



Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge

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ABSTRACT

Laboratory and pilot-scale experiments were carried out in order to evaluate the influence of thermal pre-treatment time on waste-activated sludge properties and anaerobic biodegradability. Six experimental conditions were analyzed from 0 to 30 min of hydrolysis time. Solubilization of macromolecular compounds, changes in the main sludge properties and anaerobic biodegradability of the sewage sludge were evaluated. A similar carbohydrate solubilization degree was achieved, from 53% to 70% and 59% to 75% for lab- and pilot-scale experiments, respectively. In the case of proteins, the values of solubilization were lower in the pilot-scale experiment than in the laboratory, with 31–45% and 47–70%, respectively. Ammonia and volatile fatty acid did not undergo important changes; however the sludge dewaterability enhanced at increased pre-treatment times. All the pre-treatment conditions had a positive effect with regard to anaerobic biodegradability and by fitting experimental data with a simplified mathematical model, it was concluded that the maximum biogas production rate is more influenced by the pre-treatment time than the total biogas production.

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1. Introduction

In the anaerobic digestion of waste-activated sludge (WAS), the methanogenic process is limited by the hydrolysis rate of organic suspended matter (Batstone et al., 2009; Vavilin et al., 2008). By improving the hydrolysis step, organic matter is more available to anaerobic bacteria, accelerating the digestion, increasing the volume of biogas produced and decreasing the amount of sludge to be disposed. In this context, the application of pre-treatment techniques for sewage sludge has been gaining importance in recent years, with several full-scale facilities already in operation. Among them, thermal hydrolysis is a well known method, which increases the biogas production from anaerobic digestion and the dewaterability of sludge (Kepp et al., 2000). Two are the main manipulated variables in this process: temperature and time of pre-treatment.

There is a consensus that the best range of temperature for thermal pre-treatment is within 160–180 °C, since above 180 °C non-biodegradable compounds begin to form (Neyens and Baeyens, 2003; Pérez-Elvira et al., 2006). With respect to the time of the pre-treatment, most reports indicate that this variable has no

significant influence on sludge properties, hence on the biogas production. Commonly, the time of the thermal pre-treatment is about 30 min (Bougrier et al., 2007, 2008; Fdz-Polanco et al., 2008; Wilson and Novak, 2009).

However, few studies have evaluated in-depth the influence of the pre-treatment time upon the variation of the sludge properties. Li and Noike (1992) tested 15, 30, 60 and 120 min and its impact on the biogas production. They found the total biogas production increased with increasing pre-treatment times, using a temperature of 150 °C, and the highest increase was observed between 15 and 30 min. However, they only studied its final effect but not the effect of this time on the compound's solubilization. Valo et al. (2004) used 15, 30, and 60 min and their results indicated that the treatment range of time had little influence on improving COD solubilization; however, anaerobic biodegradability of the samples was not studied. Dohanyos et al. (2004), who used rapid thermal treatment (1 min) with digested sludge conditioned in a rapid thermal reactor (RTR) at different temperatures (120–170 °C), found that the disintegration efficiency increased by increasing the temperature about 35–49% in the methane yield. As can be noted, there is a lack of information and the preliminary results seem to be contradictory.

The time of the pre-treatment is an important variable for system design as it may influence the energetic balance (Yang et al.,

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2010) and operational costs of the plant (Kalogo and Monteith, 2008). Understanding the dynamics of thermal pre-treatment may also be a valuable tool for modeling applications. Therefore, an accurate analysis of the influence of thermal pre-treatment time is a necessity. The aim of this study is to evaluate the effect of thermal pre-treatment time on the general properties of sewage sludge as well as on its anaerobic biodegradability. To do this, and in order to obtain more conclusive and reliable results, two experiments, one at lab- and another at pilot-scale were carried out.

2. Methods

2.1. Thermal hydrolysis experiment

2.1.1. Lab-scale system

The experimental set-up consisted of a manual lab-scale thermal system with a hydrolysis reactor of 0.5 L total volume, connected to a flash tank ($V = 5$ L) with outlet pipes so steam and hydrolyzed sludge could exit the flash. The lab-plant is equipped with a temperature electrode inside the reactor, one manometer placed at the top of the reactor and one peristaltic pump for feeding hydrolyzed sludge. The pump introduces 0.2 L of sewage sludge into the reactor, and then the steam valve is manually opened until pressure and temperature reach the set point, then, the steam valve is manually maintained between the set point during the established time. At the end of the reaction, the steam valve is closed and the decompression valve is opened gradually and the hydrolyzed sludge flows to the flash tank.

2.1.2. Pilot-scale system

This experiment was conducted under more controlled conditions in order to support the results from the lab-scale experiment. The experiment was carried out in an automatic pilot-scale thermal system located in the Wastewater Treatment Plant (WWTP, Valladolid, Spain). This system consisted of a feeding tank, a progressive cavity pump ($P_{max} = 12$ bar), a steam boiler, a 20 L total volume hydrolysis reactor ($V_{utile} = 10$ L) connected to a flash tank ($V = 100$ L) with outlet pipes for steam and hydrolyzed sludge. The pilot plant is equipped with automatic valves that control the steam entrance from the boiler and the sludge exit from the reactor to the flash. A data acquisition and control system is used to measure pressure and temperature and automatically controls the steam inlet and the hydrolyzed sludge exit to the flash. The pump introduces 10 L of sludge into the reactor and then the steam valve is opened until pressure and temperature reach the set point. At the end of the reaction time the decompression valve is automatically opened and the hydrolyzed sludge flows to the flash tank.

