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Dewaterability of sewage sludge by ultrasonic, thermal and chemical treatments

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Abstract

Sludges resulting from wastewater treatment processes have a characteristically high water content, which complicates handling operations such as pumping, transport and disposal. To enhance the dewatering of secondary sludge, the effect of ultrasound waves, thermal treatment and chemical conditioning with NaOH have been studied. Two features of treated sludges were examined: their rheological behavior and their dewaterability. The rheological tests consisted of recording shear stress when the shear rate increases and decreases continuously and linearly with time, and when it increases and decreases in steps. Steady-state viscosity and thixotropy were obtained from the rheological tests, and both decreased significantly in all cases with increased treatment intensity. Centrifugation of ultrasonicated and thermally treated sludges allowed the total solid content to be increased by approximately 16.2% and 17.6%, respectively. These dewatered sludges had a lower viscosity and thixotropy than the untreated sludge. In contrast, alkali conditioning barely allowed the sludge to be dewatered by centrifugation, despite decreasing its viscosity and thixotropy.

Keywords: sewage sludge; rheology; ultrasonication; thermal treatment; alkali conditioning

1. Introduction

The use of activated sludge is the most common technique to treat the organic matter present in a municipal wastewater plant. In wastewater treatment, water contamination is transferred to the sludge, which then has to be treated and disposed of properly. European legislation regarding the Urban Wastewater Treatment Directive (91/271/EEC) is leading to an important increase in sewage sludge production and strong limitation of its disposal routes. Accordingly, research into efficient sludge treatments is essential to ensure the proper management of sewage sludge and to minimize costs.

Sewage sludge consists mainly of microbial cells and water. The amount of water that can be removed from sewage sludge is very high and is about 95-99% for primary sludge and 98-99.5% for secondary sludge. Nevertheless, water removal depends not only on the dewatering process, but also on water's physical position in the sludge. Kopp and Dichtl [1] distinguished four categories of water in sewage sludge: (i) free water, which can be easily removed by sedimentation; (ii) interstitial water, which could be freed by intense mechanical forces; (iii) surface water, which is held on the surface of solid particles by adsorption and adhesion; and (iv) chemically bound water, which cannot be removed completely even by higher energies. Thus, bound water is one of the main limiting factors of water removal efficiency.

Several treatments to improve the dewatering process of sewage sludge have been put forward. These treatments partially disintegrate sewage sludge by destroying cell walls and releasing linked water and organic compounds in the liquid phase. Accordingly, treatments change the composition of the sludge and disrupt extracellular polymeric substances (EPS), which entrap the water and cause high viscosity [2]. Thus, treatments, which include physical and chemical methods, have effects on the viscosity and filterability of the sludge [3].

Thermal treatment improves the dewaterability of sludge by causing cell lysis due to pressure differences [4]. The most common treatment temperatures are between 60 and 180 °C [5],

which destroys the cell walls, making proteins easily accessible for biological degradation. Unfortunately, above 180 °C refractory COD compounds are formed [6]. Treatments at temperatures lower than 100 °C are considered low-temperature thermal treatments [7] and despite requiring longer contact times than the high-temperature treatments [8-9], they are considered effective for increasing biogas production from secondary sludge [5]. Another advantage of thermal treatments is the reduction in sludge viscosity, thereby improving sludge handling, and sludge sanitation. On the other hand, the main drawback of this treatment is its high energy requirement.

Ultrasonication of sludge is the most common mechanical treatment [10]. Ultrasonication consists of disrupting the microbial cells by applying ultrasonic waves at a frequency of 20 kHz in order to extract intracellular material. Ultrasonication causes cavitation gas-bubble generation in the liquid phase [11]. These bubbles grow to a critical size and then violently collapse, producing great hydro-shear strength, intense local heating (5,000 K) and high pressures (500 atm) in the mass of the liquid surrounding the bubbles [12-13]. Cavitation also generates free radicals that accelerate chemical reactions. In this way, the disintegration produced by ultrasonication is due to two phenomena: hydro-shear strength and sonochemical effects. Thus, ultrasonication would enhance the solubilization of organic matter, decrease sludge viscosity and increase sludge homogeneity [14-15].

