Enhancement of Waste Activated Sludge (WAS) anaerobic digestion by means of pre-treatments and intermediate treatments

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Keywords: Waste Activated Sludge (WAS), Extracellular Polymeric Substance (EPS), Lysis, Disintegraton Rate (DR).

Abstract
The consolidated fate of the excess of waste activated sludge (WAS) generated in conventional biological wastewater treatment processes is anaerobic digestion (AD). Several studies have demonstrated the efficiency of different typologies of pre-treatments in liberating the intra-cellular organic substances and make them more available for AD. However, the production of new extracellular polymeric substances (EPS) that occur during an AD process due to microbial metabolism, self-protective reaction and cell lysis partially neutralizes the benefit generated by 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 the performances of low-temperature thermal and hybrid (thermal+alkali) treatments carried out on raw WAS samples and digestate after a 10-day digestion process. For both pre-treatments and intermediate treatments operating conditions were 90 minutes, 70°C and 90°C, in the presence of low doses (4-8% of the TS matrix) of NaOH and $Ca(OH)_2$.
In both cases NaOH showed a better efficiency in liberating intracellular organic matter and break EPS bridges than $Ca(OH)_2$. Digestibility tests carried out in mesophilic conditions and batch mode revealed that the specific production of methane increased of approximately 40%, when raw WAS was treated at 70°C in combination with a dose of 4 g NaOH/100 g TS, and of more than 66% when the hybrid treatment was carried out at 90°C with the same dose of alkali. Intermediate treatments performed in the same modality on the pre-digested sample showed increases in the methane specific production of respectively 31% (70°C) and 54% (90°C). A mass balance performed using the results obtained in the digestibility tests reveled that if the digestion process of WAS was carried out in two steps (first stage on untreated WAS and second stage on intermediate treated digestate) with a duration of 10 days each, the amount of produced methane could increase of respectively 17% and 27% (90°C and 70°C) compared with the scenario that pre-treats raw sludge.

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 in 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 in WAS, most organic matters are found in insoluble microbial cells, which are packed by various microbial cell structures, such as cell walls, cell membranes and cell nuclei, which exhibit low bioavailability for the subsequent AD process (Traversi et al., 2015; Xiao et al., 2015). The efficacy of several pre-treatments were tested to improve the availability of WAS, through the disruption of cell walls, for the enzymatic attack which takes places in AD processes. In previous works (Ruffino et al., 2015, in press) we focused on traditional pre-treatments (mechanical, thermal at low temperatures, chemical in the presence of an alkali agent or combination of thermal and chemical pre-treatments) to improve the anaerobic digestion (AD) of waste activated sludge (WAS). However, also the extracellular polymeric substances (EPS) contained in WAS is believed to be a factor for poor AD of sewage sludge and its subsequent dewatering (Shana 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 of EPS is part of the biochemical composition of the activated sludge fed to the digester, the other type of EPS 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 feed but cannot prevent its production during the 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 lysis processes (Li et al., 2013; Williams et al., 2015).

Intermediate hydrolysis processes (IHPs) consist of conventional mesophilic AD followed by an 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 with pre-treatments. Only few cases study are reported in the scientific literature. For example, 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 for improved anaerobic digestion 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 inter-stage and only of 2% when applied as pre-treatment.

Some 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) on 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 on 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., in press) 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 of samples of WAS and digestate that resulted from the anaerobic digestion of WAS. Pre-treatments and intermediate treatments were carried out at 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, 2,300,000 population equivalent, p.e.) thickened to a final total solid (TS) content in the order of 4-5% from an original TS content of less than 1%. Intermediate treatments were carried out on the digestate provided by the same WWTP that treats 110 m^3/h of primary and secondary sludge with an average TS content of 2.75%. Under normal operating conditions, the WWTP operates the digestion process in mesophilic conditions with an average hydraulic retention time (HRT) of 17 days (Ruffino et al., 2014). Actually at the time at which the samples of digestate were collected the HRT of digesters was in the order of only 10 days.

Materials and Methods

2.1. WAS and digestate samples

Two kinds of substrates, WAS and digestate, were collected from the WWTP of Castiglione Torinese (NW Italy, 2,300,000 p.e.) to carry out the tests. The details of the units and processes that make up the water line and the sludge line of the plant are shown in Ruffino et al., 2014 and Panepinto et al., 2016.

