Thesis of Doctoral (Ph.D.) Dissertation

Enhancing the degradation efficiency of biomasses by magnetite nanoparticle coupled microwave irradiation and monitoring the processes with dielectric parameters

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2025

1. Introduction and Research Objectives

The continuous growth of the global population and industrial activities have led to increasing waste generation, posing a significant economic and environmental challenge. Waste management has become a critical global concern, worsened by rising energy demands. Various waste types require different treatment methods, placing a burden on economies and research development sectors. However, many waste materials contain recoverable components that, when treated appropriately, can be transformed into valuable raw materials or energy carriers, reducing overall waste volumes. The efficiency of these processes is often inadequate, necessitating the development of effective pre-treatment methods to improve the efficiency of biotransformation-based technologies. Additionally, reliable monitoring techniques are needed to ensure accurate and timely tracking of pre-treatment and utilization processes.

My doctoral research focused on two types of waste: meat industry sludge and a plant-based biomass byproduct. I aimed to enhance process efficiency and monitor these processes using dielectric parameters. The meat industry sludge samples were subjected to standalone and magnetite nanoparticle-enhanced microwave pre-treatments to increase the organic content of the liquid phase and improve biogas production potential. The lignocellulosic plant biomass byproduct underwent multi-stage biotransformation into sugars and ethanol. Anaerobic co-digestion experiments were conducted using fermentation residues and meat industry sludge to maximize biogas yield.

Given the complexity and sensitivity of these processes to initial conditions, the development of a proper monitoring method was essential.

Dielectric parameters are fundamental material characteristics influenced by physical, chemical, and biological properties. Since these material properties change during pre-treatment and utilization processes, their dielectric behavior also evolves. My primary objective was to examine how changes in dielectric parameters correlate with process indicators and to establish a reliable, rapid, and non-destructive monitoring methodology.

2. Materials and Methods

In the first phase of my research, I used meat industry wastewater sludge from a local meat processing plant as raw material. Various microwave-based pre-treatment methods were applied. For standalone microwave treatments, experiments were conducted at magnetron power levels of 250 W and 500 W with irradiation durations of 180 and 90 seconds, corresponding to an energy input of 45 kJ. For combined treatments, 5 mg/100 cm^3 magnetite nanoparticles (MNPs) were added to the sludge before microwave irradiation. The changes in soluble chemical oxygen demand (sCOD) were measured to evaluate the impact of pre-treatment. The dielectric behavior of the liquid phase was assessed using an open-ended dielectric probe connected to a vector network analyzer (VNA) over a 200-2400 MHz frequency range.

In the second phase, the pre-treated sludge samples underwent mesophilic anaerobic digestion (38±0.5°C). I monitored biogas production, apparent viscosity changes, and variations in dielectric properties within the 200-2400 MHz frequency range. Biogas methane content was measured using an OPTIMA7 biogas analyzer equipped with dual NDIR sensors. The relationship between biogas yield, rheological changes, and dielectric behavior was evaluated.

In the final phase, plant-based biomass (corn cob meal) underwent multi-stage SHF (separate hydrolysis and fermentation) processes. Enzymatic hydrolysis was conducted under controlled conditions (T = 45±0.5°C, pH = 4.8±0.2) using glycosidic enzymes (cellulase, hemicellulase, β-glucosidase). Reducing sugar concentration was measured via DNSA-based spectrophotometry, and the dielectric behavior of the hydrolysate was monitored across the 200-2400 MHz range.

Following hydrolysis, the hydrolysates were subjected to ethanol fermentation using Saccharomyces cerevisiae at 1 g/L concentration under optimal conditions (T = 35±0.5°C, pH = 5.5±0.2). Ethanol concentration was measured using a refractometric method following distillation, and dielectric properties were recorded. The solid residue from ethanol fermentation was co-digested with meat industry sludge under mesophilic conditions. Biogas production and dielectric properties were monitored to establish correlations between process efficiency and dielectric changes.