Chemical methods to reduce water content in the sludge have also been used. Advanced oxidation processes (AOPs) such as ozone oxidation, Fenton processes and hydrogen peroxide (H_2O_2) oxidation may offer promising technology for the minimization of excess sludge [2,12]. Nevertheless, these processes are considered expensive if intended to eliminate all the contaminants of the sludge. Alkali treatment is reported to provide an efficient solubilisation of the sludge and is considered an appropriate method for enhancing the biodegradation of complex organic matter [16]. Alkaline hydrolysis refers to a process in

which the pH of sludge is increased up to 12 by adding an alkali and maintained for a required time. It is a simple and highly efficient treatment [17] that can disrupt flocs and cells, and release the bound water of the sludge [18-19]. However, low doses of NaOH (<0.2 mol/L) are pointed out to deteriorate sludge dewatering ability, but this ability could be recovered gradually with the increase of NaOH dose [20]. Nevertheless, alkali treatment generates a series of drawbacks such as corrosion, odors and the need to add a chemical agent and then neutralize it. In addition, the cost of disintegrating sludge through a chemical treatment tends to be more expensive than through physical or biological treatment processes [21]. For this reason, preliminary biological processes are adopted, to minimize sludge production and thus reduce subsequent cost.

The aim of this study is to examine the influence of three treatments (ultrasonication, thermal hydrolysis and alkaline conditioning with NaOH) on the rheological profile of sewage sludge, based on the assumption that treatment will modify the rheological features of sewage sludge and enhance its dewaterability. In a previous paper it was highlighted the importance of the proper knowledge of rheology to control sludge treatment processes such as dewatering and stabilization [15]. Rheology describes the deformation of a flow under the influence of mechanical stress: viscosity, which determines the thickness of the sludge, is the basic rheological parameter.

Sewage sludge is considered a non-Newtonian fluid behaving as a pseudo-plastic fluid [22], which indicates that the viscosity decreases with the applied shear rate. It also shows thixotropic behavior, which means that the viscosity is time-dependent. Thixotropy can be measured by the hysteresis loop technique [23-24], which consists of measuring the area enclosed between the up- and down-curve obtained by linearly increasing and decreasing shear rate over time. The rheology of sewage sludge depends on sludge composition,

temperature, concentration of solids and pH [25-27] and can be modified by the application of the treatments cited above or a combination of them.

2. Materials and Methods

2.1. Sludge characteristics

In this study, secondary sewage sludge was obtained from El Prat Municipal Wastewater Treatment Plant (Barcelona, Spain). After leaving the secondary tank, the sludge was thickened by centrifugation. Prior to centrifugation, a cationic polyelectrolyte (about 1kg/ton dry sludge) was added in order to enhance sludge dewaterability [28]. Table 1 shows the physical and chemical properties of the sludge. The total and volatile solid content were measured in triplicate, and were 56.7 and 45.8 g/kg, respectively (Table 1). In the laboratory, the sludge was stored at 4 °C to minimize bacterial activity until it was used.

Sludge was also characterized by means of particle size distribution and capillary suction time (CST). Before measuring the particle size distribution, sludge was diluted in distilled water. Sludge particle size distribution was measured at room temperature by a Coulter counter (Beckman Coulter Corporation, Fullerton, CA), which provided measurements over a particle diameter range of 0.04–1,000 μ m.

The CST measurement was conducted by the Type 304M Capillary Suction Time (Triton Electronics Ltd. UK) device. This method is an easy test for measuring the dewaterability of sludge and consists of a sludge column contained in a metal cylinder centered in the middle of two concentric electrodes. The cylinder rests on a filter paper. The test starts when the water (contained in the sludge) advancing through the filter reaches the first electrode and ends when it reaches the second one. The time elapsed between the two electrodes is the CST. According to some authors, the order of mean CST of sludges is: digested sludge > activated

sludge > raw sludge > mineral sludge [29-32]. This means that digested sludge or activated sludge is much more difficult to dewater than raw sludge or mineral sludge.

Dissolved organic carbon (DOC) content of the resulting supernatants after centrifugation was obtained by filtering the samples through polyvinylidene difluoride (PVDF) membranes of 0.45 μ m, and measured with TOC-VCSN Analyzer (Shimadzu).

