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Cracow, May 11, 2026

Review
of the doctoral dissertation written by Kirill Fedorov, M.Sc. Eng.
entitled "Degradation of organic water pollutants using hybrid cavitation-based advanced chemical processes"

Introduction and Formal Characteristics of the Dissertation

The formal basis for the present review is the letter issued by the Chair of the Council of the Discipline of Chemical Sciences at Gdansk University of Technology, Prof. Marek Tobiszewski, D.Sc. Eng., dated March 12, 2026 (Ref. No. 57 WCh/Dz/2025), informing me of my appointment, in accordance with the resolution of the Council of the Discipline of Chemical Sciences of Gdansk University of Technology dated March 10, 2026, to the position of reviewer of the doctoral dissertation submitted by Mr. Kirill Fedorov, M.Sc., Eng. The aforementioned letter further stated that the dissertation had been prepared under the supervision of Prof. Grzegorz Boczkaj, D.Sc. Eng., successfully passed verification in the anti-plagiarism system, and that the doctoral degree would be conferred in the field of *exact and natural sciences* within the discipline *of chemical sciences*. The letter was accompanied by the doctoral dissertation in the form of a monograph, its electronic version (CD), and information concerning the principles governing the distinction of doctoral dissertations.

The reviewed doctoral dissertation concerns investigations into hybrid cavitation-assisted advanced chemical processes applied to the degradation of organic contaminants occurring in the aquatic environment. This dissertation presents the development and evaluation of hybrid processes combining either acoustic cavitation (AC) or hydrodynamic cavitation (HC) with advanced oxidation processes (AOPs), in which ozone (O_3) or sulfate radicals ($SO_4^{\bullet-}$) were employed for the degradation of compounds belonging to the BTEX group as well as 1,4-dioxane, an industrial organic solvent primarily used in the manufacture of paints, varnishes, resins, waxes, cellulose derivatives, and related products. In the subsequent stage of the study, HC was integrated with an advanced reduction process (ARP), involving the sulfite/UV system ($SO_3^{\bullet -}$/UV), to degrade clofibric acid (CLA), which is known to be an active metabolite of fibrate-class pharmaceuticals such as clofibrate and etofibrate, commonly administered to reduce blood lipid levels. The dissertation presents the results of investigations into the effects of (***i***) the pH of the reaction medium, (***ii***) the molar ratio of radical precursor to target contaminant, and (***iii***) the presence of inorganic anions. Furthermore, the dominant radical species were identified on the basis of radical quenching experiments, while degradation pathways of the investigated contaminants were proposed based on the identification of intermediate products using GC-MS and HPLC-UV/DAD analytical techniques. The results obtained and presented in the doctoral dissertation demonstrated that cavitation plays a crucial role in reagent activation and in the intensification of AOP and ARP processes, giving rise to a synergistic effect. In the HC/ARP system, the presence of reactive reducing species was confirmed, and their reactivity toward CLA was further supported by theoretical calculations.

The doctoral dissertation submitted for evaluation is an original monograph containing a comprehensive description of the research planned and conducted by the doctoral candidate, as well as the results obtained. The dissertation is complemented by a review of the relevant literature and a discussion of the research findings. An integral part of the dissertation consists of appropriately formulated conclusions and an outline of perspectives for further, academically interesting research. The dissertation presents the results of studies on cavitation-based processes (including their modifications), derived from five scientific publications to which the doctoral candidate made a significant contribution:

K. Fedorov, X. Sun, G. Boczkaj, Combination of hydrodynamic cavitation and SR-AOPs for simultaneous degradation of BTEX in water, *Chemical Engineering Journal*, 417, 2021, 128081, IF 16.74, DOI: https://doi.org/10.1016/j.cej.2020.128081.

K. Fedorov, M. Plata-Gryl, J. Ali Khan, G. Boczkaj, Ultrasound-assisted heterogeneous activation of persulfate and peroxymonosulfate by asphaltenes for the degradation of BTEX in water, *Journal of Hazardous Materials*, 397, 2020, 122804, IF 10.58, DOI: https://doi.org/10.1016/j.jhazmat.2020.122804.

