Initial examination of microwave pretreatment on primary, secondary and mixed sludges before and after anaerobic digestion

C. Eskicioglu, K. J. Kennedy and R. L. Droste

Department of Civil Engineering, University of Ottawa, 161 Louis-Pasteur, Ottawa, Ontario, K1N 6N5, Canada
(E-mail: eskiciog@genie.uottawa.ca; kkennedy@uottawa.ca; droste@eng.uottawa.ca)

Abstract: The effects of microwave pretreatment on disintegration and mesophilic digestion of waste activated sludge (WAS), primary sludge (PS), combined (PS + WAS) sequencing batch reactor (SBR) sludge and anaerobically digested biocake were investigated by both household and bench scale industrial types microwaves at temperatures below and above boiling point. Pretreatment variables, temperature, intensity (cooking rate) and sludge concentration had statistically significant effects on solubilization. The microwave pretreatment also increased the bioavailability of sludge components under batch anaerobic digestion and enhanced the dewaterability of pretreated sludges after digestion. However, the level of improvements in solubilization and biodegradation from different waste sludges were different. While the largest improvement in ultimate biodegradation was observed in WAS, microwave irradiation only affected the rate of biodegradation of pretreated PS samples. Similarly, relatively lower solubilization ratios achieved for combined - SBR sludge was attributed to high sludge age of extended aeration SBR unit. It is possible that initial sludge characteristics may influence final pretreatment outcomes so that general statements of performance cannot always be made.

Keywords: Anaerobic digestion; microwave pretreatment; WAS; PS, biocake

INTRODUCTION

The minimization of volume and quantity of PS and WAS produced by wastewater treatment plants (WWTPs) has become increasingly important because of the rising energy and operating costs, as well as issues related to disposal (e.g., growing opposition to land application due to pathogens and odor). Previous research on sludge minimization by Water Environment Research Federation (WERF) was primarily focused on finding cost-effective methods for sludge dewatering, since half the cost of WWTP management is spent on sludge dewatering, mainly due to the sponge-like structure of biomass and extracellular polymeric substances (EPS; such as proteins, polysaccharides and nucleic acids) in WAS, which traps water and makes it difficult to dewater (Schmitt and Flemming, 1999; Yin et al., 2004). The link between the type of cations, biopolymers and sludge digestibility was also examined. Studies suggested that anaerobic digestion would yield the best solids destruction for sludges with high iron content, and aerobic digestion can release a high magnitude of divalent cations required for floc integrity. Depending on the ratio of divalent/monovalent cations in sludge, bound protein with divalent cations improves settling and dewaterability, while sludges with high monovalent cations can be difficult to settle and dewater (Novak et al., 2003).

Recent studies have focused on destruction of floc structures and lysis of microbial cells to release biodegradable organic materials and render them more accessible to anaerobic digestion. Ultrasound (Gonze et al., 2003), mechanical (Muller et al., 2003), chemical (Chiu et al., 1997), thermal (Dereix et al., 2006), enzymatic (Barjenbruch and Kopplow, 2003) thermo-chemical (Valo et al. 2004) and ozonation (Weemaes et al., 2000) are the main categories of pretreatment methods researched to date. Microwave irradiation is a novel application for digestion pretreatment. Initial microwave studies were conducted at temperatures less than 100°C using household microwave ovens and microwave transparent containers designed for food applications. For laboratory experiments, the household microwave oven can be a relatively efficient microwave pretreatment applicator, depending on (1) the shape and size of the treatment vessel, and (2) how far the microwaves penetrate into the fluid. Household microwave ovens are designed to have good power absorption efficiency for a ~ 1 litre vessel, with ~ 1.0 cm microwave “Half-Power” penetration depth in the fluid to be heated. However, no microwave-based high-temperature (above 100°C) sludge pretreatment study has been...
reported using a programmable temperature and pressure system with closed reaction vessels. This paper analyzes the effects of microwave pretreatment on disintegration and mesophilic digestion of WAS, PS, combined (PS + WAS) SBR sludge and anaerobically digested biocake by both household and bench scale industrial types microwaves at temperatures below and above boiling point.

