MICROWAVE ENHANCED BIODEGRADABILITY OF FOOD PROCESSING WASTEWATER SLUDGE

S. Beszédes, PhD student, Department of Process Engineering, University of Szeged

L. Ludányi, Senior Researcher, Department of Process Engineering, University of Szeged

M. Ábel, PhD student, Department of Process Engineering, University of Szeged

C. Hodúr, Professor, Department of Process Engineering, University of Szeged

G. Szabó, Professor, Head of Department, Department of Process Engineering, University of Szeged

Contact: Prof. Dr. Gábor Szabó, Department of Process Engineering, Faculty of Engineering, University of Szeged, Moszkvai krt. 9., Szeged, H-6725, Hungary; Tel.: +3662546500; E-mail: szabog@mk.u-szeged.hu

SUMMARY

Food industry wastewater contains a huge amount of organic matters; therefore in sludge, originating from it, the dosed cations in the precipitation stage of wastewater line altogether with living microorganisms and organic molecules form extracellular polymeric substances (EPS). EPS fraction of sludge causes hydrophilic characteristic of sludge, and increases the difficulty achieving effective bioconversion during anaerobic digestion (AD) or aerobic biotransformation processes, e.g. composting. Numerous sludge conditioning methods were developed and investigated to improve the accessibility of organic matter for decomposing bacteria.

Microwave (MW) irradiation has been successfully applied in many fields of food technology, organic chemistry, biotechnology and also in environmental engineering. MW pre-treatment has verified positive effects on sludge disintegration and releasing of organic matter into the soluble phase, but combining of it with chemical methods, such as alkali, acid and oxidizer agents, synergetic mechanism was experienced with accelerated decomposition under aerobic and anaerobic condition, as well. Many reports deal with examination of the efficiency of MW irradiation of municipal sludge, but very few of them focus on the development of microwave pre-treatment processes for food industry sludge. Therefore, the aim of our present work is to identify the main influential operating parameters of MW pre-treatments in meat processing wastewater sludge conditioning process with optimization of them for enhanced biodegradability.

MW pre-treatments were carried out in a special designed microwave cavity resonator, in which magnetron power is variable continuously in the range of 50W to 700W. To investigate the efficiency of MW pre-treatment the process parameters studied were the microwave power level (MWPL), and the irradiated microwave energy (IMWE). Selected control parameters for MW sludge conditioning were the organic matter solubility index (SLI) calculated from the ratio of soluble to total chemical oxygen demand (COD), and the biodegradation index (BDI) determined from the change of the ratio of biochemical oxygen demand (BOD) to COD. To quantify the change in the degree of anaerobic decomposition batch mesophilic biogas production tests were carried out.

Our results verify the applicability of microwave pre-treatment procedure for food industry sludge. MW pre-treatments increased the biodegradability and biogas production of meat processing wastewater sludge (MPWS). Investigated process parameters, namely IMWE and also MWPL, had significant effect on the SLI and BDI. MW pre-treatments increased the organic matters solubility and the biodegradability of sludge, but the worsening effect of the high intensity irradiation over a certain value of IMWE was also experienced. Results from response surface modeling and optimization show that the optimal condition for MW process of MPWS for highest biodegradability with minimum energy demand was determined at 621 kJ of IMWE and at 2.6 Wg^{-1} of MWPL.

1   INTRODUCTION

Disposal and utilization of waste sludge is one of the key issues in the operation of wastewater treatment plants (WWTP), in where a large amount wastewater with high organic matter load is processed. Food processors have faced with the rigorous environmental standards related for wastewater pollutants and the increasing cost of sludge handling, as well. Beyond the volume reduction keeping in mind the cost minimizing, sludge conditioning operations may also have requirement to modify the sludge structure before further utilization. From environmental point of view the biological process can be considered obviously solution for sludge stabilization.

