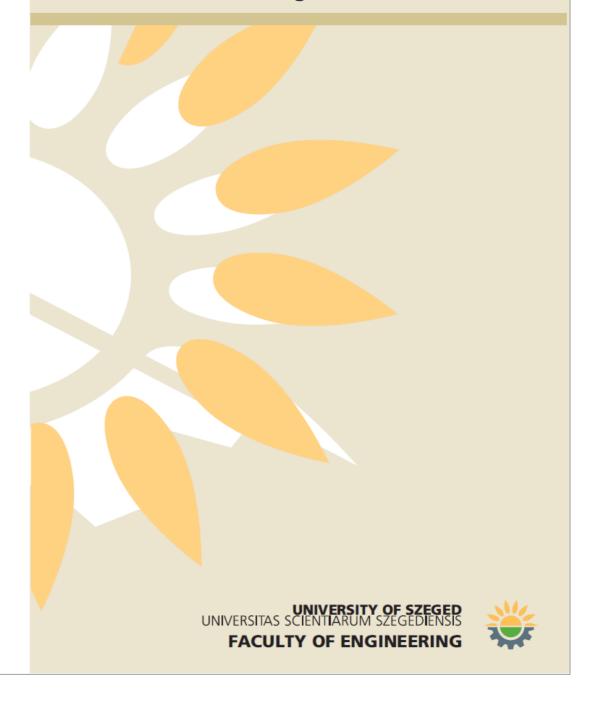
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CONTENTS

CONTENTS	PAGE
Balázs P. Szabó	
SOFT AND HARD WINTER WHEAT DEBRANNING	
Vasile Alexa, Imre Kiss, Csaba-Attila Gheorghiu	10
THE EDUCATIONAL PRACTICES AND E-LEARNING COURSES IN PERFORMING THE	
LABORATORY WORKS SPECIFICS TO THE HYDRAULICS AND PNEUMATICS APPLICATIONS	
Sorina Gabriela Şerban	17
EDUCATIONAL SOFTWARE – EFFECTIVE WAY IN TEACHING CHEMISTRY IN UNIVERSITIES	
Zsolt László Kiss, Nándor Csorba, Cecilia Hodúr, Gábor Keszthelyi-Szabó, Zsuzsanna László	22
INVESTIGATION OF AOPs AND MEMBRANE FILTRATION COMBINATION FOR WASTEWATER	
TREATMENT	
Sándor Beszédes, Petra Veszelovszki, Lajos Ludányi, Gábor Keszthelyi-Szabó, Cecilia Hodúr	27
REALTIONSHIP BETWEEN DIELECTRIC PARAMETERS AND BIODEGRADABILITY OF SLUDGE	
Anikó Türkössy	33
WHAY FAIR VALUE IS A RELEVANT RULE IN INTERNATIONAL ACCOUNTING	
Zsuzsanna H.Horváth	35
ANALYSIS THE COLOUR OF PAPRIKA POWDER WITH DIFFERENT COLOUR AGENT	
CONTENT	
Imre Kiss, Vasile Alexa	40
GENERAL OVERVIEW UPON THE MAIN APPLICATIONS OF THE IRON AND STEELMAKING	
SLAG PRODUCTS	
Imre Kiss, Vasile Alexa, 'Slobodan Stefanovic	47
ABOUT THE QUALITY ASSURANCE ACTIVITIES IMPROVEMENT IN THE ROLLING ROLL'S INDUSTRY	

REALTIONSHIP BETWEEN DIELECTRIC PARAMETERS AND BIODEGRADABILITY OF SLUDGE

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ABSTRACT

Sludge management has been one of the major parts of research and development activity of wastewater sector of environmental industry. Microwave enhanced process is considered as a novel and promising technology for efficient sludge treatment and other biomass pretreatment. Advantage of microwave irradiation over the conventional heating is verified in many scientific works, and it can already be found industrial scale applications. Nevertheless, the knowledge about dielectric parameters of food industry sludge is not sufficient, yet. Furthermore, the relationship between the dielectric properties and biodegradation has not been analyzed. Therefore our aim was to measure the dielectric constant and dielectric loss factor of meat industry sludge and investigate the possible correlation of dielectric parameters with the biodegradability indicators. Our results show, that the change in sludge structure, namely the disintegration of particles given by organic matter solubility, has effect on dielectric parameters. Therefore, the real-time measurement of dielectric properties can be a suitable method to estimate the biodegradability during a continuous industrial-scale microwave operation.

