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Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability

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Abstract

In order to enhance the efficiency of anaerobic digestion, the effects of ultrasounds, ozonation and thermal pre-treatment have been studied on waste activated sludge. The feature of this study was to carry out the comparison of the three pre-treatments in the same conditions and on the same sludge sample. Each treatment was tested in two conditions close to optimum conditions to maximise batch anaerobic sludge biodegradability. All treatments led to chemical oxygen demand and matter solubilisation and had little influence on mineral matter. In terms of solubilisation thermal pre-treatment was better than sonication or ozonation. But, in terms of batch anaerobic biodegradability, best results were obtained with ultrasounds with an energy of 6250 or 9350 kJ/kg TS and a thermal treatment at 170 or 190 °C. Moreover, treatments had effects on physico-chemical characteristics of sludge samples: apparent viscosity decreased after all treatments but the reduction was more important with thermal treatment. Median diameter of sludge flocs were reduced after sonication, increased after thermal treatment and did not change after ozonation. Finally, capillary suction time (CST) increased after ozonation, increased highly after sonication and was reduced after thermal treatment.

Keywords: Ultrasounds; Ozone; Thermal treatment; Solubilisation; Methanisation; Particle size; Viscosity; Capillary suction time; Sewage sludge

1. Introduction

At present in France, sludge production is increasing, due to the enforcement of the European legislation regarding the Urban Wastewater Treatments Directive (91/271/EEC). The research of more efficient treatment is therefore necessary. Indeed, the Directive sets limits for some of the established sanitary determinants (e.g. biological oxygen demand, suspended solids and nutrients) and imposes small town to build plant in order to treat their wastewater. This leads to an important increase in sewage sludge production. In the same time, disposal routes are subject to more legal and social constraints: land disposal is now restricted in France, incineration is quite expensive and land application (or agricultural use) is highly debated. This causes a large problem to communities and wastewater treatment plant operators.

In order to solve this problem, it is necessary to reduce sludge production to the source that is to say in the wastewater treatment plant. This is possible with anaerobic digestion. This treatment, which allows a reduction of sludge quantity of about 40–50%, has become one common method of sludge stabilisation, due to the production of biogas that makes the process profitable. In wastewater treatment plants, anaerobic digestion is generally applied to mixture of primary and secondary (waste activated) sludge. But waste activated sludge (WAS) are known to be more difficult to digest than primary sludge [1]. Anaerobic digestion process is achieved through several stages: hydrolysis, acidogenesis, methanogenesis. For WAS degradation, the rate-limiting step is the hydrolysis [2]. In order to improve hydrolysis and anaerobic digestion performance, one possibility is to use cell lyse pre-treatments. Several pre-treatments can be considered: mechanical, thermal, chemical or biological treatments [3–5]. The aim of these treatments is to solubilise and/or to reduce the size of organic compounds, and specially refractory compounds, in order to make them more easily biodegradable [6,7]. Final quantity of residual sludge and time of digestion can thus be reduced and biogas production can be increased [8–10].

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This paper deals with the comparison of three pre-treatments: ultrasounds, ozonation and thermal pre-treatment. Ultrasonic pre-treatment leads to cavitation bubbles formation in the liquid phase [11]. These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse produces intense local heating and high pressure at the liquid–gas interface, turbulence and high shearing phenomena in the liquid phase, but also formation of radicals [12,13]. Moreover, it has been proved that the degradation of excess sludge is more efficient using low frequencies: mechanical effects facilitate particles solubilisation [11].

Due to its strong oxidative properties, ozone has been used for water and wastewater treatment. During sludge ozonation, because of the complex composition of sludge, ozone decomposes itself into radicals and reacts with the whole matter: soluble and particular fractions, organic or mineral fractions [14,15]. Using ozone for sludge reduction has been widely studied. Optimal consumed ozone dose ranges from 0.05 and 0.5 g O_3/g of total solid: there is a phenomenon of mineralisation for higher ozone doses [10,16]. Moreover, ozonation modifies viscosity and settlement of sludge [17].

