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Research article

Improvement of anaerobic digestion of sewage sludge through microwave pre-treatment

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ABSTRACT

Sewage sludge generated in the activated sludge process is a polluting waste that must be treated adequately to avoid important environmental impacts. Traditional management methods, such as landfill disposal or incineration, are being ruled out due to the high content in heavy metal, pathogens, micropolluting compounds of the sewage sludge and the lack of use of resources. Anaerobic digestion could be an interesting treatment, but must be improved since the biomethanisation of sewage sludge entails low biodegradability and low methane production. A microwave pre-treatment at pilot scale is proposed to increase the organic matter solubilisation of sewage sludge and enhance the biomethanisation yield. The operational variables of microwave pre-treatment (power and specific energy applied) were optimised by analysing the physicochemical characteristics of sewage sludge (both total and soluble fraction) under different pre-treatment conditions. According to the variation in the sCOD and TN concentration, the optimal operation variables of the pre-treatment were fixed at 20,000 J/g TS and 700 W. A subsequent anaerobic digestion test was carried out with raw and pre-treated sewage sludge under different conditions (20,000 J/g TS and 700 W; 20,000 J/g TS and 400 W; and 30,000 J/g TS and 400 W). Although stability was maintained throughout the process, the enhancement in the total methane yield was not high (up to 17%). Nevertheless, very promising improvements were determined for the kinetics of the process, where the r_G and the OLR increased by 43% and 39%, respectively, after carrying out a pre-treatment at 20,000 J/g TS and 700 W.

1. Introduction

Sewage sludge is generated in the activated sludge process, which is one of the most commonly used treatment technologies in municipal and industrial wastewater treatment plants (WWTPs), and whose management represents a problem of growing importance around the world (Appels et al., 2013). The management of sewage sludge is an expensive and environmentally sensitive problem given that this waste contains heavy metals, organic micropollutants and pathogens, which have led to stringent legislation for sewage sludge applications (Hendrickx, 2009).

Anaerobic digestion is one of the available technologies for the treatment of sewage sludge given that it permits recovering energy in the form of methane, reducing mass and pathogens and removing odours (Pilli et al., 2011). Nevertheless, this technology presents several disadvantages for treating sewage sludge such as low methane production and biodegradability, along with an unfavourable kinetics of the process as the hydrolysis of this waste is slow (Bolzonella et al., 2005; Ortega et al., 2008). Moreover, variations in operational variables such as organic loading rate might cause perturbations in the inoculum/substrate ratio and lead to system failure (Labatut and Gooch, 2012; Raposo et al., 2009). This problem could be associated particularly to tourist areas or management plants which have to treat occasional organic overloads and where there are important seasonal variations in the influent to be treated, thus increasing the sewage sludge flow. To deal with the problems of daily, weekly and seasonal influent load variations, it was a tradition for many years to design oversized WWTPs to guarantee good effluent quality without much process adjustment (Gernaey et al., 1998). Nevertheless, because oversizing entails important additional investment costs, this alternative should be avoided in order to ensure the economic sustainability of

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Nomenclature

Alk	alkalinity (mg $CaCO_3$/L)
C_2	acetic acid (mg C_2/L)
COD	chemical oxygen demand (g O_2/kg)
D.L.	detection limit
FS	total fixed solids (g/kg)
GAL	glucose, sodium acetate and lactic acid solution
$N-NH_4^+$	ammoniacal nitrogen (mg/kg)
OLR	organic loading rate (g VS/L·d)
r_G	methane production rate (mL_{STP}/L·d)
sCOD	soluble chemical oxygen demand (g O_2/kg; mg O_2/kg; mg O_2/L)
STP	standard temperature and pressure conditions (0 °C, 1 atm)
t_{80}	time required to reach 80% of the total methane production (d)
TN	soluble total nitrogen (mg/kg; mg/L)
TOC	total soluble organic carbon (mg/kg)
TS	total solids (g/kg)
VA	volatile acidity (mg C/L; mg C_2/kg; mg C/kg)
VS	total volatile solids (g/L; g/kg)
$Y_{CH4/S}$	methane yield coefficient (mL_{STP} CH_4/g VS)
WWTP	wastewater treatment plant

the treatment process.

As a suitable alternative for sewage sludge management, several authors have proposed the application of different pre-treatments, such as thermal, freeze/thaw, ultrasonic and/or chemical treatments in order to facilitate the hydrolysis of this waste and reduce the hydraulic retention time (Carrère et al., 2010; Carlsson et al., 2012; Martín et al., 2015). Therefore, it might be possible to treat larger amounts of sewage sludge in the same plant through the implementation of a pre-treatment step before anaerobic digestion. Moreover, this pre-treatment system could operate only when deemed necessary.

Microwave pre-treatment is one of the pre-treatment methods proposed in the literature for the solubilisation of sewage sludge and the enhancement of biogas production during biomethanisation. However, due to the diversity of the reported results, the suitability of implementing a microwave pre-treatment is not clear. Several authors have described a positive effect of microwave pre-treatment on biogas production as a consequence of the effective solubilisation of the organic matter during the process. This technique combines the effect of increasing temperature, as usually occurs with the application of other conventional thermal pre-treatments, and the disintegration of different compounds by the breakage of hydrogen bonds attributed to the rapidly changing dipole orientation in the polarised side chains of the cell membrane macromolecules (Park et al., 2004; Appels et al., 2013). Kuglarz et al. (2013), for example, reported an improvement in methane production of around 41–52% under temperatures of 60–70 °C after a microwave pre-treatment at 700 W or 900 W, with times from 58 to 493 s. Other authors have reported that the energy consumption of the pre-treatment is not compensated by the low methane enhancement (Mottet et al., 2009; Ariunbaatar et al., 2014). Nevertheless, most of these studies focus only on the variation in the soluble fraction of sewage sludge and the effect on biogas production or the energy balance between the pre-treatment requirements and the energy derived from the obtained methane. However, it is also necessary to evaluate the enhancement of the treatment capacity after applying this pre-treatment in order to increase the flexibility of the system for seasonal or occasional variations in the flow rate and characteristics of sewage sludge. Moreover, the implementation of a microwave pre-treatment could be very interesting to reduce the investment costs of enlarging plants or avoiding extra operational costs due to the oversizing of digesters.