3. New Scientific Results

T1) I have found that the changes in soluble chemical oxygen demand (characterized by the logarithmic change compared to the control samples; log sCOD/sCOD$_c$) caused by 2450 MHz frequency microwave treatments applied to meat industry sludge standalone or in combination with magnetite nanoparticles correlates with the change in dielectric parameters measured at 500 MHZ frequency (characterized by the logarithmic change of the dielectric constant and loss factor compared to the control; log ε'/ε'$_c$ and log ε"/ε"$_c$).

Microwave pre-treatments at 2450 MHz frequency, combined with magnetic metal oxide (magnetite) nanoparticles, applied at two different power levels (250 W and 500 W) to the meat sludge raw material, increased the water-soluble chemical oxygen demand (sCOD) of the sample to different extents compared to the native (control) sample, and the logarithm of the magnitude of the increase is strongly correlated with the logarithmic change in the dielectric constant and loss factor (f = 500 MHz) describing the dielectric behavior of the sample compared to the control sample (r = 0.9941 and 0.9942, and R^2 = 0.9883 and 0.9884). Since the logarithmic function is mutually explicit, this implies that the molecular changes induced in the liquid phase by each pretreatment are directly related to the change in dielectric behavior under the conditions and boundary conditions tested ($0.05 < \log sCOD/sCODc < 0.35$; $-0.009 < \log \varepsilon'/\varepsilon'_c < 0$; $0 < \log \varepsilon''/\varepsilon''_c < 2.5$), i.e. by measuring the appropriate dielectric parameters, the efficiency of sludge pretreatment processes can be estimated - irrespective of the pretreatment process that induced these molecular changes.

T2) I have demonstrated with experimental results that the $sCOD/sCOD_c$ ratio, which indicates the organic matter content of the soluble phase compared to the native (control) sample, can be more than doubled when the 2450 MHz frequency microwave pre-treatment (at a power level of 250 W and irradiation time of 3 minutes) of the meat industry sludge is combined with the addition of magnetite nanoparticles at a concentration of 5 mg/100 cm^3.

Magnetite nanoparticle addition, combined with 250 W microwave treatment for 3 minutes, significantly increased the soluble organic content in the liquid phase. The soluble chemical oxygen demand ratio (sCOD/tCOD)

increased by 36%, significantly higher than the 8% increase observed with standalone 250 W microwave treatment. The ratio of sCOD/sCODc (the change in the soluble chemical oxygen demand compared to the control sample) showed a 2.2-fold increase, improving the original 0.3 sCOD/TCOD to approximately 0.7. This improvement likely results from a more homogeneous thermal field induced by the presence of magnetite particles, promoting higher sludge disintegration. Further studies are necessary to confirm this explanation conclusively.

T3) I established that treating meat industry sludge (with an organic content of 34.3 g/L) with magnetite nanoparticles and 2450 MHz microwave irradiation (250 W, 3 min) could increase the specific biogas yield over threefold compared to untreated sludge during mesophilic digestion (38±0.5 °C), with improved methane composition.

The combined treatment enhanced sludge disintegration, leading to higher soluble organic content in the liquid phase and improved anaerobic bioconversion efficiency. Untreated sludge yielded 88.7 $cm^3/gTCOD_{initial}$, while the sludge sample that underwent combined treatment produced 278 $cm^3/gTCOD_{initial}$, which is a significant improvement. The methane content of biogas also increased from 60% in the control to 69% in the treated sample.

T4) I have confirmed with experimental results that the continuous presence of magnetite nanoparticles during mesophilic anaerobic fermentation (38±0.5 °C) of meat industry sludge (34.3 g/L organic content) pretreated with 2450 MHz microwave energy (250 W, 3 min) can enhance the maximum biogas yield by about 40%.

The combined pretreatment, involving magnetite nanoparticle addition followed by 2450 MHz microwave irradiation, significantly improved biogas production efficiency during anaerobic fermentation. However, if the magnetite particles were completely removed before digestion, the specific biogas yield dropped by 40% (from 278 $cm^3/gTCOD_{initial}$ to 205 $cm^3/gTCOD_{initial}$). This indicates that the enhanced methane production is likely due to the previously described mechanism of iron-dependent hydrogenase activity in methanogenic bacteria, stimulated by the presence of magnetite. These findings confirm that the combined magnetite-microwave pretreatment plays a crucial role in improving both biogas yield and process efficiency.

