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Enhancement of Waste Activated Sludge (WAS) anaerobic digestion by means of pre- and intermediate treatments. Technical and economic analysis at a full-scale WWTP

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Abstract

Anaerobic digestion (AD) is the most commonly applied end-treatment for the excess of waste activated sludge (WAS) generated in biological wastewater treatment processes. The efficacy of different typologies of pre-treatments in liberating intra-cellular organic substances and make them more usable for AD was demonstrated in several studies. However, the production of new extracellular polymeric substances (EPSs) that occur during an AD process, due to microbial metabolism, self-protective reactions and cell lysis, partially neutralizes the benefit of pre-treatments. The efficacy of post- and inter-stage treatments is currently under consideration to overcome the problems due to this unavoidable byproduct.

This work compares three scenarios in which low-temperature (<100°C) thermal and hybrid (thermal+alkali) lysis treatments were applied to one sample of WAS and two samples of digestate with hydraulic retention times (HRTs) of 7 and 15 days. Batch mesophilic digestibility tests demonstrated that intermediate treatments were effective in making the residual organic substance of a 7-day digestate usable for a second-stage AD process. In fact, under this scenario, the methane generated in a two-stage AD process, with an in-between intermediate treatment, was 23% and 16% higher than that generated in the scenario that considers traditional pre-treatments carried out with 4% NaOH at 70 and 90°C respectively. Conversely, in no cases (70 or 90°C) the combination of a 15-day AD process, followed by an intermediate treatment and a second-stage AD process, made possible to obtain specific methane productions (SMPs) higher than those obtained with pre-treatments.

The results of the digestibility tests were used for a tecno-economic assessment of pre- and intermediate lysis treatments in a full scale wastewater treatment plant (WWTP, 2,000,000 p.e.). It was demonstrated that the introduction of thermal or hybrid pre-treatments could increase the revenues from the electricity sale by between 13% and 25%, in comparison with the present scenario (no lysis treatments). Conversely, intermediate treatments on a 7-day digestate could provide a gain of 26% or 32%, depending on the process temperature (70 or 90°C).

Key words: waste activated sludge (WAS); cellular lysis; two-stage anaerobic digestion; intermediate hydrolysis treatment; cost-benefit assessment

Introduction

Conventional biological treatments carried out in wastewater treatment plants (WWTPs) are intended to reduce the load of organic substances and nutrients from wastewaters before discharge in receiving water bodies. Biological treatments concentrate more than 60% of the initially diluted organic matter in waste activate sludge (WAS) that contains total (TS) and volatile solids (VS) (Garrido et al., 2013). Then, 60% of the initial energy content of the wastewater (3.2 MJ/kg TS) is transferred into WAS (with a heating value of 17.5 MJ/kg TS, according to Cano et al., 2015) and can be recovered as biogas from an anaerobic digestion (AD) process.

It is however well known that most of the organic substances in WAS are found in insoluble microbial cells, which show low bioavailability for the subsequent AD process (Traversi et al., 2015; Xiao et al., 2015). Traditional pre-treatments (mechanical, thermal, chemical or a combination of them) are intended to make the biological substrates more usable for enzymatic attack through the disruption of cell walls (Collivignarelli et al., 2015; Carrère et al., 2010; Teo, 2016). However, several authors demonstrated that also Extracellular Polymeric Substances (EPSs) in sewage sludge is a factor for poor anaerobic digestion (Shana et al., 2015; Williams et al., 2015). EPS is a part of sludge biochemical composition (carbohydrates and proteins) and two types of EPSs are involved in WAS digestion. One type is part of the biochemical composition of the activated sludge fed to the digester, the other type is released from the sludge that undergoes digestion because of microbial metabolism, self-protective reaction and cell lysis (Shana et al., 2015). The use of sludge pre-treatment technologies may only help to reduce the amount of EPS in the sludge feedstock but cannot prevent its production during an AD process due to bacteria growth, substrate consumption, self-protection of microorganisms from adverse environmental conditions or cell decay. Thus, EPS is an unavoidable by-product of the WAS digestion process. Therefore, a possible solution to deal with EPS production during sludge digestion is to make use of intermediate hydrolysis processes (IHPs, Li et al., 2013; Williams et al., 2015).

IHPs consist of conventional mesophilic AD followed by a hydrolysis process. These treatments only concentrate on the slowly degradable parts of the sludge, in contrast to pre-treatment methods. Despite the possible advantages of post/inter-stage treatments, these configurations have until now received little attention in comparison to pre-treatments. To the best of our knowledge, only very few cases study compared the performances of pre- and inter-stage (or post) treatments on sludge destined to AD. Nielsen and coauthors (2011) compared moderate thermal (80 °C), high thermal (loop autoclave at 130–170 °C) and thermo-chemical (170 °C/pH 10, KOH) pre-treatments with inter-stage treatments carried out under the same operating conditions. They concluded that thermal or thermo-chemical treatments of WAS were more effective when applied as an inter-stage treatment rather than a pre-treatment. This behavior was particularly evident for the strongest treatment condition (170 °C/pH 10, KOH), for which the increase in the methane yield was of 28%, when applied as an inter-stage, and only of 2% when applied as a pre-treatment.

A very recent study (Ortega-Martinez et al., 2016) demonstrated that thermal inter-treatment could improve the methane production by 45% and 20% compared to conventional anaerobic digestion and pre-treatments followed by anaerobic digestion, respectively. Ortega-Martinez and coauthors carried out pre- and inter-treatments in a laboratory-scale thermal steam explosion system at temperature values that ranged from 110 to 200°C and for contact times of 10, 30 and 50 minutes. Also, Shana and coauthors (Shana et al., 2011; 2013) stated the advantage of IHPs compared to pre-treatments using very hard operating conditions (165°C, 7 bar, 30 min). They demonstrated that IHPs produced 20% more biogas than pre-treatments.

Conversely, some other authors concentrated their attention only on post- or inter-stage treatments, without a comparison with pre-treatments carried out under the same operating conditions. Takashima and Tanaka (2014) demonstrated that post- and inter-stage treatment configurations showed good performances in organic matter destruction and methane production by testing acid thermal post-treatments (ATPT) at a lab scale at the temperature values of 25; 100 and 180 °C and pH of 2; 4 and 6 obtained with HCl.

Li and coauthors (2013) tested alkaline post-treatment at a lab scale. They extracted 5% of sludge from a semi-continuous digester between the 8th and the 12th hour of a 24-h digestion cycle. The sludge was disintegrated with 0.1 mol/L NaOH and returned to the digester after neutralization. The results showed that alkaline post-treatment increased the level of soluble organic substances in the extracted sludge, particularly of volatile fatty acids and polysaccharides. This process resulted in a 33% enhancement of biogas production in comparison with the control. A very recent experience (Zhang et al., 2016) demonstrated the effectiveness of free nitrous acid (FNA i.e. HNO_2, in the range of 0.77 – 3.85 mg N/L for 24 h) used to hydrolyze samples of already anaerobically digested sludge. The FNA treatment at the lowest concentration resulted in the highest increase in methane production (40%) compared to the control.

In this work, only-thermal and hybrid (thermo-chemical) processes that use alkali species (NaOH and $Ca(OH)_2$) were employed for pre-treatments and intermediate treatments. Pre-treatments and intermediate treatments were carried out at the temperature values of 20, 70, 90 °C for contact times of 1.5 hours. Pre-treatments involved samples of WAS provided by the local wastewater treatment plant (WWTP, 2,000,000 population equivalent, p.e.), thickened to a final total solid (TS) content in the order of 4.5%. Intermediate treatments were carried out on two samples of digestate, one generated in the WWTP and characterized by a hydraulic retention time (HRT) of 7 days, the other produced in a pilot scale reactor and characterized by a HRT of 15 days. Performances of pre- and intermediate treatments were compared at three levels of analysis:

1. by assessing the disintegration rate (DR) parameter, as a quick response of the efficacy of the treatment;
2. by evaluating the increase in biogas and methane production using lab-scale digesters;
3. by assessing the benefit produced by pre- and intermediate treatments, in terms of increase in the economic revenues, for a full-scale plant (2,000,000 p.e.).

2. Materials and Methods

2.1. WAS and digestate samples

Three kinds of substrates were employed for this study. The first two substrates, a WAS and a digestate, were collected from the SMAT WWTP located in Castiglione Torinese (NW Italy, 2,000,000 p.e.). The SMAT plant is a conventional WWTP, the details of the units and processes that make up the water line and the sludge line are described in Panepinto et al., 2016. The third substrate was the digestate produced in a pilot scale (300-L) apparatus.

