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Poznan, 22/09/2025

**Review of the doctoral dissertation of M.Sc. Zhila Honarmandrad entitled**: "***Management of broth after biomass hydrolysis to improve biohydrogen production***"

The review was prepared on the basis of a letter from the Chairman of the Chemical Sciences Discipline Council of the Faculty of Chemistry of Gdansk University of Technology, Dr. D.Sc. Eng Marek Tobiszewski, prof. GUT (ref. L. Dz. 180 WCh/Dz/2025) of July 18, 2025, referring to the resolution of the Chemical Sciences Discipline Council of July 15, 2025 on the appointment of reviewers in the doctoral proceedings of M.Sc. Zhila Honarmandrad.

**Description of the topic and assessment of compliance with the scientific discipline**

The doctoral dissertation submitted for review, entitled "*Management of broth after biomass hydrolysis to improve biohydrogen production*" was written by M.Sc. Zhila Honarmandrad, under the supervision of Dr. D.Sc. Jacek Gębicki, prof. GUT, at the Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdansk University of Technology.

In the doctoral dissertation, M.Sc. Zhila Honarmandrad addresses the very important and current topic of sustainable energy, whereby renewable energy sources such as solar, wind, hydropower, geothermal energy, and biomass undoubtedly play a key role. Biomass is the focus of this dissertation. As the PhD student emphasizes, a significant advantage of biomass is the ability to transform waste products, such as agricultural residues, food waste, and municipal solid waste into a valuable energy source. This waste can be burned to generate heat or converted into biofuels. Therefore, biomass, due to its carbon neutrality, plays a significant role in renewable energy. The growing demand for sustainable energy has fueled interest in biohydrogen production from lignocellulosic biomass. However, the hydrolysis and fermentation of such biomass generates various inhibitory compounds, such as furfural (FF), hydroxymethylfurfural (HMF), hydroquinone (HQ), and vanillin (VAN), which significantly hinder microbial activity and reduce biohydrogen production efficiency. Therefore, in the dissertation, the PhD student focused on the development and evaluation of the effectiveness of three new methods for removing the aforementioned inhibitors formed during the hydrolysis and fermentation of lignocellulosic biomass. The methods

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proposed by M.Sc. Zhila Honarmandrad are based on sorption systems which utilize deep eutectic solvents (DESs):
(1) hydrophobic magnetic deep eutectic solvents (HMDES),
(2) metal-organic framework with pseudo-DES (MOF@pseudo-DES),
(3) supramolecular deep eutectic solvents (SUPRADES).

The PhD student also presented the characteristics of the proposed sorption systems, optimization of sorption parameters using statistical designs (Plackett-Burman and Box-Behnken), and verified their sorption efficiency using both model and actual hydrolysates.

Consistent with the scientific literature, M.Sc. Zhila Honarmandrad's doctoral dissertation contains elements of both scientific novelty and originality in the conducted research. The PhD student's involvement resulted in her co-authorship of three articles from the JCR list with high impact factors closely related to the research of the doctoral dissertation:

- Z. Honarmandrad, K. Kucharska, M. Kaykhaii, J. Gębicki, *Removal of phenolic inhibitor compounds from hydrolysates and post-fermentation broths by using a hydrophobic magnetic deep eutectic solvent*, Journal of Environmental Chemical Engineering, 12(3), 112621 (2024). **IF=7,2**
- Z. Honarmandrad, S.S.M. Khadem, K. Kucharska, M. Kaykhaii, J. Łuczak, J. Gebicki, *Enhanced sorption of inhibitory compounds from fermentation broth using a MOF@ pseudo-DES composite*, Journal of Molecular Liquids, 421, 126845 (2025). **IF=5,2**
- Z. Honarmandrad, K. Kucharska, E. Słupek, J. Cydejko, I. Strzelczyk, M. Kaykhaii J. Gębicki, *SUPRADES: A novel approach for inhibitor compound removal from hydrolysates with concurrent enhancement of biohydrogen production*, International Journal of Hydrogen Energy, 135, 361-371 (2025). **IF=8,3**

It should be emphasized that M.Sc. Zhila Honarmandrad is the first author of the aforementioned publications, and she is also the corresponding author of one of these articles. Furthermore, the PhD student participated in two conferences: in 2022, the 64th Congress of the Polish Chemical Society in Lublin, and in 2024, the 7th International Congress on Water, Waste and Energy Management (WWEM-24) in Lisbon, Portugal.

