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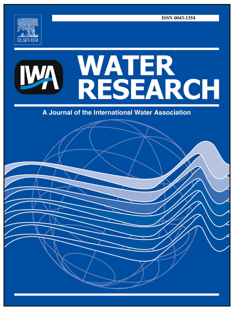

Effect of ultrasound, low-temperature thermal and alkali pre-treatments on waste activated sludge rheology, hygienization and methane potential

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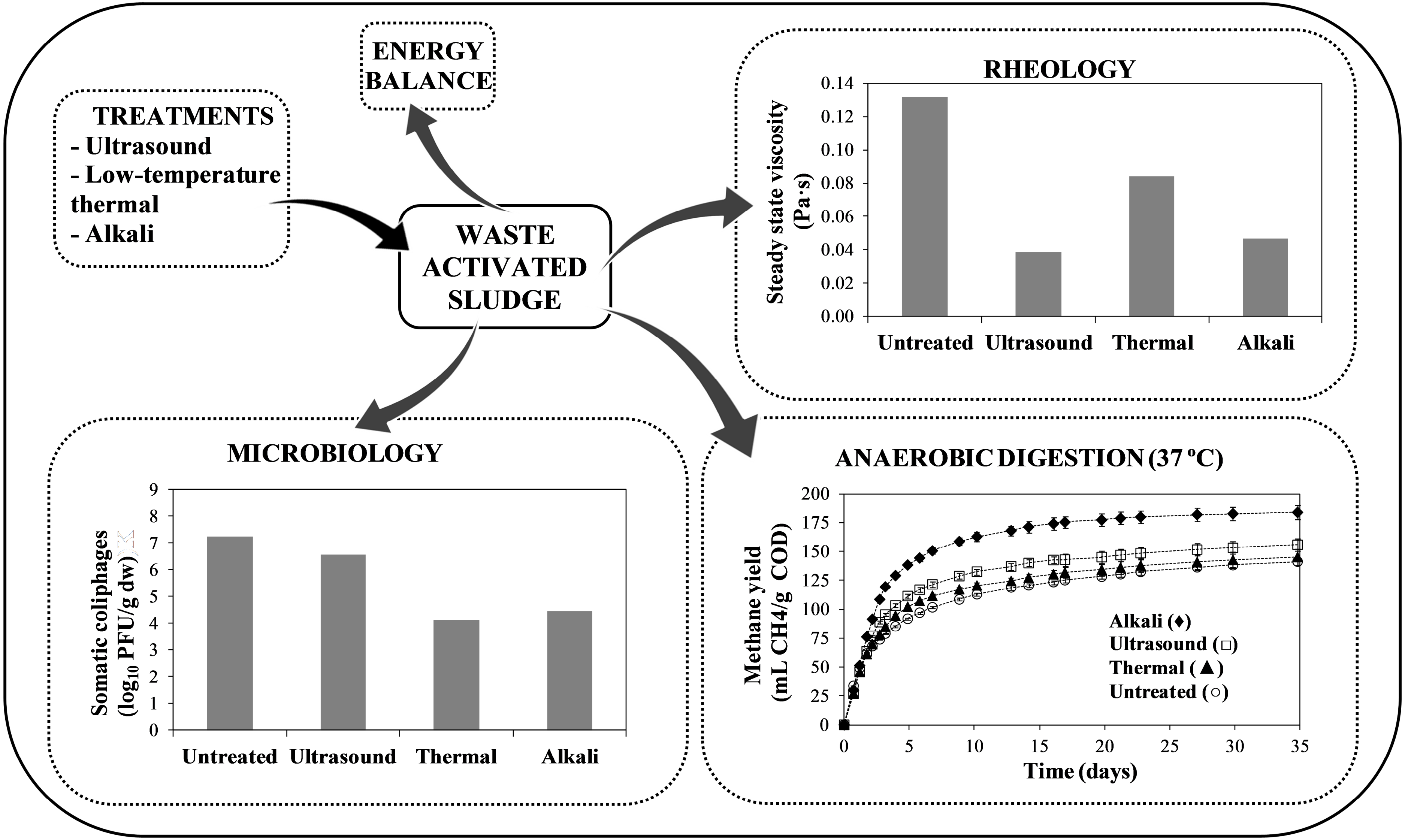
ENERGY BALANCE
TREATMENTS
- Ultrasound
- Low-temperature thermal
- Alkali
WASTE ACTIVATED SLUDGE
RHEOLOGY
Steady state viscosity (Pa·s)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Untreated
Ultrasound
Thermal
Alkali
MICROBIOLOGY
Somatic coliphages (log10 PFU/g dw)
9
8
7
6
5
4
3
2
1
0
Untreated
Ultrasound
Thermal
Alkali
ANAEROBIC DIGESTION (37 ºC)
Methane yield (mL CH4/g COD)
200
175
150
125
100
75
50
25
0
Alkali (♦)
Ultrasound (□)
Thermal (▲)
Untreated (○)
0
5
10
15
20
25
30
35
Time (days)

Effect of ultrasound, low-temperature thermal and alkali pre-treatments on waste activated sludge rheology, hygienization and methane potential

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ABSTRACT

Waste activated sludge is slower to biodegrade under anaerobic conditions than is primary sludge due to the glycan strands present in microbial cell walls. The use of pre-treatments may help to disrupt cell membranes and improve waste activated sludge biodegradability. In the present study, the effect of ultrasound, low-temperature thermal and alkali pre-treatments on the rheology, hygienization and biodegradability of waste activated sludge was evaluated. The optimum condition of each pre-treatment was selected based on rheological criteria (reduction of steady state viscosity) and hygienization levels (reduction of *Escherichia coli*, somatic coliphages and spores of sulfite-reducing clostridia). The three pre-treatments were able to reduce the viscosity of the sludge, and this reduction was greater with increasing treatment intensity. However, only the alkali and thermal conditioning allowed the hygienization of the sludge, whereas the ultrasonication did not exhibit any notorious effect on microbial indicators populations. The selected optimum conditions were as follows: 27,000 kJ/kg TS for the ultrasound, 80 ºC during 15 min for the thermal and 157 g NaOH/kg TS for the alkali. Afterward, the specific methane production was evaluated through biomethane potential tests at the specified optimum conditions. The alkali pre-treatment exhibited the greatest methane production increase (34%) followed by the ultrasonication (13%), whereas the thermal pre-treatment presented a methane potential similar to the untreated sludge. Finally, an assessment of the different treatment scenarios was conducted considering the results together with an energy balance, which revealed that the ultrasound and alkali treatments entailed higher costs.

Keywords

Waste activated sludge; Anaerobic digestion; Pre-treatment, Rheology; Hygienization; Post-treatment

1. Introduction

Mesophilic anaerobic digestion (AD) of sewage sludge, which is a mixture of primary and waste activated sludge (WAS), is a commercial reality, due to the high biodegradability of primary sludge. However, WAS, which is primarily formed by microorganisms, is more difficult to degrade through AD due to the glycan strands present in the microbial cell walls (Appels et al., 2008). Accordingly, numerous disintegration methods (e.g., ultrasound, thermal or alkali) have been employed for pre-treatment under the assumption that these methods are capable of disrupting cell walls and therefore to release the intracellular organic material into the liquid phase (Appels et al., 2008; Farno et al., 2014). The hydrolysis produced by ultrasound conditioning is due to the generation of cavitation gas-bubbles (Tiehm et al., 2001), which grow to a critical size and violently collapse, producing significant hydro-shear strength, intense local heating and high pressures in the mass of the liquid surrounding the bubbles (Bougrier et al., 2006). Additionally, cavitation generates free radicals that contribute to cell wall disruption (Foladori et al., 2007). Thermal pre-treatment has also been used to facilitate the digestion of WAS to methane because it results in the breakdown of the gel structure of the sludge and the subsequent release of the intracellular organic matter (Neyens and Baeyens, 2003). Alkali pre-treatment is also considered an appropriate method for enhancing the biodegradation of complex organic matter (Lopez-Torres and Espinosa-Lloréns, 2008). The basis of this pre-treatment is that the alkali added to the sludge reacts with the cell walls in several ways, including a saponification of the lipids in the cell walls, which causes the disruption of the microbial cells (Neyens et al., 2003).