With thermal pre-treatment, cells are broken due to pressure differences. These treatments also have the advantage of sanitising the sludge and enhancing its dewatering properties [18]. According to several authors, optimal temperature is around 170–200 °C and treatment time has little effect [2,9,19]. Moreover, when combined with anaerobic digestion, energy required to perform thermal treatment can be positively balanced by biogas production [20]. Beside, thermal treatment has effects on the viscosity and the filterability of sludge [21].

Previous works in the laboratory [22–24] were devoted to determine optimum conditions of ultrasounds, ozonation and thermal treatment. For all treatments sludge solubilisation increased with the treatment (ultrasonic specific applied energy, transferred ozone dose and temperature). In all cases, solubilisation of matter was focused on organic solids: mineral solids solubilisation was lower than organic solids solubilisation. During ozonation, total COD and total solids remained constant for an ozone dose lower than 0.15 g O_3/g TS. For higher ozone dose, total concentrations seemed to decrease. This could suggest a mineralisation phenomenon for ozone doses higher than 0.18 g O_3/g TS.

Sludge biodegradability was assessed by batch anaerobic digestion tests. In all cases, biogas production for treated samples was higher than for untreated sludge, but treated sludge was not completely biodegradable in 16–20 days. For ultrasonic specific energy between 0 and 7000 kJ/kg TS, biogas production increased with energy supplied. But for energy supplied of 7000 and 15,000 kJ/kg TS, biogas production was almost the same. The optimum ultrasonic energy was thus about 7000 kJ/kg TS [22].

Biogas production increased with ozone dose until 0.15 g O_3/g TS and then decreased. This was probably due to inappropriate acidic condition for micro-organisms or due to the formation of recalcitrant ozonation by-products. Therefore, an ozone dose of 0.15 g O_3/g TS seemed to be the most interesting [23].

In the range of temperature tested (90–210 °C), optimal temperature seemed to be 170 or 190 °C: sludge biodegradability of treated sludge increased with temperature up to 170 °C. The increase in biogas production was almost the same for 170 and 190 °C and was lower for 210 °C [24].

The objective of this study was to compare the effects of these three pre-treatments (ultrasounds, ozonation and thermal pre-treatment) on waste activated sludge, in order to improve anaerobic digestion. The feature of this work was to carry out the comparison of the three pre-treatments in the same conditions and on the same sludge sample. Solubilisation of chemical oxygen demand and matter were measured, as well as physico-chemical characteristics of sludge (pH, particles size, viscosity and filterability) and improvement of biogas production during batch anaerobic digestion.

For each treatment, we applied two conditions close to the optimal ones [22–24]:

- a specific energy of 6250 and 9350 kJ/kg TS, for sonication,
- an ozone dose of 0.1 and 0.16 g O_3/g TS, for ozonation,
- a temperature of 170 and 190 °C, for thermal treatment.

2. Experimental

2.1. *Waste activated sludge characteristics*

Experiments were carried out using flottation-thickened WAS collected from the municipal WWTP of Carcassonne (South of France). This plant had a capacity of 90,000 people equivalent, that is to say that the pollution in entrance was equivalent to 4.5 tonnes of suspended solids per day. This plant treated domestic and industrial wastewater and was operated with a high loaded aeration tank. For the experiments, sludge was diluted in order to obtain a total solid concentration (TS) of 20 g/l. The organic solids (or total volatile solids VS) content was 76% of TS.

2.2. *Pre-treatments conditions*

The ultrasonic apparatus used was an ultrasonic homogenizer Autotune 750 W (Bioblock Scientific), working with a standard probe, an operating frequency of 20 kHz and a supplied power of about 225 W. Batch experiments were carried out in beakers without temperature regulation (no cooling). Treated samples had a volume of 0.5 l. Specific supplied energy (E_s) was 6250 and 9350 kJ/kg TS. Specific energy (E_s) is defined using ultrasonic power (P), sonication time (t), sample volume (v) and initial total solid concentration (TS_0):

$$E_s = (Pt)/(v\mathrm{TS}_0) \quad (1)$$

Sludge was ozonized in batches in a bubble column. Ozone was generated from pure oxygen using an OZAT® type CFS-1 generator (Ozonia). Ozone concentrations in gas phase, before and after reaction with sludge, were measured, during the oxidation every 30 s, with UV analysers BMT 96 3 in order to calculate the amount of O_3 that was transferred. Gas flow rate was 1 l/min, ozone inlet concentration was about 30 mg/l. Reactor volume was 1 l, sample volume was 0.3 l. The transferred ozone dose was 0.10 and 0.16 g O_3/g TS.

