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Comparison of Pre-treatment Technologies to Improve Sewage Sludge Biomethanization

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Abstract

This research study evaluates various pre-treatments to improve sewage sludge solubilization prior to treatment by mesophilic anaerobic digestion. Microwave, thermal, and sonication pre-treatments were compared as these pre-treatments are the most commonly used for this purpose. The solubilization of sewage sludge was evaluated through the variation in soluble total organic carbon (sTOC, mg/L) and soluble total nitrogen (sTN, mg/L). Thermal and microwave pre-treatments increased sTOC/VS by 19.2% and 83.4% (VS, total volatile solids), respectively, after applying lower specific energy through (20 kJ/g TS, approximately) (TS, total solids) unlike the sonication pre-treatment, which required 136 kJ/g TS. Although sTN content did not increase significantly with the pre-treatments with respect to sTOC, both showed proportional trends. Sonication pre-treatments allowed the highest increase in volatile fatty acids (VFA) with respect to the raw sewage sludge (15% ΔVFA/sTOC). Methane production with and without pre-treatment was also evaluated. Methane production increased by 95% after applying sonication pre-treatment compared to the methane production of raw sewage sludge. Thermal and microwave pre-treatments entailed lower improvements (29% and 20%, respectively). Economically, thermal pre-treatments were the most viable alternative at real scale.

Keywords Mesophilic anaerobic digestion · Sewage sludge · Sonication · Microwave · Thermal pre-treatment

Introduction

The management, processing, and disposal of urban wastewater treatment plant (WWTP) sewage sludge has been and continues to be one of the greatest challenges of the wastewater

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sector [1]. Sewage sludge is difficult to manage due to the huge volume produced and the presence of undesirable compounds such as heavy metals, organic micropollutants, and pathogens [2]. These undesirable compounds could entail high environmental impacts and limit the available methods for sewage sludge management [3].

Anaerobic digestion is a treatment technology that is being developed worldwide to treat this polluting and hazardous waste [4]. This technology has several advantages such as the reduction of mass and pathogens, the removal of odors, and, more importantly, the recovery of energy as methane [5, 6]. However, the anaerobic digestion of sewage sludge should be improved as it usually entails low biodegradability and low methane production, which could limit its industrial implementation [7]. These limiting factors are generally associated with the hydrolysis stage [5, 8]. During sewage sludge hydrolysis, cell walls, which are a relatively unfavorable substrate for microbial degradation, should be ruptured in order to release readily digestible organic matter for the microorganisms.

In order to facilitate the hydrolysis phase, different pre-treatments have been proposed to solubilize the organic matter content as a previous step to the biomethanization process. Among the different pre-treatments described in the literature, thermal [9, 10], sonication [8, 11], and, to a lesser extent, microwave [4, 12] pre-treatments are the most widely proposed to improve the anaerobic digestion of sewage sludge. Thermal pre-treatment mainly solubilizes the organic matter by increasing the temperature, which solubilizes both proteins and polysaccharides [13]. Depending on the operational conditions and the sewage sludge characteristics, thermal pre-treatments could improve the anaerobic digestion of sewage sludge by 14–90% [14, 15]. By contrast, the effect of sonication pre-treatment on sewage sludge is mainly a consequence of a cavitation process rather than an increase in temperature. Sonication forms cavitation bubbles, which grow and then collapse, thus causing high shearing forces and the formation of radicals [16]. The improvement of anaerobic digestion after sonication pre-treatments has been described in a wide range from 12 up to 1700% with respect to the raw sewage sludge [17, 18]. This variation depends on the operational parameters of the sonication as well as the composition and moisture of the sewage sludge [18]. Microwave pre-treatment combines a thermal effect and a non-thermal effect [19]. The non-thermal effect involves the breakage of the cell wall as a consequence of the rapid change in the orientation of the dipoles in the polarized side chains of the cell membrane macromolecules [4]. The disintegration capacity of microwave pre-treatment has been described as higher than conventional thermal pre-treatments, resulting in higher sewage sludge floc and cell destruction [19, 20]. However, the reported improvements in the anaerobic digestion of sewage sludge using microwave pre-treatments were not significantly higher than those obtained by thermal pre-treatments. Microwave pre-treatment has been shown to improve the production of methane from sewage sludge by up to 31% [21], although lower improvement values are usual [22, 23].

