

Improving biogas production performance of dairy activated sludge via ultrasound disruption prior to microwave disintegration

M. Al Ramahi, G. Keszthelyi-Szabó and S. Beszédes

ABSTRACT

In this study, ultrasound disruption was employed to enhance the efficiency of microwave disintegration of dairy sludge. Results revealed that ultrasound specific energy input of 1,500 kJ/kg TS was found to be optimum with limited cell lysis at the end of the disruption phase. Biodegradability study suggested an enhancement in suspended solids reduction (16%) and biogas production (180 mL/gVS) in floc disrupted (deflocculated) samples when compared to sole microwave pretreatment (8.3% and 140 mL/gVS, respectively). Energy assessment to attain the 15% optimum solubilization revealed a positive net production of 26 kWh per kg sludge in deflocculated samples compared to 18 kWh in flocculated (sole microwave) samples. Thus, ultrasound disruption prior to microwave disintegration of dairy sludge was considered to be a feasible pretreatment technique.

Key words | energy efficiency, gas fuel, liquid fertilizer, methane, wastewater treatment

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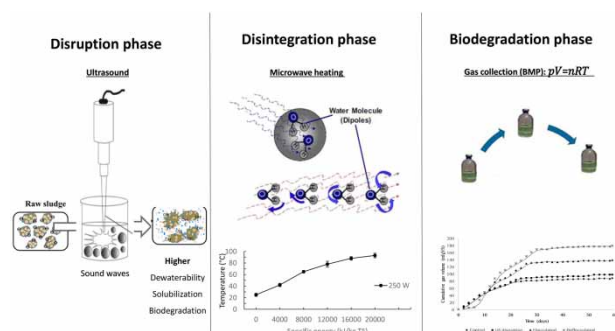
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HIGHLIGHTS

- Ultrasound disruption prior to microwave disintegration of dairy sludge is believed to be a feasible pretreatment technique.
- This efficient process solubilizes organics at energy input of 1,500 kJ/kg TS.
- This novel process enhances EPS release in sludge efficiently prior to disintegration.
- Ultrasound disruption of sludge enhances microwave disintegration rate efficiently.
- A positive net energy of 26 kWh was obtained by this novel process.

GRAPHICAL ABSTRACT



LIST OF ABBREVIATIONS

AD Anaerobic digestion
DOC Dissolved organic carbon

EPS Extracellular polymeric substances
GC Gas chromatography

doi: 10.2166/wst.2020.216

ICP	Inductively coupled plasma spectrometry
MW	Microwave
SS	Suspended solids
TN	Total nitrogen
TAN	Total ammonium nitrogen
TC	Total carbon
TOC	Total organic carbon
TS	Total solids
US	Ultrasound
VS	Volatile solids
VFAs	Volatile fatty acids

INTRODUCTION

The efficient treatment of dairy sludge is a major challenge due to its high content of proteins, carbohydrates and fats. The relative quantities of these compounds in dairy sludge are varied according to the change of wastewater components and the variable removal efficiency of wastewater treatment processes; some cause biodegradability difficulties related to sludge flocculation, which are mainly attributed to high presence of fats.

Anaerobic digestion (AD) is one of the most effective treatment techniques for waste sludge, including that generated from dairy industries. AD breaks down sludge gel networks and reduces water affinity of sludge through a biological series of hydrolysis, acidogenesis, acetogenesis and methanogenesis (Shi *et al.* 2018). Hydrolysis is the first and the rate limiting step in AD (Tyagi & Lo 2013). Hence, pretreatment techniques were suggested previously to facilitate the hydrolysis step in order to achieve a faster and more efficient disintegration process. Among those, thermal treatment has long been recognized as one of the most effective methods for sludge conditioning. But unlike the conventional heating, heating via microwave (MW) irradiation is converted directly into thermal energy through the molecular interaction with the electromagnetic field. Thus, it is expected to increase the surface area of sludge and improve the enzymatic degradation of organics (Taherzadeh & Karimi 2008). Moreover, MW irradiation is responsible for changing the positioning in the polarized side chains, which results in breakage of the hydrogen bonds, disintegration of the flocs matrix, and changing the protein structures of the microorganisms (Appels *et al.* 2013). Destruction of microorganisms occurs due to the thermal effect of MW irradiation; however, several studies have proved that MW irradiation also has an athermal effect (Tyagi & Lo 2013).