Compared to the other industrial sectors, food technologies output a great amount of wastewater because of the high water content of the raw materials processed, the commonly used dehydration operations and, additionally, the high water demand of flushing and cleaning procedures. Generally, food industry works have two-stage wastewater purification systems in Hungary, operated by mechanical and physico-chemical processes. Sludge produced in food industry wastewater purification technology consists of cellular compounds that make slow the direct biodegradation, because the cell walls protect the cells from exoenzyme breaking-down and hydrolysis. On the other hand, the extracellular polymeric substances (EPS) compose mainly from carbohydrates and proteins act as second protective layer for enzymatic degradation.

Wastewater originated from food operations contains a great amount of organic matter, and due to frequently cleaning and disinfecting procedures effluents can be characterized by a high content of surfactants and disinfecting agents, respectively. Dosed cations in wastewater purification technology are also contributed to form more resistant sludge flocs via the stronger polymeric network (McSwain et al., 2005). Therefore disruption of EPS and sludge condition for enhanced biodegradation has been important factor in the efficiency and economy of sludge handling technology. Advantage of the increased accessibility of sludge organic matter can be utilizable in the anaerobic digestion (AD) and also in the aerobic sludge conditioning, such as the composting processes.

1.1   Background

In aerobic stabilization and also during the anaerobic digestion (AD) the efficiency of the biotransformation processes can be enhanced by different pre-treatments in which the sludge has been disintegrated. Sludge particle disintegration has positive effect on the organic matter solubilization and it also helps to convert materials into easier degradable forms. Numerous pre-treatment method are known to enhance the disintegration degree, such as sonication, mechanical, chemical and thermal processes (Bougrier et al., 2008; Na et al., 2007; Yuan et al., 2010).

In the last decades, application of MW irradiation has been come into the limelight in the fields of environmental engineering, food industry, rubber industry and waste processing. The major advantage of MW heating over conventional thermal methods is the volumetric heating, which led to faster heat and mass transfer and shorter process time. Since MW heat generation is a non-contact method the surface area of irradiated materials has less significant effect on the efficiency of the processes. It can be noticed, that to achieve appropriate energy absorption homogenous electromagnetic field is needed in the cavity resonator and also inside of the irradiated material (Géczi and Sembery, 2010). High efficiency of MW treatments in the biomaterial processing and also on the rate of chemical reactions is often explained by the non-thermal effects of microwaves due to the direct interaction of electromagnetic field with molecules (Leonelli and Mason, 2010).

MW irradiation has been successfully adopted as pre-treatment method via the high energy dissipation of polar compounds of sludge. There are several studies concluding MW method advantages over the pre-treatment process operating by conventional heating (Toreci et al., 2009). Increasing effect of MW irradiation on anaerobic digestion of organic solid waste was found, considering the substrate availability a 78% improvement was achieved after MW pre-treatment (Shahriari et eal., 2012).

Microwave heating of primary municipal sludge resulted in 2.5 fold increases in soluble organic matter content related to the control (Zheng et al., 2009). Application of MW irradiation combining with oxidation process, such as ozonation, can also be considered promising technology as pre-treatment before AD of high organic matter containing but less degradable sludge (Beszédes et al., 2009).

However, effects of MW process parameters on the physico-chemical properties and structure of sludge are controversial. Some studies suggested the high power MW irradiation for enhanced organic matter solubilization and disintegration of sludge particles (Climent et al., 2007), other authors concluded lower solubilization after high intensity MW irradiation (Eskicioglu et al., 2007; Park et al., 2010).

Energy transfer carried by microwaves affect the biodegradability in two ways. Thermal effect is expressed in the increase of internal pressure of intracellular liquor caused by internal heating and rapid evaporation, that altogether can lead to cell wall disruption (Lucchesi et al., 2007). The non-thermal effect of high frequency electromagnetic field is contributed to alter the structure of macromolecules with polarization of side chains and breaking of hydrogen bounds (Park et al., 2004).

1.2   Research objectives

Over the last decade many reports can be found investigating the effects of MW irradiation on the sludge disintegration and anaerobiosis, but in very few of them were examined food industry wastewater sludge. There can be found studies reporting conflicting results regard to the optimal parameters of MW pre-treatments. Furthermore, the very few experience regarding to continuous-flow operating equipment make difficulty the scale-up of MW processes.