These pre-treatments may also have effects on sludge hygienization and therefore could be used as both pre-treatment and post-treatment, depending on the requirements of the wastewater treatment plant (WWTP). It is well-known that temperature (Mocé-Llivina et al., 2003; Ziemba and Peccia, 2011; Astals et al., 2012a) and alkali compounds (Allievi et al., 1994; Bujockzek et al., 2002) are capable in reducing the pathogen load of the sludge. In contrast, the effect of the ultrasonication is difficult to predict due to the complexity and several factors involving this treatment (Pilli et al., 2011). However, it has been reported that conventional bacterial indicators may not provide a precise indication of the fate of viruses and protozoa during sludge treatments because such pathogens survive the environmental stresses more successfully than the conventional indicators (Lucena et al., 1988; Payment and Franco, 1993). Therefore, the availability of new microorganisms able to overcome the limitations of conventional indicators is of major importance. Spores of sulfite-reducing clostridia (SSRC) have been proposed as alternative indicators of protozoan oocysts in water treatment (Payment and Franco, 1993) while bacteriophages of enteric bacteria (as somatic coliphages; SOMCPH) have been proposed as surrogates of waterborne viruses in water quality control processes (IAWPRC, 1991).

The aforementioned pre-treatments may also play an important role on WAS viscosity and filterability (Bougrier et al., 2006; Pham et al., 2010; Ruiz-Hernando et al., 2013). Accordingly, a proper understanding of the rheology, which is the discipline that addresses the deformation of fluids, is essential to control sludge treatment processes. WAS is considered a non-Newtonian fluid behaving as a pseudo-plastic fluid (Seyssiecq et al., 2007), which means that the viscosity decreases with the applied shear rate. The Ostwald–de Waele model is commonly used to represent the non-Newtonian behavior of sludge, most likely due to its simplicity and good fitting (Bougrier et al., 2006; Ratkovich et al., 2013). Other models, such as the Herschel-Bulkley model, the Bingham model or the Casson model are also valid (Estiaghi et al., 2013; Ratkovich et al., 2013). In contradistinction to the Ostwald–de Waele equation, these models are characterized by the presence of yield stress, below which the sample to analyze is not flowing. However, one fundamental problem with the concept of yield stress is the difficulty in determining the true yield stress (Labanda et al., 2007) because its determination is not univocal and can vary over a wide range depending on the equation used.

The aim of the present study is to compare the effect of ultrasound, low-temperature thermal and alkali pre-treatments on WAS rheology, hygienization and methane potential, in order to provide an overall view of feasible scenarios for WAS management. First, preliminary assays were conducted to obtain the optimum condition of each pre-treatment based on rheology (i.e., the reduction of steady state viscosity) and hygienization (i.e., the reduction of *E. coli*, SOMCPH and SSRC). Next, biomethane potential tests and the hygienization of the digested sludge were analyzed under the optimum conditions. The untreated digested sludge, obtained after 35 days of anaerobic digestion, was post-treated at the same optimum conditions applied to the pre-treatments. Finally, the economic feasibility of each treatment was conducted, and the various scenarios for sludge management were discussed.

2. Materials and Methods

2.1. Waste activated sludge and inoculum origin

The WAS and inoculum (i.e., digested sludge) samples used in this study were collected from a municipal WWTP in the Barcelona metropolitan area (Spain). At the WWTP, the

WAS was thickened by centrifugation after leaving the secondary tank. The WAS samples were collected weekly to guarantee the reliability of the microbiological tests. Samples were stored below 4 °C until their utilization.

2.2. Pre-treatments conditions

The pre-treatments studied in this research were ultrasound, low-temperature thermal and alkali. The ultrasonic apparatus used was an HD2070 Sonopuls Ultrasonic Homogenizer equipped with a MS 73 titanium microtip probe (Bandelin, Berlin, Germany; 20 kHz). The beaker containing the samples was submerged in an ice bath to prevent increases of sludge temperature due to the thermal effect of the cavitation phenomenon. The ultrasonic waves were applied at constant power and different application times to provide different specific energies (E_S): 5,000, 11,000 and 27,000 kJ/kg total solids (TS). The thermal pre-treatment was performed in a heating bath (Huber Polystat CC2) at two fixed temperatures, 70 and 80 ºC. The exposure times were 10, 20 and 30 min at 70 ºC, and 10, 15 and 30 min at 80 ºC. The time required to reach both temperatures were 10 min and was included in the exposure time, i.e., the exposure time of 15 min corresponds to 10 min heating ramp up + 5 min heating at 80 ºC. The reagent used for alkali conditioning was NaOH because it is cheaper and more efficient for sludge disintegration than KOH or $Ca(OH)_2$ (Li et al., 2008; Uma-Rani et al., 2012). The alkali pre-treatment was conducted at room temperature (approximately 25 ºC) by adding different doses of NaOH and a contact time of 24 h. Samples were subsequently neutralized with $HCl_{35\%}$ to reach a pH range of 6.5 to 7.5. The concentrations studied were 35.3, 70.6 and 157 g NaOH/kg TS. The effect of dilution due to the reagents was corrected by adding deionized water to the alkali-treated sludge samples in order to maintain a constant volume. The increase in salinity due to the alkali addition was not corrected.

The effect of the optimum condition of each pre-treatment on WAS solubilization was determined by: (i) the soluble chemical oxygen demand (sCOD) to total chemical oxygen demand (tCOD) percentage ratio (sCOD/tCOD×100) and (ii) the COD solubilization degree (SD) (Eq. 1; Table 1).

$$\mathrm{SD}\ (\%) = \frac{\mathrm{sCOD}_f - \mathrm{sCOD}_0}{\mathrm{tCOD}_0 - \mathrm{sCOD}_0} \cdot 100 \qquad (1)$$

where $sCOD_f$ is the soluble COD after the pre-treatment, $sCOD_0$ is the soluble COD before the pre-treatment and $tCOD_0$ is the total COD before the pre-treatment.

2.3. Microbiological tests

The occurrence and levels of two bacterial indicators (*E. coli* and SSRC) and one viral indicator (SOMCPH) were controlled in this research, by evaluating their indigenous populations in the sludge during the different treatment processes.

2.3.1. Bacterial enumeration

5 to 10 g of sludge were mixed in a 1:10 (W/V) ratio with phosphate buffered saline (PBS) solution at pH 7.2, homogenized with a wrist action shaker at 900 osc/min for 30 min at room temperature and centrifuged at 300 g for 3 min at 4 ºC. The resulting supernatant was utilized for analyzing both the *E. coli* and the SSRC present in the sample. For this purpose, serial dilutions were made. *E. coli* was tested by the pour plate procedure on Chromocult agar (Merck, Germany) supplemented with *E. coli*/coliforms-Selective Supplement (Merck,

Germany). Plates were incubated at 44 ºC overnight (O/N), and dark-blue/purple *E. coli* colonies were counted. For the SSRC present in the sample, the supernatant and dilutions were subjected to a thermal shock of 80 ºC for 10 min. Then, the samples were anaerobically cultured by mass inoculation in *Clostridium perfringens* selective agar (Scharlab, Spain) and finally incubated at 44º C O/N. The typical black spherical colonies with black halos were counted as SSRC. The analyses were performed in duplicate.

2.3.2. Bacteriophages enumeration

SOMCPH were extracted from sludge as described by Guzmán et al. (2007). Briefly, 5 to 10 g of the sludge sample was mixed in a 1:10 (W/V) ratio with a solution (pH 7.2) containing 10% beef extract powder (Becton Dickinson, France) and homogenized with a wrist action shaker at 900 osc/min for 30 min at room temperature. Next, the sample was centrifuged at 4,000 g for 30 min at 4 ºC. The supernatant was filtered through a 0.22 μm pore size polyethersulfone non-protein binding membrane filter (Millipore, USA). The permeate was analyzed for the presence of SOMCPH as indicated in the ISO 10705-2 standard (Anonymous, 2000). The analyses were performed in duplicate.

2.4. Rheological study

The rheometer used was a Haake RS300 control stress rheometer equipped with HAAKE Rheowin Software. The geometry used was a 4º cone and a flat stationary 35 mm-diameter plate. Measurements were conducted at 22.0 ± 0.1 ºC. The rheological behavior of the sludge under flow conditions was analyzed by shear rate step test, which consisted of shearing the sludge at a fixed shear rate for 15 minutes, time enough to reach the steady-state value (equilibrium value). The applied shear rates were: 5, 30, 125 and 300 s^{-1}. Steady-state shear stress, τ_e (Pa), was determined following a first-order kinetic equation with the shear rate step test (Ruiz-Hernando et al., 2010). The experimental shear stresses were fitted to the Ostwald–de Waele equation:

$$\tau_e = K\dot{\gamma}^n \qquad (2)$$

where $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index ($Pa \cdot s^n$) and n is the power law index (-).

Finally, the steady state viscosity was determined following Newton's equation ($\eta_e = \frac{\tau_e}{\dot{\gamma}}$).

