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# Improving sewage sludge ultrasonic pretreatment under pressure by changing initial pH

Ngoc Tuan Le, Carine Julcour, Berthe Ratsimba, Henri Delmas\*

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## A B S T R A C T

This work aimed at understanding the combined effect of sludge pH, temperature, and external pressure on the efficiency of sewage sludge ultrasound (US) pretreatment. Based on the evolution of both the degree of sludge disintegration ( $DD_{COD}$ ) and pH, application of 40 mg<sub>NaOH</sub>/g<sub>TS</sub> during 30 min was selected for chemical pretreatment. Mechanical and thermal effects induced by cavitation contributed in similar proportion to sludge disruption, but the role of the latter effect tended to be weakened after mild alkalisation of sludge. When applying external pressure,  $DD_{COD}$  was always improved, by about 10% at the optimal value of 2 bar. The optimal combination was an addition of 40 mg<sub>NaOH</sub>/g<sub>TS</sub> prior to adiabatic sonication at 2 bar, resulting in a  $DD_{COD}$  value of about 46% at 75,000 kJ/kg<sub>TS</sub> (as compared to 35% for sole US) for the investigated mixed sludge. Very short time US application yielded a drastic reduction of the volume mean particle size, mainly due to the erosion and disruption of large flocs (>90 µm), yet this was not sufficient to initiate significant subsequent COD solubilisation under stirring.

## Keywords:

Alkalization  
Sonication  
Sludge disintegration  
Chemical oxygen demand  
Particle size distribution  
Mixed sludge

## 1. Introduction

The first objective of sewage sludge treatment is to remove organic matters and water, which reduces the volume and mass of sludge and also cuts down toxic materials and pathogens. Biological, mechanical, chemical methods and thermal hydrolysis have been listed as popular techniques for sludge pretreatment (Carrère et al., 2010). Among these techniques, anaerobic digestion (AD) is the most traditional one. However, this process is limited by long sludge retention time and rather low overall degradation efficiency. Sludge mainly consists of microbial cells that limit the biodegradability of intracellular organic matters by their walls (Kim et al., 2010). Therefore, sludge disintegration pretreatment, which disrupts sludge flocs, breaks cell walls, and facilitates the release of intracellular matters into the aqueous phase, can be considered as a simple approach for improving rate and/or extent of degradation.

Ultrasonication (US) is a promising applicable mechanical disruption technique for sludge disintegration and microorganism lyses. However, US requires high energy input, generally referred as the specific energy input (ES) in kJ/kg of dried sludge, and causes great discussions due to economic issues in practical application. This high cost could be reduced by the combination with other

pretreatment methods, the adjustment of sludge properties (total solid content (TS), pH, and volume of sludge, etc.), and/or the optimisation of ultrasonic parameters (frequency, specific energy input, intensity, density, etc.), and external pressure, etc.

According to Pilli et al. (2011), the effects of sonication parameters and sludge properties on solubilisation of the chemical oxygen demand (COD) can be rated as follows: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density. This suggests that pH adjustment to a suitable value prior to US pretreatment is an important step.

Sludge cells were proved to be disintegrated and dissolved by acidic treatment. Only the acid dose significantly affected the solubilisation of sludge (Woodard and Wukash, 1994). The optimal pH values for reducing volatile suspended solids and excess sludge subsequently varied between 1.5 (Woodard and Wukash, 1994) and 3 (Neyens et al., 2003). However, acidic pretreatment alone exhibited a very low performance as compared to US pretreatment for releasing organic matters into the liquid phase. Moreover, sludge acidification was detrimental to US pretreatment performance, especially at low pH values (Apul, 2009).

On the other hand, alkaline pretreatment enhanced sludge solubilisation, anaerobic biodegradability, and methane production (Kim et al., 2003; Valo et al., 2004). Besides, the combination of alkaline and US gave better performances of TS solubilisation as compared to both thermo-acidic and US-acidic pretreatments (Liu et al., 2008). Moreover, Chu et al. (2001) showed that

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extracellular polymeric substances (EPS) and gels surrounding cells limit the efficiency of ultrasonic treatment on sludge disintegration. Adjusting the pH of sludge to alkali value promotes EPS hydrolysis and gel solubilisation. After that, cell walls cannot maintain an appropriate turgor pressure (Jin et al., 2009) and easily disrupt. Therefore, the combined alkaline-US pretreatment, based on different mechanisms of sludge disintegration (modification of structural properties and intense mechanical shear force), is expected to take advantage of both and achieve a better efficiency of sludge pretreatment. Some synergetic effects were even noticed (Kim et al., 2010). In near-neutral pH conditions (pH 7–8), waste activated sludge (WAS) solubilisation obtained from combined, chemical, and US (1.9 W/mL, 60 s) pretreatments was 18, 13.5, and 13%, respectively (Bunrith, 2008). At higher pH values (pH 11–13), the solubilisation reached 60–70% with the combined method (ES 7500–30,000 kJ/kg<sub>TS</sub>) while it never exceeded 50% in individual pretreatments (Jin et al., 2009; Kim et al., 2010). Methane production yield derived from full stream combined-pretreated sludge (pH 9, ES 7500 kJ/kg<sub>TS</sub>) was also 55% higher than that from the control (Kim et al., 2010).

