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REVIEW

of the doctoral dissertation by MSc Eng. Elvana Cako
Title of doctoral dissertation: "Hybrid g-C_3N_4-based photocatalysts for degradation of pharmaceutical micropollutants"
prepared at the Department of Process Engineering and Chemical Technology,
Faculty of Chemistry, Gdańsk University of Technology
Supervisor: Prof. Anna Zielińska-Jurek, PhD, DSc, Eng.

The reviewed doctoral dissertation concerns the development and characterization of advanced photocatalytic materials based on graphitic carbon nitride (g-C_3N_4) and their application in the degradation of pharmaceutical micropollutants in the aquatic environment.

Aquatic ecosystems play a fundamental role in sustaining life on Earth, serving not only as a source of drinking water but also as the basis for numerous natural and economic processes. Contemporary threats associated with anthropogenic water pollution, including the presence of pharmaceuticals, mean that preventive measures alone are insufficient to ensure the appropriate quality of water resources. Therefore, the subject of the dissertation is timely and falls within the dynamically developing field of research on modern water treatment technologies, particularly advanced oxidation processes (AOPs), which are regarded as one of the most promising methods for the elimination of organic micropollutants from aquatic environments.

The dissertation was prepared in English and includes abstracts in both Polish and English, as well as a list of abbreviations used throughout the dissertation together with their explanations. Remark: two different abbreviations are assigned to the same term: "SR-AOP – Persulfate-based advanced oxidation processes; PS-AOP – Persulfate-based advanced oxidation processes".

The dissertation follows a mixed (hybrid) structure, combining elements of a traditional doctoral thesis, including a literature review, research objectives and methodology, with a publication-based presentation of the author's original research results. Such a format is consistent with Article 187(3) of the Act on Higher Education and Science, which permits a doctoral dissertation to take the form of either a scientific monograph or a collection of thematically related scientific publications.

In Chapter I, the Author presents the current state of knowledge regarding water contamination by micropollutants, with particular emphasis on advanced oxidation processes, photocatalysis, and graphitic carbon nitride-based materials used for the removal of pharmaceuticals from aquatic environments. This chapter provides a solid introduction to the Author's own research and concludes with a summary and a list of cited references. While reading the literature review section, several comments came to mind:

1. The dissertation presents a broad literature review; however, in the summary section it would be worthwhile to place greater emphasis on comparative and critical aspects. In particular, it would be valuable to compare the effectiveness of the discussed AOPs, different approaches to g-C_3N_4 modification, and the obtained effects in relation to potential practical applications. Such an analysis could be illustrated using the removal of a selected pharmaceutical compound, for example carbamazepine.

2. Figure 2 presents monitoring results concerning pharmaceutical concentrations in surface waters, marine waters, biologically treated wastewater (WWTP effluents), drinking water, and groundwater within European Union countries. A lack of consistency in the presentation of numerical data is noticeable, as values are reported using different numbers of significant figures. The Author is kindly requested to explain the rationale behind the adopted level of precision. Is it related to the detection and quantification limits of the analytical methods employed, or is it a consequence of averaging data originating from different literature sources?

3. In the description of the classification of toxicity (pages 15 and 16) of pharmaceuticals and their derivatives toward aquatic organisms, information regarding the units in which LC50, EC50 and ChV values are expressed appears to be missing. Providing only numerical ranges ($>10^2$, 10^2–10^1, 10^1–10^0, $\leq 10^0$) without specifying whether they refer to mg dm^{-3} or other units makes interpretation of the results and comparison with literature data more difficult. Although it may be assumed that these units are commonly used and readily understood by specialists involved in ecotoxicity assessment, a doctoral dissertation should be written in a manner that is

as clear and accessible as possible, including for readers outside a narrow specialization. Therefore, this information should be specified more explicitly in the text.

4. On page 32, the Doctoral Candidate writes: "The introduction of iron(II,III) oxide Fe_2O_3 into g-C_3N_4 successfully formed a heterocomposite with enhanced visible-light absorption, improved charge-carrier separation, and increased reusability over six consecutive cycles [104]."The above statement contains a terminological inaccuracy, as Fe_2O_3 has been incorrectly identified as iron(II,III) oxide, whereas it corresponds to iron(III) oxide. Iron(II,III) oxide has the formula Fe_3O_4.