The main purpose of this study is to optimize the microwave pre-treatment of sewage sludge at laboratory scale and evaluate its effects on a subsequent biomethanisation process, focussing on stability, methane production yield and particularly the kinetics of the process.

2. Materials and methods

2.1. Chemical analyses

The following parameters were determined in the solid fraction of sewage sludge before and after pre-treatment: total chemical oxygen demand (COD, g O_2/kg), total solids (TS, g/kg), total fixed solids (FS, g/kg), total volatile solids (VS, g/kg) and ammoniacal nitrogen ($N-NH_4^+$, mg/kg). Soluble chemical oxygen demand (sCOD, g O_2/kg), pH and conductivity (mS/cm) were also analysed to characterise the soluble fraction of the substrate. All analyses were carried out 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 (Thompson et al., 2001). Additionally, total soluble organic carbon (TOC; mg/L) and total soluble nitrogen (TN, mg/L) were analysed using a Shimadzu TOC-VCPH combustion/non dispersive infrared analyser, which was calibrated with a standard solution of potassium phthalate prior to the TOC analyses. Separate volatile fatty acids (acetic, propionic, butyric, isobutyric, valeric, isovaleric and caproic acids) were also determined in the sewage sludge after extraction with distilled water (Thompson et al., 2001). The determination was carried out using a Hewlett- Packard HP-5890 gas chromatograph equipped with a 15 m × 0.53 mm (i.d.) Nukol-silica semicapillary column and a flame ionisation detector. The oven temperature was gradually increased from 100 to 150 °C at a rate of 4 °C/min. Helium (28.6 kPa) was used as carrier gas at a flow rate of 50 mL/min. Hydrogen (14.3 kPa) and air (28.6 kPa) were used together to ignite the flame of the FID. Additionally, the following parameters were determined in the effluents of the anaerobic reactors: pH, COD (g O_2/kg), sCOD (mg O_2/kg), TS (g/kg), FS (g/kg), VS (g/kg), TOC (mg/L), volatile acidity (VA, mg C/L), conductivity (mS/cm) and alkalinity (Alk, mg $CaCO_3$/L). All analyses were carried out in accordance with the Standard Methods of the APHA (APHA, 1989). Separate volatile fatty acids were also determined in the effluents of the digesters by the chromatographic method described previously.

2.2. Substrate

The raw material used as substrate was sewage sludge collected from the COPERO urban WWTP (Seville, Spain). A percentage as high as 85–90% of the influent of this WWTP is composed of municipal wastewater. The rest of the influent is industrial wastewater mainly derived from the agri-food industry. This WWTP generates sewage sludge at a flow rate of 500 tonnes per year, on dry basis. The sewage sludge was composed of primary and secondary sludge. The main analytical characteristics of the substrate are shown in Table 1. The sewage sludge was collected at different times from the WWTP to ensure it was fresh and to avoid uncontrolled fermentation process due to storage in the laboratory. Nevertheless, some variations in the physicochemical

Table 1
Analytical characterisation of the sewage sludge (wet weight basis) throughout the experimental time and the inoculum.

	Sewage sludge (04/28/2014)	Sewage sludge (06/04/2014)	Inoculum
pH	6.45 ± 0.04	6.71 ± 0.05	7.48 ± 0.01
Conductivity (mS/cm)	7.08 ± 0.08	2.82 ± 0.09	7.32 ± 0.01
Moisture (%)	97.7 ± 0.1	97.1 ± 0.1	98.5 ± 0.1
sCOD (g O_2/kg)	8625 ± 50	1835 ± 50	–
TS (g/kg)	22,785 ± 370	29,000 ± 450	14,735 ± 85
FS (g/kg)	5640 ± 310	5710 ± 360	4940 ± 145
VS (g/kg)	17,145 ± 200	23,290 ± 760	9795 ± 90
N–NH_4^+ (mg/kg)	1070 ± 25	560 ± 25	1065 ± 10
TN (mg/kg)	1345 ± 15	305 ± 13	894 ± 5
TOC (mg/kg)	3130 ± 140	595 ± 70	394 ± 1

characterisations were observed.

2.3. Experimental set-up

2.3.1. Microwave pre-treatment

The microwave device used to pre-treat the sewage sludge consisted of an experimental pilot microwave designed specifically for this purpose that can operate at different powers within the range of 100–900 W. The system is controlled by a computer with its own software to regulate the operational variables (time and power), as well as monitor the temperature inside the system. Aliquots of 100 g of sewage sludge, which were contained in an open container, were pre-treated under each operational condition. The pre-treatment assays were performed by fixing two different powers, 400 W and 700 W, while the specific energy applied was increased from 0 to 30,000 J/g TS in both cases. Highest powers could not be selected because the system reached the alarm temperature (100 °C) during the pre-treatment step, while lower powers lead to an unnecessary increase of pre-treatment time. Other intermediate powers were not selected as non-significant differences among results might be detected.

The samples were analysed before and after each assay and each sample was analysed in triplicate.