Previous studies have investigated the effect of MW pretreatment as a function of temperature in which high degrees of sludge solubilization were achieved correlating to high temperatures during MW pretreatment. For example, the study of Eskicioglu *et al.* (2007) investigated the effect of MW irradiation on waste activated sludge in temperatures between 50 and 96°C and concluded an enhancement in biogas production up to 16%. Nonetheless, the study of Appels *et al.* (2013) claimed an enhancement of 50% in biogas production after MW pretreatment in temperatures below 80 °C. However, the prime disadvantage of MW irradiation is its high energy consumption, which can be minimized by combining it with lower energy disruption methods such as ultrasound (US) (Pilli *et al.* 2011). Sludge exposure to US is expected to increase the rate of extracellular polymeric substances (EPS) release and increase the solubility of organics due the effect of the acoustic cavitation force (Pilli *et al.* 2011). The so-called acoustic cavitation force is initiated by the energy release upon the implosion of gas bubbles generated during US treatment. Hence, ultrasound processing is expected to enlarge the reaction boundary and break the bonds of highly polymeric substances, resulting in more efficient MW disintegration.

While most researches have focused on the effect of sole microwave pretreatment on sludge disintegration, some studies have investigated combining it with other pretreatment techniques. For example, the recent study by Kavitha *et al.* (2016) investigated the effect of disperser induced microwave pretreatment on chemical oxygen demand (COD) solubilization. Their results indicated a significant reduction of energy consumption with enhanced COD solubilization (22%) and suspended solids (SS) reduction (17%). No less importantly, the study of Yang *et al.* (2013) evaluated the effect of combining alkaline pretreatment with MW irradiation on sludge disintegration and concluded an enhancement of 66% at specific energy input of 38,400 kJ/kg TS. To date, however, only a small number of studies such as Kavitha *et al.* (2018) evaluated the effect of ultrasound disruption on microwave disintegration of sludge. Hence, further research and development is needed to understand the effect of this phase separated pretreatment on energy recovery, resources transformation and sludge biodegradability as current information is still in its infancy, with many research and methodological gaps. A pilot scale concept design of ultrasound assisted microwave disintegration was studied in this work, and the operational conditions were evaluated for dairy industry sludge treatment. The main objective was to investigate the effect of sludge disruption via US

prior to subsequent MW irradiation on sludge disintegration and energy recovery. Moreover, the effect of the pretreatment process on the aqueous phase's characteristics (AD digestate) was measured and documented.

MATERIALS AND METHODS

Dairy sludge was collected from a dairy factory in Szeged, Hungary. After sampling, three sets of samples were disrupted using a mechanical device, ultrasonicator, prior to MW disintegration. Bio-methane potential (BMP) assay was conducted for all samples; experiments are detailed as follows.

Sludge sampling and characterization

Characteristics of dairy sludge were: pH (6.89), soluble COD (SCOD) was 0.8 g/L, total COD (TCOD) was 12 g/L, soluble biological oxygen demand (BOD₅) was 160 mg/L, total BOD₅ was 7 g/L. Total solids (TS) content was 16.7 g/L. Volatile solids (VSs) content was 9.6 g/L, and SS content was 7.5 g/L. Sludge characteristics were confirmed following analytical methods.

US floc disruption

US pretreatment was carried out using Hielscher UP200S ultrasonic homogenizer (Germany) with operating frequency of 24 kHz, rated voltage (200–240 V), and rated current of 2 A. 500 mL of sludge were placed in a glass beaker without temperature adjustment (room temperature). US probe was submerged into the sludge to a depth of 2 cm. The effect US pretreatment on sludge disintegration was evaluated at different processing times (10 s, 20 s, 30 s, 40 s, 50 s, 1 min, 2 min, 3 min).

According to [Feng *et al.* \(2009\)](#) the rise in sludge temperature during US disruption (short sonication time) is not significant. Therefore, no efforts were made to control sludge temperature during experimentation. Temperature of sludge was measured after US treatment and in consistent with the literature, no significant increase was reported (<2 °C). Each set of US conditions was performed in triplicates. Results were reported as mean values with standard errors.

MW disintegration

A pretreatment experiment was performed by placing 250 mL of sludge in a microwave oven (2,450 MHz frequency). Experiments were carried in polytetrafluoroethylene

(PTFE) vessels for effective microwave dissipation in samples. A cover was employed to avoid evaporation, volatile loss and hot spots formation during MW disintegration. Tests were performed at different treatment times, ranging from 0 to 6 min.

Bio-methane potential (BMP) testing

The BMP tests were conducted in 120 mL serum bottles. The bottles were filled with 60 mL of dairy sludge with inoculum and then purged with nitrogen gas and sealed with rubber stoppers to ensure anaerobic conditions. The reactors were incubated at mesophilic conditions (37 ± 0.5 °C). Gas pressure was measured and documented every 2–5 days using a pressure meter (Lutron, PS-9302). Biogas production was determined following the ideal gas law, Equation (1):

$$pV = nRT \quad (1)$$

where p is pressure in Pascal, V is gas volume in m³, R is gas constant (8.314 J/mol·K), and T is temperature in Kelvin.