2.1.3. Thermal hydrolysis conditions

The pre-heating time (from the initial temperature up to 170 °C) can exert a significant impact on the final results. In order to minimize this effect, several preliminary hydrolysis runs were carried out, prior to the experimental runs, to pre-heat the whole system, and this way, achieve constant profiles of temperature. The temperature inside the reactors, both at the top and bottom of the reactor, and pressure, showed the same behavior in all experiments: a continuous slight decrease of temperature (up to roughly 70 °C) and a sharp pressure drop (0 bar) while the sludge feeding took place (around 15 min), followed by a sharp increase of the temperature and pressure (10 min) up to 170 °C and 8 bars, respectively, once the feeding step finishes and all the valves are closed and the vapor injections begins. This is followed by a constant period under these conditions (between 0 and 30 min), and, finally, an abrupt drop of these parameters when the steam explosion took place.

2.1.4. Waste-activated sludge and experimental conditions

Sewage sludge (or waste-activated sludge) from the WWTP (Valladolid, Spain) which serves a 233,000 population equivalent (EI) was used. The conventional wastewater treatment used in these plants consists of preliminary (sieving and sand trap) and primary treatment and secondary treatment in the activated sludge unit. Primary sludge (PS) and secondary waste-activated sludge (WAS) are mixed and thickened before undergoing mesophilic (35 °C) anaerobic digestion. With regards to the experimental conditions, both experiments were performed using the same experimental conditions with a set point of 170 °C and 8 bars (nominal conditions). Since the sludge samples were taken with a few weeks apart their characteristics were not the same and they are detailed in Table 1. Six hydrolysis times were evaluated: 0 (LPR), 5 (LP5), 10 (LP10), 15 (LP15), 25 (LP25) and 30 min (LP30). The LPR condition meant that the sludge was heated up and once the system reached 170 °C and 8 bars, was decompressed and the hydrolyzed sludge flowed to the flash tank.

2.2. Sample analysis

After pre-treatment, the volume of the pre-treated sludge is greater than the raw sludge that was fed, since part of the steam condenses into the sludge. In order to know this dilution factor, total (TS) and volatile solids (VS) concentrations in all samples were determined by heating at 105 °C during 24 h for total solids and 550 °C during 2 h for volatile solids concentration. Soluble fractions of the sludge were defined by centrifuging at 500 rpm for 5 min and then passing through a 0.45 µm cellulose filter. The organic matter concentration was measured as Chemical Oxygen Demand (COD) by titration, Total Kjeldahl Nitrogen (TKN) by digestion and oxidation, ammonia ($N - NH_4^+$) by selective electrode and total coliforms by a membrane filter, all of them according to (APHA et al., 1995). The volatile fatty acid (VFA) composition was determined by using a gas chromatography (GC) system (Agilent GC-6890), equipped with a FID detector and a DB-FFAP capillary column (30 m, 0.25 mm ID, 0.25 µm) from Agilent J&W (Ref. 122-3232E). Carrier gas (He) flow was adjusted to 1.1 ml/min. Each sample was injected automatically with a split ratio of 20:1, and the injection port temperature was 150 °C. The detector temperature was 150 °C, while the oven temperature ramp was as follows: 100 °C (5 min), then 150 °C at 10 °C min⁻¹, then 240 °C at 30 °C min⁻¹, remaining at 240 °C for 4 min. The filtered sludge was processed before injecting the sample by performing a liquid-liquid extraction with an organic phase (*tert*-butyl methyl ether, TBME) and using pivalic acid as an internal standard.

The protein content (Pc) was calculated based on the assumption that the protein contains 16% (w/w) nitrogen and taking into account TKN and $N - NH_4^+$ measurements, according to Eq. (1):

Table 1
General properties of the sewage sludge used in this study.

| Property | Lab-scale | Pilot-scale |
|------------------------------|-----------|------------------|
| TS (g/L) | 99.8 | 76.8 |
| VS (g/L) | 75.7 | 54.0 |
| TCOD (mg/L) | 108,022 | 90,168 |
| SCOD (mg/L) | 7376 | 4829 |
| TCarbohydrates (mg/L) | 13,191 | 10,868 |
| SCarbohydrates (mg/L) | 733 | 629 |
| TKN (mg/L) | 7083 | 6270 |
| TProteins (mg/L) | 41,950 | 37,807 |
| Acetic Acid (mg/L) | 191 | 110 |
| Propionic Acid (mg/L) | 278 | 186 |
| Isovaleric Acid (mg/L) | 65 | 44 |
| Coliforms (coliforms/100 ml) | n.d | 56×10^6 |
| CST (s) | n.d | 4197 |

n.d., not determined.

$$P_C = (TKN - NH_4^+) \cdot 6.15 \quad (1)$$

Soluble polysaccharides were measured as described by Dubois et al. (1956) using glucose as a standard. This method has been used in other reports for sludge analysis (Tanaka et al. 1997; Wilson and Novak, 2009).

Solubilization degree (S_D) of COD, carbohydrates and proteins were calculated according to Eq. (2):

$$S_D(\%) = \frac{M_S - M_{SO}}{M_T - M_{SO}} \cdot 100 \quad (2)$$

where M_S is the soluble concentration of compound M after pre-treatment, M_{SO} the soluble concentration of compound M in the raw sample and M_T the total concentration of compound M in the raw sample.