In our earlier work was verified that beside the applied microwave power and the irradiation time the specific intensity of irradiation has also effect on the cumulative biogas product and the kinetic of anaerobic decomposition (Beszédes et al., 2011). But increasing of irradiated energy and also the specific intensity has limited positive effect on the degree of biodegradation, therefore the optimisation of process parameters are needed.

Taking into consideration of above mentioned aspects, in our present work we focused on the investigation of microwave conditioning method for food industry sludge with defining appropriate control parameters to quantify the change in biodegradability. Our second objective was to optimize the MW process parameters such as irradiated MW energy (IMWE) and intensity of MW pre-treatment characterized by the specific MW power level (MWPL). Results obtained from optimization can provide valuable and substantial information to develop continuous flow MW equipment for sludge pre-treatments.

2   METHODOLOGY

2.1   Sludge sample

Thickened meat processing wastewater sludge (MPWS) came from the sedimentation tank of wastewater purification line of a local meat processing factory (Szeged, Hungary). Wastewater was mainly originated from flushing and cleaning operations of slaughterhouse processes, meat cutting and sausage making, and it was purified by mechanical and chemical precipitation processes.

Samples were taken from equalized sludge of one week period, collected samples was stored in closed polyethylene bags at 4°C to avoid the change in sludge structure during the freezing and thawing procedure. The basic characteristics of the raw MPWS are summarized in Table 1.

TABLE 1   **Main characteristic of raw MPWS**

TS [ww^{-1} %]	TCOD [kgm^{-3}]	SCOD [kgm^{-3}]	pCOD [kgm^{-3}]	BOD$_5$ [kgm^{-3}]	SCOD/TCOD [%]	BOD$_5$/TCOD [%]	BOD$_5$/SCOD [%]
17.31±1.9	539.87±7.6	101.27±7.3	438.6±7.7	31.39±2.1	18.76±1.1	5.82±0.6	30.9±1.3

2.2 Microwave procedure

MW pretreatments were performed in a tailor-made microwave system containing continuously irradiating magnetron with changeable power in the range of 50 W to 700 W operating at a frequency of 2450 MHz. To minimize the energy loss of sample holder polytetrafluoroethylene (PTFE) container was applied for MW treatments. To investigate the efficiency of MW pretreatment the process 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. IMWE (kJ) was calculated by the magnetron power and the irradiation time.

2.3 Statistical analysis

To study the effects of the two factors and their possible interactions on the process response surface methodology (RSM) with a central composite face centered (CCF) experimental design was performed using MODDE 8.0 statistical experimental design software (Umetrics, Sweden). For the modeling and optimization the studied factors were IMWE and MWPL, selected responses function was SLI and BDI. Based on our preliminary experiments IMWE and MWPL were varied in the range of 90 – 1050 kJ and 0.5-5 Wg^{-1}, respectively. To evaluate the reproducibility of the quadratic model fitted with multiple linear regressions (MLR) three replication at the center point were used in the experimental design. The matrix for CCF and the results of experiments are summarized in Table 2.

TABLE 2   **Experimental design for MW pre-treatments of MPWS and results**

Exp.	Run Order	IMWE [kJ]	MWPL [W g^{-1}]	SLI	BDI
N1	5	90	0.5	0.303	0.46958
N2	18	1050	0.5	0.734	0.62858
N3	14	90	5	0.175	0.48654
N4	17	1050	5	0.907	0.60208
N5	8	90	2.75	0.253	0.53265
N6	7	1050	2.75	0.903	0.66038
N7	16	570	0.5	0.751	0.85012
N8	20	570	5	0.793	0.85807
N9	9	570	2.75	0.800	0.8923
N10	11	570	2.75	0.798	0.8903
N11	4	570	2.75	0.803	0.8914
N12	15	90	0.5	0.297	0.47223
N13	10	1050	0.5	0.745	0.64289
N14	21	90	5	0.186	0.48813
N15	6	1050	5	0.899	0.61427
N16	22	90	2.75	0.267	0.52523
N17	19	1050	2.75	0.902	0.66727
N18	3	570	0.5	0.776	0.85489
N19	13	570	5	0.809	0.84482
N20	12	570	2.75	0.803	0.8913
N21	2	570	2.75	0.801	0.8921
N22	1	570	2.75	0.807	0.8935

Behavior of SL and BDI was described by second-order polynomial function. Significance and reliability of the model terms was examined by regression analysis, lack of fit tests, and analysis of variance (ANOVA).