1. INTRODUCTION

Nowadays, sludge management has a great importance because of the continuous increase in sludge output and stringent environmental standards. The presence of pathogens, heavy metals, polycyclic aromatic hydrocarbons (PAH), polychlorinated byphenyl (PCB), dioxins and other undesirable components make impossible or highly environmental risk the land application and disposal in landfills of sludge. There are known various processes to reduce the quantity of excess sludge. These processes can be sorted into 3 main group:

- Reduction in wastewater line: using oxic and anoxic stages
- > Reduction in sludge line: pre-treatments to enhance the efficiency of anaerobic digestion (AD)
- > Reduction in final waste line: incineration or pyrolysis

Among them, many research and study conclude sludge treatment using hydrolysis in AD process the most "clean" or "green" technology, because this technology do not need complex gas cleaning system (on contrary to the incineration), the final waste production of AD process is minimized, and net energy production can be achieved during a waste treatment process (Kalmár et al., 2010). The degradation of sludge under anaerobic condition is limited, and the overall efficiency of AD process is low without pre-treatment prior to hydrolysis stage of anaerobic decomposition. Numerous pre-treatment methods are known to enhance the biodegradability of sludge, such as sonication, mechanical, chemical and thermal processes (Bougrier et al., 2008; Yuan et al., 2010).

Generally, thermal treatment is readily used due to its good controllability and the widespread application of the commercial heat exchangers. Among the potential thermal pre-treatment methods microwave (MW) irradiation for sludge treatment can be considered as an intensive and efficient process, because its ability to quick heating, accelerated reaction rate, instantaneous on/off control, selective and volumetric heating mechanisms, non-contact heating method and space saving for constructed equipment (Leonelli and Mason, 2010; Beszédes et al., 2012). These specific properties of energy transfer carried out by microwaves resulted in many verified positive effects and advantage in comparison with sludge pre-treatments applying conventional heating, such as enhanced sludge disintegration, increased biogas production, rapid and stronger sanitization effect (Beszédes et al., 2011).

Increasing of 70% was found in the biogas production of organic solid waste after MW irradiation (Shahriari et al., 2012). Microwave heating of primary municipal sludge resulted in 150% increase in soluble organic matter content related to the control (Zheng et al., 2009). MW pre-treated sludge contains soluble proteins and volatile fatty acids in a higher concentration, but it has a lower soluble sugar content compared to conventional heated sample. Eskicioglu et al. (2008) established that the level of solubility depends on the type of sludge, and concluded that microwave intensity has influential parameters just for the rate of organic matter decomposition in AD process, not for the ultimate level of biodegradation.

Microwaves generates energy via the realignment of dipoles with high frequency oscillating electromagnetic field, and some part of penetrated energy is irreversible absorbed (dissipated) in the material, what resulted in temperature increase (Lakatos et al., 2005). Therefore the quantity of polar components of material has a great influence on the extent of energy absorption, therefore the energy efficiency of the MW heating process. In high water contented materials, such as wastewater sludge, the state and also the mobility of water molecules determined the dielectric properties of MW irradiated system (Tyagi and Lo, 2013).

The dielectric properties, namely the dielectric constant (ϵ ') and the dielectric loss factor (ϵ ") are important for predicting the behavior of materials during microwave processing, because both of them determine the interaction between the molecules

with the oscillating electromagnetic field (Géczi et al., 2013). Dielectric constant measure the ability of material to store the irradiated energy, the value loss factor relate to the ability of material to convert electric energy into heat. In high water contented materials, trends of the change of dielectric properties are similar with the behavior of pure water (Zheng et al., 2009). The dielectric constant of material decreased and the dielectric loss factor increased as the frequency of electromagnetic field increased in the frequency range of 2-20 GHz (Mokhtar et al., 2011). Taking into consideration the effect of moisture content of sludge it was verified that increasing of water content decrease the dielectric constant but increase the dielectric loss factor.

The most MW application aim the rapid heat generation, therefore influence of temperature on the dielectric parameters was one of the main key issues of microwave research (Szerencsi et al., 2009). Dielectric constant of sludge decreases with increasing temperature, as well as the dielectric loss factor. Contrary to the MW drying process of solid biomaterials, penetration depth (d_p) is not changed in a wide temperature range under 100°C during sludge processing, what do not decrease the energetic efficiency of the MW operation. It can be explained by the above mentioned trends in the change of ϵ ' and ϵ ", because the penetration depth is influenced by both dielectric parameters.

$$\mathbf{d}_{p} = \frac{\lambda \sqrt{\epsilon'}}{2\pi \sqrt{\epsilon'}} \left[\left(1 + \left(\frac{\epsilon''}{\epsilon'} \right)^{2} \right)^{0.5} - 1 \right]^{-0.5}$$

It is verified that during MW irradiation of wastewater sludge lipids are hydrolyzed to palmitic acid, stearic acid and oleic acid; furthermore proteins are hydrolyzed to unsaturated acids (Ahn et al., 2009). Therefore the macromolecules with low dielectric loss degrade to components with stronger polar characteristic what increase the average concentration of polar components in processed sludge resulting in enhanced MW energy absorption at a constant temperature.

