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RESEARCH ARTICLE

Effects of anaerobic digestion enhanced by ultrasound pretreatment on the fuel properties of municipal sludge

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Abstract

In this study, effects of ultrasound pretreatment on combustion characteristics and elemental composition of municipal sludge were examined for energy-based evaluation of sludge pretreatment. Waste activated sludge (WAS) from a municipal wastewater treatment plant was pretreated with ultrasound at varying durations and was subjected to anaerobic digestion in a biochemical methane potential (BMP) assay. Changes in gas production rates, calorific value (CV), elemental compositions, and ash contents of sludge samples were examined to assess the effects of pretreatment and digestion. Sonication at 0.73 W/mL enhanced gas production by 28%. Moreover, volatile solids (VS) and chemical oxygen demand (COD) removals increased from 41 to 45% and 33 to 37%, respectively. Following anaerobic digestion, CVs of samples decreased by about 18%. Sonicated samples exhibited a higher decrease. In order to quantify the change in overall energy content, total solids (TS) reduction was also taken into account. Loss was magnified as both CV and the amount of TS that would provide the overall energy were reduced. This loss was 38% for the control group and 41% for the 15 min sonicated sludge. Digestion decreased the C content of sludge by about 20% and H content by 50% due to biogas production. Ash content increased relatively as some of the combustible solids were lost due to digestion. Experimental results indicate that if sludge is to be combusted, digestion with or without ultrasound pretreatment may be disadvantageous if the aim is to maximize energy gain from sludge.

Keywords Biochemical methane potential · Calorific value · Combustion · Ultrasonication · Waste activated sludge

Introduction

As the byproduct of wastewater treatment industry, sludge production around the globe is projected to increase due to increasing wastewater production and more treatment plants starting operation (Magdziarz and Wilk 2013; Collivignarelli et al. 2019). Until recently, landfilling following dewatering used to be the common disposal approach. New regulations (such as the EU Landfill Directive), however, are limiting this old method, requiring further treatment in order to reclaim water and other resources before final disposal. It is expected that management and disposal tendencies will favor utilization of sludge in revenue-generating approaches like soil conditioning and co-combustion where the inherent value of sludge is realized (Gherghel et al. 2019). Europe is currently shifting towards using such methods (Kelessidis and Stasinakis 2012; Bianchini et al. 2016).

Three major advantages are associated with sludge co-combustion. Firstly, the energy stored in sludge is utilized instead of being wasted in a landfill, converting it into a bio-energy source. Secondly, as a part of the fuel that is combusted with sludge is replaced, co-combustion helps conserve the original fuel source. Finally, ash is produced as the remainder of sludge after co-combustion, an inert substance which is fundamentally easier to dispose. This ash can be used for various purposes including agricultural usage, cement manufacturing, and adsorbents (Onaka 2000; Donatello and Cheeseman 2013).

Combustion of sludge could be affected by several factors including moisture content, calorific value (CV), and ash content (Werther and Ogada 1999). The water part of sludge may lead to undesirable consequences during combustion like lowering of temperature, which could be prevented by drying to above 90% dry solids levels (Werther and Ogada 1999). CV is

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the energy amount that appears when a fuel is combusted. Before aerobic or anaerobic digestion, sludge is expected to have a CV of about 17.5 kJ/g, and around 10.5 kJ/g afterwards (Werther and Ogada 1999). In comparison, anthracite may have a CV of 33 kJ/g, and lignite may have a CV of 10 kJ/g. Thus, sludge could possibly yield energy comparable with a medium level coal (Hao et al. 2018).

Besides (co-)combustion, anaerobic digestion offers another method of utilizing sludge as an energy source. Although conventional digestion has been commonly used, newer approaches focus on higher loading rates and increased methane yields (Pérez-Elvira et al. 2006; Liu et al. 2018; Collivignarelli et al. 2019). Pretreatment is one option that helps to increase both methane yields and production rates through enhancing and accelerating the rate-limiting hydrolysis step (Riau et al. 2015; Paulista et al. 2019). Ultrasound application, a common pretreatment method, disrupts floc structure and ruptures the cell walls of bacteria found in waste activated sludge (WAS), dispensing soluble organic content (Lizama et al. 2017). Its mechanism involves rapid formation and collapse of cavitation bubbles, causing extreme increases in temperature and pressure, which mechanically, thermally, and chemically degrade the constituents of WAS (Tiehm et al. 2001; Badmus et al. 2018). Lizama et al. (2017) showed that ultrasound pretreatment at 35 kJ/g increased the soluble chemical oxygen demand (sCOD) concentration by 26% and consequently biogas production by 31%. Braguglia et al. (2012b), in their comparison of ultrasound and ozone pretreatments, documented that sonication increased biogas production by 20%. In another study involving a biochemical methane potential (BMP) assay, sonication was found to increase biogas production further at low food-to-microorganism (F/M) ratios (Braguglia et al. 2012b). Arun and Sivashanmugam (2018) stated that sonication at 0.6 W/mL increased the solubilization of organics. Yet, these studies have focused on biogas yields and improvements on digestion while generally disregarding whether the energy used for pretreatment could be regained afterwards.