The chemicals used for increasing the pH of sludge also affect WAS solubilisation efficacy: NaOH > KOH > Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> (Kim et al., 2003; Jin et al., 2009). Ca<sup>2+</sup> and Mg<sup>2+</sup> are key substances binding cells with EPS. As a result, their presence may enhance the reflocculation of dissolved organic polymers (Jin et al., 2009), leading to a decrease in soluble COD. On the other hand, over-concentration of Na<sup>+</sup> (or K<sup>+</sup>) was reported to cause subsequent inhibition of AD (Carrère et al., 2010).

For ambient conditions of US process, modification of external pressure was proved to change cavitation intensity (Thompson and Doraiswamy, 1999), and to improve the rate and yield of US-assisted reactions (Cum et al., 1988). However, most US experiments have been carried out at atmospheric pressure; only a few studies have been focussing on how increasing static pressure affects cavitation but they almost concern sonoluminescence. To our knowledge, we have conducted the first study about the effect of pressure (1–16 bar) on sludge US pretreatment (Le et al., 2013). We found an optimum pressure of 2 bar for sludge disintegration regardless of ES ( $P_{US}$  of 150 W), temperature, and sludge type. At this optimum pressure and over the ES range of 7000–75000 kJ/kg<sub>TS</sub>, adiabatic US was more efficient than isothermal US (with an improvement of 22–82%, 39–88%, and 33–86% for mixed, secondary, and digested sludge, respectively). These conditions were therefore applied in the present work for the mixed sludge. Solubilisation of COD, evolution of pH, and evolution of particle size distribution were examined for separate, then combined, US and alkaline pretreatments.

## 2. Materials and methods

### 2.1. Sludge samples

Mixed sludge was collected after centrifugation from Ginestous wastewater treatment plant (Toulouse, France) with a sufficient amount for all experiments in this work. Its properties, given in Table 1, were evaluated according to standard analytical methods (see § 2.3).

It was sampled in 100 g plastic boxes and preserved in a freezer. Kidak et al. (2009) reported that this preliminary maintaining step might change some physical characteristics of the sludge, but it should not significantly affect COD solubilisation results. It was confirmed in this work, the difference in sludge disintegration between fresh sludge (without freezing) and frozen sludge was less than 5% on the whole ES range (7000–75,000 kJ/kg<sub>TS</sub>).

When performing experiments, the required amount of sludge was defrosted and diluted with distilled water up to 500 mL per

**Table 1**  
Characteristics of the sludge sample.

Parameter	Value
<i>Raw sludge</i>	
pH	6.3
Total solids (TS)	270 mg/g
Volatile solids (VS)	233 mg/g
VS/TS	86.2%
<i>Synthetic sample</i>	
Total solids (TS)	28.0 g/L
SCOD <sub>NaOH 0.5 M</sub>	19.6 g/L
Total COD (TCOD)	38.9 g/L

experiment. According to our previous results (Le et al., 2013), the optimum TS concentration for sludge ultrasonic disintegration was 28 g/L.

### 2.2. Ultrasound application to original or alkalinized sludge

The US stainless steel reactor (9 cm internal diameter and 18 cm height) consisted of a cup-horn type transducer (35 mm diameter probe) and was connected to a pressurized N<sub>2</sub> bottle (Fig. 1). The sludge solution was stirred by a Rushton type turbine of 32 mm diameter, with an adjustable speed up to 3000 rpm. Cooling water was allowed to circulate in an internal coil to maintain a constant temperature ( $T = 28 \pm 2$  °C) during isothermal sonication tests.

The US system had a fixed frequency of 20 kHz, and a maximum total power of 200 W corresponding to an ultrasonic power input ( $P_{US}$ ) of 158 W. The transducer was cooled by compressed air during operation.

US tests were performed at the highest  $P_{US}$  (150 W) as it proved to be the most effective in isothermal conditions. A convenient stirrer speed of 500 rpm, as also found in previous work, was applied in all tests.

