PhD thesis

IMPROVEMENT OF BIODEGRADABILITY OF SLUDGE BY MICROWAVE PRE-TREATMENT

Sándor Beszédes

Supervisor:
Prof. Dr. Cecilia Hodúr PhD
full professor

Co-supervisor:
Prof. Dr. Gábor Keszthelyi-Szabó DSc
full professor

Doctoral School of Environmental Science
University of Szeged
Szeged

2014

1. INTRODUCTION AND BACKGROUND OF RESEARCH

Nowadays, the expectations for higher capacity and cleaning efficiency of wastewater purification technologies are growing because of the shortening of water resources. Notwithstanding of the technological development of wastewater treatment works, the amount of sludge produced is continuously increasing. Professionals of wastewater plants and environmental industry face more frequent the general problems of sludge handling, such as the storage, sanitation, utilization or disposal. Taking into consideration of the economy of the wastewater treatment technologies, the total cost of sludge handling has been equal to the cost of wastewater purification. Hence, and furthermore the environmental awareness and the more and more rigorous pollution control regulations, the research and development activity focuses on the sludge utilization processes. Sludge utilization has been realized in agriculture for composting, but in the last decades the anaerobic digestion has been widely used for this purpose, as well. With the adaptation of anaerobic digestion or other utilization processes the efficiency of wastewater works can exceed the average efficiency of the end of pipe technologies. These end of pipe technologies are only focused on the fulfilment of the requirement of environmental standards, with the application of different purification processes.

There is a need to apply sludge pre-treatments, because of the aspects of environmental protection and safety, and to make more profitable of the economy of wastewater works. The sludge pre-treatment processes aim mainly the volume reduction to reduce the cost of transportation and storage, the destruction of pathogen microorganisms to decrease the microbial risk of sludge, the removal of the toxic components of sludge to reduce the environmental risk, or the enhanced degree of further utilization efficiency. Respect to the nowadays used industrial scale sludge handling technologies the thermal pre-treatments can be considered as the more commonly used processes. The advantageous effect of thermal pre-treatment on the sludge structure have been verified and utilized for decades (Brooks, 1970; Neyens, Baeyens, 2003). The main aim for applying thermal pre-treatments is to reduce the odour load of sludge processing, to reduce the microbial risk of sludge disposal and to increase the organic matter removal efficiency of anaerobic digestion in industrial scale technologies

Previous investigations have been verified, that microwave irradiation is applicable in various material processing as an alternative method for conventional heating. The main advantages of microwave heating over the conventional heating methods are the following: rapid heat generation, volumetric heating, selecting heating mechanism in multicomponent system resulted from the different dielectric properties of components, and the very short process time demand due to the high energy intensity of microwave irradiation (Clark et al., 2000; Leadbeater, 2011). Despite the good potential of microwave irradiation for material processing and the promising results of the field of microwave research the adaptation of them in industrial scale processes has been not realized yet. Available scientific results and experiences from the microwave sludge conditioning are not enough to scale up the microwave process. Furthermore, beside these advantages, it can be concluded, that the effects and efficiency of microwave processes are not deeply enough investigated and analyzed for many types of materials. Published scientific work and research reports in the field of microwave sludge processing find microwave irradiation as an efficient method to dehydrate the sludge, and to recover some valuable component, such as some metallic compound, and microwave irradiation is suitable as pre-treatments method before anaerobic digestion to increase the biogas yield. This advantageous and beneficial feature of microwave irradiation is caused by the effect of high frequency electromagnetic field on the secondary and tertiary structure of proteins, which can manifested in the decreased stability and the enhanced disintegration degree of sludge particles (Park et al., 2010; tang et al., 2010). It has been also concluded, that the increment in the solubility of carbohydrate compounds of sludge was approximately 10-15% higher, than the improvement in protein solubilisation after microwave treatment (Appels et al., 2010).

