

Original scientific paper

TOWARDS SUSTAINABLE WASTEWATER TREATMENT: COMPARATIVE STUDY OF HYBRID ELECTROCOAGULATION PROCESSES WITH ZEOLITE, ULTRASOUND, AND MAGNET

Nediljka Vukojević Medvidović¹, Ladislav Vrsalović¹, Sandra Svilović¹, Senka Gudić¹, Ivona Čule^{1,2}

¹Faculty of Chemistry and Technology in Split, Croatia

²Institute for Public Health of the Federation of Bosnia and Herzegovina, Mostar, Bosnia & Herzegovina

ABSTRACT

This study evaluates three hybrid electrocoagulation (EC) processes with aluminium electrodes: EC-zeolite process (EC+Z), EC-zeolite-ultrasound-assisted process (EC+Z+US), and EC-zeolite-magnet-assisted process (EC+Z+MAG) for compost wastewater treatment with a large content of organic matter. The focus was on evaluating the effects of these processes on the removal efficiency of pollutants, including chemical oxygen demand (COD) and turbidity. Additionally, the study analysed the pH and temperature variations as well as electrode dissolution and corrosion to assess each hybrid process. The results revealed that the EC+Z+MAG process achieved the highest COD and turbidity decrease, indicating its superior efficiency in particle aggregation and removal. Regarding the pH and temperature, the EC+Z+US experiment exhibited the least changes in pH and temperature, while the EC+Z+MAG exhibited the highest. The EC+Z+US showed improved sludge recovery due to better particle agglomeration, while reducing electrode corrosion compared to other processes. Microscopic analysis indicated that ultrasound assistance reduced corrosion damage on the anode, while the magnetic field in the EC+Z+MAG process contributed to the formation of a dendritic structure on the cathode. Even though this study highlights the effectiveness of combining electrocoagulation with zeolite, ultrasound, and magnetic assistance to enhance wastewater treatment efficiency, further optimization of these hybrid processes is recommended to balance performance with sustainability and electrode longevity.

Keywords: hybrid electrocoagulation processes; wastewater treatment efficiency; electrode corrosion

Corresponding Author:
Nediljka Vukojević Medvidović
University of Split, Faculty of Chemistry and Technology, Split, Croatia
Ruder Bošković 35, Split, Croatia
Tel.: +385 21 329 452; fax: + 385 21 329 461
E-mail address: nvukojev@ktf-split.hr

1. INTRODUCTION

As industrial and technological activities continue to expand, the production of wastewater with complex compositions has escalated, presenting significant challenges for both the environment and water

availability [1]. Effective and economical treatment technologies are crucial for mitigating these issues and ensuring sustainable water management [2,3]. Among the various treatment methods, electrocoagulation (EC) has emerged as a

promising solution due to its simplicity, rapid process time, and ability to effectively remove contaminants such as suspended solids and organic matter [4,5]. EC works by using an electrochemical reactor, where metal electrodes dissolve anodically to generate hydroxides that destabilize and aggregate colloidal particles for removal through precipitation or flotation [2,4]. Despite its advantages, traditional EC processes face challenges like electrode fouling, corrosion, and high energy consumption [6]. To overcome these limitations, hybrid processes integrate EC with other techniques have attracted increasing attention [7]. One of the additions in the electrochemical reactor is zeolite, which is not only a strong sorbent but also reduces electrode fouling and improves overall treatment efficiency [8]. Further integration of methods such as ultrasound and magnetic fields, which can improve particle aggregation, presents these hybrid systems as capable of yielding better wastewater treatment outcomes with reduced operational costs and prolonged electrode lifespan [9,10]. This study compares the three hybrid EC processes: EC+Z (EC-zeolite process), EC+Z+US (EC-zeolite-ultrasound-assisted process), and EC+Z+MAG (EC-zeolite-magnet-assisted process) conducted using aluminium electrodes, by analysing pH and temperature change, reduction in chemical oxygen demand (COD) and turbidity, sludge recovery and electrode mass consumption. Additionally, microscopic analysis of the electrode surfaces was performed to evaluate corrosion and fouling. The goal of this study is to give useful information about the potential advantages and limitations of these hybrid processes, with the objective of optimizing the efficiency of wastewater treatment systems for both the environment and the industry.