The sample of WAS was collected from one of the secondary clarifiers placed after the biological compartment of the water line. Under the WWTP normal operating conditions, WAS has a TS content of approximately 0.8% and a VS/TS ratio of 0.7. For experimental purposes the WAS sample was thickened on a cloth filter to reach a final TS content of approximately 5%.

The sample of digestate from the WWTP was collected at the exit of one of the six anaerobic digesters employed for the treatment of sludge produced in the WWTP. Digesters are fed with sludge of different quality: primary, secondary or a mixture of two. Under normal operating conditions, the digesters work in a one-stage modality with a HRT of 17 days. However, in the period in which the digestate was sampled (March 2016), all the secondary sludge was digested in one system that combined two digesters working in a two-stage modality. Digestate was taken at the exit of the first-stage digester that had a HRT of only 7 days. Also, the sample of digestate was thickened on a cloth filter to reach a final TS content of 4.5%.

The sample of digestate collected from the 300-L digester was produced in a test that involved the WAS generated in the Castiglione Torinese WWTP. The pilot scale digester was described in detail in Fiore et al., 2016. Shortly, it had an operating volume of 240 L and worked in mesophilic conditions under an organic loading rate of approximately 2 $kgTS/m^3 \cdot d$. The HRT was of 15 days. When the sample of digestate was collected for the study, the digester had been working for 75 days. The WAS used as a feeding substrate has had an average TS content of 3.18±0.22% and an average VS/TS ratio of 0.693±0.013. Also, the digestate collected from the 300-L digester was thickened before use. The original sample had a TS content of 2.58±0.06% with a VS/TS ratio of 0.626±0.005. After thickening, the TS content increased up to 4.30%.

The characteristics of the three substrates used for the tests are summarized in Table 1. Each value was obtained as an average of three replicates.

2.2. Lysis tests

Tests of low-temperature thermal lysis and hybrid thermo-chemical lysis were performed only on the samples of WAS and digestate collected from the WWTP. The methods employed were described in detail in Ruffino et al. (2016). Tests were carried out at the three values of temperature of 20; 70 and 90°C, using two alkali agents, NaOH and $Ca(OH)_2$. Contact time was equal to 90 minutes and the mixture was stirred energetically for 1 minute every 15 minutes. The doses of alkali employed were of 4 and 8% of the TS content and came from the results of a previous work (Ruffino et al., 2016). That work was aimed at identifying the optimal alkali dosage for the treatment of WAS and demonstrated that, in the range 2-20 g alkali/100 g TS, 4-8 was the most suitable dose for a hydrolysis process.

For what concerns the sample of digestate from the 300-L digester (15-day digestate), the effect of thermo-chemical lysis was verified only for the two specific working conditions that demonstrated to be the most promising, that is (70°C; 4% NaOH) and (90°C; 4% NaOH). Samples that underwent this treatment were subsequently used for digestibility tests (see Section 2.3).

2.3. Digestibility tests

Anaerobic digestion tests were carried out using the procedures described in previous works (Ruffino et al., 2015; 2016). The tests were performed in batch mode and mesophilic conditions (35-38°C) in the apparatus shown in Figure 1. Due to the limited availability of reactors, only six tests could be carried out simultaneously. A total of five series of tests were carried out in this study. Three series of tests involved samples of WAS, one series the 7-day digestate (from the full scale WWTP) and one series the 15-day digestate (from the 300-L digester). Specifically, digestibility tests involved samples of WAS treated with thermal (70°C and 90°C) and hybrid (20-70-90°C with 4% NaOH) processes and samples of 7-d and 15-d digestate treated with hybrid (70-90°C with 4% NaOH) processes.

In each series, two samples (in two replicates) treated with lysis processes were digested with a control (untreated) sample (also in two replicates). The inoculum used for the tests was the digestate collected from the 300-L reactor (TS content of 2.58±0.06% with a VS/TS ratio of 0.626±0.005). The ratio between food and microorganisms (F/M), as TS, was in the order of 1.5 in all tests.

As in previous experiences (Ruffino et al., 2015; 2016), the biogas produced from the reactors was collected in two 5-L Tedlar® bags connected in parallel. The characterization and measure of the volume of the produced biogas was carried out daily, throughout the whole duration of the test. The characterization, that is the volumetric composition of the biogas in terms of CH_4, CO_2, O_2 and "balance" (the fraction made up of gases that are different from the first three) was obtained by flushing 500 mL of biogas through a biogas analyzer (Biogas Check, Geotechnical Instruments Ltd). The residual volume of the biogas after characterization was measured by replacing volumes of water with the residual gas and referring the obtained value to the normal conditions (273.15 K and 101.325 kPa).

2.4. Analytical methods

All the analytical parameters monitored in the lysis tests (TS, VS, pH, electric conductivity (EC), soluble COD (sCOD) and ammonium NH_4^+) were determined using Standard Methods (APHA, AWWA, WEF, 2012). Soluble COD is the fraction of COD separated after a centrifugation at 4000 rpm for 15 minutes and a subsequent filtration on a 0.45 um nylon membrane, as recommended by Roeleveld and van Loosdrecht (2002).

Specific COD value (as g O_2/g VS) was evaluated using the elemental composition of the sludge as in Van Lier et al. (2008). The elemental composition of WAS and digestate samples was determined using a Flash 2000 ThermoFisher Scientific CHNS analyzer.

3. Results and Discussion

3.1. Characterization of WAS and digestate samples

The complete physical and chemical characterization of the three substrates is shown in Table 1. As anticipated in Section 2, the thickening process, carried out with a cloth filter, produced a final TS content in the order of 4.00-5.00% in all samples. Some parameters (pH value, sCOD and ammonia concentration) were of the same order of magnitude in the three samples.

The both samples of digestate had a VS content lower than that of the WAS sample. This was because the AD process consumes biodegradable substance. Between the two samples of digestate, the substrate coming from the 300-L digester had the lowest VS/TS content, in agreement with the higher HRT (15 days vs. 7 days).

Moreover, both digestates had an EC value that was approximately three times the EC of the WAS sample (3.5 and 2.9 mS/cm vs. 1.1 mS/cm), this was probably a consequence of the release of intracellular ions due to rupture of the cell membranes during an AD process. Specific COD values for the WAS and 7-day digestate samples were quite similar. The elemental composition of the 15-day digestate was assumed equal to that of the 7-day digestate.

3.2 Results of lysis tests

The efficacy of the treatments of lysis was assessed by using the disintegration rate (DR) parameter.

$$DR = \frac{sCOD_l - sCOD_0}{tCOD_0 - sCOD_0} \cdot 100\% \qquad (1)$$

This parameter has been largely employed to evaluate the efficacy of lysis processes (Dohányos et al., 1997). It relates the soluble COD released by the lysis treatment to the particulate fraction (tCOD-sCOD) of the sludge COD, that is the fraction that can be potentially hydrolyzed during the treatment. In Equation 1 $sCOD_l$ is the soluble COD after the lysis process, $sCOD_0$ is the soluble COD of the untreated sludge and $tCOD_0$ is the total COD of the sludge.

Figure 2 shows the DR values for all the lysis treatments carried out on both the WAS and 7-day digestate samples. The results were grouped by type of treatment: only thermal, with $Ca(OH)_2$ at the doses of 4 and 8 g alkali/ 100 g TS and with NaOH at the same doses. Each group of bars reported the comparison between the WAS sample (light bars) and the 7-day digestate (dark bars) at the three operating temperature values (20, 70 and 90°C). As shown in Figure 2, the DR parameter varied from a few percent to up to 40%.

The only-thermal treatment, at the temperature of 70 °C, showed a better efficiency on digestate than on WAS. An opposite behavior was observed for the working temperature of 90°C. In fact, the increase of temperature from 70 °C to 90 °C doubled the efficiency in hydrolyzing particulate COD for the WAS sample, the DR of which increased from approximately 12% to 22%. Conversely, for the same increase in temperature, the increase of hydrolyzed COD in the digestate was only in the order of 45%, because the DR rose from 15% to 21%. The chemical treatment carried out at 20 °C was, on average, more efficient on WAS than on digestate. The trend, in most cases, reversed if the combined effect of the alkali agent and temperature was considered. The thermo-chemical treatment carried out at 70 °C was, on average, more efficient on digestate than on WAS.

DR values obtained from the hybrid lysis processes carried out on the 15-d digestate were of 9.1% and 15%, for the temperature of 70°C and 90°C respectively. These DRs were sensibly lower than the values registered for the WAS and 7-d digestate samples treated with the same operating conditions.

