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APPLICATION OF THERMAL AND MICROWAVE PRE-TREAMENTS FOR DAIRY WASTEWATER SLUDGE

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ABSTRACT: *Thermal pre-treatment has verified beneficial effects on sludge characteristic, therefore it is suitable to adopt in sludge handling technologies. Microwave method has many advantages over the conventional thermal processes; the most important properties of microwave irradiation are the rapid heating and the high intensity with reduced processing time requirement. Many reports have dealt with the examination of microwave technique in the field of municipal sludge processing, but can not be found results related to microwave treatment of wastewater sludge in continuous flow equipment. Therefore the aim of our work was to investigate the applicability of a continuously flow microwave reactor for enhanced biodegradability of wastewater sludge from dairy processing. Our results had shown that the effect of microwave irradiation on the biodegradability of sludge was higher than that of obtained from conventional heating, what make the process suitable to apply as pre-treatment method in sludge handling technologies.*
KEYWORDS: *microwave pre-treatment, wastewater, sludge, biodegradability*

INTRODUCTION

The main aim of wastewater purification technologies s is the removing of contaminants and organic components from wastewater using various methods, techniques and systems. There are known numerous physical, chemical and biological processes used to achieve efficient .removal with appropriate capacity. Beside the many advantage of novel wastewater treatment technologies, such as advanced oxidation processes, membrane operations and biological treatment, sludge handling present actual solving problem for wastewater treatment plant [1].

Sewage sludge and industrial wastewater sludge is one of the main residual waste from wastewater management. With the widespread used wastewater treatment technologies the amount of produced sludge is increasing both in the developing and industrial countries. In many branch of the food industry a huge amount of wastewater sludge is generated, mainly because of the high water demand of process technologies and the frequently used flushing and cleaning procedures. There have been developed many process to decrease the amount of different type of sludge produced in wastewater treatment or sludge lines, minimized the pathogen content and to eliminate the environmental risk of them.

Before disposing and further utilization, waste sludge need to be stabilized sufficiently to reduce organic content, odour problems and pathogen contamination. Anaerobic digestion (AD) has become one of the most popular sludge stabilization processes which reduce the volume of waste sludge and produces bio-energy. Biotransformation of organic matters into biogas has limitations in terms of long retention times, long lag-phase of decomposition and low degradation efficiency. Digestion rate is significantly influenced by the slowly biodegradable cell walls and polymeric structure of sludge formed by the extracellular polymeric substances (EPS), therefore the hydrolysis stage is considered as the rate limiting step in the AD process [2]. Many pre-treatment methods have been investigated to overcome these limitations. There is known several mechanical, chemical, enzymatic, ultrasonic assisted and thermal processes to disrupt the cell walls and EPS what is manifested in enhanced biodegradability [3].

Microwave (MW) irradiation is an alternative method to conventional thermal treatment suitable to produce rapidly focused direct heat with low transmission energy losses. Moreover, existence of so called non-thermal microwave effect are assumed arisen from the changing in dipole orientation of polar molecules, nuclear spin rotation and spin alignment manifested in restructuration of side chains and hydrogen bounds of macromolecules in high frequency alternating electromagnetic field [4]. Non-thermal effects are described in solvent free or dry media reactions or biphasic viscous systems. In high water containing materials thermal effects dominate over the non-thermal effects due to the high energy dissipation [5].

Processing in high frequency electromagnetic field has received much attention in the last decades due to the ease in operation, fast start-stop periods, and high intensity volumetric and selective heating characteristic. It can be noticed, that rapid dielectric heating is suitable for only the lossy materials with high dielectric loss factor. Nowadays there can be found many microwave method to *heat insulator type materials using facilitator such as carbon, magnetite or silicone carbide. MW is used in numerous environmental applications, such as pyrolysis, soil remediation, chemical catalysis, and remediation of hazardous wastes or wastewater sludge treatment [6]. In the environmental engineering, or also in the organic synthesis MW irradiation can be successfully applied alone, or combined with advanced oxidation processes (AOPs), heterogeneous catalysts, photocatalysis or other thermo-chemical methods [7].*

Mw irradiation was also investigated for wastewater treatment and sludge handling. The main requirements for MW applications are the good degradation efficiency for various organic pollutants and rapid heating due to the high energy absorption. Because of the high water content MW operations can answer the challenge of fast heating and it can be made suitable for cost-effective method with optimization of process parameters. The molar energy of MW irradiation (0.4 - 40J at a frequency range of 1-100 GHz) is not enough to disrupt primary or secondary chemical bounds but sufficient to alter the tertiary and quaternary structure of proteins and carbohydrates what can lead to higher biodegradability or change in chemical or enzymatic reactivity [8]. Promising results was reported on the ammonia removal using MW process. Since the dipolar polarization of polar NH_3 was manifested in removal efficiency of 80-100% processing municipal wastewater in MW assisted reactor [9].

