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Review report on the PhD thesis of Mujahid Ameen Khan entitled
„Synthesis of metallic nanoparticles for catalytic and agricultural applications"

One of the significant global challenges our world faces today is environmental pollution caused by urbanization, mining, and industrialization. Since the publication of Rachel Carson's book titled *„Silent Spring"*, there has been growing concern about the widespread distribution and bioaccumulation of persistent pollutants in water and soil. Advances in analytical methods have revealed that many anthropogenic micropollutants, such as antibiotics, can resist biological degradation and persist in conventional water treatment systems. The continuous discharge of these substances disrupts aquatic ecosystems, induces antibiotic resistance, and poses long-term toxicological risks to both aquatic organisms and humans. To address this pressing challenge, the new European Urban Wastewater Treatment Directive, introduced in 2025, mandates quaternary treatment processes that achieve at least 80% removal efficiency of micropollutants. Additionally, this environmental pressure coincides with an increasing prevalence of multidrug-resistant microorganisms, including phytopathogens that affect crops. This situation underscores the urgent need for the development of innovative and sustainable technological solutions. In this regard, the dissertation presented for defence by MSc Mujahid Ameen Khan is an interesting contribution to the development of advanced nanomaterials with catalytic and antimicrobial properties for environmental remediation and agricultural protection.

The reviewed PhD thesis is structured into three main parts: Part I, comprising the theoretical background, including the aims of the research, research questions, hypotheses, and literature overview; Part II, presenting the research described in thematically related publications constituting the core of the dissertation, including experimental methodology, results, and discussion, and Part III, containing appendices with the full texts of 3 published articles indexed in the Journal Citation Reports database forming the basis of the doctoral thesis. The IF of these

works range from 5.4 to 7.7, and the total IF is 18.5. The PhD student is the first author of all of them. The publications included in the dissertation were reviewed by experts, and their high scientific quality had already been confirmed.

Before the description of Part I, the dissertation includes a list of scientific activities of MSc Mujahid Ameen Khan, abstracts in Polish and English, and a list of acronyms and abbreviations. Furthermore, in Chapter 1, the research objectives, questions, and hypotheses are presented prior to the literature review. However, from a formal and methodological perspective, this structure weakens the narrative coherence of the dissertation, as the research questions and hypotheses are not explicitly grounded in the subsequent analysis of the literature. The development of research questions and hypotheses should arise from a thorough examination of the current state of the art, which enables the identification of research gaps. These gaps then provide the rationale for defining the scope and direction of the study.

The reader is introduced to the subject of the thesis in Chapter 2, entitled „Introduction". This chapter consists of 31 pages and provides a solid background for understanding the research problem, with particular emphasis on the use of nanomaterials and their morphological and structural properties to address contemporary environmental and agricultural challenges. A significant part of this section is devoted to cold atmospheric pressure plasma, including its fundamental principles, types of plasma systems, and the role of reactive species in nanoparticles synthesis and micropollutants degradation. Finally, in the last part of the chapter, the Candidate presents rhenium- and silver-based nanomaterials and discusses their properties and potential applications in catalysis and antimicrobial systems, emphasizing that the design of metal nanoparticles with desired physicochemical properties is strongly dependent on the selection of precursors, reducing and stabilizing agents. These parameters influence the size, morphology, stability, and functional performance of the resulting nanomaterials. Overall, this section provides a comprehensive overview of the state of the art and establishes the scientific foundation for the experimental work presented in the dissertation.

The main goals of the PhD work are presented in Chapter 3 entitled: *„Establishment of the subject matter"*, which outlines the motivation and scope of the research, linking the presence of micropollutants in the environment with the growing problem of drug-resistant phytopathogens. This part of the dissertation serves as a bridge between the general introduction and the specific research objectives, positioning the performed studies within the context of current scientific developments. Moreover, the Candidate provides an overview of cold atmospheric-pressure plasma as a method for the synthesis of metallic nanomaterials, highlighting both the potential of these systems and existing research gaps.

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Below are several detailed remarks pertaining to Part I of the dissertation, with particular reference to the theoretical background.