The reactor used for thermal treatment was a Zipperclave (Autoclave France) which temperature was controlled by PID (proportional integral derivative). The autoclave was equipped with an Hastelloy C tank. Sample volume was 0.5 l. Tested temperatures were 170 and 190 °C. For 190 °C, treatment duration corresponded to the rise in temperature (about 60 min) and for 170 °C experiments lasted 30 min more.

2.3. *Samples analyses*

2.3.1. *Solubilisation evaluation*

In order to determine sludge solubilisation, several measurements were carried out on samples, according to Standard Methods [25]. In fact, the term “solubilisation” represents the transfer (of COD or solids) from the particulate fraction of the sludge (solids after centrifugation) to the soluble fraction of the sludge (supernatant after centrifugation).

First, soluble and particulate fractions were obtained after centrifugation (Beckman J2 MC 25,000 × *g*, 15 min, 5 °C). Then, solubilisation was characterised by chemical oxygen demand (COD), solids repartition (soluble/particulate or organic/mineral).

COD was measured on the total sludge and on the supernatant, using the normalised method [25]. For this paper, COD measured on supernatant will be called “soluble COD” (CODs) and COD measured on the “solids of centrifuge” will be called “particulate COD” (CODp). COD solubilisation (S_{COD}) was calculated using the difference between soluble COD (CODs) and initial soluble COD (CODs_0), compared to the initial particulate COD (CODp_0).

$$S_{\mathrm{COD}} = (\mathrm{CODs} - \mathrm{CODs}_0)/\mathrm{CODp}_0 \times 100\% \qquad (2)$$

Solids concentrations were estimated by heating (105 °C during 24 h for total solids and 550 °C during 2 h for mineral solids concentrations). Volatile solids concentrations were deduced. Measures of total and organic solids (TS and VS) were realised on sludge and on solids after centrifugation (total and volatile suspended solids: TSS and VSS). Solids concentration of the supernatant, that is to say the soluble phase, was then deduced.

That led to the composition in the different parts in the sludge. Matter solubilisation (S_{TS}) was calculated.

$$S_{\mathrm{TS}} = (\mathrm{TSS}_0 - \mathrm{TSS})/\mathrm{TSS}_0 \times 100\% \qquad (3)$$

2.3.2. *Sludge characteristics*

Particle size measurements were realised using a laser diffraction sensor (Mastersizer 2000, from the Malvern firm). Particle size was determined using a sphere of same volume. Results were expressed in median diameter (*d*).

Viscosity measurements were carried out using a High Resolution C-VOR viscosimeter (Bohlin Instrument) connected to a computer. The system was a “plane-cone” with a diameter of 60 mm. The angle of the cone was 2° and the gap measured 70 μm. Measures were realised by increasing the shear stress from 0.01 to 8 Pa and were duplicated. Their reproductibility was good.

Capillary suction time measurements (CST) were realised using a Triton type 319 Multi-CST (Triton Electronics Ltd.). The CST permits to estimate the sludge ability to dewater:water is absorbed by CST paper by capillarity. The CST measure corresponds to the time needed for water to cross a fixed distance in the filter paper. It is often used to estimate sludge filterability.

2.3.3. *Characterisation of anaerobic biodegradability*

Batch anaerobic digestion tests were carried out to assess sludge biodegradability. For these experiments the inoculum used was a sludge treating a mixture of wine effluents (80%) and sludge (20%). The inoculum was diluted to 4 g/L of volatile suspended solids (VSS-equivalent to organic suspended solids). For each pre-treatment, samples of treated or untreated sludge were added to 400 ml of inoculum. The pollution to degrade was equivalent to 0.5 g COD/g VSS of inoculum. Plasma bottles were agitated (200 rpm) at 35°C. Several control samples were realised: a blank (water), an ethanol sample (completely biodegradable compound) and a untreated sample (raw sludge added). Biogas volume produced was measured by movement of liquid (water, pH 2, NaCl 10%).

