HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 36(1-2) pp. 11-16 (2008)

ENHANCING OF BIODEGRADABILITY OF SEWAGE SLUDGE BY MICROWAVE IRRADIATION

S. BESZÉDES, ZS. LÁSZLÓ, G. SZABÓ, C. HODÚR✉

University of Szeged, Institute of Mechanical and Process Engineering
Moszkvai krt. 5-7, HU-6725 Szeged, HUNGARY
✉E-mail: hodur@mk.u-szeged.hu

In our work we focused on the effect of the microwave energy at the aerobic and anaerobic biological degradability of sewage sludge. The sewage sludge is a multiphase system with high water content. Because of the presence of water molecules sludge is able to absorb the microwave energy efficiently. Because of the variable dielectric properties the different component of sludge heat differently, these effects cause „thermal shock". During the microwave treatment the configuration of macromolecules are varied and the cell walls of the microorganisms are opened by the thermal shock, it means the organic compounds are accessible for further biological degradable. In our experiments digested municipal sewage sludge and undigested dairy-sludge were used. Labotron 500 professional microwave equipment was used for the microwave treatment at 2450 MHz frequency. The specific microwave power level was changed between 1 to 5 W/g. Oxitop PM barometrical measurement system was used for determination of the biogas production at 40 °C, the measurement of the chemical oxygen demand (COD) of sludge was based on a potassinium-bichromate method, and a respirometric BOD meter was used for the biochemical oxygen demand (BOD) measurement (20 °C).

Our results showed that, the microwave energy could be a practical and effective alternative technique to enhance the biodegradability of sludge, because after microwave treatment increases the biodegradability from 7 up to 40% by diary sludge and from 12 up to 48 % by municipal sludge. It was found, that the originally resistant sludge after a microwave pre-treatment became more degradable, and its biogas production increased from 20-30 ml/g $_{\text{dry weight}}$ up to 500 ml/ g$_{\text{dry weight}}$. The highest microwave power level effects the highest biogas yield, but the energy balance at lower specific power level (1-2 W/g) and longer treatment time gave just notable net energy production compared to the control sample.

Keywords: sewage sludge, biodegradability, biogas, microwave pre-treatment

Introduction

Nowadays, the most limiting factor of human being has been the clear water, and for this reason the efficiency of wastewater treatment technologies has increased. But the development and the widespread using of waste water technologies causes a large increasing in the municipal and industrial sewage sludge production. Sludge represents the major solid waste from biological and physico-chemical waste water treatment processes. Handling of this waste is difficult, and gives rise to secondary collateral environmental pollution. So the amount and the environmental risk of sludge have growing.

The most common alternatives of treatment of sewage sludge are sludge landfill, cropland application, ocean dumping and incineration. But for example by agricultural using the existing landfill sites are running out of space, however secondary pollution is becoming a serious problem. For these reasons it is the most urgent challange to improved novel process to minimized final sludge quantity.

Environmental problems of sewage sludges

The municipal and for instance the food industrial sludge, because of high organic content, is a special type of biomass, thus it may be utilized in biogas production. In the case of sludge it is some limiting compounds for example hazardous heavy metals and pathogen microorganisms. The anaerobic conditions in presence of methanogenic microorganisms lead to sludge stabilization by converting a part of organic substance into biogas [1]. The carbohydrates and the lipids of sludge are easily degradable by microorganisms, while the proteins normally less accessible for biological degradation. The anaerobic digestion of sewage sludge has many advantages for example the produced biogas can be used as renewable energy source, digestion has low energy requirement (if the produced biogas is used for heating of reactor), the pathogenic microorganisms are efficiently killed and digested sludge is harmless to dispose [2-4].

The main structure of sludge consists of extracellular polymeric substance (polysaccharide, proteins), other organic and inorganic matter and microbial cells which agglomerated together. This complex flock structure of sludge is resistance to a direct anaerobic degradation since cell walls and polymeric conformation present physical and chemical barriers for microbial and enzymatic degradation [5]. The non-biodegradable polymeric structure does not only originate from cell autolysis and sludge bacterial cell but also originates from the raw wastewater. So besides the dosed chemical, the organic matter removal efficiency of applied waste water technology is determinative too. But the amount of biological degradable component of organic matter is essential not only in anaerobic digestion but in aerobic process for example in composting or in soil-bioremediation, also.

