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Increasing biogas production by thermal (70º) sludge pre-treatment prior to thermophilic anaerobic digestion

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Abstract

The objective of this work was to investigate the effect of a low temperature pre-treatment (70 ºC) on the efficiency of thermophilic anaerobic digestion of primary and secondary waste sludge. Firstly, effect of sludge pre-treatment time (9, 24, 48 and 72 h) was evaluated by the increase in volatile dissolved solids (VDS), volatile fatty acids (VFA) and biogas production in thermophilic batch tests. Secondly, semi-continuous process performance was studied in a lab-scale reactor (5 L) working at 55 ºC and 10 days solid retention time. The 70 ºC pre-treatment showed an initial solubilization effect (increasing VDS by almost 10 times after 9 h), followed by a progressive generation of VFA (from 0 to nearly 5 g·L^{-1} after 72 h). Biogas production increased up to 30 % both in batch tests and in semi-continuous experiments. Our results suggest that a short period (9 h) low temperature pre-treatment should be enough to enhance methane production through thermophilic anaerobic digestion of sludge.

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Keywords: Anaerobic Processes; Biosolid; Thermal Pre-treatment; Thermophiles; Waste-Water Treatment; Waste Treatment

1. Introduction

Anaerobic digestion is a treatment process used in many municipal wastewater treatment plants (MWWTP) for sludge stabilization. Mass reduction, methane production and improved dewatering properties of the treated sludge are the main features of the process. Slow degradation of sewage sludge is a disadvantage of anaerobic digestion, leading to high solid retention times (SRT) of 20-30 days in conventional mesophilic (37 ºC) digesters. This fact implies significant space requirements due to large digesters. Anaerobic digestion may be carried out under psychrophilic, mesophilic and thermophilic conditions (55 ºC). In general, mesophilic anaerobic digestion of sewage sludge is more widely used compared to thermophilic digestion, mainly because of the lower energy requirements and higher stability of the process. Thermophilic digestion, however, is more efficient in terms of organic matter removal and methane production [1, 2]. Moreover, it enhances the destruction of pathogens, weed seeds and insect eggs; thus enabling effluent hygienisation [3], which might be required in the short term for land application (3rd Draft EU Working Document on Sludge [4]). Increased energy requirements may be met by implementing a system allowing heat recovery from the effluent and cogeneration with biogas [5].

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Hydrolysis is the rate limiting step of anaerobic digestion of semi-solid wastes. In this step both solubilization of particulate matter and biological decomposition of organic polymers to monomers or dimers take place. Thermal, chemical, biological and mechanical processes, as well as combinations of these, have been studied as possible pre-treatments to accelerate sludge hydrolysis. These pre-treatments cause the lysis or disintegration of sludge cells permitting the release of intracellular matter that becomes more accessible to anaerobic microorganisms. This fact improves the overall digestion process velocity and the degree of sludge degradation, thus reducing anaerobic digester retention time and increasing methane production rates [6].

Mechanical sludge disintegration methods are generally based on the disruption of microbial cell walls by shear stress. Stirred ball mills, high pressure homogenisers and mechanical jet smash techniques have been used for mechanical pre-treatment application although the most used technique is sludge sonication [6-10]. Microwaves have also been used for cell lysis. However, they have been scarcely used for sludge disintegration [10-14]. The use of heat has been widely reported for the disintegration of sludge [6, 10, 15-18]. A wide range of temperatures has been studied, ranging from 60 to 270 ºC, although the most common pre-treatment temperatures are between 60 and 180 ºC, since temperatures above 200 ºC have been found responsible for refractory compound formation [15]. Pre-treatments applied at temperatures below 100 ºC are considered as low temperature thermal pre-treatments. Such pre-treatments have been pointed out as effective in increasing biogas production from both primary and secondary sludge [10, 19].

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Similarly, two-stage systems coupling a hyperthermophilic digester (68-70 ºC) and a thermophilic digester (55 ºC) have been found to be more efficient in terms of methane production compared to single stage thermophilic digesters treating primary and secondary sludge [20, 21] and cattle manure [22]. In these studies, it is suggested that thermal pre-treatment applied at temperatures around 70 ºC enhances biological activity of some thermophilic bacteria population with optimum activity temperatures in the high values of the thermophilic range. Thus, low temperature pre-treatment may be considered as a predigestion step.

In general, the efficiency of pre-treatments has been assessed by the increase of soluble organic matter (i.e. volatile dissolved solids (VDS), soluble chemical oxygen demand or soluble proteins). Some studies also focus on anaerobic biodegradability and biogas production, mainly in mesophilic batch assays [8, 13, 14, 16]. But little work has been done on the effect of sludge pre-treatment on thermophilic anaerobic digestion [10, 19], especially in continuous digesters [9, 17, 23]. To our knowledge, no such work exists for a low temperature pre-treatment of the mixture of thickened primary and secondary sludge prior to continuous thermophilic anaerobic digestion.