There are numerous works published on the topic of ultrasound (or any other) pretreatment and how it enhances anaerobic digestion (Seng et al. 2010; Tian et al. 2015). However, energy-based considerations involving sludge treatment or the treatment plants as a whole are largely ignored. Furthermore, while it is known that anaerobic digestion reduces the CV of sludge, quantification and further changes in fuel properties or elemental composition of sludge following digestion are seldom mentioned. Cano et al. (2015) suggested that energy self-sufficiency of pretreatment methods should be assessed alongside their digestion-enhancing benefits and claim that from an energy point of view, many of the pretreatment methods may not be favorable. Coupling this fact with digested sludge yielding a lower CV, a complete energy analysis of sludge treatment should be conducted, especially for treatment plants making use of (co-)combustion as a sludge management option. To our current knowledge, effects of any pretreatment method on combustion characteristics or elemental composition of sewage sludge have not been studied. With this work, we aim to present a quick and easy assay for the assessment of fuel properties of municipal sludge following pretreatment and anaerobic digestion, while filling the apparent gap in the literature concerning pretreatment and using sludge as a fuel. Within the scope of this study, sludge samples taken from a municipal wastewater treatment plant were subjected to ultrasound pretreatment and then anaerobically digested in the form of a BMP assay. CVs and C, H, N, and ash compositions were measured before and after digestion to quantify the changes in the properties of the sludge and the total amount of energy that can be harvested.

Materials and methods

Sludge samples and ultrasound pretreatment

Sludge samples for the anaerobic digestion experiments were taken from the Ankara Central Wastewater Treatment Plant. Having a design flowrate of 760,000 m^3/d, the plant employs a conventional activated sludge system. Mixed primary and secondary sludge is digested in mesophilic anaerobic digesters with 14-day solids retention time (SRT) (ASKI 2014). For experiments, sludge to be digested were taken from the WAS line and digesters provided the seed sludge.

Ultrasound pretreatment was applied at varying durations using Sartorius Labsonic P (Sartorius AG, Germany). Sonication frequency of the device was 24 kHz. Amplitude was 100%. Probe diameter and device frequency were 22 mm and 1, respectively, yielding a 255 W maximum power. Sample volume subjected to sonication was 350 mL, resulting in a 0.73 W/mL density. Temperature was controlled during sonication using ice baths. Similar to the studies performed previously by our group (Apul and Sanin 2010; Köksoy and Sanin 2010), sonication durations varied as 0, 5, 10, 15, 20, and 25 min, resulting in six different WAS types. Specific energy inputs were determined by multiplying the sonication power and duration, divided by the sonicated sample volume and its TS concentration. Table 1 shows the sonication

Table 1 Sonication durations with corresponding specific energy inputs

Sonication duration (min)	Specific energy input (kJ/g TS)
5	19.1
10	38.2
15	57.3
20	76.4
25	95.5

durations with corresponding specific energy inputs. The lower end of the range of specific energy inputs tested is compatible with the previous studies of Lizama et al. (2017) (5–35 kJ/g TS), Braguglia et al. (2012a) (9.5–45 kJ/g TS), and Tian et al. (2015) (2.5–21 kJ/g TS). The upper end of the range allowed us to explore the scarcely studied impacts of higher energy sonication which may be required for complete floc destruction and solubilization (Houtmeyers et al. 2014; Zhen et al. 2017).

Characterization and BMP setup

A total of seven different sludge samples (including the sample containing the seed sludge only) were produced for BMP assay. Initially, samples were analyzed for their total solids (TS), total suspended solids (TSS), volatile solids (VS), and volatile suspended solids (VSS) contents. Preliminary characterization of the samples used for the preparation of BMP assay are given in Table 2 in terms of averaged values and standard deviations. Overall, for WAS, TS concentrations ranged between 11,000 and 11,500 mg/L. VS concentrations were about 8500 to 9000 mg/L. Both observed ranges are typical for secondary sludge in full-scale treatment plants (WEF and ASCE/EWRI 2009).