Results obtained from different studies has often controversial establishment, furthermore the results are not comparable, because of the different geometry and structure of microwave equipment and there is not defined the power intensity of treatment. Additionally, the comparison of the efficiency of microwave operation and process parameters is difficult because the control parameters are undefined or the calculation methods are different, and the analytical methods are not standardized. There are some studies concluded the increasing of microwave power has an increasing effect on the organic matter solubility (Climent et al., 2007; Appels et al., 2010), nevertheless other studies summarized decreasing effect of the enhanced microwave power (Park et al., 2010; Toreci et al., 2009). Applying microwave treatment with high power intensity in open vessel systems, the agglomeration of partly dehydrated sludge particles are observable, because of the intensive evaporation from the surface of the sludge exposed to microwave irradiation. In this case, the change in sludge structure is considered irreversible, because the water addition after the microwave treatment is not able to resolve the organic matters (Sólyom et al., 2011). It can be also noticed, that results of studies on microwave sludge conditioning obtained mainly from municipal sludge processing, which has lower organic and dry matter content than the food industry sludge. It has been established, that microwave pre-treatments of municipal sludge enhance the organic removal efficiency of anaerobic digestion process (Appels et al., 2013) and increase the biogas production (Toreci et al., 2009).

2. AIMS OF RESEARCH

The main aim of my research work was to investigate the effects of microwave irradiation on the structure of food industry sludge, and the applicability of microwave technique as a sludge pre-treatment method. Beside the irradiation time and the magnetron power, which are the most often examined and optimized parameters for microwave treatment, the effects of irradiated microwave energy and the specific microwave power intensity were analyzed on the structure and biodegradability of sludge. Efficiency of microwave pre-treatments was characterized by the changing in the anaerobic biodegradability as well. The effect of different intensity microwave sludge pre-treatments was given by the change in biogas yield, biogas composition, and the rate of decomposition. These control parameters obtained from batch mesophilic anaerobic digestion tests. Because of the many aspects and the complexity of the research topic I defined the following sub-tasks and objectives:

- To investigate the effect of microwave irradiation on the organic matter fraction of sludge, comparing the efficiency of microwave and conventional heating methods.
- To verify the applicability and efficiency of microwave sludge conditioning method by objective control parameters.
- To determine the influence and to investigate the significance of irradiated microwave energy and specific microwave power intensity in the organic matter solubilisation and the change of biodegradability.
- To develop novel control parameters by which become measurable the changes in organic matter fraction of sludge independently from the varying characteristic or different origin of raw sludge. The developed control parameters can be the base for comparison purpose, and for modelling and optimization of microwave process.
- To investigate the possible correlation between the change of organic matter solubility, the change and the extent of biodegradability, and the dielectric parameters of sludge.
- To analyze the effect of specific microwave power level and the irradiated microwave energy, as process parameters, on the anaerobic digestion process of food industry sludge.
- To investigate the profitability of microwave sludge conditioning method by cost-benefit analysis determining of payback period for an industrial scale microwave system.

3. APPLIED METHODS

Microwave experiments were carried out in a tailor made microwave sludge processing and measuring system developed at the Process Engineering Department of the University of Szeged Faculty of Engineering. Microwave equipment has a continuously irradiating magnetron with changeable power in the range of 50 W to 700 W operating at a frequency of 2450 MHz. Power of the continuously irradiating microwave magnetron is adjustable by varying of anode voltage through a transformer with variable voltage.

To investigate the efficiency of the MW pre-treatment process the parameters studied were the microwave power level (MWPL), and the irradiated microwave energy (IMWE). MWPL (Wg^{-1}) was defined as the ratio of magnetron power to the quantity of treated sludge. MWPL and IMWE were calculated from the weight of sludge samples (m_{sl} [g]), the power of magnetron (P_m [W]), the irradiation time (τ [s]) and the percentage irradiation time period of magnetron (I [%]).