Because each digestibility test (see Section 3.2) lasted approximately one months, and only three samples could be tested together, several samples of WAS were taken to be involved in the experimental tests. WAS samples were collected from April to November 2015 from one of the secondary clarifiers placed after the biological treatment. 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 WAS samples were thickened on a cloth filter to reach a final TS content of approximately 4.5-5.0%.

One sample of digestate was collected at the exit of one of the six anaerobic digesters employed for the treatment of primary and secondary sludge produced in the WWTP. The digesters are fed with sludge of different quality: primary, secondary or a mixture of two. The sample of digestate used for the tests went from a digester fed with secondary sludge. Digesters, under normal operating conditions, work with an HRT of 17 days. However, in the period in which the sample of digestate was taken (January 2016), the HRT was only 10 days. Also the sample of digestate was thickened on a cloth filter to reach a final TS content of 4.6%.

2.2. Lysis tests

Tests of low-temperature thermal lysis and hybrid thermo-chemical lysis were performed on the sample of WAS collected in November 2015 and on the only sample of digestate according to the method described in detail in Ruffino et al. (in press). Tests were carried out at the three values of temperature of 20; 70 and 90 °C, using two alkali agents, NaOH and $Ca(OH)_2$. The contact time was equal to 90 minutes and the mixture was stirred energetically for 1 minute every 15 minutes. The employed doses of alkali were in the order of 4 and 8% of the TS content. These amounts were decided because a previous work, aimed at identifying the optimal alkali dosage for the treatment of WAS, demonstrated that, in the range 2-20 g alkali/100 g TS, 4-8 was the most suitable dose for an hydrolysis process (Ruffino et al., in press).

Operating conditions employed in the lysis tests for both WAS and digestate samples are summed up in Table 1.

Table 1. Operating conditions for low-temperature thermal and hybrid lysis tests

T °C	$Ca(OH)_2$ g alkali/100 g TS	NaOH g alkali/100 g TS	Contact time min
20	0 - 4 - 8	0 - 4 - 8	90
70	0 - 4 - 8	0 - 4 - 8	90
90	0 - 4 - 8	0 - 4 - 8	90

2.3. Digestibility tests

Anaerobic digestion tests were carried out using the apparatus and procedures described in previous works (Ruffino et al., 2015; in press). The apparatus is shown in Figure 1. It can be seen that due to the availability of reactors, six tests can be carried out in the same series. The tests were performed in batch mode in mesophilic conditions (35°C).

Figure 1. Apparatus for anaerobic digestion tests

In this work four series of tests were carried out, for a total duration of the experimentation phase of approximately four months. The first three series involved WAS samples, the fourth series samples of digestate, as shown in the scheme reported in Table 2.

Table 2. Pre-treatment or intermediate treatment condition for sample subjected to digestibility tests

Reactor/series	I	II	III	IV
1	Untreated WAS	Untreated WAS	Untreated WAS	Untreated digestate
2	Untreated WAS	Untreated WAS	Untreated WAS	Untreated digestate
3	20°C, NaOH 4%	70°C, NaOH 4%	70°C	70°C, NaOH 4%
4	20°C, NaOH 4%	70°C, NaOH 4%	70°C	70°C, NaOH 4%
5	70°C, NaOH 4%	90°C, NaOH 4%	90°C	90°C, NaOH 4%
6	70°C, NaOH 4%	90°C, NaOH 4%	90°C	90°C, NaOH 4%

As shown in Table 2, each lysis condition (pre- or intermediate) was tested in duplicate, with the exception of (70°C, NaOH 4%) that was tested in two subsequent series of tests for a total of four replicates.

The inoculum employed for the tests went from the Castiglione WWTP and had a TS content of 2.68±0.24% (average ± standard deviation on four replicates), a VS/TS ratio of 0.610±0.039 and neutral pH. In all tests the ratio between substrate (WAS or digestate) and inoculum was of 1.5±0.1, in order not to overfeed the digester and avoid an accumulation of volatile fatty acids (VFA), coming from the steps of hydrolysis and acidogenesis, in the first part of the AD process (Shana et al., 2013).