Due to the large amount of available information and the wide variety of experimental set-ups reported in the literature, it is difficult to select the most appropriate pre-treatment for sewage sludge. Therefore, it is of interest to evaluate the relation between type of pre-treatment, sewage sludge solubilization, and the effect on a subsequent biomethanization step. The main objective of this research study is to compare the most widely applied pre-treatments for the anaerobic digestion of sewage sludge. This comparison focuses on two different, though interconnected, aspects: sewage sludge solubilization and methane production improvement.

Materials and Methods

Chemical Analyses

To characterize the sewage sludge, the following chemical analyses were used: soluble chemical oxygen demand (sCOD, g O_2/kg), total solids (TS, g/kg), total fixed solids (FS, g/kg), and total volatile solids (VS, g/kg). For the characterization of the soluble fraction of the substrate, volatile fatty acidity (VFA, mg acetic acid /L) and pH were analyzed. All analyses were performed in accordance with the test methods for the examination of composting and compost developed by the US Department of Agriculture and the US Composting Council [24]. Total soluble organic carbon (sTOC; mg/L) and total soluble nitrogen (sTN, mg/L) were also determined using a Rosemount Analytical Dohrmann DC-190 carbon analyzer. The sTOC analyzer was calibrated with a standard potassium phthalate solution prior to the sTOC analyses.

The following parameters were determined in the effluents of the reactors during the anaerobic digestion assays: pH, fatty acidity (VFA, mg acetic acid /L), and alkalinity (Alk, mg $CaCO_3$/L). All analyses were carried out in accordance with the Standard Methods of the APHA [25].

Sewage Sludge

Sewage sludge composed of primary and secondary sludge was used as a substrate. The main analytical characteristics of the substrate are shown in Table 1. To ensure that the sewage sludge was fresh and prevent uncontrolled fermentation due to laboratory storage, the sewage sludge was collected at different times. Table 1 shows the mean value of the analytical characteristics determined during the experiments, although some variations in the physico-chemical characterizations were observed.

The sewage sludge was collected from the Copero urban WWTP (Seville, Spain). The flow rate of this WWTP is 500 t of sewage sludge on a dry basis per year. A high percentage (85–90%) of the influent of this WWTP is composed of municipal wastewater, while the remaining industrial wastewater influent comes mainly from the agrifood sector.

Pre-treatment Set-Ups and Procedures

For each pre-treatment, different ranges of operational variables were evaluated to optimize the relation between soluble and total organic matter. Table 2 summarizes the ranges of the

Table 1 Analytical characterization of the raw sewage sludge (wet weight basis) used for all pre-treatments

Variable	Raw sewage sludge
pH	7.74 ± 0.06
Moisture (%)	86.5 ± 0.7
sCOD (g O_2/kg)	10 ± 1
TS (g/kg)	135 ± 1
FS (g/kg)	44 ± 1
VS (g/kg)	92 ± 2
sTN (mg/kg)	2288 ± 268
sTOC (mg/kg)	2701 ± 350

assayed operational variables and the selected conditions for the subsequent anaerobic digestion test. After each pre-treatment was carried out and prior to the analysis, the samples were cooled at room temperature to prevent the loss of volatile compounds. Each sample was analyzed in triplicate.

Thermal Pre-treatment

For the thermal pre-treatment, a 75-L volume autoclave (Selecta P. Autester Mod. 437-G) operating at 120 °C and 2 atm was used. The thermal autoclave was fitted with a system to program and control the pre-treatment time. Three sewage sludge aliquots of 100 g were inserted in sealed 0.25-L volume NORMAX bottles and placed in the autoclave for each experimental time. After each pre-treatment was carried out and prior to the analysis, the samples were cooled at room temperature to prevent the loss of volatile compounds.

