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REVIEW

of the Doctoral Dissertation of MSc Elvana Cako

"*Hybrid g-C_3N_4-based photocatalysts for degradation of pharmaceutical micropollutants*"

(Supervisor: Prof. dr hab. Anna Zielińska-Jurek)

The aim MSc Elvana Cako set for her doctoral dissertation was to develop and investigate multifunctional hybrid photocatalysts based on g-C3N4 and to apply them to the degradation of pharmaceutical micropollutants in the aquatic environment. The doctoral dissertation was carried out under the supervision of Prof. Anna Zielińska-Jurek, D.Sc. The dissertation is written in English. It consists of six chapters. It also includes an abstract in English and Polish, co-author declarations for the publications on which the doctoral candidate is a co-author, and a list of those publications. The whole totals 189 pages.

The first chapter is an introduction. In it, MSc Cako describes the global problem of water pollution and discusses advanced methods for removing micropollutants from water, with particular attention to heterogeneous catalysis and its combination with an external magnetic field. The doctoral candidate describes the introduction of EU Directive 2024/3019, which imposes an obligation to apply the so-called fourth treatment stage for wastewater. However, the physical methods proposed for this purpose, such as adsorption and reverse osmosis, are problematic and ineffective in the long run. Among advanced oxidation processes (AOPs), treating contaminated water with ozone or hydrogen peroxide is likewise problematic in practice. At this point, the doctoral candidate presents heterogeneous photocatalysis as the most promising approach to wastewater treatment at the fourth stage.

My attention is then drawn to the title of subsection 2.1, "Combining of heterogeneous photocatalysis with AOPs," given that heterogeneous catalysis itself belongs to this category of methods. This subsection presents examples of combining solid catalysts with ozone, ultrasound, and electrochemical methods. Here, we also learn how the peroxydisulfate ion can

be activated to the sulfate radical (e.g., via carbon materials or UV radiation). The next subsection (2.3) describes the combination of heterogeneous photocatalysis with an external magnetic field. Notably, the emphasis is not placed on the practical advantages (magnetic catalysts are easier to separate), but on the fact that applying an external magnetic field can suppress the recombination of photogenerated charge carriers and affect their migration through the spin polarization effect. Subsection 3 describes the use of carbon materials in advanced oxidation processes (AOPs) for micropollutant degradation. Here the doctoral candidate focuses on doping graphitic carbon nitride (3.1), forming heterojunctions (3.2), modifying g-C_3N_4 with spinel ferrites (3.3), and functionalizing its surface (3.4). The first chapter closes with a summary and a list of references. In this chapter I missed a description of, or an introduction to, the concept of frustrated Lewis pairs (FLPs). This concept is known primarily from organic chemistry, considerably less so in the context of heterogeneous photocatalysts. The term FLP first appears in the aims of the dissertation, without any prior mention. In my assessment, the literature review presented in Chapter I, aside from the exception noted above, constitutes a complete body of information that explains the research aims pursued further on, the methodology applied, and the significance of the scientific problem undertaken.

In the second chapter, the doctoral candidate presents the scope of the research, the aims, and the methodology. This is also where she summarizes the contents of the dissertation (Thesis content). The following three chapters (III–V) are reprints of research papers on which the doctoral candidate is a co-author. These are three experimental papers, published in well-regarded scientific journals: *Separation and Purification Technology (IF=9.1), ACS Omega (IF=5.2), Chemical Engineering and Processing - Process Intensification (IF=4.2).* MSc Cako is also a co-author of a review paper in *Water Resources and Industry (IF=8.7).* It should be emphasized that the doctoral candidate is the corresponding author on all four papers, which attests to her substantial contribution to these publications. The final chapter, VI, describes research on surface functionalization and defect engineering in a frustrated-Lewis-pair-type heterostructure built from hydroxylated graphitic carbon nitride, g-C3N4(OH), and zinc oxide hydroxide with oxygen vacancies, ZnO(OH)-V_o.

I present my assessment of the dissertation under three headings: general comments, minor deficiencies, and questions to the doctoral candidate.

Comments:

1. In Chapter II, the description of the zeta potential analysis does not state the scattering angle used during the measurements – was it 173°, 90°, or 13°? This parameter can affect the final results and should therefore be included in the description of the research method.
2. The publications included in Chapters III–V come with supplementary materials, which are an integral part of each publication. The supplementary materials for the publications in Chapters IV and V have been included in the dissertation, but the supplementary material for the publication in Chapter III is missing.
3. It is worth noting that the doctoral candidate took part in two research internships (information on page 189). However, to properly assess this activity, the duration of each internship is not given.

Minor mistakes:

The DOI of the publication included in Chapter IV is https://doi.org/10.1016/j.wri.2024.100241, not "https://doi.org/10.1016/j.wri.2024.10024" as given in the dissertation.

The discussion of the results and their summary raise no objections. Reading the dissertation, however, prompted me to formulate a few questions, given below, which I ask the doctoral candidate to address.

Questions:

1. In the first chapter you discuss the presence of carbamazepine, acetaminophen, and ibuprofen in surface waters, seawater, wastewater, drinking water, and groundwater. You present a list of countries in which the concentrations of these pharmaceuticals pose an environmental risk (RQ > 1), including the United Kingdom, Switzerland, Poland, France, and Denmark. In your view, are these actually the countries where contamination by these pharmaceuticals is highest? Are there other factors that account for the highest recorded concentrations of carbamazepine, acetaminophen, and ibuprofen occurring specifically in these countries?
2. The optimal degradation of the pollutants studied by the doctoral candidate was achieved at a catalyst concentration of 1 g/L. Please comment on whether this value is high, low, or typical.
3. The doctoral candidate identified the main degradation products of the pollutants studied. For carbamazepine these were hydroxycarbamazepine and dioxocarbamazepine; for

acetaminophen, products with m/z 300.7, 167.5, and 167.5; and for ibuprofen, products with m/z 221, 269, 177, and 134. The doctoral candidate assessed the toxicity of the ibuprofen degradation products using ECOSAR modeling. Did the doctoral candidate carry out similar modeling for the degradation products of carbamazepine and acetaminophen? Alternatively, does the doctoral candidate know whether these compounds are more or less toxic than the parent pollutant? What experiment could the doctoral candidate propose to assess the toxicity of the degradation products experimentally?

In summary, I would like to highlight the broad scope of the research carried out by the doctoral candidate, covering the synthesis and physicochemical characterization of the photocatalysts, the evaluation of photocatalytic activity, the investigation of the photocatalytic mechanism, and the identification of degradation products. The doctoral candidate achieved the aim of the dissertation: she developed and investigated multifunctional hybrid photocatalysts based on g-C3N4 for the degradation of pharmaceutical micropollutants in the aquatic environment, and she confirmed the research hypotheses put forward.

I am fully convinced that the doctoral dissertation of Ms. Elvana Cako meets the statutory requirements for doctoral dissertations under the Act of 20 July 2018 – Law on Higher Education and Science (consolidated text: Journal of Laws of 2022, item 574, as amended). **I would ask that the High Council of the Discipline of the Faculty of Chemistry of Gdańsk University of Technology admit MSc Elvana Cako to the further stages of the proceedings for the conferral of the doctoral degree.**

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