2.4. Analytical methods

All the analytical parameters monitored in the lysis tests (TS, VS, pH, electric conductivity (EC), sCOD and ammonium NH_4^+) were determined using Standard Methods (APHA, AWWA, WEF, 2005). Soluble COD (sCOD) 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).

Total COD (tCOD) was evaluated using the elemental composition of the sludge as in Van Lier et al. (2008). At this stage only the elemental composition of the WAS sample was determined using a Flash 2000 ThermoFisher Scientific CHNS analyzer. The composition of the digestate was assumed equal to that of WAS.

3. Results and discussion

3.1. WAS and digestate samples

The complete physical and chemical characterization of the two substrates employed for the lysis tests is shown in Table 3. It has to be pointed out that all the pre-treatment tests (low-temperature thermal and hybrid) were carried out on the same WAS sample.

Table 3. Characterization of WAS and digestate employed for the tests

	TS (%)	VS/TS (%)	pH	EC (mS/cm)	tCOD (mg/l)	sCOD (mg/l)	NH_4^+ (mg/l)
WAS	4.88	0.70	6.78	1.09	46,100	210	128
Digestate	4.58	0.67	7.36	3.53	41,200	125	299

NA: not available

As anticipated in Section 2, the thickening process carried out with a cloth filter produced a final TS content in the order of 4.50-5.00% in both samples. Several parameters (pH value, sCOD and ammonia concentration) were for the both samples of the same order of magnitude. The sample of digestate had a VS content lower than the VS content of the WAS sample. This is coherent with the fact that even a not complete anaerobic digestion process consumes an amount of biodegradable substance. Moreover, digestate had an EC value that was three times the EC of the WAS sample (3.5 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 the AD process. The elemental composition of both samples was C 48.0%, H 16.9%, N 7.1% and O 37.2%. From these values the resulting tCOD was of 46,100 mg/l for the WAS sample and of 41,200 mg/l for the digestate.

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 in the literature 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 parameter value (that is the release of the sCOD compared to the particulate COD) for all the lysis treatments tested on both WAS and 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 digestate (dark bars) at the three operating temperature values (20, 70 and 90°C). As shown in figure 1, the DR parameter varied from a few percent up to 40%.

The only thermal treatment, at a temperature of 70 °C, showed a better efficiency on the 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. For WAS sample the DR increased from approximately 12% to 22%. On the other hand, for the same increase in temperature, the increase in hydrolysis of the particulate 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.

In the scientific literature there are a number of studies that report the efficacy of thermal low-temperature or hybrid thermo-chemical pretreatments on WAS, but very few examples of treatments carried out on intermediate sludge (i.e. sludge after a partial digestion process) or digestate. One case-study is reported by Li and coauthors (2013) who employed a solution 0.1 M of NaOH to treat a matrix composed of 80% primary sludge and 20% of biofilm sludge after anaerobic digestion. The concentration of TS of 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 order of magnitude of the liberated COD observed for the digestate treated at ambient temperature with NaOH in this experience was consistent with that found in Li et al. (2013). However, it has to be taken into account that Li and coauthors reported their results as sCOD instead of DR. The value of sCOD found (approximately 2,000 mg/l) was 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%.