The objective of this work was then to address the enhancement of thermophilic anaerobic digestion of the mixture of thickened primary and secondary sewage sludge, by means of a low temperature (70 ºC) pre-treatment. Firstly by studying the effect of pre-treatment time on organic matter solubilization, volatile fatty acids (VFA) generation and biogas production in thermophilic batch tests; and secondly by evaluating process efficiency in a semi-continuous lab-scale reactor at 55 ºC and 10 days RT. The effect on the hygienisation of sludge was also studied.

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2. Materials and methods

2.1. Sludge sampling and characterization

The mixture of thickened primary and secondary sludge (Table 1) used for this work was obtained from a municipal wastewater treatment plant (MWWTP) near Barcelona (Spain). Samples were collected weekly and stored at 4 ºC until use. This MWWTP serves a population of 128,000 equivalent inhabitants. The conventional wastewater treatment used in this plant consists of preliminary and primary treatment and secondary treatment in the activated sludge unit. Primary sludge (PS) and secondary waste activated sludge (WAS) are thickened and mixed (this is the sampling point), before undergoing mesophilic (38 ºC) anaerobic digestion at very high SRT (40 days) aimed to reduce the solids content and improve dewatering in a centrifuge prior to final disposal.

2.2. Low temperature (70 ºC) pre-treatment

The low temperature pre-treatment was carried out at 70 ºC in order to enhance thermal solubilization of particulate material, as well as enzymatic hydrolysis. Bearing in mind that the effect of thermal pre-treatments depends both on treatment temperature and time [24], in this work the effect of pre-treatment duration was evaluated by taking samples at different pre-treatment times (9, 24, 48 and 72 h) in order to study the combined effect.

Beakers containing 0.5 L of sludge were submersed in a thermostatic bath at 70 ºC during 9, 24, 48 and 72 h. The beakers were covered with plastic film, to avoid water evaporation, and gently stirred (Heidolph RZR1) to ensure temperature homogeneity. Samples of raw and pretreated sludge were analysed for total solids (TS), volatile solids (VS), total dissolved solids (TDS), volatile dissolved solids (VDS), volatile fatty acids (VFA) and pH.

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The effect of pre-treatment time was assessed by the increase in VDS and VFA, comparing the initial concentration of VDS and VFA in the raw sludge with those obtained after each pre-treatment time assayed. Sludge solubilization was also evaluated by the increase in the ratio soluble to total volatile solids (VDS/VS), calculated as shown in Eq. (1), where the sub-indexes refer to raw (o) and treated (t) sludge samples.

$$VDS/VS = \frac{(VDS/VS)_t - (VDS/VS)_o}{(VDS/VS)_o} \qquad (1)$$

2.3. Anaerobic batch tests

Biogas production of raw and pretreated sludge samples (at 70 ºC for 9, 24, 48 and 72 h) was initially determined by means of batch tests at 55 ºC. The objective was to study the effect of the duration of 70 ºC pre-treatment, in terms of anaerobic biodegradability and biogas production under thermophilic conditions. Anaerobic batch tests were based on Soto et al. [25], adapted according to Ferrer et al. [26].

The inoculum was thermophilic sludge from the effluent of a lab-scale 5 L continuous stirred tank reactor (CSTR), operated at 20 days SRT and 55 ºC. This digester was fed with sludge mixture (PS and WAS) from the same MWWTP as that used for the anaerobic batch tests. The substrate was either pretreated or raw sludge (control treatment). A blank treatment with only inoculum was used to determine biogas production due to endogenous respiration. Each treatment was performed in triplicate.

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Each bottle-reactor (300 mL, SIGG®) was filled with 100 g of inoculum and 50 g of substrate (the blank treatment only with 150 g of inoculum) and was subsequently purged with N_2 and sealed. The bottles were incubated at 55 ºC and biogas production was followed by the pressure increase in the headspace by means of a SMC Pressure Switch manometer (1 bar, 5 % accuracy), until biogas production ceased. Biogas samples were taken periodically for the analysis of methane content by gas chromatography.

Accumulated volumetric biogas production (mL) was calculated from the pressure increase in the headspace volume (150 mL) at 55 ºC and expressed under normal conditions (20 ºC, 1 atm). The net values of biogas production were obtained by subtracting biogas production of the blank treatment to biogas production of each treatment.

2.4. Lab-scale thermophilic anaerobic digestion

The effect of 70 ºC pre-treatment on semi-continuous process performance was studied in the experimental set-up (Fig. 1), described in Ferrer et al. [27]. It consists of a jacketed CSTR (5 L) connected to a thermostatic bath through which temperature is controlled. Semi-continuous feeding is automated via a Data Acquisition System (DAS, by STEP S.L.) which activates the feeding and extraction peristaltic pumps twice per day, giving a total volume corresponding to the RT. The volume of biogas produced is measured with a device designed by Mata-Álvarez et al. [28] and a capacitive sensor (detector) connected to the DAS. Process temperature is also monitored on-line by means of a thermal sensor submersed in the liquor and connected to the DAS. Real time data from the DAS is displayed in a PC (software by STEP S.L.).

