Wrocław University
of Science and Technology

Faculty of Chemistry

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REVIEW

of the doctoral thesis of MSc. Elvana Çako,
entitled.: *„Hybrid g-C_3N_4- based photocatalysts for degradation of pharmaceutical micropollutants"*

Formal basis for the review

The basis for the review is the Resolution of the Disciplinary Council for Chemical Sciences of the Gdansk University of Technology of May 12, 2026, and Article 190, paragraph 2 of the Act of July 20, 2018 - Law on Higher Education and Science (consolidated text: Journal of Laws of 2024, item 1571, as amended).

Introduction

The doctoral dissertation entitled: „*Hybrid g-C_3N_4-based photocatalysts for the degradation of pharmaceutical micropollutants*", was completed by MSc. Elvana Çako, at the Gdansk University of Technology. Her doctoral supervisor is Prof. Anna Zielinska-Jurek, PhD. DSc. Eng.

The doctoral dissertation submitted for review addresses an important social issue related to the pollution of the aquatic environment caused by the presence of selected pharmaceuticals. The research presented in the dissertation is related to the development of innovative materials for the degradation of selected aquatic contaminants, including ibuprofen, carbamazepine, and acetaminophen.

Overall Assessment of the Doctoral Dissertation

The reviewed doctoral dissertation was written in a hybrid format, consisting of both published scientific publications (Chapters III-V) and unpublished research results (Chapter VI). Chapters (III-VI) are preceded by a detailed literature introduction (Chapter I), a description of the scope, objectives, and methodology, and a description of the content of the doctoral dissertation (Chapter II). The subsequent chapters, i.e., Chapters III-V, represent the scientific publications incorporated into the doctoral dissertation. Chapter VI, in turn, describes the previously obtained, unpublished research results. The doctoral dissertation finishes with conclusions, after which the doctoral candidate attached statements of contribution from the co-authors of the scientific papers, followed by the research activity related to dissertation of PhD Candidate.

The doctoral thesis consists of the standard elements of this type of work, namely the title page, statement, a short description of the dissertation (including summaries in Polish and English), acknowledgments, a table of contents, a list of abbreviations, as well as statement of contribution, regarding the participation of co-authors of scientific articles in the preparation of individual publications (section

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following conclusions), as well as a presentation of the PhD student's research activity related to the dissertation.

The core of the dissertation consists of three scientific publications, published in prestigious journals from the JCR (Journal Citation Reports) list, namely:

1. Çako, E., Dudziak, S., Głuchowski, P., Trykowski, G., Pisarek, M., Borzyszkowska, A. F., ... & Zielińska-Jurek, A. (2023). *Heterojunction of (P, S) co-doped g-C_3N_4 and 2D TiO_2 for improved carbamazepine and acetaminophen photocatalytic degradation*. **Separation and Purification Technology**, 311, 123320, cited 50 times according to the *Scopus* database (accessed on 28.08.2026, without self-citations) - constituting Chapter III of the dissertation,

2. Çako, E., Gomez-Polo, C., Trykowski, G., Pisarek, M., Sikora, K., & Zielińska-Jurek, A. (2026). *Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary $ZnFe_2O_4$/(P, S)-g-C_3N_4/Two-Dimensional TiO_2 Composite*. **ACS Omega**, 11, 7486, cited 0 times according to the *Google Schoolar* database (accessed on 28.08.2026) - constituting Chapter IV of the dissertation,

3. Çako, E., Gomez-Polo, C., Kowalkińska, M., Pisarek, M., & Zielińska-Jurek, A. (2026). *Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes*. **Chemical Engineering and Processing-Process Intensification,** 222, 110740, cited 1 time according to the *Scopus* database (accessed on 28.08.2026, without self-citations) - constituting Chapter V of the dissertation.