After each measurement; gas samples were stored in gas tight 10 mL bottles. Following gas collection, gas samples were analyzed for CH₄ and CO₂ using CP-3800 gas chromatograph (Varian, Walnut Creek, CA, USA) with a 0.53 mm × 30 mm Rt-Q-Bond column (Restec, Bellefonte, PA, USA).

Energy consideration

A detailed energy assessment was done to evaluate the economic viability of the disintegration technique. The equations employed to perform energy calculations are explained in detail as the following.

Input energy includes energy applied for ultrasonic disruption and microwave disintegration. Ultrasonic energy was applied to disrupt flocs of sludge biomass, while microwave energy was consumed to disintegrate the sludge biomass during pretreatment, both were calculated using the following equation ([Yang *et al.* 2013](#)).

$$E = P \times T / (V \times TS) \quad (2)$$

where E is the input energy (kJ/kg TS), P is the input power (kW), T is the treatment time (sec), V is the volume of the sample (L) and TS is total solids in (kg/L).

These amounts do not include the energy required for thickening and mixing inside the digester, nor does it account for losses during biogas compression and

purification. However, with an optimized design and operational procedure, these amounts can be kept to a minimum.

Output energy, the energy recovered in the form of methane was calculated by the following equation (Passos & Ferrer 2015).

$$R_m = T_m \cdot \text{COD}_s \cdot Y_m \cdot (-C_E) \cdot \alpha \quad (3)$$

where R_m is the methane energy recovery (kWh), T_m is total mass of sludge (kg), COD_s is chemical oxygen demand of sludge (kg), Y_m is the yield of methane (m^3/kgCOD), C_E is the combustion energy of methane, which is equivalent to 40 MJ/m^3 , and α is the conversion factor for methane chemical energy to electricity, equivalent to 35%.

Analytical methods

The liquid phase was decanted and filtered through $0.45 \mu\text{m}$ pore size membrane discs (GN-6 Metrical, Pall Corporation) to remove colloidal solids and produce the truly soluble fraction. All analyses were duplicated and results were given as mean values with standard deviations. Whole fraction and supernatant fraction were characterized for pH, EC, SCOD, TCOD, total Kjeldahl nitrogen (TKN), TS and VS, ammonia-N, soluble proteins, and humic-like substances concentrations.

The concentrations of volatile fatty acids (VFAs) were determined using Hewlett-Packard gas chromatograph (Model 6890 plus) equipped with an Innovax capillary column and a flame ionization detector. COD, TS and VS concentrations were determined according to procedures in standard methods (American Public Health 2005). Dissolved organic carbon (DOC) and total nitrogen (TN) contents were determined by a Torch (Teledyne Tekmar, USA) combustion (HTC) type analyzer equipped with pressurized NDIR detector. BOD_5 was determined by respirometric method (Lovibond Oxidirect, Germany) at a controlled temperature of 20°C for a 5-day period. Elemental composition of carbon (C) and nitrogen (N) were determined with a Vario Max CN Element Analyzer (Elementar Analysensysteme GmbH). Elemental C was confirmed using the Walkley–Black method. TN was confirmed by TKN (American Public Health 2005). The higher heating value (HHV) was measured using bomb calorimeter (Thermo Fisher Scientific). Macro- and microelements were analyzed by ICP analyzer (PerkinElmer 7000DV ICP-OES Spectrometer, power of the radiofrequency-generator: 1,450 W) according to standard methods

(American Public Health 2005). Sodium absorption ratio (SAR) was calculated based on concentrations of Na, Ca, and Mg. Protein concentrations were determined on the supernatant using the Lowry method. Carbohydrates concentrations were determined using the anthrone method.

Statistical analysis

Statistical analysis was performed to determine differences between each parameter on the investigated characteristics. First-way ANOVA was performed at 95% confidence level; when a significant difference was detected, post hoc pair-wise multiple comparisons were calculated.