2.2. Treatments conditions

Ultrasonic, thermal and alkali treatments were conducted in this research. The reactor used for thermal treatment (Autoclave Engineers) consists of a closed tank subjected to a preset temperature in the range of 60-100 °C. Sample volume was 100 mL and a heating jacket provided the heat to the sludge contained inside the tank through the tank walls. Treatment lasted while temperature rose to the desired value (about 30 min) and was then maintained for 30 more minutes. Under these conditions, the specific energy applied ranged from 12,000 to 22,000 kJ/kg TS. Sludge was mechanically agitated during treatment time to ensure the temperature homogeneity of the sample. Finally, the samples were cooled down to room temperature before the reactor was opened.

The ultrasonic apparatus used was HD2070 Sonopuls Ultrasonic Homogenizer equipped with a MS 73 titanium microtip probe and working with an operating frequency of 20 kHz and a maximum supplied power of 70 W. The specifications of the treatment were the same as those detailed in the previous study [15]. The ultrasonic waves were applied at constant ultrasonication power and different application times to provide specific energies from 3,000 to 33,000 kJ/kg TS.

Alkaline hydrolysis was conducted at room temperature by adding different concentrations of NaOH to the sludge and subsequent neutralization after 24 hours. The concentrations studied included values within the wide range from 0.784 to 235 gNaOH/kg TS. At low NaOH

concentrations the surface electrical charges of particles is altered, which has a decisive influence on the rheology of the compound. Furthermore, high NaOH concentrations may cause hydrolysis reactions and important changes in the rheology of the system, especially in secondary sludge due to the abundance of microorganisms.

2.3. Rheological study

The rheological behavior of secondary sludge was studied by a Haake RS300 control stress rheometer (Germany), equipped with HAAKE Rheowin Software. The geometry used was a 4° cone and a flat stationary 35 mm-diameter plate, which generated defined shear rates. Measurements were conducted at 22 ± 0.1 °C.

The rheological behavior of sludge under flow conditions was analyzed by two tests, following the procedures described by Ruiz-Hernando et al. [15]: hysteresis loop test and shear rate step test.

The hysteresis loop test consisted of four steps: (1) leaving the dispersion at 5 s^{-1} for 15 minutes, (2) linearly increasing the shear rate from 0 to the maximum shear rate over 5 minutes (up-curve), (3) shearing at the maximum shear rate for 10 minutes, (4) linearly decreasing the shear rate to 0 s^{-1} over 5 minutes (down curve). The maximum shear rates analyzed were 30, 125 and 300 s^{-1} . This test was carried out in order to quantify the thixotropy with the calculation of the enclosed area between the up-curve and down-curve when shear rate is linearly increased and decreased, respectively. The shear rate step test 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 viscosity was determined following Newton's equation and a first-order kinetic equation.

As concentrated sludge tends to be a pseudo-plastic fluid, steady state viscosity follows power law dependence on the applied shear rate [15]. Thus, the experimental steady state viscosities were fitted by the Oswald–de Waele equation:

$$\eta_e = K \dot{\gamma}^{n-1} \quad (1)$$

where $\dot{\gamma}$ is the shear rate, K is the consistency index and n is the power law index.

3. Results and Discussion

3.1. Effects of the treatments on sludge viscosity and thixotropy

Fig. 1 shows the evolution of steady state viscosity with applied shear rate for untreated sludge. Steady state viscosity follows the pseudo-plastic behavior defined by Oswald's equations, following power law dependence with the shear rate. Thus, significant reduction of viscosity was observed at low shear rate, i.e. steady state viscosity decreased its value by 70.9% when shear rate was increased from 5 to 30 s⁻¹. Table 2 shows the consistency index and power law index values that best fit the experimental viscosities for both untreated and treated sludges. The higher the value of the consistency index is, the greater the apparent viscosity. The power law index is linked to apparent viscosity dependence on shear rate; n is equal to 1 for Newtonian fluids, higher than 1 for dilatant fluids and lower than 1 for pseudo-plastic fluids.

Fig. 1 also shows the hysteresis loop test for untreated sludge. The presence of the hysteresis area indicates that the sludge shows positive thixotropic behavior. Thus, shear stresses during the up-curves are higher than shear stresses during the down-curves at the same shear rate. The phenomenon of thixotropy is due to the non-instantaneous processes of disruption or reconstruction of the internal network of the sludge, composed largely of internal filamentous structures, under the effect of a shear rate. The disruption of these filamentous structures contained in the sludge is believed to be the origin of the hysteresis area [33]. Table 2 also

shows the hysteresis area and fluidity, which is calculated as the inverse of the down-curve area and can be assimilated to the inverse of viscosity. Thus, high fluidity will result in a very liquid sludge.