In the BMP experiment, three replicate bottles (each having 200 mL active volume) were used for each WAS type and seed sludge provided in Table 2, totaling 21 bottles. Following a previous work of Köksoy and Sanin (2010), F/M ratio was determined as 1 (g VS/g VSS). The seed sludge employed in this assay was already being used to digest this particular WAS in the treatment plant; thus, it was assumed to be already acclimated to this WAS. Therefore, basal medium was not added. After preparation, bottles were purged with N_2 gas (99% purity) for 10 min and sealed afterwards. Then, they were placed in a shaking incubator at 35 °C.

Analytical methods

A number of analyses were conducted to determine the initial and final conditions of sludge samples and the composition of produced biogas. For the determination of CV, sludge samples were dried at 105 °C to constant weights and sieved through a 60-mesh size sieve before being combusted in the LECO AC500 calorimeter (LECO Corporation, USA). Elemental compositions of samples were determined using LECO TruSpec CHN (LECO Corporation, USA). TS, VS, TSS, and VSS measurements were done according to the Standard Methods 2540B, 2540E, 2540D, and 2540E, respectively (APHA et al. 2005). Ash contents were analyzed following the ASTM Standard Method D3174-12 (ASTM 2012). COD and sCOD concentrations were determined using Hach COD kits and Hach DR 3900 spectrophotometer (Hach Company, USA) in accordance with the USEPA-approved dichromate method (Jirka and Carter 1975). For sCOD determination, samples were filtered following the Standard Method 2540D (APHA et al. 2005); then, the remaining liquid was used. Biogas productions were measured using a water displacement unit. Biogas composition was measured with Agilent 6890N gas chromatograph using a thermal conductivity detector (TCD) (Agilent Technologies, Inc., USA).

Results and discussion

Increase in sCOD concentrations

Ultrasound pretreatment is known to solubilize a part of particulate organics (Pérez-Elvira et al. 2006; Show et al. 2006). Shown in Fig. 1 are the sCOD concentrations in percentage with respect to specific energy input in comparison with other ultrasound pretreatment studies that have reported sCOD concentrations with varying energy inputs. Data obtained in this study are given as averaged concentrations with standard deviations. Up to 35 kJ/g TS input, our sCOD results seem to agree with the studies used for comparison, except with those of Lizama et al. (2017) where solubilization was lower than all the other studies. Beyond that point, as mentioned before, we were able to show how higher energy inputs influence the solubilization of organics in WAS. In our case, sonication increased the sCOD concentrations rapidly up to 57.3 kJ/g TS specific energy input (corresponding to 15 min sonication). Afterwards, concentrations dropped below that of

Table 2 Preliminary characterization of sludge samples after pretreatment processes

Sludge type	TS (mg/L)	VS (mg/L)	TSS (mg/L)	VSS (mg/L)
ADS (seed sludge)	22,527 ± 93	11,633 ± 41	21,800 ± 348	11,388 ± 151
WAS—no sonic.	11,453 ± 90	9033 ± 38	9151 ± 94	7254 ± 211
WAS—5 min sonic.	11,053 ± 50	8547 ± 52	9042 ± 188	7196 ± 179
WAS—10 min sonic.	11,273 ± 143	8780 ± 166	9098 ± 127	7243 ± 144
WAS—15 min sonic.	11,073 ± 164	8573 ± 127	8947 ± 141	7150 ± 241
WAS—20 min sonic.	11,433 ± 84	8827 ± 155	9044 ± 199	6832 ± 285
WAS—25 min sonic.	11,513 ± 124	8853 ± 152	9222 ± 207	6799 ± 116