2.3.2. Anaerobic digestion

The experimental set-up used for the anaerobic digestion of pre-treated sewage sludge consisted of eight 1.0-L Pyrex complete mixing reactors working under mesophilic temperature (35 °C) in batch mode. The reactors were equipped with four connections to load feedstock, ventilate the biogas, inject inert gas (nitrogen) to maintain the anaerobic conditions and remove effluent. The content of the reactors was magnetically stirred and temperature was maintained at 35 °C by a thermostatic jacket containing water. The volume of methane produced during the process was measured using 1.0-L Boyle-Mariotte reservoirs connected to each reactor. To remove the CO_2 produced during the process, tightly closed bubblers containing a NaOH solution (6 N) were connected between the two elements. The volume of methane displaced an equal measurable volume of water from the reservoirs, which was measured with a test tube. This volume was corrected in order 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 from the COPERO plant (Table 1). The methane production rate of the inoculum was found to be 44 mL_{STP} CH_4/(g VS·h) (Field et al., 1988).

2.3.2.1. Anaerobic digesters. Experimental procedure. The anaerobic reactors were initially loaded with 7.8 g VS/L of anaerobic sludge. In order to bio-stimulate the inoculum prior to the experiments and to determine methanogenic activity, the reactors were first fed with a synthetic solution composed of glucose, sodium acetate and lactic acid (GAL) at concentrations of 50 g/L, 25 g/L and 21 mL/L, respectively. During this initial period, the organic load added to the reactors was gradually increased from 0.50 to 1.50 g VS/L over a 15-day period.

Several sets of experiments using raw and pre-treated sewage sludge were carried out in batch mode in such a manner that the load added to the digesters was increased from 1.0 g VS/L to 5.0 g VS/L, with intervals of 0.50 g VS/L in each assay. Each load was assayed at least in triplicate. In all cases, the volume of methane was measured as a function of time and samples were taken and analysed before and after feeding. The solid fraction of digestate (which included microorganisms and non-biodegraded substrate) was recovered from the samples by centrifugation at 2000 rpm and recirculated into the digesters. The duration of each experiment was equal to the time interval required for maximum gas production and VS removal. In the experiments with the highest loads, this time was up to 80 h. All the experiments, including start-up, biomass acclimatisation and waste treatment, were carried out over a 90-day period.

2.4. Calculation

2.4.1. Organic loading rate

The organic loading rate (OLR) relates the amount of waste added to the reactors with the reactor volume and time. The operational conditions used in this study allow the added substrate to be biomethanised as much as possible. Consequently, OLR was calculated considering the substrate concentration added to the reactors and the time required to reach 80% of the total methane production for each load.

$$OLR = \frac{[Added\ load]}{t_{80}} \tag{1}$$

where *[Added load]* is the concentration of sewage sludge added to the reactors (g VS/L) and t_{80} is the time required (d) to reach 80% of the total methane production for each load. This methane production percentage was selected to extrapolate the results obtained in discontinuous mode to a full-scale plant which usually operates in continuous or semi-continuous mode.

2.4.2. Methane production rate

The methane production rate values (r_G) were determined from t_{80} (d), the methane volume (G; mL_{STP}) generated at t_{80} and considering the volume of the reactor (V; L) according to equation (2):

$$r_G = \frac{G}{V \cdot t_{80}} \tag{2}$$

2.5. Software

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

3. Results and discussion

3.1. Solubilisation of organic matter through microwave pre-treatment

As described previously, the solubilisation of organic matter is the main objective of microwave pre-treatment. Solubilisation was measured through the variation in sCOD, TOC and TN in the soluble fraction of the sewage sludge for each pre-treatment condition.

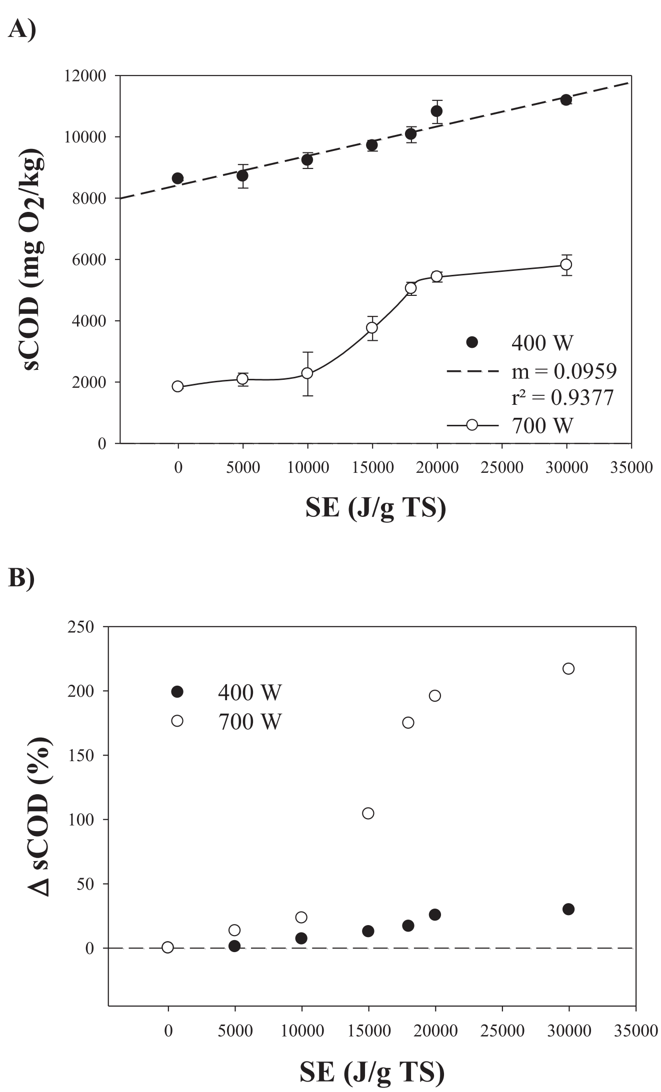

Fig. 1. **(A)** Variation in sCOD (mg O_2/kg) with specific energy applied (J/g TS). **(B)** Percentage of variation in sCOD (%) with the specific energy applied (J/g TS).