2.5. Chemical analytical methods

Analyses of the total fraction were performed directly on the samples or dilutions. For analyses of the soluble fraction, the samples were centrifuged at 1,252 g for 10 minutes and the supernatant was filtered through a regenerated cellulose 0.45 µm filter (CHM® SRC045025Q). TS, volatile solids (VS), tCOD and sCOD were determined following the guidelines given by the standard methods 2540G and 5220D (APHA, 2005). The losses of volatile fatty acids (VFA) compounds during the solids determination were taken into account and combined to give the final TS and VS values (Astals et al., 2012a). The pH was measured with a Crison 5014T pH probe. Individual VFA (acetate, propionate, butyrate and valerate) were analyzed by an HP 5890-Series II chromatograph equipped with a capillary column (Nukol™) and a flame ionization detector (Astals et al., 2012b). The ionic profiles were determined in an 863 Advanced Compact IC Metrohm ionic chromatographer using Metrosep columns.

2.6. Biomethane potential tests

Biomethane potential (BMP) tests were carried out at mesophilic temperature conditions following the stages defined by Angelidaki et al. (2009). The BMP tests were performed in 115 mL serum bottles, closed with a PTFE/butyl septum, which was fixed by an aluminum crimp cap. The bottles were filled in with 60 mL of inoculum and 13 mL of WAS sample (untreated or treated), which met an inoculum to substrate ratio of 2 in VS-basis considering the untreated WAS VS value. A control blank with only inoculum was measured to determine the background effect of the inoculum. Before sealing the bottles, all digesters were flushed with nitrogen for one minute (3 L/min). Finally, digesters were placed in a water bath at 37 ± 1 ºC. The bottles were manually mixed by swirling twice daily. All samples were tested in triplicate.

The biogas production during the running test was measured by using a vacuumeter (Ebro – VAM 320) after discarding the overpressure generated during the first hour. The methane content of the biogas accumulated in the bottle headspace was analyzed at each sampling event by a Shimadzu GC-2010+ gas chromatograph equipped with a capillary column (Carboxen®-1010 PLOT) and a thermal conductivity detector. Finally, methane production over time was obtained by multiplying the biogas production, subtracting the vapor pressure and converted to standard temperature and pressure conditions (i.e., converted to 0 ºC and 1 atm) by the percentage of methane in the biogas.

2.7. Model implementation and data analysis

Mathematical analysis of the BMPs was based on the IWA Anaerobic Digestion Model No. 1 (ADM1; Batstone et al., 2002). WAS degradation was modeled using first-order kinetics because the hydrolysis step is considered the rate-limiting step during WAS degradation (Appels et al., 2008) (Eq. 3).

$$r_{was} = f_{was} \cdot k_{hyd,was} \cdot X_{was} \quad (3)$$

where r_{was} is the process rate (mL CH_4/L·day), f_{was} is the substrate biodegradability (-), $k_{hyd,was}$ is the first order hydrolysis rate constant of the WAS (day^{-1}), and X_{was} is the WAS concentration (g COD/L).

The model was implemented in Aquasim 2.1d. Parameter estimation and uncertainty analysis were simultaneously estimated, with a 95% confidence limit, as was the case for Batstone et al. (2003 and 2009). Uncertainty parameters (f_{was} and $k_{hyd,\ was}$) were estimated based on a one-tailed t-test with standard error around the optimum, and non-linear confidence regions were also tested to confirm that the linear estimate was representative of true confidence (Jensen et al., 2011). The objective function was the sum of squared errors (χ^2) of averaged data from triplicate experiments.

3. Results and Discussion

3.1. Effect of the pre-treatments on the hygienization and rheological profile of the WAS

An initial set of assays was carried out to determine appropriate conditions of each treatment for further biomethanization studies. This selection was performed based on the hygienization and rheological characterization of sludge. Different microbiological results were obtained with the three pre-treatments conducted (Fig. 1). For the ultrasound, small changes in the levels of microbial indicators were found, even at the highest E_S applied (27,000 kJ/kg TS). Thus, the ultrasonication conditions tested in this research were not effective enough to achieve hygienization. Because the effect of temperature was nullified by the ice bath, the disinfection mechanism was exclusively related to cell wall disruption due to cavitation, a phenomenon that is influenced by several factors (Pilli et al., 2011). According to Foladori et al. (2007) and Cui et al. (2011), ultrasonication appeared to have two effects: a first step, in which the sludge flocs were dissipated, and the microbial cells attached to the solids were released; and a second step, in which the walls of the exposed cells were disrupted. Thus, it is conceivable that the specific energies applied were effective enough to dissipate sludge flocs but not for killing bacteria and spores or for inactivating bacteriophages. However, to confirm this, more research is required. For thermal treatments, better results were obtained at 80 ºC compared with 70 ºC (data not shown for 70 ºC). At 80 ºC, the three microbial indicators behaved differently: there was a slight reduction for SSRC (0.84 $\log_{10}$ of reduction), approximately 5 $\log_{10}$ of reduction for SOMCPH and a very high grade of hygienization for *E. coli* (> 4.01 $\log_{10}$ of reduction). In fact, after 15 min, the *E. coli* population significantly dropped below the detection limit of the technique (2.02 $\log_{10}$ CFU/g dw or 4.00 CFU/g ww), satisfying normal levels accepted by the EPA (US Environmental Protection Agency, 2003) and the 3rd official draft from the EU (Environment DG, EU, 2000) for land application of the biosolids. These behaviors are similar to those described by Mocé-Llivina et al. (2003), showing a great sensitivity of *E. coli*, a moderate sensitivity of SOMCPH and a good resistance of SSRC toward thermal treatment. In this context, the use of the three microbial indicators may offer a complete interpretation of the effect of thermal treatments on the microbial population of the WAS. For alkali pre-treatment, the disinfecting effect of high pH was previously confirmed

(Allievi et al. 1994; Bujoczek et al. 2002). In the present work, a similar pattern of inactivation in the three indicators was found after alkali treatment. The highest concentration of NaOH (157 g/kg TS) exhibited an extreme pH (approximately 12) during the 24 h treatment and was lethal for all three microorganisms. Therefore, the required hygienization levels for *E. coli* were accomplished, with a value of 3.20 $\log_{10}$ CFU/g dw (95.6 CFU/g ww) for a reduction of 2.57 $\log_{10}$. Likewise, SOMCPH and SSRC levels were reduced by 2.79 and 1.72 $\log_{10}$, respectively. Unexpectedly, increases in SSRC and *E. coli* levels (1.04 $\log_{10}$ and 0.87 $\log_{10}$, respectively) were observed with the application of 35.3 g NaOH/kg TS. This reproducible result is not described in this study and is currently being investigated. It is important to note that bacteria could experience multiple physiological states; this fact may prevent the measurement of actual concentrations. In contrast, viruses can only be infective or not infective, simplifying their use as indicators. Additionally, the levels of the three parameters as a mean of 8 replicates were calculated for the untreated WAS: 5.99 $\log_{10}$ CFU/g dw of *E. coli* (s=0.22); 7.02 $\log_{10}$ PFU/g dw of SOMCPH (s=0.34); and 6.07 $\log_{10}$ CFU/g dw of SSRC (s=0.16).

For rheological characterizations, all pre-treatments were conducted on the same WAS sample (45.9 ± 0.2 g TS/L) because rheological properties of sludge are highly conditioned by the TS content (Pollice et al., 2006; Laera, et al., 2007). All of the analyzed WAS samples (untreated and treated) exhibited pseudoplastic behavior. Fig. 2 shows the evolution of the steady state shear stress as a function of shear rate for the untreated and three treated sludges, together with their respective fittings to the Ostwald-de Waele model (Eq. 2). The good fit of the experimental data showed the capability of the model to reproduce the pseudoplastic response of the WAS. Fig. 3 shows variations in the steady state viscosity when increasing treatment intensities at a shear rate of 300 s^{-1}. The steady state viscosity was significantly reduced with the treatments because the treatments changed the overall sludge properties, including the composition, structure, strength and size of the sludge flocs (Neyens and Baeyens, 2003; Bougrier et al., 2006; Pham et al., 2010; Ruiz-Hernando et al., 2013; Farno et al., 2014). The greatest reduction of the steady state viscosity was observed (71% reduction) after ultrasonication at an E_S of 27,000 kJ/kg TS. Thermal treatment is known to degrade cell wall membranes due to pressure difference, resulting in a lower viscosity and in an improvement of the filterability (Bougrier et al., 2008). However, for the thermal conditions evaluated in this study (80 ºC for 10, 15 and 30 min) the reduction of the steady state viscosity was lower than after ultrasonication, likely due to the shorter heating exposure times. Additionally, no significant differences in viscosity reduction were observed between the three heating exposure times. To be specific, after a contact time of 10 min, the steady state viscosity was reduced by 35%, which was not significantly different from that of the exposure times of 15 (36%) and 30 min (38%). For low doses of NaOH, the alkali treatment exhibited the lowest reduction of the steady state viscosity (33%), whereas at higher doses the reduction was greater (65%).