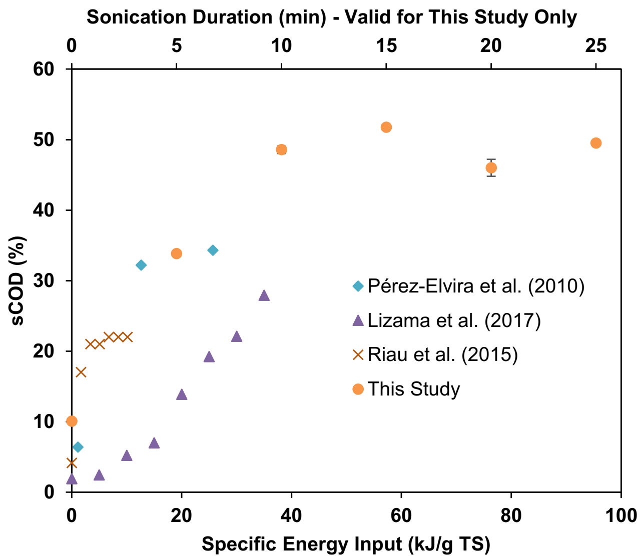

Fig. 1 Soluble COD concentrations in percentage with respect to increasing specific energy inputs, compared with the values calculated from other studies (Pérez-Elvira et al. 2010; Riau et al. 2015; Lizama et al. 2017)

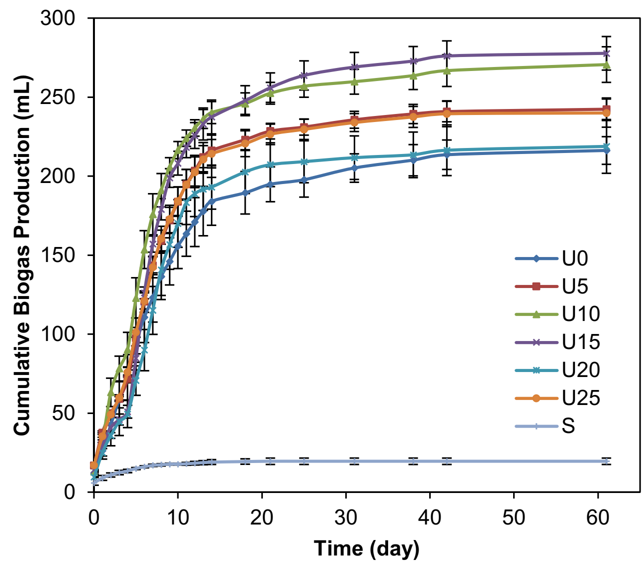

Fig. 2 Cumulative biogas production from the BMP samples (averages of three replicates)

10 min at 20 min sonication, then, finally increased again at 25 min. The same decrease and following increase were observed in a different study by our group which involved WAS from the same treatment plant (Apul and Sanin 2010). This phenomenon was attributed to the complex sono-chemical reactions that may lead to recapturing of the organics within flocs and cell damage resulting in inhibited activity (Apul and Sanin 2010; Zheng et al. 2019). Results presented by Zheng et al. (2019) also show minor increases in suspended solid concentration with increased sonication duration (or energy input); however, their findings are not sufficient in describing the phenomenon either. Another cause, as suggested by Apul and Sanin (2010), involves local thermal reactions, which may occur even in temperature-controlled experimental setups. Foladori et al. (2010) argues that cell membrane disintegration begins only after 30 kJ/g TSS; thus, our higher energy inputs may have triggered membrane breakage alongside floc disruption (which occurs below 30 kJ/g TSS) causing disaggregation of smaller cell groups. In this occurrence, flocs may have reformed in small clusters, leading to decreased soluble organics. Either case, in the figure, it can be seen that sonication beyond 57.3 kJ/g TS (which corresponds to 15 min sonication for our case) does not provide additional increase in solubility despite higher energy consumption.

Cumulative biogas and methane productions

In BMP tests, biogas production and its composition were measured daily for the first 14 days. Afterwards, as biogas production diminished, the frequency of measurements decreased, and the experiment was concluded on the 61st day. Shown in Fig. 2 are the average cumulative biogas production values for the samples, with error bars showing the standard deviations from multiple measurements. Biogas production values show that ultrasound pretreatment increased the yield for all sonication durations as anticipated. Fifteen minutes of sonication (U15), providing 57.3 kJ/g TS of specific energy, provided the highest biogas production at 277.7 mL. U10 was close behind with 270.6 mL. Following them, U5 produced 242.4 mL, U25 produced 240.0 mL, U20 produced 218.8 mL, while the control group with no pretreatment produced 216.3 mL. In comparison of biogas productions, although U15 had the highest value, U10 was within one standard deviation while requiring only two-thirds of the ultrasound energy. Among the tested sonication durations, 20 min and 25 min were relatively inefficient. U20 and U25 had lower biogas productions than U5, U10, and U15, making both redundant based on higher energy consumption for sonication as well as lower gas production. The cumulative biogas production results show that solubilization achieved by ultrasound pretreatment influenced biogas formation directly as samples with higher sCOD concentrations yielded higher production. Compared with the control (U0), U15 (57.3 kJ/g TS energy input) had the highest increase with 28% while U10 (38.2 kJ/g TS energy input) had 25% and U5 (19.1 kJ/g TS energy input) had 12%. Lizama et al. (2017) reported 31.4% increase in biogas production following an ultrasound energy input of 35 kJ/g TS, while Braguglia et al. (2012b) stated 27.2% increased production after 2.5 kJ/g TS energy input. Our results showed comparable biogas production increases; however, it was not possible to observe a linear relationship between the increase in biogas production and energy inputs neither for our results nor for the studies compared.

