REVIEW

of reviewer on thesis of
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 dissertation addresses the design of photocatalysts and photo-Fenton catalysts derived from modified metal–organic frameworks (MOFs) to tackle the escalating challenge of organic micropollutants in aquatic environments. Pesticide residues such as neonicotinoids (e.g., imidacloprid) and triazines (e.g., atrazine) are persistent, biologically active, and frequently detected at low concentrations that evade conventional treatment. Advanced oxidation processes (AOPs) driven by light and/or H_2O_2 offer energy-efficient routes to degrade such compounds, yet their practical deployment depends on catalysts that are both highly active under mild conditions and sufficiently robust for repeated use. In this context, MOFs are uniquely positioned: their crystalline porosity, high specific surface area, and modular chemistry allow rational tuning of active sites, band energetics, and interfacial properties relevant to radical generation and charge separation.

The work's focus on two complementary strategies - (i) constructing MOF/semiconductor heterojunctions (NH_2-MIL-125/TiO_2) and (ii) introducing controlled defect states into Fe-MOFs via tannic-acid modification and thermal treatment (M88A@TA-2) - directly targets known limitations of traditional photocatalysts and heterogeneous Fenton systems. Heterostructures can narrow effective band gaps and promote charge separation under visible light, while defect engineering in Fe-MOFs enhances active-site density and facilitates redox cycling for efficient H_2O_2 activation. The thesis further underlines application relevance by demonstrating high removal efficiencies for representative pesticides, improved utilization of oxidants, activity across a broad pH window, and mechanistic validation via scavenger assays and EPR spectroscopy identifying •OH and $^1O_2$ as key reactive oxygen species.

By linking synthesis, multi-modal characterization (XRD, SEM/TEM, FTIR, XPS, BET, UV–Vis DRS), and kinetic performance, the study advances the translation of MOF-based catalysts from conceptual promise to operationally meaningful performance metrics. Given regulatory pressures and the need for scalable, light-driven water-purification technologies, the exploration of MOF/semiconductor composites and defect-engineered MOFs constitutes a timely and significant contribution, providing design principles and empirical evidence that support the deployment of MOF-based AOPs for resilient removal of organic contaminants from water.

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 NH_2-MIL-125/TiO_2 based on MOF semiconductors was synthesized, which combines the high light absorption capacity of NH_2-MIL-125 and the high oxidation capacity of TiO_2, which provides 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 NH_2-MIL-125/TiO_2 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 H_2O_2. 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" 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 dissertation stands out for its coherent structure, transparent narrative, and reader-friendly exposition. The writing maintains a rigorously scientific register and employs contemporary terminology consistent with accepted norms in chemical technology and engineering. The candidate demonstrates thorough command of the subject area, communicating aims, methods, and findings with precision and economy.

The document is organized into an introduction, four core chapters, final conclusions, and a reference list, totaling 133 pages.

The introductory section articulates the relevance of the topic, defines the aim and tasks, and specifies the object and subject of the study. It surveys the current landscape of MOF-based catalysts for water treatment, delineates the work's scientific novelty and practical value, and lists validation efforts, publications arising from the research, and instances of implementation.

Chapter One opens with a synopsis of leading technologies for eliminating organic pesticide pollutants from aqueous media, together with their inherent limitations. It proceeds to analyze advances in employing MOF-derived materials for

photocatalytic and photo-Fenton degradation of organic species in water. Methods for tuning and improving MOF catalysts are reviewed, with emphasis on the development and prospects of MOF/semiconductor composites and defect-engineered MOFs.

Chapter Two provides a detailed account of the synthesis protocols for the composite photocatalyst NH_2-MIL-125/TiO_2 and the defect-rich photo-Fenton catalyst M88A@TA-2. It then compiles an extensive characterization suite: morphology and phase analysis by XRD, SEM, TEM, and N_2 adsorption–desorption; chemical-structure verification via FTIR, XPS, and TGA; and optical characterization using UV–Vis DRS. This chapter also specifies the experimental procedures for applying the materials in photocatalytic and photo-Fenton tests, and the analytical methods for quantifying pesticide levels in water by liquid chromatography.