Enhancement of biodegradability was evaluated by comparison of biogas volumes produced by treated and untreated samples. Biogas ratio is biogas volume produced with treated sludge divided by biogas volume produced with untreated sludge. Moreover, the biodegradability percentage was estimated by comparing the biogas volume produced with sludge (treated or not) to the biogas volume produced with ethanol. For all substrates, volumes of biogas were reported to the introduced COD (quantity of pollution to degrade).

3. Results and discussion

3.1. *Effects of pre-treatments on matter and COD solubilisation*

During these comparative tests, total COD and TS concentrations remained almost constant for all treatments, except for thermal treatment at 170 °C (sludge slightly stuck on the lyse reactor walls). COD concentration was 15.0 g O_2/l (standard deviation: 1.0 g O_2/l); TS one 18.9 g/l (S.D.: 1.1 g O_2/l). Treatments led to a transfer from particles to supernatant. Fig. 1 presents results obtained in terms of COD and TS solubilisation.

For each technique, COD solubilisation and TS solubilisation were quite similar: almost 15% for sonication, 20–25% for ozonation and 40–45% for thermal treatment. Thus solubilisation results were very different according to used techniques. Solubilisation is much more higher with thermal treatment than with sonication or ozonation. Moreover, for a given technique, there were few differences between the two chosen operating conditions, which were relatively close.

Pre-treatments led to a modification of the repartition of the solids (Fig. 2). For all treatments, total mineral solids concentration was almost constant: sonication, ozonation or thermal

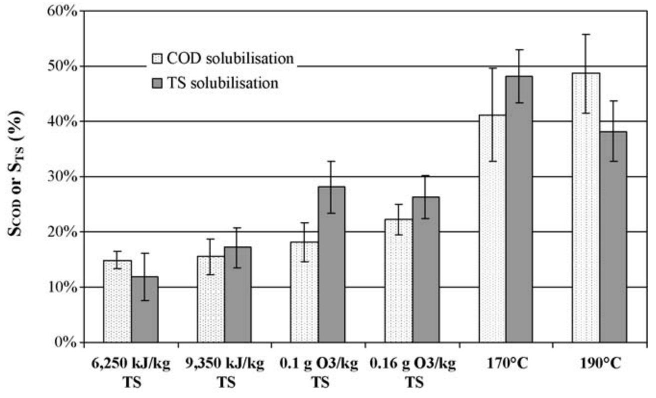

Fig. 1. COD and TS solubilisation after various pre-treatments (mean of three measurements ± S.D.).

treatment did not lead to a mineralisation phenomenon in those conditions. Moreover, mineral concentration in particles seemed to be almost constant to: 3.8 g/l (S.D.: 0.3 g/l). Therefore, it means that mineral solids were only slightly affected by pre-treatments: mineral solids solubilisation was very low (less than 10%). At the opposite, organic solids were highly affected by treatment. Organic solids concentration in particles decreased strongly from 14.4 g/l in raw sludge to 11–12 g/l for sludge treated with ultrasounds, 9–10 g/l for sludge treated with ozone and around 7 g/l for thermally treated sludge. Thus, specially for thermal treatment, particular fraction of sludge became more mineral. The ratio VSS/TSS decreased from 78% for raw sludge to 73% for sludge treated with ultrasounds or ozone and 66% for thermally treated sludge.

In conclusion, thermal treatment was the most efficient treatment in terms of matter solubilisation and sonication and ozonation led to almost the same results (lower than for thermal treatment).

3.2. *Effects of pre-treatments on physico-chemical characteristics of waste activated sludge*

Lyse pre-treatments led to modification of the physico-chemical characteristics of sludge. For instance, pH decreased with ozonation or thermal treatment, in order to reach a value of 5.8. This can be explained by the formation of acidic compounds. On the other hand, for sonication, pH was not modified. Thus, it seems that sonication, ozonation and thermal treatment do not act in the same way. Ozonation and thermal treatment led to the modification of sludge composition: organic compounds were directly affected by treatment. In fact, it seems that lipids were degraded in order to form volatile fatty acids, which decreased the pH [24].