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) and NRVZ power sensors. For the calculation of ε' the incident (P_h) and reflected (P_r) was used.

$$\varepsilon' = \sqrt{\frac{P_r}{P_h}}$$

Magnetron of dielectrometer operates at a frequency of 2450 MHz. The loss tangent (δ) was calculated from the reflection coefficient (Γ) and the phase shift (ϕ), and the dielectric loss factor was determined from the tgδ.

$$\delta = arc\ \ tg\left(\frac{|\Gamma|\sin\varphi}{1-(|\Gamma|\cos\varphi)}\right) - arc\ \ tg\left(\frac{|\Gamma|\sin\varphi}{1+(|\Gamma|\cos\varphi)}\right)$$

$$\varepsilon'' = tg\delta \cdot \varepsilon'$$

Carbonaceous biochemical oxygen demand (BOD) tests were carried out in a respirometric BOD system (BOD Oxidirect, Lovibond, Germany) thermostated at a temperature of 20±0.2°C (TS606, WTW). BOD analysis was according to the APHA5210D method. To ensure the consistency of the experiments, BOD seed microbe capsules (Cole Parmer, USA) were used for the measurements.

The chemical oxygen demand (COD) was measured by the standardized colorimetric dichromate method using HACH test cuvettes, according to USEPA 5520D method. For the thermal digestion ET108 (Lovibond) thermoblock was used for 2 hours at 150°C. The COD was measured colorimetrically using PC Checkit photometer with inner calibration for COD measurement.

The total chemical oxygen demand (TCOD) was measured from the total sludge matrix. The soluble organic matter content was given as the soluble chemical oxygen demand unit (SCOD). SCOD was determined after separation of soluble from solid fraction by centrifugation (RCF of 32000 g for 15 minutes, MPW-350 centrifuge) and pre-filtration (0.45 μm Millipore cellulose-acetate disc filter).

To quantify the anaerobic biodegradability of sludge samples batch mesophilic anaerobic digestion (AD) tests were used. AD tests were carried out in a WTW Oxitop-C 110 laboratory scale measuring system containing 12 continuously stirred anaerobic reactors equipped by pressure-mode sensors. To ensure the 35±0.5°C temperature during the biogas tests the measuring system was placed to a thermostat cabinet. The pH of the samples was adjusted to 7.2.

The inoculums (seed sludge) were taken from an operating mesophilic anaerobic digester and acclimatized to the pre-treated sludge in order to reduce the initial lag-phase of the anaerobic process. Since my main object was to examine the effect of microwave pre-treatment on the control parameters, the condition of the batch anaerobic fermentation (dry matter content of fermentation broth, temperature, concentration of inoculums, pH, etc.) was the same in all tests.

4. NOVEL SCIENTIFIC RESULTS

T1) Microwave pre-treatments under atmospheric pressure increase the organic matter solubility and aerobic biodegradability of food industry sludge in a higher extent and by shorter process time demand, than that of obtained from conventional heating process at atmospheric pressure. These advantages make the microwave method suitable to enhance the efficiency of further biological utilization of sludge.

The SCOD/TCOD ratio, as the measure of the soluble fraction to total organic matter of sludge, can be increased from 9,7% to over 30% for dairy sludge, and from 29% to 45% for meat processing sludge by microwave pre-treatments, respectively. The aerobically degradable organic matter concentration, given by the biochemical oxygen demand (BOD) parameters, had an increment of 4-fold and 3-fold for dairy, and meat processing sludge, as well.

T2) The effect of microwave sludge conditioning process on the concentration of biodegradable materials, and on the solubility of organic matters of food industry sludge is also significantly influenced by the process parameter of specific microwave power intensity (given as the ratio of magnetron power to the quantity of processed sludge), beside the irradiation time.

The specific microwave power intensity, in the range of 0.5-5 Wg^{-1}, has a significant effect on the increment of SCOD/TCOD and BOD/COD ratio, which quantifies the change in the solubility of sludge organic matter, and the biodegradable fraction of organic matters, respectively.