The research contained in Ms. Zhila Honarmandrad's doctoral dissertation was funded by the National Science Centre under the OPUS research project no. UMO-2021/41/B/ST8/02395.

Moreover, according to the Scopus database (data as of September 15, 2025), M.Sc. Zhila Honarmandrad is the co-author of a total of 16 research articles (although not all of them were presented in the doctoral dissertation). Her Hirsh index is 10, and the number of

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citations across all publications is 521, which I consider impressive at this stage of her scientific development.

The scope of her doctoral dissertation encompasses chemical sciences, including issues related to the use of instrumental techniques (HPLC-DAD, GC-TCD-FID), as well as the synthesis of new sorption systems based on deep eutectic solvents and their characterization (using techniques such as FT-IR, TGA, SEM, BET, XRD). Therefore, I think that the research topic undertaken by the PhD student is consistent with the discipline of chemical sciences.

**Substantive Assessment of the Doctoral Dissertation**

The doctoral dissertation is written in English. The dissertation appears to contain all required sections, but the standard division into chapters has not been followed. Chapter 1, entitled "*Introduction*," is followed by chapters 2-7, which constitute the literature section of the dissertation, although they are not named as such. Chapter 8 presents the aim of the doctoral dissertation and the research tasks. Chapter 9, titled "*Materials and Methods*," contains all the relevant information that should be included in the experimental section. The following chapters (10-15) alternate between the discussion of the results and conclusions for the three tested sorption systems - HMDES, MOF@pseudo-DES, and SUPRADES - and Chapter 16 presents their comparative evaluation. Next are: Chapter 17 – "*Summary, Scientific Novelty, and the Purpose of the Doctoral Dissertation*" (I do not understand why the purpose of the dissertation reappears), Chapter 18 – "*General Conclusions*," and Chapter 19 – "*Future Research Directions.*" I think there are too many summaries and conclusions in the doctoral dissertation, especially since they are often repeated. It would be sufficient to summarize the research only once at the end of the dissertation. The dissertation is supplemented by: "*Abstract*," "*Table of Contents*," "*List of Figures*," "*List of Tables*," "*References*" and "*Achievements*." In total, the dissertation is 131 pages long. The work is characterized by a moderate proportion of the research section to the entire dissertation (the literature section – 32 pages, the experimental section and discussion of results – 73 pages). Unfortunately, there are many pages that are only half-filled or contain a figure/graph while the rest of the page is blank (e.g. pages: 30, 46, 55, 58, 59, 60, 61, 65, 78, 79, 80, 81, 82, 83, 91, 95, 96, 97, 102, 103). The bibliography contains 220 references (numbered according to first use in the text), which consist of scientific literature, such as publications, book chapters, and conference proceedings.

In the literature section, M.Sc. Zhila Honarmandrad presented the most important introduction to the topic of doctoral dissertation, which includes: non-renewable fuels and the effects of their use, renewable fuels and their types as well as advantages, types of biomass, biohydrogen and its production methods, lignocellulose as a raw material for

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biohydrogen production, fermentation inhibitors, methods for removing inhibitory compounds from the hydrolysis of lignocellulosic biomass, deep eutectic solvents and their classification and application in bioprocessing and inhibitor removal.

The literature section was written in a very general and rather disorganized manner, with numerous repetitions of the same information. For example, information regarding fossil fuels and their impact on greenhouse gas emissions is described in paragraph 3 of Section 2 and then repeated at the beginning of Section 2.1. However, the same information is cited in a different reference. Another example: Subsection 4.1.2.1.2. "*Biological Processes*" – The first and last sentences of this chapter contain the same information, just presented differently. There are numerous repetitions of the same definitions throughout the reference section.

