the silica gel samples modified with nickel oxide increased tenfold. Does this refer to the capacity for copper ions or for methylene blue?

9. The dissertation text contains a number of mechanical errors — such as full-size instead of subscript indices, inconsistent designations of specific surface area (BET). In Chapter 3, the notation DMSN-1.5, -3, -5 is not explained (the reader has to refer back to Chapter 2). In Fig. 3.5 and Fig. 3.9, the results of the pore structure analysis of the obtained materials are presented: in the first figure, the X-axis is labeled as pore diameter, while in the second figure — as pore radius.

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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