In the scientific literature, there are several studies that report the efficacy of thermal low-temperature or hybrid thermo-chemical pre-treatments on WAS (Carrère et al., 2016; Zhen et al., 2017) or other substrates (Passos et al., 2017), but very few examples of treatments carried out on intermediate sludge (i.e. sludge after a partial digestion process) or digestate. Among these, Li and coauthors (2013) found a value of sCOD in the order of 2,000 mg/L, after the treatment with a 0.1 M NaOH solution of a substrate produced by the digestion of 80% primary sludge and 20% of biofilm sludge. The concentration of TS in the digested sludge was in the order of 20 g/l, so the employed alkali dose should have been of 20 g NaOH/100 g TS. The value of sCOD found by Li and coauthors (2013) must be referred to an estimated tCOD equal to 20-22,000 mg/l, consistent with a TS content of 2%, to obtain a final DR of 10%. This result was in line with the outcome of the tests carried out at ambient temperature in the present study.

The increase in pH value in samples that underwent a lysis treatment was an inevitable result of the alkali addition. As shown in Figure 3, the final pH value depended on the type and dose of chemical used for the test and, for a lesser extent, on the type of substrate (WAS or digestate). The highest pH values, in the order of 10-11 pH units, were found for samples treated with NaOH at the dose of 8 g NaOH/100 g TS at 20

°C. Such a dose, in the order of 0.1 M, should produce a final pH value of approximately 13 pH units. In fact, for each liter of treated sludge, there was approximately 45-48 g of TS and a dose of NaOH of 3.6 – 3.8 g was employed for tests (i.e. approximately 0.1 moles, NaOH MW = 39.997 g/mol). However, the liberation of sCOD, rich in organic acids, aided in buffering the increase of pH. The final pH value resulted from a balance between the addition of alkali agent and the buffering capacity of the substrate. The buffer phenomenon occurred in all series of treatments and was slightly more evident for the samples of WAS. In fact, for those samples, the release of soluble COD was on average higher than for the digestate.

Treatment with alkali (or the combination alkali-low temperature), in addition to causing an evident basification, also determined an increase in the electrical conductivity (EC) for most part of the samples. Figure 4 shows the ratio between the EC after the lysis treatment and the EC of the untreated samples, of 1.09 mS/cm for the WAS and 3.53 mS/cm for the digestate, respectively, as shown in Table 1. Lysis pre-treatments carried out on WAS determined an increase in the EC for all treatment conditions. Values of EC increased up to 3-5 times when the samples of WAS were treated with doses of NaOH.

The hybrid treatment with NaOH on digestate produced increases in the EC values of quite limited extent (1.2-1.7 times the reference value). Conversely, intermediate treatments on digestate produced a reduction in the EC value when the treatment was carried out with only heat or by combining heat and $Ca(OH)_2$. In fact, EC reduced from 3.53 mS/cm (for the untreated sample) to 2.85 mS/cm (-20%, for the sample treated at 20°C with 4% of $Ca(OH)_2$) to 1.74 mS/cm (-50%, for the sample treated at 20°C with 8% of $Ca(OH)_2$). The EC decrease was much more pronounced for the lowest temperature values. Decrease in EC may be due to the generation of calcium salts, with very low solubility, and subsequent precipitation.

3.3 Anaerobic digestion tests

AD tests carried out in this and in a previous work (Ruffino et al., 2016) showed a substantial variability in the specific production of biogas and methane of the raw WAS sample (i.e. not subjected to any treatment) from one series of tests to another. The specific biogas production amounted to values in the order of 0.257±0.020 $Nm^3/kg\ VS_{added}$ (average on five different raw WAS samples), while the specific production of methane was 0.166±0.015 $Nm^3/kg\ VS_{added}$, with methane volumetric percentages that ranged between 61 and 67%. In order to compare the results obtained in the different series of tests, all the specific methane production (SMP) curves have been scaled on a reference untreated WAS sample characterized by a specific production of methane equal to the average value (0.166 $Nm^3/kg\ VS_{added}$) found over all series.

Curves of Figure 5 show the evolution of SMP for WAS samples treated under different conditions (only-thermal or a combination of thermal and alkali treatments). Digestibility tests lasted 21 days. After that time the tests were considered completed since the daily marginal production of biogas or methane was less than 1% of the overall production (VDI Standard 2006). The only-thermal treatment carried out on the WAS sample determined an increase in SMP of 14% for the temperature of 70°C and of approximately 20% for the temperature of 90°C. These observations were in line with the results of a previous study (Ruffino et al., 2015) carried out on WAS samples collected from the same WWTP and subjected to thermal pre-treatments. In that case, SMP increases of 21% and 31% were recorded after thermal pre-treatments processes carried out for 3 hours at 70 and 90 °C respectively. The tests described in that study differed from those reported in the present study not only for the duration of the pre-treatment (180 minutes vs. 90 minutes) but also for the ratio between substrate and inoculum. In the old tests this ratio was in fact in the order of 2.5.

A comparison between only-thermal and hybrid pre-treatments carried out at the same temperature value demonstrated that hybrid pre-treatments were more effective in biogas/methane production. Hybrid pre-treatments produced an SMP increase of 40% and 66% for the sample treated at 70 °C and 90°C respectively. The SMP increase was calculated with reference to the untreated sample.

Figure 6 compares the curves of SMP obtained for WAS and the two samples of digestate treated under the same operating conditions (thermo-alkali with 4% NaOH at temperature values of 70°C and 90°C). Untreated digestate with a HRT of 7 days produced approximately 16% less methane than the sample of untreated WAS (0.143±0.003 $Nm^3\ CH_4/kg\ VS_{added}$ vs. 0.166±0.015 $Nm^3\ CH_4/kg\ VS_{added}$). When the 7-day digestate was subjected to a hybrid process, its SPM increased by 31% and 54% at 70°C and 90°C respectively. The 7-day digestate treated at 70°C with 4% NaOH generated 0.185±0.003 $Nm^3\ CH_4/kg\ VS_{added}$.

Conversely, SMP rose to 0.223±0.002 Nm^3 CH_4/kg VS_{added} when the hybrid treatment was carried out at 90°C. These percentage increases were of the same order of magnitude of those found by Boni and coauthors (2016). They tested ultrasonication in order to make the organic matter contained in lignocellulosic AD residues usable for new AD processes and they obtained a maximum gain in biogas production in the order of 30%. It has to be pointed out that the digestate employed for the tests in Boni et al. (2016) had a residual SMP in the order of 0.150 Nm^3 CH_4/kg VS_{added}, similar to the 7-day digestate used in this work. Conversely, Sambusiti and coauthors (2015) did not observe a beneficial effect of thermal and alkaline post-treatments in enhancing methane potentials of digestates from agricultural residues.

SMP of the 15-day digestate was approximately 250% less than that of the untreated WAS (0.047±0.001 Nm^3 CH_4/kg VS_{added} vs. 0.166±0.015 Nm^3 CH_4/kg VS_{added}). Hybrid treatments at 70 and 90°C could increase SMP by respectively 131 and 184% compared to the untreated digestate sample. However, that increase was not sufficient to equal the specific production of the untreated WAS. SMPs of the 15-day digestate were in fact of 0.109±0.005 Nm^3 CH_4/kg VS_{added} and 0.134±0.004 Nm^3 CH_4/kg VS_{added}, when intermediate treatments were carried out at 70 and 90°C, respectively.

These results demonstrated that a significant amount of organic matter could not be converted to methane and carbon dioxide in a 15-day mesophilic AD process. TS and VS content of the sample used for the tests was respectively in the order of 2.58% and 1.62% (VS/TS = 0.626). TSs and VSs of the substrate fed to the digester 15 days before (i.e. untreated WAS) were 3.33% and 2.27% respectively (VS/TS = 0.681). That means that the VS reduction observed in the 300-L digester was in the order of only 30%. This was in line with the results reported in some studies that demonstrated that a 15-day AD process carried out in mesophilic conditions could degrade no more than 30-40% of the overall organic substrate (Nielsen et al., 2011; Takashima and Tanaka, 2014).

Figure 7 shows the possible result of the combination of an AD process carried out on an untreated WAS sample and the subsequent application of intermediate treatments to 7-day and 15-day digestates. A 7-day AD process carried out on an untreated WAS sample could extract approximately 65% of the ultimate methane content. If the AD process lasted 15 days, the amount of methane extracted rose to 95% (see Figures 5 and 6).