Chapter Three reports on the properties and catalytic performance of the NH_2-MIL-125/TiO_2 composite. XRD confirms the coexistence of reflections from both TiO_2 and NH_2-MIL-125, indicating successful composite formation. FTIR spectra of the composite closely match those of pristine NH_2-MIL-125, suggesting that the MOF's chemical framework remains intact. SEM images show TiO_2 nanoparticles distributed over the MOF surface, further supporting the intended architecture. UV–Vis DRS reveals band gaps of approximately 3.36 eV for TiO_2, 2.68 eV for NH_2-MIL-125, and 2.58 eV for the composite. The reduced gap in the composite implies a tuned band structure and enhanced photoresponse relative to the individual constituents.

Chapter Four examines the physicochemical attributes of the defect-engineered M88A@TA-2 and validates its effectiveness in photo-Fenton degradation of pesticides. Phase and morphology were assessed by XRD, SEM, TEM, and BET analyses, showing that tannic-acid modification followed by thermal treatment yields a porous, loosely packed structure with abundant lattice defects. FTIR, TGA, and XPS indicate that the primary MOF framework is preserved after modification at 200 °C, while defect density increases, exposing additional carboxyl functionalities; TGA and XPS data corroborate this defect enrichment. UV–Vis DRS and valence-band XPS demonstrate a narrowed band gap and stronger light absorption in M88A@TA-2. Catalytic trials identify M88A@TA-2 as the top performer among the prepared materials, attributed to its surface area, defect population, and favorable optical properties; it also operates across a broad pH range with efficient H_2O_2 utilization. Reactive-species trapping and EPR measurements indicate that •OH and $^1O_2$ are the principal ROS involved in atrazine degradation over M88A@TA-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 Scoups.

The results of the dissertation were also tested 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.

Thus, the scientific results described in the dissertation are fully covered in the applicant's scientific publications.

Disadvantages and comments on the dissertation.

1. The assignment of the TiO_2 component to a "main rutile phase" is stated without quantitative backing, despite the use of commercial P25, which is typically a mixed anatase/rutile material. Rietveld refinement or at least peak-area ratios would strengthen the conclusion and allow correlating phase composition with activity trends in Figure 3.6. In addition, the claim that the NH_2-MIL-125 phase remains unaffected by TiO_2 loading would be more convincing if lattice parameter refinements or peak broadening analysis (Scherrer/Williamson–Hall) were provided, not only qualitative peak presence. As written, the reader cannot fully assess whether subtle framework distortions or preferred orientation effects occurred. The qualitative narrative is plausible, but quantitative crystallographic analysis would provide a stronger mechanistic bridge to optical and kinetic data. Finally, mention of the (101) TiO_2 peak increase with TiO_2/TPOT ratio is useful, yet it would benefit from intensity normalization to an internal standard.

2. The SEM panel shows nanoscale TiO_2 decorating the MOF and describes good dispersion and heterogeneous structure formation. Yet, the discussion relies on qualitative observation; a particle-size histogram or interparticle spacing distribution (from multiple micrographs) would provide a more rigorous basis for claims about improved TiO_2 contact with pollutants. Similarly, EDS mapping or line scans on the composite would help visualize Ti/O/N spatial distributions to corroborate the "well dispersed" assertion. Absent such metrics, it remains difficult to quantify how morphology co-varies with catalytic performance across loadings. The narrative link between dispersion and activity (Figure 3.6) is reasonable but would be stronger with quantitative image analysis. Overall, the figures are informative; adding statistics would elevate reproducibility.

