

REVIEW

by the official opponent of the dissertation
Zhou Zhentao

on the topic **“Research on Modified MOF Materials
for Water Pesticide Pollutant Purification”**,
presented for the degree of Doctor of Philosophy

in the field of knowledge 16 Chemical and Bioengineering
in specialty 161 Chemical Technology and Engineering

Relevance of the dissertation topic.

This work focuses on the development of photocatalysts and photo-Fenton catalysts based on modified metal-organic framework (MOF) materials. Given the increasingly serious problem of organic water pollution, the development of photocatalysts and photo-Fenton catalysts based on novel porous materials is an important and promising research area. MOFs, as a novel material, possess a porous structure and generally possess strong light absorption capabilities, making them very promising photocatalysts and photo-Fenton catalysts. Therefore, the development and synthesis of MOF/semiconductor composite photocatalysts, as well as the synthesis of defective MOF-photo-Fenton catalysts through defect engineering, and the study of their performance in removing organic pollutants from water are of great significance for the practical application of MOF materials in water purification.

Evaluation of the scientific validity, reliability, and novelty of the dissertation results.

The scientific novelty of the results of the dissertation research is as follows.

A new composite photocatalyst $\text{NH}_2\text{-MIL-125/TiO}_2$ based on MOF semiconductors, was synthesized. This composite combines the high light absorption capacity of $\text{NH}_2\text{-MIL-125}$ with the high oxidation capacity of TiO_2 , providing thereby providing greater photocatalytic activity.

A novel and facile synthesis method, using tannic acid modification and calcination steps, was developed to synthesize the defect-rich M88A@TA-2 material. This material exhibits high photo-Fenton catalytic activity for pollutant degradation and exceptionally high H_2O_2 utilization efficiency, significantly reducing oxidant consumption in the photo-Fenton process. Furthermore, the proposed mechanism for

the photo-Fenton degradation of atrazine by the M88A@TA-2 catalyst provides valuable insights for future research in the field of photo-Fenton catalysis. The practical significance of this study lies in the development of NH₂-MIL-125/TiO₂ composite material with excellent photocatalytic activity and the establishment of optimal conditions for its synthesis, which lays the foundation for its future large-scale production. In addition, a simple synthesis method for the highly efficient photo-Fenton catalyst M88A@TA-2 was developed in this dissertation. The results showed that M88A@TA-2 has exceptional photo-Fenton activity for the decomposition of organic pollutants and effectively utilizes the oxidant H₂O₂. In addition, M88A@TA-2 exhibits strong pH adaptability, which will reduce energy consumption, capital expenditure and reagent costs during the treatment of complex water environment, demonstrating its significant potential for application in photo-Fenton processes.

Scientific research was carried out by the applicant at the Department of Inorganic Substances Technologies, Water Treatment and General Chemical Technology of the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" (Ukraine) within the framework of the project "Synthesis of low-cost ceramic membranes of the controlled design for mobile MF/UF/NF systems" (State registration number 0123U102670) under the supervision of Professor, Doctor of Technical Sciences Tetiana Dontsova.

In summary, the scientific task set in the dissertation work to obtain functional materials based on modified MOF materials for photocatalytic and photo-Fenton catalytic applications has been fully accomplished, and the applicant has fully mastered the methodology of scientific activity.

Assessment of the content of the dissertation, its completeness and adherence to the principles of academic integrity.

In terms of its content, the dissertation work of the applicant Zhou Zhentao fully complies with the higher education standard in specialty 161 "Chemical Technology and Engineering" and the research areas in accordance with the educational program "Chemical Technology and Engineering".

The dissertation is a completed scientific work and demonstrates the applicant's personal contribution to the scientific direction of developing functional materials based on modified MOF.

Having reviewed the similarity report based on the results of checking the dissertation for textual matches, it can be concluded that Zhou Zhentao's dissertation is the result of the applicant's independent research and does not contain elements of falsification, compilation, fabrication, plagiarism and borrowing. The ideas, results and texts of other authors used have proper references to the appropriate source.

Language and style of presenting results.

The dissertation is written in English.

The presented material is distinguished by its logical consistency, clarity, and accessibility of presentation. The style of the dissertation is scientifically sound, employing modern terminology that adheres to established standards in the field of chemical technology and engineering. The dissertation candidate demonstrates a deep understanding of the research topic and presents the results clearly and concisely.