The selection of the optimum condition of each treatment is detailed below. Because no ultrasonication condition resulted in a noticeable reduction of microbial indicators, the optimum condition for this treatment responded exclusively to rheological criteria. Accordingly, an optimum E_S of 27,000 kJ/kg TS was selected because it displayed the maximum reduction in viscosity. The optimum condition for the low-temperature thermal treatment was 80 ºC for 15 min because it resulted in sludge hygienization. Moreover, very little difference in viscosity reduction was detected between 15 and 30 min of heating exposure time at 80 ºC. For alkali treatments, the optimum condition selected was 157 g NaOH/kg TS (252 meq/L; pH 12.4) because it allowed the hygienization of the sludge and noticeably reduced the viscosity. The optimum conditions are abbreviated as US-WAS (ultrasonicated WAS), T-WAS (low-temperature thermally treated WAS) and NaOH-WAS (alkali-treated WAS).

3.2. Biomethane potential tests

To determine the effect of the pre-treated WAS on AD, the previously determined optimum conditions for each pre-treatment and the untreated WAS were analyzed by physicochemical characterization (Table 1) and biomethane potential tests (Fig. 4a). As shown by the sCOD/tCOD ratio and the SD (Table 1), all pre-treatments were able to solubilize particulate organic matter from the WAS. Specifically, ultrasound and low-temperature thermal pre-treatments presented similar efficiencies (approximately 11%) which were lower than the efficiency obtained by the alkali pre-treatment (approximately 15%). Nevertheless, the alkali pre-treatment presented a loss of 5 g COD/L due to organic matter mineralization, a phenomenon not detected in the ultrasound and low-temperature thermal pre-treatments. The SD obtained by ultrasound pre-treatment is in agreement with that reported by Kim et al. (2013a) when dosing at a similar E_S (approximately 25,000 kJ/kg TS) but is lower than that reported by Bougrier et al. (2006), who used a lower E_S (6,250 and 9,350 kJ/kg TS) and reached an SD of 15 ± 3%. The differences between the SD values may be related to the pre-treatment performance (e.g., no cooling during ultrasonication) and the sludge TS concentration (Carrère et al., 2010). Regarding the low-temperature thermal pre-treatment, the SD reached in the present study is lower than that reported by Kim et al. (2013b), likely due to the lower exposure time. The authors reported an SD of 23 and 27% when pre-treating WAS for 6 h at 60 and 75 ºC, respectively. The SD achieved through alkali pre-treatment was significantly lower than the values found in the literature, where an SD of approximately 30% was reported for WAS pre-treated with alkali at pH 12 and room temperature. Specifically, 1 h after dosing with 65 meq KOH/L (at a sample pH 12), Valo et al. (2004), recorded an SD of 31%. This value is similar to the result reported in Navia et al. (2002), in which an observed SD of 32% was obtained after dosing with 80 meq/L NaOH for 24 h (WAS from a kraft mill). Similarly, Jiang et al. (2010), evaluated the effect of the treatment time and pH on WAS solubilization. At pH 12, the authors recorded increases of the SD of 21 and 33% after 0.5 h and 24 h, respectively, of pre-treatment time.

Although the optimum pre-treatment conditions, in terms of methane production, may be those that present a high COD solubilization and low organic matter mineralization, increased solubilization does not always lead to an enhanced methane potential (Kim et al., 2013a). Therefore, BMP tests are needed to assess the effect of the pre-treatments on AD. The effect of the pre-treatments on methane production was evaluated through the modeling of the BMP tests (Fig. 4b). The 95% confidence region for biodegradability (x-axis) and apparent hydrolysis rate (y-axis) indicated that each pre-treatment had a different effect on WAS biodegradability. T-WAS (0.38 ± 0.1) presented similar biodegradability as WAS (0.37 ± 0.3), whereas US-WAS (0.42 ± 0.2) and NaOH-WAS (0.49 ± 0.1) presented increases of 13% and 34%, respectively, on WAS biodegradability and their final methane potential. The low increase of WAS biodegradability after pre-treatment, when compared with the literature, may be related to the selection of the pre-treatment conditions. In the present study, the strength and exposure time of each pre-treatment was based on rheological and hygienization criteria, rather than on the increase of the methane yield. For instance, through low-temperature thermal pre-treatments (60-80 ºC), increases of the biogas production by 20-40% have been reported when pre-treating WAS over 0.5 to 1.5 h (Hiraoka et al., 1984; Li and Noike, 1992; Wang et al., 1997). Likewise, increases of the biogas production between 40 and 50% have been achieved through ultrasound pre-treatment, even though lower E_S (5,000-9,350 kJ/kg TS) were applied (Bougrier et al., 2006; Braguglia et al., 2008). This may be related to the TS concentration (64.2 ± 0.2 g/L) and viscosity of the WAS because increased viscosity (linked to a higher TS concentration) hinders the formation of cavitation bubbles (Carrère et al., 2010). Moreover, in the present study, the WAS sample was cooled down during ultrasonication, thereby avoiding the thermal effect. The literature is less consistent regarding the effect of alkali pre-treatment on the biogas potential at room temperature. Penaud et al. (1999) demonstrated an increase in biodegradability by approximately 40% after adding 125 meq NaOH/L. In contrast, Valo et al. (2004), reached a pH of 12 after adding 65 meq KOH/L, but did not observe any significant improvement on WAS biodegradability.

Similar SDs, but different biodegradabilities, reached by T-WAS and US-WAS showed that some parts of the cell wall were weakened but not solubilized during the pre-treatments. However, because the pre-treatment conditions applied to the WAS did not affect the hydrolysis rate, it can be understood that most of the methane production still came from the particulate organic matter (Fig. 4b). Finally, a possible inhibitory effect due to a high sodium concentration (3.6 g Na^+/L) on NaOH-WAS digestion, which is reported within the moderate inhibition sodium concentrations for mesophilic methanogens (Chen et al., 2008), may had been masked by the dilution effect (approximately 1/4) of the inoculum.

3.3. Hygienization effect of the mesophilic anaerobic digestion aided by pre- and post-treatments

Although AD has been designed for increasing biogas production and solids destruction, it also plays a role in pathogen inactivation (Ziemba and Peccia, 2011), and pre-treatment optimization may help in this purpose. The occurrence of indicators after the BMP tests in the pre-treated sludges is shown in Fig. 5. It is worth remembering that, in order to perform the BMP tests, the untreated and the pre-treated WAS were mixed with digested sludge and therefore the microbiological tests were made on these mixtures. For *E. coli*, the reductions achieved by the entire processes (i.e., pre-treatments + mesophilic AD) provided results below the detection limit of the technique (< 2.02 $\log_{10}$ CFU/g dw or < 4.00 CFU/g ww), successfully overcoming the levels of hygienization established by the EPA and EU. Specifically, for ultrasound pre-treatment, *E. coli* reduction was due to the single effect of the AD because this pre-treatment did not sanitize the sludge (relevant data corresponding to the single effect of AD are shown in Fig. 6). For the SOMCPH, the three configurations generated similar results: 2.32, 2.45 and 2.47 $\log_{10}$ reductions for ultrasound, low-temperature thermal and alkali, respectively. Finally, as was observed in the preliminary assays (section 3.1), unexpected results for SSRC were found after digestion of the ultrasonicated and alkali pre-treated sludge, resulting in an increase of 1.62 $\log_{10}$ and 1.80 $\log_{10}$, respectively. However, SSRC did not experience similar changes with the low-temperature thermal pre-treatment. As for preliminary assays, this increase in the SSRC concentration after AD is currently being investigated. From the three configurations studied in this section, the thermal pre-treatment followed by mesophilic AD seems to be the best option in terms of hygienization.

