UNIWERSYTET IM. ADAMA MICKIEWICZA W POZNANIU
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Review of the doctoral dissertation of M.Sc. Eng. Kirill Fedorov entitled:

„Degradation of organic water pollutants using hybrid cavitation-based advanced chemical processes" / "Degradacja organicznych zanieczyszczeń wody z zastosowaniem hybrydowych zaawansowanych procesów chemicznych wykorzystujących zjawisko kawitacji"

prepared at the request of the Chair of the Council of the Discipline of Chemical Sciences, Gdańsk University of Technology.

Subject of the Doctoral Dissertation

The development of civilization, together with industrialization and the continuous growth of industrial production, contributes to the growing scale of environmental problems. Aquatic ecosystems are particularly vulnerable, as increasing concentrations of various toxic and problematic chemical compounds are being observed in water environments. Of particular concern are the so-called refractory pollutants, i.e. substances characterized by high resistance to degradation and removal, which are typically eliminated from municipal and industrial wastewater only to a limited extent when conventional biological treatment processes are employed. In view of the growing awareness of the risks associated with the inefficient removal of these chemical compounds from wastewater, the scientific community continues to seek novel methods capable of achieving more effective elimination of such contaminants. The research presented in this doctoral dissertation clearly fits within this global research trend. It includes not only the development of new approaches for the removal of persistent organic pollutants from water, but also the identification of factors affecting their efficiency, and the recognition of possible limitations and practical challenges associated with their use. In my opinion, the research topic addressed in this dissertation is important from the perspective of fundamental research and fully justified in light of the increasing degradation of water resources.

General Information

The doctoral dissertation was prepared under the supervision of dr. hab. inż. Grzegorz Boczkaj, Associate Professor at Gdańsk University of Technology. The dissertation was written in English and prepared in the form of a monograph, beginning with a title page, author declarations, abstracts in Polish and English, acknowledgements, a table of contents, a list of figures, a list of tables, and a list of abbreviations. The main part of the dissertation consists of a literature review (48 pages), a description

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of the research objectives, a description of research methods and experimental conditions (10 pages), a results and discussion section (54 pages), and a final chapter presenting conclusions as well as future perspectives and the potential future development of hybrid processes (4 pages). The last sections present a summary of the doctoral candidate's scientific achievements and a list of literature references cited throughout the dissertation. The dissertation has been prepared in a careful, clear, and logically structured manner. Some minor errors are present, including punctuation errors, missing figure labels (e.g., Figure 11, p. 70), inconsistencies in figure captions (Figure 22, p. 86), or incomplete information regarding experimental conditions (e.g., the lack of information about reaction time in caption to Figure 8, p. 65). However, these minor issues do not affect the clarity of the content or the scientific value of the dissertation. The abstracts are concise, informative, and accurately reflect both the content of the dissertation and the subject of the research.

Evaluation of the Doctoral Dissertation

The first major section of the dissertation, presented as a literature review, briefly explains the need for wastewater treatment and provides a broad overview of the different treatment stages, ranging from physical and biological methods to chemical treatment approaches. Particular attention is given to advanced chemical processes that are directly related to the research presented in the dissertation, namely ozonation, sulfate radical-based oxidation methods, and chemical treatment methods involving sulfites and UV irradiation. This section clearly explains factors affecting the efficiency of the discussed methods, such as oxidant concentration, the pH of the aqueous matrix, and the presence of other chemical species, including organic matter and selected inorganic compounds (mainly anions commonly present in wastewater and water systems). The final part of literature review focuses on the phenomenon of cavitation and its practical applications, including water treatment, with particular emphasis on hybrid processes in which cavitation significantly improves the efficiency of contaminant removal in the presence of various oxidants, such as H_2O_2, ozone, and PMS. The literature review section is comprehensive, includes 235 literature references, and is scientifically sound and well prepared. This section contains a few minor inaccuracies, which do not affect its overall scientific quality or comprehensibility. One example is an inconsistency in the classification of adsorption methods, which are considered in one part as physical method and in another as chemical method. Another inconsistency concerns the preparation of carbon-based adsorbents, where the doctoral candidate states that these materials can be obtained by "calcination" at 900 °C. While the use of high temperature is fully justified, such processes are usually carried out under an inert atmosphere to prevent combustion or oxidation of the carbon material. The term calcination usually refers to heating at high temperature in an oxidizing atmosphere (e.g., air), which would typically result in oxidation of carbon-based materials. Nevertheless, this minor inaccuracy, which concerns a topic outside the doctoral candidate's main area of expertise, does not reduce the scientific value of the dissertation. I would like to emphasize that such comprehensive literature review demonstrates the author's broad knowledge of techniques and methods used in wastewater treatment. I do have some minor reservations regarding