**MATERIALS AND METHODS**

**Waste sludges pretreated**

The experimental setup was assembled and operated at the University of Ottawa (ON, Canada). Waste sludges [thickened WAS (TWAS), PS and anaerobically digested biocake] were taken from the Robert O. Pickard Environmental Centre (ROPEC) wastewater treatment plant located in Gloucester (ON, Canada). ROPEC has preliminary and primary treatment followed by a conventional aerobic activated sludge unit operated at an average sludge retention time (SRT) of 5 d. Ferric chloride is added to WAS for P removal prior to WAS thickening. TWAS and PS are blended in a 58.42 v/v ratio and undergo mesophilic anaerobic sludge digestion to produce a stabilized biosolids product for disposal. PS [4% total solids (TS), w/w] was obtained from primary clarifiers following preliminary pretreatment and TWAS (5.4% TS, w/w) was obtained from the thickener centrifuge downstream of the activated sludge unit. Biocake used in this study was the final product of mesophilic sludge (PS+WAS) digesters and dewatered to 30% TS (w/w) at ROPEC.

ROPEC - TWAS was characterized as young sludge based on the 5 d SRT of the activated sludge unit and supported by the relatively high volatile solids (VS)/TS ratio of about 0.70. In order to analyze the effects of sludge type and sludge age of activated sludge unit, where the sludge is taken, on the pretreatment efficiency, microwave pretreatment was also applied to a combined (PS + WAS) extended aeration SBR sludge with an SRT of 12 d. Combined SBR sludge was obtained from WWTP in Rockland (ON, Canada) which incorporates course and fine screening, solids degritting followed by aerobic treatment and settling in an SBR. The SBR sequence is: fill (2.67 h), mix (3.33 h), settle (1 h) and decant (1 h) with a SRT of 12 d and food to microorganisms ratio of 0.24. Sludge collected during the settle phase was approximately 1.5-3% TS. Characterization of sludges pretreated is given in Table 1.

**Table 1. General characteristics of waste sludges pretreated.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ROPEC - TWAS</th>
<th>ROPEC - PS</th>
<th>Rockland - SBR sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH [-]</td>
<td>6.49</td>
<td>6.9</td>
<td>6.1</td>
</tr>
<tr>
<td>TS [% (w/w)]</td>
<td>5.40</td>
<td>4.16</td>
<td>1.5-3%</td>
</tr>
<tr>
<td>VS [% (w/w)]</td>
<td>3.77</td>
<td>0.338</td>
<td>1.40</td>
</tr>
<tr>
<td>VS/TS*100 [%]</td>
<td>69</td>
<td>8.1</td>
<td>~50</td>
</tr>
<tr>
<td>TCOD [mg/L]</td>
<td>41, 667</td>
<td>52, 614</td>
<td>22,921</td>
</tr>
<tr>
<td>SCOD [mg/L]</td>
<td>2, 357</td>
<td>1289</td>
<td>321</td>
</tr>
<tr>
<td>SCOD/TCOD*100 [%]</td>
<td>6</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>NH₃-N [mg/L]</td>
<td>536</td>
<td>145</td>
<td>-</td>
</tr>
<tr>
<td>¹Alkalinity [mg/L]</td>
<td>919</td>
<td>220</td>
<td>-</td>
</tr>
<tr>
<td>²TVFA [mg/L]</td>
<td>913</td>
<td>914</td>
<td>-</td>
</tr>
</tbody>
</table>

¹TS, VS: total and volatile solids; TCOD, SCOD: total and soluble chemical oxygen demand, respectively
²Bicarbonate alkalinity in units of mg/L as calcium carbonate (CaCO₃)
³TVFA: total volatile fatty acids (summation of acetic, propionic, butyric acids), no duplicate measurements
Microwave pretreatment of waste sludges

Household type microwave oven. During initial studies, microwave irradiation was applied by a household type microwave oven (Panasonic NN-S53 with inverter, 1,460 W, 2,450 MHz and 12.24 cm wavelength, cavity size of 278 mm x 469 mm x 470 mm) equipped with a rotating tray. Microwave pretreatment of the ROPEC - PS and Rockland - SBR sludge was carried out in a shallow 2-L (25 x 15 x 2, 7.5 cm; 850 mL of sample size) and ROPEC-TWAS was microwaved in 1-L (19 x 12 x 4.4 cm; 500 mL of sample size) polypropylene containers for each pretreatment temperature, respectively. Sludge temperature was measured with a series of 5 thermocouple probes (T-type, fine-gauge Teflon Polytetrafluoroethylene, response time of 0.5 s, Labor Technical Sales Inc., ON, Canada) inserted in the middle of the sample connected to a module for analog-to-digital conversion and recorded by a laboratory computer system (LabVIEW Software Version 6, National Instruments, Co., Austin, TX, USA). The recorded temperature was the highest temperature recorded after vigorous mixing. Once the desired temperatures were reached, samples were removed from the heat source (no holding time).

