UNIVERSITY OF LJUBLJANA | FS Faculty of Mechanical Engineering

Ljubljana, July 23rd, 2026

Subject: Report on the PhD Thesis "Degradation of organic water pollutants using hybrid cavitation-based advanced chemical processes" submitted by Kirill Fedorov

I was nominated as an examiner of the thesis "Degradation of organic water pollutants using hybrid cavitation-based advanced chemical processes" submitted by Kirill Fedorov. As a member of the jury, I'm submitting my evaluation report.

Introduction

The doctoral thesis addresses the timely and scientifically relevant topic of advanced water treatment technologies based on cavitation-assisted chemical processes.

The thesis investigates several hybrid cavitation-based systems by combining acoustic or hydrodynamic cavitation with both advanced oxidation processes and the emerging advanced reduction processes. The work includes the degradation of representative organic pollutants, including volatile aromatic hydrocarbons, 1,4-dioxane, and the pharmaceutical contaminant clofibric acid. In addition to evaluating degradation performance under various operating conditions, the candidate also examines the reaction mechanisms through radical quenching experiments, identification of degradation intermediates, and theoretical calculations.

Evaluation of the thesis

The core of the thesis consists of 5 chapters. In total it has 146 pages. In the literature review chapter, the candidate compiled over 250 references. I assess that the candidate prepared a comprehensive literature review and selected appropriate sources, which were meaningfully incorporated into the different chapters, predominantly introduction, of the dissertation. In doing so, the candidate demonstrated a good understanding of the research topic addressed in the doctoral work. During his PhD studies the candidate published as a first author no less than 6 journal papers and coauthored several more. This indicates his involvement in the respective research field.

In the *first chapter*, the candidate gives a literature review, an overview of the scientific background and motivation behind the current thesis. The candidate first introduces wastewater treatment methods. He divides them into physical, biological and chemical methods. Emphasis is placed on cavitation where he discusses the phenomenon from a single bubble to acoustic and hydrodynamic manifestation of bubbles. He continues to show the role of cavitation in hybrid methods for water and wastewater treatment.
The chapter concludes with an overview on how integrated sequence of physical, biological and chemical methods can be used to effectively accomplish the removal of suspended solids, organic matter, nutrients and pathogenic microorganisms in wastewater treatment plants. He however highlights that the new and stricter standards demand the development of new strategies, which include advanced chemical processes, namely, advanced oxidation and reduction processes. Finally, he puts cavitation to the spotlight and gives the motivation of the present work.

The *second chapter* shortly introduces the research aims and objectives. Briefly these are: i) to assess the effectiveness of cavitation alone and in combination with advanced oxidation and reduction processes, ii) to evaluate the influence of key operating parameters, including reagent concentration and solution pH, on pollutant degradation, iii) to investigate the effect of common inorganic ions on the efficiency of the developed treatment processes, iv) to identify the dominant reactive species and elucidate the degradation mechanisms and pathways of the target pollutants and v) to evaluate the potential of hydrodynamic cavitation in advanced reduction processes and verify the reductive degradation pathway using theoretical calculations.
One can for sure state that the set goals are extremely ambitious and achieving them in a given time frame was a challenging task.

Chapter 3 presents the materials, experimental procedures, analytical methods, and computational approaches employed throughout the dissertation. The materials section describes the chemicals used in the experiments, including the selected model pollutants - BTEX compounds, 1,4-dioxane, and clofibric acid, Also various oxidants and reductants such as persulfate, peroxymonosulfate, sodium percarbonate, ozone, and sulfite. High-purity reagents and ultrapure water were employed throughout the study to minimize experimental uncertainties.
A significant part of the chapter is devoted to the experimental setups. Two complementary cavitation technologies were investigated: hydrodynamic cavitation and acoustic cavitation. The hydrodynamic cavitation reactor, based on a Venturi geometry, was integrated with recirculation, pressure and temperature control, UV irradiation, and ozone dosing, allowing the study of several hybrid treatment processes under controlled conditions. The acoustic cavitation experiments utilized both conventional ultrasound and a specially designed dual-frequency ultrasonic reactor, enabling comparison of different ultrasonic operating modes and their influence on cavitation intensity and pollutant degradation.
The experimental methodology was designed to systematically investigate the influence of key operating parameters, including oxidant or reductant concentration, solution pH, cavitation intensity, ozone dosage, and reaction time. In addition, the effects of common inorganic ions and