Sonication Pre-treatment

For the sonication pre-treatment, a 6.0-L volume Selecta P. 3000513 ultrasonic cleaning bath was used under the following conditions: 25 °C, atmospheric pressure, and a power generator of 150 W. The ultrasound system was fitted with a system to program and control the pre-treatment time. Sewage sludge aliquots of 30 g contained in sealed 0.25-L NORMAX bottles were placed in the basin of the device. The basin contained tap water where the ultrasonic rays were generated at each pre-treatment time. The bottles were shaken manually every 5 min during the pre-treatment to minimize gradients in the sample.

Microwave Pre-treatment

An experimental pilot microwave was used for the microwave pre-treatment. The device, which was designed specifically for this pre-treatment, operates at different powers in a range of 100–900 W [22]. The system is computer controlled and equipped with software to regulate the operational variables (time and power) and monitor the temperature inside the system. Sewage sludge aliquots of 100 g were placed in a container and pre-treated under each operational condition.

Anaerobic Digestion Procedure

Once the operational conditions were selected, anaerobic digestion tests were performed to determine the biomethane potential of the raw sewage sludge and the sewage sludge subjected to the different pre-treatments. The biomethane potential of the raw and pre-treated sewage sludge was evaluated in duplicate in 1.0-L working volume Pyrex completely mixed reactors

Table 2 Ranges of operational conditions employed in the sewage sludge pre-treatments

Pre-treatment	Duration (min)	Specific energy applied (kJ/g TS)	Power (W)	Temperature (°C)
Thermal	0–60 *(15)*	0–145 *(36)*	–	120
Sonication	0–60 *(45)*	0–136 *(102)*	150	30
Microwave	0–2.1 *(1.4)*	*20*	0–900 *(700)*	< 80

Selected conditions within the range shown in parentheses operating in parallel under mesophilic temperature (35 °C) and in batch mode. The reactor content was mechanically stirred, and the temperature was maintained by a thermostatic jacket containing water at 37 °C. The volume of methane produced during the process was measured using 1.0-L Boyle-Mariotte reservoirs connected to each reactor. The biogas produced from the sewage sludge was passed through a 6 N NaOH solution to capture CO_2. The remaining gas was assumed to be methane. The volume of methane displaced an equal measurable volume of water from the reservoirs. This volume was corrected to remove the effect of water steam pressure, and the measured methane was then expressed at standard temperature and pressure conditions (STP: 0 °C and 1 atm).

The reactors were inoculated with anaerobic sludge, which was obtained from a full-scale anaerobic reactor used to treat sewage sludge at the Copero plant (Seville, Spain). The methane production rate of the inoculum was 44 mL STP CH_4/(g VS·h), and the main physicochemical characteristics were $pH = 7.47 \pm 0.04$ and $Alk = 10,555 \pm 50$ mg $CaCO_3$/L.

Software

Sigma-Plot software (version 11.0) was used to create the graphs, perform the statistical analysis (mean value and standard deviation), and fit the experimental data to the tendency lines presented in this work.