2. EXPERIMENTAL

Compost wastewater. The initial wastewater was characterized by pH of 3.95, electrical

conductivity of 1.9 mS/cm, turbidity of 251.67 NTU, COD of 1642.06 mg O₂/L, and total solids concentration of 3.08 g/L, previously reported in the literature [11].

Electrodes: aluminium alloy series 2000 (AA2007) with Al=92.58%, Cu=3.84% was used [11].

Zeolite (Z): Synthetic zeolite (<40 µm) from Alfa Aesar [12] was crushed, sieved, granulated, and added at 15 g/L.

EC-hybrid system setup: Three different hybrid process carried out in a electrochemical cell equipped with aluminium electrodes were investigated: EC+Z, EC+Z+US, and EC+Z+MAG. Ultrasound was applied by placing the electrochemical cell in an ultrasonic bath (Agrolab DU100 of 40 kHz), while magnetic assistance was achieved using a 0.55T NdFeB magnet positioned beneath the reactor. The experiments were conducted under fixed conditions, including a current density of 0.0182 A/cm², the addition of 0.5 g/L NaCl as an electrolyte, an electrode distance of 3 cm, at mixing speed of 250 rpm and a contact time of 30 minutes. pH and temperature were continuously monitored, while the reduction in COD and turbidity, sludge recovery, and electrode mass consumption were measured at the end of the process for comparative analysis. Changes in electrode mass were determined through weighing, while electrode surfaces were analysed using a light microscope (MXFMS-BD, Ningbo Sunny Instruments Co.) with 50× and 200× magnification with bright field (BF) and dark field (DF), and a Canon EOS 1300D camera.

3. RESULTS AND DISCUSSION

3.1 Performance evaluation of hybrid wastewater treatment processes

The performance of different hybrid processes in wastewater treatment was evaluated by comparing pH and temperature change during each hybrid process which reflect the electrochemical reactions and energy inputs involved, and reduction of COD and turbidity which are crucial

indicators of the effectiveness of contaminant removal and colloidal particle destabilization. The results are compared on Figs. 1 and 2.

During wastewater treatment using different hybrid processes, both pH and temperature exhibit an increasing trend, although the rate

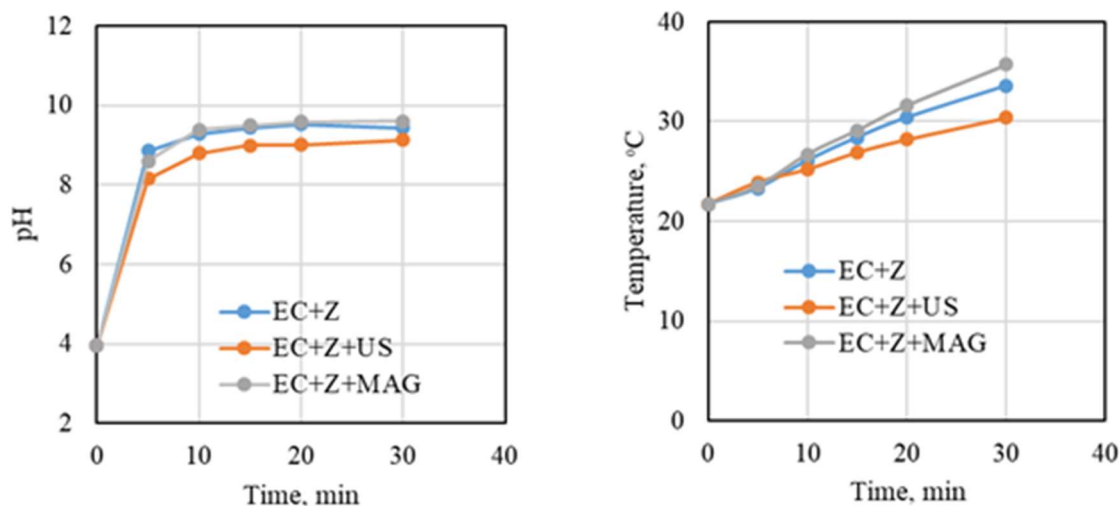


Figure 1. Comparison of pH values and temperature change during wastewater treatment by different hybrid processes