K. Fedorov, L. Kong, C. Wang, G. Boczkaj, High-performance activation of ozone by sonocavitation for BTEX degradation in water, *Journal of Environmental Management*, 363, 2024, 121343, IF 8.4, DOI: https://doi.org/10.1016/j.jenvman.2024.121343.

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K. Fedorov, M. P. Rayaroth, N. S. Shah, G. Boczkaj, Activated sodium percarbonate-ozone (SPC/O3) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water, *Chemical Engineering Journal*, 456, 2023, 141027, IF 13.3, DOI: https://doi.org/10.1016/j.cej.2022.141027.

K. Fedorov, C. Wang, N. S. Shah, G. Boczkaj, Boosting the radicalinduced reductive degradation of clofibric acid in water: Synergistic effect of SO_3^{2-}/UV and hydrodynamic cavitation (HC), *Journal of Environmental Management*, 391, 2025, 126506, IF 8.4, DOI: https://doi.org/10.1016/j.jenvman.2025.126506.

The analysis of the statements regarding authorship and the contributions of the individual authors (included at the end of the publications) demonstrates that the doctoral candidate significantly contributed to each publication through, among others: the development of the research concept and methodology, the design and validation of analytical methods, the performance of experimental studies, the collection, analysis, interpretation, and visualization of research data, and the preparation of both preliminary and final versions of the manuscripts. The doctoral candidate also participated in manuscript formatting and content revision aimed at improving readability and scientific accuracy. Furthermore, in all publications, the doctoral candidate is listed as the first author, and the articles have been published in high-impact scientific journals such as *Chemical Engineering Journal*, *Journal of Hazardous Materials*, and *Journal of Environmental Management*.

Formally, the doctoral dissertation contains 146 pages and is divided into seven chapters, including a list of the doctoral candidate's scientific achievements and the bibliography. The dissertation contains 44 figures, 6 tables, and 255 literature references, as well as a list of abbreviations and acronyms, which facilitates the reading and comprehension of the thesis.

Evaluation of the Aim and Subject Matter of the Doctoral Dissertation

When assessing the aim and subject matter of the doctoral dissertation, it should be noted that the growing global demand for high-quality water, driven by the dynamic development of industry and the exponential increase in population, currently represents one of the key challenges of contemporary science. Additionally, it should be emphasized that the problem of water resource scarcity is further exacerbated by widespread anthropopression manifested by the presence of anthropogenic chemical contaminants in the hydrosphere. In this context, the identification and implementation of highly efficient methods for the removal

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of pollutants from water and wastewater, as well as their monitoring in the aquatic environment, are critical for ensuring long-term hydrological security. Wastewater treatment methods are selected depending on the types of contaminants present and may include physical, chemical, and biological approaches (e.g., anaerobic methane fermentation, which removes a substantial organic load with simultaneous biogas production, combined with posttreatment under aerobic conditions using activated sludge or biological filters, ensuring effective removal of nitrogen and phosphorus compounds). In practice, several methods are typically combined to achieve increased treatment efficiency. However, conventional methods or their combinations do not always provide sufficient effectiveness, which is associated with the limited susceptibility of certain contaminants to removal or biodegradation. These limitations are particularly evident in the case of specific industrial wastewaters, but they also concern municipal wastewater, which contains micropollutants, i.e., substances occurring in the aquatic environment at low concentrations (from ng/L to μg/L), including pharmaceuticals and personal care products, per- and polyfluoroalkyl substances (PFAS), pesticides, biocides, plasticizers, phthalates, and others.

The issue in question requires attention to at least three aspects: (***i***) conventional biological wastewater treatment plants are not designed to remove these contaminants, as a result of which they enter rivers and lakes in varying concentrations; (***ii***) these substances accumulate in the tissues of living organisms, leading to biomagnification along the trophic chain; and (***iii***) even trace amounts of certain compounds may mimic or block hormones, causing feminization in fish or fertility disorders in mammals.