RESULTS AND DISCUSSION

Determination of the specific energy input for US disruption

EPS release is expected to enhance biomass disintegration potential and increase the biodegradation rate during AD (Wang *et al.* 2014). A sequential increment in EPS release was achieved via US up to $1,500 \text{ kJ/kg TS}$ indicating the end of the floc disruption phase (Figure 1). US processing generated a momentum in the growth of the microscopic bubbles, a phenomenon that referred to the cavitation effect. The cavitation effect led to the formation of hydroxyl radicals, which attack the sludge floc matrix and disrupt it (Kim Lee & Park 2014). As a result, EPS matrix transformed into the soluble form resulting in higher concentrations in the aqueous phase as seen in Figure 1. In other words, the sonication forces on sludge decreased the firmness of the suspended solids, which led to the lysis of cells and the release of intracellular components into the aqueous phase (Kavitha *et al.* 2018). The initial concentrations of dissolved EPS in dairy sludge were under the detection limit ($>50 \text{ mg/L}$) and increased to about 111 mg/L at the end

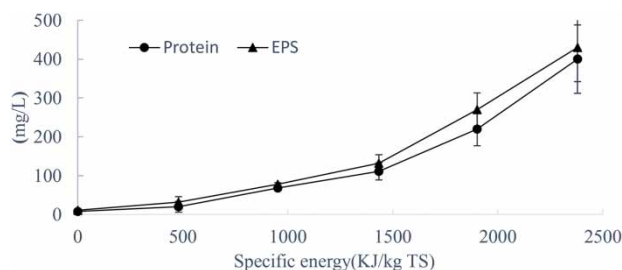


Figure 1 | Effect of ultrasound disruption with different energy input on floc disruption. Error bars represent the standard errors.

of the disruption phase. Afterwards, a rapid increase was observed in which the concentrations have increased to an average of 270 mg/L at specific US energy input of 2,000 kJ/kg TS, implying the beginning of the disintegration phase. To examine the change of phase from floc disruption to cell lysis, DNA concentrations were determined and showed a mild increase from 0 to 29 mg/L which prove that the extraction of exogenous EPS in the absence of cell lysis was possible below US input energy of 2,000 mg/L. Similar to EPS, concentrations of soluble protein increased during US pretreatment. Results of EPS release are similar to those obtained by (Kavitha *et al.* 2018) at lower energy input, probably due to the difference in energy considerations and the primary sludge characteristics.

US disruption effect on SCOD release and SS reduction

In addition to protein and EPS release, SCOD is another important index to evaluate the efficiency of sludge solubilization. US disruption improved the bioavailability of particulate materials by increasing the rate of SCOD release as evident in Figure 2. SCOD release increased rapidly with the increase in specific energy up to 1,300 kJ/kg TS. These results are in similar trend to those obtained by (Gayathri *et al.* 2015). The rapid increase in SCOD release is attributed to higher vulnerability of sludge for US effect in the disruption phase. However, the decrease in SCOD release at the end of the disruption phase was due the diminution of easily disintegrable organics. Another indication of the pretreatment efficiency on sludge stability is SS reduction. A

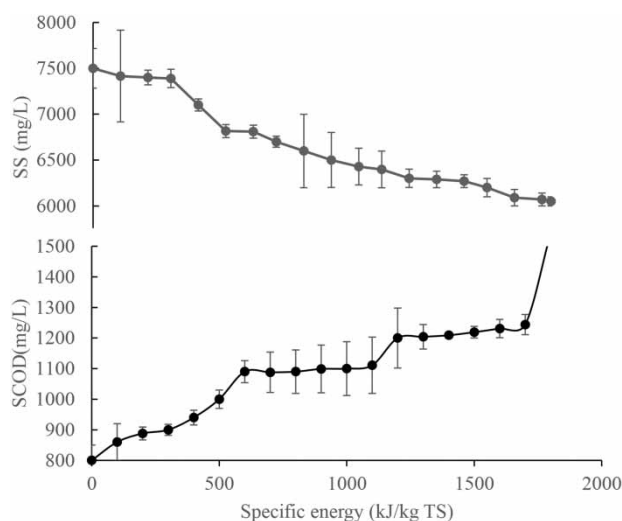


Figure 2 | Effect of ultrasound disruption on COD solubilization and SS reduction. Error bars represent the standard errors.

rapid decrease in SS concentrations was observed during the first stage of US pretreatment (Figure 2). The main reason of the mass reduction in sludge during US disruption was the intense release of extracellular and intracellular matters (Gayathri *et al.* 2015). A slower trend in SS reduction was observed beyond the disruption phase attributed to higher compression forces due to higher intensity of gas bubbles formation (Uma Rani *et al.* 2014). Similar conclusions were observed in previous literature (Gallipoli *et al.* 2014).

Effect of MW irradiation on sludge temperature

Sludge temperature is an essential parameter due its effect on sludge physical and chemical characteristics during MW disintegration (Eskicioglu *et al.* 2007). Figure 3 shows the effect of microwave irradiation on sludge temperature. Evaporation has occurred gradually during the pretreatment process resulting in carbonization of the humic substances of the organic matters (Jones *et al.* 2002). The rapid heating of the particles during the pretreatment process was resultant by the molecular rotation; mainly because of the high frequency electromagnetic radiation interacting with the dipolar molecules of the organic matters (Yan *et al.* 2010). However, high temperatures means higher energy consumption, which was uneconomical for sludge application (Shi *et al.* 2018). Hence, it was insignificant for further application of MW disintegration beyond the boiling point.