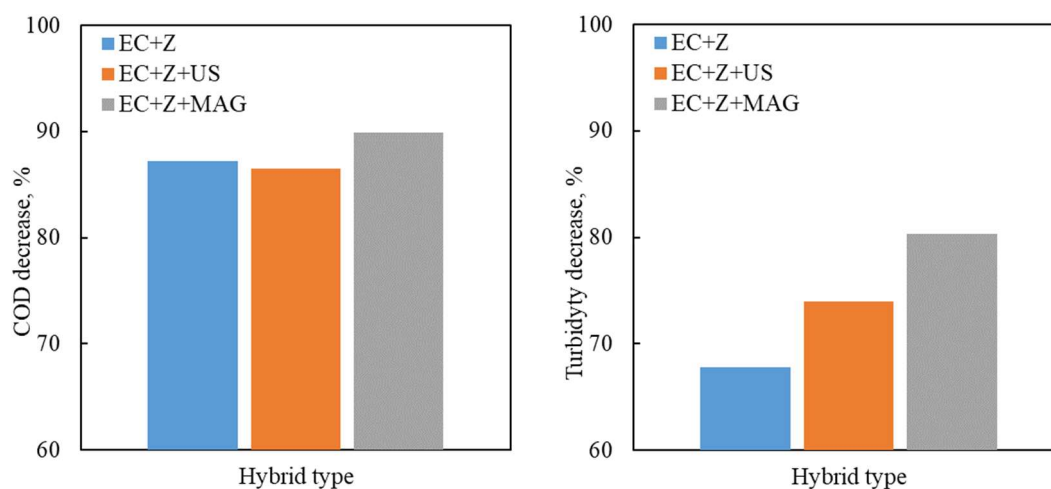


Figure 2. Comparison of COD and turbidity decrease by different hybrid processes

of change varies depending on the process (Fig. 1). Evidently, ultrasound – enhanced mixing and surface cleaning effects that occur during the EC+Z+US, may influence on lower increase of pH and temperature. Conversely, the EC+Z+MAG showed a higher increase in temperature which can be attributed to magnetohydrodynamic (MHD).

The magnetic field interacts effect with the electric field between electrode, generating Lorentz forces that enhance fluid motion and turbulence. This increased mixing promotes higher energy dissipation and conversion into heat within the electrochemical cell.

Additionally, the movement of charged species under the influence of the magnetic

field can disrupt their directed movement and lead to localized heating near the electrodes, further contributing to the overall temperature increase [13].

The results of COD and turbidity decreases percentage highlight differences among the hybrid processes. For COD, the EC+Z+MAG achieved the highest efficiency at 89.87%, followed by the EC+Z at 87.21% and the EC+Z+US at 86.49%. For turbidity removal, the EC+Z+MAG process also performed the best with 80.37%, followed by the EC+Z+US process at 73.95% and the EC+Z process at 67.8%. The superior performance of the EC+Z+MAG process in both COD and turbidity decrease percentage can be attributed to the MHD effect introduced by the magnetic field [13,14]. These effects enhance mixing, and particle collision rates, leading to more effective aggregation of colloidal particles, which improves removal efficiency. The slightly lower COD decrease percentage in the EC+Z+US process might result from the ultrasonic energy and particle dispersion rather than contributing significantly to the generation of additional reactive species [15]. However, ultrasound likely improves turbidity removal by increasing the interaction between particles and electro-generated coagulants.

The comparatively lower turbidity removal efficiency of the EC+Z process is likely due to the absence of external forces (magnetic field or ultrasound), which play a critical

role in enhancing particle interactions. Although synthetic zeolite provides adsorption and ion exchange capabilities, its effectiveness is limited without additional energy inputs to improve particle destabilization and aggregation, especially in such complex initial wastewater with very high organic load. Overall, the EC+Z+MAG process demonstrates the most effective hybrid approach, particularly for applications requiring high efficiency in both COD reduction and turbidity removal.

3.2 Sludge recovery and electrode consumption for different hybrid types

Evaluating sludge recovery (combination of metal oxides and hydroxides with a bound organic part and saturated zeolite) and electrode consumption is crucial in understanding the efficiency and sustainability of different hybrid EC processes. These parameters are influenced by factors such as particle aggregation, fouling effects, and the involvement of external factors like ultrasound, magnetic fields and zeolite addition. This section will compare and analyse the sludge recovery and electrode consumption for the different hybrid processes, shedding light on the interplay between these factors and their impact on the overall efficiency of wastewater treatment. The results are compare in Fig. 3.