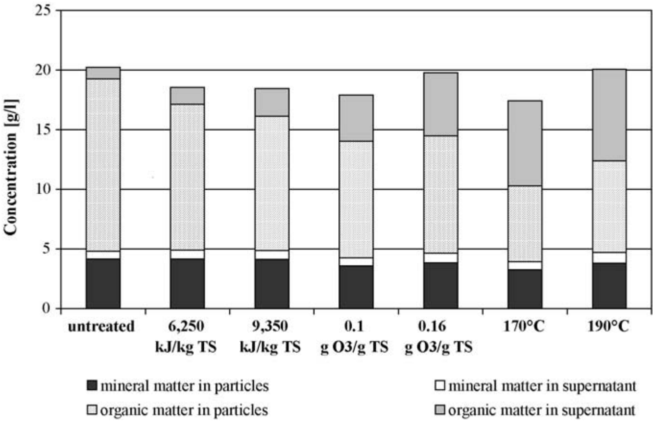

Fig. 2. Solids repartition before and after treatment: means of three values. Errors were equal to 2–3% for all measurements.

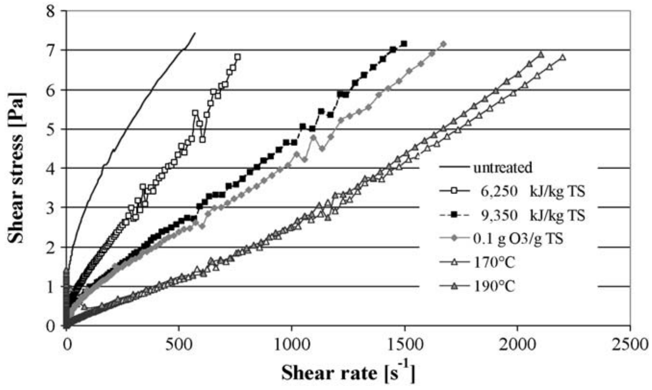

Fig. 3. Shear stress versus shear rate, for treated and untreated sludge samples.

Treatments also had effects on rheology of sludge. WAS are generally non-Newtonian fluids: the shear stress (τ) is not linearly related to the shear rate ($\dot{\gamma}$) as shown in Fig. 3.

The treated sludge curves were lower than the curve for untreated sludge. That means that apparent viscosity ($\tau/\dot{\gamma}$), for a given shear rate, decreased with treatments. For instance, for a shear rate of $100\,s^{-1}$, the apparent viscosity of raw sludge was 0.034 Pa s, and it decreased to 0.009–0.014 Pa s for sonicated or ozonized sludge and to 0.003 Pa s for thermally treated sludge. In the same time, it seemed that rheology curve for thermally treated sludge became more linear. This could mean that sludge tended to become more Newtonian after thermal treatment. In order to verify this hypothesis, we used a rheology model. According to literature, the Ostwald de Waele model is the most used model in the case of sludge [26,27].

$$\tau = k\dot{\gamma}^n \qquad (4)$$

In this model, k is a constant, linked to the structure: the higher the value is, the higher the apparent viscosity. The structure index n is linked to the apparent viscosity dependence to shear rate: n equals to 1 for Newtonian fluids. Table 1 presents model parameters, which were determined by fitting experimental data. The table also presents the apparent viscocity measured for two different shear rates. So, during experiment, k constant strongly decreased with treatments: k was divided by 10 for sonicated and ozonized sludge and by 100 for thermally treated sludge. In the same time, the structure index n increased from 0.42 to 0.89 for thermally treated sludge. Sludge became therefore more Newtonian and apparent viscosity decreased strongly: viscosity was divided by 16, for a shear rate of $56\,s^{-1}$, for sludge thermally treated at 170 °C. Thus treated sludge should be easier to pump.

An other modification due to pre-treatment was particles size. Table 2 presents median diameter for treated or untreated sludge.