Only a handful of studies can be found in the literature that evaluated the effect of MW disintegration temperature on AD batch reactor performance, and they give conflicting results. For example, Liu *et al.* (2016) evaluated MW irradiation at 100 °C and their results showed a significant increase in sludge dewaterability after MW pretreatment. On the other hand, Vergine Zábranská & Canziani (2014) claimed that increasing sludge temperature under MW

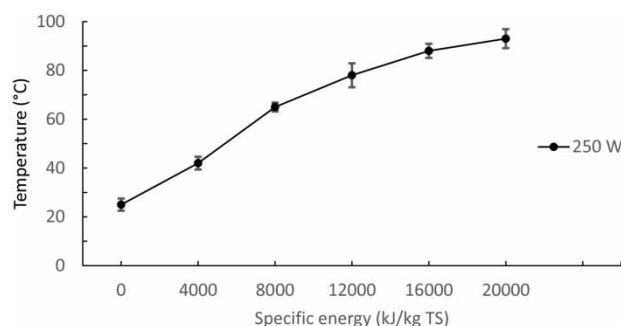


Figure 3 | Effect of microwave irradiation specific energy on sludge temperature.

irradiation from 72 to 93 °C did not improve sludge disintegration significantly and hence, MW disintegration at low temperatures were the most cost-effective in terms of COD solubilisation per unit energy. In this study, however, the optimal MW disintegration conditions were determined according to the amounts of SCOD that were released to the aqueous phase as discussed in the following section.

Determination of the optimal specific energy input for MW disintegration

MW irradiation is expected to increase COD solubilization and SCOD release by breaking down the complex floc structures and increase the biodegradability of organic molecules. Figure 4 shows the effect of MW irradiation on COD solubilization and SCOD release in dairy sludge. Interestingly, US disruption (deflocculated sludge) resulted in higher trend of SCOD release. Initial SCOD concentrations of deflocculated sludge were on average 1,090 mg/L and increased to their maximum value at 1,780 mg/L at specific energy input of 12,000 kJ/kg TS, no increase in SCOD release was observed afterwards. The lower trend in SCOD release was obtained for flocculated sludge, starting at 800 mg/L, with a maximum value of 1,389 mg/L at the same specific energy input of 12,000 kJ/kg TS. The intense increase in SCOD release during MW disintegration was due to intense hydrolysis of large organic molecules caused by MW irradiation. These findings are consistent with those obtained previously (Park *et al.* 2004; Saha Eskicioglu & Marin 2011), in which higher levels of hydrolysis were achieved after MW disintegration at low temperatures ($T < 96$ °C). In the current study, sludge solubilization (SCOD/TCOD) has increased from 0.07 ± 0.01 to 0.12 ± 0.01 in flocculated sludge, and from 0.09 ± 0.01 to 0.15 ± 0.01 in deflocculated sludge subsequent to MW disintegration (Figure 4). The noticeable decrease in SCOD

release beyond 93 °C (20,000 kJ/kg TS) was attributed to higher intensity of chemical reactions such as dehydration and decarboxylation. The optimum solubility of 15% achieved in this study was lower than that achieved by (Kavitha *et al.* 2016), in which 22% solubility was optimized for municipal waste activated sludge; probably due to the higher presence of non-soluble organics in dairy sludge.

SS reduction during microwave disintegration

SS reduction increased progressively for both deflocculated and flocculated sludge over the course of MW pretreatment (Figure 5). Mass content decreased by 7.4% and 8.3% in deflocculated and flocculated sludge, respectively. The high rate of SS reduction during MW disintegration in sludge was due the liquefaction of readily biodegradable matters (Kavitha *et al.* 2016). However, lower SS values obtained in deflocculated sludge suggests its better adeptness to MW disintegration. Hence, the existence of unstable flocs in flocculated sludge reduced its disintegration potential through MW irradiation whereas flocs disruption via US prior to MW irradiation resulted in higher SS reduction. No significant increase in SS reduction was obtained beyond specific energy input of 16,000 kJ/kg TS. These outcomes are similar to those obtained by the previous study of Kavitha *et al.* (2016). *P*-value for SS concentrations was less than (0.05) revealing significant variation between deflocculated and flocculated sludge.