Fig. 1A shows the variation in the concentration of sCOD (mg O_2/kg) in the sewage sludge after carrying out a microwave pre-treatment under different operational conditions (different specific energy applied and power). As can be seen, the sCOD content in sewage sludge was enhanced at increasing the specific energy applied for both powers. Specifically, the sewage sludge pre-treated at 400 W showed an increase in sCOD from around 8600 mg O_2/kg to 11,175 mg O_2/kg for specific energy inputs from 0 to 30,000 J/g TS, respectively. For this applied power, the increase in sCOD in the sewage sludge is virtually linear at increasing the specific energy ($r^2 = 0.9377$). Nevertheless, in the pre-treatment of sewage sludge at 700 W, sCOD increased markedly at specific energy inputs higher than 10,000 J/g TS, reaching a mean value of 5620 ± 270 mg O_2/kg at specific energy inputs higher than 20,000 J/g TS, while the sCOD without pre-treatment was 1835 ± 50 mg O_2/kg. Therefore, higher energy inputs are not recommended given that more energy consumption does not entail higher waste solubilisation. By relating the highest variation in sCOD to the solid concentration of the raw sewage sludge, an enhancement of 0.113 and 0.137 mg O_2/g TS was obtained at 400 W and 700 W, respectively. This indicates that pre-treatment at 700 W is more effective, even with a higher initial solid concentration (around 21% higher). Fig. 1B shows the variation of sCOD in % for each power at different specific energy inputs. As can be seen, there is a significantly higher increase at 700 W, which rose to 215%, while the variation was very limited at 400 W, reaching a variation of only around 25% and 30% for a specific energy input of 20,000 J/g TS and 30,000 J/g TS, respectively. These results are in line with those described by Appels et al. (2013), who reported an increase in sCOD of around 214% after carrying out a microwave pre-treatment at 800 W and a specific energy applied of around 8300 J/kg TS. This shows that higher power could allow the reduction of the specific energy required for the process. Nevertheless, it is necessary to assess the feasibility of the implementation of this pre-treatment through an anaerobic digestions test since solubilisation does not necessary entail enhanced methane production. This fact might be a consequence of the low biodegradability of the solubilized compounds, which might even be inhibitors (Climent et al., 2007; Carlsson et al., 2012).

In addition, Fig. 2 shows the variation in the TN concentration (mg/kg) in the sewage sludge after carrying out the microwave pre-treatment. The increases observed in TN concentration were around 290 and 420 at 400 W and 700 W, respectively, for the different specific energies applied. By relating these variations with the total solid concentration of the raw sewage sludge, the net

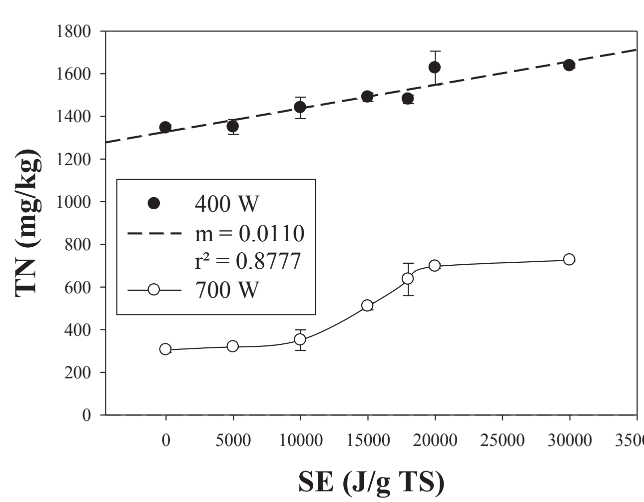

Fig. 2. Variation in TN (mg/kg) with specific energy applied (J/g TS).

solubilisation of TN was 0.0127 and 0.0145 mg TN/g TS at 400 W and 700 W for the highest specific energies applied, respectively. The difference at both powers is equivalent to that obtained for the solubilisation of COD, thus implying that the microwave pre-treatment affects the whole substrate.

Fig. 3A and B shows the relation between soluble organic matter and nitrogen for each assay independently of the pre-treated sewage sludge (see Table 1). As can be seen, the pairs of sCOD-TOC and TN-sCOD points can be fitted to a straight line in both cases. Therefore, the increase in the carbon present in the soluble fraction is proportional to the solubilisation of nitrogen, indicating that the pre-treatment had an effect over the whole substrate. More specifically, the proportion between sCOD and TOC remains constant at around 2.64 mg COD/mg TOC for the different assays, which is very close to the theoretical oxygen demand. Likewise, the TN/sCOD ratio also remains virtually constant in a proportion around 0.15 mg TN/mg COD. In comparison to the same ratio obtained from the initial characterisation of the raw sewage sludge, it can be observed that the pre-treatment maintained the proportion between both nutrients (nitrogen and organic matter) in liquid phase. This fact corroborates that the microwave pre-treatment is not selective to the solubilisation of a specific type of compound, but affects the whole solid substrate.