The effects of three variables; microwave pretreatment temperature (T, °C), microwave intensity (I, % of total microwave power) and concentration of waste sludge pretreated (C, % total solids) were investigated on both sludge solubilization (SCOD/TCOD ratio) and mesophilic digestion. Table 2 indicates the microwave pretreatment variables and levels studied for different waste sludges.

Table 2. Microwave (household type) pretreatment variables and levels studied.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ROPEC - TWAS</th>
<th>ROPEC - PS</th>
<th>Rockland SBR sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave temperature (T)</td>
<td>50, 75, 96°C</td>
<td>35, 65, 90°C</td>
<td>45, 65, 85°C</td>
</tr>
<tr>
<td>Microwave intensity (I)</td>
<td>50, 100%</td>
<td>40, 80%</td>
<td>60, 80, 100%</td>
</tr>
<tr>
<td>Sludge concentration (C)</td>
<td>1.4, 5.4%</td>
<td>1, 4% TS (w/w)</td>
<td>1.5, 2.8, 4.0% TS (w/w)</td>
</tr>
</tbody>
</table>

*TS: total solids; T: sample temperature; I: microwave intensity; C: sludge concentration

Laboratory scale industrial microwave oven. Microwave Accelerated Reaction System (MARS-5, CEM Corporation, 0-1250 W, 2450 MHz frequency, max temperature: 260°C, maximum pressure: 500 psig (33 bars) equipped with fibre optic temperature and pressure probes within the cavity and a turning carousel with a maximum of 14 pressure sealed vessels (XP-1500) of 100 mL each) was used to study the microwave effects on TWAS and biocake samples at temperatures above the boiling point. A total of 500 g of TWAS was cooked in 10 vessels (50 g TWAS per vessel) rotating on the carousel. MARS-5 operates with a focused MW irradiating beam and is capable of heating and holding at desired cooking (or temperature ramp) rates and holding times. After target temperatures were reached, samples were removed from the heating source (no holding time at desired temperatures) and cooled down to room temperature in closed vessels to avoid evaporation of organics and then stored at 4°C in the fridge.

Biochemical methane potential (BMP) tests

The anaerobic degradabilities of control (un-pretreated) and microwave pretreated sludge samples were determined by batch mesophilic BMP tests in a 0.5 or 1-L borosilicate glass graduated media bottles (Wheaton bottles with polypropylene caps, screw cap size of 45 mm, WWR, Montreal, QC, Canada) based on Owen et al. (1979). Nitrogen sparging was applied to batch reactors when sludge and inoculum were mixed to prevent exposure to air and reactors were sealed after addition of an equal mixture of NaHCO3 and KHCO3 to achieve an alkalinity of 4000-9000 mg/L as CaCO3. Batch reactors were kept in a temperature controlled incubator shaker (PhycroTherm, New Brunswick Scientific Co. Inc., NB, Canada) at 35 ± 1°C and mixed at 50-90 rpm to keep the bacteria - sludge mixture in suspension. Once biogas production ceased, reactors were uncapped to terminate the BMP assays and stored in a 4°C refrigerator until final sludge characterization. Inoculums used...
in BMP assays were initially acclimatized to harshest microwave pretreatment temperatures in three separate semi-continuous digesters (SRTs ~ 20 d) fed with pretreated ROPEC - TWAS (at 96°C), ROPEC - PS (at 85°C) and Rockland - SBR sludge (at 85°C) for a period of 3 to 6 months.

Analysis
Standard Methods procedure 2540G (APHA, 1995) was used for TS/VS analysis. Colorimetric COD measurements were performed based on Standard Methods procedure 5250D (APHA, 1995) with a Coleman Perkin-Elmer spectrophotometer Model 295 at 600 nm light absorbance. Before SCOD determination, sludge samples were centrifuged (for 20 min at 5856 RCF) and filtered through membrane disc filters with 1.2 m first and then with 0.45 m pore sizes. Reactor pH, total volatile fatty acids (VFAs; summation of acetic, propionic and butyric acids) and biogas composition (nitrogen, methane and carbon dioxide percentage) were monitored weekly during the batch anaerobic digestion. Total VFAs were measured by injecting supernatants into a HP 5840A GC with glass packed column (Chromatographic Specialties Inc., Brockville, ON, Canada, Chromosorb 101, packing mesh size: 80/100, column length x ID: 304.8 cm x 0.21 cm) and a flame ionization detector (oven, inlet and outlet temperatures: 180, 250 and 350°C, respectively, carrier gas flowrate: 25 mL helium/min) equipped with HP 7672A autosampler (van Huyssteen, 1967). Biogas composition was determined with an HP 5710A GC with metal packed column (Chromatographic Specialties Inc., Brockville, ON, Canada, Porapak T, packing mesh size: 50/80, column length x OD: 304.8 cm x 0.635 cm) and thermal conductivity detector (oven, inlet and outlet temperatures: 70, 100 and 150°C, respectively) using helium as the carrier gas (flowrate: 25 mL/min) (Ackman, 1972). Dewaterability of sludge samples digested in control and pretreated reactors was tested by a Capillary Suction Timer [Model 440, Fann Instrument Company, TX, USA] based on Standard Methods Procedure 2710G (APHA, 1995).