Gas chromatography was used to assess the composition of biogas. Depicted in Fig. 3 are the cumulative methane

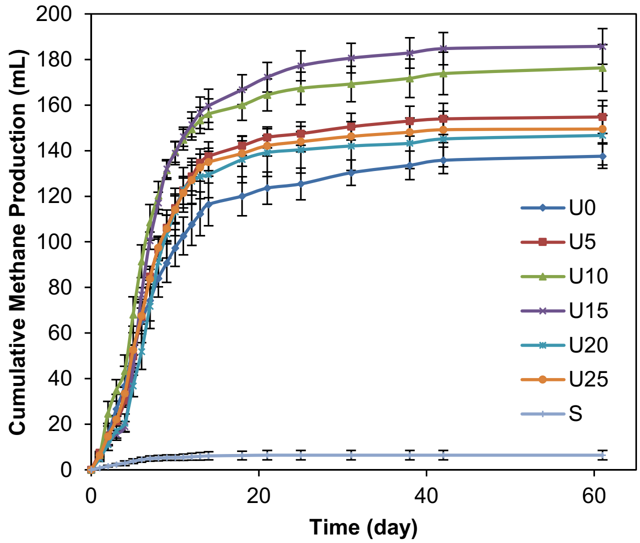

Fig. 3 Cumulative methane productions from the BMP samples (averages of three replicates)

productions throughout the experiment duration (61 days). Values on the graph are the averages of methane productions from each replicate bottle corresponding to the same sludge type, with error bars showing standard deviations. The highest cumulative methane production was for U15 at 185.7 mL. This was followed by U10 with 176.3 mL, and U5 with 154.8 mL. U25 and U20 had 149.5 mL and 146.7 mL methane production, respectively. The production of the control group (U0) was 137.6 mL. Observations for methane production agree with the total biogas production results given earlier. The highest sCOD increase, seen for U15 (57.3 kJ/g TS energy input), resulted in 35% increase in methane production, followed by 28% for U10 (38.2 kJ/g TS energy input) and 13% for U5 (19.1 kJ/g TS energy input). Since the corresponding increases for methane are higher than the increases in biogas production, it is possible to say that more of the produced biogas was methane. This shows that ultrasound increased not only the overall gas production but also the methane content of the produced biogas. Pérez-Elvira et al. (2010) reported 41% increase in methane production following an ultrasonic energy input of 25.7 kJ/g TS, while 10.9% increase was observed by Tian et al. (2015) after 9 kJ/g TS. As was the case with biogas production, although we observed significant increases in methane, it was not possible to establish a linear relationship between specific energy inputs and increases in methane production. Reduced benefits at 20 and 25 min of sonication are apparent for methane production as well. These observations are conforming with a prior work of Apul and Sanin (2010), where a comparable decrease was documented for sonication durations longer than 15 min. Over 61 days, the seed sludge (S) produced 19.5 mL of biogas (less than 10% of U0) and 6.4 mL of methane (less than 5% of U0). Along with the fact that almost all VS in the seed was in particulate form (Table 2), this showed the limited activity of the seed (Angelidaki et al. 2009) and therefore supported its suitability of usage in this BMP experiment.