There are many possibilities to improve the digestibility and aerobical biodegradability of sludge. Mechanical, thermal, ultrasound, chemical, thermo-chemical and enzymatic pre-treatment methods can enhance the extent and the rate of biological degradation [6-8]. It is verified the thermal pretreatments improve pathogen destruction and dewaterability process of sludge, too [9, 10]. The value of biodegradability (BD) is commonly characterized by the BOD/COD ratio. COD is the chemical oxygen demand; the quantity of oxygen required oxidation by chemical oxidant. The soluble COD (sCOD) indicate the water soluble part of COD. BOD is the biochemical oxygen demand, the quantity of oxygen consumed by aerobic microorganisms due to carbonaceous oxidation at a standard temperature (20 °C).

The anaerobic degradability batch mesophilic biochemical methane potential (BMP) tests are used with applying of acclimated inoculums of methanogenic bacteria at mesophilic temperature range (25–45 °C).

Possibilities of microwave technic in sewage sludge treatment

Microwave heating is used as a popular alternative to conventional heating mainly due to considerable reaction time reducing effect. In conventional heating a large part of process time is needed to heat the vessel before the heat is transferred to the sample, while microwave irradiation heats matter directly.

The microwave equipment generally uses 2450 MHz frequency with a 12.24 cm operating wavelength. The microwave magnetron with 900 MHz operating frequency is used for industrial scale heating and drying of solid and low water content matter on the ground of larger penetration ability [11]. Nowadays microwave digestion methods have been developed for different sample types such as environmental, biological, geological and metallic matrices [12]. Applications of microwave-assisted techniques in many fields of analytical methods, such as sample drying, moisture measurements and extraction processes are used.

Besides the examination of microwave irradiation on biological system the microwave oven reaction engineering (MORE) demonstrates promising results, for example in synthesis of organic molecules.

The microwave irradiation has thermal and athermal effect. The thermal effect can be attributed heat generation in the matter due to rotation of dipole molecules or ionic conduction. Ionic conduction is the electrophoretic migration of ions when an electromagnetic field is applied. Dipole rotation means realignment of dipoles with the applied fields, for example at 2450 MHz the dipoles align and randomized $4.9 \cdot 10^9$ times per second and this forced molecular motion results heat. In many applications these two mechanisms have been applied simultaneously. Due to high water content the sewage sludge can absorb microwave energy efficiency. Microwave irradiation causes increasing of kinetic energy of water molecules, thus the boiling point is reached rapidly.

Although the quantum energy of microwave radiation is too low ($1.05 \cdot 10^{-5}$ eV) to break the chemical bounds but some structures can be altered by the energies carried by microwaves. For example the athermal effect of microwave radiation is caused by polarized parts of macromolecules, it results breakage of hydrogen bound. Therefore, for instance the microwave irradiated microbial cell shows greater damage than convective heating cells to a similar temperature. A sample with non-homogenous structural characteristics and different dielectric properties is possible to produce a selective heating of some areas or components of material, it is known as superheating effect. The intensive microwave heat generation and the different dielectric properties of compounds of cell wall lead to a rapid disruption of extracellular polymer network and residue cells of sludge [13].

However the cell liquor and extracellular organic matter within polymeric network can release into the soluble phase, hereby increase the ratio of accessible and biodegradable component. During the intensive microwave heating the odorous compounds of sludge e.g. volatile fatty acids were reduced too.

To summarize, by application of microwave treatment could be achieve a higher flock and cells destruction compared to conventional heating, this effect could be manifested by difference ratio of soluble and total COD and the increased rate of biogas production [14]. But it is had to notice that the temperature control of a microwave pre-treatment process causes some practical difficulties because the conventional thermistors cannot provide accurate temperature measurement, since the local superheating effect within the sample due the interaction of thermistor and thermocouple with electromagnetic field [15]. In the microwave technique widely used infrared thermometer can measure only the surface temperature of sample. By the glass fiber instruments can be measured more exact values of temperature distribution of matters but by a sample with a low moisture content and varying, non homogenous structure, the method is less applicable in practice.