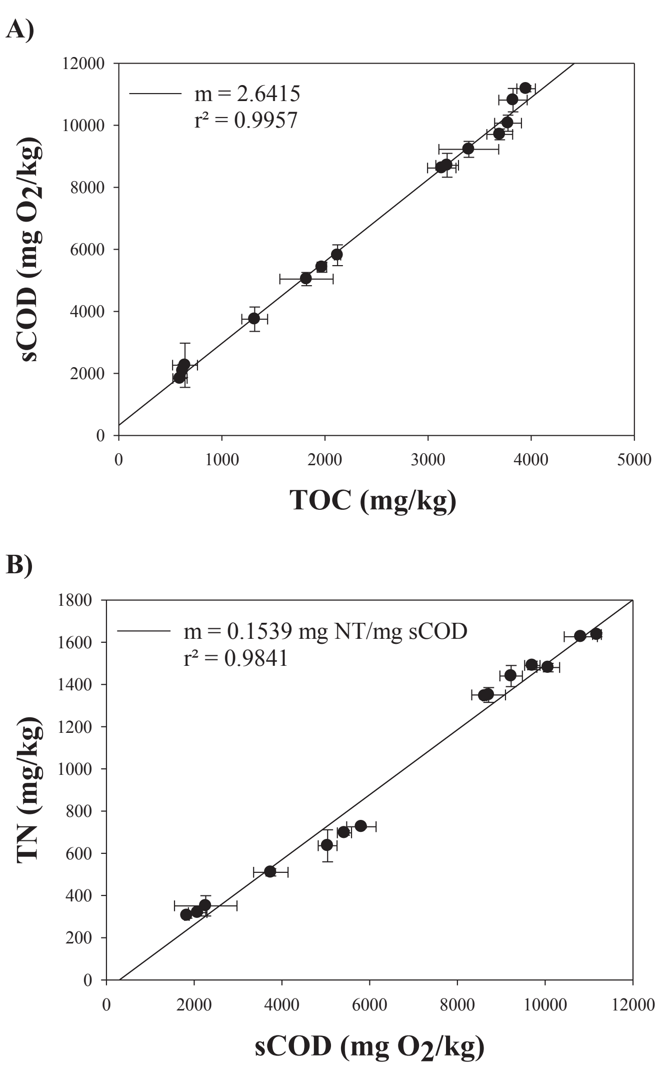

Fig. 3. **(A)** Plot of sCOD (mg O_2/kg) against the TOC (mg/kg) for pre-treatments at 400 W and 700 W. **(B)** Plot of TN (mg/kg) against the sCOD (mg O_2/kg) for pre-treatments at 400 W and 700 W.

3.2. *Effect of microwave pre-treatment over the volatile acid concentration*

The increase in VA (especially acetate) in the waste is directly related to methane yield improvement (Tiehm et al., 1997). Therefore, the concentration of short chain organic volatile acids (C_2–C_6) was determined in the sewage sludge samples after carrying out the pre-treatment under different conditions. Table 2 shows the C_2–C_6 concentration values for each specific energy and power applied to the sewage sludge. As can be seen, the initial VA concentration (sewage sludge without pre-treatment) was markedly higher for the sewage sludge treated at 400 W than 700 W (in accordance with the higher sCOD). However, according to the variation in VA after each pre-treatment, 400 W pre-treatments increased the C_2–C_6 VA concentration from 3890 ± 60 mg C_2/kg to 4740 ± 103 mg C_2/kg, while 700 W pre-treatments enhanced this concentration from 563 ± 32 mg C_2/kg to 1546 ± 36 mg C_2/kg. These variations led to increases of around 22% and 175%, respectively. Furthermore, the enhancement of specific energy entailed an increase in the VA up to values of around 20,000 J/kg TS, while higher specific energy was not very effective at either applied powers. These VA generation values were higher than the results obtained by Park and Ahn (2011), who reported an increase of around 10% in the VA concentration after a pre-treatment of 1000 W at 4 min. This difference might be explained by the maximum temperature fixed by these authors (80 °C), while in the present research work the temperature was fixed at 100 °C. Furthermore, the increase in VA concentration entails a decrease in the pH values of the sewage sludge. This decrease was more marked for the sewage sludge pre-treated at 700 W, whose pH varied from 6.71 ± 0.05 to 6.50 ± 0.09, in line with the higher increase in the VA. Nevertheless, pH values remained virtually constant in the sewage sludge pre-treated at 400 W with a mean value of 6.44 ± 0.02. Therefore, although the pre-treatment would entail the higher availability of easily biodegradable compounds and an increase in VA concentration, the decrease in the pH in the substrate could lead to the risk of acidification of the subsequent biomethanisation process (Motte et al., 2015).

It is also important to note that the increase in VA concentration was in line with the higher effect on the sCOD and TOC concentrations described in Section 3.1. Fig. 4 shows the linear relation between the VA and TOC concentration after carrying out each pre-treatment. As can be seen, most of the 85% of the value pairs fit correctly to a straight line within a confidence interval of 95%. Moreover, the slopes of the straight lines, which depend on the relation between the C_2–C_6 VA and TOC, indicate the VA yield from the solubilisation processes. Specifically, the VA yield was 0.3558 mg C_{VA}/mg TOC and 0.2105 mg C_{VA}/mg TOC for 400 W and 700 W, respectively. As can be seen, the ratio mg C_{VA}/mg TOC for 400 W is markedly higher than the values obtained for 700 W (in absolute values). This fact indicates that after carrying out the pre-treatment at 400 W more soluble compounds were in the form of volatile acids. Nevertheless, in relative terms the highest percentage improvement of VA corresponded to 700 W, as previously mentioned, due to the initial organic matter concentration in each substrate.

3.3. *Stability of anaerobic digestion of pre-treated and raw sewage sludge*

Once the microwave pre-treatment conditions were optimised with the experimental set-up used, the anaerobic digestion of raw

Table 2
Separate organic volatile acid concentration (mg C_2/kg) for each pre-treatment condition.