T5) I have determined that during the mesophilic anaerobic digestion of native and microwave-treated (2450 MHz) 51.4 g/L organic content meat industry sludge, the characteristic reduction in the apparent viscosity of the fermentation medium coincided with the distinct phases of biogas fermentation (lag, log, stationary).

The apparent viscosity continuously decreased during digestion, correlating with biogas volume production and the distinct fermentation phases. This indicates that by measuring the rheological properties of the meat industry sludge during anaerobic fermentation, we can gather information about the phase the anaerobic fermentation is currently in.

T6) Dielectric measurements during mesophilic digestion (38±0.5 °C) of 51.4 g/L organic content meat sludge demonstrated that the characteristic changes in dielectric constant (in the interval of 82.75 to 77.02) and loss factor (in the interval of 0.01 to 9.88) at 200-2400 MHz frequency range persisted until the onset of the stationary phase.

The dielectric constant gradually decreased until the 12th day, marking the start of the stationary phase. The discrete frequency associated with maximum dielectric constant shifted towards higher frequencies. The loss factor also decreased continuously, and its spectrum steepened at higher frequencies as fermentation progressed. A strong correlation was observed between the complex dielectric behavior (ε'/ε'') and cumulative biogas volume (R^2 = 0.977-0.9866, r = 0.9884-0.9933), indicating that molecular changes in the medium manifest as measurable dielectric changes, suitable for tracking biogas fermentation.

T7) I established that during both the lignocellulose-to-reducing sugar enzymatic bioconversion (0-24300 g/L sugar-concentration range) and reducing sugar-to-bioethanol bioconversion (0-0.5 V/V% ethanol concentration range), the measurement of the dielectric constant at 900 MHz can be applied to monitor the progression of these processes.

During enzymatic hydrolysis, the reducing sugar concentration increase corresponded to a local minimum in the dielectric constant at 900 MHz. The dielectric constant decreased proportionally to glucose concentration increases, showing strong correlation (r = 0.987-0.989, R^2 = 0.9736-0.9781). During ethanol fermentation, the dielectric constant's minimum value increased as ethanol concentration increased (and glucose concentration decreased), again showing strong correlation (r = 0.989-0.997, R^2 = 0.979-0.993).

T8) I determined that during the co-fermentation of 34.3 g/L organic content meat sludge and SHF fermentation residues of plant byproducts, dielectric constant changes measured at 200-2400 MHz can be used to monitor the process, considering both the maximum points of the dielectric constant values and the corresponding frequency shifts.

A strong correlation was observed between biogas yield – which directly implicates the efficiency of the co-fermentation process - and the dielectric behavior changes ($r = 0.981\text{-}0.996$, $R^2 = 0.963\text{-}0.993$), both for the control, and the microwave treated meat industry sludge samples. The maximum value of the dielectric constant decreased continuously during the anaerobic digestion, with the corresponding frequency shifting towards higher values. This indicates that the application of dielectric measurements can provide indirect information about biogas yield and the co-fermentation process efficiency.

4. Scientific publications related to the thesis

- **Jákói Z,** Lemmer B, Hodúr C, Beszédes S. Microwave and Ultrasound Based Methods in Sludge Treatment: A Review.

  Applied Sciences. 2021; 11(15):7067. https://doi.org/10.3390/app11157067

  Q2, IF=2,5, WoS-citation: 10

  https://www.webofscience.com/wos/woscc/full-record/WOS:000681864800001

- **Jákói, Z.,** Hodúr, C., Beszédes, S. Dielektromos mérések alkalmazási lehetőségei biomassza-hasznosítási eljárásokban.

  Membrántechnika és Ipari Biotechnológia, 2022; 13(2), 14-20.