Effects of anaerobic digestion on the properties of sludge samples

TS, VS, and COD concentrations of the samples before and after anaerobic digestion, as well as removal percentages, are given in Table 3 with standard deviations. Similar in all samples, TS removal was 25% on the average. Increased solubilization provided by ultrasound pretreatment enhances the removal of organics as evident in improved VS and COD removals. For all sludge samples, VS destruction amounts followed the same order as in biogas and methane productions. U15 having the highest biogas and methane yield also had the highest VS removal at 45%. VS removal rates for other samples were as follows: U10 resulted in 43.9% reduction, U5 and U25 followed that with 43.1%, and U20 yielded 42.4% removal. U0 had 41.0% VS removal on the average, lower than all the pretreated samples. In other ultrasound pretreatment studies, Braguglia et al. (2011) reported 8% improvement in VS removal while Seng et al. (2010) observed 11% enhancement. For our case, improvements were 5, 7, and 10% for U5, U10, and U15, respectively. COD removal

Table 3 Average TS, VS, and COD concentrations and COD removal percentages at the end of the BMP assay period. Subscripts "i" and "f" denote initial and final conditions, respectively

Label	TS_i (mg/L)	TS_f (mg/L)	TS removal (%)	VS_i (mg/L)	VS_f (mg/L)	VS removal (%)	COD_i (mg/L)	COD_f (mg/L)	COD removal (%)
U0	15,853 ± 93	11,982 ± 85	24.4	9631 ± 126	5684 ± 77	41.0	15,200 ± 94	10,242 ± 145	32.6
U5	15,996 ± 103	11,871 ± 65	25.8	9849 ± 119	5607 ± 25	43.1	15,675 ± 102	10,250 ± 114	34.6
U10	15,893 ± 63	11,633 ± 137	26.8	9851 ± 46	5529 ± 110	43.9	15,942 ± 103	10,208 ± 47	36.0
U15	15,982 ± 180	11,571 ± 45	27.6	9953 ± 90	5478 ± 55	45.0	16,200 ± 108	10,275 ± 82	36.6
U20	15,709 ± 149	11,602 ± 113	26.1	9720 ± 95	5596 ± 80	42.4	15,783 ± 42	10,792 ± 48	31.6
U25	16,118 ± 62	11,864 ± 112	26.4	9973 ± 102	5671 ± 79	43.1	16,067 ± 77	10,658 ± 81	33.7
S	9876 ± 122	8671 ± 64	12.2	5058 ± 23	3847 ± 57	23.9	8208 ± 12	7317 ± 31	10.9

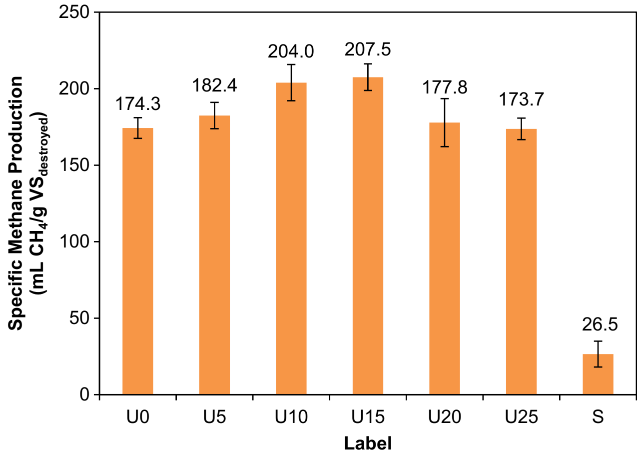

Fig. 4 Average specific methane productions for different sludge samples

ranged between 31.6 and 36.6% for the pretreated sludge. Analogous to VS removals, U15 displayed the highest COD removal (36.6%). U10 followed that with 36.0%, along with 34.6% and 33.7% for U5 and U25, respectively. However, contrasting biogas and methane productions and VS removals, COD removal in U0 was higher than U20. The drop in sCOD concentration at 20 min sonication seems to have a negative effect both on biogas production and organic removal degree. If the reduction in sCOD was due to floc reformation as discussed before, it may explain this behavior. This consistency between reduced sCOD concentration, reduced biogas and methane production, and lower organic removals shows that this occurrence is not an experimental error but rather an actual effect of sonication beyond 60 kJ/g TS energy input. The reductions in sCOD, methane production, and organic removal following higher energy inputs warrant further research.