There can be found papers dealing with the effect of microwave conditioning on the sludge characteristic. Wojciechowska [10] concluded that microwave irradiation is appropriate to decrease the specific resistance of sludge to filtration. Microwave irradiation in combination with acidic hydrolysis or oxidants is suitable to enhance the degree of nutrient recovery [11]. MW treatments have obvious effect on disintegration of sludge particles and therefore affect the organic matter solubilisation. Considering the effect of MW power on solubilisation conflicting results are reported. Some authors concluded that higher MW power led to higher degree of solubilisation [12], while others reported opposite trends of sludge disintegration [13].

Connection between the change in solubilisation and the degree of anaerobic biodegradation was also verified. In the study of Eskicioglu et al. [14] effects of MW irradiation on the organic matter solubilisation and methane production from thickened waste activated sludge were investigated. The results indicated linear correlation between the degree of solubilisation and the applied temperature. The highest solubilisation was found after MW heating of sludge to 175°C. Under this condition 54% of the ultimate chemical solubilisation ratio was achieved and the cumulative biogas production was about 31% higher than that of obtained from control sample. Microwave irradiation was also successfully adopted in order shorten the initial lag-time of anaerobic digestion [2].

Beyond the many report on disinfection ability and effective dehydration capability for bio-materials, mechanisms and effects of microwave irradiation during sludge conditioning is not fully understood yet. Very few scientific works have focused on the investigation of the effect of MW irradiation on the biodegradability of food industry wastewater sludge Furthermore, there is no found study related to sludge conditioning carried out in continuously flow microwave reactor. Therefore, our research has aimed to investigate the effect of MW pre-treatment on wastewater sludge from dairy processing comparing the efficiency of conventional heat treatment and continuous MW operation.

MATERIALS AND METHODS

Thickened wastewater sludge originated from physico-chemical wastewater purification technology of a dairy factory. Samples were fresh collected from the settling tank, and were stored at 4°C prior to processing. The sludge samples had an average total solid (TS) content of 5.1 ± 0.2 w/w% measured by drying to constant rate standard method at 105°C.

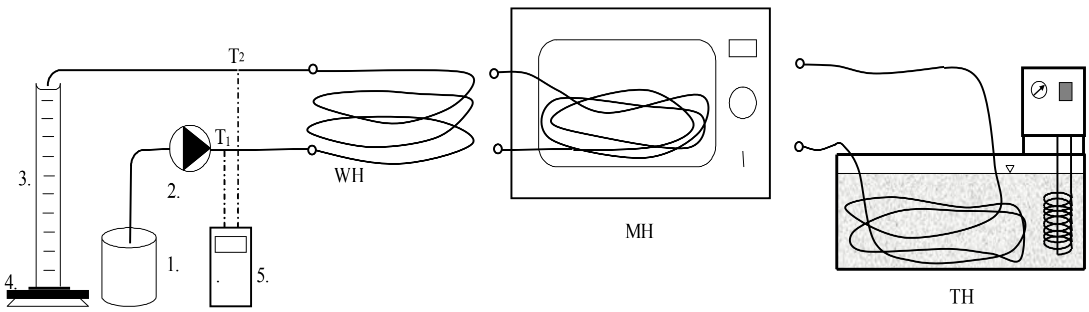

Fig.1 . Schematic diagram of measuring and sampling
1-sludge tank, 2-feed pump, 3-sample container, 4- scale, 5- thermometer,

Conventional heat treatment (TH) was carried out in a temperature controlled water bath. For microwave pretreatments (MH) a tailored Whirlpool AT314 microwave oven with 900W nominal power at 2450 MHz operating frequency was used. During the treatment sludge samples were heated up to a temperature of 80 C° in continuous operation, temperature was controlled and recorded by Almemo

2590 thermometer. Sludge was flowed by Stenner 85M5 peristaltic pump through flexible silicon pipe (inner diameter of 8 mm). Control samples (WH) were obtained from the same measuring system without heating.