  MTA-classification „A" – IV. Section of Agricultural Sciences

- **Jákói Z**, Hodúr C, Beszédes S. Monitoring the Process of Anaerobic Digestion of Native and Microwave Pre-Treated Sludge by Dielectric and Rheological Measurements.

  Water. 2022; 14(8):1294. https://doi.org/10.3390/w14081294

  Q1, IF=3, WoS-citations:5

  https://www.webofscience.com/wos/woscc/full-record/WOS:000786882900001

- **Jákói Z.P**, Lemmer B, Dobozi R, Hodúr C, Beszédes S. Using Dielectric Constant Measurement to Monitor Ethanol Fermentation and Anaerobic Co-Digestion of Lignocellulosic Biomass.

  Fermentation 2023; 9(10):902
  https://doi.org/10.3390/fermentation9100902

  Q2, IF=3,3, WoS-citations: 2

  https://www.webofscience.com/wos/woscc/full-record/WOS:001089882700001

- **Jákói, Z.P.,** Hodúr, C., Beszédes, S. Magnetic iron oxide nanoparticle enhanced microwave pretreatment for anaerobic digestion of meat industry sludge.

  Scientific Reports, 2024, 14, 10723. https://doi.org/10.1038/s41598-024-61423-6

  D1, IF=4,996, WoS-citations: 1

  https://www.webofscience.com/wos/woscc/full-record/WOS:001218726300028

Total IF: 13,796

Total no. of WoS-citations: 18

Other scientific papers, total citations (MTMT):
https://m2.mtmt.hu/gui2/?type=authors&mode=browse&sel=10062259&view=dataSheet (MTMT-identifier: 10062259)

5. Selected conference presentations

- 26th International Symposium on Analytical and Environmental Problems, international conference, presentation of scientific research (**oral speech in English**), Szeged, Hungary, 23-24th November, 2020. (Presentation: Application of microwave-assisted fenton-reaction for enhanced organic matter removal in wastewater treatment)

- International Conference on Science, Technology, Engineering and Economy - ICOSTEE 2022, international conference, presentation of scientific research (**oral speech in English**), Szeged, Hungary, 24th March, 2022. (Presentation: Advanced Processes in Wastewater Sludge Treatment)

- 50. Műszaki Kémiai Napok Jubileumi Konferencia, international conference presentation of scientific research (**oral speech in Hungarian**), Veszprém, Hungary, 26-28th April, 2022 (Presentation: Biogázfermentáció nyomon követése dielektromos és reológiai mérési módszerekkel)

- XXXV Scientific - Professional Conference of Processing and Energy in Agriculture, **invited (plenary) speech in English**, Palics, Serbia, 23-28th April, 2023 (Presentation: Enhancing the Anaerobic Digestion of Sludge with Combined Pre-treatment Methods)

- International Conference on Science, Technology, Engineering and Economy - ICOSTEE 2024, **oral speech in English**, Szeged, Hungary, 31st May, 2024 (Presentation: Enhancing the Biodegradability of Meat

Industry Sludge with Metal Nanoparticles Coupled Microwave Irradiation)

- 2nd TwiNSol-CECs Workshop, **oral speech in English**, Novi Sad, Serbia, 7th June, 2024 (Presentation: Dielectric monitoring in enhanced wastewater sludge utilization processes)

6. Acknowledgements

I express my profound gratitude to my supervisors, Prof. Dr. Cecilia Hodúr and Dr. habil. Sándor Beszédes, for their invaluable support throughout my doctoral journey. I extend my thanks to my colleagues at the Faculty of Engineering, University of Szeged, particularly those at the Department of Biosystems Engineering. Special thanks to Dr. Erzsebét Illés for providing the essential magnetite nanoparticles and her scientific expertise.

Additionally, I am immensely thankful to my family—my dear parents, siblings, my partner Réka Dobozi, and her family—for their unwavering support, encouragement, and motivation throughout this journey, often going above and beyond when needed.

Finally, I wish to thank my past self for persevering through challenges and never giving up, and to my future self, I say: this is just the beginning!