For each experiment, a constant volume of synthetic sludge sample (0.5 L) was poured into the stainless steel reactor. Five different sonication times corresponding to five values of ES (7000, 12,000, 35,000, 50,000, and 75,000 kJ/kg<sub>TS</sub>) were tested.

$$ES = (P_{US} * t) / (V * TS)$$

with ES: specific energy input, energy per total solid weight (kJ/kg<sub>TS</sub>),  $P_{US}$ : US power input (W),  $t$ : sonication duration (s),  $V$ : volume of sludge (L), and TS: total solid concentration (g/L).

According to previous studies (Kim et al., 2003; Jin et al., 2009), NaOH was used for adjusting the pH of sludge. Regarding the treatment sequence, “alkalination followed by ultrasonic pretreatment” was more effective than the reverse combination, as it allows the US treatment to benefit from the weakening of the sludge matrix. Conversely, the disrupted floc fragments could be re-aggregated into compact structures by the subsequent NaOH treatment (Jin et al., 2009). Consequently, the former procedure was chosen for alkaline-US experiments.

A given amount of NaOH was added into the fixed volume of sludge to ensure the same condition of chemical application. The kinetics of sludge disintegration by NaOH was first investigated to select a convenient a holding time corresponding to the most significant COD release (cf. § 3.1.1). Sonication was then applied to alkalinized sludge samples and the effects of NaOH dose, ES in the range of 0–75,000 kJ/kg<sub>TS</sub>, temperature profile (isothermal/adiabatic conditions), and external pressure (atmospheric pressure/optimal pressure of 2 bar in accordance with previous results) were examined in order to improve sludge disintegration.

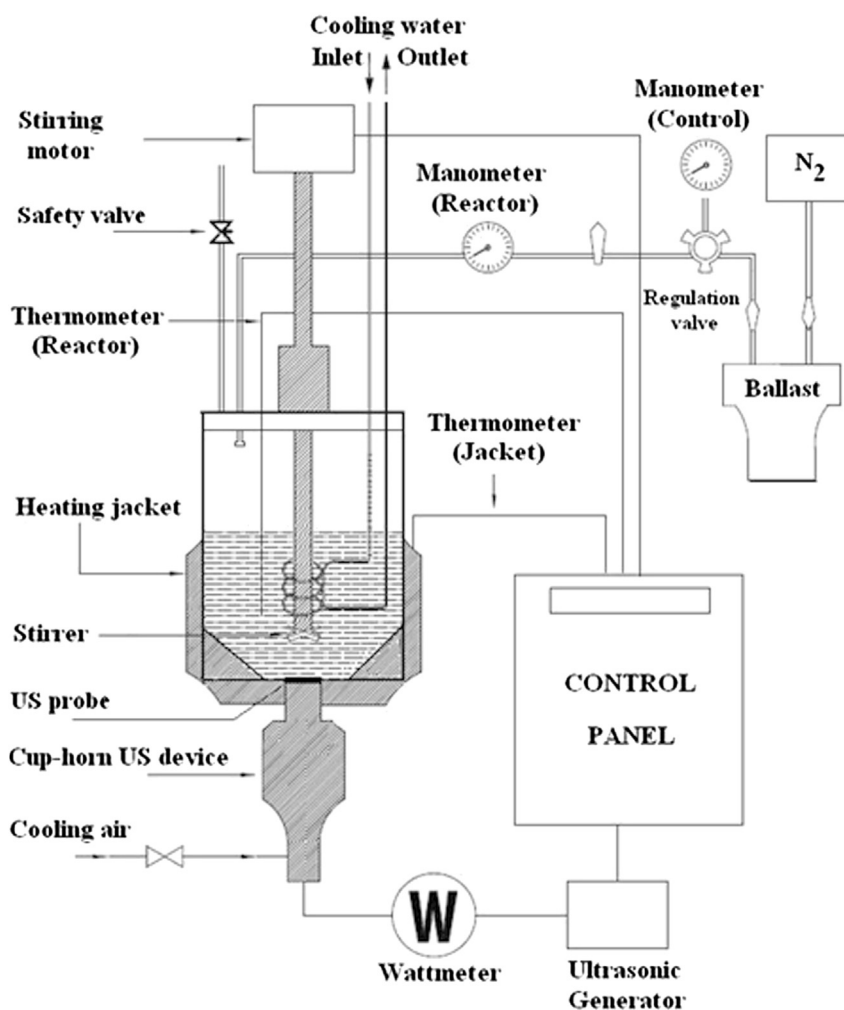


Fig. 1. Ultrasonic autoclave set-up.

### 2.3. Analytical methods

**Total and volatile solid contents** (TS and VS, respectively) were measured according to the following procedure (APHA, 2005): TS was determined by drying a well-mixed sample to constant weight at 105 °C and VS was obtained from the loss on ignition of the residue at 550 °C.