Microwave irradiation was carried out using nominal magnetron power of 900W. The continuous through-flow microwave unit was developed by the modification of a domestic microwave oven. The wastewater sludge was flown in the silicon pipe in the microwave cavity. Desired temperature was varied by the length of the silicon pipe and the volumetric flow rate of the feeding pump. The temperature can be measured before and after the heat treatment outside of the high frequency electromagnetic field.

To ensure the comparability of the heat treatments, a method with equal duration time and temperature was developed. With the adjustment of the water bath temperature the same temperature profile with the same flow rate can be achieved than that of obtained in microwave heating method. The measuring procedure was suitable to compare the effect of different heating method using the same operating condition.

Organic matter content of processed sludge was characterized by the chemical oxygen demand (COD) parameter. COD was measured by colorimetric dichromate method using COD test cuvettes after centrifugation (6000 rpm, 20 min). For sample preparing a 0.45μm disc filter (Millipore) was used. Digestion was carried out in a thermoreactor (VELP Scientifica, Germany) at 180°C for 180 minutes. For the COD assay a LOVIBOND PC Checkit (Germany) photometer was used. In order to eliminate the positive errors of the measurements dechlorinating agent was added into the samples.

Biodegradable part of organic matters was estimated by the biochemical oxygen demand (BOD). BOD was measured in a respirometric BOD meter (LOVIBOND Oxidirect, Germany), samples were thermostated at 20 °C for 5 days. To ensure the consistency of the experiments, BOD Seed microbe capsules (Cole Parmer, USA) were used for the experiments and the pH of all samples was adjusted to 7.2. The prepared samples were diluted with the buffer solution (containing K_2HPO_4, KH_2PO_4, Na_2HPO_4, $CaCl_2$, $FeCl_3$, NH_4Cl), using dilution factor of 10. In order to avoid the errors originating from the oxygen uptake of nitrification process n-allylthiourea solution was dosed to the samples in a concentration of 2 μmol·L^{-1}.

RESULTS AND DISCUSSION

Results obtained from microwave heating (MH), conventional heating (TH) and the characterization of non-treated sample (WH) are summarized in Table 1. Chemical oxygen demand (COD) was measured in triplicates; the ability of organic matters to biological degradation was expressed by the ratio of five days biochemical oxygen demand (BOD_5) to average value of COD.

Table 1. Results obtained from different sludge pre-treatments

Pre-treatment	COD [mgL^{-1}]					BOD_5 [mgL^{-1}]	BOD/COD [%]
	1	2	3	Average	SD		
WH	3630	3600	3680	3636.7	40.4	201	5.5
	3780	3880	3870	3843.3	55.1	273	7.1
	3820	3910	3780	3836.7	66.6	268	7.0
	3580	3610	3620	3603.3	20.8	241	6.7
MH	3940	4010	3970	3973.3	35.1	1509	28.0
	4090	4460	4290	4280.0	185.2	874	24.4
	4010	4030	4020	4020.0	10.0	778	29.4
	3960	3830	4030	3940.0	101.5	1044	26.5
TH	3870	3800	3870	3846.7	40.4	598	15.5
	3930	3930	3910	3923.3	11.5	489	12.5
	3830	3780	3930	3846.7	76.4	875	18,3
	3360	3350	3390	3366.7	20.8	784	17,7

Results of our experimental research and analytical measurements show that despite of the high organic matter content of sludge (70% on dry matter basis) biochemical oxygen demand indicate low biodegradability. Our experiences are verified that dairy industry sludge contains organic components in a high concentration which affect negatively the microbial decomposition; therefore the efficiency of further biological utilization of sludge is limited.

Data show that the COD of different pre-treated samples was not changed, because the applied microwave and conventional heat treatment have not effect on the total concentration of organic matters determined by chemical oxidation method. Applied analytical method was not suitable to measure the difference between the total amount of organic matters and that of in soluble phase due to the low dry matter content of sludge. Based on preliminary results conventional thermal pre-treatments and MW pre-treatments as well were concluded suitable to enhance organic matter solubility [8, 11] but this effect was not detectable in our experiments using the standard analytical methods.

Our experimental results presented that effects of both the microwave process and the conventional heating has manifested in a higher BOD compared to the control samples. Increment of BOD was significantly the highest after MW pre-treatment, compared to the untreated sample (BOD value of 245 mgL^{-1}) the microwave irradiated sludge had biodegradable organic matter concentration of 1050 mgL^{-1}. Conventional thermal pre-treatment has also advantageous effect on BOD, but increasing was lower than that of obtained from microwave processing.