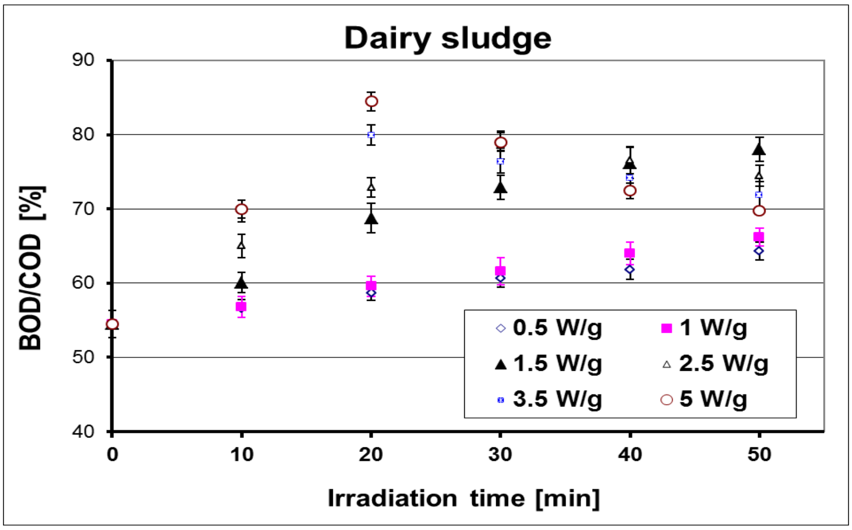


Fig. 1: Change in BOD/COD ratio during microwave treatment of dairy sludge as the function of irradiation time. (microwave power intensity range of 0.5-5 Wg^{-1})

T3) The biodegradation index (BDI), developed to measure the aerobic biodegradability and the solubility index (SLI), developed to quantify the change in organic matter solubility are suitable to investigate and optimize the process parameters of microwave sludge pre-treatment method.

The solubility index (SLI) and the biodegradation index (BDI) are calculated from the total organic matter content (given by the TCOD), the soluble organic matters content (SCOD) and the biochemical oxygen demand (BOD), measuring them initially (0), at a given time (t) and from the parameters of maximum biodegradable sample (max).

$$SLI = \frac{\left(\frac{SCOD}{TCOD}\right)_t - \left(\frac{SCOD}{TCOD}\right)_0}{\left(\frac{SCOD}{TCOD}\right)_{max} - \left(\frac{SCOD}{TCOD}\right)_0} \quad [-] \qquad BDI = \frac{\left(\frac{BOD}{SCOD}\right)_t - \left(\frac{BOD}{SCOD}\right)_0}{\left(\frac{BOD}{SCOD}\right)_{max} - \left(\frac{BOD}{SCOD}\right)_0} \quad [-]$$

SLI and BDI of sludge can be estimated by the following equations, which are verified to MWPL and IMWE range of 0,5-5 Wg^{-1}, and 90-105 kJg^{-1}.

$$SLI = 0.8085 + 0.301x_1 + 0.014x_2 + 0.0706x_1x_2 - 0.237x_1^2 + 0.036x_2^2$$

$$BDI = 0.8921 + 0.071x_1 - 0.002x_2 - 0.298x_1^2 + 0.043x_2^2$$

where X1 and X2 coded the IMWE and MWPL, respectively.