2.4   Analytical methods

The sludge samples were analyzed for total solid content (TS), total and soluble chemical oxygen demand (TCOD and SCOD) and five days biochemical oxygen demand (BOD_5). Total solid content (TS) was measured by drying to constant rate at 105°C. TCOD from the total MPWS matrix was measured triplicate using colorimetric standard method (APHA, 2005). SCOD was determined after separation of soluble from solid fraction by centrifugation (12,000 rpm for 10 minutes) and prefiltration (0.45 µm Millipore disc filter).

To evaluate the organic matter solubilization following MW treatment and to eliminate differences originating from different characteristic of raw sludge the dimensionless solubilization index (SLI) was calculated as follows:

$$\mathbf{SLI} = \frac{(\mathbf{SCOD} / \mathbf{TCOD})_t - (\mathbf{SCOD} / \mathbf{TCOD})_i}{(\mathbf{SCOD} / \mathbf{TCOD})_{max}} \tag{1}$$

Maximum achievable solid solubilization quantified by COD measurement after NaOH addition into the sample in a concentration of 2 mol L^{-1} and applied contact time of 48 hours at a controlled temperature of 50°C.

The change in the ability of organic matter for biological degradation resulted by MW treatment was characterized by the dimensionless biodegradation index (BDI) with the following equation:

$$\mathbf{BDI} = \frac{(\mathbf{CBOD}_5 / \mathbf{SCOD})_t - (\mathbf{CBOD}_5 / \mathbf{SCOD})_i}{\mathbf{CBOD}_{5\,max} / \mathbf{SCOD}_{max}} \tag{2}$$

Subscript 5 means the time of degradation during the tests. BOD_5 tests were carried out in a respirometric BOD system (BOD Oxidirect, Lovibond, Germany) at 20°C for five days with dosing of n-allylthiourea in a concentration of 12 µmol L^{-1} to avoid the nitrification process. BOD_{5max} was measured from the sample with the highest solid solubilization.

Batch mesophilic biogas production tests were carried out triplicate in plasma bottles equipped by Oxitop-C barometrical measuring head (WTW GmbH, Germany). Methane concentration in biogas was measured by Airtox biogas analyzer (Fresenius Umwelttechnik GmbH., Germany).

3   RESULTS AND DISCUSSION

To find the effect of MWPL and IMWE on quality parameter of MWPL described by solubilization index (SLI) and biodegradation index (BDI) second-order equations were developed. Multiple regression analysis of the experimental data yielded the following regression model for target function of SLI (Eq. 3) and BDI (Eq. 4). IMWE and MWPL parameters are encoded as x_1 and x_2, respectively.

$$\mathbf{SLI} = 0.8085 + 0.301x_1 + 0.014x_2 + 0.0706x_1x_2 - 0.237x_1^2 + 0.036x_2^2 \tag{3}$$

$$\mathbf{BDI} = 0.8921 + 0.071x_1 - 0.002x_2 - 0.298x_1^2 + 0.043x_2^2 \tag{4}$$

Terms with positive sign show that variables or interactions of them had positive effect on the control parameter, negative signs present that increasing of operating parameters led to disadvantageous effect. Equations with significant terms remained show that both of the factors have linear and quadratic effect on the value of control parameters studied. Interaction among variables of IMWE and MWPL was not significant for BDI at the 5% α level, but it was significant for SLI. The correlation coefficient R is defined as the ratio of explained variation to the total variation and is a measure of the goodness of fit. The value of R^2 for SLI Eq. (3) and also for BDI (Eq.4) was higher than 0.9 indicating a relatively high degree of correlation between the predicted and observed values.