Curves 1 (in diagrams a and b of Figure 7) represent the time evolution of SMP of the WAS samples that underwent a hybrid process carried out at 70 or 90°C. Curves 2 combine the SMP due to a 7-day AD process carried out on an untreated WAS sample with the SMP due to an intermediate treatment carried out on a 7-day digestate. Finally, curves 3 combine the result of a 15-day AD process carried out on an untreated WAS sample with the results of an intermediate treatment of a 15-day digestate.

Figure 7a demonstrates that the combination of AD plus hybrid intermediate treatment at 70°C made possible to produce the same amount of methane (i.e. 0.233 Nm^3 CH_4/kg VS_{added}), obtained with the hybrid pre-treatment carried out on WAS, in a shorter time. In fact, the final SMP recorded after a 20-day one-stage AD process was obtained already after 12 days from the beginning of the tests. When pre- or intermediate treatments were carried out at 90°C (see Figure 7b), a (7+8)-day process that includes a first-stage AD, an intermediate treatment and a second-stage AD was necessary to equal the production obtained from a WAS sample subjected to pre-treatment and subsequently digested for 20 days.

The outcomes of the experimentation demonstrated that, for both temperature values (70 and 90°C), a process that combines an intermediate treatment of a 7-day digestate with a two-stage digestion with an overall length of 20 days (7+13), could produce more methane than the sequence of pre-treatment and AD with the same duration. Specifically, the intermediate treatment carried out at 70°C produced 0.286 Nm^3 CH_4/kg VS_{added} vs. 0.232 Nm^3 CH_4/kg VS_{added} generated using the pre-treatment (+23%). Conversely, the intermediate treatment carried out at 90°C produced 0.317 Nm^3 CH_4/kg VS_{added} vs. 0.274 Nm^3 CH_4/kg VS_{added} (+16%).

As shown in Figure 7, in no cases (70 or 90°C) the combination of AD of untreated WAS, intermediate treatment of a 15-day digestate and subsequent second-stage digestion made possible to obtain a SMP higher than those obtained with pre-treatments. In fact, the SMP of the combined system could equal that of the pretreated sludge only if the combined process had a whole length of 30 days or more.

4. Technical assessment

The technical and economic assessment carried out in this Section was referred to the full scale SMAT WWTP located in Castiglione Torinese. The treatment scheme for pre- and intermediate treatments is shown in Figure 8.

It is well known that a mesophilic AD process is self-sustainable if the heat generated by the process is sufficient to heat the sludge from the ambient (approx. 15°C) to the process (38°C) temperature and keep the temperature constant into the digester. In fact, one part of the heat provided must offset the heat losses, through the digester walls, due to the exchange with the exterior environment. The heat losses can be evaluated by considering the geometry of the digester, the materials employed for its construction and the temperature of soil (15°C) and exterior environment (as monthly averages, as reported in UNI 10349 rule, Ruffino et al., 2014). This assessment considered the heat losses with the outside in the worst case (i.e. winter condition). For one digester, they amounted at 158.5 MJ/h.

The sludge flow rate was of 58.8 m^3/h, for both primary and secondary sludge, under normal operating conditions of the WWTP. It was also assumed that the average VS/TS ratio was 0.7 for both kinds of sludge.

All the thermal balances performed to assess the technical sustainability of pre- and intermediate treatments considered:

- a thermal efficiency of the combined heat and power (CHP) unit of 0.42;
- an electrical efficiency of the CHP unit of 0.42;
- an efficiency in the thermal exchange processes of 1;

In the case of pre-treatments, heat must obviously be provided also for thermal (or hybrid) hydrolysis. If the sludge is thermal treated, its extra heat can be conveniently used to heat primary sludge (see Figure 8). In the case of pre-treatments, secondary sludge heated at 70 or 90°C, after hybrid treatment, was mixed with primary sludge (at ambient temperature). Both types of sludge were then digested with a HRT of 20 days.

A complete thermal balance for the pre-treatment scenario must include:

$Q_{HYD\_P} + Q_{LOSS} + Q_{PRIM} = Q_{AD} + Q_{HYD\_SLUD}$

- Q_{HYD_P}, is the thermal power necessary to heat the secondary sludge from the ambient to the pre-treatment temperature (70 or 90°C) and maintain the process for the fixed contact time (1.5 hours);
- Q_{LOSS}, are the heat losses (integrated over time) with the exterior environment during the AD process;
- Q_{PRIM}, is the thermal power necessary to heat the primary sludge from the ambient to the digester (mesophilic) temperature;
- Q_{AD}, is the thermal power generated in the AD process;
- Q_{HYD_SLUD}, is the thermal power available, after secondary sludge hydrolysis, to heat the primary sludge before digestion.

If the TS content of the primary sludge was fixed to 3.5%, positive terms of the thermal balance equaled the negative terms when the TS content of the secondary sludge was of 3.7%, at 70°C, and 4.9%, at 90°C, respectively.

In the case of intermediate treatments, as shown in Figure 8, the secondary sludge fed the first-stage digester (HRT = 7 days) after a pre-thickening process. This process increased the sludge TS content up to 2.75%. Consequently, the mass flow rate of dry solid was 1617.5 kg/h. The secondary sludge was then digested for 7 days and subsequently treated at 70 or 90°C with alkali (NaOH 4%). Heated sludge was mixed with the cold primary sludge and them both were finally digested with a HRT of 13 days.

A complete thermal balance for the intermediate treatment scenario must include:

$Q_{WARM} + Q_{LOSS1} + Q_{HYD\_I} + Q_{PRIM} + Q_{LOSS2} = Q_{AD1} + Q_{AD2} + Q_{HYD\_SLUD}$

- Q_{WARM}, is the thermal power necessary to heat the secondary sludge from the ambient to the digester (mesophilic) temperature in the first-stage AD;
- Q_{LOSSi}, are the heat losses (integrated over time) with the exterior environment in the first- and second-stage digesters;

- Q_{HYD_I}, is the thermal power necessary to warm the digestate, from secondary sludge, from mesophilic to the intermediate treatment temperature (70 or 90°C) and maintain the process for the fixed contact time (1.5 hours);
- Q_{PRIM}, is the thermal power necessary to warm the primary sludge from the ambient to the digester (mesophilic) temperature;
- Q_{ADi}, is the thermal power generated in the first- and second-stage AD process;
- Q_{HYD_SLUD}, is the thermal power available, after the intermediate hydrolysis of the digestate from the secondary sludge, to warm the primary sludge before digestion.

Figure 9a shows the thermal power (kW) required and available, as a function of the TS content of the secondary sludge, for the scenario that considers intermediate treatments at 70 and 90°C. The positive terms of the thermal balance equaled the negative terms when the TS content of secondary sludge was respectively of 3.25%, at 70°C, and 4.25%, at 90°C. As in the previous case, it was assumed that the TS content of the primary sludge before digestion was in the order of 3.5%. It was also assumed that the TS of the secondary sludge was not altered by the first-stage AD process.

If a focus is made only on the stage of mixing between primary and secondary (after first-stage digestion and IHP) sludge, it can be demonstrated that not in all cases the heat carried by the secondary sludge after IHP was sufficient to warm the primary sludge to the temperature value required for the second-stage AD process. In detail, when the digestate from the first-stage AD was treated at 90°C (see Figure 9b), the heat supplied by this flux was sufficient to warm the primary sludge for any digestate TS content (up to 6.5%). Conversely, when the first-stage digestate was treated at 70°C, only TS values of less than 4.25% may guarantee the thermal self-sustainability of the mixing stage.

5. Economic analysis

Tests carried out in this and in a previous work (Ruffino et al., 2016) demonstrated that, for low temperature values (<100°C) and low dosage of alkali (4%), a combination of thermal and alkali pre-treatments was more effective than a single treatment. However, alkali used for the treatment has a cost of 0.3 €/kg (Solvay, 2016). The increase in methane, and the consequent increase in the produced heat and electricity, must balance the reagent cost. As shown in Section 3.1, the treatment with alkali increased the pH to values in the order of 8.5 – 8.8, depending on the process temperature. In a previous experience, it was demonstrated that pH values not too far from neutrality (i.e. in the order of 8.5) did not adversely affect the performance of the AD process (Ruffino et al., 2016). In fact, the inoculum could buffer the increase in pH due to the alkali effect. Then, acidic agents were considered not to be necessary in the implementation of hybrid pre-treatments.