Fermentation study

Proteins and carbohydrates are the main organics in sludge composition. In the hydrolysis phase, proteins convert into peptides and amino acids, and then to organic acids, NH_3 and CO_2 , while carbohydrates transform into

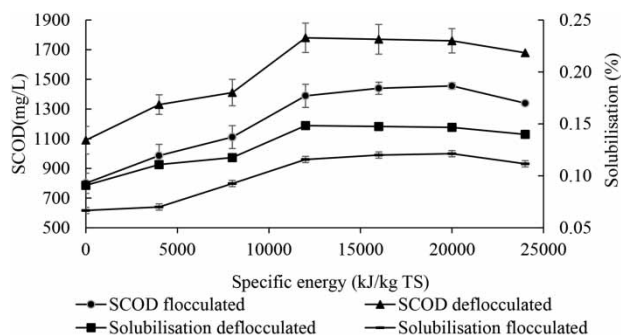


Figure 4 | Effect of microwave disintegration on COD solubilization and SCOD release. Error bars represent the standard errors.

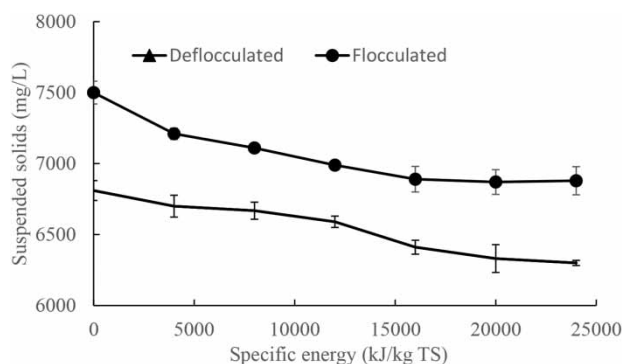


Figure 5 | Effect of microwave disintegration on the SS reduction. Error bars represent the standard errors.

polysaccharides (Kavitha *et al.* 2016). The quantity of proteins in dairy sludge exhibited an increment during MW disintegration from 50 mg/L to 200 mg/L and 400 mg/L, in flocculated and deflocculated sludge, respectively. While carbohydrates concentrations increased from 5 mg/L to 24 mg/L and 59 mg/L, in flocculated and deflocculated sludge, respectively. Higher solubility of polymers such as proteins and carbohydrates cause higher rates of VFAs generation (Jiang *et al.* 2007). The importance of VFAs comes from its representation of a major class of organics in sludge intermediate products during the course of AD and hence, their production and consumption balance is vital for an efficient AD process. High VFAs accumulation can cause low methane production and, subsequently, less energy gain (Pastor-Poquet *et al.* 2019). The effect of MW disintegration on VFAs generation is presented in Table 1. As seen, the relative increase of butyric acid was the most significant (784%), followed by iso-butyric acid (213%) and acetic acid (167%). Similar observations were obtained by (Appels *et al.* 2013).

Solid–aqueous phase characterization

The concentrations of all parameters studied were, on average, higher in treated slurry, indicating higher solubility into the aqueous phase after the pretreatment process (Table 2). C concentrations increased significantly after MW disintegration, as the caloric value of sludge, suggesting that there were no losses in total C during MW irradiation. On the contrary to C, N concentrations decreased significantly in response to raising temperatures and spontaneously changed the C/N ratio. High total ammonia–nitrogen (TAN) concentrations in the aqueous phase indicate high TAN release. TAN accounted for about 33–37% of TN present in the aqueous phase after the pretreatment process, with undetectable concentrations of NO₂

Table 1 | The effect of MW disintegration on VFAs concentrations in flocculated sludge

Parameter (mg/L)	Raw sludge (flocculated)	Disintegrated sludge (sole MW treatment)	Relative increase (%)
Acetic acid	371 ± 30 ^a	999 ± 49 ^b	167
Propionic acid	53 ± 10 ^a	133 ± 77 ^b	151
Butyric acid	61 ± 21 ^a	539 ± 72 ^b	784
Iso-Butyric acid	319 ± 19 ^a	992 ± 119 ^b	213
Caproic acid	140 ± 25 ^a	340 ± 87 ^b	143
Total VFAs	944	3,003	218

^{a,b}Statistical differences are indicated by different superscript letters.