Sludge dewaterability was evaluated by means two measurements: *Filterability* (This is an internal method established from the experiments in sludge characterization in the *Department of Chemical Engineering and Environmental Technology, at the University of Valladolid*), defined as the viability of sludge to flow through a filter, measured by forcing the sludge to pass through a filter under a given pressure. The filtration constant (FC) was calculated using the slope (m) from plotting filtrate volume (V^2) versus filtration time (t) and the area of the filtering paper (A), according to Eq. (3). *Capillary suction time* (CST) was measured to evaluate sludge dewatering behavior since it indicates how fast sludge releases its water. A long CST means a high cake specific resistance. The CST determined using a Triton Electronics Ltd. (Type 319). A stainless-steel tube with an inner radius of 0.925 cm and Whatman No. 17 filter paper was used. The filter paper was taken as the time (in s) needed to wet the filter paper from a radius of 6–12 cm. Sludge samples were analyzed 3 times and the results were averaged before being standardized to the TS concentration.

$$FC = \frac{m}{A} \quad (3)$$

2.3. Anaerobic biodegradability tests

2.3.1. Experimental set-up

Batch anaerobic digestion tests were carried out to assess pre-treated sludge biodegradability. All the experiments were carried out at 35 ± 0.6 °C in a thermostatic room and seeded with anaerobic sludge from a pilot-scale mesophilic anaerobic digester fed with the same raw secondary sewage sludge that the one used in the hydrolysis experiments, with a TS concentration of 22.25 ± 0.1 gVS/L and a VS concentration of 12.28 ± 0.08 gVS/L. Serum bottles of 160 mL of volume and an F/I (feeding/inoculum) ratio between 0.5 and 0.8 gVS/gVS was used for all the experiments. Biogas production was measured manually by a pressure transmitter (Druck, PTX 1400, range 1 bar) in the head space of each reactor. After the daily pressure measurement, the biogas in the head space was released, which reduced the pressure in the head space to atmospheric pressure. These pressure differences were converted into biogas volume, using the ideal gas Law and standard conditions ($P = 1$ bar and $T = 0$ °C). Biogas composition was measured by gas chromatography through the injection of 1 mL of sample directly into the column.

2.3.2. Parameters determination

Experimental data, i.e., the cumulative methane production was fitted to Reaction Curve model for an evaluation of the kinetic parameters. The objective of this part was to apply a simplified model in order to obtain some parameters that allow us to make a comparison of the results. This function has been used mainly for control purposes, since it is considered that any process may

be analyzed as a system receiving inputs and generating outputs. However, this equation has been applied successfully in some reports of anaerobic biodegradability tests (Donoso-Bravo et al., 2010; Pérez-Elvira et al., 2010).

$$B = P \cdot \left(1 - \exp \left(\frac{-Rm(t - \lambda)}{P} \right) \right) \quad (4)$$

where B is the methane production (ml/gVS) P is the maximum methane production (mL/gVS), Rm maximum biogas production rate (mL/gVS·d), λ the lag time (d) and t the time of the assay (d). Nonlinear optimization by the least squares procedure is applied to calculate the unknown parameters by minimizing a cost function that measures the difference between the experimental measurements and the corresponding simulated value (the values obtained with the linearization method are used as initial values in the simulation process). Matlab® 7.0 was used to solve the least squared procedure.

3. Results and discussion

3.1. Property variations

3.1.1. Initial sludge composition

According to the initial characterization of the raw sludge (Table 1) and the theoretical formula for COD yield (see Table 2), protein represents 55–60% and carbohydrates 13–15% of the total COD for both lab and pilot experiments. This agrees with other WAS compositions found in literature, although the protein content in this study is a little bit higher than those reported. The surplus of COD must be due to the lipid content, which usually is around 15–25% (Bougrier et al., 2008; Tanaka et al., 1997).

3.1.2. Time of pre-treatment effect

In general terms, the results obtained from lab- and pilot-scale experiments bear a resemblance to each other, which strengthens the conclusion that can be drawn from this study. Figs. 1 and 2 show chemical composition of the soluble fraction of the pre-treated sludge samples at lab- and pilot-scale, respectively, for the experimental conditions studied. In both cases, a similarly sharp rise in the soluble COD concentration was accomplished, after heating the sludge to 170 °C and the steam explosion in the flash tank (LPR condition), which indicates that decompression plays a key role in sludge hydrolysis. At lab-scale, a continuous increase in soluble COD up to 15 min of reaction time was attained, after that a constant value was maintained up to 30 min. In the case of the pilot-scale experiment, a slight increment in the soluble COD was obtained as the time of reaction increased; however, no significant differences were observed among LPR and LP30. These results agree, in part, to those reported by Valo et al. (2004), but in this study the importance of the decompression step is stated, as well as a more detailed time influence determination between 0 and 30 min. In any case, temperature seems to have a greater effect on the COD solubilization than time does, in accordance with the soluble COD profiles presented at different temperatures in several studies (Bougrier et al., 2008; Wilson and Novak, 2009).

With regard to the nitrogen compounds, ammonia concentrations did not undergo relevant changes in all the experimental conditions, though a slight increasing tendency was observed in the lab experiment. In any case, the released ammonia was low in terms of the potential for inhibition. These results indicate that proteins were mostly solubilized instead of degraded. On the other hand, proteins were clearly solubilized into the soluble fraction after the pre-treatment. The greatest increment was attained between LSP and LPR, which coincide with soluble COD values.

Table 2

COD balance of the thermal pre-treatment experiment at lab- and pilot-scale.