The **degree of sludge disintegration** ( $DD_{COD}$ ) was calculated by determining the soluble chemical oxygen demand after strong alkaline disintegration of sludge ( $SCOD_{NaOH}$ ) and the chemical oxygen demand in the supernatant before and after treatment ( $SCOD_0$  and  $SCOD$ , respectively):

$$DD_{COD} = (SCOD - SCOD_0) / (SCOD_{NaOH} - SCOD_0) * 100(\%)$$

(Nickel and Neis, 2007).

To measure the  $SCOD_{NaOH}$ , used as a reference to evaluate the efficiency of organic matter solubilisation under US/chemical treatment, the sludge sample was mixed with 0.5 M NaOH at room temperature for 24 h (Li et al., 2009). Besides, total chemical oxygen demand (TCOD) was also measured by potassium dichromate oxidation method (standard AFNOR NFT 90–101).

Prior to SCOD determination, the supernatant liquid obtained after sedimentation was filtered under vacuum using a cellulose nitrate membrane with 0.2 µm pore size. The filtered liquid was subjected to COD analysis as per Hach spectrophotometric method.

The change in the SCOD indirectly represents the quantity of organic carbon that has been transferred from the cell content (disruption) and solid materials (solubilisation) into the external liquid phase of sludge. The experiments were triplicated and the coefficients of variation (CV) were about 5%.

The **particle size distribution (PSD)** of sludge before and after treatment was determined by using a Malvern particle size analyzer (Mastersizer, 2000; Malvern Inc.), a laser diffraction-based system (measuring range from 0.02 to 2000 µm). Each sample was diluted approximately 300-fold in osmosed water, before being pumped into the measurement cell (suction mode). The PSD was based on the average of five measurements showing deviations of less than 3%. Optical properties of the material were set as default (refractive index 1.52, absorption 0.1) appropriate for the majority of naturally occurring substances (Minervini, 2008; Bieganski et al., 2012). Only in the small particle range (i.e. for particle diameter smaller than 10 µm), the refractive index dependence becomes significant (Govoreanu et al., 2009). Moreover it was checked that these mean optical properties led to a weighted residual parameter of less than 2% as recommended by the manufacturer.

Since the primary result from laser diffraction is a volume distribution, the volume mean diameter  $D[4,3]$  (or de Brouckere mean diameter) was used to illustrate the mean particle size of sludge.

### 3. Results and discussion

#### 3.1. Effect of chemical pretreatment on $DD_{COD}$

The effect of chemical pretreatment on  $DD_{COD}$  was investigated by adding NaOH doses of 22, 40, 47, and 77  $\text{mg}_{\text{NaOH}}/\text{g}_{\text{TS}}$  to the mixed sludge solution (for comparison, 714  $\text{mg}_{\text{NaOH}}/\text{g}_{\text{TS}}$  were used for the measurement of the reference  $\text{SCOD}_{\text{NaOH}}$ ). These samples were labelled sol. 22, sol. 40, sol. 47, and sol. 77, respectively. The evolution of pH and  $DD_{COD}$  of the samples, measured at room temperature, is shown in Table 2.

##### 3.1.1. Kinetics of alkaline sludge disintegration and effect of NaOH dose

According to Kim et al. (2010), chemical pretreatment usually acts faster than other methods. Indeed, in all cases, alkaline treatment resulted in a fast solubilisation of COD, more than 50% of the maximal observed yield being achieved within 10 min, followed by a quasi-plateau after 30 min. Therefore, a holding time of 30 min was selected for subsequent experiments combined with US. During this period, the pH of the sludge samples dropped by about one pH unit as shown in Table 2.

$DD_{COD}$  increased continuously with NaOH dose in the investigated range. However, for overall process economy (related to chemicals used in pretreatment stage as well as in subsequent neutralisation required for AD), NaOH addition should be limited. Moreover, high concentrations of  $\text{Na}^+$  were reported to cause subsequent inhibition of AD (Carrère et al., 2010). Recommended values for NaOH dose vary between 50 and 200  $\text{mg}_{\text{NaOH}}/\text{g}_{\text{TS}}$  to ensure that NaOH is in excess and achieves a significant enhancement of  $DD_{COD}$  (Kim et al., 2003; Bunrith, 2008; Jin et al., 2009). However, after 30 min,  $DD_{COD}$  value from sol. 40 was almost double of that from sol. 22, but close to that from sol. 47. In other words, an increase of the NaOH amount from 40 to 47  $\text{mg}_{\text{NaOH}}/\text{g}_{\text{TS}}$  resulted in a pH jump of nearly one unit, without significant effect on COD solubilisation. Considering this pH transition (and its final value), a dose of 40  $\text{mg}_{\text{NaOH}}/\text{g}_{\text{TS}}$  could be selected as a critical NaOH dose for chemical disintegration of sludge.