On the other hand, through the degradation of cell walls in sludge, the phospholipids from disrupted lipid bi-layer are liberated (Banik et al., 2003) what increase the concentration of polar compounds in sludge liquor enhancing further the extent of MW energy absorption. The ion content of sludge liquor is also increased because of the broken cell walls, what provoke the enhanced intensity of ionic migration in oscillating electromagnetic field. Some study concluded that the low intensity MW irradiation is suitable to polarize the side-chains of macromolecules which possible result in the broken of hydrogen bounds (Park et al., 2004).

Our main aim was to examine how affect MW irradiation the biodegradability and solubility of organic matter fraction of sludge. Furthermore, the relationship between the dielectric parameters and the change in sludge structure and biodegradability was also investigated.

2. MATERIALS AND METHODS

Investigated wastewater sludge was originated from meat industry with a total solid (TS) content of 9.7 %, initial total COD of 105.9 kgm⁻³, and soluble COD of 20.1 kgm⁻³. Chemical oxygen demand (COD) from the total MPWS matrix was measured triplicate using colorimetric standard method (APHA 5520D, 2005). Soluble chemical oxygen demand (SCOD) was determined after separation of soluble from solid fraction by centrifugation (12,000 rpm for 10 minutes) and pre-filtration (0.45 µm Millipore disc filter). Biochemical oxygen demand tests (BOD₅₎ were carried out in a respirometric BOD system (BOD Oxidirect, Lovibond, Germany) at 20°C for 5 days.

Dielectric constant (ϵ ') and dielectric loss factor (ϵ '') were determined in a tailor made dielectrometer equipped with a dual channel NRVD power meter (Rohde & Schwarz). Magnetron of dielectrometer operates at a frequency of 2450 MHz. ϵ ' and ϵ '' was calculated from the reflection coefficient (Γ), phase shift (ϕ), incident (P_i) and reflected (P_r) power with the following equations:

$$\begin{split} \epsilon' &= \sqrt{\frac{P_r}{P_i}} \\ \Gamma &= \frac{P_r}{P_i} \\ A &= |\Gamma| \sin \phi \end{split} \qquad \begin{split} \Theta &= \frac{\pi}{2} arc \ tg(\Gamma) \\ B &= 1 - \left(|\Gamma| cos \phi\right) \\ \delta &= arc \ tg\left(\frac{A}{B}\right) - arc \ tg\left(\frac{A}{C}\right) \\ tg\delta &= \frac{\epsilon'}{\epsilon''} \end{split}$$

Measurements were carried out in static mode with low MW power and short exposition time to avoid the temperature increasing of the sample. The quantity of sample was 185 g in every experiments.

3. RESULTS AND DISCUSSION

Wastewater sludge contains water in a high concentration, therefore behavior of investigated dielectric parameters i.e. dielectric constant (ϵ ') and dielectric loss factor (ϵ ") has theoretically a similar trend to water as a function of temperature. Our experimental results presented, that in spite of the high moisture content, the change in ϵ ' and ϵ " was different from the water.

Increasing the temperature of sludge the value ϵ ' and ϵ " decreased, but over a certain value of sample temperature both dielectric parameter show an increasing tendency in the temperature range of 50-80°C (Fig. 1.). It can be noticed, that this phenomena has effect on the penetration depth, because the ratio of ϵ " to ϵ ' was changed.

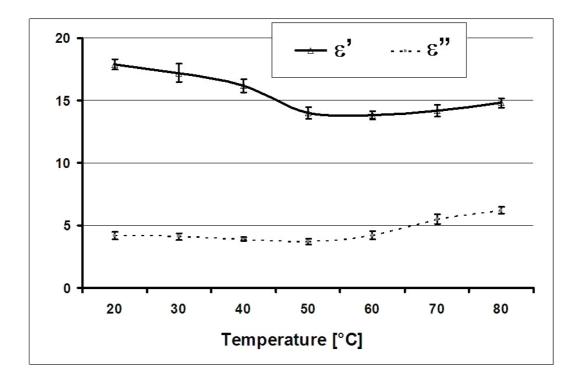


Figure 1. Dielectric constant (ε ') and dielectric loss factor (ε ") as the function of temperature

Fluctuation of dielectric parameters can occur when boiling point is reached during the heating, or air bubbles are arisen in the fluid (Bogdal and Loupy, 2008). But in our cases the temperature range was chosen under boiling point, and air bubbles were detected neither visually nor by the fluctuation of measured reflected power data. Breaking point of ϵ ' and ϵ " curve was occurred approximately in the same temperature range.