the overall concept of this section, especially in relation to the specific subject of the doctoral research. In my opinion, too much attention is devoted to processes that are not directly investigated in the dissertation, such as physical and biological treatment methods. At the same time, the review provides only a relatively limited discussion of the rationale for selecting the model contaminants used in the study, the challenges associated with their removal, and previous research on hybrid processes involving cavitation. Consequently, the current literature review does not sufficiently highlight the main innovative aspects of the presented research in relation to the existing body of literature. At the same time, I would like to stress that, despite the above minor reservations, the author introduces the topic of cavitation in an interesting and competent manner, including its use in water treatment. This indirectly demonstrates very good understanding of this phenomenon by the author and its strong awareness of the potential application of cavitation for the removal of organic contaminants from aqueous matrices.

The research objectives are described in a clear and well-structured manner. The main challenge addressed in this dissertation was the evaluation of the effect of cavitation on the degradation efficiency of selected organic compounds in the presence of various oxidants, including PMS, PS, and ozone. An important part of the study was also the investigation of the effect of cavitation on the degradation efficiency of CLA in the presence of sulfites and UV irradiation, as a model process involving reactive chemical species with reducing rather than oxidizing properties. The conducted research aimed to improve the understanding of the factors affecting the degradation efficiency of selected model organic compounds in the investigated hybrid processes, to identify the key reactive species generated under specific reaction conditions and responsible for effective contaminant degradation, and to analyze the degradation pathways of the selected model compounds. Addressing these research questions required the application of numerous experimental techniques, which demanded not only knowledge and experience in the design and execution of water treatment experiments, but also expertise in analytical chemistry, especially in sample preparation methods. The research was therefore interdisciplinary in nature and demonstrates the doctoral candidate’s broad technical competence, as well as very good preparation for further independent scientific work. The scientific problems addressed in this dissertation are fully aligned with current international research trends in fundamental studies focused on the development and mechanistic understanding of innovative hybrid methods for the removal of organic contaminants from aqueous matrices.

The chapter describing the experimental conditions is concise and contains the key information necessary to understand the applied research methods and the way in which the contaminant degradation experiments were carried out. However, considering that the dissertation was prepared in the form of a monograph, some minor details that would support a more complete understanding of the experimental work are missing. For example, the purity of the chemicals is provided only for selected reagents. Moreover, the description of the experimental procedures does not specify which reagents were used to adjust the pH of the aqueous matrix before the experiments. I would like

to emphasize, however, that these comments refer only to minor technical details and do not imply that the experimental descriptions are incomplete or lack scientific rigor.