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Prior to the experiments with pretreated sludge, the digester had been working at 55 ºC for one year, fed with the same sludge mixture described above, at decreasing SRT from 30 to 10 days, at which it was maintained under steady-state conditions for 2 months. This is the control treatment to which experiments with pretreated sludge were compared. Keeping the same flow rate of 500 $mL\cdot day^{-1}$ (which corresponds to a SRT of 10 days), the digester was subsequently fed with pretreated sludge (at 70 ºC, for 9, 24 and 48 h), with a total experimental duration of 6 months.

Process performance was followed by on-line measurement of biogas production and by periodical analyses (twice per week) of influent and effluent sludge samples (TS, VS, VFA, pH and alkalinity) and biogas samples (% CH_4). Process efficiency under steady state conditions for each treatment assayed was evaluated in terms of biogas and methane production rates ($L\cdot L_{reactor}^{-1}\cdot day^{-1}$) and yields (($L\cdot g\ VS_{fed}^{-1}$ or $L\cdot g\ VS_{removed}^{-1}$), as well as organic solids (VS) removal (Table 2). VS removal was calculated according to Eq. (2), where the sub-indexes refer to the influent (i) and effluent (e) sludge.

$$VS_{removal}(\%) = \frac{VS_i - VS_e}{VS_i} \quad (2)$$

Total VFA were calculated as the sum of individual VFA analysed (expressed as g·L^{-1}).

2.5. Analytical methods

The solids content of sludge was determined according to Standard Methods [29] procedure 2540G. TS and VS were determined directly from sludge samples, whereas TDS and VDS were determined from the supernatant of samples centrifuged at 7000 rpm. Supernatants underwent filtration through 1.2 µm nominal pore size glass fibber filters (Albet FVC047, Spain). The particulate fractions, total suspended solids (TSS) and volatile suspended solids (VSS) were subsequently deduced. pH, alkalinity and VFA (acetic, propionic, iso-butyric, n-butyric, iso-valeric and n-valeric acids) were also analysed from the filtrate supernatant. Samples for VFA analysis were further filtered through a 0.45 µm nylon syringe filter.

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VFA and biogas composition were determined by gas chromatography (Perkin-Elmer AutoSystem XL Gas Chromatograph). For VFA analysis, the chromatograph was equipped with a capillary column (HP Innowax 30 m × 0.25 mm × 0.25 µm) and a flame ionisation detector (FID). Helium (He) was used as carrier gas, with a split ratio of 13 (column flow: 5 mL·min^{-1}). The oven was kept at an initial temperature of 120 ºC for 1 min, it was subsequently increased at a constant ratio of 10 ºC·min^{-1} to 245 ºC and maintained for 2 min. The temperatures of the injector and detector were 250 ºC and 300 ºC, respectively. The system was calibrated with dilutions of commercial (Scharlau, Spain) VFA (acetic, propionic, iso-butyric, n-butyric, iso-valeric and n-valeric acids) with concentrations in the range of 0-1000 mg·L^{-1}. Detection limit of VFA analysis was 5 mg·L^{-1}. Biogas composition was determined with a thermal conductivity detector (TCD), by injecting gas samples into a packed column (Hayesep 3 m 1/8 in. 100/120). The carrier gas was He in splitless mode (column flow: 19 mL·min^{-1}). The oven was maintained at a constant temperature of 40 ºC. Injector and detector temperatures were 150 ºC and 250 ºC, respectively. The system was calibrated with pure samples of methane (99.9 % CH_4) and carbon dioxide (99.9 % CO_2).

Escherichia coli were quantified by the methodology ISO 16649:2000 and the results were expressed as colony forming units per mL (CFU·mL^{-1}). In the case of *Salmonella sp*., only presence or absence was determined by the methodology NF-V08-052 and the results were presence or absence per 50 mL of sample.

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3. Results and discussion

3.1. Sludge composition

General characteristics of the feeding sludge, mixture of thickened PS and WAS, are summarised in Table 1. TS content was around 39 g·L^{-1} (3.9 %) and total VS around 29 g·L^{-1} (2.9 %), with a VS/TS ratio of 0.74 (74 %), a high organic content typical from fresh non-stabilized materials. Furthermore, only a small proportion of this organic material was soluble, as shown by the low volatile dissolved solids to total volatile solids ratio (0.05 VDS/VS), which may be indicating that little hydrolysis had occurred. This matches with the almost absence of volatile fatty acids (VFA), meaning very scare fermentative activity. The only VFA detected were acetate and propionate.

3.2. Low temperature (70 ºC) pre-treatment

The expected effect after thermal pre-treatment of sludge was an increase in soluble materials, with interest focused on soluble organic solids (i.e. VDS), thus enhancing hydrolysis. Since the feeding sludge was a mixture of thickened PS and WAS, and WAS consists of a complex activated sludge floc structure, the disruption of this structure may release biopolymers such as proteins or sugars from the floc into the soluble phase [13]. At the same time, disruption of microbial cells from WAS should lead to their solubilization into carbohydrates, proteins, lipids and even lower molecular weight products like VFA [24].