##### 3.1.2. Comparison of sole ultrasonic and sole chemical pretreatment of sludge

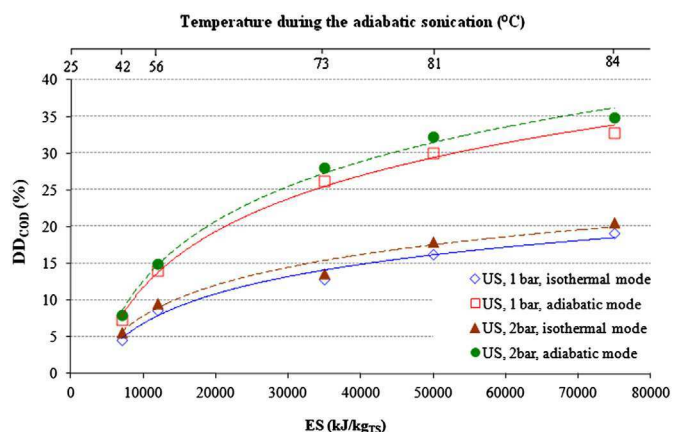
Fig. 2 recalls the main results of US treatment carried out on the mixed sludge using  $P_{\text{US}}$  of 150 W, with various thermal conditions (isothermal/adiabatic) and external pressures (atmospheric/optimal value of 2 bar) (Le et al., 2013).

Conversely to chemical treatment which showed a fast COD solubilisation (after 30 min as abovementioned),  $DD_{COD}$  gradually increased during the 2 h of sonication.

The efficiency of US resulted nearly equally from mechanical and thermal effects induced by cavitation as  $DD_{COD}$  of mixed sludge obtained dropped from 32.8% under adiabatic conditions to 19.1% at a controlled temperature of 28 °C after 2 h of sonication. When applying external pressure, the degree of sludge disintegration was slightly improved, by about 10% at the optimal value of 2 bar.

**Table 2**  
Chemical pretreatment of mixed sludge (room temperature).

	Holding time (min)					
	0.5		10		20	
	pH	$DD_{COD}$ (%)	pH	$DD_{COD}$ (%)	pH	$DD_{COD}$ (%)
Sol. 22	9.6	6.4	7.3	8.6	9.5	10.7
Sol. 40	10.2	11.5	13.3	9.4	17.0	18.3
Sol. 47	11.1	13.0	15.8	10.1	19.3	21.0
Sol. 77	12.2	24.4	26.3	11.0	29.0	30.4



**Fig. 2.** Mixed sludge disintegration under US pretreatment: evolution of COD solubilisation as a function of applied specific energy ( $TS = 28 \text{ g/L}$ ,  $P_{\text{US}} = 150 \text{ W}$ ). The upper y-axis indicates the evolution of temperature during the adiabatic sonication (final  $T$  for each corresponding ES value).

After 30 min under NaOH treatment, the volume mean diameter  $D[4,3]$  of mixed sludge was 288, 247, 203, and 133  $\mu\text{m}$  for sol. 22, sol. 40, sol. 47, and sol. 77, respectively, compared to 370  $\mu\text{m}$  for the untreated sample. For the same time under controlled temperature sonication,  $D[4,3]$  dropped to about 100  $\mu\text{m}$ . However, with the exception of sol. 22, a much higher  $DD_{COD}$  was achieved by chemical treatment. This could be explained that apart from causing the disintegration of floc structures and cell walls, hydroxyl anions also resulted in extensive swelling and subsequent solubilisation of gels in sludge (Kim et al., 2003). The higher the pH, the more easily the processes of natural shape losing of proteins, saponification of lipid, and hydrolysis of RNA occur (Li et al., 2008; Carrère et al., 2010). Obviously, selection of NaOH dose must also be based on the pH of sludge after chemical pretreatment that should comply with subsequent treatment – methanisation requiring a narrow range between 6.5 and 8 (Kim et al., 2003).