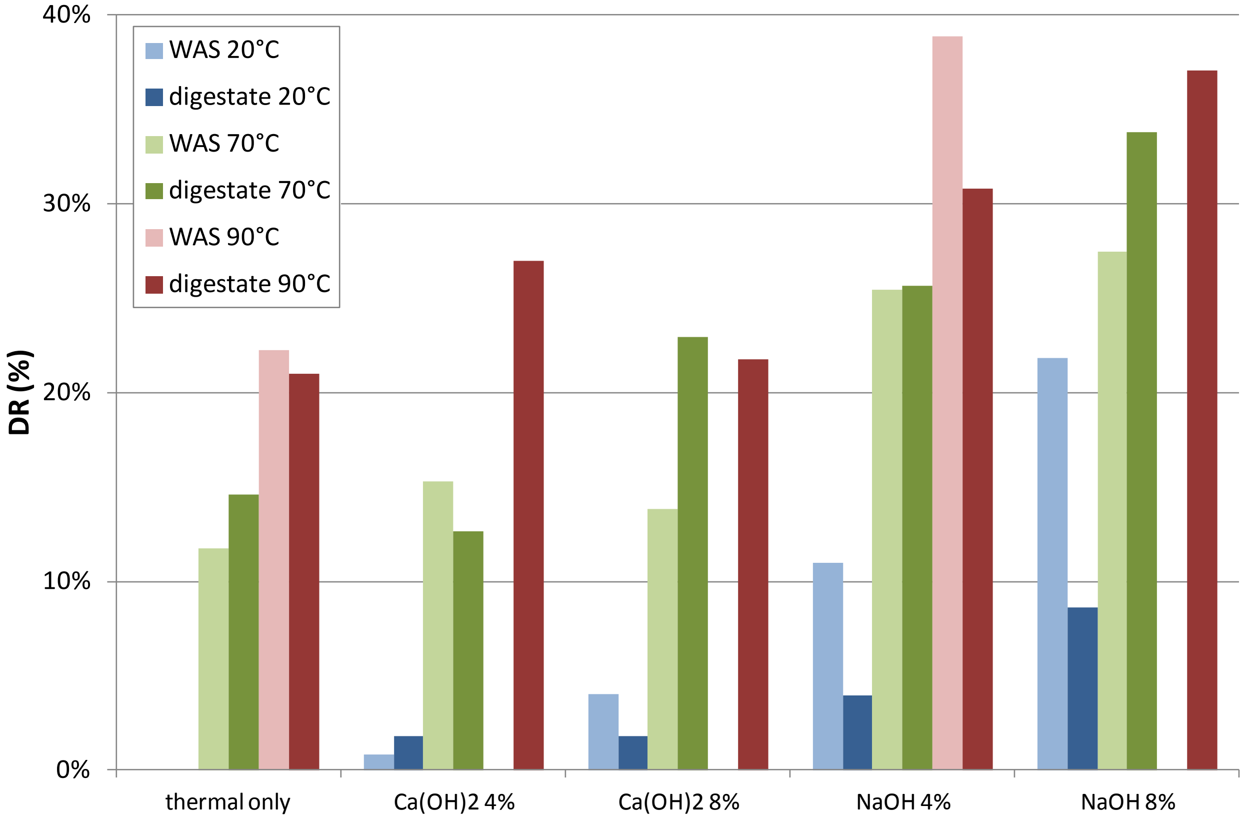

Figure 2. DR resulting from the lysis tests

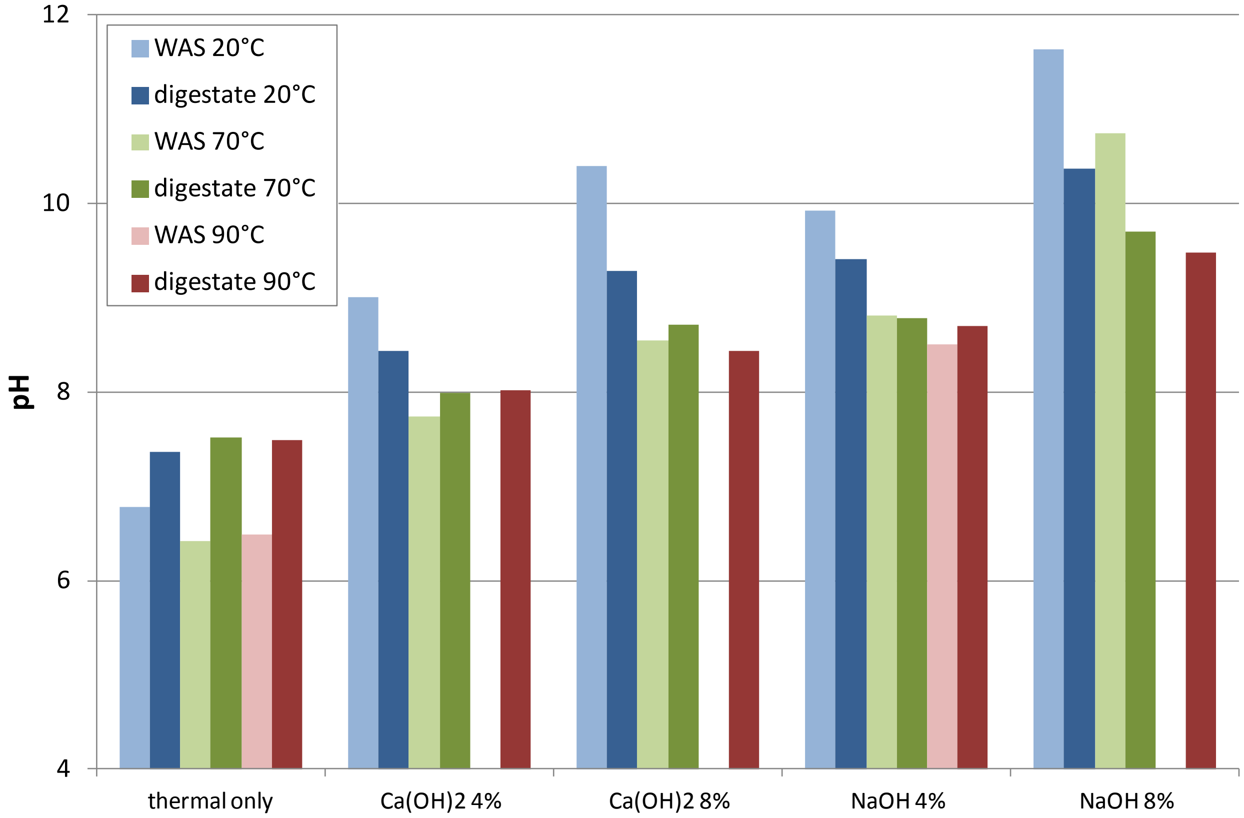

Figure 3. pH values resulting from the lysis tests

The amount of alkali added to the sample of WAS or digestate inevitably determined an increase of the pH value. As shown in Figure 3, the final pH value depends 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. It could be interesting to note that such a dose of alkali agent (in the order of 0.1 M) should produce a final pH value of approximately 13 pH units. However, the liberation of soluble COD, rich in organic acids, aided in buffering the increase of pH and the final pH value results 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 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 EC after the lysis treatment and the EC of the untreated samples (respectively of 1.09 mS/cm for the WAS and 3.53 mS/cm for the digestate, as shown in Table 4). 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 samples of WAS were treated with doses of NaOH.

Hybrid treatment on digestate with NaOH produced increases in the EC values of quite limited extent (1.2-1.7 times the reference value). On the other hand, 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 lower temperature values. Decrease in EC may be due to the generation of calcium salts, with very low solubility, and subsequent precipitation of those.

The treatment with alkali agents at 20 °C had little effect on ammonia release from treated WAS. The concentration of ammonia, in fact, remained approximately constant at values of 110-120 mg/l. On the other hand, the ammonia concentration in the digestate was in of the order of 300 mg/l. In the case of digestate, there was an evident relation between the concentration of ammonia and EC after treatment. Moreover, a decrease of ammonia concentration was observed for digestate samples treated at increasing doses of $Ca(OH)_2$. For both WAS and digestate samples an increase of the ammonium concentration for systems treated at 70 °C (most evident for the digestate) and a subsequent general decrease, when the treatment was carried out at 90 °C, was observed. Such an evidence could be justified by referring to the Maillard process (Eskicioglu et al., 2007, 2008; Kuglarz et al., 2013). Furthermore, the ammonia concentration depends on the balance of the species NH_3/ NH_4^+. It must be assumed that the concentration of ammonia observed after treatment results from a balance between the Maillard process and the equilibrium of ammonia, that is influenced by the pH value and that depends, in turn, on the balance between the dose of the alkali agent and the amount of released organic acids.