Consequently, the identified and intensively studied areas of the negative impact of micropollutants on human health include (***i***) endocrine disruption, (***ii***) the global spread of antimicrobial resistance, and (***iii***) increasing organ toxicity and neurotoxicity associated with long-term exposure. Therefore, the current strategy of the European Union is based on a shift from the classical control of basic sanitary parameters of wastewater towards a "*zero pollution*" paradigm and the development of "*water resilience*" in the context of observed environmental changes. This includes the mandatory introduction of tertiary and quaternary wastewater treatment stages, the extension of producer responsibility schemes, the implementation of pollution prevention strategies at the source (including REACH restrictions on microplastics), and the introduction of harmonized analytical methodologies for the

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identification of previously unmonitored substances, such as total PFAS, endocrine-disrupting compounds, and microplastics.

The doctoral candidate formulated the research aims and objectives presented below.

1. Assess the effectiveness of single and combined processes for the degradation of selected water pollutants and determine the role of cavitation in the developed processes.
2. Evaluate the effect of operating parameters, such as oxidant/reductant concentration and solution pH, on the degradation efficiency of pollutants and interpret the results.
3. Examine the effect of common inorganic ions on the degradation efficiency of the developed processes.
4. Verify the presence of radical species via a quenching method selecting specific scavenging agents. Elucidate the predominant radical species responsible for the degradation of the pollutant. Identify the transformation products using GC-MS and propose a reaction mechanism to describe the degradation pathway.
5. Evaluate the potential of HC in ARPs based on studies on combined HC/SO_3^{2-}/UV and verify the reductive pathway of CLA degradation using DFT calculations.

In the context of the environmental conditions outlined above, I have no doubts that the aims, scope, and subject matter of the doctoral dissertation have been formulated correctly and are fully justified, not only from a scientific perspective but also in the context of contemporary challenges in environmental engineering as well as global socioeconomic problems. I would like to explicitly emphasize that the research problem undertaken by the doctoral candidate concerning the degradation of contaminants in the aquatic environment is fully aligned with current research priorities and the dynamically evolving legislative policy of the European Union.

Furthermore, it should be noted that the formulated research objectives are characterized by a high degree of innovativeness, and their implementation holds significant application potential. The subject matter of the dissertation is highly original and demonstrates the doctoral candidate's ability to adopt a comprehensive approach to the development of research concepts, methodologies, and the planning of scientific investigations.In this context, undertaking the implementation of the formulated research tasks and addressing the original scientific problems is assessed as purposeful and fully justified.

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Assessment of methodological correctness and research competences

In Chapter 3, the doctoral candidate presents the applied research methodology, describing five experimental procedures, namely, HC-SR-AOPs, AC-SR-AOPs, AC-O_3-AOPs, and HC-O_3-AOPs. In addition, the candidate provides a thorough and precise description of sample preparation methods as well as the analytical techniques used for the determination of the investigated contaminants, including GC-FID, GC-MS, UHPLC, UHPLC-UV-DAD, as well as methodologies for experimental design and data analysis using CCD/RSM, together with the potential application of DFT calculations. Both the research methodology and the analytical and computational procedures are described in great detail. The planned research methodology is characterized by a high level of sophistication and strong logical coherence. The applied approaches, i.e., the combination of hydrodynamic cavitation and acoustic cavitation with advanced oxidation and reduction processes, constitute an optimal solution employed by the doctoral candidate for the degradation of the investigated contaminants. The selection of matrices and model pollutants of varying chemical structures enabled the execution of experiments that are highly valuable from a scientific and exploratory perspective, leading to well-founded and reliable scientific conclusions. The detailed methodological description ensures the reproducibility of the conducted experiments. The doctoral candidate utilized 255 literature sources which are state-of-the-art and appropriately selected without raising any reservations. The candidate refers to the latest scientific reports and makes use of publications from high-impact scientific journals. The selection of references is appropriate, contributing to the completeness and comprehensiveness of the bibliography. The proper selection of literature provides a solid theoretical foundation for the planned and conducted research as well as for the discussion of results presented in the subsequent chapters of the dissertation. The literature analysis was carried out in a critical manner, and the candidate appropriately discussed the obtained results in the context of the current state of knowledge.