#### 3.2. Effect of NaOH addition prior to sonication

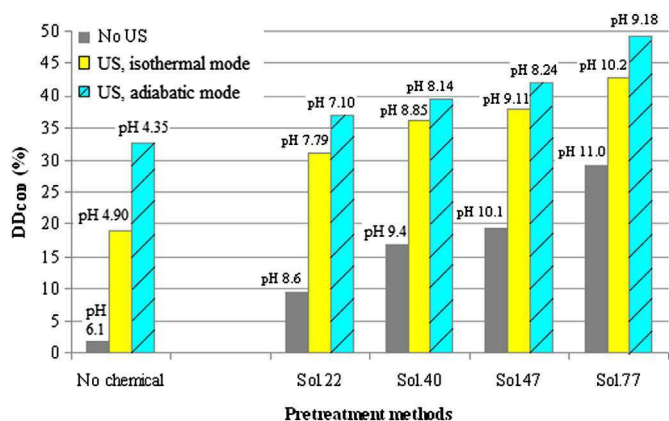
##### 3.2.1. Combined chemical – ultrasonic pretreatment of sludge at atmospheric pressure

Different mixed sludge samples were prepared by adding increasing doses of NaOH (as per sol. 22 to sol. 77) and letting react for 30 min under stirring before applying US for 2 h.

Fig. 3 compares the final  $DD_{COD}$  values of the combined pretreatment to those of the US pretreatment, with and without cooling. As expected, alkali-ultrasonic pretreatment was the most effective technique for sludge disintegration, and the resulting efficacy was nearly the sum of individual alkali and US pretreatments when sol. 22 or sol. 40 were kept under isothermal conditions (28 °C). Jin et al. (2009) also observed such a result. Alkalis significantly reduced the differences observed between the controlled and uncontrolled temperature modes of US treatment. It is also worth noting that under US, the differences resulting from the addition of different NaOH amounts tended to vanish. Therefore, addition of a small NaOH dose (as per sol. 22 or sol. 40) should be indeed the best option for the whole process.

##### 3.2.2. Combined chemical – ultrasonic pretreatment of sludge under pressure

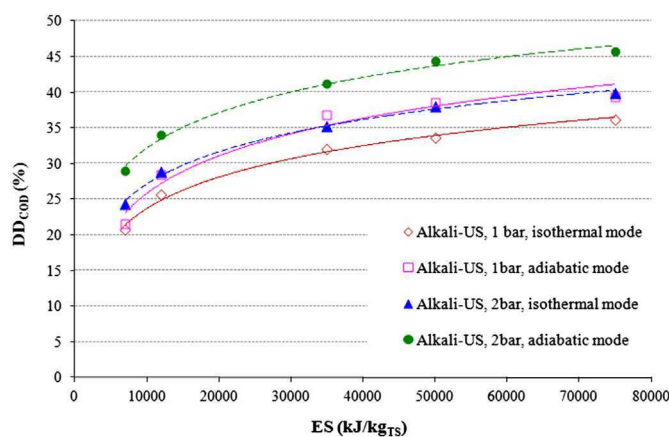
Some positive effect of external pressure was observed in our previous work, with an optimal pressure of about 2 bar. Hence, some experiments were also carried out under this external pressure value. In the previous experiments (cf. § 3.2.1), after 2 h of



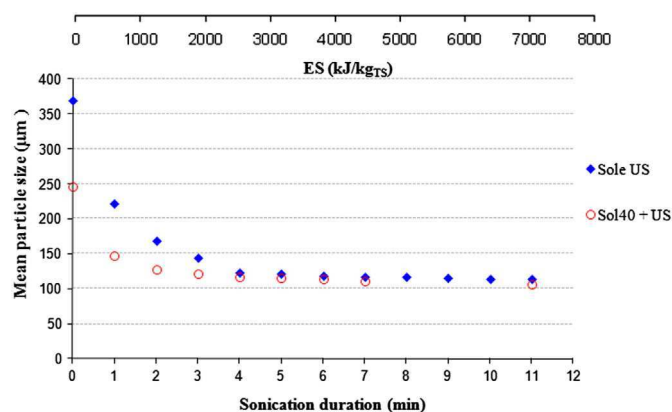
**Fig. 3.** Comparison of different methods for mixed sludge disintegration (TS = 28 g/L):  $P_{US} = 150$  W, sonication duration = 117 min, NaOH dose = 0–77 mg<sub>NaOH</sub>/g<sub>TS</sub> (holding time = 30 min), and atmospheric pressure. Final pH value after treatment is also indicated on top of each corresponding bar.

sonication, the pH of the different alkalinized mixed sludge solutions varied between 7.8 and 10.2 under cooling and between 7.1 and 9.2 under adiabatic condition. The upper values are too high for a subsequent valorisation by methanisation according to the above-mentioned pH range of AD. Therefore, subsequent US experiments at different ES (or sonication duration) combining all parameters (pH adjustment, isothermal/adiabatic modes, and external pressure application) were conducted for sol. 40 only. The results are shown in Fig. 4.