For the economic analysis, it was assumed that all the heat produced by the digesters was used to sustain the whole system (combination of hydrolysis and digestion), according to the working conditions fixed in Section 2.1. In this way, the employment of an auxiliary fuel can be completely avoided. The plant's managers can sell the net produced electricity at the price of 0.217 €/kWh, that includes the public subsidy (0.077 €/kWh). Therefore, the economic value of the methane used to produce electricity was equal to 0.885 €/Nm^3 CH_4.

The economic revenues of the plant in the absence of pre- or intermediate processes for the treatment of secondary sludge was in the order of 530 €/h (Ruffino et al., 2014). The introduction of thermal or hybrid pre-treatments in the full scale WWTP could increase the revenues from electricity sale between 13% and 25%. Conversely, intermediate treatments on a 7-day digestate could provide a gain of 26% or 32%, depending on the process temperature (70 or 90°C, see Table 2). Only the scenario that considered the use of alkali at ambient temperature (20°C) determined a worsening in the economic performance of the plant. In this case, the value of the electricity produced from AD was not sufficient to compensate for the costs of alkali and acid reagents. In fact, under this scenario, the pH resulting after the hybrid hydrolysis was too high (9.9) and it had to be corrected with the addition of an acid before digestion.

Conclusions

This paper wanted to demonstrate the superiority of intermediate lysis treatments compared to traditional pre-treatments carried out under the same operating conditions. Intermediate treatments could make the residual organic substance of a partially digested sludge usable for a second-stage AD process. To the best of our knowledge, until now only very few studies have focused on the comparison of the performances of these two operating schemes. This work can get some clues for a more effective treatment of sewage sludge in a full scale WWTP.

The analysis was carried out at three levels. Values of DR, specific productions of biogas and methane, and final revenues from the electricity sale were determined by performing tests on WAS and digestates, with HRTs of 7 and 15 days respectively, and by using the tests' outcomes for a full-scale cost-benefit assessment.

It was demonstrated that:

(1) when results were reported in terms of DR values, thermal and hybrid lysis treatments were on average more effective on a digestate than on a WAS. This outcome was particularly evident when mild treatments (i.e. carried out at 70°C or in the presence of $Ca(OH)_2$) were applied;

(2) intermediate treatments were effective in making the residual organic substance of a 7-day digestate usable for a second-stage AD process. In fact, under this scenario, the methane generated in a two-stage AD process, with an in-between intermediate treatment, was 23% and 16% higher than in the scenario that considers traditional pre-treatments, with 4% NaOH, at 70 and 90°C respectively. Conversely, in no cases (70 or 90°C) the combination of a 15-day AD process of untreated WAS followed by an intermediate treatment and a second-stage AD, made possible to obtain SMPs higher than those obtained with pre-treatments.

(3) the introduction of thermal or hybrid pre-treatments in a full scale WWTP (2,000,000 p.e.) could increase the revenues from the electricity sale between 13% and 25%, in comparison with the present scenario. Conversely, intermediate treatments on a 7-day digestate could provide a gain of 26% or 32%, depending on the process temperature (70 or 90°C).

Acknowledgments

This paper is dedicated to the memory of prof. Giuseppe Genon.

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List of Figure legends

Figure 1. Apparatus for anaerobic digestion tests

Figure 2. DR values after lysis processes

Figure 3. pH values after lysis processes

Figure 4. EC/EC_0 values after lysis processes

Figure 5. Time evolution of SMP for WAS samples pre-treated under different operating conditions

Figure 6. Time evolution of SMP obtained for WAS and the two samples of digestate (7-day and 15-day) treated under the same operating conditions

Figure 7. Curves 1. Time evolution of SMP of WAS after a hybrid process carried out at 70°C (a) or 90°C (b). Curves 2. Combination of the cumulative SMP due to a 7-day AD process on untreated WAS with the SMP due to an intermediate treatment on a 7-day digestate (a, 70°C; b, 90°C). Curves 3. Combination of the SMP due to a 15-day AD process on untreated WAS with the SMP due to an intermediate treatment on a 15-day digestate (a, 70°C; b, 90°C).

Figure 8. Treatment scheme for pre- and intermediate treatments

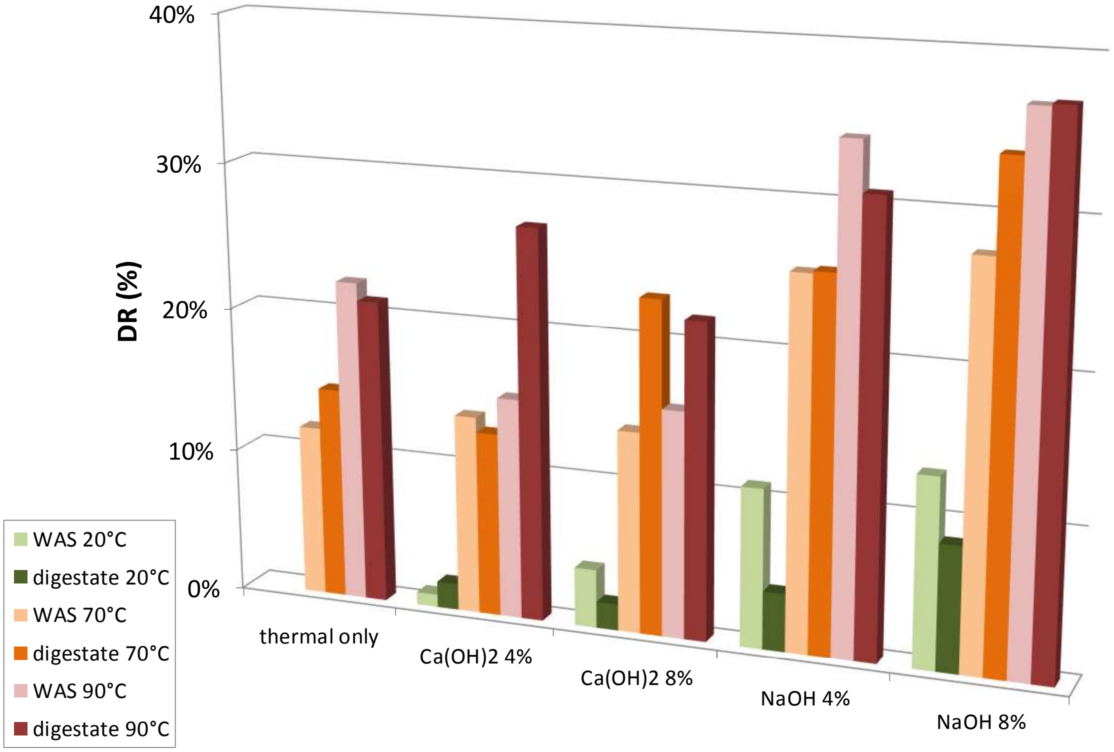
Figure 9. Thermal power (kW) required and available for IHPs (a) and thermal balance for the mixing of primary and secondary sludge (b) as a function of the TS content of the secondary sludge

List of Table legends

Table 1. Characteristics of the three substrates used for the experimentation

Table 2. Summary of the results obtained from digestibility tests and economic analysis