The effectiveness of post-treatments in the sanitation of digested sludge has been thoroughly studied in the literature (Allievi et al., 1994; Bujoczek et al., 2002; Astals et al., 2012a). The microbiological results for the three post-treatments applied after mesophilic AD are displayed in Fig. 6. The digestion was sufficient to meet the *E. coli* requirements established by the normative, reaching reductions of more than 3.78 $\log_{10}$. These results were below the detection limit of the technique, making impossible to evaluate the *E. coli* reductions achieved by the assayed post-treatments. In contrast, the SSRC levels were not changed due to the mesophilic AD or post-treatments. A single mesophilic AD reduced SOMCPH levels by 1.88 $\log_{10}$, and the combination of AD followed by the low-temperature thermal and alkali post-treatments resulted in reductions of 3.42 $\log_{10}$ and 2.56 $\log_{10}$, respectively. However, no additional effect was observed with ultrasound post-treatment with respect to a single AD. Taking into account that *E. coli* levels decayed below detection limits and that SSRC levels remained unchanged, the level of SOMCPH was the parameter that allowed the evaluation of the efficacy of post-treatments. Therefore, as was the case for pre-treatments, the low-temperature thermal post-treatment seems to be the best option for hygienization.

3.4. Assessment of the feasibility of the treatments in a WWTP

By considering an energy balance with the assessment of the different treatment scenarios an estimate can be made to determine whether the energy (i.e., electricity and heat) required by the pre-treatment can be recovered through the improved methane production. However, these estimates rely exclusively on laboratory data; therefore, the results would not be entirely conclusive for an operational WWTP. Moreover, it should be considered that the heat balance is highly influenced by the solid concentration; therefore, a concentrated WAS will lead to a better balance, while a diluted sludge will lead to a worse balance (Carrère et al., 2012). The assessment is based on a novel WWTP approach, where the primary sludge and WAS are digested separately to increase the opportunities to use digested WAS in agriculture.

Ultrasound treatment (27,000 kJ/kg TS) was able to solubilize organic matter and improve WAS specific methane production, but was not able to disinfect the WAS. Therefore, the most reasonable configuration for ultrasonication would be to use it as a pre-treatment prior to AD and composting or thermal post-treatment (if the digestate is intended for use as fertilizer). The electricity balance of the ultrasound pre-treatment shows that an increase in methane production (15 mL CH_4/g COD) results in an increased electrical production of 240 kJ/kg TS, which is very low when compared to the supplied energy (27,000 kJ/kg TS). Nevertheless, on an industrial scale, this difference would be lower due to the higher efficiency of commercial ultrasonic devices.

Low-temperature pre-treatments (< 100 ºC) are characterized by a low energy demand, which may be supplied by a combined heat and power (CHP) unit fueled with biogas (Passos et al., 2013). On the one hand, the heat required to increase the WAS from 15 to 80 ºC were estimated to be 4.6 MJ/kg TS, assuming a WAS specific heat of 4.18 kJ/kg/ºC, a density of 1000 kg/m^3, and 8% of the process heat losses (Astals et al., 2012a). On the other hand, the heat produced by the CHP unit after burning the biogas was 3.6 MJ/kg TS, which represents the energy required to increase the WAS temperature from 15 to approximately 65 ºC. The value was obtained assuming a 35,800 kJ/kg TS methane caloric value and a 0.55 CHP unit yield for heat generation (Astals et al., 2012a; Passos et al., 2013). However, if a 80 ºC pre-treatment is required, it would be necessary to install a sludge-to-sludge heat exchanger, where the pre-treatment effluent would be used to pre-heat WAS. The energy recovered in the sludge exchanger should be at least the 23% of the heat contained by the pre-treated WAS, which is below than the 80-85% efficiency reported for this type of unit (Astals et al., 2012a; Carrère et al., 2012). As shown in the BMP tests, the low-temperature thermal pre-treatment scarcely increased the biodegradability of the WAS, possibly due to the shorter contact time. It is likely that a longer exposure time would result in an increase of the methane production and induce an improvement of the energy balance (Li and Noike, 1992). Nonetheless, a higher capital cost would be required due to the larger digester volume. Additionally, both the thermal pre-treatment and the post-treatment were successful in reducing the microbiological parameters. However, the pre-treatment does not guarantee hygienization after the AD. Therefore, the configuration for this treatment seems to depend on the final destination of the sludge: if the sludge is intended for agriculture, it should undergo post-treatment to satisfactorily meet the current microbiological levels for land application. If the sludge is not intended for agriculture, it may be appropriate to perform a pre-treatment (the effect of the exposure time should be further investigated) to enhance the AD.

Alkali conditioning (157 g NaOH/kg TS) has been successful in improving methane production, and has reduced the levels of *E. coli* below the limits established by the EPA and EU. However, as a pre-treatment, it unexpectedly increased the levels of SSRC after AD and required neutralization prior to AD. In addition, it resulted in a negative economic balance. The selling price of industrial NaOH and HCl are highly variable, but average at 300 and 200 €/ton, respectively (Solvay, 2013). Consequently, dosing 157 g NaOH/kg TS and 218 g $HCl_{35\%}$/kg TS for their subsequent neutralization requires 0.094 €/kg TS and 0.044 €/kg TS, respectively. The sum of the reagents cost (0.138 €/kg TS) was much larger that the incomes generated through the extra methane production. Specifically, 43 mL CH_4/g COD will represent an extra electricity production of 680 kJ/kg TS that, at a tariff of

0.10 €/kWh, will lead to a revenue of 0.019 €/kg TS. Another drawback linked to alkali pre-treatment is the rising sodium concentration in the digester, which can drive the AD process to inhibition (Mouneimne et al., 2003; Carrère et al., 2012); therefore, the use of NaOH as a pre-treatment is rather limited.

Finally, it is worthwhile to note that the treatments reduced the energy of pumping due to the decrease on WAS viscosity. Specifically, ultrasound, thermal and alkali treatments reduce the energy of pumping from 14 kJ/kg TS (no treatment) to 1.8, 6.0 and 2.5 kJ/kg TS, which corresponds to a reduction of approximately 90, 60 and 80%, respectively. This approach was obtained assuming a sludge flow velocity of 0.2 m/s, a pipeline length of 500 m and a pipeline internal diameter of 150 mm. These specifications are obtained from a WWTP with a capacity of two million population equivalents (420,000 m^3/day). Clearly, the energy required for pumping the untreated sludge (14 kJ/kg TS) is considerably lower than the cost of the discussed treatments. On the other hand, although it was not quantified, it is conceivable that the decrease in viscosity improved the mixing in the digester and allowed the realization of high solids AD, thus enhancing the final biogas production and the energy balance.

4. Conclusions

Waste activated sludge was pre-treated and post-treated through ultrasound, low-temperature thermal and alkali conditioning to provide an overall view of feasible scenarios for waste activated sludge management. The selection of the optimum condition of each pre-treatment was based on hygienization and rheological results. On the one hand, the three treatments reduced the viscosity of the sludge, and this reduction was greater when increasing the treatment intensity. On the other hand, the low-temperature thermal and alkali treatments but not ultrasound treatment allowed the hygienization of the sludge. The effects of the three optimum treatment conditions were compared in terms of the anaerobic digestion improvements and hygienization. Ultrasound increased the sludge biodegradability and the specific methane production (13%), but did not succeed in hygienization, suggesting that the most appropriate configuration for ultrasonication is as a pre-treatment before treatment in the anaerobic digester. The low-temperature thermal treatment barely increased the sludge biodegradability, but allowed hygienization, which suggests that it would be more suitable as a post-treatment. However, the use of longer contact times would increase the chances for use as a pre-treatment. Alkali treatment increased the methane production (34%) and was successful in hygienization because it reduced the levels of *E. coli* below the limits established by the EPA and EU. However, when used as a pre-treatment, it resulted in a high amount of sodium because of the high concentrations of NaOH required, which may inhibit anaerobic digestion. The energy balance revealed that under the tested conditions, the ultrasound and alkali treatments required higher operating costs. Finally, it is noteworthy that SOMCPH was an appropriate microbial indicator for evaluating the different sludge treatments and would be a suitable candidate to complement *E. coli* measurements.

Acknowledgments

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Table 1. Characterization of the raw and pre-treated WAS. Errors represent standard deviations.