The same conclusions prevailed regarding the effect of temperature and alkalinisation, but at 2 bar of external pressure, the overall process was still improved: up to about 46% of  $DD_{COD}$  after 2 h of sonication of sol. 40. The final pH of 7.6 was also suitable for AD. The solubilisation performance depicted in Fig. 4 was somewhat lower than that reported by Jin et al. (2009) (about 45% with 99 mg<sub>NaOH</sub>/g<sub>TS</sub> and ES 12000 kJ/kg<sub>TS</sub>) and Kim et al. (2010) (50–60% for pH 9–10 and ES < 30,000 kJ/kg<sub>TS</sub>). Apart from the higher NaOH doses applied, it could be due to different experimental conditions as compared to the present work: substrates (WAS (Jin et al., 2009; Kim et al., 2010) vs. mixed sludge), US apparatus (probe system (Jin et al., 2009; Kim et al., 2010) vs. cup-horn system), US intensity and US density reflected by  $P_{US}$ , probe diameter, and volume of sludge per experiment (300 W (Kim et al., 2010) vs. 150 W; 6 mm (Jin et al.,



**Fig. 4.** Mixed sludge disintegration under alkali-US pretreatment: evolution of COD solubilisation as a function of applied specific energy (TS = 28 g/L,  $P_{US} = 150$  W, NaOH dose = 40 mg<sub>NaOH</sub>/g<sub>TS</sub>).



**Fig. 5.** Mean particle size evolution of mixed sludge (based on  $D[4,3]$ ) during the early stage of (alkali-)US pretreatment:  $P_{US} = 150$  W, controlled  $T$  (28 °C), and atmospheric pressure.

2009) vs. 35 mm of probe diameter; 0.1 L (Jin et al., 2009; Kim et al., 2010) vs. 0.5 L of sludge).

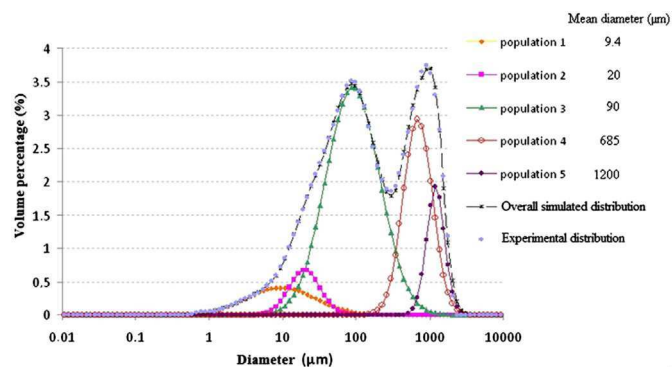
### 3.3. Particle size reduction

As abovementioned in § 3.1.2, US pretreatment is very effective in reducing the sludge particle size, which accelerates the hydrolysis stage of AD and enhances the degradation of organic matters. Main reduction of  $D[4,3]$  was observed within a much shorter duration compared to the time required for a significant COD release in the aqueous phase. Other works (Chu et al., 2001; Gonze et al., 2003; Show et al., 2007) came to the same conclusion.

In order to observe more precisely the particle size reduction, experiments were carried out with particle size sampling at much shorter time of sonication. The results (Fig. 5) show that the combination of US and chemical treatment accelerated the size reduction, but the final  $D[4,3]$  value was almost the same, about 100 µm.

According to the work of Gonze et al. (2003), the particle size distributions were deconvoluted into five populations, each following a log-normal distribution. The treatment was performed using OriginPro 8.6 (OriginLab). An example is given in Fig. 6 for the raw mixed sludge: a very small extra peak might be distinguished around 1 µm, but its contribution was always so low that it could not be adequately detected. Therefore, its contribution was neglected.

Fig. 7a shows the evolution of each population contribution during the US treatment: two macro-floc populations – population



**Fig. 6.** Deconvolution of PSD of raw mixed sludge.

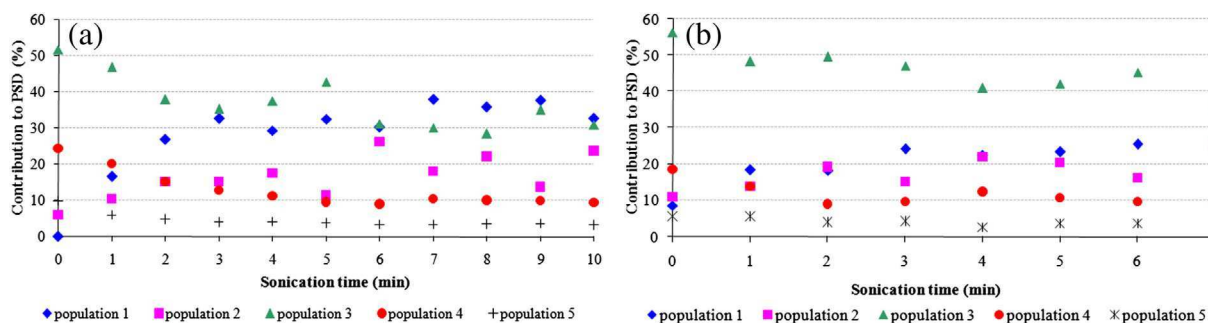


Fig. 7. Contribution of each population to PSD of mixed sludge during short sonication: (a) without addition of NaOH and (b) using 40 mg<sub>NaOH</sub>/g<sub>TS</sub> ( $P_{US} = 150$  W, controlled  $T$  at 28 °C, and atmospheric pressure).