All treated sludges showed shear thinning and thixotropy, like untreated sludge. Treatments will typically affect rheological behavior by modifying overall sludge properties, including structure, size of sludge flocks and sludge composition [2]. The effect of treatments on the rheology of the sludge is shown in Figs. 2 and 3.

The steady state viscosities measured at 30 s^{-1} are given in Fig. 2 for the three treated sludges. Significant reduction of the steady state viscosity was observed after all treatments. The lowest steady state viscosity was registered for thermal treatment ($0.14 \text{ Pa}\cdot\text{s}$), representing a reduction of 93.5% in comparison with untreated sludge. Similar results were observed at the rest of the applied shear rates, although the differences in viscosity were less significant at higher shear rates due to the pseudo-plastic behavior of the sludge.

Table 2 shows the values of consistency and the power law indexes of the Oswald–de Waele equation that best fits the experimental data for the three treatments. The consistency index decreased and the power law index increased (but always remained below unity, indicating deviation from Newtonian behavior) with treatment intensity, showing a reduction in shear-thinning behavior. The reduction in the consistency index was non-linear, as high treatment intensities involve lower decrease.

Table 2 also shows the hysteresis area and fluidity for each treatment. Hysteresis area values cannot be compared with the values in the literature, since each author used a different hysteresis loop to analyze the hysteresis area. Fig. 3 shows the hysteresis area reduction resulting from the application of the three treatments to the sludge with respect to the untreated sludge for the loop with the maximum shear rate of 300 s^{-1} . The hysteresis area reduction increased with treatment intensity and the maximum reduction (around 94%) was

observed at the highest specific energy of both ultrasound (33,000 kJ/kg TS) and thermal treatment (22,000 kJ/kg TS). Moreover, as shown in Table 2, fluidity increased with the increase in treatment intensity. Then, the sludge analyzed in this study may have been formed by a relevant filamentous structure and the effect of the treatments disrupted the filaments to achieve a weakened structure with lower hysteresis area values. Alkali treatment led to a lesser reduction of viscosity and thixotropy of the sludge in comparison with the other two treatments likely due to the reduction of the action of inter-particle interactions between sludge flocs and their components.

3.2. Effects of the treatments on sludge dewaterability

The dewaterability of sludge was analyzed at one (hereafter called the “dewatering condition”) of the above conditions discussed for the three treatments. The dewatering condition selected for ultrasound treatment was 27,000 kJ/kg TS, because the reduction in viscosity was almost the same as for 33,000 kJ/kg TS (Fig. 2), and obviously the expenditure was lower. The resulting supernatant was measured in terms of DOC, which value was 2.51g/kg (Table 3). For thermal treatment, the dewatering condition selected was 15,000 kJ/kg TS, because it allowed a reduction in viscosity even higher than the dewatering condition selected for ultrasound treatment (Fig. 2). In addition, this specific thermal energy corresponds to a temperature of 70 °C, which is reported to provide large reductions in pathogen indicators and for increasing biogas production in mesophilic and thermophilic digestion of secondary sludges [5, 34-35]. The dewatering condition for alkali treatment was 157 gNaOH/kg TS (or 0.2 mol/L), because the reduction in viscosity was comparable to the dewatering condition selected for ultrasound treatment (Fig. 2). In addition, doses of NaOH lower than 0.2 mol/L are considered to deteriorate sludge dewatering [20]. The resulting supernatant of the thermally and alkali dewatered sludges showed DOC values of 5.63 and 6.72 g/kg, respectively (Table 3), which far exceeded the result obtained for ultrasonication.

Thus, the chances are that thermal and alkali treatments will enhance sludge disintegration for subsequent anaerobic digestion, even better than ultrasonication. Dewatered sludges were obtained by centrifugation (2,000 g for 30 minutes) of the treated sludges at the dewatering conditions, following by the removal of the free water by decantation. Then, the rheological changes of dewatered sludges were compared with the untreated sludge and with treated sludges at the dewatering conditions. Some physical features of the dewatered sludges (total solid content, *TS*, and total volatile solid content, *VS*) are shown in Table 3. The total solid content increased by 16.2% for the dewatered sludge previously ultrasonicated and by 17.6% for the dewatered sludge previously heated. Alkali treatment resulted in little increase in *TS* content because of poor phase separation after centrifugation.