- The lack of page numbering makes it difficult to navigate the dissertation and to refer to specific sections.
- The phrase „Aligning with the green chemistry principles" is general and somewhat declarative. It would benefit from a more explicit connection to specific principles (e.g., avoiding hazardous reagents and using renewable feedstocks).
- In several parts of the thesis, imprecise and informal wording is used, which reduces the clarity of the discussion. From a terminological perspective, the use of the term "granular properties" appears imprecise in the context of nanomaterials and would benefit from replacement with more specific terminology, such as „structural" or "physicochemical properties". In that case, it is not clear whether this refers to crystallite size, grain structure, or general morphological features of nanoparticles. „*Optimally develop"* - unclear whether optimization refers to catalytic activity, particle size, stability, or other measurable parameters. The term „fine-tuned" may be somewhat overstated and should be supported by more precise justification; „structure-activity interpretation" should be replaced with „structure-activity relationships".
- The reported in Chapter 2 production volume of nitroaromatic compounds appears unrealistic. A value of 1 billion tons per year is not consistent with the known scale of production of these specialty chemicals, which is typically several orders of magnitude lower (in the range of millions of tons annually). The Candidate should verify this information and provide a reliable reference. The Reviewer has made an effort to trace the origin of the cited information regarding the production volume of nitroaromatic compounds [Gupta et al., Water 16 (2024)], and it was found that the reported value has been propagated from secondary literature, where it was cited from another review article [Kulkarni et al., J. Environ. Manag. 85 (2007)]. Notably, in that original source, no primary reference supporting this numerical value was provided. This highlights a broader issue of uncritical citation practices in the literature. It underscores the importance of carefully verifying reported data, especially when quantitative values are involved.
- Additionally, minor editorial issues are noted (e.g., punctuation inconsistencies and stylistic repetitions), which do not affect the scientific content but slightly reduce the overall clarity of the text.

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The second part of the dissertation presents a coherent synthesis of the scientific output forming the basis of the doctoral thesis. The Candidate summarizes the results of published studies, with particular emphasis on the design and development of Re and Ag metallic nanocatalysts using cold atmospheric pressure plasma-assisted and green synthesis approaches. The Candidate systematically examines the effect of synthesis parameters on the physicochemical properties of metallic nanoparticles and correlates these characteristics with catalytic efficiency, reaction kinetics, and antibacterial activity. The research methodology aligns with the research goals and the research hypothesis. However, the lack of direct references to the specific publications that underpin reported research findings slightly reduces the clarity and transparency of this section.

The first publication is devoted to the optimisation of the synthesis process of Re nanoparticles using a Box–Behnken design of experiments. The research is based on the hypothesis that the catalytic properties of carbohydrate-stabilized Re nanoparticles can be enhanced by adjusting their composition and morphology. In this regard, the main objective of this work was to study the effect of Re(VII) ion concentration, solution flow rate, and discharge current as the operating parameters of the cold atmospheric pressure plasma to control the physicochemical properties of Re NPs and thereby improve their catalytic performance in the reduction of nitroaromatic compounds. In relation to the presented findings, I would like to ask whether the stability and reusability of the catalytic material were evaluated. In particular, was the effect of catalyst aging on the oxidation state of Re species and their catalytic performance investigated?

The second article focuses on the enhanced catalytic decomposition of furazolidone and chloramphenicol, which are commonly used as medical and veterinary antimicrobial agents. In this regard, a dielectric barrier discharge cold atmospheric pressure plasma (DBD-CAPP) system was used for the simultaneous synthesis of Re NPs and the generation of reactive oxygen and nitrogen species in treated water. It was demonstrated that DBD-CAPP treatment of the samples leads to efficient degradation of the pharmaceutical compounds, accompanied by hydrogenation of their nitro substituents. However, since no comparative studies were performed to evaluate the efficiency of pharmaceutical degradation in the presence of Re species at oxidation states other than Re(VII), it remains unclear whether the role of Re is limited solely to the reduction of nitro groups or it also contributes more broadly to the overall degradation efficiency of the investigated organic compounds. Despite the extensive characterization and the broad range of studies, the results do not provide a sufficiently clear answer to this question.