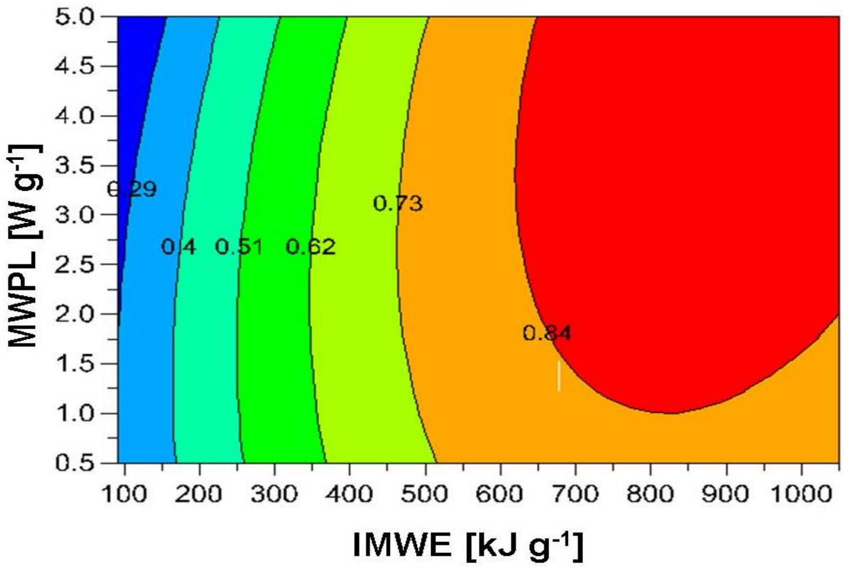


Fig. 2: Contour plot for solubility index (SLI) generated by the constructed mathematical model

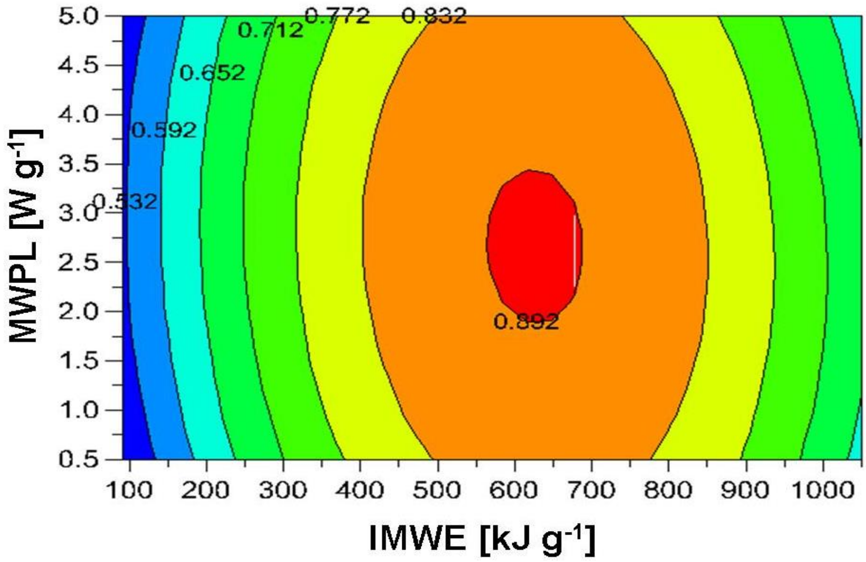


Fig. 3: Contour plot for biodegradation index (BDI) generated by the constructed mathematical model

T4) Improvement of biogas yield in the anaerobic digestion process of food industry sludge, and the increment of methane concentration are significantly influenced by the specific microwave power intensity.

The biogas yield which has a low value for raw sludge can be increased to 19-fold and 1.2-fold for dairy and meat processing sludge, compared to the initial value of untreated samples. Application of the most effective process parameters, the methane content of biogas from dairy and meat processing sludge is increased by minimum 25% after microwave pre-treatment.

T5) Microwave irradiation, as the pre-treatment of anaerobic digestion of food industry sludge, is suitable to decrease the digestion time due to the accelerated biogas production rate and intensified anaerobic decomposition.

The initial lag-phase of anaerobic digestion process can be shortened by 80% and 75% for dairy and meat processing sludge, respectively. The increment of the average biogas production rate calculated from the 5 days linear period of the 30 days total fermentation process was 20-fold and 3-fold for dairy and meat processing sludge.