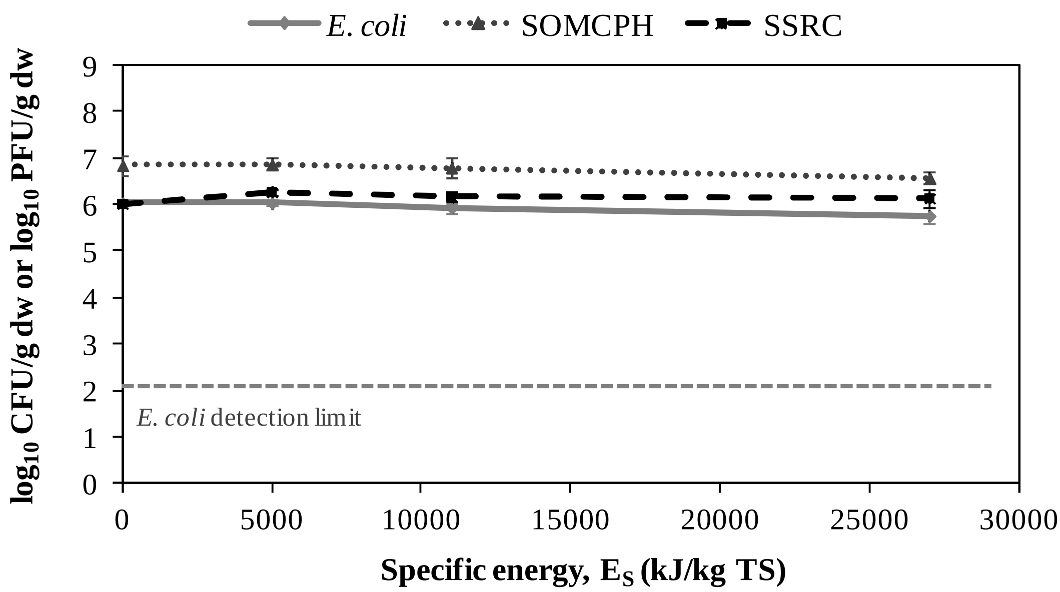
	Units	WAS	US-WAS	T-WAS	NaOH-WAS
Waste characterisation					
TS	g/L	64.2 ± 0.2	65.7 ± 0.1	64.6 ± 0.1	72.3 ± 0.1
VS	g/L	52.9 ± 0.2	53.9 ± 0.1	53.0 ± 0.1	49.5 ± 0.2
tCOD	g O_2/L	80.9 ± 0.4	80.5 ± 0.3	81.6 ± 0.5	75.7* ± 0.4
sCOD	g O_2/L	0.9 ± 0.1	10.3 ± 0.2	9.6 ± 0.2	12.1** ± 0.1
pH	-	6.5 ± 0.1	6.4 ± 0.2	6.4 ± 0.2	7.5 ± 0.1
VFA	mg/L	223 ± 10	952 ± 16	293 ± 21	560 ± 18
Acetate	mg/L	165 ± 4	634 ± 5	249 ± 18	481 ± 14
Propionate	mg/L	22 ± 5	197 ± 9	25 ± 8	22 ± 3
Butyrate	mg/L	23 ± 1	53 ± 4	19 ± 2	31 ± 2
Valerate	mg/L	13 ± 1	68 ± 1	n.d.***	26 ± 2
Pre-treatment solubilisation efficiency					
sCOD/tCOD	%	1.1 ± 0.1	12.8 ± 0.2	11.7 ± 0.2	16.0 ± 0.2
SD	%	-	11.8 ± 0.4	10.8 ± 0.6	14.0 ± 0.6

* Obtained by multiplying the SV by 1.53 g COD/g VS due to chloride interference in the COD analysis

** Obtained after removing the chloride COD determined in tCOD analysis

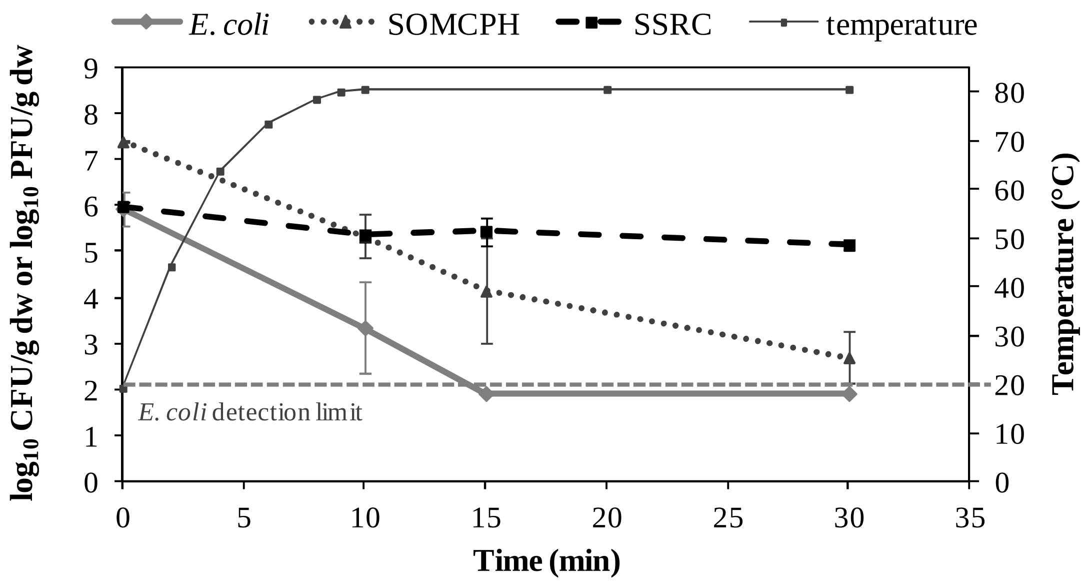
*** n.d. non-detected (<10 mg/L)

A



E. coli
SOMCPH
SSRC
log10 CFU/g dw or log10 PFU/g dw
E. coli detection limit
Specific energy, ES (kJ/kg TS)

B



E. coli
SOMCPH
SSRC
temperature
log10 CFU/g dw or log10 PFU/g dw
Temperature (°C)
E. coli detection limit
Time (min)

C

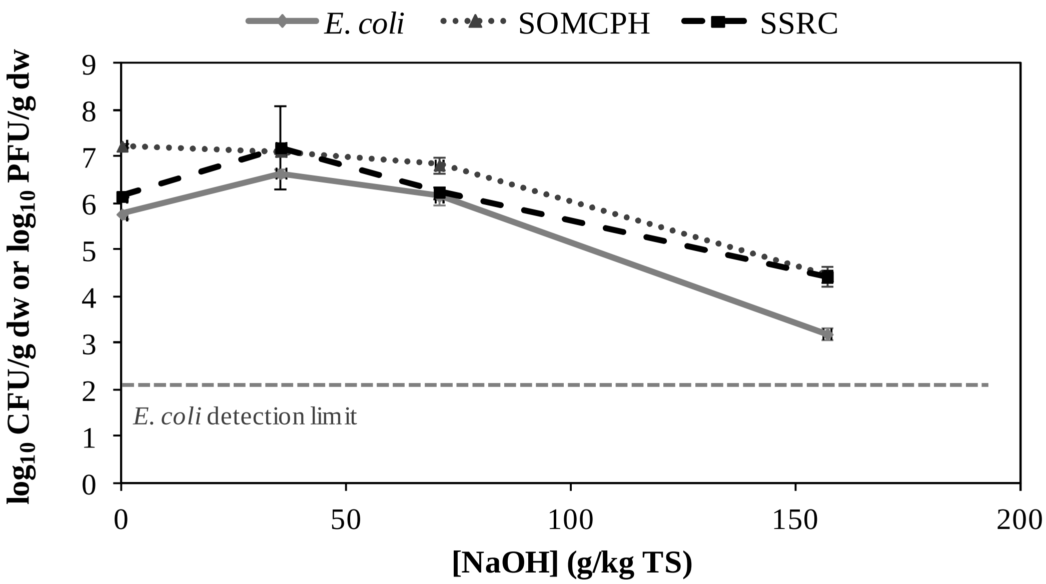


Fig. 1. Effect of the ultrasound, low-temperature thermal and alkali treatments on indicator populations (*E. coli*, SOMCPH, and SSRC). A: ultrasound conditions; B: thermal conditions; C: alkali conditions. Error bars represent standard deviations.