As expected, TDS and VDS concentrations increased after thermal pre-treatment at 70 ºC. An increase from around 1.5 $g \cdot L^{-1}$VDS in the raw sludge to 11.9-13.9 $g \cdot L^{-1}$ VDS after 9, 24 and 48 h thermal pre-treatment was detected (Fig. 2), resulting in an increase in VDS/VS ratio from 0.05 to 0.44-0.48. This means that the proportion of soluble to total organic matter increased by almost 10 times, from 5 % to almost 50 % after 70 ºC pre-treatment. Regarding VFA concentration, it increased along pre-treatment time, from about 0 in the raw sludge to nearly 5 $g \cdot L^{-1}$ after 72 h thermal pre-treatment. After 24 h acetic and propionic acids were the main VFA generated, whereas butyric and valeric acids were mostly detected after 48 h (Fig. 3).

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Comparing the evolution of VDS and VFA (Fig. 2), it is clear that there was a sharp increase in VDS, which was followed by a progressive generation of VFA after 24 h. According to this, sludge solubilization due to 70 ºC pre-treatment would occur rapidly, reaching a maximum concentration of VDS within 9-24 h. Other studies indicate that even shorter periods (30-60 min) are needed for WAS solubilization at 60-80 ºC [24, 30]. On the other hand, longer pre-treatments at 70 ºC may favour the activity of thermophilic or hyperthermophilic bacteria, promoting enzymatic hydrolysis and resulting in a predigestion step [20-22]. The relentless increase in VFA after 9 h, and especially after 24 h, might result from the aforementioned process.

3.3. Anaerobic batch tests

Biogas production under thermophilic conditions was initially assessed by means of anaerobic batch tests using raw and pretreated sludge samples. Fig. 4 shows the evolution of net accumulated biogas production during the 37 days of assay. Initial biogas production rate (indicated by the slope of the curve) up to day 7 was similar in all cases, except for the 72 h pretreated sludge. However, at day 10 (which corresponds to the SRT assayed in the continuous process) accumulated production was nearly 300 mL for 9, 24, and 48 h pretreated samples, whereas for the control treatment it was around 200 mL, representing an almost 50 % volume increase. Final values were somewhat higher for the 9 h treatment (30 % increase) followed by the 24 and 48 h treatments (15 % increase). Gavala et al. [19] found increased thermophilic methane potential after 70 ºC pre-treatment, but only for primary sludge samples, whereas production rate was increased both with primary and secondary sludge samples.

Lower values for 72 h treated sludge could be related to process inhibition caused by initial accumulation of VFA. The concentration of VFA in the sludge after 72 h of thermal pre-treatment was remarkably high (4.86 $g \cdot L^{-1}$), even higher than in the thermophilic inoculum used for the tests (2.12 $g \cdot L^{-1}$). This initial accumulation was not observed after shorter pre-treatments (9-48 h) in which final VFA concentration were much lower (0.32-2.86 $g \cdot L^{-1}$). In addition, partial biodegradation of organic compounds

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during pre-treatment itself might be responsible for lower final biogas volume; as suggested by lower VS and VDS in Fig. 3.

3.4. Performance of thermophilic anaerobic digestion

Table 2 shows characteristics and operational parameters during semi-continuous thermophilic anaerobic digestion of raw sludge and 70 ºC pretreated mixture of primary and secondary waste sludge.

3.4.1. Thermophilic anaerobic digestion of raw sludge at 10 days RT

Thermophilic digestion of raw sludge after 1 year of operation at decreasing SRT from 30 to 10 days (data not shown), and over 2 months at the lowest SRT of only 10 days, proved to be very stable.

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Average efficiencies were around 27 % and 33 % for TS and VS removal, respectively; biogas production rate around 0.63 $L \cdot L^{-1} \cdot day^{-1}$ and methane content in biogas around 64 % (Table 2). Our results are quite consistent with those obtained under similar conditions, treating WAS at 8-12 days SRT [23], or the mixture of PS and WAS at 15 days SRT [9] and 20 days SRT [19]. However, from the comparison of these results it is clear that VS removal is lower at 10 days SRT (33 % vs. 46 and 52 % at 15 and 20 days RT, respectively). On the other hand, biogas production rate is considerably higher (0.63 vs. 0.58 and 0.43 $L \cdot L^{-1} \cdot day^{-1}$ at 15 and 20 days SRT, respectively). This suggests that lower SRT are more efficient in terms of energy production, but less efficient in terms of effluent stabilization; as predicted by kinetic models when hydrolysis is the rate-limiting step of anaerobic digestion [31]. Hence, depending on sludge final disposal (i.e. land application) a stabilisation post-treatment such as composting may be appropriate to further stabilise the effluent.

Higher VS concentration in the effluent should possibly be related to a certain accumulation of VFA in the effluent, especially propionate, which degradation tends to be slower than the rest [32]. Apparently, though, this did not affect process stability. In fact, despite being high compared to mesophilic sludge (in which VFA concentration is typically low or even not detected); VFA concentration was still low compared to other thermophilic digesters with stable operation at SRT between 15 and 75 days [33]. Stable operation in spite of relatively high VFA concentration might be attributed to high buffer capacity in the system (i.e. alkalinity) and to the fact that anaerobes were already adapted to high OLR (~ 3 g VS $L^{-1}\cdot day^{-1}$) working at 10 days SRT.

