

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 dissertation is devoted to the development of sorption materials based on natural and artificial raw materials for the protection of water from contamination by heavy metal ions and organic dyes. Among promising adsorbents, modified silicas stand out for their efficiency, while clay minerals and technogenic silicates, such as thermal power plant waste (fly ash), are distinguished by their availability and low cost. Such types of inorganic carriers can be relatively easily modified with zero-valent iron particles, metal oxides or oxyhydroxides, and organosilicon compounds using standard laboratory equipment and conventional synthesis methods. The use of fly ash as a source of silicon and aluminum makes it possible, under certain synthesis conditions, to obtain a zeolitic layer on the surface of aluminosilicate microspheres, which exhibits adsorption capacity toward metal ions. At the same time, this approach can partially address the environmental problem of waste utilization. The preparation of so-called "low-cost" materials based on accessible natural aluminosilicate raw materials (saponite) in granulated form significantly improves the technological feasibility of the sorption process. Therefore, investigating the features of obtaining materials based on modified synthetic silicas and aluminosilicates, as well as studying the physicochemical patterns of heavy metal and cationic dye removal from water, represents a relevant ecological challenge.

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: scanning electron microscopy with energy-dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffraction analysis, X-ray photoelectron and infrared spectroscopy, low-temperature nitrogen adsorption-desorption method, differential thermal and gravimetric analyses, inductively coupled plasma atomic emission spectrometry, and spectrophotometric method.

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

- the features of adsorbents obtaining based on dendritic silica and commercial silica gel with improved structural and sorption characteristics have been

studied by modifying their surface 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 determined for producing granulated "low-cost" adsorbents that are stable in aqueous environments;

- a mesoporous sorption material with a deposited zeolitic layer was obtained from technogenic aluminosilicate waste (fly ash) using conventional synthesis methods and readily available laboratory equipment;

- the physicochemical features of copper compound and methylene blue removal by the obtained adsorbing materials were studied, and their potential use for effective water purification from such pollutants was established.

- 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 corresponding 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 topics, programs, and plans, the aim and objectives of the study, the research methods used, 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 an analytical review of the literature sources related to the research topic, namely a wide range of developed adsorption materials for the purification of water from contamination by heavy metal ions and

organic dyes. Methods for obtaining mesoporous adsorbents based on synthetic silicas as well as natural and artificial aluminosilicate raw materials are considered.

The second chapter describes the methodologies for obtaining dendritic mesoporous silica nanoparticles (DMSN) and samples coated with layers of zero-valent iron particles and an organosilicon compound. In addition, it presents the methods for preparing commercial silica gel modified with nickel oxide, granulated samples based on the layered silicate (saponite) and the biopolymer (sodium alginate), as well as mesoporous adsorbents with a zeolite layer deposited from fly ash. The research methods employed in this dissertation are also presented.

The third chapter of the dissertation focuses on the synthesis of dendritic mesoporous silica nanoparticles (DMSN) and the modified samples obtained by coating them with layers of zero-valent iron particles and 3-aminopropyltriethoxysilane. Their morphology, structural and sorption characteristics, and adsorption capacity for the removal of heavy metal ions (copper) from aqueous solutions were studied. The influence of synthesis time (1.5, 3, and 5 hours) on the formation of monodisperse silica microspheres with controlled structural and physicochemical properties (DMSN-1.5; DMSN-3; DMSN-5) was determined. It was confirmed that the synthesized samples contained all the vibrational bands of Si-OH, O-Si-O, and Si-O-Si characteristic of amorphous SiO₂. It was also established that the silica microspheres possess a mesoporous structure, and their specific surface area decreases with synthesis time increasing, attaining 504, 452, and 308 m²/g for DMSN-1.5, DMSN-3, and DMSN-5, respectively. Based on the obtained data, it was shown that the optimal synthesis time is 1.5 hours.

Section 3.2 presents experimental data describing the properties of the adsorbent (Fe⁰@DMSN) obtained by depositing zero-valent iron particles onto the surface of DMSN-1.5. Successful modification of silica was confirmed by scanning and transmission electron microscopy, X-ray diffraction analysis, and infrared spectroscopy. The mesoporous structure of the obtained materials was studied by low-temperature nitrogen adsorption-desorption. It was established that the specific surface area of the modified material is smaller than that of the original DMSN, which is due to Fe⁰ particles occupying or partially blocking the pore channels. The maximum adsorption capacity of Fe⁰@DMSN toward copper ions at pH = 5.7 was found to be 39.8 mg·g⁻¹, which is significantly higher than that of the original DMSN-1.5 (0.7 mg·g⁻¹).

Section 3.3 presents the results of the study of the characteristics and properties of the amino-functionalized adsorbent obtained by chemically modifying dendritic mesoporous silica nanoparticles with 3-aminopropyltriethoxysilane (DMSN-NH₂). The attachment of amino groups to the surface of the silica particles was confirmed by infrared spectroscopy. It was shown that this material has a mesoporous structure and can quickly and effectively remove copper ions from aqueous media within the studied pH range. It was found that coordination bonds are formed between Cu²⁺ ions and amino groups. It was also determined that regeneration of the spent sorbent is possible, allowing it to be reused.