Figure 1. Apparatus for anaerobic digestion tests



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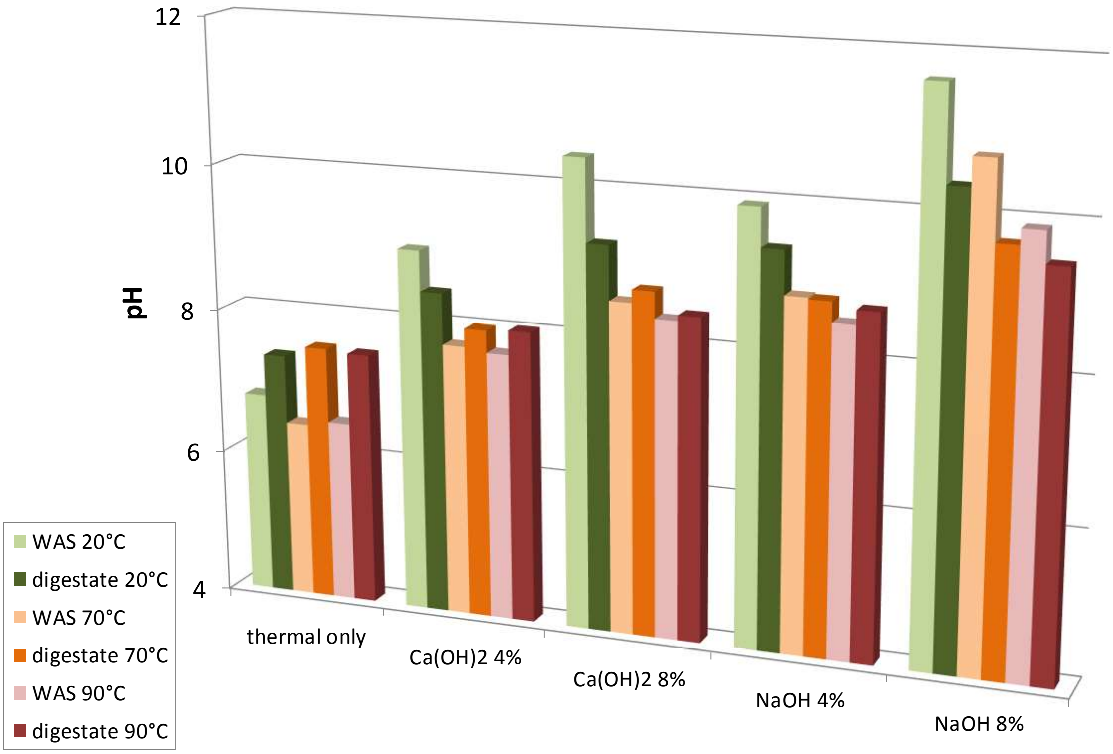
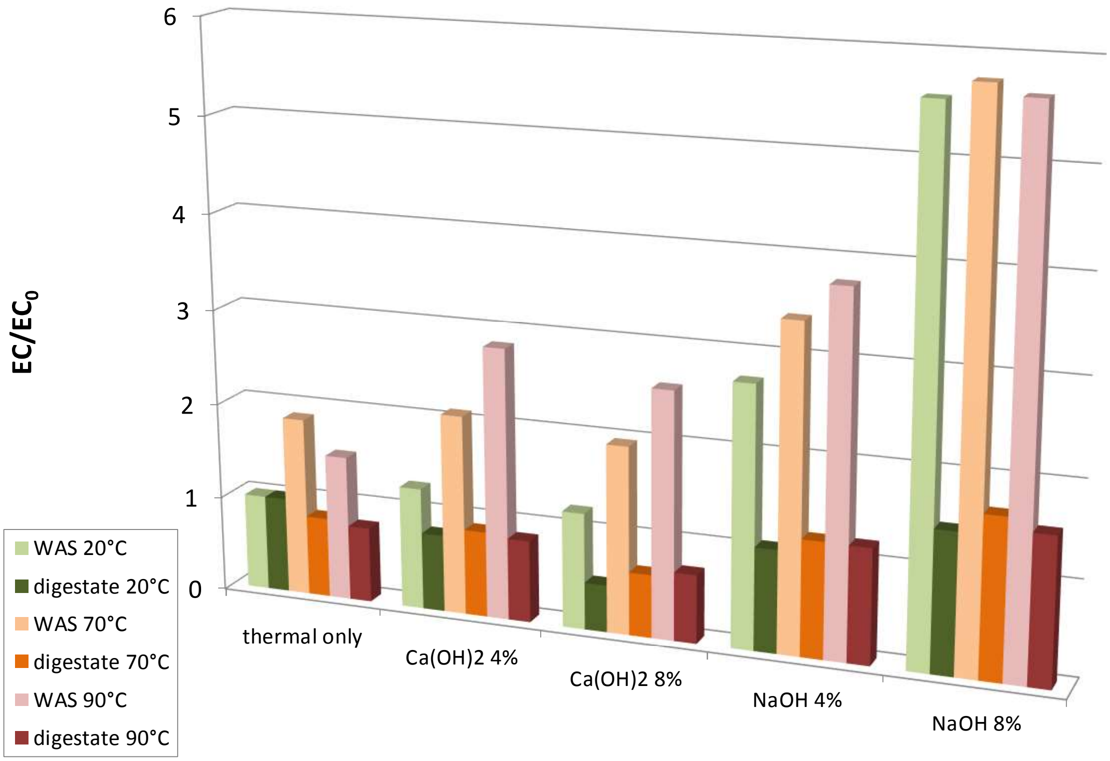


Figure 3. pH values after lysis processes



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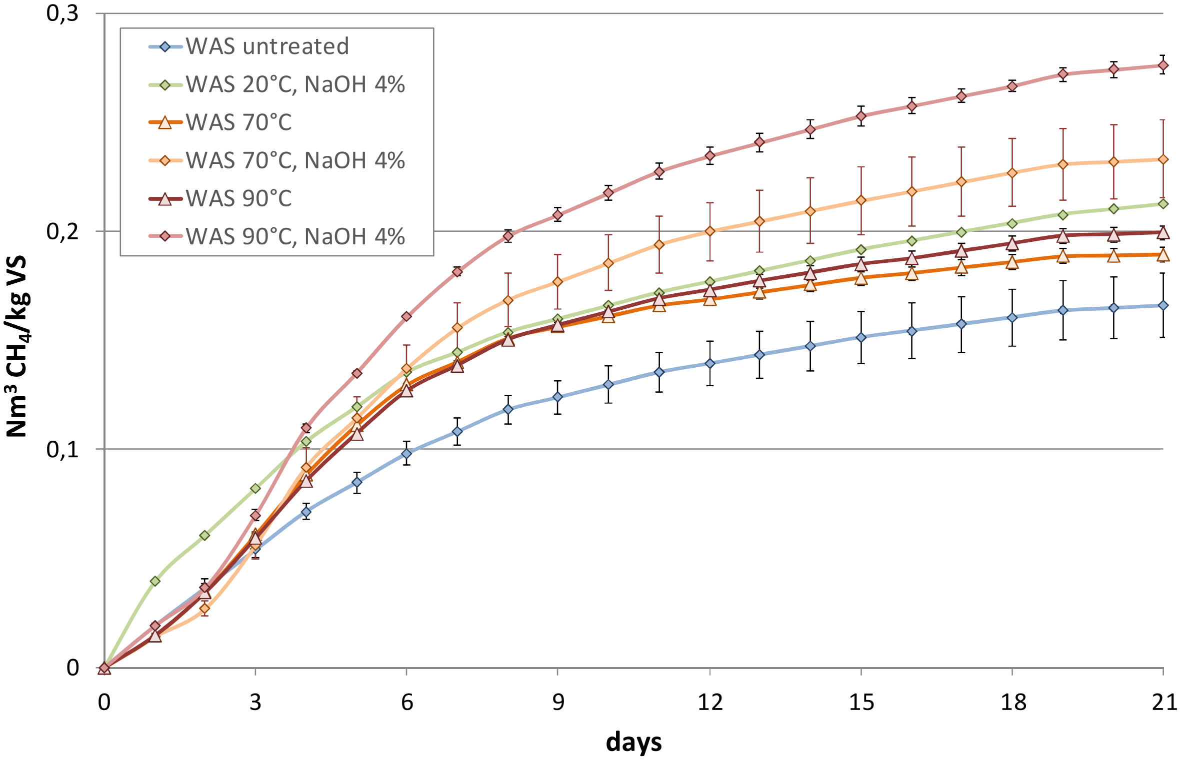

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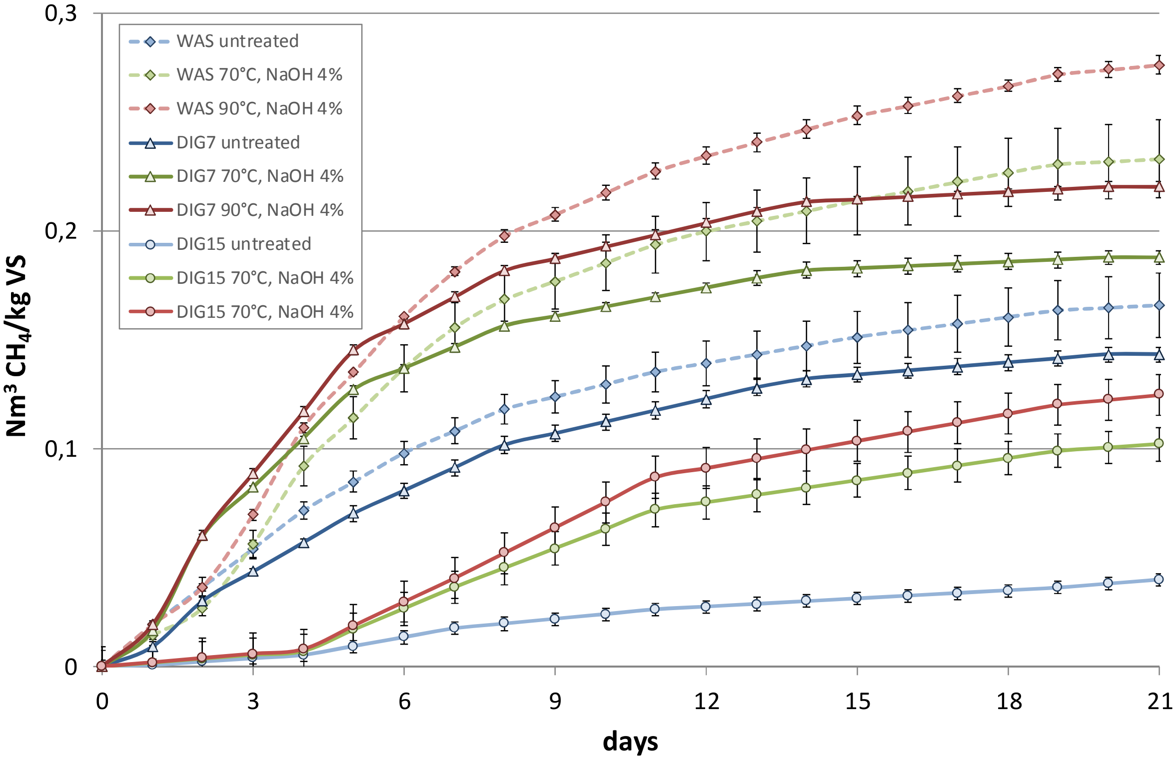