Regarding effluent hygienisation, pathogens concentration was reduced from $>10^6$ CFU to absence per mL for *E. coli*; whereas *Salmonella* was always absence per 50 mL (both in raw and digested sludge samples), which was also found by Zábranská et al. [3]. From a sanitary point of view, this effluent would fulfil the requirements for land application proposed in the 3rd Draft EU Working Document on Sludge [4]. Destruction of pathogens from primary or secondary waste sludge through one and two-stage thermophilic digestion has also been reported by other authors [20, 21, 23].

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3.4.2. Thermophilic anaerobic digestion of 70 ºC pretreated sludge at 10 days SRT

The results with pretreated sludge (Table 2) clearly show that the process was more efficient in terms of biogas production and yield in all cases, with increases in the range of 30-40 %, following the tendency observed in the batch tests. Lower increase with the 24 h pre-treatment (10%) may be attributed to lower VS content in the influent sludge obtained from the MWWTP during this experimental period. Notice that, in spite of the variability of solids concentration in the influent sludge, solids concentration in the effluent is fairly similar for all treatments. Apparently, the higher the VS fed, the higher the VS removed, and the higher the biogas production. According to this, under the conditions assayed, increasing solids concentration in the influent sludge up to of 55 g TS·L^{-1} and 30 g VS·L^{-1}, allows to increase biogas production (i.e. energy production) maintaining the quality of the effluent. Biogas yield (i.e. biogas produced per VS fed) was also enhanced in all cases, being some 30 % higher with pretreated sludge (0.28-0.30 L·gVS$_{fed}$$^{-1}$) than with raw sludge (0.22 L·gVS$_{fed}$$^{-1}$). The same pattern described for biogas production applies to methane production. Moreover, methane content in biogas was also always higher after sludge pretreament, around 69 % vs. 64 % with raw sludge.

According to our results, it seems that 70 ºC sludge pre-treatment has similar effects in subsequent thermophilic digestion regardless of pre-treatment time. If no additional benefits are obtained, the shorter the pre-treatment time, the lower the costs related to energy consumption and reactor volume. Therefore, 9 h pre-treatment should be enough to enhance thermophilic digestion of sludge at 10 days RT. Two-stage systems coupling a hyperthermophilic digester (68-70 ºC, 2-3 days RT) and a thermophilic digester (55 ºC, 12-13 days RT) have also been found to be more efficient in terms of methane production than single stage thermophilic digesters (55 ºC, 15 days RT) treating primary and secondary sludge [20, 21] and cattle manure [22]. In such studies it is suggested that positive effects of low temperature pre-treatments upon thermophilic digestion are related to the fact that they accelerate hydrolysis-acidogenesis by promoting the activity of thermophilic bacteria, resulting in the so-called predigestion step. Our study shows that 70 ºC pre-treatment time as well as the overall SRT of thermophilic anaerobic digestion can be further reduced, maintaining the efficiency in terms of biogas and methane production. Other pre-treatments such as ultrasounds are

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more effective at enhancing mesophilic than thermophilic sludge digestion [9], which has been attributed to higher hydrolysis rate under thermophilic conditions, thus reducing the benefits from sludge solubilization prior to digestion process.

From an energetic point of view, full-scale application of low temperature sludge pre-treatment is amongst the less energy demanding pre-treatments, since influent sludge might be heated up to 70 ºC by means of a heat-exchanger, using the waste heat from a conventional heat and power generation unit fuelled with biogas. According to theoretical energy balances, the extra energy requirements would be fully covered by the energy generated from the extra methane production [21].

4. Conclusions

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A thermophilic lab-scale digester was operating for over 6 months treating raw and pretreated (70 ºC) mixture of primary and secondary waste sludge. From this period of study the following conclusions can be drawn:

(1) Sludge solubilization due to a low temperature (70 ºC) pre-treatment can increase VDS concentration as much as 10 times (from ~1.5 g VDS·L^{-1} in raw sludge to ~12.73 g VDS L^{-1} in pretreated samples), representing an increase from around 5 % to 50 % in the ratio VDS to total VS. This effect occurred already after the shorter pre-treatment times assayed (9 and 24 h). However, VFA generation was only enhanced after 24 h, which might be regarded as threshold for the so-called predigestion step. From this moment, VFA concentration increased along pre-treatment time, up to a maximum concentration of nearly 5 g VFA·L^{-1} after 72 h.

(2) Biogas production in thermophilic batch tests showed that initial biogas production rate was similar for raw sludge and for 9, 24 and 48 h pretreated sludge samples.

However, at day 10 accumulated biogas productions were 50 % higher for 9, 24, and 48 h pre-treatments, and final values were 30 % higher for 9 h pre-treatment, and 15 % for 24 and 48 h pre-treatments. Lower production in the 72 h pre-treatment could be related to initial inhibition caused by VFA accumulation, and to partial biodegradation of solubilized compounds during thermal pre-treatment.