The next chapter presents the scope of the research, the research objectives of the dissertation, and the adopted research methodology. The scope of the research has been clearly defined and focuses on the development of novel photocatalytic materials based on graphitic carbon nitride (g-C_3N_4) for the removal of pharmaceutical compounds from aquatic environments. The logical connection between the main objective and the proposed research hypotheses deserves special recognition. The Author proposed a comprehensive approach involving three material modification strategies: non-metal doping, heterojunction formation, and chemical functionalisation. The six research hypotheses form a coherent research pathway, leading from the modification of the g-C_3N_4 structure and improvement of its optoelectronic properties, through the construction of advanced heterostructures and magnetic systems, to the development of frustrated Lewis pair (FLP) materials and their integration with persulfate activation processes. Particularly valuable is the inclusion of application-oriented aspects, such as the possibility of photocatalyst recovery using a magnetic field and the enhancement of its stability and reusability.

After defining the research objectives, the Author presented a clear and logically organised research plan, illustrated schematically in Figure 9. This plan enables the tracking of subsequent stages of the work and the assessment of the degree of fulfilment of the proposed research hypotheses.

The research methodology was developed very comprehensively and includes:

• advanced material synthesis methods (calcination, hydrothermal methods, freeze-drying),

• a wide range of characterisation techniques (XRD, BET, UV-Vis, FTIR, XRF, Raman, XPS, TEM/SEM, PL),

• electrochemical and optical studies,

• photocatalytic activity tests,

• numerical modelling and DFT calculations.

In my opinion, the presented methodology is adequate for achieving the stated objectives and enables a comprehensive assessment of the influence of individual modifications on the photocatalytic activity of the materials. It is also worth emphasising that, in addition to enhancing the degradation efficiency of micropollutants, mechanistic aspects related to charge carrier separation, generation of reactive oxygen species, and activation of oxidants were also considered. Such a broad approach should be assessed very positively, as it enables a multidimensional analysis of the investigated systems.

Comments regarding this part of the dissertation:

1. In the paragraph describing the application of WDXRF for the analysis of P and S in graphitic carbon nitride g-C_3N_4, the Author refers to the standard PN-EN 15308:2010; however, this standard does not concern the methodology of analysis using this technique. The cited standard relates to the determination of polychlorinated biphenyls (PCBs) using gas chromatography. The Author is kindly asked to provide the appropriate standard.

2. In Section 2.3, it is stated that "samples were collected at time intervals of −30, 0, 15, 30, 60 and 120 min". It appears that these values refer rather to sampling time points than to time intervals between successive measurements. It would be advisable to clarify this wording.

3. The effect of PS-AOP processes was investigated using two different activators: persulfate (PDS) for the $ZnFe_2O_4$/(P,S)-g-C_3N_4/2D TiO_2 system and peroxymonosulfate (PMS) for the ZnO(OH)-V_0/g-C_3N_4(OH) system. The Author is kindly requested to justify the choice of different oxidants for the individual systems. Was this decision based on the properties of the obtained photocatalysts, preliminary studies, or literature reports? The use of different activators may hinder the direct comparison of the efficiency of individual materials and the assessment of the influence of the photocatalyst structure itself on the process.

4. In Equation 2 on page 65, used to calculate the synergy index, the meaning of the symbols employed is not explained. Although it may be inferred that k denotes the reaction rate constant, all quantities appearing in the equation should be defined in the text in order to ensure clarity and unambiguity.

5. The description of the procedure used for determining leached iron requires clarification. According to the manufacturer's documentation, the Hach LCK 521 test is based on the 1,10-phenanthroline method, whereas the dissertation refers to a reaction with ferrozine. The ferrozine method is indeed widely used for the determination of Fe(II) and can be applied to the analysis of iron in aqueous solutions. However, the issue is not whether ferrozine can be used, but whether it was actually used in the LCK 521 test.