Results and Discussion

Organic Matter Solubilization by Different Pre-treatments

The implementation of a pre-treatment phase aims to achieve a higher reduction of the sewage sludge during a subsequent anaerobic digestion process. The enhanced degradation of sludge in anaerobic digesters is reflected in higher organic matter removal and improved methane/biogas production [14]. These enhancements have been reported to be a consequence of the higher availability of readily digestible compounds due to the solubilization of sewage sludge during the pre-treatment step [26]. Sewage sludge solubilization was evaluated through the variations in sTOC (Fig. 1a) and sTN (Fig. 1b) for the proposed pre-treatments. As can be seen, sTOC increased significantly after applying 36 and 20 kJ/g TS through thermal and microwave pre-treatments, respectively. The increase in sTOC and sTN may be due to the fact that these techniques improve the solubilization of organic matter. Yang et al. [27] reported that approximately 10% of the tCOD of primary sludge was converted to sCOD after thermal pre-treatment. Moreover, microwave pre-treatment not only affects sewage sludge by increasing temperature, but the polarity of the macromolecules also changes because different compounds disintegrate due to the breakage of hydrogen bonds [4, 12]. By contrast, the sonication pre-treatment required higher specific energy (i.e., 136 kJ/g TS) to reach variations in sTOC similar to those obtained for the thermal and microwave pre-treatments. This difference could be due to the solubilization mechanism attributed to sonication pre-treatments mentioned previously [16]. Although the thermal pre-treatment was apparently the best method to increase sTOC, this increase should be expressed with respect to the VS content in the raw material. An increase of 19.2%, 20.8%, and 83.4% in sTOC/VS was observed with the thermal, sonication, and microwave pre-treatments, respectively. Under the experimental conditions evaluated, the microwave pre-treatment was the best pre-treatment to increase sTOC. Figure 1b shows that variations of sTN presented a similar trend to the variations described for sTOC. The increase in sTN with respect to the raw sewage sludge could be due to the degradation of proteins during the pre-treatment step [28]. Thermal and microwave pre-treatments reach a maximum increase in sTN at relatively low severe conditions, although the thermal pre-treatment did not significantly increase the sTN concentration (lower than 10% compared to 40% in the microwave pre-treatment). The sonication pre-treatment required specific energies higher than 100 kJ/g TS to significantly increase sTN in the sewage sludge [3].

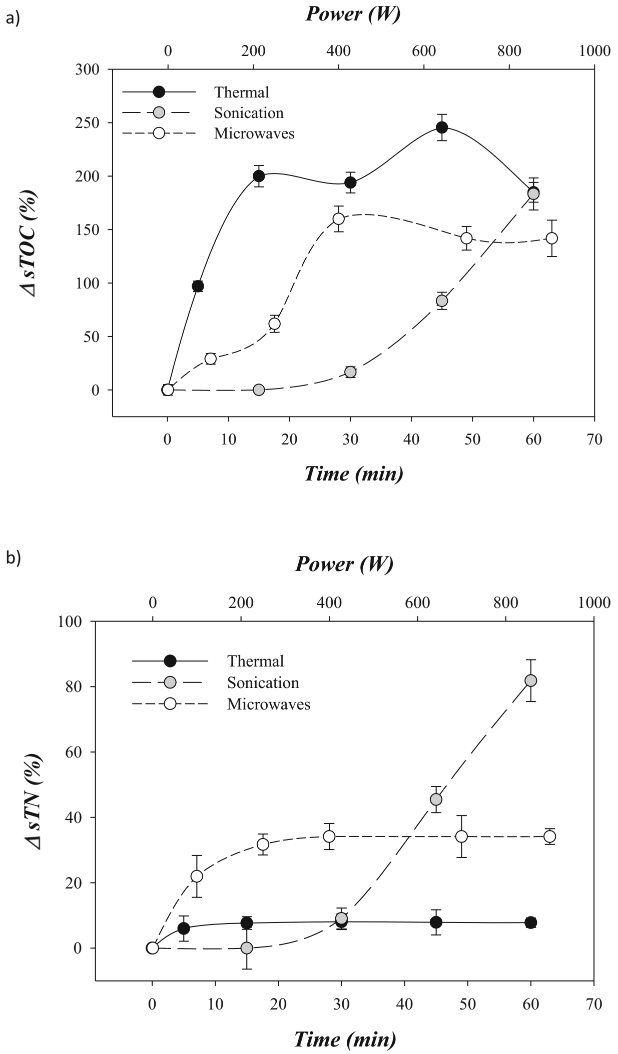

Fig. 1 **a** Percentage of variation in sTOC (%) with the power applied (W) and time (d) for each pre-treatment. **b** Percentage of variation in sTN (%) with the power applied (W) and time (min) for each pre-treatment