Table 1
Parameters of Oswald de Waele model and apparent viscosity

Treatment	k	n	μ_{ap} (Pa s)	
			For $\dot{\gamma} = 50\,s^{-1}$	For $\dot{\gamma} = 300\,s^{-1}$
Untreated	0.494	0.42	0.051	0.018
Ultrasounds (E_s = 6250 kJ/kg TS)	0.044	0.75	0.016	0.010
Ozonation (0.1 g O_3/g TS)	0.043	0.65	0.011	0.006
Thermal treatment (170 °C)	0.0047	0.89	0.0031	0.0026

Table 2
Median diameter of particles before and after treatments (mean of five measurements)

	d (μm)
Untreated	36.3
Sonication	
6250 kJ/kg TS	10.7
9350 kJ/kg TS	9.6
Ozonation	
0.1 g O_3/g TS	33.2
0.16 g O_3/g TS	32.6
Thermal treatment	
170 °C	76.8
190 °C	77.1

For the applied energies, sonication decreased median diameter from 36 μm for raw sludge to 10 μm: that is to say a decrease of 70%. On the contrary, thermal treatment led to an increase in the diameter. Ozonation did not seem to affect particles size. These modification meant that sonication broke aggregates, flocs and maybe cells [29]. On the other hand, thermal treatment led to particles agglomeration. This could suggest that the rise in temperature led to the creation of chemical bonds.

Treatments also led to a modification of the sludge filterability. Table 3 shows CST measures for the different treatments. The three treatments did not have the same effect on filterability. Sonication and ozonation increased strongly the CST value, whereas, thermal treatment decreased it. This can maybe be linked to the particles size. But, in priori, particles size is not the only parameter having an impact on CST. Indeed, particles size remained constant with ozonation.

Sonication, by decreasing particles size, led to the damage of filterability. This confirms results obtained by Chu et al. [28]. They observed an increase of the CST, which they explain by an increase of the bound water linked to the particles surface: as the particles diameters were lower, the surface of contact was higher and the quantity of bound water too. On the other hand, thermal treatment led to the release of more water, by breaking the sludge structure. The reached temperature could have effect on hydrogen bonds, which gave structure to sludge. By modifying this structure, it was possible to release a part of the initial bound water. Moreover, thermal treatment was initially used as a dewatering pre-treatment [18].

Table 3
CST measures before and after treatments (mean of three values ± S.D., except for ozonation, 1 value)

	CST (s)
Untreated	151 ± 2
Sonication	
6250 kJ/kg TS	733 ± 19
9350 kJ/kg TS	680 ± 47
Ozonation	
0.1 g O_3/g TS	382
Thermal treatment	
170 °C	39 ± 1
190 °C	29 ± 4

3.3. *Effects of pre-treatments on batch anaerobic digestion*

The aim of pre-treatments is to improve sludge anaerobic digestion. Therefore, batch anaerobic digestion tests were realised in order to choose the best treatment. Fig. 4 presents results of batch anaerobic digestion tests. All pre-treatments allowed a biogas production equal or higher than for untreated sludge, but total produced biogas volume remained lower than for ethanol (totally biodegradable substrate). All sludge samples were not completely biodegradable in 24 days. However, for thermal treatment and sonication, final biogas volumes produced with treated sludge were only slightly lower than the biogas volume produced with ethanol.

For sonication, results obtained for the two conditions of treatment were identical during the whole test. It was the same for thermal treatment but both samples of ozonized sludge showed little difference. Table 4 presents the biogas production enhancement, the methane content and the biodegradability

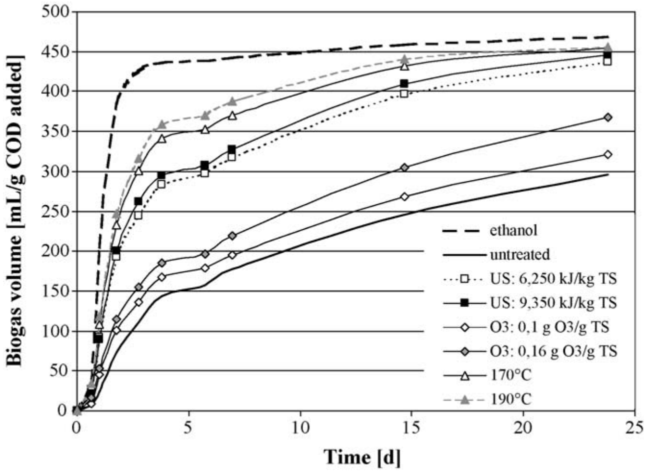

Fig. 4. Batch anaerobic digestion tests.

