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ENHANCING AND MONITORING THE ANAEROBIC DIGESTION OF WASTEWATER SLUDGE

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Abstract
The most important key of wastewater treatment is the treatment of the wastewater sludge. Anaerobic fermentation is an effective solution for the treatment. *I*t can lower the organic content of the sludge while a renewable energy source – biogas – is produced at the same time. Our research is focused on the applicability of rheological and dielectric measurements to study if these measurements can monitor the proccess of anaerobic digestion. Moreover, microwave pre-treatment was used on the wastewater sludge to examine its effect on anaerobic digestion. Our experimental results represent that the microwave irradiation can intensify the total biogas yield by 15% during anaerobic fermentation. Furthermore, microwave irradiation was effect on viscosity, it reduced the viscosity of the fermentation media by 13%. It has been confirmed that dielectric and rheological measurements are capable of monitoring the anaerobic digestion because there is a correlation among dielectric parameters, biogas yield and absolute viscosity of the fermentation media. Changes in the dielectric parameters and absolute viscosity show similar trends, which can be explained by the connection with biogas production.

Introduction
One of the ecologically dominant problems nowadays is the large amount of waste which is a result of industrialization and growing population. Wastewaters from various origin also form a group of wastes and the proper treatment of these wastewaters plays a particularly important role in terms of the nature and the mankind as well. By subjecting the accumulated wastewaters to appropriate treatments, it is possible to reduce the use of natural energy sources, such as petroleum, coal or natural gas which are being depleted. Biologically produced alternatives - such as biofuels - offer an opportunity to solve this, as the use of biomass means significantly smaller ecological footprint. [1]
The most essential purposes of thermal treatment techniques are to reduce the moisture content of the sludge, minimize its microbial risk and improve their fermentability. As an alternative of tradicional heat transfer methods, the examination of microwave irradiation has become more and more common in recent decades, due to its fast, selective and efficient heating mechanism that can enhance several biotechnological and environmental processes. [2]
Anaerobic digestion is a promising and effective method in wastewater sludge treatment, as it can be used to remove toxic substances, reduce the volume of the sludge and produce biogas. During anaerobic digestion specific microorganisms transform the organic content of the substrate into methane (40-65%), carbon-dioxide (30-55%) and other gaseous compounds (0,3-1%). [3] The production can be divided into three different stages of microbiological activity, which are built on each other and can not be separated under natural conditions (Figure 1). [4]
In the stage of hydrolysis, complex carbohydrates, lipids and proteins are transformed into sugars, fatty acids, and amino acids with their help of polymer-decomposing bacteria. In the next acidification phase the previous various compounds are used by acetogenic bacteria to

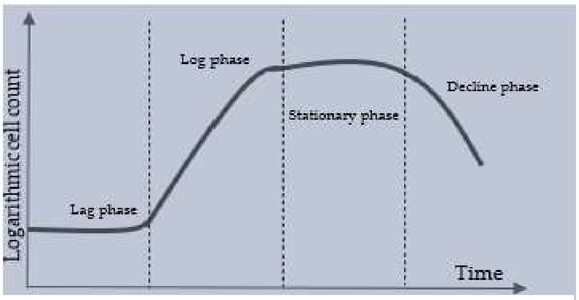


Figure 1. Different phases of biogas formation in a batch fermenter [7]

produce organic acids and alcohols, then these are almost completely modified into acetic acid. In the last stage, the so-called methanogenesis, the main component of the biogas – the methane gas – is produced by methanogenic bacteria. [5] Several key factors affect the successful completion of biogas fermentation, for example the C:N:P ratio of the substrate, the temperature, total solid concentration, pH, and the bioavailability of compounds which are involved in biochemical transformation. [6] [7].

Dielectric behaviour of normal materials largely depends on their physicochemical structure and the frequency (*f*) and strength (*E*) of the electromagnetic field they are interacting with. Given the equation

$$\frac{D}{E} = \varepsilon,$$

we can see that the absolute permittivity of a material is the ratio of the electric displacement (*D*) that was caused by the electric or electromagnetic field *E*. Polarization however does not occur instantaneously in these materials; therefore the electric displacement (*D*) can be interpreted as a phase shift. Since complex numbers allow to define magnitude and phase in the same time, the absolute permittivity of a material should be treated as a complex function of the frequency:

$$\varepsilon = f(\varepsilon_C(\omega))$$

As any complex function, complex permittivity can be separated to its real and imaginary part:

$$\varepsilon_C(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

ε' refers to the dielectric constant which indicates the electric energy storing capability of a given material, while ε'' is the dielectric loss factor. The latter contains the so-called dielectric loss (due to the rotation and vibration of permanent and induced dipolar molecules) and the effective conductive loss (due to the ionic displacement of charged particles). These dielectric properties greatly depend on the physicochemical structure of a given material, and can significantly change when this structure undergoes any form of transformation – for example, during a fermentation process. Measuring the dielectric properties of wastewater sludge is non-destructive, quick, and chemical-free method. Taking the change of dielectric properties as a basis, then changes taking place during the fermentation process can be monitored. Another potential method to analyse the efficiency of anaerobic digestion is to measure changes in dynamic viscosity. A number of biochemical reactions take place in the various phases of the anaerobic digestion, therefore changes in absolute viscosity of the fermentation media are expected to occur.

Experimental

For the anaerobic digestion experiments, we used wastewater sludge originated from a local meat processing plant as raw material in a volume of 90 cm^3 with 10 cm^3 of inoculum seed sludge added to guarantee the proper microbiological environment. Anaerobic fermentation was carried out under thermostatic conditions at a temperature of 38 °C. The samples were incubated in 250 cm^3, continuously stirred laboratory glass reactors, sealed by PTFE septum. Measurements were taken every second day. On top of the reactors WTW Oxi-Top IDS/B automatic manometric measuring heads were put, which could indicate the amount of biogas production by monitoring the absolute gas pressure during the digestion. To observe the changes in the dielectric constant (ε') and the dielectric loss factor (ε") a DAK 3.5 (Speag, Switzerland) dielectric probe connected to a ZVL-3 (Rhode&Schwarz, Germany) VNA was used, which enables testing in the range of 200 to 2400 MHz. To derermine the absolute viscosity of the fermentation liquid, RP1 rotary viscosimeter at a speed of 200 rpm was used, which provides examination in the range of $20\text{-}13\cdot10^6$ mPas.

Microwave treatment was carried out in a Labotron 500 laboratory batch microwave equipment, which generates electromagnetic waves at the frequency of 2.45 GHz. The treatments were carried out at the power level of 250W and the radiation time of 720 seconds and 30-30 seconds on/off cycle to achieve better temperature homogenity.

Results and discussion

Firstly, we studied the applicability of viscosity measurement to both control and microwave-irradiated samples and investigated how the microwave irradiation affects the biogas production dynamics.

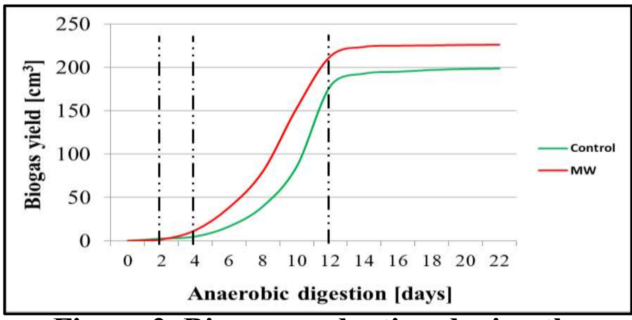


Figure 2. Biogas production during the anaerobic digestion

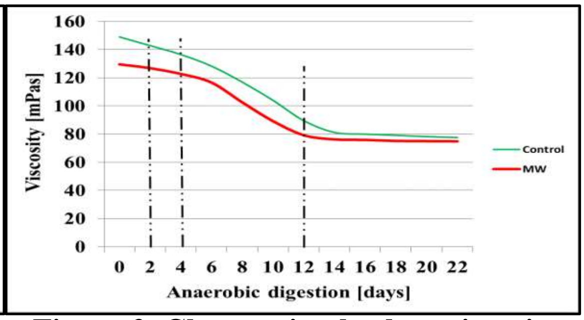
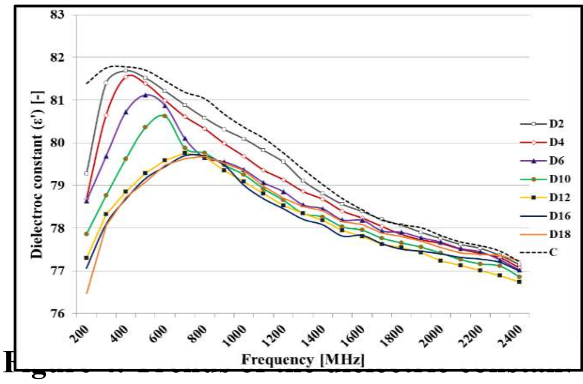
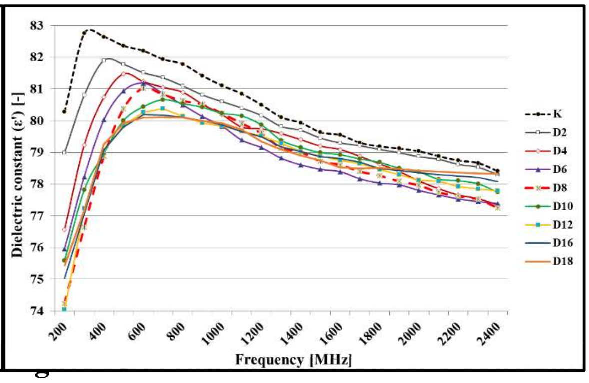