The dissertation consists of an introduction, 4 chapters, conclusions, and a list of references. The total length of the dissertation is 133 pages.

The introduction substantiates the relevance of the research topic, formulates the goal, objectives, object and subject of the work. The state of research on MOF-based catalysts in water purification applications is summarized. The scientific novelty and practical significance of the results obtained are determined, and information about testing, publications on the topic of the dissertation and the implementation of the results is provided.

The first chapter begins by presenting the main modern methods for removing organic pesticide contaminants from water and the problems encountered by these methods. It then reviews the current state of research on the use of MOF-based catalysts for photocatalytic and photo-Fenton catalytic removal of organic contaminants from water. This chapter also explores methods for modifying MOF-based catalysts, with a particular focus on research achievements and prospects for the application of MOF/semiconductor composite catalysts and defective MOF catalysts.

The second chapter describes in detail the synthesis methods of the MOF/TiO₂ composite photocatalyst (NH₂-MIL-125/TiO₂) and the defective MOF photo-Fenton catalyst (M88A@TA-2). In addition, the section focuses on the characterization of the obtained materials. These include methods for characterizing the morphology and phase structure using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and nitrogen adsorption-desorption; characterization of the chemical structure using infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA); characterization of optical properties using ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). This section also describes specific experimental procedures for applying materials in photocatalytic and photoFenton catalytic experiments, as well as methods for determining pesticide contaminant concentrations in water using liquid chromatography.

The third chapter presents the characteristics and catalytic activity test results of the $\text{NH}_2\text{-MIL-125/TiO}_2$ composite. The XRD results show that $\text{NH}_2\text{-MIL-125/TiO}_2$ has both X-ray and $\text{NH}_2\text{-MIL-125}$ characteristics, indicating the formation of a composite material. The FTIR results confirm that the spectrum of $\text{NH}_2\text{-MIL-125/TiO}_2$ is almost identical to that of pure $\text{NH}_2\text{-MIL-125}$, indicating that the design of the composite material does not affect the chemical structure of the MOF. In addition, the SEM images of $\text{NH}_2\text{-MIL-125/TiO}_2$ show TiO_2 nanoparticles dispersed on the surface of $\text{NH}_2\text{-MIL-125}$, further confirming the successful synthesis of the composite material. The UV-Vis DRS results show that the band gap of TiO_2 is approximately 3.36 eV, the band gap of $\text{NH}_2\text{-MIL-125}$ is approximately 2.68 eV, and the band gap of the $\text{NH}_2\text{-MIL-125/TiO}_2$ composite is approximately 2.58 eV. The band gap of the composite material is smaller than that of the two individual components, indicating that the combination of the composite material can optimize the band structure and provide higher light efficiency.

In *the fourth chapter*, the physicochemical structure of the defective M88A@TA-2 was characterized and its efficiency in photo-Fenton catalytic removal of pesticides from water was verified. The morphology and phase structure of the obtained material were characterized using XRD, SEM, TEM and BET methods. The results showed that the modification with tannic acid and the sintering process resulted in a loose and porous structure of M88A@TA-2 with a large number of defects in its crystal structure. The chemical structure of the obtained material was analyzed using FTIR, TGA and XPS. The FTIR results showed that the modification with tannic acid and sintering at 200°C did not destroy the main chemical structure of the MOF, but M88A@TA-2 was rich in defects, exposing more carboxyl groups. TGA and XPS further confirmed the higher number of defects in M88A@TA-2 . The band structure and optical absorption properties of the obtained material were characterized by UV-Vis DRS and valence band potential spectroscopy XPS. The results showed that the modified M88A@TA-2 material exhibited a narrower energy band and stronger optical absorption. Catalytic activity tests showed that M88A@TA-2 exhibited the best photo-Fenton catalytic activity among all the prepared materials due to its high specific surface area, numerous defects, and excellent light absorption properties. In addition, M88A@TA-2 exhibited a wide pH range and high H_2O_2 utilization. Reactive oxygen species (ROS) scavenging experiments and EPR measurements showed that the main ROS species involved in the photo-Fenton degradation of ATZ M88A@TA-2 were OH and $^1\text{O}_2$.

The dissertation work is designed in accordance with the requirements of the Order of the Ministry of Education and Science of Ukraine dated January 12, 2017 No. 40 "On Approval of Requirements for the Design of a Dissertation".