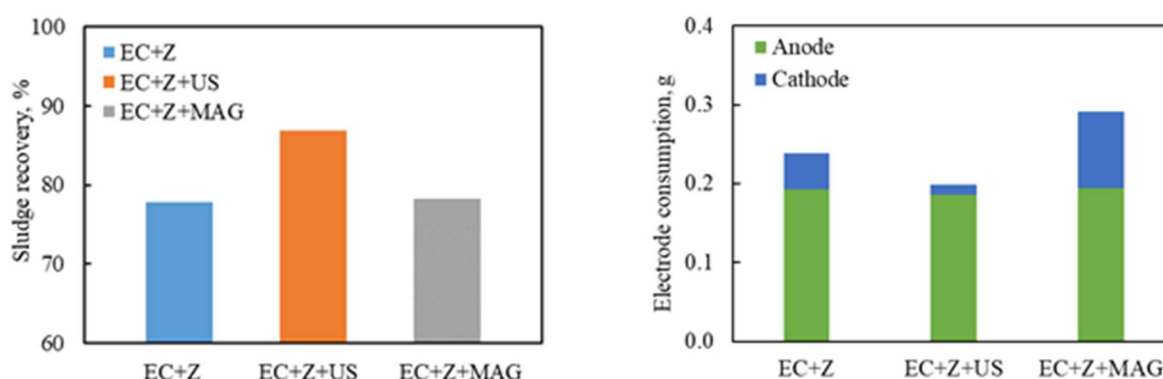


Figure 3. Comparison of: a) sludge recovery; b) electrode consumption for different hybrid types

The sludge recovery and electrode consumption results for the various hybrid processes indicate different trends. The highest electrode sludge recovery percentage is observed in the EC+Z+US at 86.85%, which suggests that the ultrasound assists in better aggregation and settling of the sludge. This can be attributed to the increased interaction between particles under the influence of ultrasonic waves, which enhances the floc formation [16]. In contrast, the EC+Z and the EC+Z+MAG show lower recovery rates of 77.83% and 78.24%, respectively. The slightly higher recovery in the EC+Z+MAG process compared to EC+Z could be due to the MHD effects, which help in the better aggregation of particles, although it still does not match the performance of ultrasound in sludge recovery [13,14].

Regarding the electrode consumption, the results show the expected trend of higher consumption of the anode compared to the cathode, as the EC process typically involves the sacrificial dissolution of the anode. Specifically, the EC+Z shows an anode consumption of 0.1929 g, which is slightly higher than the EC+Z+US at 0.1857 g, while almost identical to EC+Z+MAG at 0.1937 g, indicating that the magnet does not significantly affect the dissolution rate of the anode. On the other hand, the EC+Z+US process exhibits the lowest anode consumption, likely due to ultrasound-enhanced mass transfer, which limits ion accumulation and fouling near the anode, suppresses the formation of aggressive microenvironments, and prevents excessive anodic dissolution [17].

Regarding the cathode consumption, it is visibly lower than the anode consumption across all processes. The EC+Z+US process shows the lowest cathode consumption at 0.0136 g, which is significantly less than the EC+Z process (0.0456 g) and the EC+Z+MAG process (0.0976 g). The EC+Z+MAG process

has a notably higher cathode consumption. In contrast, the EC+Z+US process demonstrates better performance in reducing cathode wear, which suggests that ultrasound assistance mitigates fouling on the cathode surface by enhancing mass transfer and reducing ion accumulation, ultimately lowering consumption.

3.3 Microscopic analysis of electrode surface damage after performance of hybrid processes

The corrosion of electrodes during EC processes significantly impacts the efficiency and longevity of the treatment system. A detailed analysis of the electrode surfaces can provide valuable insights into the mechanisms driving corrosion and the influence of different hybrid processes. In this study, the surfaces of the electrodes after various hybrid processes, including EC+Z, EC+Z+US, and EC+Z+MAG, were examined using optical microscopy at 50× and 200× magnification with bright field (BF) and dark field (DF). By comparing the damage to both the anode and cathode surfaces, we aim to understand how ultrasound and magnetic assistance influence corrosion patterns, particularly focusing on reducing damage, changes in surface structure, and potential improvements in electrode performance. The results are compared in Figs 4 and 5.