(3) Sludge pre-treatment at 70 ºC enhanced biogas and methane productions in lab-scale digesters working at 55 ºC and 10 days RT. Biogas yield was some 30 % higher with pretreated sludge (0.28-0.30 $L\cdot gVS_{fed}^{-1}$) than with raw sludge (0.22 $L\cdot gVS_{fed}^{-1}$). Methane content in biogas was also higher after sludge pretreament, around 69 % vs. 64 % with raw sludge.

(4) The comparison of thermophilic anaerobic digestion of raw sludge at 10 days SRT with other studies at 15 and 20 days SRT shows that lower SRT are more efficient in terms of energy production, but less efficient in terms of effluent stabilization. This suggests that, depending on sludge final disposal, a stabilisation post-treatment such as composting may be appropriate to further stabilise the effluent.

(5) Regarding effluent hygienisation, the thermophilic digester treating raw sludge at 10 days SRT was capable of reducing *E. coli* from $>10^6$ CFU in the raw sludge to absence per mL in the digested effluent, whereas *Salmonella* was always absence per 50 mL (both in raw and digested sludge).

(6) Our results suggest that a short period (9 h) low temperature (70 ºC) pre-treatment should be enough to enhance biogas and methane production through thermophilic anaerobic digestion of sludge. The assessment of even shorter pre-treatment times should be considered in future research studies.

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Table 1

Composition of the mixture of thickened primary and secondary waste sludge

Parameter	Value
TS (g·L^{-1})	38.97
VS (g·L^{-1})	28.87
VS/TS	0.74
TDS (g·L^{-1})	2.54
VDS (g·L^{-1})	1.51
VDS/TDS	0.59
VDS/VS	0.05
pH	7.96
Total VFA (g·L^{-1})	0.11
Acetate (g·L^{-1})	0.06
Propionate (g·L^{-1})	0.05
iso-Butyrate (g·L^{-1})	0.00
n-Butyrate (g·L^{-1})	0.00
iso-Valerate (g·L^{-1})	0.00
n-Valerate (g·L^{-1})	0.00

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Table 2

Average feed and digested sludge characteristics and operational parameters during semi-continuous thermophilic anaerobic digestion with raw and 70 ºC pretreated sludge (mixture of thickened primary and secondary waste sludge)

Parameter	70 ºC Treatment time (h)			
	0	9	24	48
Operating conditions				
Temperature (ºC)	55			
SRT (days)	10			
Flow rate ($mL\cdot day^{-1}$)	500			
Feed composition				
TS ($g\cdot L^{-1}$)	38.53 ± 6.26	55.47 ± 11.75	38.33 ± 9.90	54.43 ± 4.43
VS ($g\cdot L^{-1}$)	30.08 ± 2.89	30.45 ± 3.59	26.59 ± 6.63	27.88 ± 2.12
VS/TS	0.78	0.55	0.69	0.51
pH	6.92 ± 0.18	6.67 ± 0.46	7.28 ± 0.29	7.15 ± 0.18
Effluent composition				
TS ($g\cdot L^{-1}$)	31.17 ± 4.93	34.87 ± 5.92	33.95 ± 5.43	36.88 ± 5.64
VS ($g\cdot L^{-1}$)	19.93 ± 1.88	18.95 ± 2.29	19.64 ± 3.52	18.56 ± 1.69
VS/TS	0.64	0.54	0.58	0.50
Total VFA ($g\cdot L^{-1}$)	2.40 ± 0.42	1.27 ± 0.38	2.07 ± 0.45	1.42 ± 0.34
Acetate ($g\cdot L^{-1}$)	0.32 ± 0.13	0.15 ± 0.10	0.67 ± 0.23	0.40 ± 0.29
Propionate ($g\cdot L^{-1}$)	1.14 ± 0.12	0.88 ± 0.09	1.11 ± 0.17	0.86 ± 0.10
iso-Butyrate ($g\cdot L^{-1}$)	0.30 ± 0.13	0.05 ± 0.08	0.09 ± 0.04	0.07 ± 0.04
n-Butyrate ($g\cdot L^{-1}$)	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00
iso-Valerate ($g\cdot L^{-1}$)	0.53 ± 0.09	0.18 ± 0.13	0.19 ± 0.14	0.11 ± 0.02
n-Valerate ($g\cdot L^{-1}$)	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
pH	8.22 ± 0.10	8.27 ± 0.10	8.32 ± 0.13	8.25 ± 0.12
Removal efficiency				
TS removal (%)	26.89 ± 6.07	31.16 ± 15.44	28.35 ± 15.38	30.66 ± 8.70
VS removal (%)	33.23 ± 5.49	36.55 ± 5.72	24.64 ± 9.09	32.61 ± 4.27
Biogas characteristics				
Biogas production ($L\cdot L_R^{-1}\cdot day^{-1}$)	0.63 ± 0.06	0.87 ± 0.17	0.69 ± 0.18	0.81 ± 0.15
Biogas production ($L\cdot L_{fed}^{-1}\cdot day^{-1}$)	6.06 ± 1.01	9.15 ± 1.51	7.43 ± 2.23	8.45 ± 1.33
Biogas yield ($L\cdot gVS_{fed}^{-1}$)	0.22 ± 0.04	0.30 ± 0.04	0.28 ± 0.05	0.29 ± 0.05
Biogas yield ($L\cdot gVS_{removed}^{-1}$)	0.61 ± 0.16	0.82 ± 0.17	0.81 ± 0.13	0.94 ± 0.14
Methane production ($L\cdot L_R^{-1}\cdot day^{-1}$)	0.40 ± 0.04	0.56 ± 0.22	0.48 ± 0.14	0.59 ± 0.05
Methane yield ($L\cdot gVS_{fed}^{-1}$)	0.15 ± 0.05	0.18 ± 0.08	0.18 ± 0.02	0.12 ± 0.10
Methane yield ($L\cdot gVS_{removed}^{-1}$)	0.44 ± 0.11	0.49 ± 0.23	0.41 ± 0.26	0.40 ± 0.35
Methane content (%)	63.73 ± 3.52	69.77 ± 3.36	68.73 ± 5.48	67.84 ± 5.13
Experimental period				
Duration (days)	60	40	40	40