Control sample has an average percentage ratio of BOD to COD of 6.6 ± 0.73%. With conventional thermal pre-treatment and microwave pre-treatments BOD/COD ratio increased up to 18.3 ± 2.25%, and 27.1 ± 2.14, respectively. Increment of the concentration of biologically degradable organic matter content can be explained by the disintegration of particles [10]. Decreased particle size result a higher specific surface area for microbial decomposition, and also for enzymatic processes [7].

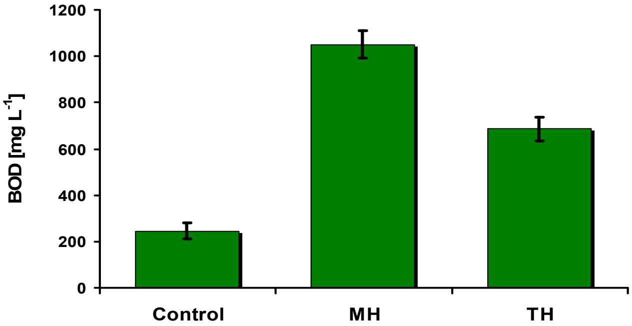

Figure 1. Change in BOD after different pre-treatment

In other hand, with destruction of cell walls the resistance to direct degradation of organic matter was decreased. Furthermore the intracellular liquor containing organic matters can liberate to the intercellular space, where the efficiency and the rate of enzymatic decomposition is enhanced [11]. Both of the above mentioned phenomena have a verified positive effect on the amount and the rate of biological degradation.

The calculated values of BOD/COD indicate the percentage ratio of biodegradable part of total organic matter content, independently from the original characteristic of wastewater samples. Figure 2 show that BOD/COD increased after the microwave and the conventional heating operation, as well. Therefore both of them are suitable to enhance the aerobic biodegradability of wastewater originating from dairy processing.

Conventional thermal heating could increase biodegradability expressed in BOD/COD parameter from an average value of 6.5% to above 18%, and biodegradable part of organic matter of sludge was enhanced over 25% after microwave pre-treatment. Microwave irradiation has also accelerated the biological transformation (data not shown). Reason for enhanced biodegradation is the disruption of resistant cell walls and therefore the easier and larger scale accessibility of organic matters for decomposing bacteria. Enhanced biodegradation provoke a higher degree of anaerobic degradation, as well, which can be manifested in higher biogas yield and accelerated biogas production.

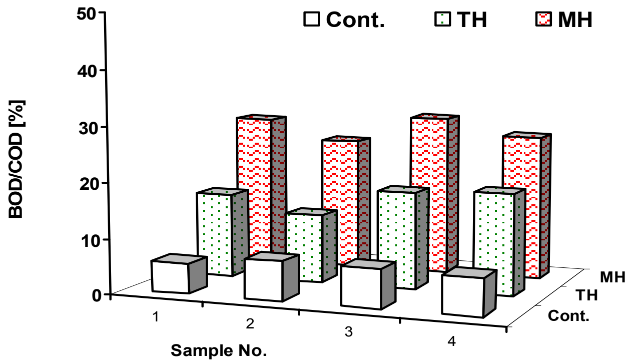

Figure 2. BOD/COD value of processed sludge as a function of treating methods

CONCLUSIONS

As summarizing of our results it can be concluded that microwave pretreatment could enhance the biodegradability of processed dairy wastewater in a higher extent than the conventional heating. The low biodegradability of raw sludge, namely BOD/COD ratio of 6.5%, could be increased to over 25%. Experimental results provoked microwave conditioning method applicable prior to biological waste handling processes such as composting or anaerobic digestion.

It can be noticed, that sludge contain water, fat, proteins, detergents and other components in soluble and also in particulate form with different dielectric- and sedimentation properties which provoke operation problems and make difficult to ensure the homogeneity of electromagnetic field in the processed material and also to achieve the optimal flow pattern.

Taking into consideration the specific requirement of sludge and other fluids with high solid content for the design of continuous flow microwave equipment the application of static mixers in the tube exposed to microwave irradiation could increase the homogeneity of processed material and also contribute to achieve more uniform heating. From energetically point of view, optimization of microwave process parameter such as flow rate, temperature, and pH adjustment is needed to increase the energy absorption ad decrease the energy loss.

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