RESULTS AND DISCUSSION
Pretreatments with household type microwave oven

Solubilization of waste sludges: The level of floc and macromolecule disintegration in pretreated sludges were represented by SCOD/TCOD values. Solubility of ROPEC - TWAS was significantly (p< 0.05) increased with pretreatment temperature (50, 75, 96°C), sludge concentration pretreated (1.4, 5.4% TS) and decreased with microwave intensity (50, 100% total microwave power). Microwave pretreatment of TWAS resulted in 3.6 ± 0.6 and 3.2 ± 0.1 fold increases in SCOD/TCOD ratios at high (5.4% TS) and low sludge (1.4% TS) concentrations, respectively (data not shown). Pretreatment results indicated a potential of damaging floc structure and releasing 4.2, 4.5 fold higher soluble proteins, sugars over controls along with nucleic acid release (Eskicioglu et al., 2007a).

In raw ROPEC - PS, most COD was associated with the solid phase rather than soluble phase, as evidenced by the rather low SCOD/TCOD concentration in the control PS samples (Table 1). The increase of SCOD concentration after microwave pretreatment of PS was caused by aggregating deagglomeration and the transfer of organic substances from non-soluble material into soluble material. To explore the linear relationship between SCOD increase and microwave irradiation scenarios (Table 2), SCOD concentrations are plotted as a function of the pretreatment temperature (Figure 1). For PS, pretreated at TS of 4% and at microwave intensity of 80%, SCOD concentration increased 1.4 fold from 1390 mg/L in raw PS to 3304 mg/L at 90°C. Other microwave scenarios bear a strong similarity in terms of SCOD concentration improvement (Figure 1).
Figure 1. Effect of microwave temperature, microwave intensity and sludge concentration on SCOD concentration of ROPEC - Primary Sludge (TS: total solids, SCOD: soluble chemical oxygen demand).

The solubilization of Rockland - SBR sludge after pretreatment was also tested. The SCOD/TCOD ratio of control samples was approximately 1.4%. Among the microwave scenarios tested (Table 2), maximum SCOD/TCOD ratio obtained was approximately 7% at microwave temperature and intensity of 85°C and 60% of total power, respectively, for samples with 4% TS. Based on results on Rockland – SBR, only, microwave pretreatment temperature was found to have a statistically significant (p< 0.05) effect on the SCOD/TCOD ratio. Results suggested that the type of sludge (PS, WAS or combined), activated sludge plant (conventional, nitrification, etc.) or SRT of the activated sludge unit as well as other plant operating procedures that could effect EPS and divalent cation compositions which determine the floc structure and strength of activated sludges, respectively, all may have some impact on microwave solubilization and final digester performance.

Anaerobic digestion studies: At a microwave pretreatment temperature of 96°C, mesophilic (33 ± 2°C) batch digesters fed with ROPEC – TWAS achieved 15 ± 0.5 and 20 ± 0.3% increases in cumulative biogas productions (CBPs) over controls after 19 d of digestion at low (1.4% TS) and high (3% TS) TWAS concentrations. Microwave intensity did not significantly (p> 0.05) affect the biogas productions at similar pretreatment temperatures. Later experiments with continuous-flow digesters fed with ROPEC – TWAS (3% TS) verified the microwave effect with 23% higher VS removals at an SRT of 5 d (Eskicioglu et al., 2007a).

Batch mesophilic reactors digesting microwave pretreated ROPEC - PS with 4% TS also showed improvements not only in the extent but in the rate of biogas production (Figure 2). At a pretreatment temperature of 90°C and 4%TS concentration, digesters produced 450 mL biogas per 500 mL PS per day, which was 37% higher than that from the untreated sludge. The same digesters required 27 days to the end of the exponential phase, which was about 30% less than the control sample. In most of the microwave scenarios, cumulative biogas production from PS pretreated at 35 and 65°C presented no obvious improvement compared to the untreated samples. Furthermore, after given sufficient digestion time, none of the pretreated samples showed substantial improvement in biogas production at the end of the 50 days of digestion (Figure 2). Again, different microwave pretreatment intensities (80 and 40%) did not significantly affect biogas production from ROPEC – PS (results are not shown). Pretreatment of Rockland – SBR sludge samples to temperatures less than 65°C did not result in conclusive improvements in overall biogas production. However, pretreatment to 65, 75 and 85°C resulted in 10.8, 10.9 and 16.2% improvements, respectively, in overall biogas production compared to controls.
Figure 2. Cumulative biogas production from ROPEC – Primary Sludge with 4% total solids pretreated at 80% microwave intensity (35, 65, 90°C indicate the pretreatment temperatures).