Evaluation of the content of the dissertation, scientific value and originality

The structure of the doctoral dissertation is correct, logical, and typical for research-based theses. It also includes a literature review, aims and scope of the study, materials and methods, results and discussion, conclusions and perspectives for further research, as well as a bibliography. The dissertation has been carefully written, the sequence of presented content is appropriate, and a clear logical order of presentation is maintained throughout.

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The research results were presented by the doctoral candidate in five subsections. In Chapter 4.1, the candidate presented hydrodynamic cavitation (HC) coupled with sulfate radical-based advanced oxidation processes (SR-AOPs) to investigate the potential application of HC for the activation of PS and PMS. The efficiency of the developed HC/PS and HC/PMS processes was evaluated in the context of BTEX degradation by monitoring the concentration of target compounds in treated samples. The studies included BTEX degradation using HC, HC/PS, and HC/PMS at different molar ratios of reagents. After selecting the optimal ratio, the HC/PS and HC/PMS systems were further investigated in the presence of inorganic anions and radical scavengers. Subsequently, model solutions containing BTEX were individually treated using HC/PS and HC/PMS, and the samples were analysed by HPLC-UV/DAD to identify intermediate products, based on which degradation pathways were proposed. In Chapter 4.2, the doctoral candidate presented results demonstrating the potential of acoustic cavitation (AC) for the activation of PS and PMS. For this purpose, BTEX degradation was conducted under AC conditions induced by ultrasound in the presence of PS and PMS at different rotational speeds. The efficiency of BTEX degradation was then evaluated using US/PS and US/PMS systems, including the addition of asphaltenes. Studies on US/PS/ASPH and US/PMS/ASPH included radical quenching experiments and tests of the reusability of asphaltenes. In Chapter 4.3, cavitation was induced in sonoreactors generating low-frequency dual ultrasound (LFDUS) operating at 40 kHz and 120 kHz, as well as high-frequency dual ultrasound (HFDUS) at 80 kHz and 200 kHz. BTEX degradation was carried out under various single- and dual-frequency ultrasound processes, as well as hybrid processes assisted by ozone (O_3), to determine the synergistic effect in LFDUS/O_3 and HFDUS/O_3 systems. The influence of pH, radical scavengers, and inorganic anions on BTEX degradation efficiency in LFDUS/O_3 and HFDUS/O_3 systems was evaluated. A degradation pathway for BTEX was also proposed. The hybrid cavitation–ozonation process is presented in Chapter 4.4. In this case, the process represents a modified version of the peroxone system (H_2O_2/O_3) combined with HC, using a stable and safe alternative to hydrogen peroxide, namely sodium percarbonate (SPC). This study evaluated the efficiency of the HC/SPC/O_3 process in the degradation of 1,4-dioxane. The synergistic effect was investigated by comparing degradation in single and hybrid processes. The performance of HC/SPC/O_3 was then assessed in the presence of scavengers and typical water matrix constituents, and a degradation pathway for 1,4-dioxane was proposed. Finally, Chapter 4.5

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presents the results obtained in the attempt to develop a hybrid cavitation-based advanced reduction process (ARP). In this study, HC coupled with SO_3^{2-}/UV was tested for the degradation of clofibric acid (CLA). The synergistic effect was evaluated through degradation experiments conducted in single and hybrid systems, and the influence of water matrix components was also examined. Furthermore, radical quenching experiments were performed using specific reducing species scavengers. The reductive degradation pathway of CLA was determined based on intermediates identified by GC-MS analysis and supported by theoretical DFT calculations.