3. The UV-Vis DRS/Tauc analysis reports band gaps of 3.36 eV (TiO_2), 2.68 eV (NH_2-MIL-125), and 2.58 eV (composite), and concludes improved visible-light response. Two issues merit comment: (i) the Tauc model requires clarity on the assumed transition (direct vs indirect) for each material; (ii) the composite shows lower absorption intensity while still exhibiting enhanced activity, which seems counterintuitive if carrier generation alone controlled kinetics. These points should be reconciled by explicitly stating the Tauc exponent used and by invoking heterojunction charge separation as the dominant factor, not simply absorption magnitude. Additionally, the text would benefit from reminding readers that Kubelka–Munk transforms were applied and spectra were replicated. This would align the optical narrative with the kinetic gains of the composite seen later.

4. Using TG residual mass to infer TiO_2 wt.% across composites is practical but assumes complete combustion of organics and neglects potential lattice oxygen loss in TiO_2 at elevated temperature. The text partially acknowledges a small high-temperature mass change for TiO_2 itself; hence, uncertainties in the inferred TiO_2 fraction may be non-negligible. Cross-validation with an elemental/metal assay (e.g., ICP-OES for Ti) would remove ambiguity and allow tighter correlations with activity. Despite this, the observed monotonic trend in residual mass versus nominal TiO_2 loading is convincing. The TG-based estimates are thus acceptable as semi-quantitative, provided their limitations are noted.

5. There appears to be a discrepancy between the methods and the plotted series: Section 2.4.1 specifies IMD at 5 $mg \cdot L^{-1}$, whereas the caption to Figure 3.6 states 10 $mg \cdot L^{-1}$ for the depicted kinetics (50 mg catalyst, 50 mL, 60 min dark, 90 min light). Such inconsistency can confuse readers regarding comparability across experiments and the absolute rate constants reported. If different concentration sets were used for different series, this should be stated explicitly where the figure is discussed. Otherwise, the kinetic comparison across materials may be misinterpreted as being performed at a single concentration. Clarification would also help in benchmarking to the literature.

6. Kinetic analyses employ a pseudo-first-order model, which is standard; however, adsorption capacities differ notably among samples (e.g., NH_2-MIL-125 vs composites), potentially biasing apparent rate constants if initial states are not strictly comparable. The 60-min dark equilibration helps, but reporting the amount adsorbed at $t=0^+$ (post-dark) would make the initial conditions explicit. In the Fe-MOF photo-Fenton part, triplicate runs and error bars (SD) are specified; the same graphical treatment across all photocatalytic figures would aid consistency. Comparing M88A@TA-2 with homogeneous photo-Fenton is a strong point; still, normalizing k to H_2O_2 consumption or surface area could add mechanistic clarity. Overall, the use of $\ln(C_0/Ct)=kt$ is appropriate; making adsorption baselines explicit would sharpen comparisons.

7. The analysis showing that k(ATZ) increases 32.8× while the H_2O_2 consumption rate rises only 8.3× is an important efficiency metric for M88A@TA-2. It would be useful to report the stoichiometric efficiency (mol ATZ degraded per mol H_2O_2 consumed) and, if possible, the carbon balance (e.g., TOC) to further substantiate selectivity toward mineralization vs partial oxidation. As is, the conclusion that the catalyst uses H_2O_2 more efficiently is well supported, but the environmental significance would be clearer with these additional metrics. This is especially relevant when comparing with homogeneous photo-Fenton. Still, the presented differential increase ($\approx 4\times$ in utilization efficiency) convincingly argues for improved ROS generation pathways.

8. The combined scavenger tests (SOD, TBA, histidine) and EPR spin-trap measurements (DMPO-•OH, TEMP-$^1O_2$, DMPO-$\bullet O_2^-$) provide a coherent picture in which $^1O_2$ and •OH dominate, with $\bullet O_2^-$ contributing weakly. A minor concern is that scavenger concentrations and potential secondary reactions (e.g., TBA's selectivity) are not shown alongside the kinetic curves; including doses and controls directly on the plots would improve transparency. Nevertheless, the EPR signatures (1:2:2:1 quartet for DMPO-•OH; triplet for TEMP-$^1O_2$) substantiate the assignments. The methodological details (x-band settings, capillary procedure, timing) are described with sufficient specificity to ensure reproducibility. Overall, the ROS identification strategy is appropriate and well executed.

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".

Reviewer:

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