Microscopic analysis of the electrode surfaces after the hybrid processes reveals distinct patterns of corrosion damage, which vary based on the type of hybrid process applied. At both 50× and 200× magnification, the images show clear signs of damage to both the anode and cathode surfaces of the electrodes, with noticeable differences between the processes. For the EC+Z process, almost the entire surface of the aluminium anode was significantly damaged, with visible signs of both general corrosion and pitting corrosion.

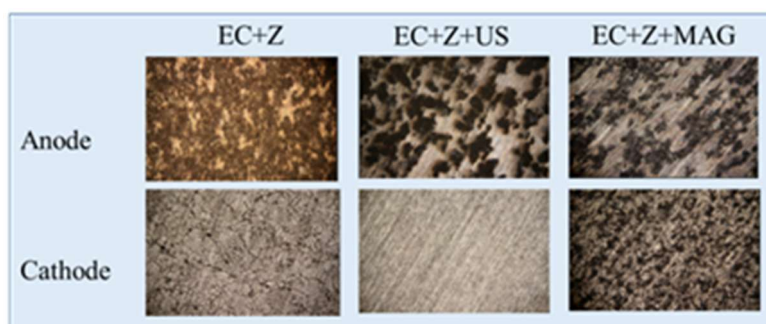


Figure 4. Optical microscopic surface analysis of electrodes (magnification 50x, bright field BF) after performance of different hybrid types

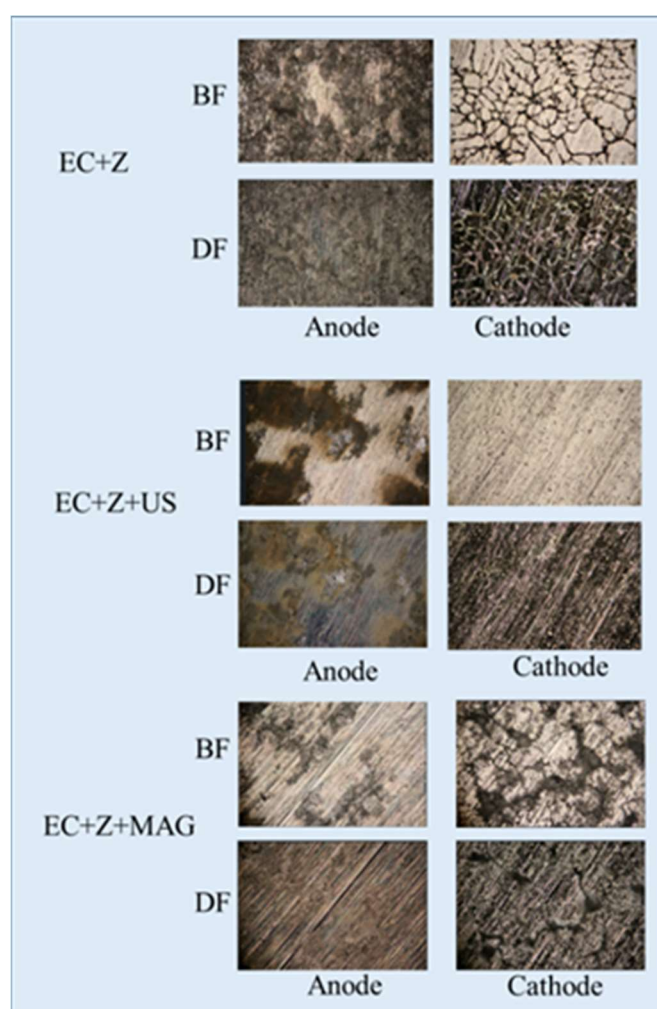


Figure 5. Microscopic surface analysis of the electrodes surface (magnification 200x, bright field BF, and dark field DF) after performance of different hybrid types

The pitting corrosion, in particular, suggests localized areas where metal dissolution occurred more aggressively. In contrast, the application of ultrasound assistance (US)

resulted in a reduction of this corrosion damage on the anode, indicating that the ultrasound helped mitigate some of the aggressive anodic dissolution [14]. However,

the magnetic assistance (MAG) process exacerbated the damage on the anode surface, possibly due to the increased turbulence and enhanced particle interaction, leading to further erosion of the anodic material.