Another question arises from the conclusion that Re NPs exhibit excellent catalytic potential for „deactivating, decomposing, and converting nitro-based compounds” into amino derivatives. In

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this context, it would be valuable to clarify which of these processes is dominant under the studied conditions. In particular, do these pathways compete with one another, or do they occur sequentially? Furthermore, which process is considered more relevant from an application perspective: the selective conversion to amino compounds or the complete degradation of the target pollutants? Were the Re species stable during consecutive catalytic cycles, or did they undergo redox transformations that could influence their activity?

The third publication focuses on the development of a controlled synthesis method of silver nanoparticles. In this regard, water-based coffee brews containing biologically active compounds such as caffeine, chlorogenic acids, aliphatic acids, polysaccharides, and amino acids having diverse functional groups were used as both reducing and stabilizing agents, avoiding the use of organic solvents, pH modifiers or intensive extraction procedures. The aim was to minimize the use of stabilizing agents and avoid potential oversaturation, which can hinder the nanoparticles' surface availability and activity. In this regard, the effects of different brewing methods on the physicochemical properties of the obtained Ag NPs, including their size distribution, morphology, surface charge, and colloidal stability, were systematically investigated. The antibacterial properties of Ag NPs exposed to cold atmospheric pressure plasma post-purification were further discussed and attributed to a synergistic effect between the nanoparticles and plasma-generated reactive species. However, it remains unclear whether this effect can be unambiguously ascribed to plasma-generated reactive species. Alternative parameters, such as nanoparticle size, surface characteristics, reaction medium pH, or the presence of reactive species in solution (e.g., NO_3^- or other plasma-induced products), may also contribute to the observed antibacterial activity. Could the Candidate clarify whether the observed enhancement in antibacterial activity results from plasma-generated reactive species, or from changes in nanoparticles morphology and solution composition, and whether appropriate control experiments were performed to distinguish these effects? I would like to raise one additional comment. According to the third research article in the monothematic cycle of publications, the absorption spectra of silver species presented in Figure 3 should be extended to a broader spectral range to provide a more comprehensive characterization of the system, as an absorption band around 250 nm would allow evaluation of the reduction efficiency of Ag^+ ions to metallic silver (Ag^0).

Despite the above-mentioned critical and polemical remarks, I consider the presented dissertation to be a valuable study demonstrating the potential applications of cold atmospheric pressure plasma-assisted synthesis of rhenium nanoparticles and silver nanoparticles without the use of additional stabilizing agents or organic solvents in environmental remediation and the control of phytopathogens.

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The main achievements of the PhD thesis of MSc Mujahid Ameen Khan are:

- Demonstrating the correlations between cold atmospheric pressure plasma operating parameters and the physicochemical properties of the obtained Re NPs, including size distribution, surface charge, and rhenium oxidation state;
- Demonstrating that dielectric barrier discharge cold atmospheric pressure plasma treatment of the samples enables both the degradation of nitro-based antimicrobial agents and the catalytic hydrogenation of their nitro groups;
- Demonstrating that bioactive compounds present in coffee, even at low concentrations (0.1%), can act as effective reducing and stabilizing agents for the synthesis of silver nanoparticles;
- Demonstrating that bioactive compounds present in coffee enable the formation of stable, predominantly spherical, and monodisperse Ag NPs, with their physicochemical properties dependent on the extraction method;
- The development of technological solutions for the degradation of micropollutants and the deactivation of phytopathogens.

Overall, the reviewed doctoral dissertation addresses important and current topics and presents a valuable contribution to the field of plasma-assisted nanotechnology and green synthesis methods of metallic nanoparticles. The Candidate has demonstrated proficiency in several important techniques for the synthesis, characterization, and testing of catalysts. The results of his work have been presented in the form of 3 scientific publications and an oral presentation at a conference. It is also worth emphasizing that selected studies included in the dissertation were conducted within the framework of an NCN research project, and the Candidate is a co-author of 3 additional scientific publications in this research area.

Taking the above into account and positively assessing the scientific value of the submitted doctoral dissertation, I conclude that it meets the requirements set for doctoral theses specified in Art. 187 of the Law on Higher Education and Science in Poland of July 20, 2018 (in Polish: Prawo o szkolnictwie wyższym i nauce, Dz.U. z 2018 r. poz. 1668 ze zm.), and I request the Scientific Council at the Wroclaw University of Science and Technology to admit the PhD student to further stages of doctoral dissertation defense.

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