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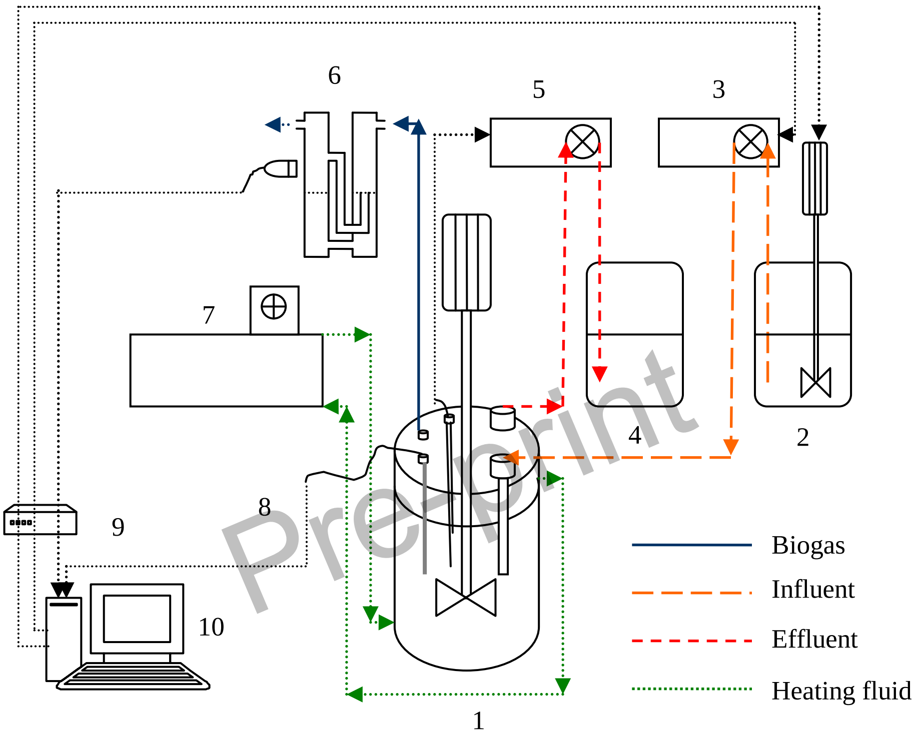

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Fig. 1. Schematic diagram of the experimental set-up.

1) Reactor; 2) Influent storage; 3) Feed pump; 4) Effluent storage; 5) Extraction pump;6) Gas meter; 7) Thermostatic bath; 8) Temperature sensor; 9) Data acquisition system; 10) PC.