After reviewing the research results presented by the doctoral candidate in chapters 4.1–4.5, I have no doubt that the subject matter of the doctoral dissertation falls unequivocally within the field of *exact and natural sciences*, specifically within the discipline of *chemical sciences*. Nevertheless, in addition to the clearly dominant chemical aspects, it also encompasses research topics situated within the field of *engineering and technical sciences*, particularly the discipline of *environmental engineering, mining and energy*, related to water and wastewater treatment. In this context, I would like to emphasize the clearly interdisciplinary nature of the dissertation.

The doctoral dissertation is an original and valuable work, and the research results obtained by the doctoral candidate have been presented in the context of the current state of knowledge. They significantly expand existing knowledge regarding the possibilities of designing and applying novel cavitation-based advanced chemical processes to degrade contaminants present in water and wastewater. It should also be emphasized that the doctoral candidate designed, constructed, and applied (presumably with significant assistance from the dissertation supervisor) laboratory-scale technological systems used in the experimental studies.

The evaluated doctoral dissertation undoubtedly demonstrates the candidate's general theoretical knowledge in the field of *exact and natural sciences*, specifically *chemical sciences*, as well as the ability to independently conduct scientific research.

The reviewed doctoral dissertation constitutes a genuine and original solution to a scientific problem. The most important scientific achievements of the doctoral candidate include: (***i***) the development of novel cavitation-based advanced chemical processes and their application to the degradation of selected contaminants, (***ii***) the determination of the efficiency of these processes, the kinetics of contaminant degradation, and the dominant

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radical species involved in these reactions, and (***iii***) the identification of possible degradation pathways of the investigated contaminants.

Comments and questions for discussion

While reading the doctoral dissertation, I noticed minor errors, typos, and inconsistencies that do not affect its substantive value. Some of them, mainly of debatable nature, as well as questions to which I will expect answers during the public defence, are presented below.

1. Instead of "siarczynowy", it should be "siarczanowy(IV)".
2. The list of abbreviations and acronyms does not include all those used in the dissertation.
3. In my opinion, the review of wastewater treatment methods involving coagulation has been written in a very concise manner. The doctoral candidate limited the discussion to aluminium- and iron-based coagulants while completely omitting innovative coagulants that have been intensively investigated and even applied in practice, such as zirconium (Zr), titanium (Ti), cerium (Ce), and lanthanum (La) compounds. Furthermore, the doctoral candidate did not include relevant literature data concerning the removal of clofibric acid (CLA) by coagulation processes, directly related to the subject matter of the dissertation.
4. The doctoral candidate states, presumably on the basis of references [78,79], that alkaline reagents such as metal hydroxides, carbonates, and ammonia are added to neutralize acidic wastewater. I cannot agree with the inclusion of ammonia for this purpose, as its use would lead to a significant increase in the concentration of ammoniacal nitrogen in wastewater, which is subject to regulatory limits. In general, elevated levels of total nitrogen are already observed in industrial wastewater, and in the case of low-pH effluents, the use of ammonia would result in a substantial increase in this parameter. The doctoral candidate should have verified the cited source prior to its inclusion in the dissertation.
5. The doctoral candidate uses common nomenclature for chemical compounds, e.g. "lime", "soda ash", etc. I recommend adopting terminology consistent with IUPAC nomenclature requirements, and optionally providing common (industrial) names in parentheses where appropriate.