Fig. 4 shows the evolution of steady-state viscosity as a function of the shear rate for the three sludges (untreated, treated and dewatered) for the treatments studied. The steady state viscosity of dewatered sludges also follows the Oswald–de Waele equation and was higher than that of treated sludges and lower than that of untreated sludge, although the solid concentration was higher. Table 2 also shows the consistency index and power law index of the three dewatered sludges. The consistency index decreased by 44.4% for the dewatered sludge previously ultrasonicated and by 45.8% for dewatered sludge previously heated, over untreated sludge, and increased by 105% and 272%, respectively, over conditioned sludges. The water extraction after centrifugation of alkali-treated sludge was minimal and therefore the consistency index of this dewatered sludge was very similar to their corresponding treated. As observed in Table 2, the power law index for the dewatered sludges is again lower than one, so the main difference in steady state viscosity are observed at a low shear rate. Then, ultrasound and thermal treatments reduced significantly the viscosity of the sludge by improving the dewatering process. As a consequence of the treatment, the bacteria cells break down, releasing intra-cellular organic matter such as extracellular polymeric substance (EPS)

and bound water to the medium. Thus, the internal structure changes due to the reorganization of the sludge flocs with the EPS and free water molecules. EPS, which are produced during the metabolism and autolysis of sludge biomass, are believed to be one of the most important factors affecting sludge dewaterability [36]. There is evidence that high concentrations of EPS increase the viscosity of the sludge [37] and block its dewaterability [38]. Alkali treatment reduced the viscosity of the sludge practically without increasing the free water content. Possibly, the increase in pH broke down the cellular walls, releasing water and other intracellular compounds, but the interaction between the organic matter and water molecules was strong enough to worsen the dewatering process.

Regarding thixotropy, the hysteresis loops of treated and dewatered sludges are shown in Fig. 5 and the corresponding hysteresis areas and fluidities are given in Table 2. Dewatered sludges have a lower hysteresis area than untreated sludge, which corresponds to a reduction of 69.0% for dewatered sludge previously ultrasonicated and 32.6% for dewatered sludge previously heated, and fluidity increased by 62.7% and 32.9%, respectively. Nevertheless, as the solid content of dewatered sludges was higher than that of untreated sludge (Table 1 and 3), the sludge resulting from dewatering was more concentrated but also more manageable. Thus, regarding dewatered sludges, both ultrasound and thermal treatment led to a reduction in viscosity at similar levels, but the reduction of the hysteresis area was significantly higher in the case of ultrasound.

Then, the three treatments reduced the viscosity and thixotropy of sludge by different dewatering mechanisms. The dewatered sludge resulting from ultrasound treatment was less significantly viscous and its thixotropy was almost wholly avoided. Thermal treatment had a lower impact on internal structure and the resulting dewatered sludge showed significant thixotropic behavior, but low viscosity. After centrifugation, the thermally treated sludge

increased the solid content and the sludge flocs were linked strongly enough to give a thixotropic relaxation time.

To evaluate the effect of the treatments on the size of the sludge bioflocs, particle size distribution was evaluated on the basis of the percentage of the particle diameter by volume of the sample. Size distribution within the range of 0.04–2,000 μm of particles was analyzed with a particle size scanning laser. Fig. 6 shows the profiles of the particle size distribution of the untreated and treated sludges for the dewatering conditions described above. All sludge particles were smaller than 1,000 μm . The main particle size for the untreated sludge was between 2 and 200 μm and the mean particle size was 56.9 μm . The particle size profiles of treated sludges vary widely, depending on the treatment. The results given in Table 4 express the particle sizes that correspond with 10%, 50% and 90% of the size histogram; i.e. in the case of untreated sludge, 90% of the volume consists of particles smaller than 111 μm , 50% consist of particles smaller than 47.9 μm , and 10% consist of particles smaller than 11.8 μm . In the case of ultrasound treatment, the volume of particles decreased by over 60.9%, with a mean size of 22.3 μm . Thermal and alkali treatment only decreased the volume of particles by 9.90% and 1.60% and their mean sizes were 51.3 μm and 56.0 μm , respectively. Table 4 also shows the standard deviation (SD) and coefficient of variation (CV). Therefore, thermal and alkali treatments did not break down the sludge flocs or the internal structure, although the viscosity was reduced significantly after treatment. In contrast, ultrasonication waves provided the greatest disruption of the internal structure of the sludge. The reduction in particle size by the application of ultrasonic waves was observed by other authors [2, 12]. Of course, this reduction depends not only on the specific ultrasonic energy supplied, but also on the sludge features. This reduction in particle size due to the ultrasound treatment is directly related to the reduction of both apparent viscosity and thixotropy. Pham et al. [2] found that ultrasonicated sludge improved the disruption kinetic constant, and that the apparent viscosity