This chapter concludes with Section 3, in which the Author summarises the experimental part of the dissertation presented in Chapters 3, 4 and 5. It serves as a guide to three original scientific publications addressing the formulated research problems. These papers have been published in journals indexed in the JCR database, with a total Impact Factor of 17.2. In every publication, the Doctoral Candidate is the first author, and the submitted declarations of the co-authors confirm her leading role in conducting the research and preparing the results.

Chapter 3 consists of the publication entitled "Heterojunction of (P, S) co-doped g-C_3N_4 and 2D TiO_2 for improved carbamazepine and acetaminophen photocatalytic degradation", published in 2023 in Separation and Purification Technology. This work is devoted to the synthesis and characterisation of (P,S)-g-C_3N_4/TiO_2 heterocomposites intended for the photocatalytic degradation of pharmaceuticals under solar irradiation. It was demonstrated that co-doping g-C_3N_4 with phosphorus and sulfur, combined with the formation of a heterojunction with nanosheet TiO_2 structures, leads to improved light absorption, more efficient charge carrier separation, and enhanced photocatalytic activity. Structural and spectroscopic studies confirmed the successful preparation of the target materials, whereas PL and EIS analyses indicated improved charge transfer within the heterostructure. The best-performing composite enabled complete degradation of carbamazepine within 30 min and acetaminophen within 60 min. Analysis of the degradation mechanism using LC-MS techniques and DFT calculations made it possible to identify intermediate products and propose degradation pathways for the studied compounds, which in my opinion is highly valuable. Particular emphasis should also be placed on the fact that the proposed TiO_2/(P,S)-g-C_3N_4 heterocomposite was obtained using relatively simple and potentially scalable synthesis methods and exhibited high activity and stability.

Chapter 4 represents the publication entitled "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", published in 2026 in ACS Omega. This work concerns the development of a $ZnFe_2O_4$/(P,S)-g-C_3N_4/2D TiO_2 heterocomposite designed for the photocatalytic degradation of carbamazepine. Due to its magnetic properties, this composite can be relatively easily removed after the process. It was demonstrated that the combination of zinc ferrite, co-doped g-C_3N_4, and nanosheet TiO_2 improves UV-Vis light absorption, enhances charge carrier separation, and enables facile recovery of the photocatalyst using a magnetic field. The highest activity was observed for the composite containing 10% TiO_2. The additional application of persulfate significantly increased process efficiency, allowing 99.5% removal of carbamazepine within 15 minutes and achieving 74% mineralisation. Mechanistic studies indicated the important role of hydroxyl, sulfate, and superoxide radicals. The photocatalyst retained high stability and reusability, which, together with its easy recovery, highlights its application potential in the treatment of waters contaminated with persistent pharmaceutical pollutants.

Chapter 5 represents of the publication entitled "Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes", published in 2026 in Chemical Engineering and Processing – Process Intensification.

This chapter is devoted to the comparison of two methods for intensifying the photocatalytic degradation of ibuprofen: persulfate-assisted photocatalysis and photocatalysis assisted by an external magnetic field. The studies were conducted using the $ZnFe_2O_4$/(P,S)-g-C_3N_4/2D TiO_2 heterocomposite, whose structural, optical and magnetic properties were confirmed by a series of physicochemical characterisation techniques. It was demonstrated that heterojunction formation improves UV-Vis light absorption and suppresses charge carrier recombination.

The obtained heterocomposite enabled complete degradation of ibuprofen within 60 minutes, achieving higher efficiency than its individual components. The application of persulfate further accelerated the process, resulting in complete degradation within 30 minutes and increasing the mineralisation degree to 66%. Sulfate, hydroxyl, and superoxide radicals were shown to play the predominant role in the degradation process. The application of a magnetic field improved process kinetics by enhancing charge carrier separation; however, this effect was weaker than that observed for persulfate activation.

The comparative analysis made it possible to identify the advantages and limitations of both process-intensification strategies. The developed heterocomposite was characterised by high activity, recoverability resulting from its magnetic properties, and potential applicability for the efficient removal of persistent pharmaceutical pollutants from water.