Materials and methods

In our experiments two different sewage sludge were used. The municipal sewage sludge was from an urbanwaste water treatment plant (Hódmezővásárhely, Hungary). The sludge was the residual solid phase of the biological waste water management technology, the average moisture content was 53.4 w/w%. The industrial sewage sludge was originated from the waste water treatment plant of a local dairy works (Sole-Mizo Ltd., Szeged, Hungary). In the case of dairy sewage sludge a phyico-chemical waster water technology was applied and the water content of sludge was 58.2 w/w%.

The microwave pre-treatments were performed in a Labotron 500 (Buchner-Guyer AG, Switzerland) professional microwave equipment, at 2.45 GHz frequency, at 100 to 500 W microwave power. The turntable of microwave equipment compensated for the non-uniform heat distribution. The microwave irradiation time was 10 to 40 minutes. The applied specific microwave power level was 1, 2 and 5 W/g, which was adjusted by the ratio of magnetron power and the quantity of treated sludge. The power of magnetron is changeable continuously 100 to 500 W by toroidal-core transformer, the quantity of sludge was constant 100 g. The disk-form sludge samples were placed invariably in 2 cm layer because of penetration depth of microwave radiation. Poly-tetrafluor-ethylene (PTFE) vessels (6 cm internal diameter) were used on account of efficient microwave penetration and absorption. Cover was applied to prevent the evaporation during the irradiation. The convective heat-treatment was performed in automatic temperature controlled laboratory heater equipment (Medline CM 307, UK) at 95 °C. The surface temperature of sludge an Infracam (FLIR InfraCAM-SD, Sweden) was determined after microwave irradiation.

Chemical oxygen demand (COD) was measured according to the dichromate standard method in COD tests with an ET 108 digester and a Lovibond PC CheckIt photometer. The biochemical oxygen demand (BOD) measurements were carried out in a respirometric BOD meter (BOD Oxidirect, Lovibond, Germany), at 20 °C. To ensure the consistency of the results BOD microbe capsules (Cole Parmer, USA) were used for measurements. Biodegradability during 5 days (BD_5%) was characterized by the following expression:

$$BD_5\% = \frac{BOD_5}{COD} \times 100\%$$

The cumulative biogas production tests were performed in batch mode under mesophilic conditions, at 40 °C for 30 day, in a temperature controlled anaerobic digester with Oxitop Control type pressure mode measuring system (WTW Gmbh, Germany). The digesters were inoculated with an acclimated anaerobic sludge from a biogas reactor of municipal wastewater treatment plant (Hódmezővásárhely, Hungary) in order to eliminate the possible lag-phase of biological degradation process. After inoculation nitrogen gas was flowed through the reactor to prevent exposure to air. For methane determination the measurements were performed parallel in two vessels: one of them contained CO_2 absorber, the other measured the total gas pressure. The resulting pressure difference is proportional to the CO_2 concentration; the remaining overpressure is proportional to the methane concentration. The composition of produced biogas also was measured by gas chromatographic and mass spectrometric method (Agilent 6890N-5976 GC-MS).

The net energy product (NEP) of processes with microwave pre-treatments can be calculated by the equation [16]:

$$NEP = q_{comb} \times m_{methane} - P_m \times \tau$$

where NEP is the net energy product [J], q_{comb} is the combustion heat [J/kg] of methane, $m_{methane}$ the mass of the produced methane [kg], P_m the power of microwave magnetron [W], τ the time of microwave irradiation [s].

Results and discussion

The surface temperature of samples was measured by infracam, and the average temperature and standard deviation were represented in the following table.

Table 1: The surface temperature of microwave irradiated sludge after treatments

MW Power level	**Surface temperature [°C]**			
	10 min.	*20 min.*	*30 min.*	*40 min.*
1 W/g	75,7 ± 2,9	83,5 ± 1,8	89,2 ± 1,6	90,2 ± 1,3
2 W/g	79,3 ± 2,2	86,7 ± 1,4	89,6 ± 1,1	91,7 ± 0,7
5 W/g	83,6 ± 0,8	89,1 ± 0,9	90,8 ± 0,3	92,8 ± 0,4

In the first series of our experiments the effect of microwave irradiation on biodegradability of sewage sludge was investigated at different specific microwave power level. Besides the specific power level the effect of irradiation time was studied too. The biodegradability of untreated dairy and municipal sewage sludge was 7% and 12% respectively. It was found that without pre-treatment either municipal or dairy industrial sludge was resistant to aerobical biological degradation.