| Compound | Abbreviation | Theoretical formula | | | | COD conversion (gCOD/gcompound) | | |
|------------------------|--------------|--------------------------|-----|-----|-----|---------------------------------|-------------|---------|
| Carbohydrate | CH | $C_6H_{9.95}O_5P_{0.05}$ | | | | 1.191 | | |
| Protein | Pr | $C_4H_{6.1}O_{1.2}N$ | | | | 1.439 | | |
| Acetic Acid | Ac | $C_2H_4O_2$ | | | | 1.066 | | |
| Propionic Acid | Pro | $C_3H_6O_2$ | | | | 1.512 | | |
| Isovaleric Acid | IsV | $C_5H_{10}O_2$ | | | | 2.037 | | |
| Experimental condition | COD | | | | | COD_{sum} | COD_{exp} | Dif (%) |
| | | CH | Pr | Ac | Pro | IsV | | |
| <i>Laboratory</i> | | | | | | | | |
| LSP | 873 | 3710 | 410 | 846 | 266 | 6104 | 7376 | 20.8 |
| LPR | 9375 | 31,093 | 361 | 887 | 341 | 42,058 | 37,715 | -10.3 |
| LP5 | 8871 | 34,585 | 504 | 833 | 403 | 45,195 | 46,270 | 2.4 |
| LP10 | 11,429 | 39,891 | 548 | 976 | 458 | 53,301 | 54,006 | 1.3 |
| LP15 | 10,572 | 45,774 | 540 | 850 | 456 | 58,191 | 56,385 | -3.1 |
| LP25 | 7243 | 43,669 | 530 | 843 | 402 | 52,686 | 56,137 | 6.5 |
| LP30 | 8766 | 44,013 | 500 | 726 | 372 | 54,378 | 55,121 | 1.4 |
| <i>Pilot</i> | | | | | | | | |
| LSP | 749 | 2551 | 117 | 281 | 90 | 3787 | 4829 | 27.5 |
| LPR | 8986 | 18,778 | 93 | 156 | 132 | 28,144 | 30,430 | 8.1 |
| LP5 | 9026 | 18,344 | 133 | 158 | 152 | 27,813 | 29,682 | 6.7 |
| LP10 | 8145 | 21,910 | 178 | 154 | 157 | 30,543 | 35,083 | 14.9 |
| LP15 | 10,071 | 22,915 | 235 | 165 | 142 | 33,528 | 34,801 | 3.8 |
| LP25 | 7987 | 25,726 | 316 | 156 | 115 | 34,299 | 36,923 | 7.6 |
| LP30 | 9843 | 24,828 | 383 | 162 | 95 | 35,311 | 40,149 | 13.7 |

Similar protein behavior was observed by Bougrier et al. (2008) and Wilson and Novak (2009) as a function of temperature. Carbohydrates were also strongly solubilized under the LPR condition in

comparison with the raw sample. However, a clear behavior can not be observed with increasing pre-treatment times when applying thermal hydrolysis at 170 °C.

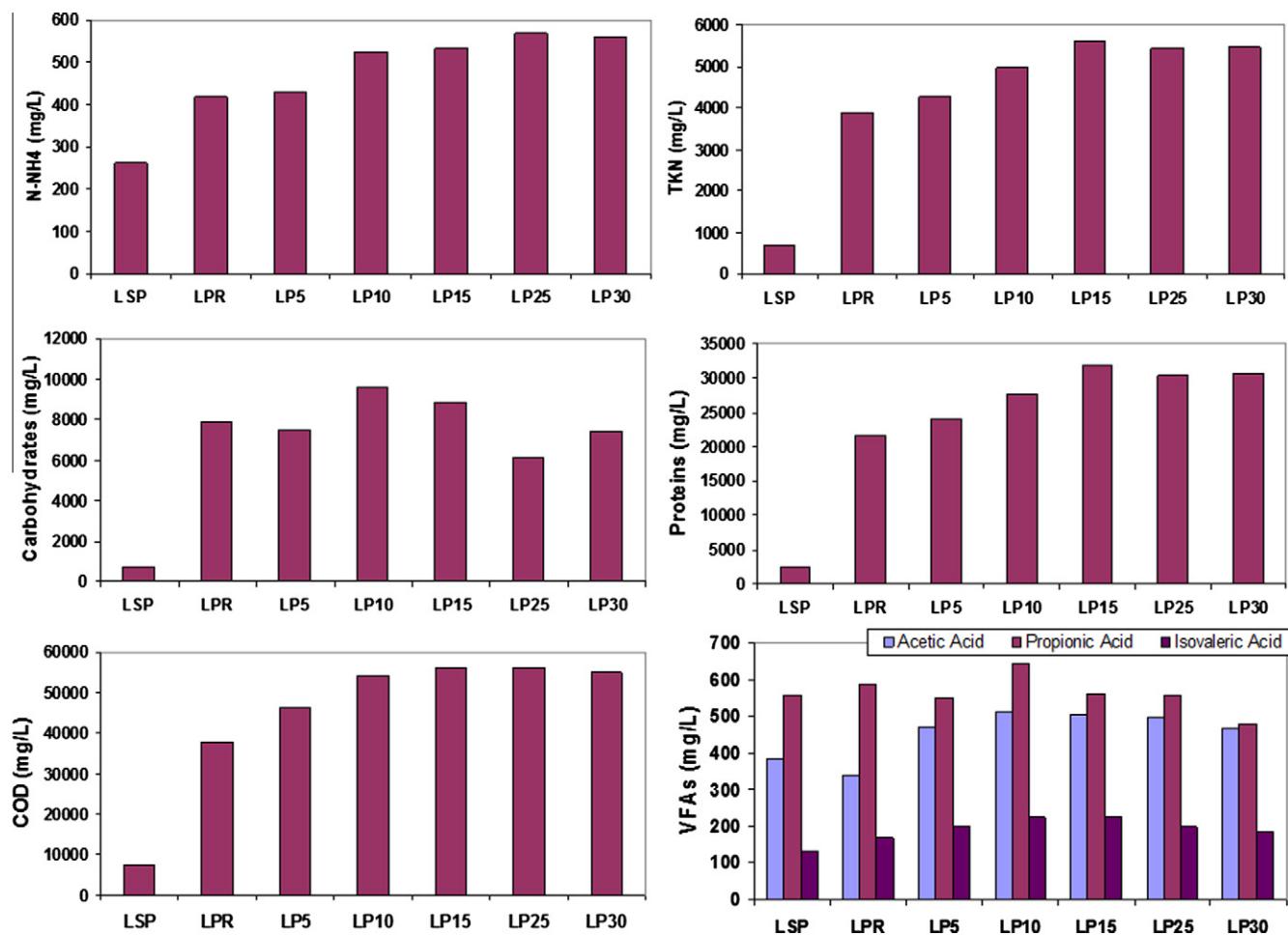


Fig. 1. Chemical composition of the soluble fraction of raw sludge (LSP) and thermal pre-treated sludge at different times in a lab-scale hydrolysis system.