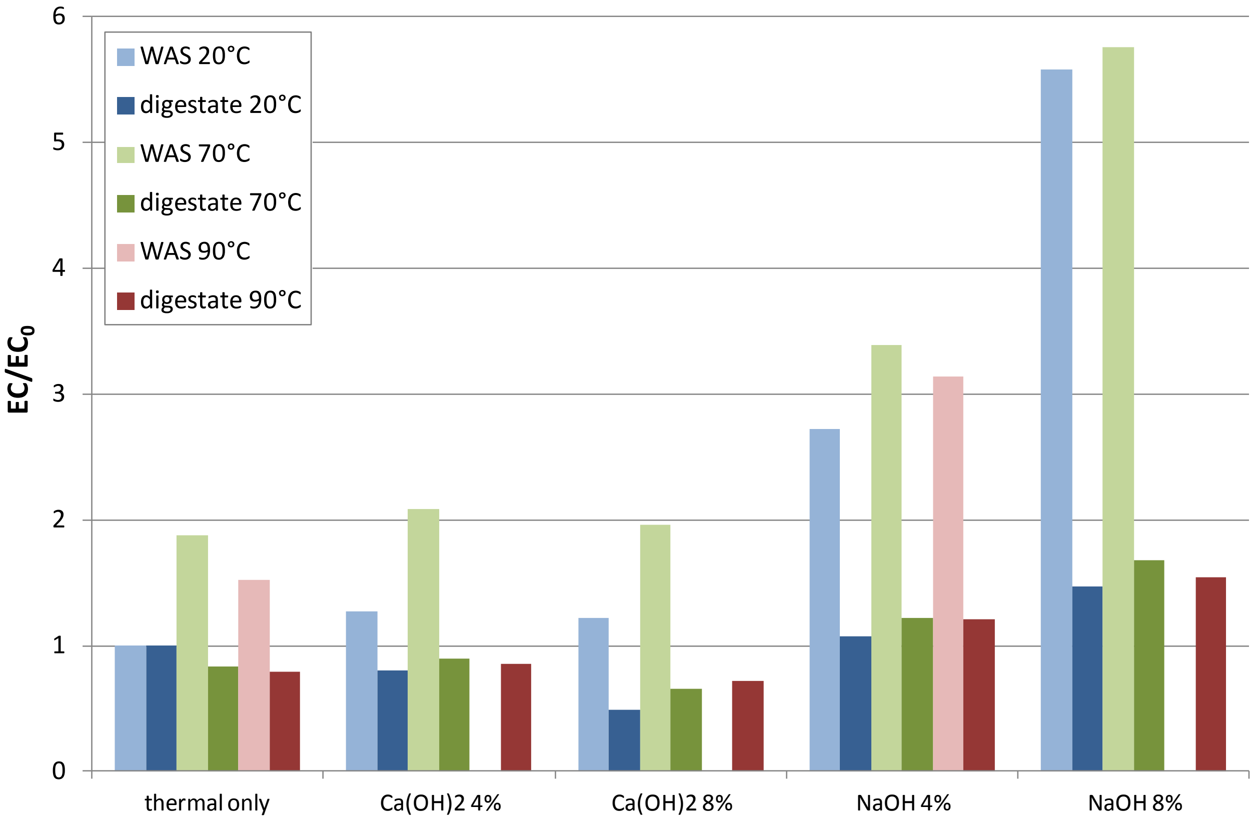

Figure 4. Ratio between EC after lysis treatments and the EC of the untreated samples

3.2. Anaerobic digestion tests

The series of anaerobic digestion tests on WAS performed in this work and in a previous work (Ruffino et al., in press) demonstrated a strong variability of the specific production of biogas and methane for the raw WAS sample (i.e. not subjected to any treatment). The specific biogas production amounted to values in the order of 0.257 ± 0.048 Nm^3/kg VS (average on five different raw WAS samples), while the specific production of methane was 0.166 ± 0.036 Nm^3/kg VS, with methane volumetric percentages that ranged between 61 and 67%.

In order to compare the results obtained in the different series of tests, all methane specific yield 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) found over all series.

Curves of Figure 5 show the evolution of the methane specific production 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 test was considered completed since the daily marginal production of biogas or methane was less than 1% of the overall production (VDI Standard 2006). For all curves the difference between the two (or more) replicates carried out on the same sample was of very reduced entity and error bars are not visible.

The only-thermal treatment carried out on the WAS sample determined ad increase in the methane specific yield of 14% for the temperature of 70 °C and of approximately 20% for the temperature of 90 °C. These observations are 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 pretreatments. In that study increases in the methane specific yields of 21% and 31% were recorded after thermal pretreatments processes carried out at respectively 70 and 90 °C for 3 hours. Tests

described in that study differed from tests reported in this study not only for the duration of pretreatment (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 increase in the methane specific yield of 40% for the sample treated at 70 °C and of more than 66% for the sample treated at 90 °C. The increase in the methane specific yield was calculated with reference to the untreated sample.