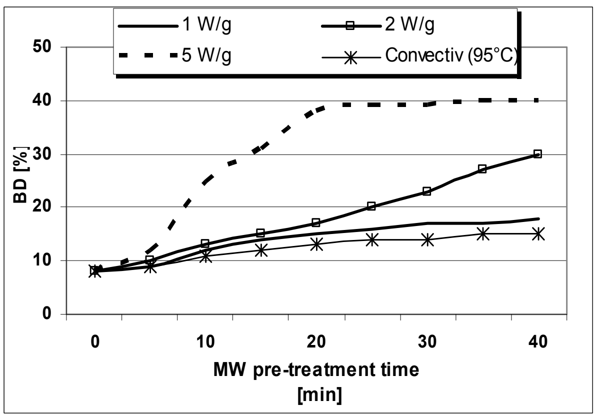

Figure 1: Biodegradability (BD%) of dairy sewage sludge after microwave and convective pre-treatments

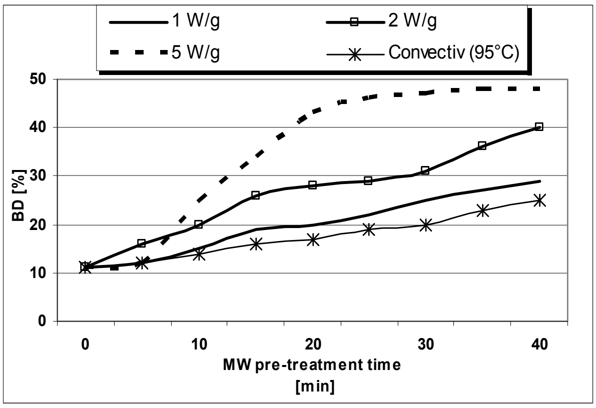

Figure 2: Biodegradability (BD%) of municipal sewage sludge after microwaveand convective pre-treatments

The low biodegradability of municipal sewage sludge was caused by large-scale degradable organic material removal of previous biological waste water treatment. The residual components, which was concentrated in the sludge, was less degradable or more resistant to microbial or enzymatical degradation. The structure of dairy sludge, formed by interaction of extracellular polymeric substance and applied chemicals, caused less accessible property for biological decomposition. For comparison the convective heat pre-treatment was examined. The convecive treatment at 95 °C caused increasing in biodegradability, but this effect was less effective than pre-treatment at lowest microwave power level.

The microwave pre-treatments increased the biodegradability of investigated sludge. Microwave irradiation at low power level (1 W/g) had a sligh effect on biodegradability, especially at sludge originated from dairy industry, but the higher microwave power level and enhanced irradiation time seemed to be more efficient. At highest applied power level (5 W/g) a saturation value of biodegradability was observed. In the case of municipal sludge the ratio of biodegradable component was enhanced from 8 % up to 40 % after 30 minutes irradiation at 5 W/g. The same microwave pre-treatment increased the value of BD% to 48 % at dairy sewage sludge. Enhancing of biodegradability may be linked to solubilization of organic matter which was indicated by the increased sCOD/COD ratio, besides the digestion effect of microwave irradiation on cell wall of residual died and alive microorganisms.

Besides the change of biodegradability the effect of microwave irradiation on anaerobic digestion was investigated, the digestionable was characterized by cumultive methane production, which were depicted on *Figs 3-4,* in the case of pre-treatment at 1 W/g and 5 W/g .

Similar to aerobical biodegradation the microwave pre-treatment improved the anaerobical decomposation performance and the increased irradiation time enhanced the biogas- and methane production of pre-treated sewage sludge related to control. The untreated control samples had very small (15–30 cm^3) methane production, but after a 40 minute long, 1 W/g MW pre-treatment enhanced the methane production up to 200 cm^3 at municipal sludge and up to 250 cm^3 at dairy sludge. The convectie heat-treatment had a substantially smaller effect on anaerobic biodegradation than microwave irradiation since the smaller biogas product. After a 40 minutes heat-treatment at 95 °C a 25% enhancing of biogas product was experienced by both sludge, but these enhancing was significantly smaller than after a 20 minutes microwave irradiation, although the average temperature of microwave iradiated sludge was just about 83 °C.