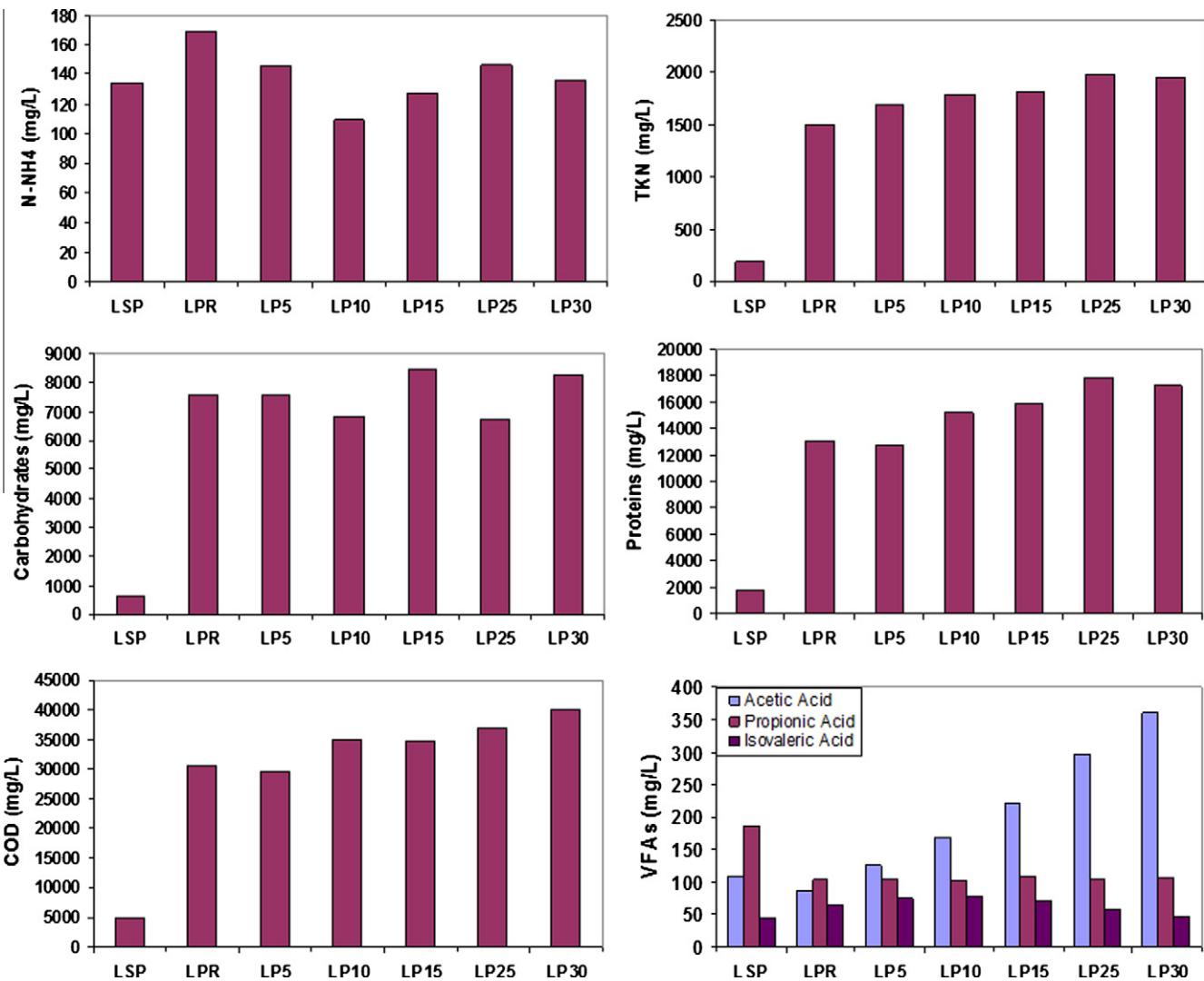


Fig. 2. Chemical composition of the soluble fraction of raw sludge (LSP) and thermal pre-treated sludge at different times in a pilot-scale thermal hydrolysis system.

Three VFAs were detected in all the samples: acetic, propionic and isovaleric acid; Moreover, insignificant quantities of butyric and isobutyric acid (<40 mg/L) and valeric acid (<20 mg/L) were found in some experiments. Because of some differences in the storage conditions of the raw sludge, the initial concentration of VFA was higher in the lab-scale experiment than in the pilot one. Acetic acid showed an increasing profile in the pilot-scale experiment, which might come from both protein or lipids degradation, although more likely from lipids due to the apparently null lipid concentration after pre-treatments (See COD balance in Table 2). Furthermore, it has been demonstrated that VFA yields from lipids is greater than from proteins in thermal pre-treatment at 170 °C (Wilson and Novak, 2009).

Fig. 3 presents the solubilization degree of COD, carbohydrates and proteins, taking into account their initial particulate fraction (Eq. (2)). It can be observed that there were similar carbohydrates solubilization degrees, within 53–70% and 59–75% for lab- and pilot-scale experiments, respectively. In the case of proteins, despite the fact that solubilization profiles were similar, the values were lower in the pilot-scale experiment (between 31% and 45%) than in the lab one (between 47% and 70%). Since the particulate protein content in sludge was very similar, these results may be due to the fact that in the lab-scale experiment, temperature was controlled manually, and sometimes it rose over 175 °C due to inertial effects, and it has been demonstrated that temperatures over 170 °C pro-

mote solubilization of proteins more than carbohydrates (Bougrier et al., 2008; Wilson and Novak, 2009). COD solubilization shows a similar behavior to that of proteins since proteins are the main contributor to the COD.