of ultrasonicated sludge reached its steady state value faster than untreated sludge. Therefore, ultrasonic waves weaken the strength of the internal structure by disrupting the flocs and/or the bacteria cells [39], which implies releasing EPS and free water into the bulk solution.

These structural changes were checked by the variations in sludge filterability. Fig. 7 shows the change in CST (Capillary Suction Time) with specific energy applied by ultrasonication and thermal treatment. CST simply indicates how quickly the sludge releases its free water content and is often used to characterize sludge dewaterability. Usually, a high value of CST will result in high cake-specific resistance. In Fig. 7, an increase in CST with an increase in specific ultrasound energy is clearly observed. Therefore, the dewaterability of sludge deteriorated sharply after ultrasonic treatment. This could be attributed to the formation of shorter flocs weakening the strength of the internal structure by the retention of the released water after treatment and to a great amount of water becoming attached to the large surfaces provided by the small particles after ultrasonication [40]. According to the literature, an ultrasonic specific energy beyond 4,400 kJ/kg TS significantly deteriorates sludge dewaterability [41].

On the other hand, thermal treatment decreased CST value. This may be because the EPS released by the treatment formed a new internal network with floc size similar to the untreated sludge, which leaves part of the free water to give a thixotropic structured sludge [4]. The CST value for alkali conditioning was too high to be recorded. This might be closely related to the near-impossibility of removing water from the sludge after centrifugation. Erdinçler et al. [18] reported that ultrasound and thermal treatment improved the dewaterability of sludge, while alkali and NaCl treatments did not do so. Dogan and Sanin [42] also reported that CST values increased with alkaline (pH 10–12.5) treatment. Li et al. [43] concluded that low doses of NaOH (lower than 0.2 mol/L) treatment deteriorated sludge dewatering ability, while this ability could be restored to some extent by treatment with a high dose. Furthermore, Ca(OH)_2

treatment was found to be more appropriate for improving sludge dewatering ability, despite being less efficient than NaOH for sludge disintegration, because calcium cations enhance the re-flocculation of soluble organic polymers, which would counteract the sludge disintegration effect.

Although the three treatments led to a decrease in viscosity and thixotropy, only ultrasound and thermal treatment allowed the removal of considerable water from the sludge. In general, the choice of one treatment over another depends on parameters such as energy costs, chemical consumption, sanitation, type of sludge (activated or primary sludge) and the simplicity of installations, among others. For instance, alkali treatment is by far the cheapest treatment, but it was observed that it blocks sludge dewatering. The specific energies for thermal treatment were calculated by an energy balance, and the specific energies for ultrasound treatment were calculated by keeping the ultrasonic power constant and exposing it at different durations. Specifically, for the dewatering conditions established, the cost linked to ultrasound treatment was almost twice the cost of thermal treatment. In addition, the introduction of ultrasound treatment on an industrial scale would be significantly more expensive.

Finally, it would be pertinent to remark that more experimental work has to be done before the structural changes observed in sewage sludge during treatments can be fully understood. This study is now under way in our laboratories and will be explained in a future publication.

4. Conclusions

Secondary sewage sludge was processed by three different treatments, in order to study whether these treatments improved the sludge dewatering process. It was shown that each treatment had a different effect on the physical properties of the sludge. The main conclusions arising from this study were as follows:

All sludges analyzed (untreated, treated and dewatered) showed shear thinning and thixotropic behavior, which means that they had a connected internal structure formed by biological flocs, intra-organic matter, water and other compounds.