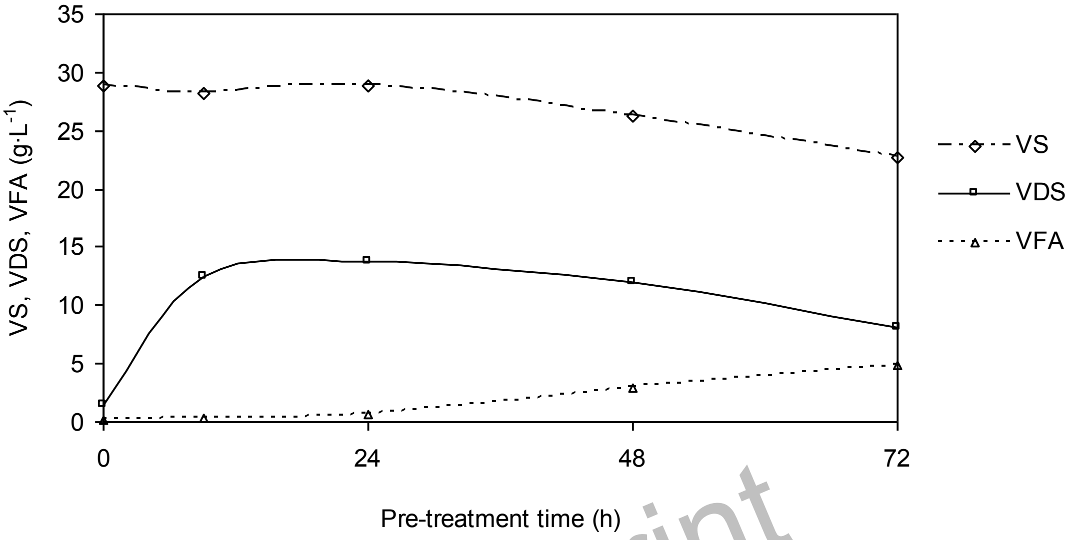

Fig. 2. Evolution of volatile solids (VS), volatile dissolved solids (VDS) and volatile fatty acids (VFA) along 70 ºC treatment time (9, 24, 48 and 72 h).

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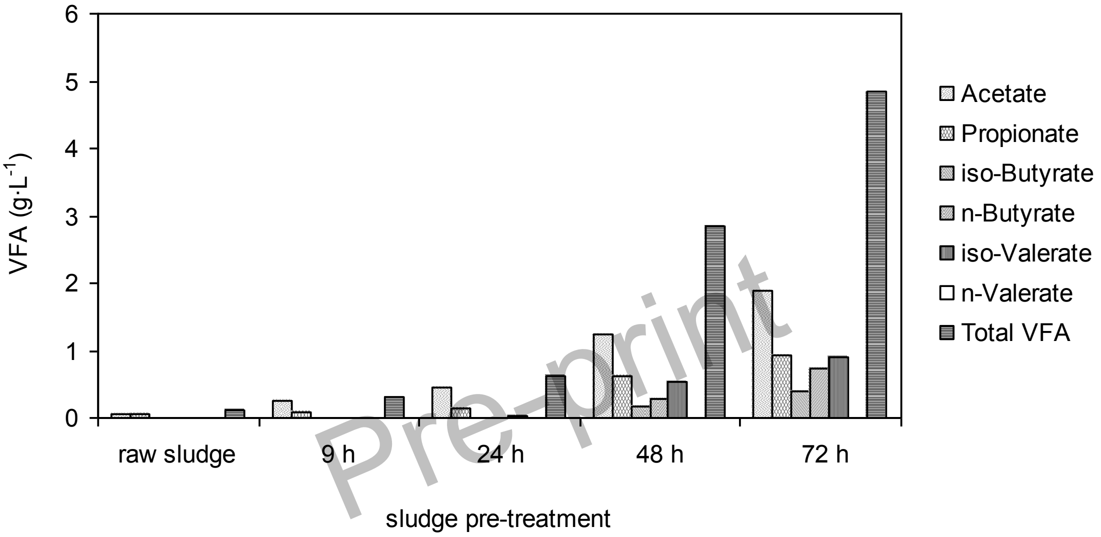

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Fig. 3. Generation of individual volatile fatty acids (VFA) and total VFA along 70 ºC treatment time (9, 24, 48 and 72 h).

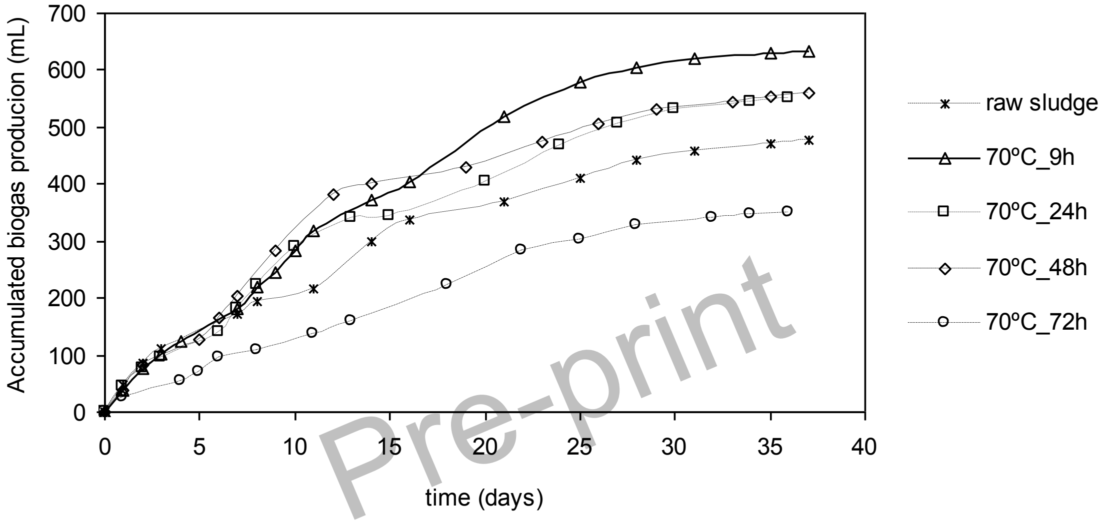

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Fig. 4. Biogas production in thermophilic anaerobic biodegradability tests with raw and 70 ºC pretreated sludge (9, 24, 48 and 72 h).