In this section, the Reviewer notes the absence of a short list of publications included in the doctoral thesis, which, in the Reviewer's opinion, should have been provided at the beginning of the dissertation rather than at the end. This is particularly relevant because, in the final part of the thesis, in the section "*Research activity related to dissertation*", the Candidate lists four scientific papers. Besides, the above-mentioned scientific publications pointed by the Reviewer as the thesis's core, the Candidate also includes the publication: Çako, E., Gunasekaran, K. D., Rajendran, S., & Zielińska-Jurek, A. (2024). *Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants degradation.* Water Resources and Industry, **31**, 100241, as a scientific paper related to the research activity related to the dissertation. However, this paper, being a literature review, was not included in the dissertation, submitted for review. Having in mind the selected statements of contribution to the scientific work of the co-authors, namely Dr. Kumaravel Dinesh Gunasekaran, Prof. Dr. Saravanan Rajendran, MSc. Çako, and Prof. Dr. DSc. Eng. Anna Zielińska-Jurek, the above-mentioned scientific work is reported as part of the dissertation.

1. Please explain why the publication by Çako, E., Gunasekaran, K. D., Rajendran, S., & Zielińska-Jurek, A. (2024). Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants

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degradation. Water Resources and Industry, 31, 100241, was not included in the doctoral dissertation as a part of it (in accordance with the description of the work content presented by the Candidate on pages 69-82), even though this work was listed in the section "Research activity related to dissertation".

The dissertation also presents a description of the results of research work, which is a continuation of experimental work on graphitic carbon nitride-based materials, used for the degradation of selected organic pollutants from the aquatic environment.

2. Why did the PhD student decide not to include a brief description of Chapter VI in Chapter II, subchapter 3, despite briefly describing the scientific papers that constitute the basis for Chapters III, IV, and V?

A detailed description of the structure of the doctoral dissertation. The dissertation begins with an Introduction (Chapter I), in which the Candidate describes with great precision the significant problems associated with global environmental pollution by pharmaceuticals, such as carbamazepine, ibuprofen, and acetaminophen, providing the concentrations of these organic compounds in samples, taken from selected water sources and/or from wastewater treatment plants. The presented values are really important for determining the levels of these organic compounds in the aquatic environment. Subsequently, the doctoral Candidate shows the ecotoxicological properties of aqueous solutions, illustrating in great detail values such as $LC_{50,\ 48\ h}$, $LC_{50,\ 96\ h}$, and $EC_{50,\ 96\ h}$ for carbamazepine and acetaminophen; however, the Reviewer did not find any corresponding data for ibuprofen.

3. Please define the data of $LC_{50,\ 48\ h}$, $LC_{50,\ 96\ h}$ for ibuprofenu in the view of selected biological models.

Afterwards, the Candidate describes the advanced oxidation processes used for micropollutants removal from aquatic environment, with particular emphasis on the combination of heterogeneous photocatalysts with advanced oxidation methods or with an external magnetic field. It should be highlighted that detailed description of the aforementioned methods of contaminant removal made by Candidate is noteworthy; however, it might be worthwhile to present the most important characteristics of a given contaminant removal method in the form of a separate Table.

Particular attention should also be given to the detailed description of possibilities of application carbon nitride-based materials in the advanced oxidation processes for micropollutants removal. This subsection was prepared by Candidate in an orderly manner, however, minor editorial errors could be found in some part of the text. Mentioned editorial errors are associated with the interchangeable use of oxide names and oxide symbols, instead of consistent use of a single, clearly defined nomenclature within the dissertation. This part is finished by the Reference's list, however, in the Reviewer's opinion not in the all cases of references, the full bibliographic data were given. This not effect on the possibilities of locate the proper work in scientific databases such as e.g. Scopus or WoS, however, might constitutes an inconsistency (references no. 13, 16, 67, 70, 127, 131, 132).

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In summary, the Introduction to the dissertation were presented in the clear and reliably manner, however, additional presentation in the form of Table *e.g.* the properties of the defined method of pollutants' removal would be highly appropriate.

In the Chapter II, the PhD Student shows *i.e.,* the scope, objectives, and methodology. According to the provided synthesis' protocols of chemical compounds,

4. Could you please clarify whether the synthesis procedures for g-C_3N_4 , (P,S)-g-C_3N_4, 2D TiO_2, and the (P,S)-g-C_3N_4/2D TiO_2 were developed in the laboratory or were they based on previously published literatures' reports?