Volatile Fatty Acids Release Through Different Pre-treatments

Among the solubilized organic matter, an increase in short-chain volatile fatty acids is directly related with the enhancement of the methane yield during subsequent methane production [3, 8]. Total VFA was analyzed in the raw sewage sludge and after carrying out the different pre-treatments. Figure 2 shows the variations of VFA after the proposed pre-treatments compared to the raw sewage sludge. As can be seen, the thermal pre-treatments led to the highest increase in VFA, with improvements of up to 100% with respect to the raw sewage sludge. By contrast, VFA only increased around 75% with the microwave and sonication pre-treatments in relation to the raw sewage sludge (Fig. 2). However, the increase in VFA should be expressed with respect to the raw material (ΔVFA/sTOC). In this line, the sonication pre-treatment showed the highest increase in ΔVFA/sTOC (15%). The increase in VFA was reached at a power higher than 400 W during the microwave pre-treatment, whereas lower powers did not result in a significant increase in VFA. By contrast, the increase in VFA after the sonication pre-treatments followed a linear trend, although a specific energy of around 136 kJ/g TS was necessary to achieve a 75% increase in VFA.

Although VFA removal is essential in biomethanization, it is usually associated to volatile organic compounds (VOCs) and odor emissions [29]. These emissions from open facilities might be considered due to their impact on occupational health and environmental hygiene [30]. Pre-treatments, especially sonication, are generally carried out in open facilities. Moreover, in the case of thermal and microwave pre-treatments, where the pre-treated sewage sludge acquires a specific temperature, VOCs and VFA could be desorbed if the sewage sludge is not directly digested. This could be the main reason for the low increase in VFA after the application of both pre-treatments. According to Ge et al. [31], the VFA concentration increased three fold when the reactor temperature increased from 60 to 65 °C.

It is also important to note that the similar solubility of organic matter is not indicative of a similar composition. Moreover, the presence of short-chain organic acids or volatile fatty acids, which are quickly metabolized by the *acetogenic bacteria*, is essential to improve the

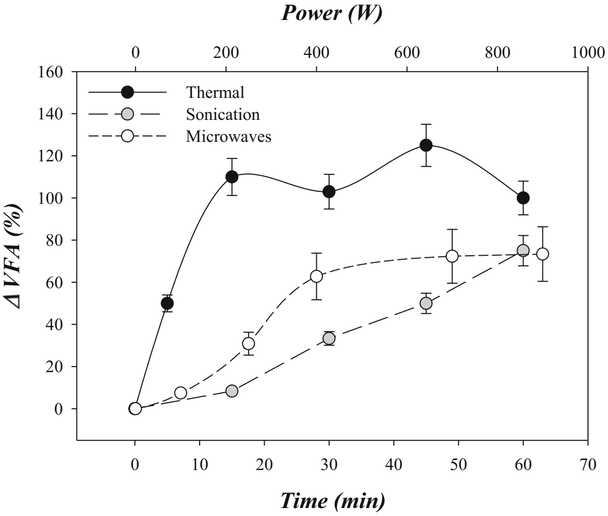

Fig. 2 Percentage of variation in VFA with power (W) against time (min) for the thermal, sonication, and microwave pre-treatments

methane and carbon dioxide production at the end of the biomethanization process through the use of pre-treatment technologies. For this reason, it is very important to study the evolution of this kind of organic matter.

Figure 3 shows the variation in the VFA/sTOC ratio for each pre-treatment compared to the raw sewage sludge. The observed decrease in the VFA/sTOC ratio for the thermal and microwave pre-treatments was due to the high increase in sTOC, which was considerably higher than the sTOC contained in the raw sewage sludge. By contrast, the VFA/sTOC ratio increased by up to 14% following a 30-min sonication pre-treatment (i.e., 51 kJ/g TS). When higher specific energy was applied, a marked decrease in the VFA/sTOC ratio was observed. This might be due to the higher temperature of the pre-treated sewage sludge, which produces a loss of this kind of VOCs (Fig. 3). The decrease in the VFA/sTOC ratio indicated that although the VFA concentration increased with the thermal pre-treatment, the solubilization of other carbon compounds was predominant for sewage sludge [9].