Chapter 6 is devoted to the development of a novel photocatalytic heterostructure of the frustrated Lewis pair (FLP) type, composed of hydroxylated graphitic carbon nitride g-C_3N_4(OH) and oxygen-vacancy-containing zinc hydroxyoxide ZnO(OH)-V_o. The Doctoral Candidate proposed an innovative approach to charge carrier separation based not on conventional band alignment but on electrostatic interactions between Lewis acid and Lewis base centres.

Structural, spectroscopic and electrochemical investigations confirmed successful surface functionalisation and the formation of the FLP heterostructure. It was demonstrated that hydroxylation of g-C_3N_4 and the introduction of oxygen vacancies into ZnO(OH) improve light absorption, facilitate charge transport, and suppress electron-hole recombination. DFT calculations confirmed the existence of strong interfacial interactions and the formation of an internal electric field responsible for efficient charge carrier separation.

The developed material exhibited very high activity in the photocatalytic degradation of carbamazepine, enabling its complete removal within 60 minutes. The additional application of peroxymonosulfate (PMS) reduced the time required for complete degradation to 30 minutes. Mechanistic studies revealed a significant contribution of hydroxyl, sulfate, and superoxide radicals. The obtained system was also characterised by good stability and reusability without significant loss of activity.

The presented results confirm that rational surface functionalisation combined with defect engineering may lead to the development of a new class of highly active FLP heterostructures, representing a promising alternative to conventional semiconductor heterojunctions in the removal of persistent pharmaceutical contaminants from water.

Summary

Chapters 3-6 present a coherent series of studies devoted to the design of modern photocatalytic materials intended for the removal of pharmaceuticals from water. The Doctoral Candidate demonstrated that appropriate modifications of g-C_3N_4, the formation of heterojunctions with nanostructured TiO_2, and the incorporation of zinc ferrite $ZnFe_2O_4$ lead to improved light absorption, more efficient charge carrier separation, and enhanced photocatalytic activity.

Particularly valuable are the studies on magnetic materials enabling easy photocatalyst recovery and the comparison of different process-intensification methods, such as persulfate activation and the application of a magnetic field. The novel FLP heterostructure concept also deserves special attention, in which charge separation occurs through Lewis acid-base interactions rather than through conventional band alignment.

The obtained materials were characterised by high efficiency in the degradation and mineralisation of pharmaceuticals, good stability, and the possibility of repeated use. The research results constitute a valuable contribution to the development of environmental photocatalysis and indicate the potential practical application of the developed systems in water treatment processes.

The summary highlights the advantages of all applied material modification strategies; however, it does not clearly indicate which of them had the greatest impact on improving photocatalytic activity. It would be worthwhile to attempt a comparison of the effectiveness of doping, heterojunction formation, incorporation of a magnetic component, and the FLP concept, and to indicate which of these strategies proved the most beneficial and what mechanistic factors were responsible. Such a synthetic comparison would facilitate the assessment of the actual contribution of individual modifications to the observed increase in photocatalytic activity.

Questions to the Doctoral Candidate

1. Which of the applied material modification strategies (doping, heterojunction formation, incorporation of a magnetic component, or the FLP concept) had the greatest impact on improving photocatalytic activity and why?
2. What are the possibilities for scaling up the synthesis of the developed materials and implementing them in real wastewater treatment systems?
3. Were the identified intermediate products of pharmaceutical degradation evaluated with respect to their environmental toxicity, and what conclusions can be drawn from such an analysis?

The above comments are of a discussion-oriented nature and in no way diminish the high scientific value of the dissertation, which constitutes an original and valuable research achievement in the field of photocatalytic removal of pharmaceutical micropollutants from aquatic environments.

Final conclusion

The reviewed doctoral dissertation constitutes a valuable scientific study of high substantive quality and significant cognitive importance. The work confirms the ability of MSc Eng. Elvana Cako to conduct independent scientific research, interpret the obtained results, and publish them in reputable scientific journals.

In my opinion, the doctoral dissertation submitted by MSc Eng. Elvana Cako, entitled "Hybrid g-C3N4-based Photocatalysts for Degradation of Pharmaceutical Micropollutants", satisfies the requirements laid down in Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science (Journal of Laws of 2024, item 1571, as amended). Accordingly, I recommend that the Candidate be admitted to the subsequent stages of the doctoral degree proceedings.