Values of determination coefficient $R^2_{(adj)}$ represent that about 90% of the total variations are explained by the fitted models, which show a good prediction ability. Results of the ANOVA of created regression model show that the model and the treatment differences are significant, which is represented by the low probability values (p) and the computed

F value. The lacks of fit F values were not significant relative to the pure error at a level of 0.05; furthermore, predicted R^2 was close to the adjusted R^2.

Results of response surface analysis show that the increment of SLI was limited. Maximal SLI was obtained if irradiated MW energy reach IMWE value of 650 kJ and MW intensity was over MWPL of 1 Wg^{-1}, higher value of irradiated energy or higher intensity of MW treatment caused any further increment in the SLI. Trends of our experimental results are in good agreement with that of reported by Ahn et al. (2009) and Eskicioglu et al. (2007), respectively; but in our work was focused on the effects of different MWPL on sludge characteristic and the absolute value of differences in SLI was due to the different type of processed sludge.

In the case of BDI contour plot indicate the optimum region for maximum biodegradability in IMWE range of 550-700 kJ, and MWPL range of 1.75-3.5 Wg^{-1}, respectively (Fig.1.).
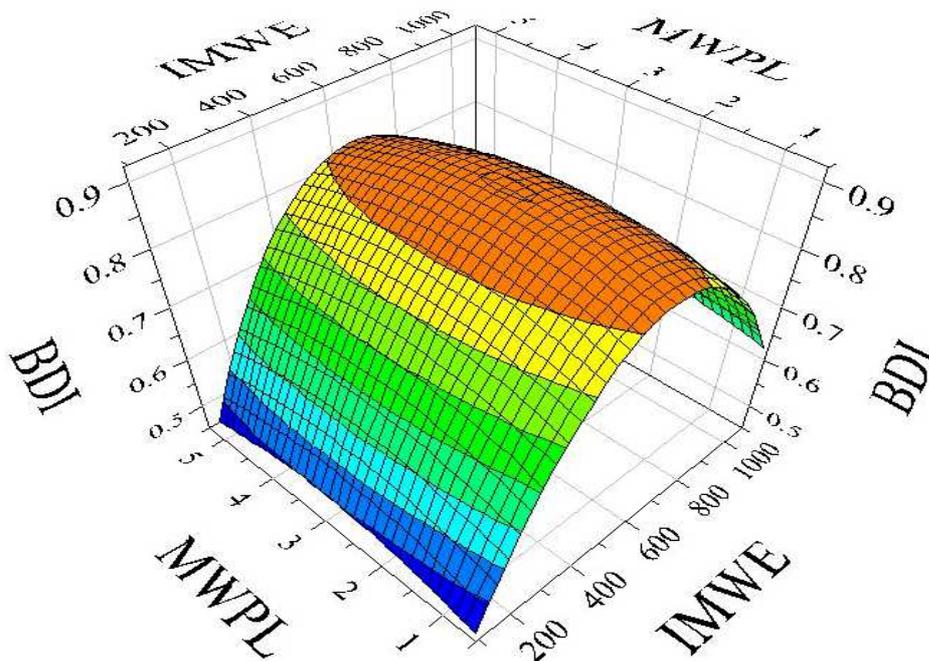

FIGURE 1   **Response surface for BDI**

Contrary to the results related to SLI, if the MW pre-treatment was carried out with higher intensity than the optimum region, or the irradiated energy was higher than that of it, decreasing of BDI was occurred.

In the study of Toreci et al. (2009) was concluded that increasing of MW power led to higher biogas production from secondary municipal sludge. In our case, MW pre-treatments increased also the cumulative biogas product from MPWS, but the worsening effect of high MWPL over a certain value of IMWE was also experienced, similar to the tendency of the change in BDI. Compare to the untreated control sample the most favorable MW pre-treated MPWS produce approximately 80% higher biogas. Our results show, that both IMWE and MWPL affect the efficiency of AD process, as well.

It can be noticed, that the intensive MW operations are known as high energy demanding processes. In order to examine the energy efficiency of MW process the net energy products of pre-treated MPWS samples were also calculated by Eq. (5).

$$\Delta E = (q_{comb} \times V_{methane}) - (P_{magnetron} \times \tau_{irradiation}) \tag{5}$$

In the calculations, 40 MJ·(Nm)$^{-3}$ average volumetric energy content for methane was used; the magnetron power varied by the intensity of irradiation.