Subsection 3.1. "*Types of Renewable Fuels*" should be entitled "*Types of Renewable Resources and Energy Sources*". Furthermore, each of the subsections: 3.1.1. "*Biomass Fuels*," 3.1.2. "*Solar Energy*," 3.1.3. "*Wind Energy*," 3.1.4. "*Hydropower*," and 3.1.5. "*Geothermal Energy*" contain only one or two sentences and a figure. I think that, at the level of a doctoral dissertation, this is definitely insufficient, especially considering the amount of scientific literature cited. Subsection 3.2. should be titled "*Advantages and Disadvantages of Renewable and Nonrenewable Energy Sources*" instead of "*Advantages of Using Renewable Fuels*."

Section 4, "*Biomass*" is structured in a particularly illogical manner, as it contains subsections up to 4.1.2.2.1.1., making it very difficult for the reader to navigate between subsections. Topics related to lignocellulose, for example, could be treated as a separate chapter, which would simplify the "row" of subsections.

Section 5, "Green Solvents" and 5.1.1. "*Deep eutectic solvents*" cite reference number 81, which does not concern deep eutectic solvents. Subsection 5.1. "*Liquid-liquid extraction*" should be included in subsection 4.1.2.2.1.4. as one of the methods for removing inhibitors. Subsection 5.1.2. "*Application of DES in Bioprocessing*" contains only one sentence. Section 7 entitled "*Summary of New Methods for Removing Inhibitors from Fermentation Broth*" as well as the subsections 7.1. "*Hydrophobic Magnetic DES*" 7.2. "*Supramolecular DES*" and 7.3. "*Metal-Organic Frameworks Combined with Pseudo-DES.*" consist of 2-3 sentences and reiterate the definitions of this types of DESs, which were already described in previous sections. Furthermore, HMDES, MOF@pseudo-DES, and SUPRADES are sorption systems for inhibitor removal, not methods - as was often defined by the PhD student.

I think the literature section of the doctoral dissertation is by far its weakest point. There are numerous repetitions of the same statements, and the composition of subsequent sections

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and subsections is chaotic. Considering the number of bibliographic references cited by the PhD student, one would expect more scholarly considerations.

Positive aspects of the literature section include the tables that summarize the advantages and disadvantages of renewable and non-renewable energy sources (Table 1), lignocellulose processing methods (Table 2), and inhibitor removal methods (Table 3), which were prepared in a very professional and readable manner. Although it would have been worthwhile to include a list of references which used to prepare the tables. Most of the figures in the doctoral dissertation were also aesthetically pleasing, with attention to detail.

The aim of M.Sc. Zhila Honarmandrad's doctoral dissertation was to develop and evaluate new and efficient sorption methods for removing inhibitors (HQ, HMF, FF, and VAN) formed during the hydrolysis and fermentation of lignocellulosic biomass. These inhibitors negatively impact the microbial activity and biohydrogen production. Therefore, three sorption systems were tested to remove them in both model and actual hydrolysates: HMDES (ferrofluid), MOF@pseudo-DES (solid), and SUPRADES (liquid). Their potential for repeated use and their impact on fermentation were also determined. The goal was to not only remove the inhibitors but also to improve the biohydrogen production efficiency.

In her doctoral dissertation, M.Sc. Zhila Honarmandrad did not put forward any research hypotheses. To achieve the goals of the dissertation, the PhD student presented the research tasks: (1) "*Comprehensive literature review on the formation of inhibitors during biomass hydrolysis and their impact on fermentation efficiency*", (2) "*Synthesis of novel green solvents, including HMDES, SUPRADES and MOF@pseudo-DES*", (3) "*Physicochemical characterization of the developed systems using techniques such as FTIR, XRD, SEM, BET and TGA for pseudo-DES@MOF and density, viscosity and surface tension measurements for SUPRADES*", (4) "*Optimization of extraction conditions to obtain maximum inhibitor removal using statistical models like Plackett-Burman and Box-Behnken designs*", (5) "*Comparison of performance of the proposed green solvents with conventional methods in terms of efficiency, selectivity and reusability*", (6) "*Application of the optimized systems to real fermentation broths to validate performance under practical conditions*," (7) "*Evaluation of biohydrogen production improvement after detoxification, confirming the positive effect of inhibitor removal on microbial hydrogen generation*".