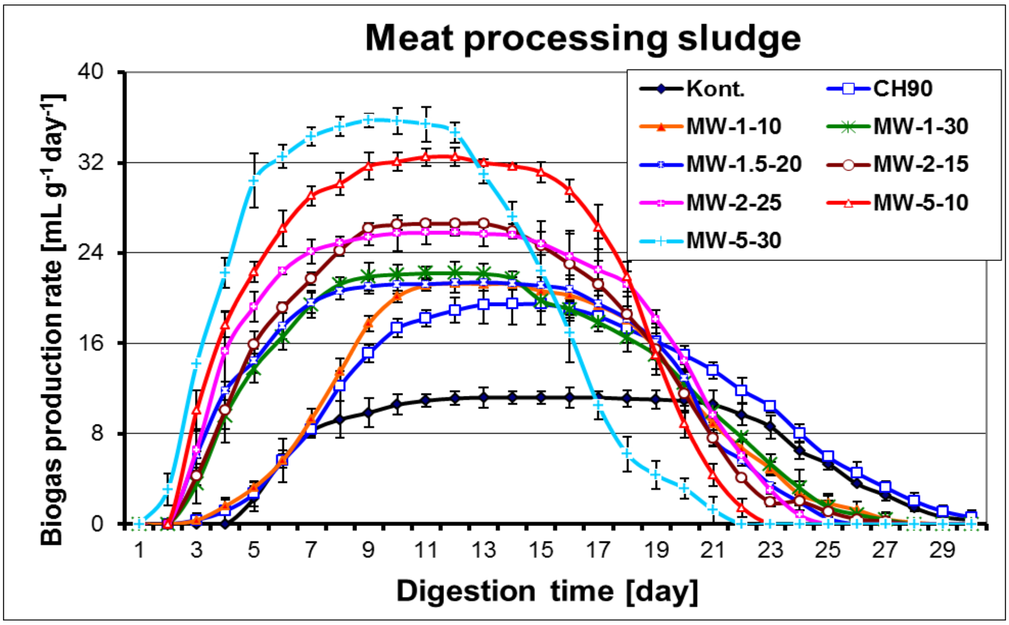


Fig. 4: Biogas production rate as the function of digestion time and pre-treatments

T6) The optimum range of process parameters of microwave sludge conditioning process is different from the viewpoint of energetic efficiency that of obtained for maximum biogas yield or maximum methane production. Determination of energy efficiency is needed to analyze and optimize the microwave pre-treatment process.

Energy efficiency (ΔE) of microwave pre-treatment followed by anaerobic degradation process can be calculated as the difference between the combustion heat (q_{comb}) of the produced methane (V_{CH4}) and the microwave power demand of process (P_{mag}) and the irradiation time (τ).

$$\Delta E = \frac{(q_{comb} \cdot V_{CH_4}) - (P_{mag} \cdot \tau)}{m_{sludge}} \quad \left[J\ g^{-1}\right]$$

Energetic efficiency is estimated by the mathematical model containing IMWE (X_1) and MWPL (X_2) process parameters.

$$\Delta E = 326.12 - 27.29X_1 - 237.74X_2 - 4.017X_1^2 - 470.79X_2^2 - 385.9X_1X_2 \quad \left[J\ g^{-1}\right]$$