Table 2 presents the COD balance for all experimental conditions at lab and pilot scale. The balance was done by using two theoretical formulas for carbohydrate and proteins, which have been used in studies about sewage sludge (de Gracia et al., 2006; Grau et al., 2007). Most of the balances close quite well, with a difference of less than 8% with respect to the experimental value. However, in some cases this difference was not low, for instance in LSP for both experiments, which can be due to the COD contribution of lipids in the soluble fraction.

3.1.3. Physical and biological variations

Total coliforms were not detected in any experimental conditions; hence the hygienization process is assured in all cases. With regards to the dewaterability properties, pressure and capillary filterability of the pre-treated sludge samples are shown in Fig. 4. From Fig. 4A it can be noted that FC increases with increasing pre-treatment time, reaching the highest value at 30 min (LP30), which indicates that under this condition the best filterability is obtained. Similar results were seen for CST (Fig. 4B) since the lowest time (related to the TS concentration) was achieved for LP30.

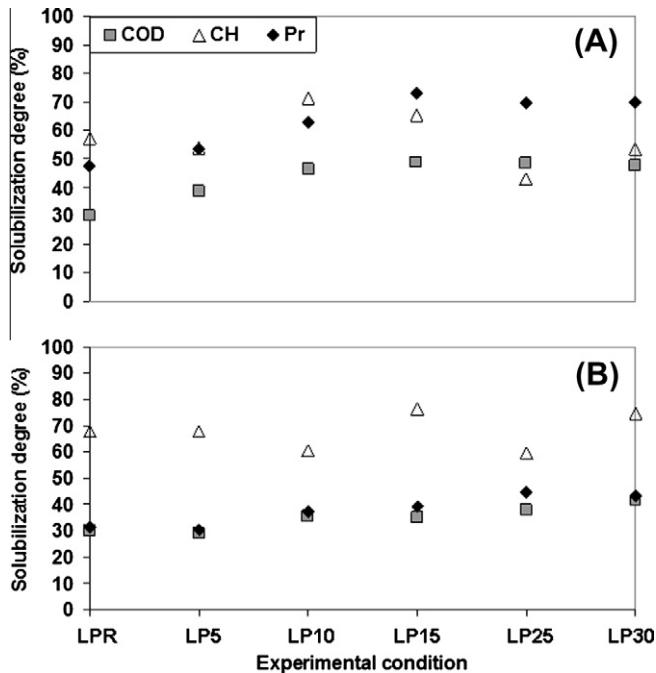


Fig. 3. Solubilization degree of COD, carbohydrates and proteins after thermal pre-treatment experiments at several hydrolysis times. (A) Lab- (B) Pilot-scale.

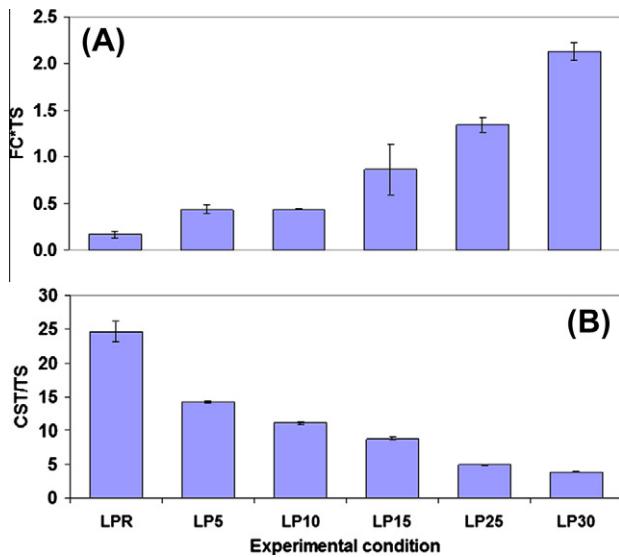


Fig. 4. Dewaterability properties of the thermal pre-treated sludge in the pilot-scale system at different pre-treatment times. (A) Pressure filterability (B) Capillary filterability.

Normally, sludge stabilization in anaerobic digesters is followed by dewatering processes, which may reach around 7% of the energy requirements in conventional activated sludge WWTP (Metcalf and Edy, 2003). The reduction of dewatering costs by enhancing sludge dewaterability is of major importance that is why the evaluation of this parameter is necessary. However, it has to be taken into account that the dewatering process is normally carried out after anaerobic digestion, thus, the sludge undergone to filtration does not have the same properties as the pre-treated sludge. Nevertheless, it has been reported that an increase in the sludge dewaterability is transferred to the anaerobic digested sludge as well (Eskicioglu et al., 2008). On the other hand, it is worth to note that sludge with a proper dewaterability may also provide advantages

in terms of sludge transport to the digester due to the changes in its viscosity.

3.2. Anaerobic biodegradability

The cumulative methane production from the anaerobic batch digestion of thermal pre-treated sludge for both experiments is presented in Fig. 5. In general, the profiles and the maximum values agree with those that have been reported for thermal pre-treatment conditions (Donoso-Bravo et al., 2010; Bougrier et al., 2006). As can be observed, all the pre-treatment conditions had a positive effect with regard to increasing the biogas production. Nevertheless, a less significant improvement was achieved for the pilot-scale experiment which must be related to the lower solubilization of proteins after the pre-treatment. Among the experimental conditions evaluated, a slight increase in the total biogas production is observed at increasing pre-treatment times, as well as, a rise of the initial slope in the cumulative production. These results were assessed more thoroughly by means kinetic parameters estimation from the model fitting with the experimental data. These parameters are presented in Table 3.