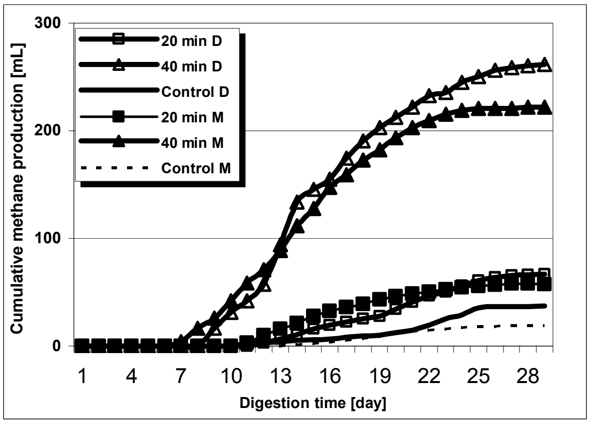

Figure 3: Methane production of sludge after 1 W/g microwave pre-treatment
(D-dairy sewage sludge, M-Municipal sewage sludge)

The applied microwave treatment both given sludge could decreased the lag-phase period of digestioning process. The higher specific microwave power caused higher increasing in the methane production and higher decreasing in the period of lag-phase.

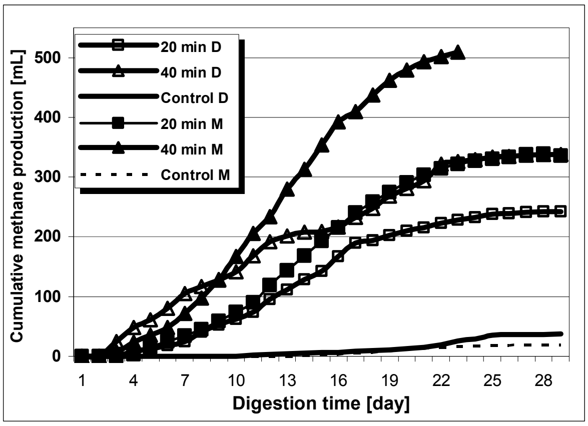

Figure 4: Methane production of sludge after microwave pre-treatment at 5 W/g
(D-dairy sewage sludge, M-Municipal sewage sludge)

Enhancing of microwave power level to 5 W/g resulted an increasing in the methane production 500 cm^3 by 40 minutes pre-treatment at municipal sludge. Approximately the same biogas yield was achieved by 5 W/g specific MW level at 40 minute long treatment at dairy sludge as it was achived with a 20 minute long MW treatment at municipal sludge. To a first approximation a longer process time and a higher microwave power level seemed to be optimal.

After all not only the biogas production itself, but the other energetical parameters must be take into consideration. By assessing the energy of extra-methane produced and calculation of energy requirements of microwave pre-treatments the energy balance of MW enhanced treatment was investigated, and the efficiency of process was characterized by net energy prouction (NEP).

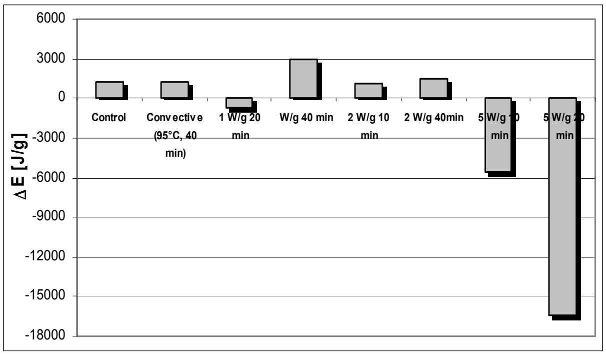

Figure 5: Energy balance of pre- treatments of dairy sewage sludge

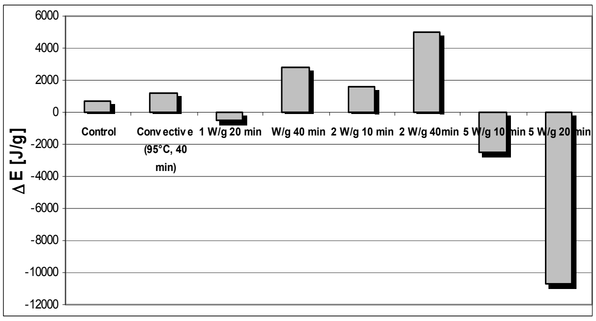

Figure 6: Energy balance ofpre- treatments of municipal sewage sludge

In spite of large energy demand of microwave treatments, there is optimal specific microwave power which produce positive energy balance. In comparison with optimal parameters of methane production different results can be obtained by calculate the energy balance of the treatments.