Publication of the results of the dissertation work.

The scientific results of the dissertation are covered in 3 scientific publications of the applicant, among which: 1 of the scientific publications was included in the list of Ukrainian scientific publications on the date of publication, 2 – in the international citation database Scopus. The results of the dissertation were also presented at 2 scientific professional conferences.

The dissertation's publications are of high scientific quality. The published results fully reflect the content of the dissertation, meet its goals and objectives, and confirm the applicant's personal contribution to obtaining new scientific and practically significant results. The publications derived from the dissertation exhibit high scientific quality. The results presented align with the dissertation's content, meet its objectives, and demonstrate the applicant's significant contribution to achieving new scientific and practically relevant results. Thus, the scientific results described in the dissertation are fully covered in the applicant's scientific publications.

Shortcomings and comments on the dissertation.

1. On the P. 30. author says that “Compared to microfiltration and ultrafiltration membranes, nanofiltration and reverse osmosis membranes have smaller pore sizes, with molecular weight cutoffs (MWCO) of 0.001 to 0.008 μm and less than 0.001 μm , respectively”. RO membranes are not characterized by MWCO in micrometers. MWCO is a value measured in daltons.

2. In the chapter 2.1.2 Synthesis method of $\text{NH}_2\text{-MIL-125/TiO}_2$ composite material (P. 54) author writes that “0.56 g of $\text{NH}_2\text{-BDC}$ (3.1 mmol) and 0.6 mL of $\text{NH}_2\text{-BDC}$ (2 mmol) were added to the solution, and the mixture was stirred until the $\text{NH}_2\text{-BDC}$ was completely dissolved”. Why was the same substance added twice in g and in ml?

3. On Figure 2.6. “Photocatalytic experimental process and experimental equipment” not specified at what wavelength was the irradiation performed?

4. After the materials and methods section, a list of publications is provided, which includes a link <https://doi.org/10.1016/j.envres.2025.122499>. This article is a review, so it should be cited after section 1, not 2.

5. On the Fig 3.5 Thermogravimetric analysis of the samples should have been presented in a differential form. In order to clearly see the main temperatures of mass loss. The main ranges of mass loss are not explained.

6. Have you observed the formation of iron hydroxides during the Fenton reaction?

7. Is it appropriate to compare homogeneous and heterogeneous catalysis in the Fenton reaction, since the constant depends on the amount of catalyst. How was the concentration of Fe^{2+} selected in this case (Fig 4.15)?

8. Why wasn't the mechanism of pesticide photodegradation investigated on samples with titanium oxide?

I believe that the expressed remarks are not decisive and do not reduce the overall scientific novelty and practical significance of the results and do not affect the overall positive assessment of the dissertation work.

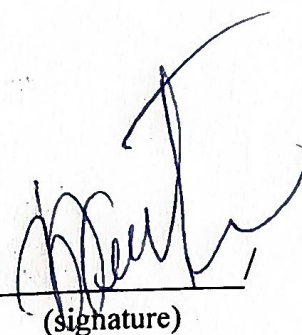
Conclusion about the dissertation work

I believe that the dissertation work of the Doctor of Philosophy degree applicant Zhou Zhentao on the topic "Research on Modified MOF Materials for Water Pesticide Pollutant Purification" is performed at a high scientific level, does not violate the principles of academic integrity and is a completed scientific research, and by the totality of the set of theoretical and practical results of which solves a scientific problem that is of significant importance for the field 16 Chemical and Bioengineering. The dissertation work in terms of relevance, practical value and scientific novelty fully complies with the requirements of the current legislation of Ukraine, as provided in paragraphs 6-9 of the "Procedure for awarding the degree of Doctor of Philosophy and revoking the decision of a one-time specialised academic council of a higher education institution or scientific institution on awarding the degree of Doctor of Philosophy", approved by the Resolution of the Cabinet of Ministers of Ukraine dated January 12, 2022 No. 44.

The applicant Zhou Zhentao deserves to be awarded the degree of Doctor of Philosophy in the field of knowledge 16 Chemical and Bioengineering in the specialty 161 "Chemical Technology and Engineering".

Official opponent:

Associated professor of National
University of Kyiv-Mohyla Academy /


(signature)

Viktoriia KONOVALOVA

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Особистий підпис
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