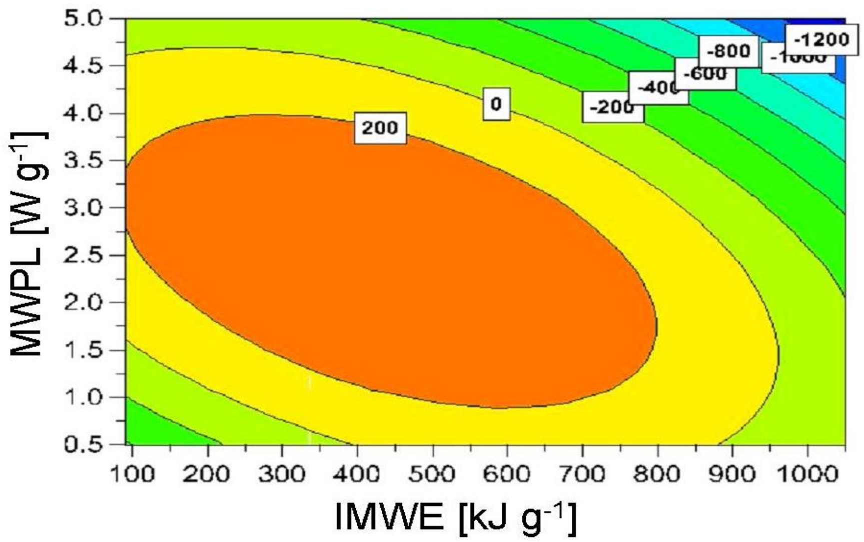
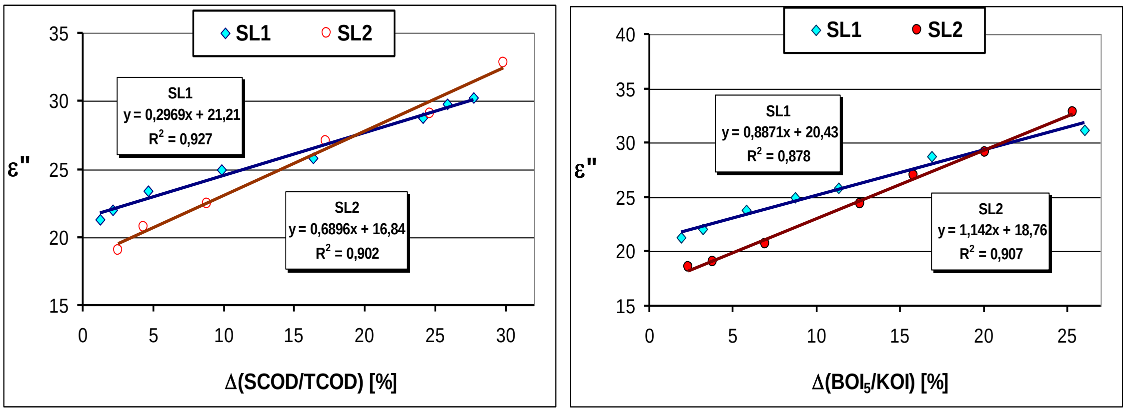


Fig. 5. Contour plot for energy-efficiency (ΔE) generated by the constructed model

T7) Dielectric loss factor which is one of the main influential parameter of microwave heating efficiency has a good correlation with the change of organic matters solubility and biodegradability of food industry sludge. Measurement of dielectric parameters during the microwave sludge conditioning process is appropriate to estimate instantaneously the change in biodegradability.

Based on my results, the change in organic matters solubility given as the ratio of SCOD to TCOD, and the change of biodegradability characterized by the BOD/COD ratio has a strong positive correlation (R^2>0.9; ill. R^2>0.85) with the change of dielectric loss factor (ε'').



a) b)

Fig. 6: Relationship between the organic matter solubility (a), biodegradability (b) and the dielectric loss factor (ε'')

5. SCIENTIFIC PUBLICATIONS RELATED TO THE THESIS

1) **Biogas production of ozone and/or microwave-pretreated canned maize production sludge**
   Beszédes S., Kertész Sz., László Zs., Szabó G., Hodúr C.
   Ozone Science & Engineering 31(3) (2009) 257-261; IF: 1.252
2) **Comparison of the effects of microwave irradiation with different intensities on the biodegradability of sludge from the dairy- and meat-industry**
   Beszédes S., László Zs., Horváth H. Zs., Szabó G., Hodúr C.
   Bioresource Technology 102(2) (2011) 814-821; IF: 4.980
3) **Effects of microwave pretreatments on the anaerobic digestion of food industrial sewage sludge**
   Beszédes S., László Zs., Szabó G., Hodúr C.
   Environmental Progress & Sustainable Energy 30(3) (2011) 486-492; IF: 1.649
4) **Microwave enhanced biodegradability of meat processing wastewater sludge**
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   Accepted paper (2013 aug.); IF:1.258*
   Abstract available: http://omicron.ch.tuiasi.ro/EEMJ/pdfs/accepted/33_46_Beszedes_13.pdf
5) **Application of response surface methodology to optimize microwave sludge conditioning for enhanced biogas production**
   Beszédes S., Ábel M., László Zs., Szabó G., Hodúr C.
   Annals of Faculty Engineering Hunedoara-International Journal of Engineering 9(2) (2011) 189-193 (ISSN: 1821-4487)