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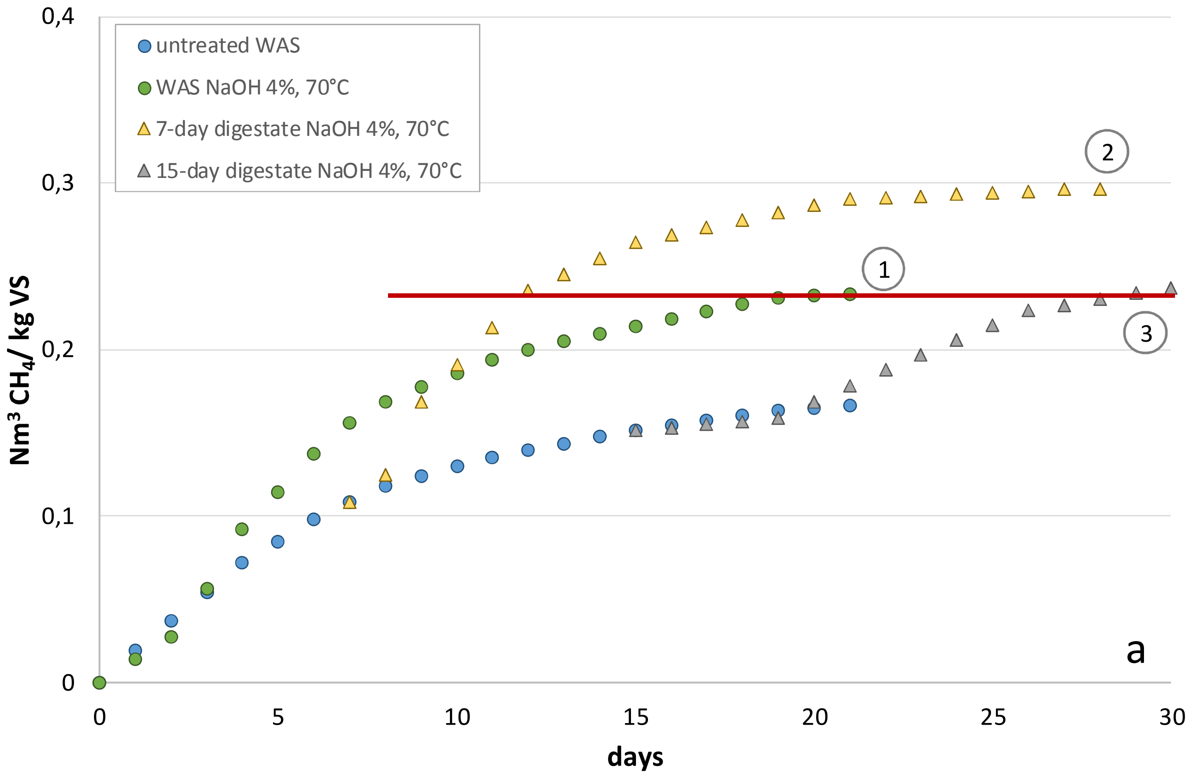

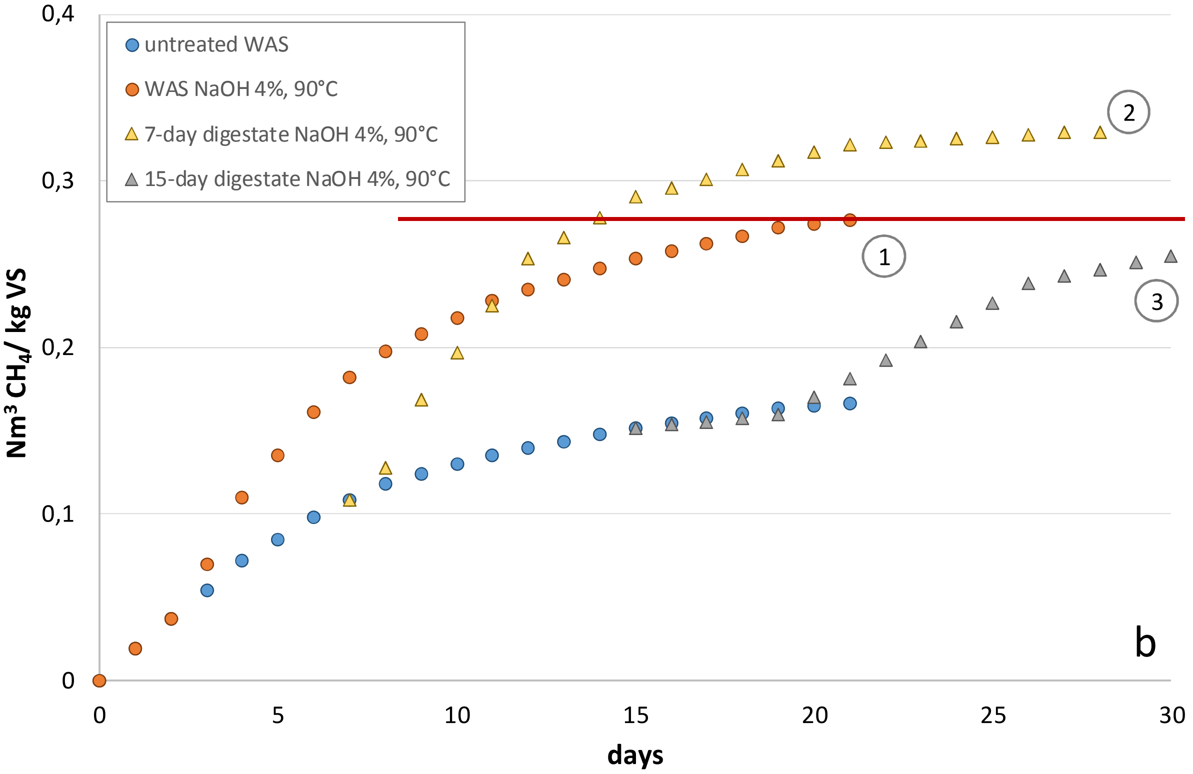

Figure 7. Curves 1. Time evolution of specific methane production of WAS after a hybrid process carried out at 70°C (a) or 90°C (b). Curves 2. Combination of the cumulative SMP due to a 7-day AD process on untreated WAS with the SMP due to an intermediate treatment on a 7-day digestate (a, 70°C; b, 90°C).