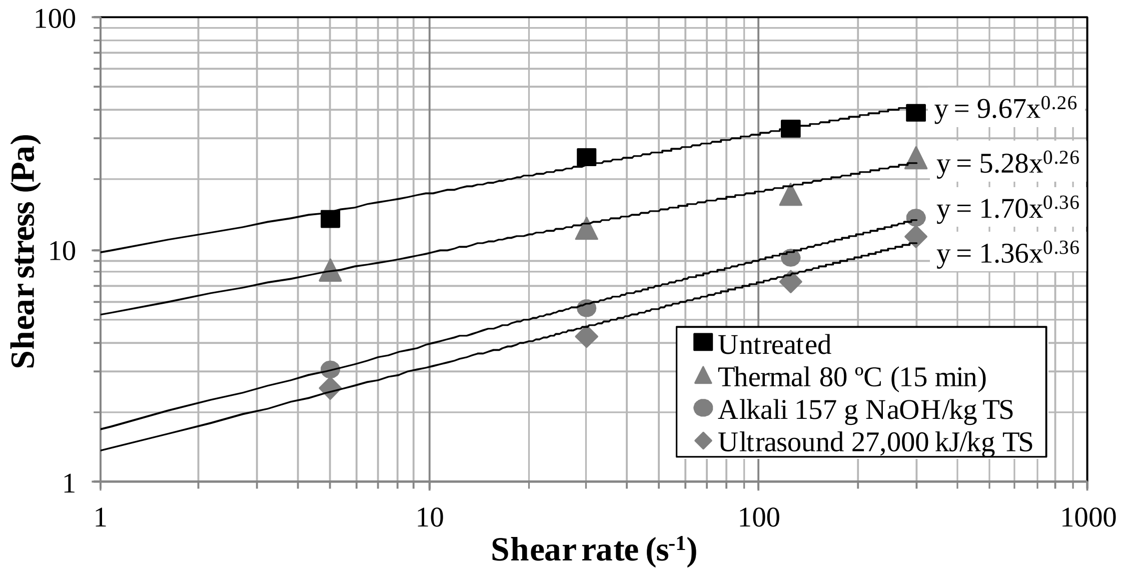


Fig. 2. Steady state shear stress as a function of shear rate for the untreated and three treated sludges (ultrasound: 27,000 kJ/kg TS; thermal: 80 ºC for 15 min; alkali: 157 g NaOH/kg TS). The solid lines correspond to the fit to the Ostwald-de Waele power-law model.

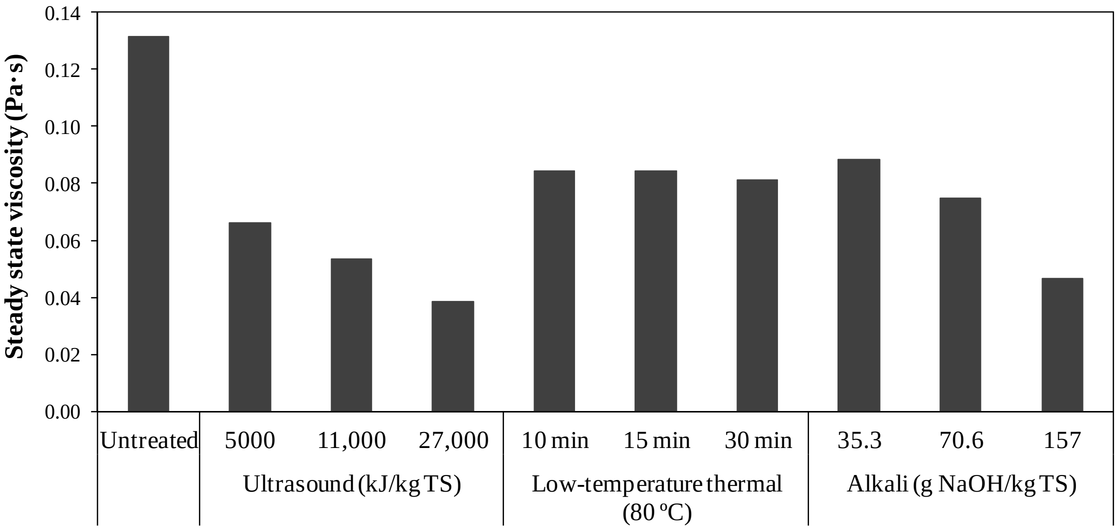


Fig. 3. Steady state viscosity at a shear rate of 300 s^{-1}.

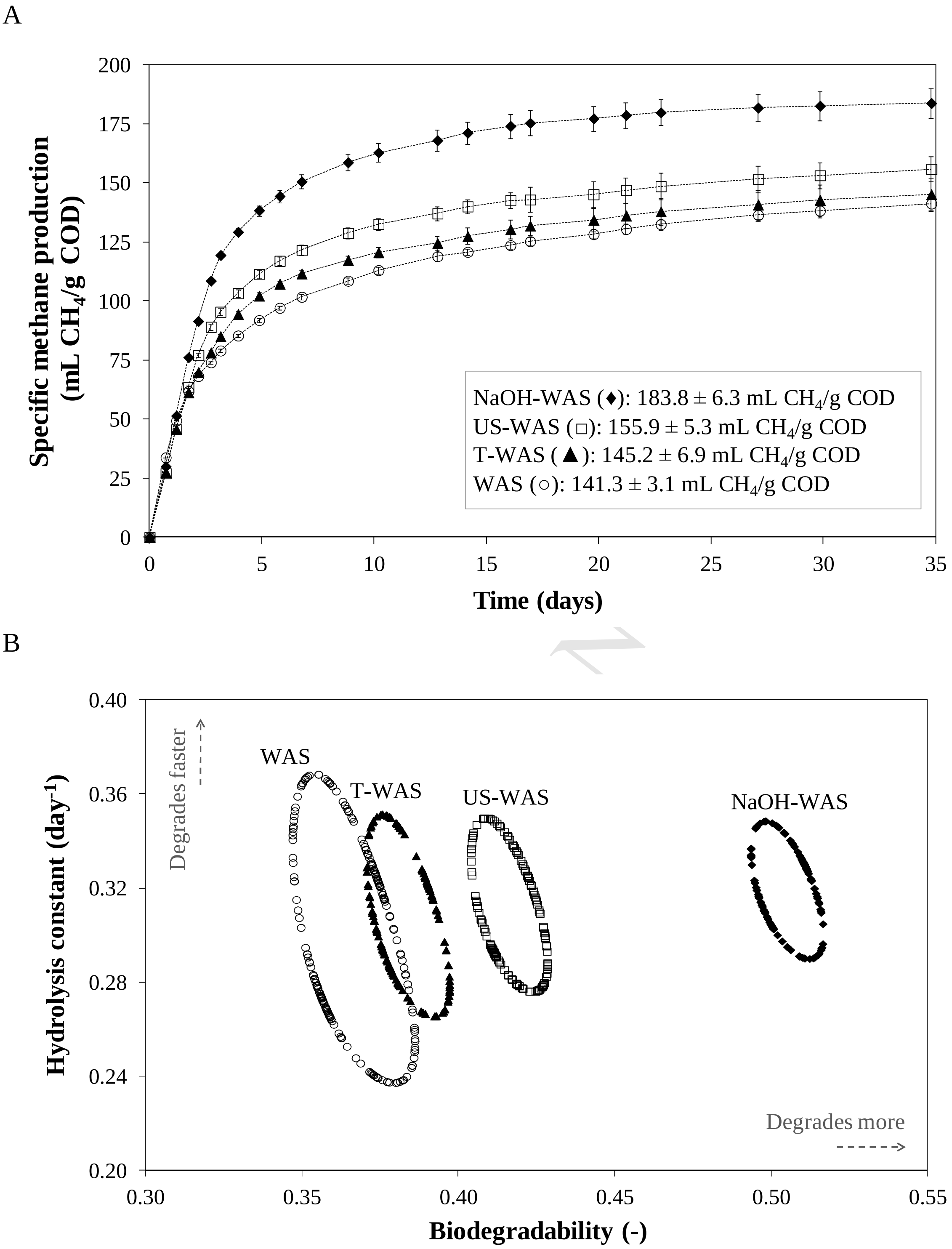
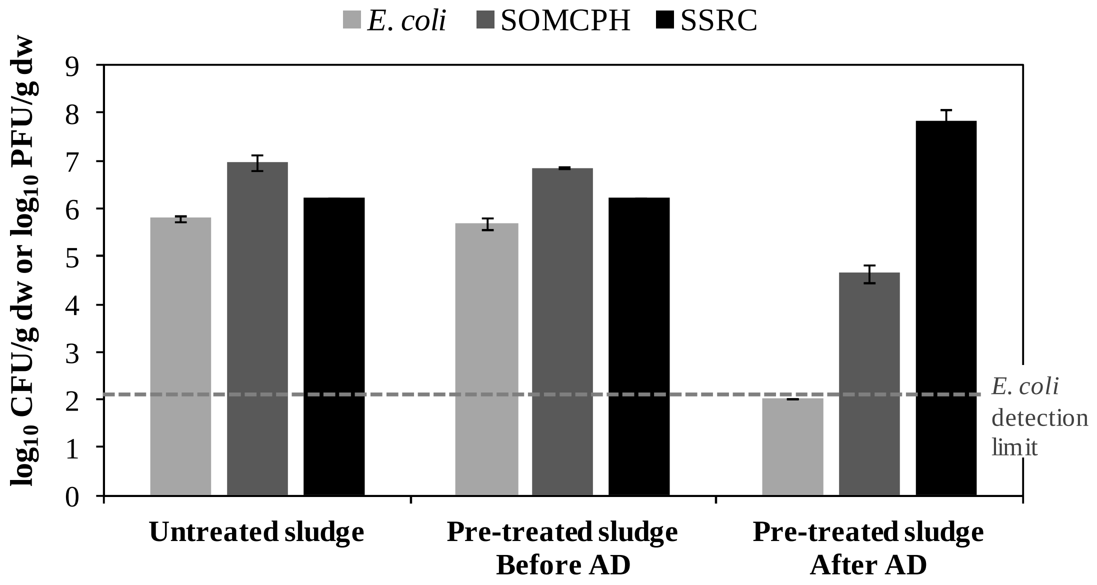
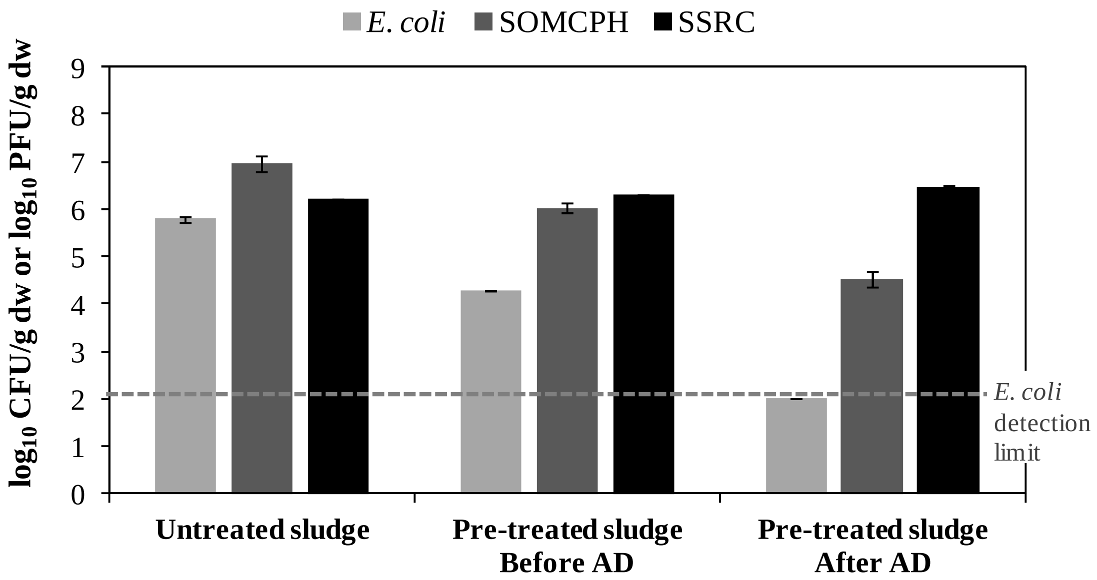