The presentation of the results is clear and divided into thematic subchapters. According to the author, these subsections are based on results obtained during the doctoral project and previously published in scientific papers in which, as stated in the dissertation, the doctoral candidate served as the first and leading author. This organization of the whole section is transparent and facilitates understanding of the presented content. At first impression, however, it somewhat resembles the structure commonly used in commentaries accompanying a collection of publications submitted as the basis for a doctoral degree. Each thematic subsection focuses on understanding the effect of cavitation on the efficiency of contaminant degradation in the presence of selected oxidant (precursor for the generation of reactive species), including PMS/PS, O_3, or O_3/SPC. The discussion is structured in a relatively consistent manner across the individual subchapters and comprises an analysis of contaminant degradation efficiency in the presence of selected oxidant and/or hybrid systems, a discussion of experiments with the use of various scavengers aimed at identifying the reactive species responsible for efficient pollutant degradation under selected reaction conditions, an evaluation of the influence of various anions and/or organic matter on pollutant removal rates, and an analysis of the proposed degradation pathways of the model contaminants. The conclusions presented are in general well supported by experimental data and an appropriate number of control experiments. Regarding the interpretation of the results and the conclusion concerning synergistic effects, I have only one point of concern related to the interpretation of the results presented in Figure 15 (page 76), associated with the US/PMS and US/PS processes in the presence of asphaltenes (ASPH). In this case, a synergistic effect is clearly observed for the degradation of benzene and toluene, as the degradation efficiency in the hybrid process is significantly higher than in the corresponding reference experiments. However, in the case of ethylbenzene and o-xylene, a very high removal efficiency was also observed in systems where ASPH was used in the presence of PMS/PS alone (ASPH/PS and ASPH/PMS) or under ultrasonic treatment alone (ASPH/US). This raises the question of whether the observed effect in this case should also be interpreted as a true synergistic effect, or rather as an additive effect. Based on the presented data, this question cannot be answered conclusively, as the conversion of ethylbenzene and o-xylene after the relatively long reaction time shown in the figure is already quite high for ASPH/PS, ASPH/PMS, and ASPH/US. I would like to emphasize that my intention is not to question the possible occurrence of synergism, but rather to indicate that, in my opinion, the presented experimental data are insufficient to conclusively support this conclusion. It is possible that the results obtained after shorter reaction times, or at lower conversion levels, would provide more convincing evidence. Nevertheless, this is the only one interpretative issue for which I have minor reservations. Overall, in my assessment, the results obtained by the doctoral candidate and presented in the dissertation provide a detailed and convincing explanation of the effect of cavitation on contaminant degradation under different reaction conditions, using various cavitation-inducing

approaches in combination with different oxidants. Overall, the presented results demonstrate that the hybrid processes enabled nearly complete mineralization when sufficiently long reaction times were applied. The obtained findings therefore indicate that the developed hybrid processes represent a highly promising approach for the removal of the investigated model contaminants from water. In addition, the results allowed for a detailed understanding of the influence of oxidant concentration and the presence of other ions or organic matter on contaminant removal efficiency, as well as the identification of possible degradation pathways of the investigated model compounds. In light of these findings, it can be concluded that all research objectives were achieved, providing valuable scientific data that advance fundamental knowledge on hybrid cavitation-based advanced chemical processes and their application for removing selected contaminants from aqueous matrices. One of the particularly interesting and scientifically innovative aspects of the dissertation is the demonstration that ASPH can be effectively used to enhance BTEX degradation in hybrid cavitation-based processes. In my opinion, the presented findings make a meaningful contribution to understanding not only the potential of the investigated hybrid processes, but also their limitations and practical constraints in the removal of selected contaminants. A certain limitation is the lack of experiments performed at relatively low contaminant concentrations and the lack of studies using real wastewater samples. However, considering the potential analytical challenges and the possible difficulties in interpreting more complex datasets, the scope of the performed research is fully justified, and the absence of such experiments should not be regarded as a significant weakness. Some reservations also concern the analysis and discussion of the proposed degradation pathways. The author proposes degradation pathways for the model compounds, but does not present experimental evidence that would allow direct verification of these interpretations or confirm the presence of the proposed intermediate products. In general, these considerations remain speculative and appear to be based on probable transformation pathways inferred from literature, although the relevant references supporting these assumptions are not explicitly provided. This is an approach sometimes encountered in interdisciplinary studies, where the main research objective is not a detailed mechanistic investigation of degradation pathways, but rather the identification of possible intermediates and the evaluation of their toxicity. In my opinion, when only a limited number of intermediate products have been identified, the interpretation of such results should be presented in a more cautious manner. Although the figure captions related to these results clearly indicate that the proposed pathways are only possible degradation routes, the discussion in the main text of the dissertation is considerably more definitive and, in my view, not fully justified based on the presented data.

The main part of the dissertation concludes with a chapter presenting conclusions and future perspectives. In my opinion, the structure of this section is somewhat unconventional and resembles a summary rather than a set of clearly formulated conclusions. In my opinion, the chapter lacks a clear and synthetic presentation of the main scientific achievements and the key conclusions resulting from the research carried out during the doctoral studies. Rather than merely summarizing the individual

chapters, it should provide an integrated scientific perspective on the investigated research problem and the overall findings of the dissertation. It should be emphasized that this critical remark refers primarily to the style in which the conclusions are presented and the insufficient emphasis given to the most important achievements, rather than to any deficiencies in scientific merit.