Similar to the investigation of SLI and BDI, RSM was used for modeling and energy optimization of MW process. Fitted mathematical model to predict ΔE was given by Eq. (6).

$$\Delta E = 326.12 - 27.29X_1 - 237.74X_2 - 4.017X_1^2 - 470.79X_2^2 - 385.9X_1X_2 \qquad (6)$$

Results of our calculations show, that despite of higher biogas yield the MW pre-treatment at higher MWPL and using increased IMWE were not favorable from energetically aspects (Fig. 2.).
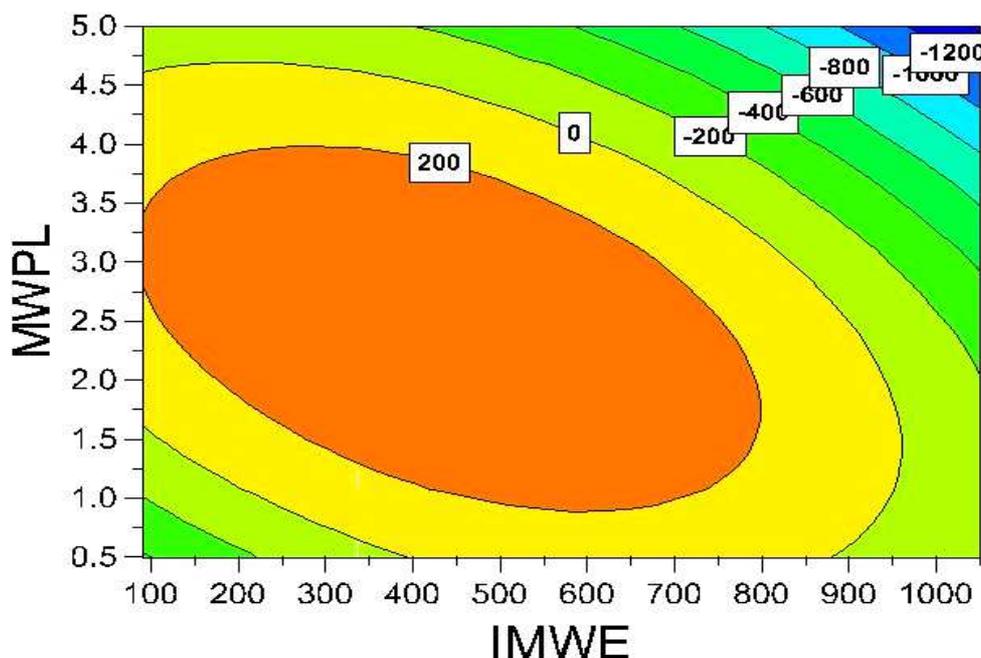

FIGURE 2   **Contour plot for ΔE**

Over a certain value of MWPL and IMWE the surplus of biogas production could not compensate the higher energy demand of the more intensive MW process. Using the fitted model and based on the date obtained from the response surface analysis the optimal condition of MW process of MPSS for highest biogas product with minimum irradiated energy and lowest MWPL were determined at IMWE of 621.9 kJ at MWPL of 2.684 Wg^{-1}. Considering the option to vary the operating parameter of MW pre-treatment optimum range of IMWE and MWPL was concluded as 600-650 kJ and 2.5-3.0 Wg^{-1}, respectively.

4   CONCLUSIONS

In present work the effects of MW irradiation on the solubilization, and biodegradability of MPWS, furthermore the energy efficiency of MW pre-treatment followed by AD were examined. Investigated operating parameters were the irradiated microwave energy (IMWE) and microwave power level (MWPL). Dimensionless solubility index (SLI) and biodegradation index (BDI) and the net energy product (ΔE) of biogas production from microwave irradiated sludge were defined as control parameters.