Table 2 | The effect of MW disintegration on the aqueous–solid phase characterization for dairy sludge

Parameters	Raw sludge	Flocculated	Deflocculated
C	59 ± 0 ^a	65.4 ± 2.3 ^b	67.1 ± 0.3 ^b
N	4.5 ± 0.2 ^a	5.1 ± 0.5 ^a	3.7 ± 0 ^b
C/N	9.3	9.8	15.9
TS	37 ± 7.8 ^a	30.6 ± 6.8 ^b	30.8 ± 1.8 ^b
HHV	23 ± 1 ^a	29 ± 0 ^b	29 ± 0 ^b
<i>Aqueous phase</i>			
pH	6.85 ^a	5.38 ^b	5.29 ^b
EC (ms/cm)	3	4	3.3
DOC (mg/L)	822 ± 101 ^a	4,993 ± 205 ^b	5,523 ± 74 ^b
<i>Macronutrients</i>			
TN (mg/L)	140 ^a ± 70	229 ^b ± 70	266 ^b ± 10
TAN (mg/L)	50 ^a ± 7	76 ^b ± 3	90 ^c ± 0
P (mg/L)	36 ^a	156 ^b	116 ^b
K	195 ^a	624 ^b	672 ^b
<i>Secondary nutrients</i>			
Ca	290 ^a ± 6	439 ^b ± 11	607 ^c ± 19
Mg	284 ^a ± 6	522 ^b ± 2	414 ^b ± 10
S	98 ^a	150 ^b	130 ^b
<i>Micronutrients</i>			
Cu	32 ^a	85 ^a	76 ^a
Na	859 ^a	668 ^a	654 ^a
Zn	13	20	30
SAR ^c	8.6 ^a	5.1 ^b	5.0 ^b

^{a,b}Statistical differences are indicated by different superscript letters.

^cNa +/(0.5 * (Ca²⁺ + Mg²⁺))^{0.5} where all concentrations are in meq/L.

and NO₃. The rest of N fraction are believed to be aliphatic and aromatic nitrogenous compounds as documented in previous literature (Danso-Boateng *et al.* 2015).

N and P nutrients recovery is essential during wastewater treatment process as they are considered scarce and non-renewable (Shi *et al.* 2018). High concentrations of macronutrients in the aqueous phase were reported, such as N, P and K (Table 2). On the other hand, the concentrations of micronutrients such as Mg and Ca, were as low as 280–300 mg/L, while S concentrations were less than 100 mg/L. Other micronutrients such as Zn and Cu were detected at even lower concentrations, 13 mg/L and 32 mg/L, respectively. In general, the concentrations of Mg, Ca, Cu and K increased after MW disintegration due to hot water leaching. These results are consistent with those obtained previously (Pérez-Cid Lavilla & Bendicho 1999; Kuo Wu & Lo 2005). For more detailed discussion in

the effect of MW irradiation on nutrients and heavy metals recovery, the reader is advised to refer to the study of Tyagi & Lo (2013).

SAR is another measurement to determine the effect of AD slurry on soil clays when used in irrigation, and it can be calculated by measuring the concentrations of Na in relation to those of Ca and Mg. The aqueous phase of dairy sludge had a moderately high SAR (Table 2). However, higher recovery of Mg and Ca after MW disintegration resulted in a slightly lower SAR. Another indication of the effect of MW disintegration in sludge solubility is DOC. It is noticeable that DOC concentrations increased significantly from 822 mg/L to 4,993 mg/L and 5,523 mg/L for flocculated and deflocculated sludge, respectively. The increase was attributed to the reduction of the particle size during US processing and the raise of sludge temperature during MW disintegration (Pilli *et al.* 2011). Further investigation is needed to explore methods to lower DOC concentrations and EC values without affecting the concentrations of nutrients and heavy metals.

The decrease in sludge pH after the pretreatment corresponded to high production of VFAs which was the main reason of low methane production during the first stage of AD (Ahn Shin & Hwang 2009; Yang *et al.* 2015; Pastor-Poquet *et al.* 2019). However, the currently observed values are more acidic than previously reported for dairy sludge (Yadav *et al.* 2009). The high acidity obtained in the present study is most likely due higher intensity of VFAs production, as demonstrated in Table 1.

Biodegradability assessment

The results of the BMP assay are presented in Figure 6. The relatively low biogas production in the first stage of BMP assay (0–10 d) in the pretreated samples was due to high generation of VFAs as a result of more intense hydrolysis. Clearly, methane production was trivial in the first 10 days as a consequence of poor methanogenesis (Pastor-Poquet *et al.* 2019). Subsequent to 10 days, the production of biogas experienced a significant enhancement in deflocculated samples. Over the total period of 60 days, an average increase of 50 mL/gVS was observed in MW disintegrated samples (flocculated sludge). The increase was almost 90 mL/gVS (compared to control) with US disruption (deflocculated sludge). Methane concentrations in all samples remained constant at approximately 60–65%.