The variation of the total biogas production and the maximum biogas production rate with respect to the results obtained for raw sludge are shown in Fig. 6. As can be noticed, the pre-treatment time has greater influence over the maximum methane production rate than it does over the total biogas production, for both experiments. The first effect (slope increase) must be related to the fact that the biomass is growing and producing biogas, at a higher specific growth rate, since more soluble organic matter is available after pre-treatment. The second effect (total biogas increase) implies that part of the inert organic matter, which could not be degraded in the test with raw sludge, turned into available organic matter, both particulate and/or soluble. In this case, the higher

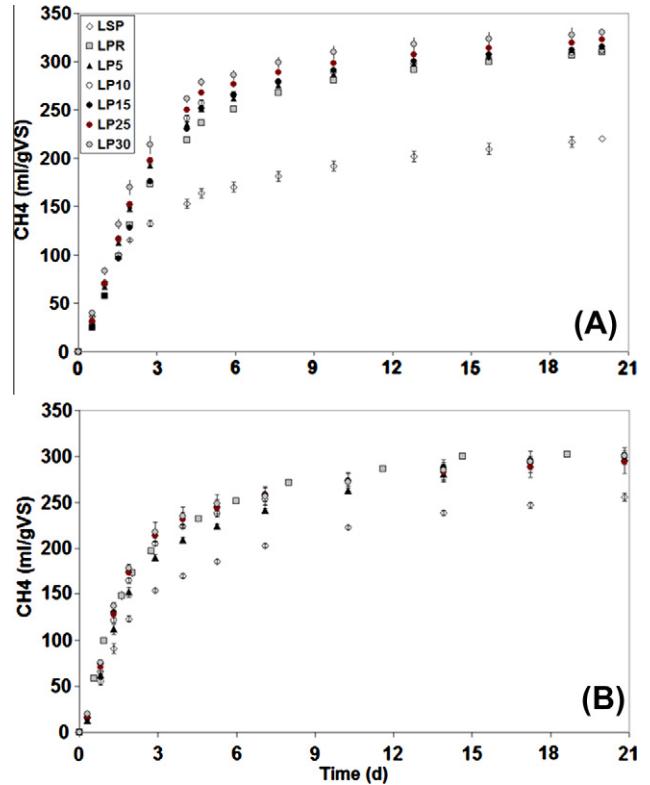


Fig. 5. Methane production profile from the anaerobic biodegradability batch test of thermal pre-treated sludge at various pre-treatment times. (A) Lab- (B) Pilot-scale.

Table 3

Kinetic parameters calculated by the fitting process between the reaction curve model and the experimental model from the anaerobic biodegradability test of raw and thermal pre-treated sewage sludge.

| | Lab-scale | | | | Pilot-scale | | | |
|------|-----------|--------|-----------|-------|-------------|--------|-----------|-------|
| | P | Rm | λ | R2 | P | Rm | λ | R2 |
| LSP | 205.97 | 75.84 | 0 | 0.982 | 241.39 | 77.45 | 0 | 0.989 |
| LPR | 304.12 | 92.24 | 0.14 | 0.995 | 289.96 | 119.93 | 0 | 0.992 |
| LP5 | 307.23 | 104.94 | 0.12 | 0.994 | 282.33 | 99.58 | 0.03 | 0.987 |
| LP10 | 305.75 | 111.23 | 0.13 | 0.994 | 284.82 | 116.54 | 0.06 | 0.990 |
| LP15 | 312.47 | 97.82 | 0.18 | 0.994 | 286.12 | 128.21 | 0.06 | 0.989 |
| LP25 | 316.99 | 113.01 | 0.14 | 0.994 | 281.37 | 129.47 | 0.07 | 0.991 |
| LP30 | 324.36 | 124.53 | 0.10 | 0.996 | 283.61 | 135.28 | 0.05 | 0.988 |

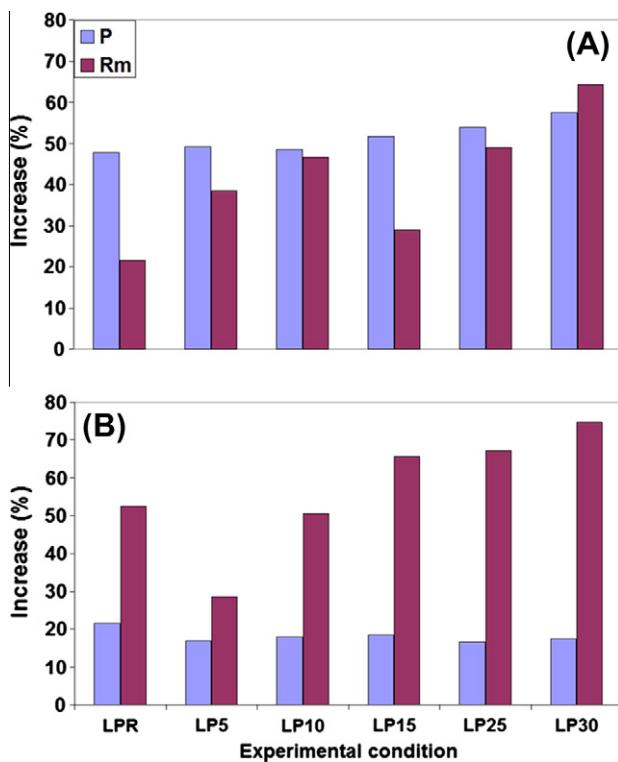


Fig. 6. Increase of the biogas production (P) and the maximum biogas production (Rm), according to the model fit for each experimental condition used in the thermal pre-treatment experiment with respect to tests with raw sludge. (A) Lab- (B) Pilot-scale.

initial slope at increases pre-treatment times may mean that particulate organic matter was converted into soluble material, which explains the increment in the initial rate at increasing time of pre-treatment; however, a quite low fraction of inert organic matter was transformed into both, slowly or readily degradable compounds.