On the cathode surface, after the EC+Z and EC+Z+MAG processes, a dendritic structure (cracked layer) was observed. This dendritic corrosion is likely caused by the cathodic reduction of organic compounds, the evolution of hydrogen gas, and the formation of hydroxide ions (OH^-), which together chemically attack the cathode surface. The dendritic structures, commonly associated with metal stress under such conditions, were particularly evident after the EC+Z+MAG process, suggesting more severe cathodic reactions in the presence of the magnetic field. However, when ultrasound assistance (US) was applied, the dendritic structure on the cathode disappeared. The reduction in dendritic corrosion features under ultrasound assistance highlights its role in mitigating surface damage and improving the overall longevity of the electrodes in the treatment process.

4. CONCLUSION

This study compares the performance of hybrid EC processes, namely EC+Z, EC+Z+US, and EC+Z+MAG, in wastewater treatment, focusing on their effects on pH and temperature change, COD and turbidity reduction, sludge recovery, electrode consumption, and surface corrosion.

The analysis of pH and temperature trends reveals that the EC+Z+US minimizes pH increase due to enhanced mixing and reduced cathodic reactions, while the EC+Z+MAG causes a greater temperature rise, attributed to MHD effects and localized heating near the electrodes. The EC+Z+MAG process exhibited the highest COD and turbidity reduction percentage, indicating its superior performance in particle aggregation and removal. The introduction

of the magnetic field increased the aggregation of particles, though it also caused more significant electrode surface interaction, leading to slightly higher electrode consumption, particularly on the cathode. Conversely, the EC+Z+US process enhanced sludge recovery and reduced electrode corrosion, particularly on the anode, compared to other processes. Microscopic analysis of the electrode surfaces revealed varying degrees of corrosion damage across the different hybrid processes. The EC+Z process caused significant pitting and general corrosion on the anode, while the EC+Z+US process reduced this damage. On the cathode, the EC+Z+MAG process led to the formation of a dendritic structure, likely due to aggressive cathodic reactions, which was alleviated by the ultrasound assistance.

This study highlights the potential of combining electrocoagulation, using an aluminum electrode, with zeolite (EC+Z) as a baseline process, with additional enhancements through magnetic assistance (EC+Z+MAG) or ultrasound (EC+Z+US). The results indicate that EC+Z+MAG is particularly effective for COD and turbidity decrease, while EC+Z+US shows promise in enhancing sludge recovery and minimizing electrode damage. Future research should explore further optimization of these hybrid processes to balance performance with long-term sustainability and electrode longevity.

Acknowledgments

The results presented in this paper were funded by institutional funds from the Faculty of Chemistry and Technology, University of Split, Croatia, and were conducted as part of the Croatian-Slovenian bilateral project "Augmentation, Intensification, and Development of New Integrated Wastewater Treatment Processes".

Conflict of Interest

The authors declare no conflict of interest.