In order to find possible explanation for the experienced phenomena, the change in the structure of sludge the fractionation of organic mater content was performed by COD measurement. Ratio of soluble chemical oxygen demand (sCOD) to total COD (tCOD) correlates with disintegration degree of sludge particles and breaking of cell walls (Ahn et al., 2009). Our experimental results show that sCOD/tCOD parameter start to increase at the same temperature range that was critical for the dielectric parameters (Fig. 2.).

With breaking of cell walls and disintegration of sludge particles led to a partial decomposition of sludge matrix (Bougrier et al., 2008). Therefore the intracellular components are released to intercellular space, furthermore a part of bounded water liberate increasing the free water content. Sludge originated from wastewater treatment technology contains different ions and organic and inorganic compounds, therefore with change in sludge structure led to enhanced ionic migration.

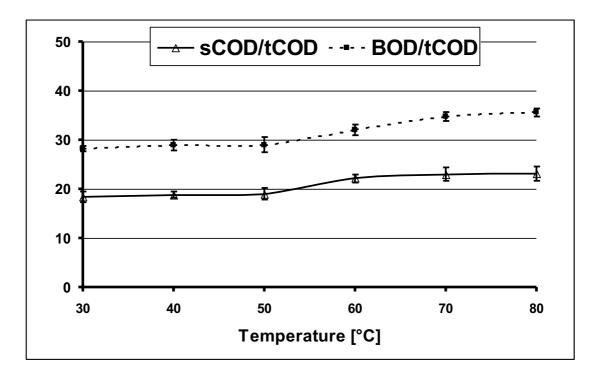


Figure 2. Change of organic matter solubility and biodegradability

Above a certain temperature, when sludge disintegration reach a critical value, the change of dielectric parameters are more influenced by the ionic migration than the dipole rotation (Leonelli and Mason, 2010). Since, this phenomena is occurred based on the thermal effect of microwave irradiation, the effect of temperature on ϵ ' and ϵ " is expected to further intensified by the decreased viscosity what increase the mobility of liberated ion in fluids.

On the other hand, the change in solubility of organic matter has also effect on biodegradability. The correlation between solubility and biodegradability has been verified earlier (Beszédes et al., 2009). The biodegradable fraction of organic matter was also enhanced by the temperature increase. Enhanced biodegradability of processed meat industry sludge was confirmed by BOD/tCOD data (Fig. 2.).

In the next series of experiments sludge sampling was performed in every 3 minutes for BOD analysis and samples were cooled to 20 °C before ϵ ' and ϵ '' measurement. These experimental set up was applied to examine the correlation between the change of biodegradability and dielectric parameters. Considering of experimental results, direct correlation between ϵ ' and BOD/tCOD was not found for meat processing sludge in the applied power and temperature range. The relationship between ϵ ' and biodegradability given by BOD/tCOD was presented in Fig. 3.

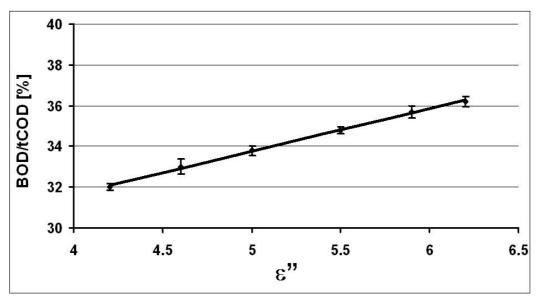


Figure 3. Relationship between dielectric loss factor and biodegradability

Results of experiments show, that the change in biodegradable fraction of organic matters of meat processing sludge is in relationship with the change of dielectric loss factor (ϵ "). In the investigated temperature range (30-80°C) a good linear correlation (R²>0.8) was obtained between the ϵ " and the biodegradability indicator (BOD/tCOD).

The correlation was established just for that phase of microwave process when sludge disintegration start to increase. Taking into consideration of the results of our experiments can be concluded, that electrical parameters, such as dielectric loss factor in present work, are appropriate to the short-time measurement of the change of biodegradability of sludge during microwave processing.

4. CONCLUSION

In our work the dielectric constant (ϵ ') and the dielectric loss factor (ϵ ") was measured for a meat processing wastewater sludge. There was found, that ϵ ' and ϵ " decreasing with increasing temperature, but over a certain value (50°C approximately) start to increase. This behavior of dielectric parameters is in a relationship with the structural change of sludge, which was characterized by the sCOD/tCOD ratio.

Our experimental results verified that the change in the value of dielectric loss factor correlate with the biodegradability of sludge. Correlation between the electrical parameters and biodegradability indicators enable to develop a real-time and inline measuring and control system for continuous flow microwave sludge conditioning technology.

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