Effect of Different Pre-treatments on Anaerobic Digestion

Table 2 summarizes the operational conditions employed in the proposed sewage sludge pre-treatments. As can be seen, the selected duration of the pre-treatment processes varied considerably. While the microwave pre-treatment was applied for only 1.4 min, the optimal time selected for the thermal and sonication pre-treatments was 15 and 45 min, respectively. The optimal times reported in the literature for the application of microwaves varies from 30 to 60 min at a temperature range of 160–180 °C [32].

Although the lowest specific energy (kJ/g TS) was applied in the microwave pre-treatment, this process required a power of 700 W in contrast to the sonication (150 W) or the thermal pre-treatment, which does not require power provided that a waste thermal stream is valorized. Table 3 shows the mean pH and VFA/Alk ratio values for the raw and pre-treated sewage sludge obtained during the anaerobic digestion processes. The optimal pH values for methanogenic activity usually ranged from 6.5 to 7.5 [33]. As can be seen in Table 3, the pH was

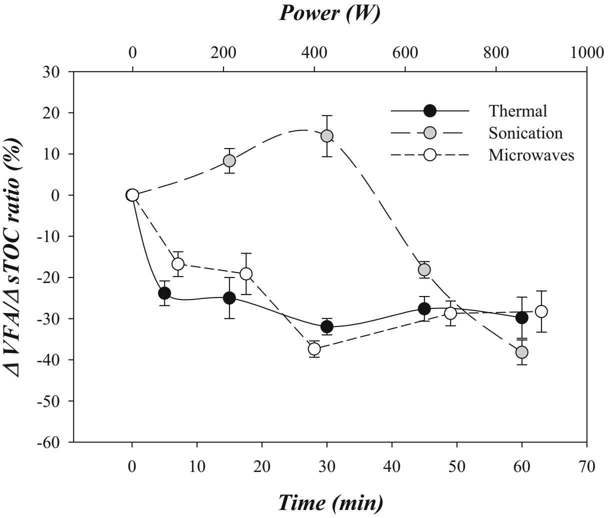

Fig. 3 A Plot of ΔVFA/sTOC ratio (%) against time (min) and power (W) for the thermal, sonication, and microwave pre-treatments

Table 3 Operational variables of the anaerobic digestion compared to the specific energy applied in each pre-treatment

	Pre-treatments					
	Thermal		Sonication		Microwave	
Specific energy (kJ/g TS)	36		102		20	
$\Delta Y_{CH4/S}$ (%)	29		95		20	
	Raw	Pre-treated	Raw	Pre-treated	Raw	Pre-treated
pH	7.74 ± 0.06	7.78 ± 0.11	7.74 ± 0.06	8.02 ± 0.21	7.74 ± 0.06	7.92 ± 0.13
VFA/Alk ratio	0.05 ± 0.02	0.06 ± 0.02	0.07 ± 0.02	0.21 ± 0.02	0.13 ± 0.01	0.06 ± 0.02

slightly alkaline, which was probably due to the high alkalinity provided by the waste (around 3200 mg $CaCO_3$/L). As a result of the high alkalinity provided by the sewage sludge, the VFA/Alk ratio values were always lower than 0.30–0.40, thus indicating no risk of acidification and that the process operated favorably [34]. The higher VFA/Alk ratio obtained during anaerobic digestion after the sonication pre-treatment compared to the thermal and microwave pre-treatments could be due to the higher specific energy applied during this pre-treatment (Table 3). Moreover, during the selected sonication pre-treatment, the VFA/sTOC ratio decreased less than for the selected thermal and microwave pre-treatments (18% vs. 25% and 29%, respectively) (Fig. 3). Therefore, the higher amount of short-chain acids with respect to the soluble and readily digestible organic matter could be related with the higher VFA/Alk ratio during anaerobic digestion.