Pretreatments with bench scale industrial type microwave oven (MARS-5)

Solubilization of waste sludges: Pretreatment of ROPEC – TWAS at temperatures above and below boiling point (at 50, 75, 96, 120, 150 and 175°C, temperature ramp of 1.2-1.4°C/min) by MARS-5 disintegrated the complex floc structure of TWAS and achieved SCOD/TCOD ratios of 9 ± 0, 12 ± 1, 21 ± 0, 24 ± 1, 28 ± 3, 24 ± 1 and 35 ± 1% at pretreatment temperatures of control, 50, 75, 96, 120, 150 and 175°C, respectively. At 175°C, pretreated sludge samples reached 54% of the ultimate solubilization ratio of ROPEC – TWAS (65 ± 0.6%) obtained with harsh chemical treatment (2 mol NaOH/L in two weeks contact time).

Microwave – MARS-5 was also used to disintegrate the anaerobically digested biocake samples above the boiling point (125, 150, 175°C). In addition to variation in pretreatment temperature, the effects of heating rate [fast (7.8°C/min), medium (3.9°C/min), slow (1.95°C/min)] and biocake TS concentration [high (30% TS, w/w) and low (15% TS, w/w)] on biocake solubilization were examined. At similar heating rates and pretreatment temperatures, the SCOD/TCOD ratios were always higher for the 15% TS compared to those of 30% TS biocake samples. At the slowest rate of 1.95°C/min, 15% TS biocake achieved 5.4, 6.7, and 11 fold higher SCOD/TCOD ratios over controls at pretreatment temperatures of 125, 150, and 175°C, respectively. Similarly, for the biocake with 30% TS, 2.1, 3.6 and 6.1 fold higher SCOD/TCODs over controls were observed. For both concentrations, increasing the heating rate (shorter exposure to microwave irradiation) decreased improvements in SCOD/TCOD ratios (Figure 3).

Figure 3. Effect of high temperature microwave irradiation on ROPEC - biocake solubilization [125, 150, 175°C indicate the pretreatment temperatures].
Anaerobic digestion studies: At a pretreatment temperature of 175°C, mesophilic batch reactors digesting ROPEC - TWAS (3% TS) produced 31 ± 6% higher biogas compared to the controls and dewaterability of pretreated TWAS (at 175°C) was enhanced by 75%. BMP tests are currently underway to determine the biodegradation potential of pretreated ROPEC - biocake. MARS-5 was also successful in achieving identical temporal heat profiles as observed in conventional heating (water bath) for ROPEC – TWAS and allowed evaluation of athermal (non-thermal) effects of microwave irradiation on floc disintegration and anaerobic digestion (Eskicioglu et al., 2007b).

CONCLUSIONS
The results from preliminary microwave studies indicated that microwave irradiation has a potential of destroying the complex floc structure of secondary sludges and macromolecules in primary sludges. The microwave pretreatment also increases the bioavailability of sludge components under batch anaerobic digestion and enhances the dewaterability of pretreated samples after digestion. However, the level of improvements in solubilization and biodegradation from different waste sludges were different. While the largest improvement in ultimate biodegradation was observed in ROPEC – TWAS, microwave irradiation only affected the rate of biodegradation of pretreated PS samples possibly because hydrolysis was not a limiting factor for ultimate anaerobic PS digestion. Similarly, relatively lower solubilization ratios achieved for Rockland – SBR sludge was attributed to higher sludge age of SBR unit and the type of samples (primary + secondary). It is possible that initial sludge characteristics may influence final pretreatment outcomes so that general statements of performance cannot always be made. Eventually, once the yields of various treatment scenarios are determined, a cost/benefit analysis needs to be done to determine practicability.

ACKNOWLEDGMENTS
The authors thank NSERC, BIOCAP Canada and Environmental Waste International Corporation for financial support. The authors express their gratitude to graduate students Jiang Zheng, Gabriel Thibault, Malik Bayusuf and Isil Toreci for their help in data generation.

REFERENCES