Since removal amounts of organics vary from one reactor to another, a comparison of reactors is made based on a normalized parameter such as specific methane production. It is calculated as mL of methane produced from g VS destroyed. Results are presented in Fig. 4, with values in averages and errors bars showing the standard deviations of specific methane productions. Overall, the range is between 173.7 $VS_{destroyed}$ (for U25) and 208 mL/g $VS_{destroyed}$ (for U15). When compared with the 174 mL/g yield of U0, a specific energy input of 19.1 kJ/g TS for U5 resulted in 5% increased yield, 38.2 kJ/g TS for U10 resulted in 17% increase, and a specific energy input of 57.3 kJ/g TS for U15 resulted in 19% increase. In comparison, Tian et al. (2015) reported 9.9% increase in yield following a specific energy input of 9 kJ/g TS, and Seng et al. (2010) observed 12.8% increase after a specific energy input of 3.8 kJ/g TS. Instead of methane, Lizama et al. (2017) reported 219.5 mL/g VS biogas yield following 35 kJ/g TS sonication energy input. For our case, 38.2 kJ/g TS energy input (U10) resulted in a biogas yield of 313 mL/g VS. Therefore, despite the fact that we utilized more energy for ultrasound degradation, we were able to achieve higher solubilization—as evident from Fig. 1—which, in turn, provided enhanced methane yields.

Initial and final CVs of the sludge samples are given in Table 4. Anaerobic digestion resulted in an overall loss of 18%. Similar to gas productions and organic removals, U15 and U10 had higher CV losses. Nonetheless, the differences in CVs are less striking and this time, the order with respect to sonication durations diverges from the order apparent in other parameters. An additional issue with regard to energy from sludge combustion is that digestion not only reduces the overall CV but also total combustible solids alongside. With the reduction in both CV and the solids amount that contributes to CV, total energy loss is magnified. For our case, the overall energy potential of a sample both before and after digestion can be calculated by multiplying the CV, TS concentration, and active volume of that sample. Comparison shows that about 40% of the total energy that will be released during sludge combustion is lost because of anaerobic digestion. Sonication durations of 10 and 15 min, which provided the highest benefits in terms of biogas and methane productions and organic removals, resulted in the highest overall reduction in energy that can be released during combustion.

Combustion of the biogas and its energy yield is also considered alongside sludge combustion. Table 5 shows the

Table 4 Changes in the average CVs of samples. Subscripts "i" and "f" denote initial and final conditions, respectively

Label	CV_i (J/g TS)	CV_f (J/g TS)	CV reduction (%)	TS removal (%)	Combustion energy reduction (%)*
U0	13,426 ± 169	11,029 ± 41	17.9	24.4	37.9
U5	13,401 ± 23	10,883 ± 21	18.8	25.8	39.7
U10	13,393 ± 126	10,807 ± 116	19.3	26.8	40.9
U15	13,502 ± 301	10,970 ± 93	18.7	27.6	41.2
U20	13,414 ± 183	10,945 ± 134	18.4	26.1	39.7
U25	13,468 ± 320	10,849 ± 83	19.4	26.4	40.7
S	11,527 ± 62	10,016 ± 62	13.1	12.2	23.7

*Calculated per BMP bottle

Table 5 Overall reduction of the energy yield of sludge by anaerobic digestion enhanced with ultrasound pretreatment

Label	Energy of sludge before digestion (J)*	Energy of sludge after digestion (J)*	Energy from biogas (J)*	Overall reduction (%)
U0	42,568	26,430	4288	27.8
U5	42,872	25,838	4824	28.5
U10	42,571	25,144	5496	28.0
U15	43,158	25,387	5790	27.8
U20	42,144	25,397	4572	28.9
U25	43,415	25,743	4660	30.0
S	22,768	17,370	200	22.8

*Calculated per BMP bottle

overall loss in the energy that can be harvested from the sludge per BMP bottle. Energy from biogas was calculated using the CV of methane (50 MJ/kg). Final results indicate that by digesting the non-pretreated sludge, 27.8% of the total energy is lost. Ultrasound pretreatment further increases this loss up to 30%.

The changes in the elemental compositions of samples are given in Fig. 5. C, N, and H contents of each sludge sample were measured before and after digestion, and the mass-based removal percentages are given in the figure. Common with VS and COD removals, sonicated samples showed higher removal percentages—as more of the C and H were used in methanogenesis. Previous studies have scarcely documented the changes in elemental composition of sludge during anaerobic digestion. Thus, the C, H, and N contents of our samples were instead compared with the ranges for both raw and digested sludge compiled from various studies. The observed C, H, and N percentages of our sludge were found to be in agreement with the ranges of 29.7 to 31.8% for C, 3.4 to 4.3% for N, and 3.5 to 4.2% for H in dry basis (Thipkhunthod et al. 2005; Boran et al. 2008; Casajus et al. 2009). The ash contents of samples seemed to increase as the biodegradable portion of total solids was reduced with anaerobic digestion. Initial and final ash contents in terms of percent of dry solids are provided in Fig. 5 as well.