Methane production during anaerobic digestion with and without the proposed pre-treatments was also evaluated. Table 3 shows the methane production values for each pre-treatment compared to the anaerobic digestion of raw sewage sludge. As can be seen, the sonication pre-treatment resulted in the highest improvement. Specifically, methane production was 95% higher for the raw sewage sludge pre-treated with sonication than without the pre-treatment. The thermal and microwave pre-treatments entailed lower improvements (29% and 20%, respectively). Figure 4 shows a clear relation between the specific energy applied (kJ/g TS) and the enhancement of methane production (ΔY_{CH4}/S, %), regardless of the selected

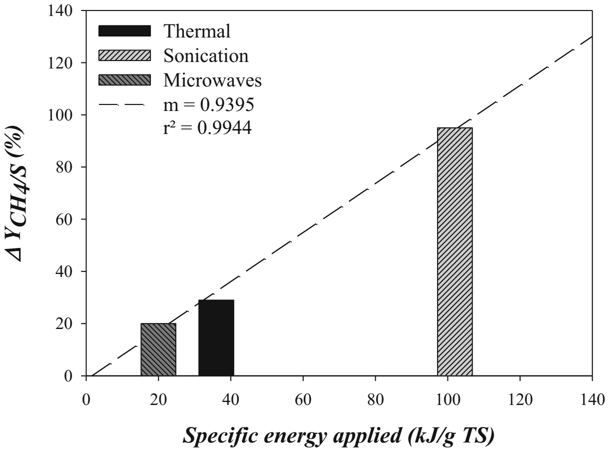

Fig. 4 Increase in methane production yield (ΔY_{CH4}/S, %) against the specific energy applied in each selected pre-treatment

Table 4 Effects and drawbacks of thermal, sonication, and microwave pre-treatments of sewage sludge according to the literature

Pre-treatment	Effects	Drawbacks	References
Hydrothermal [38, 39]	The volatile solid removal efficiency increased by 15%, leading to gas production of 260 mL_{STP} CH_4/g COD (180 °C for 30 min)	High-energy demand Increase of temperatures	Li, C., et al., 2018 Liu, J. et al., 2018
Thermal [40]	Thermal pre-treatment (175 °C and 30 min) allowed an improvement of around 90% and 80% in the maximum biogas production rate and the total volume produced, respectively	High-energy demand	Donoso-Bravo, et al., 2010
Low-energy microwave [41]	Low-energy microwave pre-treatment (14,000 kJ/kg TS) increased in 20–35% the biodegradability of sewage sludge.	High-energy demand Narrow influence area (scalability)	Ebenezer, et al., 2015
Microwave [42]	MP increased sCOD/tCOD ratio and biogas production more than conventional heating. The results obtained suggest that microwaves are beneficial for solubilization and subsequent anaerobic digestion The results show an increase of 5–27% in the specific methane yield from 260 to 290 mL_{STP} CH_4/g initial VS	Microwave utilization for volumetric heating in wastewater treatment industry is at an early stage. Therefore, radiation containment, reactor scalability, and technology deployment for sludge pre-treatment may require sophisticated engineering and design	Bozkurt and Apul, 2020
Sonication [40]	Improvement of 40% in the total biogas production by applying 12,400 kJ/kg TS	The maximum biogas production rate remained relatively constant	Donoso-Bravo, et al., 2010
Sonication [39, 43]	The application of sonication pre-treatment (15,111 kJ/kg TS) increased by 6.7% biogas production and an increase of 4.1% in total solid and 3.7% in volatile solid removal. The obtained methane yield was 0.590 m^3_{STP} CH_4/kg VS	Regular maintenance of same part of equipment High-energy demand and high-tech system Limitation of operating condition (e.g., 10% lower total solid)	Liu, J. et al., 2018 Ormaechaea, et al., 2018

pre-treatment. This relation could be conditioned by the duration of the pre-treatments since the times were selected according to the solubilization of the sewage sludge in order to avoid an unnecessary waste of energy.