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6. In the manuscript body, the chemical formula of sodium bicarbonate is written as $Na(HCO_3)_2$, whereas it should be $NaHCO_3$.
7. In the chapter on chemical precipitation, the doctoral candidate provides examples of compounds (Na_2BDP and $BDETH_2$) that may be used for the precipitation of heavy metals from industrial wastewater; however, these compounds are not applied in practice. The doctoral candidate could have included reagents that are actually used in real-world applications, such as sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, and sodium trithiocarbonate, which would have given this part of the literature review a more up-to-date character. There is a substantial body of scientific and technical literature regarding their properties and applications.
8. The doctoral candidate uses notations such as "mgO_3/mgDOC", whereas the correct form should be "mg O_3/mg DOC".
9. The doctoral candidate did not formulate research theses/hypotheses in the dissertation. Although this is not obligatory, in my opinion it constitutes a key part of a scientific thesis.
10. Why did the doctoral candidate use a BTEX model solution at a concentration of 50 ppm (in procedure 1) and 40 ppm (in procedure 2)? What was the rationale behind selecting these concentration values, and on what basis were they determined? Do these concentrations correspond in any way to the levels typically found in industrial wastewater?
11. Why was 0.5 g/L of asphaltenes added to the model solution in procedure 2? How was this dosage determined? Was the selected asphaltene dose based on prior optimization studies? If so, how to perform such preoptimization?
12. How did the doctoral candidate determine the input parameter values (Table 1), i.e., the molar ratio of the reducing agent (sulfite) to the contaminant, pH, and the reaction time? Were these values previously preoptimized? Were preliminary experiments carried out? If so, how were these experiments conducted?
13. The effectiveness of BTEX degradation (in model solutions) using the HC/PS and HC/PMS systems decreased due to the presence of carbonates, sulfates, and chlorides in the tested solutions, with the lowest efficiency observed in the case of carbonates. Chlorides and sulfates occur in industrial wastewater at significant concentrations, often exceeding regulatory limits. Carbonates may be present in slightly alkaline

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wastewater. How can the real impact of the mentioned ions on BTEX removal efficiency be verified? What experiments should be performed in this case? Can the influence of these ions on process efficiency be eliminated, and if so, how can they be eliminated?

14. Similar dependencies (as above) were observed by the doctoral candidate during the study of LFDUS/O_3 and HFDUS/O_3 processes. In these cases, the strongest inhibitory effect was observed for sulfate ions, followed by chlorides and carbonates. Considering the above conditions, how can the real impact of these ions on BTEX removal efficiency be determined? What experiments should be performed in this case? Is it possible to eliminate the influence of these ions on process efficiency, and if so, how to do it?

15. In Table 5, the doctoral candidate presented estimated costs of cavitation-based AOPs applied for BTEX degradation, along with the sources of these costs. Is it possible to reduce the costs of chemical oxidants (PS, PMS), and if so, how? Is it possible to reduce the energy costs required in these processes, and if so, what solutions could be applied? In other words, is it possible to reduce operating costs associated with energy consumption and reagent use?

16. Does the doctoral candidate see the possibility of applying the developed methods/processes on a larger (industrial) scale? If so, what conditions would need to be met, not only in terms of equipment and apparatus, but also regarding the composition of raw and treated wastewater? Would any residual excess oxidants in the wastewater need to be removed before directing the effluent to biological treatment? How could this excess be removed from the wastewater?

Conclusions

The doctoral dissertation written by Mr. Kirill Fedorov, MSc. Eng. entitled *"Degradation of organic water pollutants using hybrid cavitation-based advanced chemical processes"*, prepared under the supervision of Prof. Grzegorz Boczkaj, PhD, DSc Eng., represents an original solution to a scientific problem and provides innovative insights into the synergy between cavitation phenomena and oxidation–reduction processes for pollutant removal thus introducing valuable new knowledge and contributing to the development of the chemical sciences discipline. The dissertation is characterized by a high scientific standard and undoubtedly demonstrates the doctoral candidate's general theoretical knowledge in the

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exact and natural sciences, especially in the discipline of *chemical sciences*, as well as his ability to independently conduct research.

In conclusion, I state that the reviewed doctoral dissertation fully meets the customary and legal requirements set out in Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science (Journal of Laws 2018, item 1668, as amended). Therefore, with full conviction, I submit to the Scientific Council of the Discipline of Chemical Sciences at the Gdansk University of Technology a motion to admit Mr. Kirill Fedorov MSc. Eng. to the next stages of the doctoral procedure, including the public defence.

PODPIS ZAUFANY
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18.05.2026 13:32:20 GMT+0200
Dokument podpisany elektronicznie podpisem zaufanym

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