5. With regard to the $ZnFe_2O_4$ material, how did the Candidate confirm that the material obtained exhibited magnetic properties (page 58)?

6. Please provide a Table giving for which materials the following experimental techniques such as XRD, BET, DR/UV-Vis, PL, XRF, FTIR, TEM, SEM, EDS, XPS, EIS, among others, were employed

Also, in following Chapter, the Candidate presents the content of the dissertation, indicating which articles constitute its core, while the experimental results are described in the final Chapter. The Reviewer has the following questions regarding this section:

7. Please specify the scientific novelty of the papers included in Chapters III–V in relation to the other scientific works described in the literature.

8. Please provide a comparison of the effectiveness of the developed methods for the removal of selected pharmaceuticals from aqueous solutions, in the view to the other methods described in the literature used for their removal.

9. Why did the Candidate choose $ZnFe_2O_4$ as a material with magnetic properties instead of e.g., Fe_3O_4?

10. How were the magnetic properties of the analyzed material determined?

11. With regard to page 80, on what basis were the positions of the bands in the FTIR spectrum assigned?

In summary to this part of the dissertation, I believe it was prepared in a thoughtful manner that also highlights the social importance of experimental works, conducting in the scientific team of Prof. Dr. DSc. Eng. Anna Zielińska-Jurek.

<u>Evaluation of the research papers forming the basis of the doctoral dissertation</u>

Since the doctoral dissertation was prepared in a hybrid format, below I present an evaluation of the scientific papers (Chapters III–V) as well as the unpublished research findings (Chapter VI) that form the basis of the doctoral dissertation.

Research article by Çako, E., Dudziak, S., Głuchowski, P., Trykowski, G., Pisarek, M., Borzyszkowska, A. F., ... & Zielińska-Jurek, A. (2023). *Heterojunction of (P, S) co-doped g-C_3N_4 and 2D TiO_2 for improved carbamazepine and acetaminophen photocatalytic degradation*. **Separation and Purification Technology**, 311, 123320, describes the synthesis of a new type of photocatalyst based on carbon graphitic nitride, co-doped with phosphorus and sulfur, incorporated into the structure of two-dimensional titanium(IV) oxide, used for the solar-driven degradation of carbamazepine and acetaminophen, as examples of compounds resistant to biodegradation. The resulting photocatalyst was characterized in detail

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using a range of experimental techniques, including XRD, FTIR, PL, DR/UV-Vis, XPS, and TEM. Afterwards, the potential applications of the developed photocatalyst for the removal of carbamazepine and acetaminophen were compared. The reactive species responsible for the degradation of these organic compounds were also defined. The degradation products were further identified using LC-MS, and the obtained results were compared with DFT calculations. The presented study is particularly important, because it describes the characteristics of the developed photocatalyst in great detail and identifies and explains its potential applications in the removal of carbamazepine and acetaminophen. **With regard to this work, I ask the Candidate to answer the following questions:**

- *12. Given the possibility of using the photocatalyst for up to six cycles of degradation, how, if at all, could the durability of the resulting photocatalyst be increased?*
- *13. Was the S and P quantitative content determined in the tested samples?*
- *14. Referring to Fig. 7, why was 350 nm chosen as the excitation wavelength?*

In the paper by Çako, E., Gomez-Polo, C., Trykowski, G., Pisarek, M., Sikora, K., & Zielińska-Jurek, A. (2026). *Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary $ZnFe_2O_4$/(P,S)-g-C_3N_4/Two-Dimensional TiO_2 Composite*. **ACS Omega**, 11, 7486, describes a dual approach to the effective photodegradation and mineralization of carbamazepine, with the use of a ternary $ZnFe_2O_4$/(P,S)-*g*-C_3N_4/two-dimensional TiO_2 composite. The research presented in this scientific publication was conducted with the utmost precision, as evidenced by the use of numerous experimental techniques to characterize the obtained materials. From an economic standpoint, it is extremely important to determine the possibility of reusing the materials over several cycles, which is discussed in this paper. Furthermore, it is economically important to calculate the costs of conducting the processes; in this case, the purification costs associated with photocatalysis, persulfate-assisted catalysis, as well as the use of persulfate alone. In this study, a comprehensive research cycle was presented, beginning with the synthesis of materials, their characterization, determining the possibility of their application for carbamazepine degradation, explaining the mechanisms and showing the carbamazepine degradation path as a result of using the appropriate material, as well as determining the suitability for reuse and costs defining.