Table 4
Biogas production enhancement, methane content and biodegradability percentage, at the end of the test (day 24)

Treatment	Untreated	Ultrsound		O_3		Thermal treatment	
		6250 kJ/kg TS	9350 kJ/kg TS	0.1 g O_3/g TS	0.16 g O_3/g TS	170 °C	190 °C
Biogas enhancement	1	1.51	1.53	1.08	1.25	1.59	1.59
Methane content (%)	75	73	74	77	74	71	70
Methane production (mL CH_4/g COD_{added})	221	325	334	246	272	333	328
Biodegradability (%)	63	93	95	70	78	95	94

percentage, at the end of the test (day 24). For sonication and thermal treatment, results obtained in terms of biogas production enhancement were similar to those obtained in previous work with the same sludge and in almost the same conditions [22,24]. On the contrary, results obtained with ozone treatment were surprising. At the end of the experiments (day 24), biogas volume produced with sludge treated with an ozone dose of 0.16 g O_3/g TS was only 1.25 times higher than volume produced with untreated sludge. Previously, this enhancement was equal to 2.58 [23]. This could be due to inhibitory conditions (to much ozone remained in the soluble phase), to the formation of refractory compounds, to a not well-adapted inoculum or to ozone consumption by reduced compounds of the sludge. An other explanation could also be the initial biodegradability percentage of raw sludge. For the previous studies with ozone [23], initial biodegradability was around 35%. For this comparative series of tests, initial biodegradability was 63%. This variation of anaerobic biodegradability could be explained by variations in sludge composition and/or in used inoculum.

Moreover, it seems that thermal treatment slightly decreased methane content: it passed from 75% for raw sludge to 70% for thermal treatment. On the other hand, sonication and ozonation did not affect the methane content. After 24 days of tests, sludge was almost totally biodegradable with sonication and thermal treatment: biogas volume produced with treated sludge was equal to almost 95% of the volume produced with ethanol, but it has to be reminded that initial sludge biodegradability was high. Treatments also permitted to accelerate sludge degradation. For untreated sludge, it took 24 days to produced 300 ml of biogas per gram of COD added, and only 3 days for thermally treated sludge, 6 days for sonicated sludge and around 15–18 days for ozonized sludge (depending transferred ozone dose). These results can have important consequences in continuous anaerobic digestor operation. Indeed, sludge lysis pre-treatments can be used either to maximise biogas production (and to minimise residual sludge amount) or to accelerate sludge anaerobic digestion and to treat more sludge in a given digestor by reducing sludge retention time (SRT). The 24 days needed to produce 300 ml of biogas per gram of COD added in batch test are of the same order of magnitude as classical SRT of raw sludge (generally 20 days). Fig. 4 shows that the same volume of biogas could be produced with a SRT of 3 and 5 days with a thermal or ultrasonic pre-treatment. However, such low SRT could lead to methanogenic micro-organisms washing out. Finally, Fig. 4 shows that a SRT of 15 days could be a good choice if thermal or ultrasound is applied. It would allow to reduce classical SRT of 25% and to increase biogas production.

Fig. 5 presents methane production versus COD solubilisation, for the three treatments (day 24). A COD solubilisation of 20% led to a methane production increase of 147 ml CH_4/g COD_{added} for sonication and around 40–45 ml CH_4/g COD_{added} for ozonation or thermal treatment. Slopes of curves have been calculated, despite of the little number of experimental points. Indeed, previous separate studies have shown that, for all the treatments used, methane or biogas production was linearly correlated with COD solubilisation [24]. Therefore, ultrasounds allowed a weak solubilisation of COD and a high biodegradability, whereas, ozonation allowed a weak solubilisation and a weak biodegradability and thermal treatment a strong solubilisation and a strong biodegradability. The values determined for slopes allowed us to make suppositions about biodegradability of treated sludge. So, it seemed that treatments were controlled by different mechanisms.