The application of ultrasonic waves to the sludge significantly reduced its viscosity, thixotropy and mean particle size, while its capillary suction time was increased. Nevertheless, ultrasonication treatment improved the dewatering process by increasing the total solid content of the sludge after centrifugation.

Thermal treatment reduced viscosity, thixotropy and the capillary suction time, but did not modify mean particle size significantly. It is important to note that although the dewatered sludge previously heated showed less thixotropic behavior than untreated sludge, its thixotropy could still be considered high, which means that this dewatered sludge had a strong internal structure with high free water content.

- Alkali conditioning reduced the viscosity and thixotropy of the sludge, but the mean particle size remained almost constant and the capillary suction time increased considerably. Thus, this treatment did not increase the free water content and hindered the sludge dewatering process, despite the important decrease in viscosity. Possibly, filterability was reduced by alkali-treated sludge forms weakening the network where the water molecules were strongly trapped.

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Figure captions

Fig. 1. Steady state viscosity and hysteresis loop as a function of shear rate for untreated sludge.

Fig. 2. Steady state viscosity of untreated and treated sludges at a shear rate of 30 s^{-1} . Ultrasound treatment: 3,000, 7,000, 17,000, 27,000 and 33,000 kJ/kg TS; Thermal treatment: 12,000, 15,000, 17,000, 20,000 and 22,000 kJ/kg TS; Alkali treatment: 0.784, 7.84, 78.4, 157 and 235 gNaOH /kg TS.

Fig. 3. Hysteresis area reduction of treated sludges at a shear rate of 300 s^{-1} . Ultrasound treatment: 3,000, 7,000, 17,000, 27,000 and 33,000 kJ/kg TS; Thermal treatment: 12,000, 15,000, 17,000, 20,000 and 22,000 kJ/kg TS; Alkali treatment: 0.784, 7.84, 78.4, 157 and 235 gNaOH /kg TS.

Fig. 4. Evolution of steady state viscosity with shear rate for (a) untreated and ultrasonicated sludge at 27,000 kJ/kg TS, (b) thermally treated sludge at 15,000 kJ/kg TS, and (c) alkali-treated sludge at a concentration of 157 gNaOH/kg TS, and the corresponding dewatered sludges, which were obtained by centrifugation of the previously treated sludges.

Fig. 5. Hysteresis loops for (a) untreated and ultrasonicated sludge at 27,000 kJ/kg TS, (b) thermally treated sludge at 15,000 kJ/kg TS, and (c) alkali-treated sludge at a concentration of

157 gNaOH/kg TS, and the corresponding dewatered sludges, which were obtained by centrifugation of the previously treated sludges.

Fig. 6. Particle size distribution of untreated and treated sludges at the dewatering conditions.

Ultrasound: 27,000 kJ/kg TS. Thermal treatment: 15,000 kJ/kg TS. Alkali treatment: 157 gNaOH/kg TS

Fig. 7. Capillary Suction Time (CST) for ultrasonicated sludge and thermally treated sludge.

Table 1

Physical and chemical properties of the untreated secondary sludge.

TS (g/kg)	56.7 ± 0.7
VS (g/kg)	45.8 ± 0.3
Elemental analysis	$C_5H_{8.5}N_{0.9}P_{0.05}$
pH	6.45 ± 0.03
Conductivity (mS/cm)	3.03 ± 0.05
tCOD (g/kg)	61.3 (0.2)
sCOD (g/kg)	0.90 (0.18)