EE (J/g TS)	C_2	C_3	C_4	iC_4	C_5	iC_5	C_6
400 W							
0	1885 ± 19	981 ± 2	438 ± 10	213 ± 8	145 ± 4	230 ± 16	< D.L.
5000	950 ± 31	1028 ± 26	449 ± 3	240 ± 4	180 ± 2	259 ± 15	< D.L.
10,000	2001 ± 75	1077 ± 13	474 ± 21	248 ± 4	189 ± 4	286 ± 8	< D.L.
15,000	2099 ± 55	1089 ± 14	483 ± 11	255 ± 4	191 ± 2	287 ± 4	< D.L.
18,000	2182 ± 32	1135 ± 16	501 ± 6	263 ± 2	201 ± 16	311 ± 1	< D.L.
20,000	2199 ± 7	1160 ± 44	495 ± 34	271 ± 14	180 ± 5	285 ± 17	< D.L.
30,000	2331 ± 81	1185 ± 81	464 ± 14	294 ± 25	182 ± 13	284 ± 24	< D.L.
700 W							
0	298 ± 42	156 ± 25	37 ± 7	40 ± 6	< D.L.	32 ± 5	< D.L.
5000	628 ± 58	155 ± 14	< D.L.	< D.L.	< D.L.	37 ± 2	< D.L.
10,000	560 ± 38	218 ± 28	81 ± 5	114 ± 11	62 ± 3	41 ± 3	< D.L.
15,000	785 ± 28	345 ± 17	81 ± 4	116 ± 9	< D.L.	51 ± 2	< D.L.
18,000	814 ± 49	331 ± 11	86 ± 4	166 ± 12	85 ± 7	52 ± 1	< D.L.
20,000	822 ± 51	264 ± 15	160 ± 4	155 ± 13	45 ± 3	52 ± 4	< D.L.
30,000	884 ± 38	335 ± 18	130 ± 8	142 ± 11	< D.L.	55 ± 5	< D.L.

*D.L.: Detection limit.

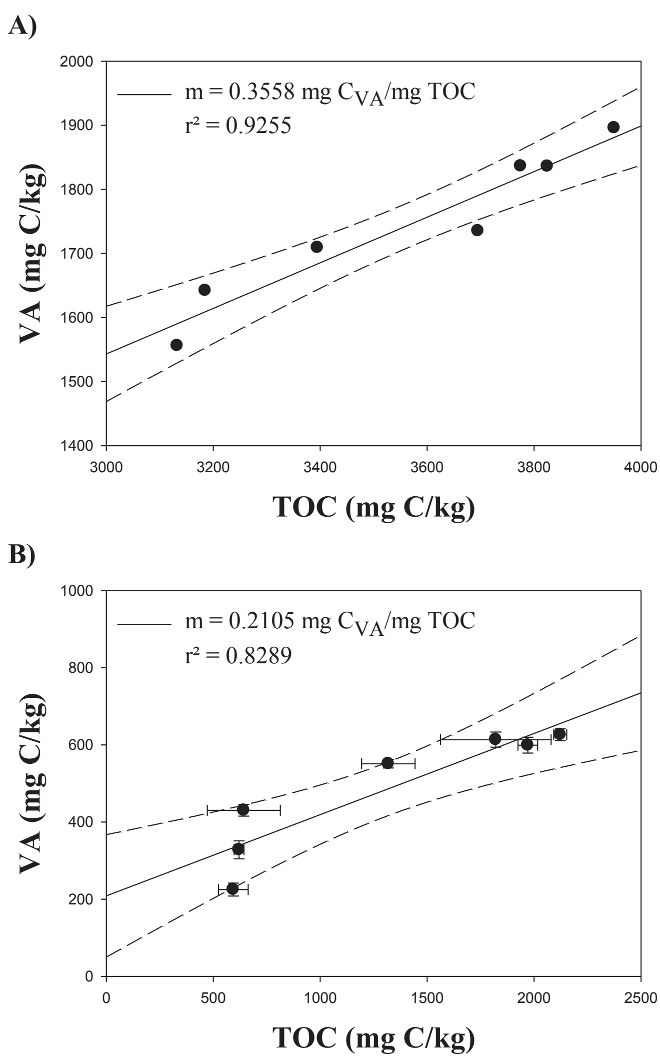

Fig. 4. Plot of the VA (mg C/kg) against the TOC (mg C/kg) for pre-treatments at 400 W **(A)** and at 700 W **(B)**.

and pre-treated sewage sludge was investigated to evaluate the variation in the treatment operational variables related with time and the added organic load. In accordance with the results obtained previously, the operational variables fixed for the pre-treatment of sewage sludge are described in Table 3. These operational variables were selected according to the variations in the soluble compounds described previously, ensuring maximum solubilisation without the unnecessary waste of energy. The reactors treating the raw sewage sludge were operated as a reference to determine the effect of the microwave pre-treatment over the biomethananogenic potential of the sewage sludge. Firstly, the stability of biomethanisation of the raw and pre-treated sewage sludge was monitored through the variation in pH, alkalinity, VA and sCOD in the digesters at the end of each load. Fig. 5A shows the variation in pH against the added load for the different pre-treatment conditions. As can be seen, the pH values were similar for the raw and the pre-treated sewage sludge under the different conditions, with values slightly higher than the optimal for methanogenic activity at the lowest loads (Wheatley, 1990; Liu et al., 2008). The highest pH values determined for the pre-treated sewage sludge were a consequence of the highest alkaline values. Specifically, the mean alkalinity values for loads of 1 g VS/L were 5475 ± 5 mg $CaCO_3$/L and 6440 ± 75 mg $CaCO_3$/L for the raw and pre-treated sewage sludge, respectively. No significant differences in the pH or alkalinity values were observed between the different pre-treatment conditions. Alkalinity was due to the presence of inorganic carbon in the form of carbonate and bicarbonate, as well as the solubilisation of different compounds such as nitrogen. In fact, the TN concentration increased from around 946 ± 26 mg/L to 1500 ± 5 mg/L (an enhancement higher than 55%). Furthermore, Fig. 5B shows the VA/Alk ratio values for the different added loads with raw and pre-treated sewage sludge. As can be seen, the values were markedly lower than 0.30–0.40, which are the limits established for the correct operation of anaerobic digestion processes without the risk of acidification (Balaguer et al., 1992). Therefore, the proposed pre-treatments did not entail the acidification of the process as a consequence of the solubilisation of acidic compounds.