With ultrasound pretreatment and anaerobic digestion experiments, we could observe that ultrasound applications at 0.73 W/mL for 5, 10, and 15 min improved the biodegradation potential of sludge. VS and COD removals, and biogas and methane productions were increased. We were also able to quantify the changes in the CV and elemental composition of the sludge, showing that anaerobic digestion reduces the overall energy potential that can be obtained through combustion. Furthermore, we observed that digestion following ultrasound pretreatment further reduced both the CV and the amount of combustible solids in the sludge.

Since the sludge management trends are focusing on valorization (Gherghel et al. 2019), classifying sludge not as a waste but as a byproduct and a resource, we expect that co-combustion to exploit the energy potential of sludge may become common, not just in developed countries, but in the developing world as well. While anaerobic digestion being a sustainable method itself offers benefits in terms of energy generation and reduction of the amount of sludge, its compatibility with a combustion process that follows should be evaluated case by case based on specific conditions, such as the necessity of drying, which could be very energy intensive (Kurt et al. 2015). Our study shows that anaerobic digestion, even when enhanced by ultrasound pretreatment, may not produce enough energy from biogas combustion to offset the

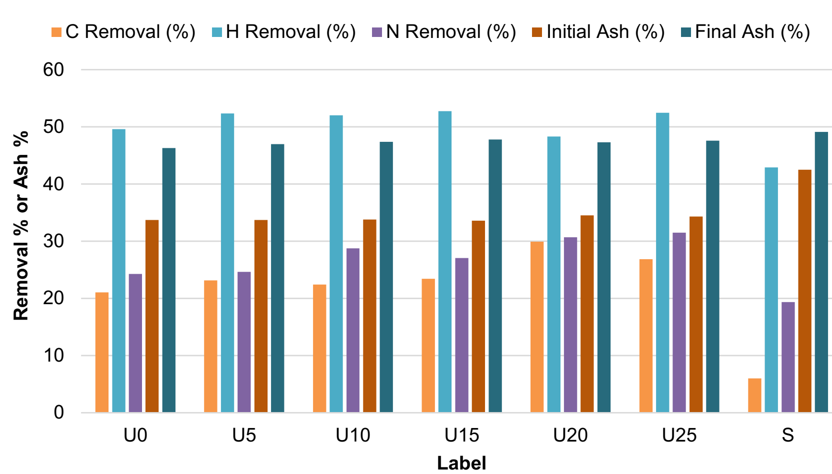

Fig. 5 Changes in the C, H, and N contents of sludge samples along with initial and final ash contents

losses in comparison with sludge combustion. Thus, if the aim is to extract the maximum energy potential of sludge, it may be worthwhile to avoid digestion and combust sludge while it retains its organics and high CV, which rivals that of coal. As a result, it may be worthwhile to conduct studies such as ours to quickly and accurately assess whether the methane potential of a sludge or its energy yield during combustion would be a better usage alternative in beneficial use of the energy potential of a given sludge.

Conclusions

The overall results of the experiments demonstrate that sonication will increase soluble organics, enhance organic removal, and improve biogas and methane productions. Compared with the control group, 15 min of ultrasound pretreatment at 0.73 W/mL increased the concentration of sCOD by more than 4.6 times, improved VS removal and COD destruction by 9.8% and 12.3%, respectively, and resulted in 35% increased methane yield. Yet, significant energy consumption of ultrasound pretreatment is also of concern and it should be viewed advantageous only if the produced energy from subsequent anaerobic digestion is higher or of more commercial value (being from a renewable source). Furthermore, if combustion is applied following digestion, increased methane yield may not be sufficient to offset the increased loss in CV and TS of sludge, as was in our case. Alongside the implications on energy balances, other effects of pretreatment on the rest of sludge treatment scheme—such as dewaterability or drying—should be considered in decision-making on beneficial usage of sludge. As for the CV of the sludge, a loss of about 18% was observed for all samples. The overall loss in energy potential was magnified by the reduction in the amount of combustible solids to 40% on the average.

As the value of sludge increases because of its use as a sustainable energy source, its management and ways of exploiting its energy content will become more important. With this study, we present a relatively quick and straightforward method of determining how the fuel properties of sludge could change following anaerobic digestion with or without pretreatment. While our results may favor combustion without digestion, different types of sludge and treatment conditions could indicate anaerobic digestion as more advantageous. Overall, decisions on sludge treatment to increase the overall energy yield should depend on complete energy balances and be evaluated on a case-by-case basis.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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