Low methane generation in sole US treated samples is attributed to the lack of easily accessible substrates due to insufficient pretreatment. At the same time, methane production in MW disintegrated samples was higher due to higher availability of the released organics. However, flocculated sludge generated less methane than deflocculated, which could be related to slower hydrolysis of organics. Higher methane production in deflocculated sludge is a clear indicator that US disruption increased the availability of organic substrates within the biomass, which led to enhanced conversion of organics during methanogenesis (Shi *et al.* 2018). These outcomes were similar to those obtained by Kavitha *et al.* (2018), with the exception at the first phase as they reported a significantly higher methane production in the first 12 days of the BMP assay, unfortunately,

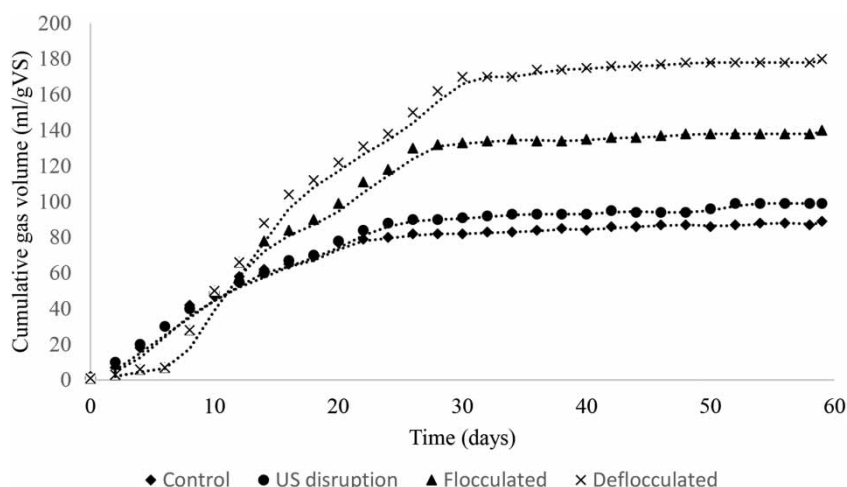


Figure 6 | Plot showing cumulative biogas production of different pretreatments.

Table 3 | Energy balance

Parameter (per kg of sludge)	Deflocculated	Flocculated	Unit
Energy content of methane	30	23.5	kWh
Energy applied	3.75	5.55	kWh
Net energy production	26.25	17.95	kWh

they did not report the pH values nor the VFAs concentrations. The amount of methane produced in this study was expressed in terms of VS. Mass balance calculations revealed higher VS removal corresponded with higher methane production in the pretreated samples implying that higher fractions of VS were converted to methane.

Energy assessment

Energy equilibrium results are presented in Table 3. To calculate total energy consumption, the energy employed for US and MW pretreatment were taken into account. However, the energy needed for stirring and heating the reactors during AD were not included as they depend mainly on operational design. A 15% optimum solubilization was determined as an index to investigate the energy consumption. Total energy employed per kg sludge to attain the 15% solubilization were 5.55 kWh and 3.75 kWh in flocculated and deflocculated sludge, respectively. Hence, nearly 70% of the input energy was consumed to attain the desired solubilization via US disruption prior to MW disintegration, due to lower energy input when compared to MW disruption of sludge. The input energy of the combined process obtained in this study was lower than previously obtained Ebenezer *et al.* (2015), which is connected to long pretreatment times required to attain the desired solubilization in dairy sludge. A positive net energy of about 26 kWh per kg sludge was obtained in the combined treatment, higher than that obtained by Kavitha *et al.* (2018) due to differences in energy considerations and sludge initial characterization. Based on the obtained results, it can be confirmed that sludge disruption via US prior to MW disintegration is believed to be a cost effective, feasible process. However, the applicability of the pretreatment process depends mainly on the amount of energy that can be recovered in the form of heat.

CONCLUSION

Ultrasound assisted microwave disintegration was perceived as an efficient technique for sludge disintegration. The

efficiency of ultrasound disruption prior to microwave disintegration was evaluated in terms of suspended solids reduction, chemical oxygen demand removal and bioenergy recovery. A higher SS reduction and chemical oxygen removal was achieved by ultrasound assisted microwave disintegration when compared to sole microwave pretreatment of dairy sludge. In addition, the combined pretreatment (US + MW) achieved higher methane potential. Energy balance revealed that ultrasound disruption prior to MW disintegration was more profitable than sole MW pretreatment of dairy sludge with net energy production of 26 kWh per kg sludge compared to 18 kWh per kg sludge, respectively.

ACKNOWLEDGEMENTS

This work was supported by the Hungarian Science and Research Foundation (OTKA contract number K115691) and the 'Sustainable Raw Material Management Thematic Network – RING 2017', EFOP-3.6.2-16-2017-00010 project. The first author especially thanks the support provided by the Stipendium Hungaricum Scholarship Programme.

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First received 4 February 2020; accepted in revised form 23 April 2020. Available online 5 May 2020