Table 2

Table 2
Rheological parameters

Ultrasonic specific energy (kJ/kg TS)	K (Pa s ⁻ⁿ)	n	Maximum shear rate of 300 s ⁻¹		Maximum shear rate of 125 s ⁻¹		Maximum shear rate of 30 s ⁻¹	
			Hysteresis area (Pa s ⁻¹)	Fluidity×10 ⁵ (Pa ⁻¹ s)	Hysteresis area (Pa s ⁻¹)	Fluidity×10 ⁵ (Pa ⁻¹ s)	Hysteresis area (Pa s ⁻¹)	Fluidity×10 ⁵ (Pa ⁻¹ s)
0	29.7 ± 1.4	0.196 ± 0.098	4176	5.31	1251	12.8	121	70.2
3,000	19.6 ± 1.2	0.206 ± 0.051	2007	6.64	750	19.1	58.5	118
7,000	17.5 ± 1.3	0.195 ± 0.071	1359	7.66	511	26.9	52.0	139
17,000	15.6 ± 1.4	0.188 ± 0.077	580	8.57	217	27.8	16.1	163
27,000	8.06 ± 1.61	0.261 ± 0.106	502	11.9	96	36.6	18.6	246
27,000*	16.5 ± 1.3	0.194 ± 0.056	1295	8.63	209	24.0	56.2	124
33,000	7.84 ± 1.52	0.266 ± 0.100	276	11.8	20	36.4	5.47	243
Thermal specific energy (kJ/kg TS)								
12,000	8.83 ± 0.79	0.259 ± 0.056	939	11.5	244	35.9	12.4	227
15,000	4.33 ± 0.61	0.314 ± 0.116	801	19.1	243	51.8	12.7	418
15,000*	16.1 ± 0.6	0.237 ± 0.107	2816	7.05	1218	23.5	1.21	572
17,000	2.92 ± 0.89	0.315 ± 0.027	580	27.5	116	85.1	6.05	828
20,000	2.33 ± 0.71	0.295 ± 0.083	544	37.9	104	120	75.3	133
22,000	1.43 ± 0.54	0.355 ± 0.148	224	44.3	62.0	144	10.6	1057
Alkali concentration (gNaOH/kg TS)								
0.784	29.9 ± 1.4	0.156 ± 0.087	1802	8.47	421	24.8	32.9	146
7.84	21.4 ± 1.7	0.216 ± 0.133	1505	9.01	338	25.9	22.3	149
78.4	15.5 ± 1.4	0.228 ± 0.084	925	11.3	243	36.0	15.9	226
157	6.18 ± 1.58	0.258 ± 0.109	723	24.4	73.0	76.9	1.03	514
157*	6.51 ± 1.82	0.196 ± 0.098	1925	9.05	450	44.2	15.6	299
235	3.46 ± 1.79	0.316 ± 0.140	573	32.7	124	103	6.01	719

*Dewatered sludges were previously (a) ultrasonicated at 27,000 kJ/kg TS, (b) thermally treated at 15,000 kJ/kg TS and (c) alkali-treated at a concentration of 157 gNaOH/kg TS and subsequently neutralized.

Table 3

Physical and chemical properties of the dewatered sludges previously treated (27,000 kJ/kg TS for ultrasonication, 15,000 kJ/kg TS for thermal treatment and 157 gNaOH/kg TS for alkali treatment).

	TS (g/kg)	VS (g/kg)	DOC (g/kg) [*]
Dewatered sludge after ultrasonication	65.9±1.3	53.4±0.2	2.51 (0.06)
Dewatered sludge after thermal treatment	66.7±0.5	54.0±0.1	5.63 (0.15)
Dewatered sludge after alkali treatment	61.6±0.8	48.0±0.3	6.72 (0.08)

^{*}Dissolved organic carbon (DOC) measurements were performed on the supernatant after centrifugation and correspond to the fraction of TOC that passes through a 0.45- μ m-pore-diam filter.

Table 4

Particle sizes for untreated and treated sludges for the dewatering conditions established.

	d ₁₀ (μm)	d ₅₀ (μm)	d ₉₀ (μm)	Mean particle size (μm)	SD (μm)	CV ¹ (%)
Untreated sludge	11.8	47.9	111	56.9	35.7	62.7
Ultrasonicated sludge ²	0.87	8.15	57.8	22.3	22.7	102
Thermally treated sludge ²	13.0	39.8	101	51.3	34.9	68.0
Alkali- treated sludge ²	14.3	52.6	101	56.0	33.9	60.5

¹ Coefficient of variation, SD/mean particle size.² Sludges treated at the dewatering conditions (a) ultrasonicated at 27000 kJ/kg TS, (b) thermally treated at 15000 kJ/kgTS and (c) alkali-treated at a concentration of 157 gNaOH/kgTS and subsequently neutralized.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

The conditioning of a secondary sludge is studied.

Three treatments were used: ultrasound waves, heat and chemical conditioning with NaOH.

The effect of the three treatments was analysed by means of rheology, particle size distribution and CST.

Ultrasound waves and heat conditioning improved the dewaterability of the sludge.