Figure 3. Changes in absolute viscosity during anaerobic digestion

Our results show (Figure 2 and 3) that the biogas production dynamic follows the stages represent in Figure 1 in terms of control and microwave irradiated samples, and at around day 12 the stationary phase sets. In case of viscosity, it declines gradually in both control and the microwave-treated samples, as the biochemical environment changed, which shares intense similarities in tendency with the curves of the biogas yield. The microwave irradiation resulted overall higher biogas yield during the whole fermentation process and the maximum achievable volume was approximately 230 cm^3 compared to the control sample, where the maximum volume was 200 cm^3. It can also been seen that microwave irradiation shortened the lag and the log phase by 1-2 days, so microorganisms could adapt to the fermentation environment more easily. When the stationary phase sets the viscosity also become nearly constant, so the changing of the biochemical environment in the different stages of the anaerobic digestion are in connection with overall viscosity of the fermentation media. In rheological properties the microwave irradiation resulted lower viscosity values during the whole fermentation by approximately 13% in average, as it was expected.



of the not-treated samples



of the microwave irradiated samples

Secondly, the examination of the dielectric properties of the fermentation media during the anaerobic digestion was the focal point of our research. It can be clearly seen that the values of the dielectric constant gradually decreases in low-frequency both of control and treated samples during the whole digestion, until the 12th day of the fermentation. The frequency which correlates to the maximum ε' increases in both cases, until the 12th day of the fermentation. After that the differences of the frequency of the ε' are starting to shrink and in higher frequency ranges (1200-2400 MHz) the dielectric constant of the 12th day media becomes the lowest. Because of reaching the stationary phase the biochemical environment becomes steady-state and no significant changes occur, so the differences in the dielectric constant cease as well. In case of the microwave irradiated samples the values of the maximum dielectric constant are a bit higher, and the differences are a bit more observable in the lower frequency range (200-600 MHz). The reason is the structural changes causes by the microwave irradiation. Microwave-treated and non-treated samples show similarities, the maximum points of the dielectric constant shift towards higher frequencies during the whole fermentation, until the 12th day, when the stationary phase sets.

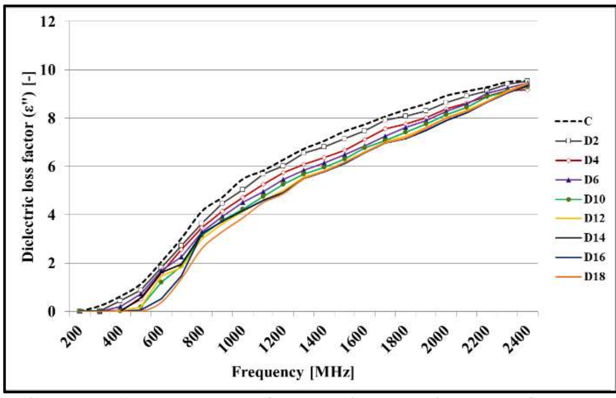


Figure 6. Trends of the dielectric loss factor of the non-treated samples

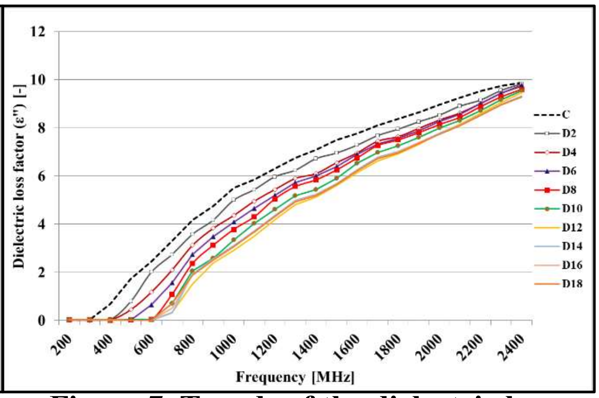


Figure 7. Trends of the dielectric loss factor of the microwave irratiated samples