In the case of sonication, the COD solubilised (approximately 20%) was almost totally and rather quickly biodegradable. At the same time, ultrasounds acted on the particular material. Particles size decreased and exchange area between particles and liquid phase increased. Particular COD thus became more easily available to micro-organisms and the biodegradability of particles improved but remained rather slow. For thermal treatment, solubilised COD (approximately 50%) was also almost totally and rather quickly biodegradable, but a small fraction remained slowly biodegradable. Moreover, considering the particular part

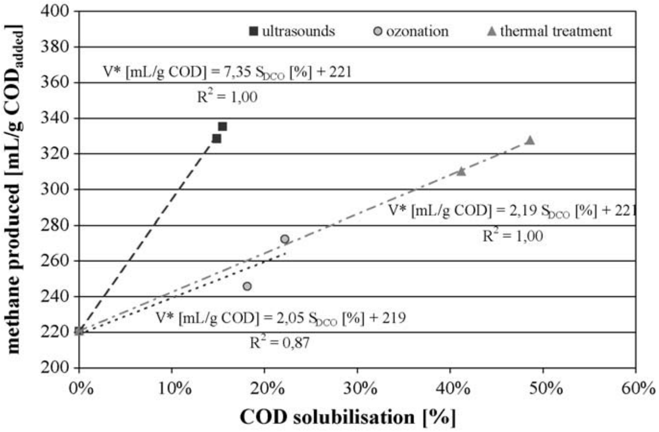

Fig. 5. Methane production versus COD solubilisation, for the three treatments (day 24).

of sludge, thermal treatment had less impact than the sonication: the accessibility of CODp seemed to be less modified than for the sonication. In the case of ozonation, COD was weakly solubilised (approximately 20%) and CODp biodegradability was little modified (same level as for thermal treatment).

So, the sonication main action was focused on particles accessibility, whereas, thermal treatment was mainly centred on compounds solubilisation.

4. Conclusion

All three techniques led to solids solubilisation and to anaerobic biodegradability enhancement. In terms of solubilisation, thermal treatment was the most efficient. In the same time, thermal treatment led to a strong decrease of apparent viscosity, a strong increase in filterability and an increase in particles diameter. Sonication led to a decrease in particles size, in apparent viscosity and in filterability. Ozonation also led to a decrease in apparent viscosity and filterability, but had no effect on particles size.

In terms of anaerobic biodegradability, pre-treatments led to an enhancement of biogas production. Nevertheless, for ozonation, this enhancement was low, but raw sludge biodegradability was very high (60%). This was probably due to inhibitory conditions or refractory compounds. On the contrary, sludge became almost completely biodegradable within a 24 days batch with sonication (6250 or 9350 kJ/kg TS) and thermal treatment (170 or 190 °C). This was the result of two different mechanisms. Ultrasounds led to little solubilisation of sludge and to particle size reduction, which allowed to enhance the particulate fraction biodegradability. Thermal treatment main effect was solid solubilisation and did not affect remaining particulate biodegradability.

It was therefore impossible to find out the best treatment among sonication and thermal treatment: there was not enough difference between sludge biodegradability results. So, in order to chose one treatment rather than the other, it is necessary to consider other parameters like costs, sanitation, simplicity of installations, . . .

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Appendix A. Nomenclature

COD	chemical oxygen demand ($g\,O_2/l$)
CODp	COD in particles ($g\,O_2/l$)
$CODp_0$	initial COD in particles ($g\,O_2/l$)
CODs	soluble COD ($g\,O_2/l$)
$CODs_0$	initial soluble COD ($g\,O_2/l$)
CST	capillary suction time (s)
d	median diameter (μm)
E_s	specific supplied energy (kJ/kg TS)
k	constant of Oswald de Waele model ($Pa\,s^n$)
n	structure index of Oswald de Waele model
P	power (W)
S.D.	standard deviation
SCOD	COD solubilisation (%)
STS	total solid solubilisation (%)
t	treatment time (s)
TS	total solids (g/l)
TS_0	initial total solids (g/l)
TSS	total suspended solids (g/l)
TSS_0	initial total suspended solids (g/l)
v	sample volume (l)
VS	volatile or organic solids (g/l)
VSS	volatile or organic suspended solids (g/l)
WAS	waste activated sludge
WWTP	wastewater treatment plant

Greek symbols

$\dot{\gamma}$	shear rate (s^{-1})
τ	shear stress (Pa)

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