15. With regard to Fig. 5 and Fig. 6, how many times were analyses performed to determine the effect of the masking compound and to measure the hydroxycoumarin content?

In turn, in the paper by Çako, E., Gomez-Polo, C., Kowalkińska, M., Pisarek, M., & Zielińska-Jurek, A. (2026). *Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes*. **Chemical Engineering and Processing-Process Intensification,** 222, 110740, the Authors clearly demonstrate the potential for using photocatalysts to facilitate the degradation of ibuprofen as well as methyl orange with the assistance either an external magnetic field or persulfate. Noteworthy is the comprehensive research approach, which

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involved a detailed characterization of the physicochemical, granulometric, and magnetic properties of the relevant materials. It is also important to determine the influence of each component of the resulting composite on the efficiency of ibuprofen and methyl orange degradation. The research conducted provided answers to questions regarding the selection of the most effective method for removing contaminants from aqueous solutions; however, I would appreciate further clarification.

- *16. How was the QSAR model used to determine acute and chronic toxicity?*
- *17. With regard to Fig. 4, how many times were the experiments conducted to determine the effect of a magnetic field and photocatalysis on the degradation of methyl orange and ibuprofen?*

In Chapter VI, the Candidate describes the functionalization of the surface of hydroxylated g-C_3N_4 to obtain a frustrated Lewis pair structure. For this purpose, the Candidate selected oxygen-deficient ZnO(OH). The granulometric properties od used in the following experiment compounds were characterized in details using experimental techniques such as XRD, FTIR, FESEM, and XPS. Subsequently, the resulting system, as well as its individual components, were used to determine the photocatalytic degradation of carbamazepine, among others. Please clarify:

- *18. In accordance to Fig. 6.6, please propose a mechanism for the removal of carbamazepine using the ZnOH-V_o/g-CN-OH.*

Following this section of the thesis, the Candidate included Conclusions, where the most important achievements of dissertation were presented.

Final conclusions

Revised doctoral thesis entitled *„Hybrid g-C_3N_4-based photocatalysts for degradation of pharmaceutical micropollutants*”, is an innovative scientific approach on the development of innovative hybrid photocatalysts based on *g-C_3N_4* for the removal of selected micropollutants from the aquatic environment. The most important achievements, presented in the dissertation, are:

- the synthesis, characterization, and application of the (P,S)-g-C_3N_4/two-dimensional TiO_2 photocatalyst for the solar-driven degradation of carbamazepine and acetaminophen,

-the production, evaluation of properties, and application of a ternary $ZnFe_2O_4$/(P,S)-g-C_3N_4/two-dimensional TiO_2 for the effective photodegradation and mineralization of carbamazepine, with determining the stability of the used material, identifying the degradation products of carbamazepine, and determining the costs of the photocatalytic process conduction, the costs of persulfate-assisted photocatalysis, and the costs of persulfate application,

-preparation, characterization, and demonstration of the applicability of $ZnFe_2O_4$/(P,S)-g-C_3N_4/two-dimensional TiO_2 as a photocatalyst for the degradation of ibuprofen and methyl orange, enhanced by an external magnetic field or by persulfate,

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-obtaining a frustrated Lewis pair structure for the photocatalytic degradation of carbamazepine.

In my opinion, the doctoral dissertation submitted for evaluation meets the substantive and formal requirements of the Act of July 20, 2018, on Higher Education and Science (consolidated text: Journal of Laws of 2024, Item 1571, as amended) and **I hereby request that it be admitted to the subsequent stages of the doctoral proceedings.**

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