Assessment of the Doctoral Candidate's Scientific Achievements

When evaluating the dissertation as a whole, I would like to emphasize that the clarity of the discussion concerning the selection and optimization of the reaction conditions, together with the careful design of the control experiments necessary to verify the observed synergistic effects, demonstrates the doctoral candidate's scientific maturity and readiness to conduct research at a high scientific level, including the design and execution of experiments as well as the critical analysis of the obtained results. This is indirectly supported by the fact that the results were published in well-recognized journals such as *Chemical Engineering Journal* and *Journal of Environmental Management*, where clear novelty and high scientific quality are key publication criteria. The doctoral candidate's publication record includes six papers as first author, five papers as a co-author, and three book chapters related to the application of cavitation in water treatment processes. The doctoral candidate has also participated in two scientific conferences. This publication record is significant and can be considered outstanding for a researcher at such an early stage of his academic career.

Questions to the Doctoral Candidate

Despite the high scientific value of the research presented in the dissertation, the presented results raise several questions which, in my opinion, have not been fully clarified.

1. Scavenger experiments are widely recognized as a standard method for evaluating the role of different active species in degradation of contaminants. However, there are also reports highlighting certain limitations and uncertainties associated with this approach. Did the doctoral candidate consider supporting the conclusions drawn from the scavenger experiments with additional analytical techniques, such as EPR spectroscopy? Would it be feasible to apply EPR studies with spin-trapping probe molecules such as DMPO or TEMP to identify ROS generated under the reaction conditions used in this doctoral work?

2. The doctoral candidate observed a significant decrease in the efficiency of ASPH-based hybrid processes over consecutive reaction cycles; however, relatively little attention was given to the characterization of the spend solid material when explaining this loss of activity. Did you observe any significant mass loss of ASPH after its separation from the post-reaction mixture? Did you evaluate the stability of these samples by characterizing spend solid material separated from post-reaction mixtures? Did you check the possible degradation of ASPH and the release of the as-formed ASPH degradation products into water matrix using methods more sensitive than UV-Vis? I would appreciate the candidate's comments on this issue.

3. The prices of PS and Oxone used for the process cost estimation appear to be relatively low (p. 92). On what basis were these values estimated? Which suppliers and reagent purities were considered?

4. In the case of hybrid methods involving PS and PMS, I would appreciate the candidate's comments regarding the potential problems or environmental concerns associated with sulfate residues remaining in the treated water.

5. The doctoral candidate observed that the presence of humic acid (HA) significantly reduced the efficiency of CLA degradation in the HC/SO_3^{2-}/UV system, and this decrease was mainly explained by UV light absorption by HA, reduced light penetration, and lower generation of reactive species. Did the candidate also consider the possibility that HA reacted directly with the generated reactive species, thereby competing with CLA and contributing to the observed decrease in efficiency of CLA degradation?

6. In relation to Experimental Procedure 5, could the author clarify how the dissolved oxygen concentration was monitored to ensure effective removal of oxygen from the aqueous matrix after argon purging?

7. Is the observed dual role of ASPH in hybrid SR-AOPs attributable to the unique properties of this material, or could similar behavior also be expected for other solid materials capable of adsorbing the investigated model contaminants?

I would like to emphasize that these questions arise primarily from scientific curiosity and do not reduce the scientific value of the results or conclusions presented in the dissertation.

Final Recommendation

In conclusion, based on my overall evaluation of the doctoral dissertation written by M.Sc. Eng. Kirill Fedorov, I conclude that the reviewed dissertation makes a meaningful contribution to the development of the discipline of Chemical Sciences, particularly in advancing fundamental knowledge concerning the application potential, advantages, and limitations of hybrid cavitation-based advanced chemical processes, in which significant enhancement of contaminant degradation in aqueous matrices can be achieved. I also state without reservation that the dissertation under review meets all formal and customary requirements for doctoral dissertations. I therefore recommend that the Council of the Discipline of Chemical Sciences at Gdańsk University of Technology accept the dissertation and proceed with the next stages of the doctoral examination process.

Yours sincerely,

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Dokument podpisany przez
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