Although acidification processes were not detected, Fig. 6A shows the accumulation of soluble compounds in the digesters at

Table 3
Operational variables fixed to pre-treat the sewage sludge fed to each digester.

Exp. No.	Power (W)	SE (J/g ST)	Pre-treatment time (s)
1	0	0	0
2	400	30,000	173
3	400	20,000	115
4	700	20,000	66

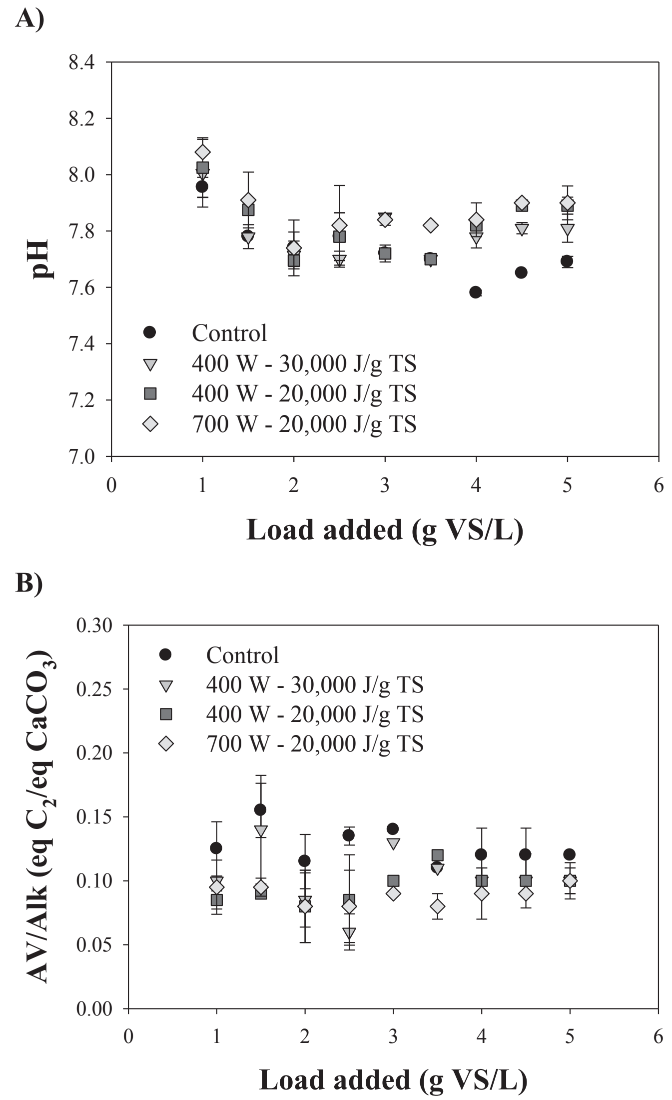

Fig. 5. Variation in pH (A) and VA/Alk ratio (eq acetic acid/eq $CaCO_3$) (B) with the load added to the reactors (g VS/L).

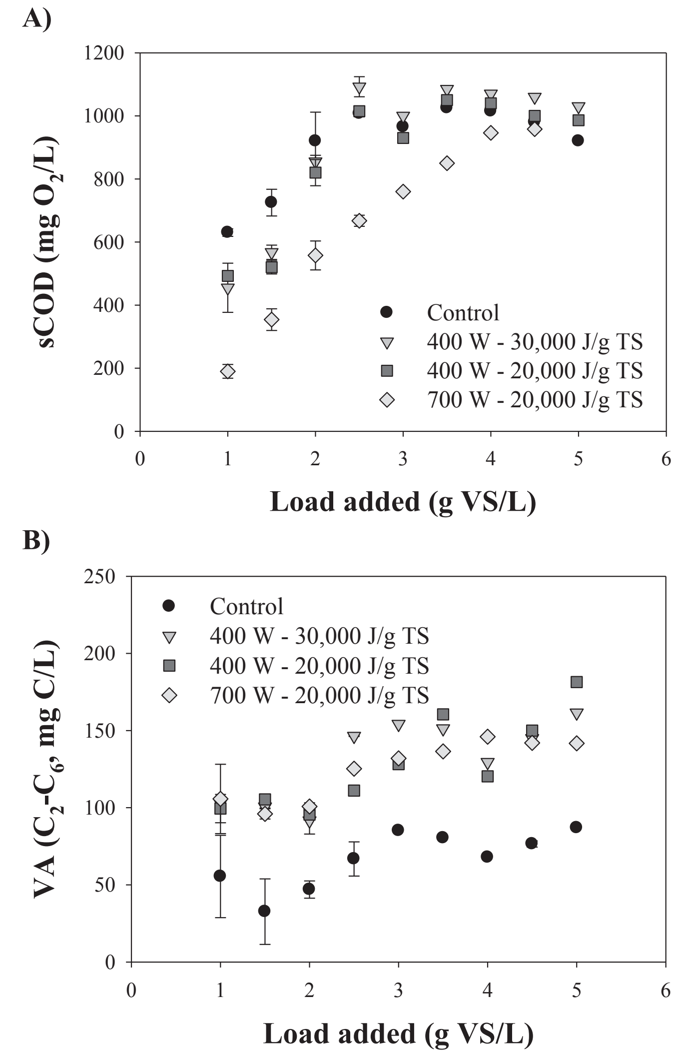

Fig. 6. Variation in sCOD (mg O_2/L) **(A)** and VA (C_2–C_6) (mg C/L) **(B)** with the load added to the reactors (g VS/L).

increasing the added load for the different pre-treatment conditions. The sCOD increased from 200 mg O_2/L to 1100 mg O_2/L. This behaviour was similar for the raw sewage sludge and the proposed pre-treatments. Specifically, Fig. 6B shows that the accumulation of VA in the digesters was lower than 100% of the initial concentrations in all cases. Therefore, the accumulation of soluble compounds might primarily correspond to complex or non-biodegradable soluble compounds, while most short chain acids were degraded during the biomethanisation process. Moreover, the VA concentration was lower in the digesters fed with raw sewage sludge, in line with the solubilisation of these compounds in the pre-treatment step of the sewage sludge feed to the other digesters.