Fig. 4. Results obtained from the BMP tests: (A) Cumulative methane production curves and (B) Confidence regions for biodegradability (f_{was}) and hydrolysis constant ($k_{hyd, was}$). Error bars represent standard deviations.

A


E. coli
SOMCPH
SSRC
log10 CFU/g dw or log10 PFU/g dw
9
8
7
6
5
4
3
2
1
0
E. coli detection limit
Untreated sludge
Pre-treated sludge Before AD
Pre-treated sludge After AD

B


E. coli
SOMCPH
SSRC
log10 CFU/g dw or log10 PFU/g dw
9
8
7
6
5
4
3
2
1
0
E. coli detection limit
Untreated sludge
Pre-treated sludge Before AD
Pre-treated sludge After AD

C

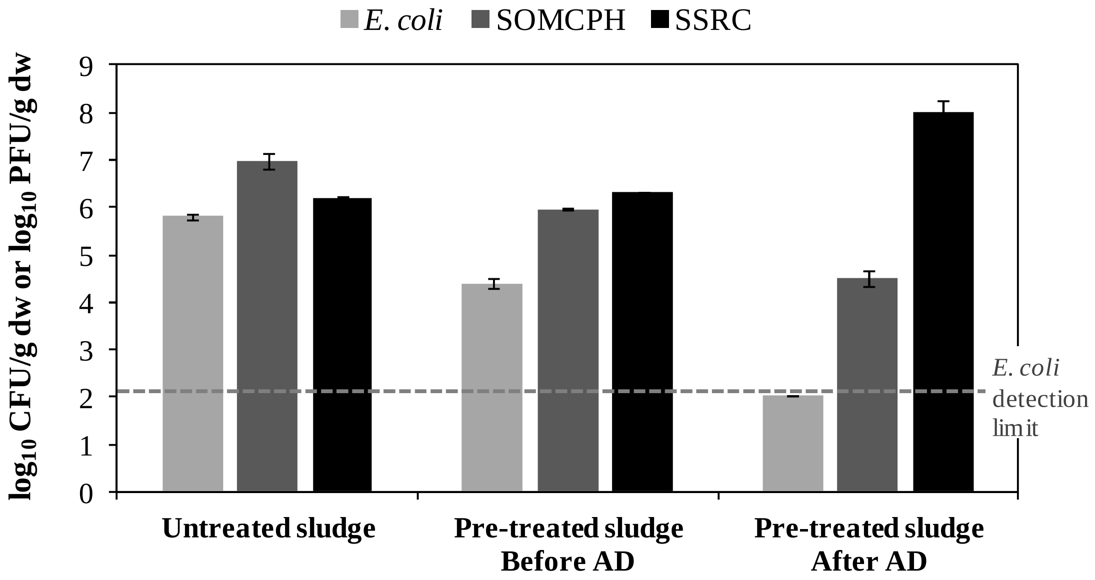


Fig. 5. Effect of different pre-treatments and the AD on the microbial populations present in sludge. A: ultrasound pre-treatment; B: low-temperature thermal pre-treatment; C: alkali pre-treatment. Error bars represent standard deviations.

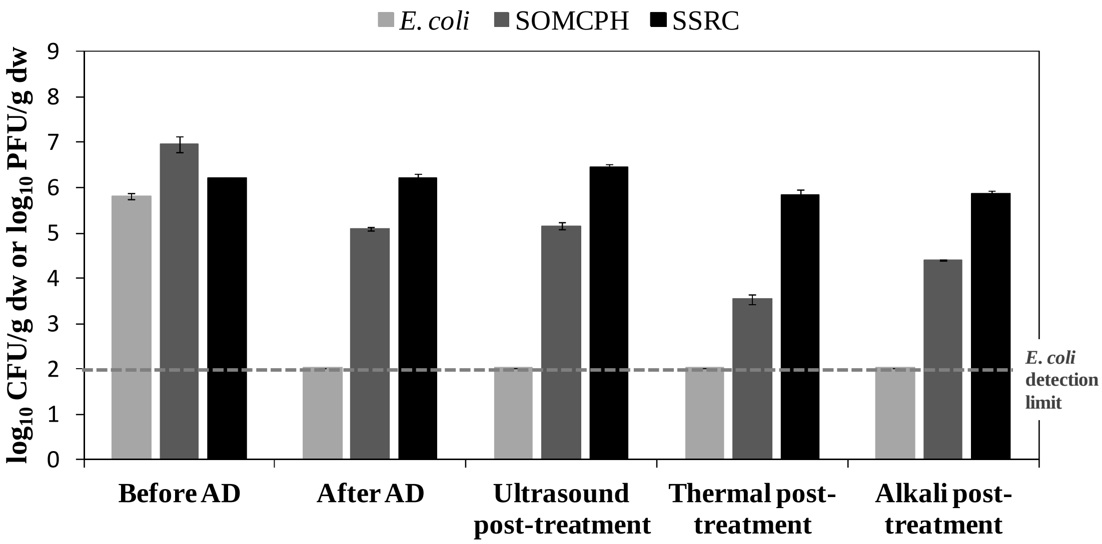


Fig. 6. Effect of the anaerobic digestion and different post-treatments on the microbial populations present in sludge. Error bars represent standard deviations.

- Thermal and alkali conditioning but not ultrasonication allowed WAS hygienization.
- The three pre-treatments were able to reduce the viscosity of WAS.
- Alkali and ultrasound pre-treatments increased WAS biodegradability.
- Thermal pre-treatment barely increased WAS biodegradability.
- Under tested conditions, ultrasound and alkali treatment entailed high costs.