4. Conclusions

Several conclusions can be drawn from this study, in which a nominal temperature of 170 °C was used: (1) steam explosion (8 to 0 bars) exerts the most significant influence on the macromolecular solubilization rather than the time of exposure at those conditions. (2) Hydrolysis time (from 0 to 30 min) has little positive influence on sludge solubilization. (3) Dewaterability of the pre-treated sludge improved with increasing time and sludge hygienization is assured for all conditions. (4) Thermal pre-treatment

between, 0 and 30 min, enhanced the anaerobic biodegradability of the sewage sludge. (5) The maximum biogas production rate is influenced more by the pre-treatment time than is total biogas production.

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References

- APHA, AWWA, WPCF., 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. Washington DC.
- Batstone, D.J., Tait, S., Starrenburg, D., 2009. Estimation of hydrolysis parameters in full-scale anaerobic digesters. *Biotechnol. Bioeng.* 102 (5), 1513–1520.
- Bougrier, C., Albasi, C., Delgenes, J.P., Carrère, H., 2006. Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. *Chem. Eng. Process.* 45, 711–718.
- Bougrier, C., Delgenes, J.P., Carrère, H., 2007. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. *Biochem. Eng. J.* 34, 20–27.
- Bougrier, C., Delgenes, J.P., Carrère, H., 2008. Effects of thermal treatments on five different waste activated sludge sample solubilisation, physical properties and anaerobic digestion. *Chem. Eng. J.* 139, 236–244.
- de Gracia, M., Sancho, L., García-Heras, J.L., Vanrolleghem, P., Ayesa, E., 2006. Mass and charge conservation check in dynamic models: application to the new ADM1 model. *Water Sci. Technol.* 53 (1), 225–240.
- Dohanyos, M., Zabranska, J., Kutil, J., Jenicek, P., 2004. Improvement of anaerobic digestion of sludge. *Water Sci. Technol.* 49 (10), 89–96.
- Donoso-Bravo, A., Pérez-Elvira, S., Fdz-Polanco, F., 2010. Application of simplified models for anaerobic biodegradability tests. Evaluation of pre-treatment processes. *Chem. Eng. J.* 160, 607–614.
- Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28 (3), 350–356.
- Eskicioglu, C., Kennedy, K.J., Droste, R.L., 2008. Initial examination of microwave pretreatment on primary, secondary and mixed sludges before and after anaerobic digestion. *Water Sci. Technol.* 57 (3), 311–317.
- Fdz-Polanco, F., Velázquez, R., Pérez-Elvira, S.I., Casas, C., del Barrio, D., Cantero, F.J., Fdz-Polanco, M., Rodríguez, P., Panizo, L., Serrat, J., Rouge, P., 2008. Continuous thermal hydrolysis and energy integration in sludge anaerobic digestion plants. *Water Sci. Technol.* 57 (8), 1221–1226.
- Grau, P., de Gracia, M., Vanrolleghem, P.A., Ayesa, E., 2007. A new plant-wide modelling methodology for WWTPs. *Water Res.* 41 (19), 4357–4372.
- Kalogi, Y., Monteith, H., 2008. State of science report: energy and resource recovery from sludge. Final report of the Global Water Research Coalition.
- Kepp, U., Machenbach, I., Weisz, N., Solheim, O.E., 2000. Enhanced stabilisation of sewage sludge through thermal hydrolysis – three years of experience with full scale plant. *Water Sci. Technol.* 42 (9), 89–96.
- Li, Y.Y., Noike, T., 1992. Upgrading of anaerobic-digestion of waste activated-sludge by thermal pretreatment. *Water Sci. Technol.* 26 (3–4), 857–866.
- Metcalf & Edy.Inc., 2003. *Wastewater engineering: treatment and reuse.* by: George Tchobanoglous, Franklin L Burton, H. David Stensel. fourth ed. revised McGraw Hill, Boston.
- Neyens, E., Baeyens, J., 2003. A review of thermal sludge pre-treatment processes to improve dewaterability. *J. Hazard. Mater.* 98, 51–67.
- Pérez-Elvira, S.I., Nieto-Diez, P., Fdz-Polanco, F., 2006. Sludge minimisation technologies. *Rev. Environ. Sci. Biotechnol.* 5, 375–398.
- Pérez-Elvira, S.I., Ferreira, L.C., Donoso-Bravo, A., Fdz-Polanco, M., Fdz-Polanco, F., 2010. Full-stream and part-stream ultrasound treatment effect on sludge anaerobic digestion. *Water Sci. Technol.* 61 (6), 1363–1372.
- Tanaka, S., Kobayashi, T., Kamiyama, K., Bildan, M., 1997. Effects of thermochemical pretreatment on the anaerobic digestion of waste activated sludge. *Water Sci. Technol.* 35 (8), 209–215.
- Valo, A., Carrère, H., Delgenes, J.P., 2004. Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion. *J. Chem. Technol. Biotechnol.* 79, 1197–1203.
- Vavilin, V.A., Fernández, B., Palatsi, J., Flotats, X., 2008. Hydrolysis kinetics in anaerobic degradation of particulate organic material: an overview. *Waste Manag.* 28, 939–951.
- Wilson, C.A., Novak, J.T., 2009. Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water Res.* 43 (18), 4489–4498.
- Yang, X.Y., Wang, X., Wang, L., 2010. Transferring of components and energy output in industrial sewage sludge disposal by thermal pretreatment and two-phase anaerobic process. *Bioresour. Technol.* 101 (8), 2580–2584.