other water constituents were evaluated to assess the robustness of the developed processes under conditions representative of real water matrices.
Considerable emphasis was placed on elucidating degradation mechanisms. Radical quenching experiments using selective scavengers were performed to identify the dominant reactive species responsible for pollutant degradation. Reaction intermediates were identified using chromatographic techniques, allowing the proposal of degradation pathways for the investigated pollutants. Analytical methods included gas chromatography with flame ionization and mass spectrometric detection (GC-FID and GC-MS) as well as high-performance liquid chromatography (HPLC), providing both quantitative and qualitative information on pollutant transformation.
The methodology was further strengthened by the application of statistical optimization using Response Surface Methodology (RSM) and Central Composite Design (CCD), enabling systematic evaluation of process parameters and their interactions. Finally, Density Functional Theory (DFT) calculations were employed to support the interpretation of the advanced reduction process by identifying the molecular sites susceptible to reductive attack and validating the proposed degradation mechanism.

Chapter 4 presents the main scientific results of the dissertation and provides a comprehensive discussion of the performance and mechanisms of hybrid cavitation-based advanced oxidation and reduction processes for the degradation of persistent organic pollutants. It consists of 5 parts, each showcasing one distinctive process.
In the first part hydrodynamic cavitation is combined with persulfate and peroxymonosulfate for the degradation of BTEX compounds. The results demonstrate that cavitation significantly enhances oxidant activation, resulting in pronounced synergistic effects and improved degradation efficiencies compared with the individual processes. This is followed by an investigation of acoustic cavitation-assisted sulfate radical oxidation, where both conventional and dual-frequency ultrasound are evaluated. The influence of operating parameters, including oxidant dosage, pH, and ultrasonic conditions, is systematically examined to identify optimal treatment conditions and maximize radical generation. The chapter continues with studies of cavitation-assisted ozone-based advanced oxidation processes. Acoustic cavitation coupled with ozonation is shown to improve ozone utilization and pollutant degradation, while the integration of hydrodynamic cavitation, ozone, and sodium percarbonate demonstrates an efficient hybrid treatment concept capable of achieving enhanced oxidation through multiple radical generation pathways. In addition to evaluating pollutant removal, the author investigates the influence of common inorganic ions and water matrix constituents, providing valuable insight into the applicability of these technologies under realistic treatment conditions. The final section introduces an innovative application of hydrodynamic cavitation in advanced reduction processes through its combination with sulfite and ultraviolet irradiation for the degradation of clofibric acid. The developed $HC/SO_3^{2-}/UV$ process demonstrates that cavitation can effectively intensify reductive degradation pathways, extending the application of cavitation beyond conventional oxidation-based treatment. The degradation mechanism is investigated using radical scavenging experiments, identification of transformation products, and Density Functional Theory (DFT)

calculations, providing strong experimental and theoretical support for the proposed reaction pathways.
It must be emphasised that each part is supported by a publication in a journal with the candidate as a first author. A major strength of the chapter is the integration of performance evaluation with mechanistic interpretation. Rather than focusing solely on degradation efficiencies, the candidate systematically identifies the dominant reactive species, proposes degradation pathways, and explains the observed synergistic effects based on the chemistry of cavitation and radical formation.

Finally, a publication list of the candidate is shown – an impressive number of papers which he published as a first author and additional ones as a coauthor. The thesis concludes with the list of references.

In accordance with the above written report, I find the thesis well written with a clear contribution to science. The dissertation combines experimental process development with mechanistic investigations, providing a comprehensive understanding of the role of cavitation in intensifying advanced chemical treatment technologies. I am

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for the candidate to defend it.

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