3.4. Methane production yield and kinetics

One of the main objectives of carrying out a pre-treatment step prior to the biomethanisation of sewage sludge is the enhancement of the methane yield coefficient ($Y_{CH4/S}$) and the kinetics of the process. In this regard, the enhancement of the methane yield obtained through the proposed microwave pre-treatment was quite low. Concretely, the methane yield coefficient obtained for raw sewage sludge was 111 ± 4 mL_{STP} CH_4/g VS, while the application of a microwave pre-treatment of 20,000 J/kg TS entailed an enhancement in methane yield coefficient of up to only 118 ± 5 mL_{STP} CH_4/g VS at both powers (around 6% higher). The increase in applied specific energy to 30,000 J/kg TS entailed a methane yield coefficient of 130 ± 6 mL_{STP} CH_4/g VS; an enhancement of up to 17%. Considering that mean EU-28 electricity price for industry in 2014 was EUR 0.12 per kWh, the application of proposed microwave pre-treatment could entail an energy cost from 0.67 to 1.00 €/kg of dry substance (EUROSTAT, 2016). These costs are higher than the required by other pre-treatments systems such as the sonication system described by Martín et al. (2015), who reported an energy requirement of 0.43 €/kg of dry substance after the optimization of the pre-treatment conditions. Therefore, it could be highly recommended to optimize the energy consumption of the microwave pre-treatment to make its implementation more attractive.

Although the total methane production might indicate that the sewage sludge pre-treatment is not viable, the enhancement of the methane production rate (r_G) and the allowed organic loading rate must also be taken into account, given that at full-scale the operation is usually in continuous mode. Table 4 shows the r_G values obtained for different OLR for raw and pre-treated sewage sludge. As

Table 4
OLR and r_G for the different pre-treated sewage sludge added to the digesters.

Power (W)	Specific energy (J/g TS)	OLR (g VS/L·d)	r_G (mL_{STP}/L·d)
0	0	1.49 ± 0.31	145 ± 22
400	20,000	1.68 ± 0.36	169 ± 44
400	30,000	1.76 ± 0.33	201 ± 48
700	20,000	2.06 ± 0.20	206 ± 25

can be seen, significant differences can be obtained by pre-treating the sewage sludge before the biomethanisation step in both operational variables, especially for the pre-treatment at 700 W. Concretely, r_G reached a value of 145 ± 22 mL_{STP} $CH_4/L_{reactor}$·d in the treatment of raw sewage sludge, while the maximum r_G obtained for the sewage sludge pre-treated at 700 W reached a value of 206 ± 25 mL_{STP} $CH_4/L_{reactor}$·d (around 43% higher). The improvements obtained after pre-treating the sewage sludge at 400 W were lower, reaching percentages of improvement of 18% and 39% for pre-treatments of 20,000 and 30,000 J/kg TS, respectively. A similar behaviour could be described for the OLR. The OLR increased from 1.49 ± 0.31 g VS/$L_{reactor}$·d to 2.06 ± 0.20 g VS/$L_{reactor}$·d after carrying out the microwave pre-treatment at 700 W (an enhancement of up to 38%). Therefore, solubilisation by the microwave pre-treatment improved the hydrolysis of the sewage sludge and minimised the time required for this step. The hydrolysis of solid compounds leads to the generation of soluble COD partially in the form of VA, which are carbonaceous soluble compounds, and even acetate under intensive pre-treatment conditions. The biomethanisation process is improved as a consequence of the solubilisation of different compounds (affecting kinetics), and due to the type of compounds (improving the process yield). Presumably, in the light of the results the hydrolysis is the most influenced step as the physical state of the organic matter is markedly affected. This is especially interesting for WWTPs with marked seasonal variations in the volume of wastewater and hence the sewage sludge to be treated, such as those in tourist areas, or to absorb occasional increases in the influent flow. The implementation of microwave pre-treatment technology might also be a suitable alternative to the oversizing of WWTPs, as it permits adapting pre-existing plants to higher influent wastewater flows.

4. Conclusions

The most relevant conclusions of this research are described in what follows:

- The soluble compounds increased at increasing the specific energy up to 20,000 J/g TS, which was considered the optimal specific energy. Higher energy input did not entail a greater solubilisation effect under the study conditions.
- At the different specific energies applied, solubilisation was more effective for a power of 700 W than at 400 W. Concretely, the increase in sCOD was 0.113 and 0.137 mg O_2/g TS at 400 W and 700 W, respectively.
- The microwave pre-treatment affected the whole organic matter, resulting in an increase in the TN of 0.0127 and 0.0145 mg TN/g TS at 400 W and 700 W. Moreover, the increase in the TOC and the TN shows a linear relation with the increase in sCOD.
- The increase in the soluble compounds did not compromise the stability of the biomethanisation process, which did not exceed the recommended thresholds at the different load concentrations.
- Although the enhancement in the total methane yield did not compensate the energy requirements of the pre-treatment step, the r_G and the OLR increased up to 43% and 39%, respectively.

Therefore, this technology could be a very interesting option for WWTPs with a variable sewage sludge flow to avoid oversizing in the plant design or to adapt pre-existing plants to higher influent flows, with the consequent economic and environmental benefits.

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