With the exception of the highest microwave power level (5 W/g) the invested microwave energy was balanced by extra methane energy and moreover in the case of dairy sewage sludge at a 40 minute long treatment at 1 and 2 W/g specific power level and in the case of municipal sewage sludge also 40 minute long duration of irradiation of 1 W/g specific power level was beneficial compared to control sample and conventional convective heat-treated sample. Therefore, at the different born sludge investigated the lower specific microwave power level used were more advantageous regarding the energy efficiency of sludge pre-treatments by microwave irradiation.

Conclusion

The application of microwave irradiation has advantages in sludge treatment processes. The microwave pre-treatments can enhance more efficiently the aerobical biodegradability and biogas yield than the convective heat pre-treatments. The efficiency of treatments is dependent on the applied specific microwave power level and the time of irradiation. Our results showed that despite of the quantity of produced biogas the lower specific microwave power level usage could be recommended from energetically aspect.

ACKNOWLEDGEMENTS

This work was supported by the Hungarian National Office of Research and Technology (NKTH) and the Agency for Research Fund Management and Research Exploitation (KPI) under contract No. RET-07/2005, and GVOP 3.2.1.2004-04. 0252/3.0 project.

REFERENCES

1. BOUGRIER C., DELGENES J. P., CARRERE H.: Chemical Engineering Journal 139 (2008) 236-244
2. BANIK S., BANDYOPADHAY S., GANGULY S.: Bioresource Technology 87 (2003) 155-159
3. GAVALA H. N., YENAL U., SKIADAS I. V. WESTERMAN P., AHRING B. K.: Water Research 37 (2003) 5461-4572
4. WATENABE H., KITAMURE T., OCHI S., ORTEGA S., OZAKI M.: Water Science Technology 36 (1997) 239-246
5. ESKICIOGLU C., KENNEDY K. J., DROSTE R. L.: Water Research 40 (2006) 3725-3736
6. WANG Q., KUNINOBU M., KAKIMOTO K., OGAWA H., KATO Y.: Bioresource Technology 68 (1999) 309-313
7. STASTA, P., BORAN, J., BEBAR, L., STEHLIK, P., ORAL, J.: Applied Thermal Engineering 4 (2005) 241-250
8. BOUGRIER C., DELGENES J. P., CARRERE H.: Process Safety and Environmental Protection 84(B4) (2006) 280-284
9. WOJCIECHOWSKA E.: Water Research 39 (2005) 4749-4754
10. NEYENS E., BAEYENS J.: Journal of Hazardous Materials B98 (2003) 51-67
11. GABRIEL, C., GABRIEL, S., GRANT, E., HALSTEAD, B., MINGOS, D.: Chemical Society Reviews *27 (1998)* 213-223
12. JONES, D. A., LELYVELD, T. P., MAVROFIDIS, S. D., KINGMAN, S. W., MILES, N. J.: Resources, Conservation and Recycling (2002) 75-90

13. ESKICIOGLU C., TERZIAN N., KENNEDY K. J., DROSTE R. L., HAMODA M.: Water Research 41 (2007) 2457-2466
14. CLIMENT M., FERRER I., BAEZA M., ARTOLA A., VAZQUEZ F., FONT.: Chemical Engineering Journal 133 (2007) 335-342
15. VESHETTI, E., MARESCA, D., SANTARSIERO, A., OTTAVIANI, M.: Microchemical Journal 59 (1998) 246-257
16. BESZÉDES S., KERTÉSZ SZ., LÁSZLÓ ZS., GÉCZI G., HODÚR C., SZABÓ G.: Proceedings of 5th International Congress on Food Technology (2007) Vol. 3. 441-446