Given that the improvement in methane production is clearly related to the specific energy applied in each pre-treatment, the efficient generation of the required energy seems to be key for ensuring the economic viability of the process. Other authors have used a cogeneration biogas engine and obtained an energy efficiency of 39% for electricity and 45% for thermal energy production [35]. However, energy efficiency could reach values of up to 80% when only thermal energy is recovered [36]. Therefore, thermal pre-treatment, whose energy requirements can be supplied as thermal energy, could be more economically interesting than sonication or microwave pre-treatments, which require high amounts of electricity. In this sense, recent developments on thermal municipal sludge pre-treatment technologies to enhance its anaerobic digestion at full scale were evaluated by Kor-Bicakci and Eskicioglu [37]. The authors emphasized the current efforts to improve strategies for energetic optimization of thermal pre-treatment technologies. They highlighted also the current lack of commercially microwave and sonication technologies for sewage sludge disintegration at full scale.

In order to recover the applied energy in the form of methane, the current energy efficiency of thermal, sonication, and microwave pre-treatments must be improved. However, a pre-treatment can be implemented in WWTPs located in areas with seasonal population variations to improve the organic matter hydrolysis in the biomethanization process (limiting stage for sewage sludge). In this sense, although there are no economic benefits in terms of energy recovery, the WWTP might increase its treatment capacity.

Finally, Table 4 compiles a comparison among sonication, microwave, and thermal pre-treatments according to the literature. As can be seen, several authors reported improvements in the maximum biogas production rate and the total volume produced after applying thermal [38–40], sonication [38–40, 43], or microwave [42] pre-treatments. However, current study, as a novel result, presents the relationship between the increase of methane production (%) and the specific energy applied (kJ/g TS) for the three pre-treatments (thermal, microwave, and sonication), under similar experimental conditions. It is worth noting that the experiments were conducted with the same sewage sludge as raw material. On the other hand, as shown in this study, the highest increase in the biodegradability of sewage sludge was obtained after applying microwave pre-treatment. The literature [39, 41, 42] also mentioned the results obtained with the application of one specific pre-treatment. However, to the best of our knowledge, a comparative study of these technologies has not been carried out under similar experimental conditions, and they are only compared in different reviews. With regard to the drawbacks of these pre-treatments, the difficulty of scalability of sonication [39] and microwave [42] pre-treatments at full scale is remarkable, which might favor the possibility of applying thermal pre-treatment when strategies for energetic optimization are desired.

Conclusions

As regards sewage sludge solubilization, the application of a microwave pre-treatment was the most efficient as it permitted obtaining the highest amount of soluble organic matter, expressed as an increase in the initial sTOC/VS (a 83.4% increase with respect to the raw sewage sludge) with low energy requirements (20 kJ/g TS) under the experimental conditions evaluated. However, the sonication pre-treatment was the most adequate to obtain a considerable increase in VFA, which has a direct relationship with the methane production yield.

This study showed that methane production was mostly influenced by the amount of specific energy applied. Therefore, the highest increase in methane production was also obtained with the application of a sonication pre-treatment. However, the costs associated with sonication pre-treatment would be the highest among the evaluated pre-treatments. Therefore, thermal pre-treatment could be the most attractive alternative prior to biomethanization at real scale because the methane that is produced could be used to generate heat that could then be reused in the thermal pre-treatment, thus reducing the costs of the total process.

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Authors' Contributions ASM, JASL, and MAMS conceived and designed the study. AS performed the experiments and analyzed the data. AS and MCGM wrote the paper. MCGM, ASM, JASL, and MAMS reviewed and edited the manuscript. All authors read and approved the manuscript.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no competing interests.

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