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1) **The possibilities of bioenergy production from whey**
   Beszédes S., László Zs., Szabó G., Hodúr C.
   Journal of Agricultural Science and Technology 4(1) (2010) 62-68 (ISSN: 1939-1250)
2) **Berry pectins: Microwave-assisted extraction and rheological properties**
   Bélafi-Bakó K., Cserjési P., Beszédes S., Csanádi Zs., Hodúr C.
   Food and Bioprocess Technology 5(3) (2012) 1100-1105; IF: 4.115
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4) **Maximum recovery of different types of berry byproducts**
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   Journal on Processing and Energy in Agriculture 13(4) (2009) 312-314 (ISSN:1821-4487)
5) **Enhanced enzymatic saccharification of agri-food sloid wastes by microwave pre-treatment**
   Beszédes S., Ábel M., szabó G., Hodúr C., László Zs.
   Annals of Faculty Engineering Hunedoara-International Journal of Engineering 9(3) (2011) 453-458 (ISSN: 1821-4487)

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1) **Increasing of biodegradability and digestibility of dairy sludge by microwave treatment**
   Beszédes S., László Zs., Szabó G., Hodúr C.
   5th International Technical Symposium on Food Processing, Monitoring Technology in Bioprocesses and Food Quality Management (Potsdam, Németország, 2009.08.31-2009.09.02) pp.: 315-323 (ISBN.978-300-028-811-1)

2) **Toroid-rezonátor fejlesztése szennyvíziszapok mikrohullámú kondicionálására**
   Beszédes S., Ludányi L., Koltai A., Szabó G.
   7. Magyar Szárítási Szimpózium (Gödöllő, Magyarország, 2011.04.07-2011.04.08) pp.:12-13 (ISBN: 978-963-269-212-8*) (in Hungarian)*

3) **Biogas production from food industry wastewater sludge intensified by microwave irradiation**
   Beszédes S., Ábel M., László Zs., Szabó G., Hodúr C.
   Bioenergy and Other Renewable Energy Technologies and Systems (BRETS 2011): 33 International Symposium of Section IV of CIGR (Bucuresti, Románia, 2011.06.23-2011.06.25) *Paper PS307 (8p) (ISBN 978-606-521-686-0)*

4) **Application of microwave toroidal cavity resonators for conditioning of food industry wastewater sludge**
   Beszédes S., Ludányi L., Veszelovszki P., Hodúr C., Szabó G.
   ISEKI Food 2011 - Bridging Training and Research for Industry and the Wider Community: 2nd International ISEKI Food Conference (Milan, Olaszország, 2011.08.31-2011.09.02) p..170 (ISBN 978-889-059-890-6)

5) **Microwave treatment as a tool for enhanced waste valorisation**
   Beszédes S., Kovács-Veszelovszky P., Ludányi L., Hodúr C., Szabó G.
   Synergy in the Technical Development of Agriculture and Food Industry, Abstracts of the II International Conference of the CIGR Hungarian National Committee. (Gödöllő, Magyarország, 2011.10.09-2011.10.15) pp.: 65-71 (ISBN 978-963-269-249-4)

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ACKNOWLEDGEMENTS

I am especially like to thank the valuable help of my Supervisors, who inspired and encouraged me during my research work.

I am grateful to all the people who have helped my work with the thesis.

This research was realized in the frames of TÁMOP 4.2.4. A/2-11-1-2012-0001 „National Excellence Program – Elaborating and operating an inland student and researcher personal support system convergence program" The project was subsidized by the European Union and co-financed by the European Social Fund.