Chapter 4 presents the results of adsorption removal of copper ions and the organic dye (methylene blue) from aqueous solutions using adsorbents based on commercial silica gel and nickel oxide with different mass ratios of components ($\text{SiO}_2@0.5\text{NiO}$ and $\text{SiO}_2@\text{NiO}$). The successful deposition of nickel oxide on the surface of silica and the mesoporous structure of the materials were confirmed. It was shown that the specific surface area of the adsorbents decreases with nickel oxide content increase from 411 m^2/g to 186 m^2/g for $\text{SiO}_2@0.5\text{NiO}$ and $\text{SiO}_2@\text{NiO}$, respectively. It was established that for the modified samples the degree of Cu^{2+} removal increases with pH, with maximum sorption values observed at pH 5.5, reaching 0.9 mg/g and 1.7 mg/g for $\text{SiO}_2@0.5\text{NiO}$ and $\text{SiO}_2@\text{NiO}$, respectively. It was also found that methylene blue removal from solution occurs rapidly. The maximum adsorption capacity for the sample with a mass ratio of SiO_2 to NiO (1:0.5) was 19.3 mg/g .

Chapter 5 presents data on the removal of copper ions from contaminated waters using sorbents based on aluminosilicates (natural saponite and technogenic fly ash). Granulated samples were obtained using ferrihydrite-modified saponite and sodium alginate, as well as a mesoporous adsorbent with a zeolite layer deposited on fly ash. The rheological behavior of saponite suspensions containing different amounts of biopolymer was studied. The conditions necessary for granulation were determined based on the obtained data. It was established that the amount of sodium alginate added to the suspension affects the stability of the granules in aqueous environments significantly. The thermal properties of the obtained adsorbents were investigated and their potential for use in the purification of contaminated waters from copper ions was demonstrated. The morphology, phase, and chemical composition of sorbents based on aluminosilicate microspheres with a zeolite layer were characterized. It was found that deposition of the zeolite phase on the surface of fly ash particles increases the copper sorption 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 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. Titration of benzoic acid in 0.05 N toluene with KOH solution in the presence of bromothymol blue indicator was used to determine the concentration of functional groups (-OH) on the surface of silica materials (page 73, 2.2.6 Methods for determining of the content of functional groups on the surface of samples. Determination of the content of functional groups (-OH)). Could the author clarify what accuracy of this method taken into account usage of bulky organic substances (toluene and benzoic acid) which may have difficulties at penetration into the small pores of sorbent.

2. Some of the isotherms of low-temperature nitrogen adsorption-desorption on synthesized materials have a shape of type II with H3 hysteresis loop according to the IUPAC classification (Figs. 3.9 and 3.16). It is necessary to explain why the author describes them as type IV and what is the origin of the hysteresis loop.

In addition, the statement concerning H3 hysteresis loop "The nature of the hysteresis loop allows us to ascertain that the porous structure of all samples is constituted by spherical particles of homogeneous size..." (page 81, Fig. 3.4) is doubtful.

3. At description of adsorption removal of copper (II) from water by amino-functionalized dendritic mesoporous silica nanoparticles (page 93) the author claims that "The absence of a peak in the $\nu \sim 3000 \text{ cm}^{-1}$ region, which belongs to the symmetrical stretching of the -N-H bond, may be due to the low intensity of amine groups originating from APTES functionalization...". It is not clear what does it mean "low intensity of amine groups". Could the author explain this assumption in details?

In Fig. 4.8 the adsorption band corresponding to the valence vibrations in silanol groups of silica framework is not registered? How this can be explained?

4. What is the experimental error of the adsorption measurements presented in this study? How it was taken into account at the analysis of experimental data by kinetic and equilibrium adsorption models?

5. It is necessary to explain why the adsorption capacity for copper cations decreases with pH increase from 3 to 6 considering the surface chemistry of the adsorbents and protolytic state of surface functional groups.

6. Adsorption removal of copper (II) and methylene blue was studied from water by NiO-modified silica gel. Could the author clarify the protolytic state of functional groups present on nickel oxide surface at studied pH value and the nature of interactions of these groups with adsorbates species. Why the degree of Cu^{2+} removal increases with pH rise? How the methylene blue adsorptive removal depends on pH?

7. The dissertation is written in good English, which makes it easy to follow. However, there are some expressions that could be improved. In addition, the author erroneously refers to article [173] instead of [172] in the description of amino (-NH₂) groups content determination (page 73, 2.2.6 Methods for determining of the content of functional groups on the surface of samples). The title of Chapter 4 "Modified

commercial silica gel used for heavy metal ions and organic dyes removal from aqueous solutions” may be misleading. It gives impression that adsorption of several heavy metals and dyes was studied by author instead of copper cations and methylene blue.

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.

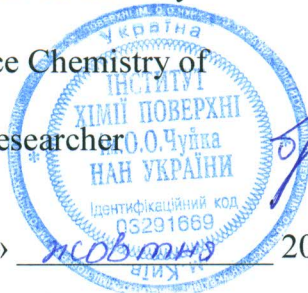
The applicant Yu Junjie fully deserves to be awarded the degree of Doctor of Philosophy in the field of knowledge 16 Chemical and Bioengineering, specialty 161 Chemical Technologies and Engineering.

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