Our results show that the control sample has the highest dielectric loss factor during the entire frequency range in non-treated and treated samples as well. This means that a reasonable amount of absorbed energy was turned into heat during the measurement. During the fermentation process the value of the dielectric loss factor become lower in every measurement point, until the 12th day of the fermentation, after which differences start to cease, just like in the case of the dielectric constant. Because of the biochemical changes during the fermentation, the values of the dielectric loss factor are starting to increase intensively at a well-defined frequency, but this point varies with the day of the fermentation. In case of microwave-treated samples the values of the ε" are higher than in case of non-treated samples, especially in the lower frequency range and the differences between the fermentation days are more observable. Moreover, the values of the dielectric loss factor are starting to increase at higher frequencies compared to non-treated samples. It can be also explained with the biochemical changes during the fermentation, because larger molecules are breaking down into smaller and smaller ones.

Conclusions

In our work we studied two monitoring techniques – dielectric and rheological measurements – to discover if they are capable of identifying and tracking the various stages of the anaerobic digestion of the sludge originated from meat industry. It was verified that the biogas production follows the stages of the anaerobic digestion in each case and the standalone microwave irradiation could intensify the maximum biogas yield by 15%. Absolute viscosity measurements share strong similarities with dynamics of the biogas volume, so these rheological measurements are able to identify and follow the different stages of the fermentation in terms of non-treated and pre-treated samples too. Because of the disintegration of the sludge, which was caused by the microwave pre-treatment the measured viscosity was lower than in case of the non-treated samples. The suitability of the measurement of the dielectric constant (ε') and dielectric loss factor (ε") for monitoring the process of the anaerobic digestion has been proven both in the case of non-treated and pre-treated samples. As the fermentation moves forward dielectric properties become lower and lower, until the 12^{th} day of the fermentation, when the stationary phase sets. Furthermore, the frequency that is in connection with the highest dielectric constant value becomes higher as the fermentation progresses, until the 12^{th} day of the fermentation. This means that the starting point of the stationary phase of the fermentation is determinable with this method. Based on our results the dielectric properties are due to the biochemical changes that occur in the fermentation media due to the absorbed microwave energy.

Acknowledgements
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References
[1] Lachassagne, D., Soubrand, M., Casellas, M., Gonzalez-Ospina, A., & Dagot, C. (2015). *Impact of sludge stabilization processes and sludge origin (urban or hospital) on the mobility of pharmaceutical compounds following sludge landspreading in laboratory soilcolumn experiments. Environmental Science and Pollution Research, 22(21), 17135–17150.*
[2]Ngo, P. L., Udugama, I. A., Gernaey, K. V., Young, B. R., & Baroutian, S. (2021). *Mechanisms, status, and challenges of thermal hydrolysis and advanced thermal hydrolysis processes in sewage sludge treatment. Chemosphere, 281, 130890*
[3] Ding, Y.; Guo, Z.S.; Hou, X.G.; Mei, J.X.; Liang, Z.L.; Li, Z.P.; Zhang, C.P.; Jin, C. *Performance Analysis for the Anaerobic Membrane Bioreactor Combined with the Forward Osmosis Membrane Bioreactor: Process Conditions Optimization,Wastewater Treatment and Sludge Characteristics. Water 2020, 12*
[4] Refai, S., Wassmann, K., & Deppenmeier, U. *Short-term effect of acetate and ethanol on methane formation in biogas sludge. Applied Microbiology and Biotechnology, Vol. 98, pp 7271–7280 (2014)*
[5] Antoine Prandota Trzcinski, *Advanced biological, physical and chemical treatment of waste activated sludge CRC Press; 1st edition, 2018* 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, 1294.*
[6] Cheng, Y.C.; Li, H. *Rheological behavior of sewage sludge with high solid content. Water Science and Technology 2015, 71, 1686-1693*
[7] 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, 1294.*