REFERENCES

- [1] T.A. Tella, B. Festurs, T.D. Olaoluwa, A.S. Oladapo, Chapter 15: Water and wastewater treatment in developed and developing countries: Present experience and future plans. In: O.O. Ayeleru, S. Pandey, A. O. Idris, P. A. Olubambi (eds), *Smart Nanomaterials for Environmental Applications*, Elsevier, 2024, pp. 351-385, doi.org/10.1016/B978-0-443-21794-4.00030-2
- [2] M. Jyotsana, A. Suchita, A. Anfal, The Treatment of Wastewater, Recycling and Reuse -Past, Present, and in the Future, *International Journal of Science and Research (IJSR)*, 12(11) (2023) pp. 210-222, 10.21275/SR231013064713
- [3] J.A. Silva, Wastewater Treatment and Reuse for Sustainable Water Resources Management: A Systematic Literature Review, *Sustainability*, 15 (2023), 10940 doi.org/10.3390/su151410940
- [4] S. Jo, R. Kadam, H. Jang, D. Seo, J. Park, Recent Advances in Wastewater Electrocoagulation Technologies: Beyond Chemical Coagulation, *Energies*, 17 (2024), 5863 doi.org/10.3390/en17235863
- [5] K.P. Sandeep, C.S. Satish, R.N. Bikshandarkoil, A. Perumal, K.D. Harish, S. Amit, S. Diwakar, N. Mohd, R. Satish, S. Deepak, S. Shamal, D. Savita, K.P. Abhinesh, State of the art review for industrial wastewater treatment by electrocoagulation process: Mechanism, cost and sludge analysis, *Desalination and Water Treatment*, 321 (2025), 100915 doi.org/10.1016/j.dwt.2024.100915
- [6] B. Sriram, K. Abhinav, K. Jyoti, K. Ruthviz, V. Jayaprakash, A state-of-the-art review of the electrocoagulation technology for wastewater treatment, *Water Cycle*, 4 (2023), pp. 26-36 doi.org/10.1016/j.watcyc.2023.01.001
- [7] Z. Al-Qodah, M. Tawalbeh, M. Al-Shannag, Z. Al-Anber, K. Bani-Melhem, Combined electrocoagulation processes as a novel approach for enhanced pollutants removal: A state-of-the-art review. *Science of The Total Environment*, 744 (2020), 140806, 10.1016/j.scitotenv.2020.140806
- [8] S. Svilović, N. Vukojević Medvidović, L. Vrsalović, A. Kulić, Combining natural zeolite and electrocoagulation with different electrode materials – electrode surface analysis and Taguchi optimization, *Applied Surface Science Advances*, 12 (2022), 100330 doi.org/10.1016/j.apsadv.2022.100330
- [9] S. Svilović, N. Vukojević Medvidović, L. Vrsalović, S. Gudić, A.-M. Mikulandra, Ultrasonically Assisted Electrocoagulation Combined with Zeolite in Compost Wastewater Treatment. *Processes*, 12 (2024), 951, doi.org/10.3390/pr12050951
- [10] N. Medvidović, L. Vrsalović, S. Svilović, S. Gudić, S. Bućma. Magnetically Assisted Electrocoagulation Combined with Zeolite: Opportunities and Challenges in Compost Wastewater Treatment. In: I. Karabegovic, A. Kovačević, S. Mandzuka (eds), *New Technologies, Development and Application VII. NT 2024. Lecture Notes in Networks and Systems*, Cham, Springer, 2024, 1070, doi.org/10.1007/978-3-031-66271-3_61
- [11] N.Vukojević Medvidović, L. Vrsalović, S. Svilović, S. Gudić, I. Čule, Sono- and Zeolite-assisted electrocoagulation for compost wastewater treatment: does ultrasound power make a difference? *Minerals* 14 (2024), 1190, doi.org/10.3390/min14121190
- [12] N. Vukojević Medvidović, L. Vrsalović, S. Svilović, K. Magaš, D. Jozić, A. Čović, Electrocoagulation Combined with Synthetic Zeolite—Does the Size of Zeolite Particles Matter? *Minerals* 13 (2023), 1141 doi.org/10.3390/min13091141.
- [13] S. Yongwen, L. Hong, Y. Han, G. Yuanfeng, Z. Cunman, Magnetic field-assisted electrocatalysis: Mechanisms and design strategies. *Carbon Energy*, 6 (2024), 575, doi:10.1002/cey2.575
- [14] N. Yasri, M. Nightingale, K.J. Cleland, E.P.L. Roberts, The impact of a magnetic field on electrode fouling during electrocoagulation, *Chemosphere*, 303 (2022), 135207, doi: 10.1016/j.chemosphere.2022.135207
- [15] S. O. A. Nassar, M. S. Yusoff, H. Halim, N. H. Mokhtar Kamal, M. J. K. Bashir, T. S. B. A. Manan, H. A. Aziz, A. Mojiri, Ultrasonic (US)-Assisted Electrocoagulation (EC) Process for Oil and Grease (O&G) Removal from Restaurant Wastewater. *Separations* 10 (2023), 61 doi.org/10.3390/separations10010061
- [16] H. Zhang, M. Du, H. Hu, H. Zhang, N. Song, A Review of Ultrasonic Treatment in Mineral

- Flotation: Mechanism and Recent Development, *Molecules* 29 (2024), 1984
doi.org/10.3390/molecules29091984
- [17] A. Hassani, M. Malhotra, V.A. Karim, S. Krishnan, P.V. Nidheesh, Recent progress on ultrasound-assisted electrochemical processes: A review on mechanism, reactor strategies, and applications for wastewater treatment, *Environmental Research*, 205 (2021), 112463, 0.1016/j.envres.2021.112463