Many colloquialisms are used in the sections discussing the results, e.g., "*ambient temperature*", "*precisely measured quantity*" (without specifying mass/volume), "*compared to the spectra of pristine HMDES*", "*duality in solubility preference*", "*extensive hydrogen bonding between the constituents*" etc.

Furthermore, the PhD student used the HPLC-DAD technique in experiment, but she did not present the basic validation parameters of the developed method for determining HQ, HMF, FF, and VAN (such as the linearity range, determination coefficients, calibration

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curve equation, limit of detection and limit of quantification). Please provide a chromatogram of the standards at λ=284 nm and chromatograms for selected samples. Error bars are not provided in all graphs presented in the experimental section. Was only one measurement performed for each parameter? Were multiple replicates performed, allowing the standard deviation to be calculated?

Why were menthol (as HBA) and nonanoic acid (as HBD) selected for the synthesis of HMDES and SUPRADES? In turn, why was choline chloride chosen for the synthesis of MOF@pseudo-DES? What factors were considered during the selection of DESs for synthesis? Have DESs with different structures or different HBD to HBA molar ratios been tested in these systems? What was the basis for the conclusion that the developed and used HMDES, SUPRADES, and MOF@pseudo-DES materials are "*green*", "*environmentally friendly*," and "*sustainable*"? Such terms frequently appear, especially in summaries.

Based on the obtained results, please propose a mechanism for the interactions between the inhibitors (HQ, HMF, FF, and VAN) and the sorption systems.

Are the FT-IR spectra sufficient to monitor possible structural changes in subsequent cycles of use of the proposed sorption systems?

In summary of doctoral dissertation, M.Sc. Zhila Honarmandrad emphasizes that each of the developed sorption methods has advantages. However, in a comparative analysis, the doctoral student indicates that HMDES is best suited for rapid, reusable, and scalable operations, SUPRADES for biohydrogen-focused pretreatment, and MOF@pseudo-DES for selective detoxification under mild conditions.

Furthermore, the doctoral student states that the proposed methods based on HMDES, SUPRADES, and MOF@pseudo-DES offer efficient, sustainable, and customizable solutions for removing inhibitory compounds from fermentation broth. Their use leads to increased fermentation efficiency and improved product yields, making them a promising advantage in biomass processing and biohydrogen production. It can be concluded that the stated goal of the doctoral dissertation has been achieved, and the planned tasks have been completed.

Moreover, in section 17 M.Sc. Zhila Honarmandrad emphasizes that the research presented in the doctoral thesis focusing on the use of HMDES to remove four inhibitors before and after fermentation is a scientific novelty and represents one of the first described advances in this topic.

**Summary and Final Conclusion**

In her doctoral dissertation, M.Sc. Zhila Honarmandrad dealt with topics that were not only very important and contemporary in scientific terms, but also allow for the practical application of research results to modify and improve the processes for removing inhibitors

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formed during the hydrolysis and fermentation of lignocellulosic biomass. In the framework of the doctoral dissertation, new sorption systems based on deep eutectic solvents - HMDES, MOF@pseudo-DES and SUPRADES - were synthesized, characterized, and applied for the removal of fermentation inhibitors. These systems offer promising solutions for increasing the efficiency of biohydrogen production. They also provide a basis for further experiments in this area. The doctoral dissertation is written in a rather chaotic manner, lacking appropriate scientific terminology and containing numerous repetitions and summaries. However, I would like to acknowledge M.Sc. Zhila Honarmandrad's contribution to such scientifically important issues in improving biohydrogen production, especially since this research was published in three high impact factor articles. **I evaluate the doctoral dissertation positively**, but I ask that the PhD student responds to all my comments and questions.

In conclusion, I declare that the reviewed doctoral dissertation of M.Sc. Zhila Honarmandrad entitled "*Management of broth after biomass hydrolysis to improve biohydrogen production*", meets the criteria for doctoral dissertations specified in Article 187 of the Act of July 20, 2018, the Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended). Therefore, I request the Chemical Sciences Discipline Council of the Faculty of Chemistry, Gdansk University of Technology, to admit M.Sc. Zhila Honarmandrad to the next stages of the doctoral process.

Justyna Werner