4 and 5 of 685  $\mu\text{m}$  and 1200  $\mu\text{m}$ , respectively – could be distinguished in the mixed sludge, both their mean diameter and contribution significantly decreased during the first 4 min of sonication. Their diameter dropped to about 400  $\mu\text{m}$  and 650  $\mu\text{m}$ , respectively, while their contribution was divided by a factor 2.5 to 3. Conversely, the size of populations 1 to 3 (about 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , and 90  $\mu\text{m}$ , respectively) remained almost constant during short US treatment. It seems thus that the decrease of the largest macro-flocs proceeded mainly according to erosion mechanism, while population 3 was disrupted into micro-flocs (population 1).

After the 30 min NaOH pretreatment (using 40 mg<sub>NaOH</sub>/g<sub>TS</sub>), the diameters of population 1 and 4 were reduced by about 20% as compared to raw mixed sludge and the contributions of populations 4 and 5 were reduced by a factor 1.3 and 1.8, respectively (in favour of population 2) (Fig. 7b). However, their evolution under subsequent sonication remained similar as without NaOH addition. In this condition, mean diameter of population 4 and 5 dropped to 400 and 600  $\mu\text{m}$ , respectively, while that of populations 1 to 3 kept almost unchanged.

For a further comprehension of the relationship between mean particle size reduction and COD solubilisation, additional experiments with and without pH adjustment (40 mg<sub>NaOH</sub>/g<sub>TS</sub>) were carried out in the following conditions: US were applied during the first minute or the first 4 min, and then only the stirrer was continuously operated under cooling. Despite these two sonication durations resulted in distinct  $D[4,3]$ , especially under natural pH (Fig. 5), no differences were observed in terms of  $DD_{COD}$  afterwards (Fig. 8). These short US pretreatments only provided a small initial jump of COD release, but did not modify its evolution. Therefore, it proves that the strong reduction of mean particle size observed at low ES was not sufficient to affect COD solubilisation as expected by the different process dynamics.

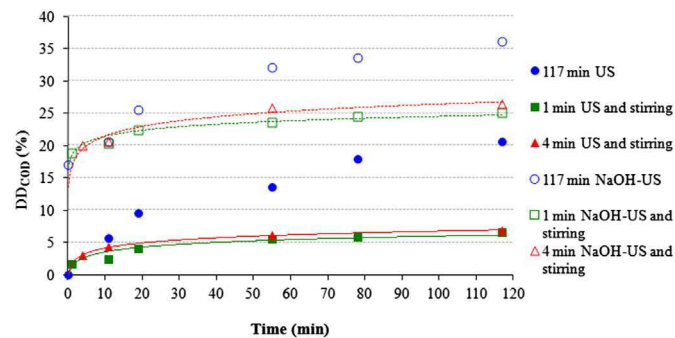


Fig. 8. Effect of short sonication time on mixed sludge disintegration with and without addition of NaOH (40 mg<sub>NaOH</sub>/g<sub>TS</sub>):  $P_{US} = 150$  W, controlled  $T$  (28 °C), and atmospheric pressure.

#### 4. Conclusions

This work proved that US pretreatment of sewage sludge benefits from the combined effects of generated heat, mild alkalisation, and also external pressure application, which was not investigated in earlier works. It was confirmed that under controlled temperature condition, US and alkali pretreatments have distinct **mechanisms of action on sludge**, resulting in different kinetics of COD release and additive effects for low NaOH dose. Conversely, the chemical pretreatment hid the positive effect of the heat generated by US under adiabatic condition. It was also shown that the fast reduction of sludge mean particle size observed at low ES is not sufficient to explain the effect of US on COD solubilisation.

Addition of low NaOH dose, between 22 and 40 mg<sub>NaOH</sub>/g<sub>TS</sub>, is recommended, that significantly improved COD release under subsequent US treatment while resulting in a final pH value suitable for subsequent methanisation. In the later condition,  $DD_{COD}$  yield reached up to 46% at 75,000 kJ/kg<sub>TS</sub> as compared to 35% for sole US.

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