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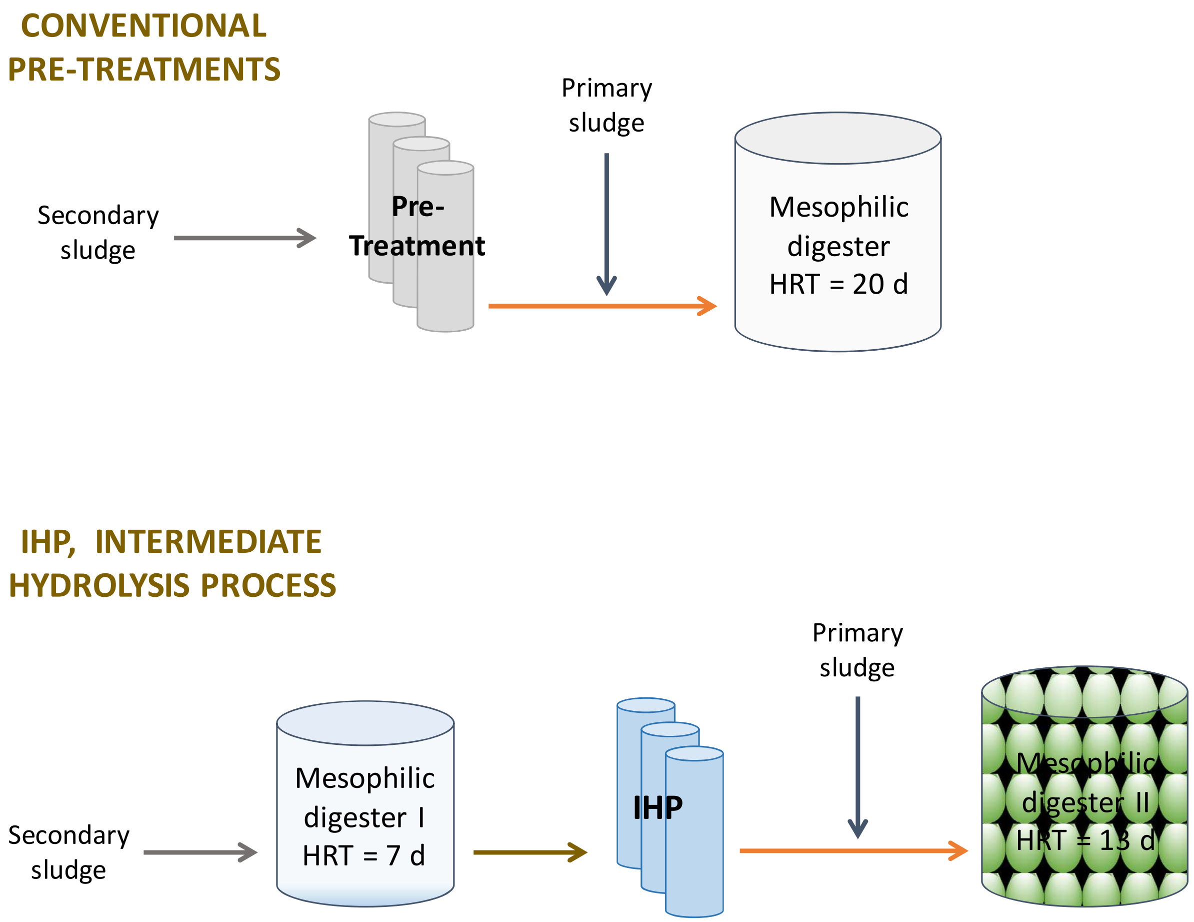

CONVENTIONAL PRE-TREATMENTS

IHP, INTERMEDIATE HYDROLYSIS PROCESS

Figure 8. Treatment scheme for pre- and intermediate treatments

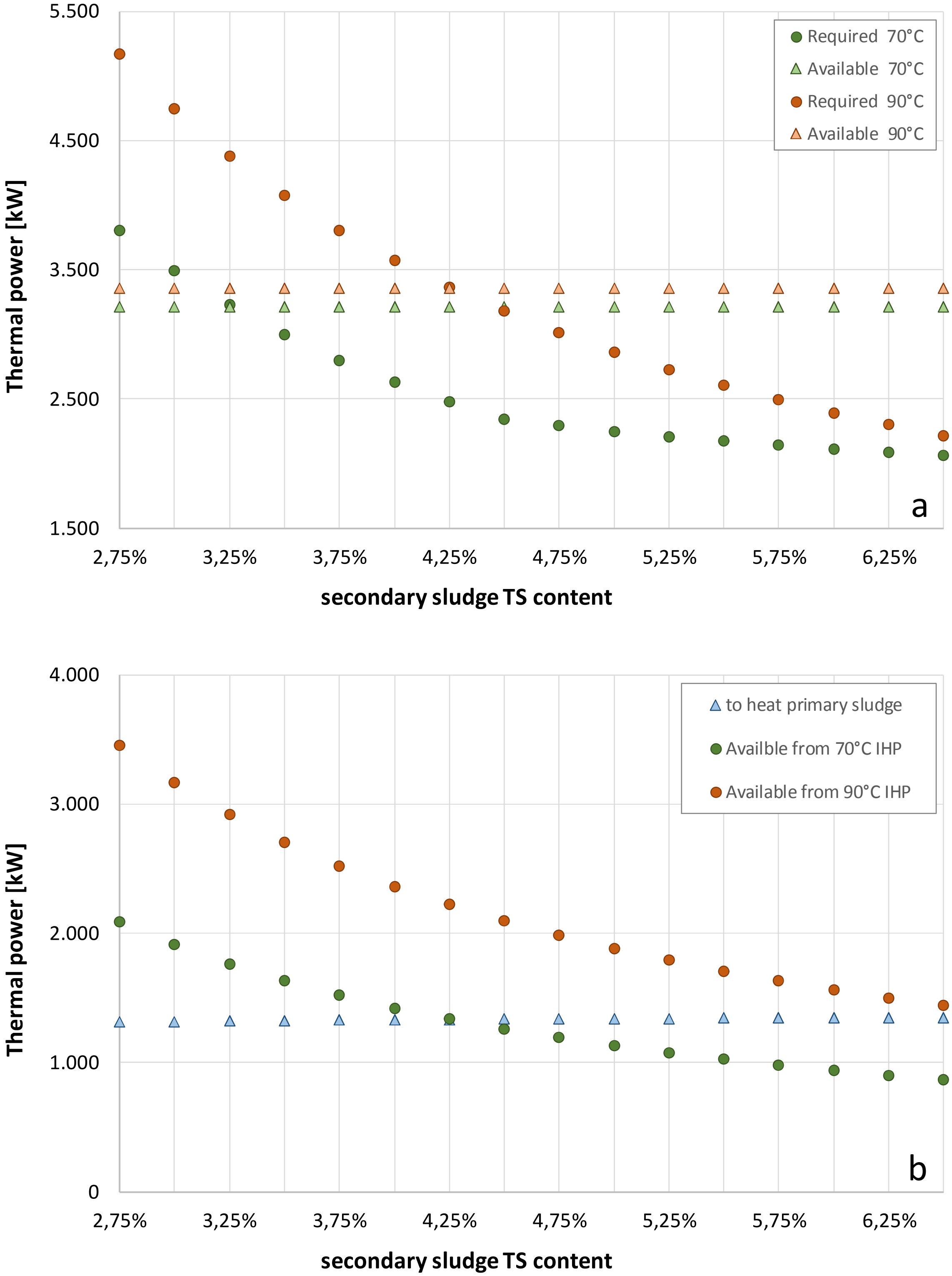

Figure 9. Thermal power (kW) required and available for IHPs (a) and thermal balance for the mixing of primary and secondary sludge (b) as a function of the TS content of the secondary sludge

	TS (%)	VS/TS (%)	pH	EC (mS/cm)	C (%)	H (%)	N (%)	S (%)	O (%)	gO_2/gVS	tCOD (mg/l)	sCOD (mg/l)	NH_4^+ (mg/l)
WAS	4.88	0.70	6.78	1.09	49.2	6.65	7.77	0.82	35.6	1.347	46,000	210	128
7-day Digestate	4.58	0.67	7.36	3.53	49.6	6.77	7.64	0.77	35.3	1.372	42,100	125	299
15-day Digestate	4.30	0.63	7.56	2.88	NA	NA	NA	NA	NA	NA	37,200	525	35

NA: not available

Table 1. Characteristics of the three substrates used for the experimentation

Treatment	Final pH value	CH_4 specific production ($Nm^3/kg\ VS_{added}$)	Increase in CH_4 specific production (%)	Increase in the revenue (%)
Untreated WAS	6.78	0.166	-	-
20°C, NaOH 4% (*)	9.93	0.212	+ 28.0	-5.3
70°C	6.42	0.189	+ 14.2	+13.2
70°C, NaOH 4%	8.81	0.233	+ 40.5	+17.2
90°C	6.49	0.199	+ 20.1	+16.0
90°C, NaOH 4%	8.51	0.276	+ 66.6	+24.5
7-day digestate, 70°C, NaOH 4%	8.79	0.287	+ 72.7	+26.4
7-day digestate, 90°C, NaOH 4%	8.70	0.317	+ 91.3	+32.3

(*) addition of HCl at a dose of 1.5 g HCl/ 100 g TS required to decrease the pH value up to 8.5

Table 2. Summary of the results obtained from digestibility tests and economic analysis