Our results show that MW irradiation is suitable method for conditioning of food industry sludge. Effect of MW pre-treatments on the solubilization and biodegradation was influenced by both the irradiated MW energy (IMWE) and the specific MW power level (MWPL). Increasing of IMWE and MWPL has a positive effect on biodegradability, but over a certain value of them the value of BDI was worsened. Results of optimization based on the constructed mathematical models obtained from response surface analysis show that the optimal condition of MW process of MPSS for highest biogas product with minimum irradiated energy and lowest MWPL were determined as IMWE range of 600-650 kJ at MWPL of 2.5-3.0 Wg^{-1}.

5 ACKNOWLEDGEMENTS

REFERENCES

Ahn, J.H., Shin, S. G., Hwang S. (2009): *Effect of microwave irradiation on the disintegration and acidogenesis of municipal secondary sludge*. Chem. Eng. J. 153, 145-150.

Beszédes, S., Kertész, Sz., László, Zs., Szabó, G., Hodúr, C. (2009): *Biogas production of ozone and/or microwave-pretreated canned maize production sludge.* Ozone Sci. Eng. 31(3), 257-261.

Beszédes S., László Zs., Horváth Zs. H., Szabó G., Hodúr C. (2011): *Comparison of the effects of microwave irradiation with different intensities on the biodegradability of sludge from the dairy- and meat-industry.* Biores. Techn. 102, 814-821.

Bougrier, C., Delgenes J. P., Carrere H. (2008): *Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion.* Chem. Eng. J. 139(2), 236-244.

Climent, L., Ferrer, I., Baeza M., Artola A., Vázquez F., Font X. (2007): *Effect of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions.* Chem. Eng. J. 133, 335-342.

Eskicioglu, C., Terzian N., Kennedy K., J., Droste, R., L., Hamoda M. (2007): *Athermal microwave effects for enhancing digestibility of waste activated sludge.* Wat. Res. 41, 2457- 2466.

Géczi, G., Sembery P. (2010): *Homogeneous heating in the inhomogeneous electric field.* Bulletin of Szent István Univev. 309-317.

Leonelli C., Mason T.J. (2010): *Microwave and ultrasonic processing: Now a realistic option for industry.* Chem. Eng. Proc. 49, 885-900.

Lucchesi, M.E., Smadja, J., Bradshaw, S., Louw, W., Chemat, F. (2007): *Solvent free microwave extraction of Ellataria cardamomum L.* J. Food. Eng. 79, 1079-1086.

McSwain, B.S., Irvine, R.L., Hausner, M., Wilderer, P.A. (2005): *Composition and distribution of extracellular polymeric substances in aerobic flocs and granular sludge.* Appl. Env. Microbiol. 71(2), 1051-1057.

Na, S., Kim, Y.U., Khim, J. (2007): *Physicochemical properties of digested sewage sludge with ultrasonic treatment.* Ultrason. Sonochem. 14, 281-285.

Park, B., Ahn, J.H., Kim, J., Hwang, S. (2004): *Use of microwave pretreatment for enhanced anaerobiosis of secondary sludge*. Wat. Sci. Techn. 50, 17-23.

Park W.J., Ahn J.H., Hwang S., Lee C. K. (2010): *Effect of output power, target temperature, and solid concentration on the solubilization of waste activated sludge using microwave irradiation.* Biores. Tech. 101, 13-16.

Shahriari, H., Warith, M., Hamoda, M., Kennedy, K.J. (2012): *Anaerobic digestion of organic fraction of municipal solid waste combining two pretreatment modalities, high temperature microwave and hydrogen peroxide.* Wast. Manag. 32, 41-52.

Toreci, I., Kennedy, K.J., Droste, R.L. (2009): *Evaluation of continuous mesophilic anerobic sludge digestion after high temperature microwave pretreatment.* Water Res. 43, 1273-1284.

Yuan, H., Zhu, N., Song, L. (2010): *Conditioning of sewage sludge with electrolysis: Effectiveness and optimizing study to improve dewaterability.* Biores. Techn. 101, 4285-4290.

Zheng, J., Kennedy, K.J., Eskicioglu, C. (2009): *Effect of low temperature microwave pretreatment on characteristic and mesophilic digestion of primary sludge.* Env. Techn. 30, 319-327.