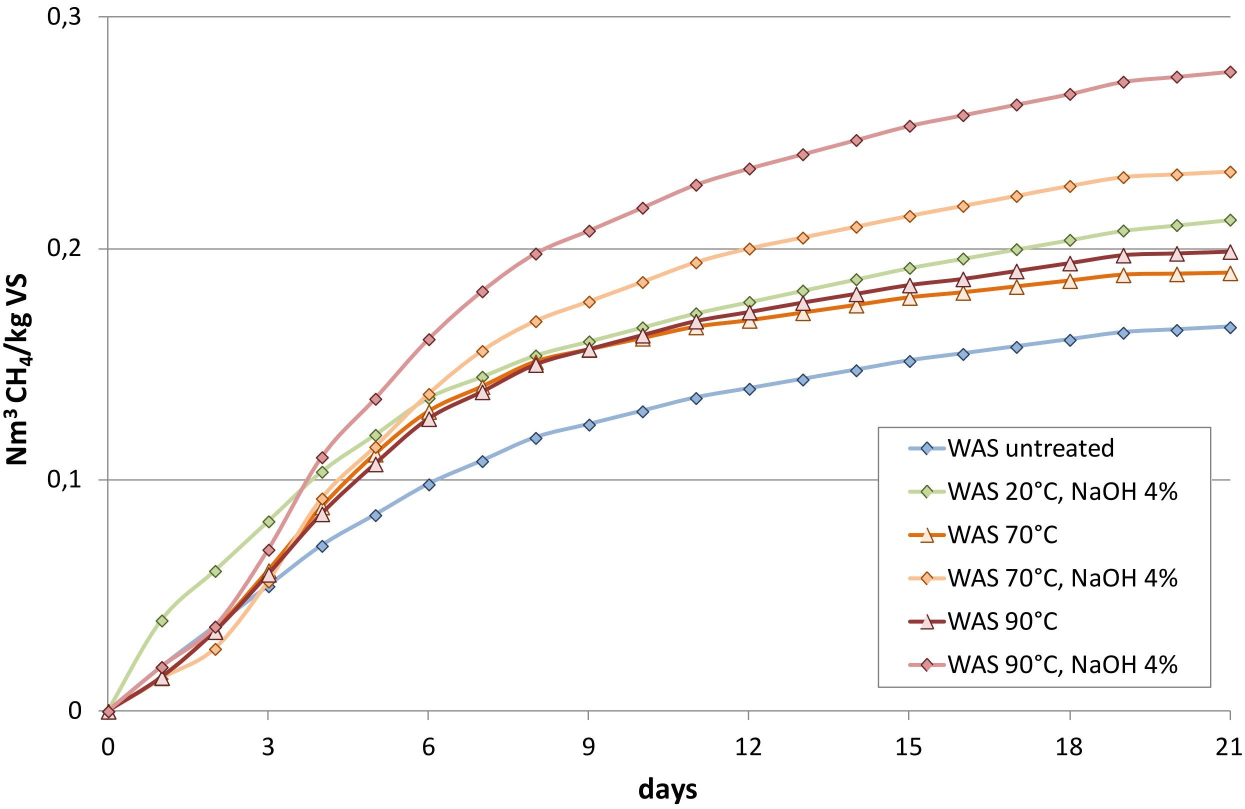

Figure 5. Evolution of the methane specific production for WAS samples treated under different conditions.

Curves of Figure 6 show the results of digestibility tests carried out on WAS (untreated and treated with an hybrid process at 70 and 90 °C) and digestate (same treatment). Although the digestate sample was already a product of a digestion process, when submitted to digestibility tests it continued to produce biogas and methane.
The specific methane yield of the untreated WAS was of 0.166 Nm^3/kg VS. The hybrid treatment caused an increase in the specific production of methane of approximately 40% for the sample treated at 70 °C and of more than 66% for the sample treated at 90 °C. The percentage of methane in the biogas generated in all digestibility processes that involved WAS was in the order of 60-70%.

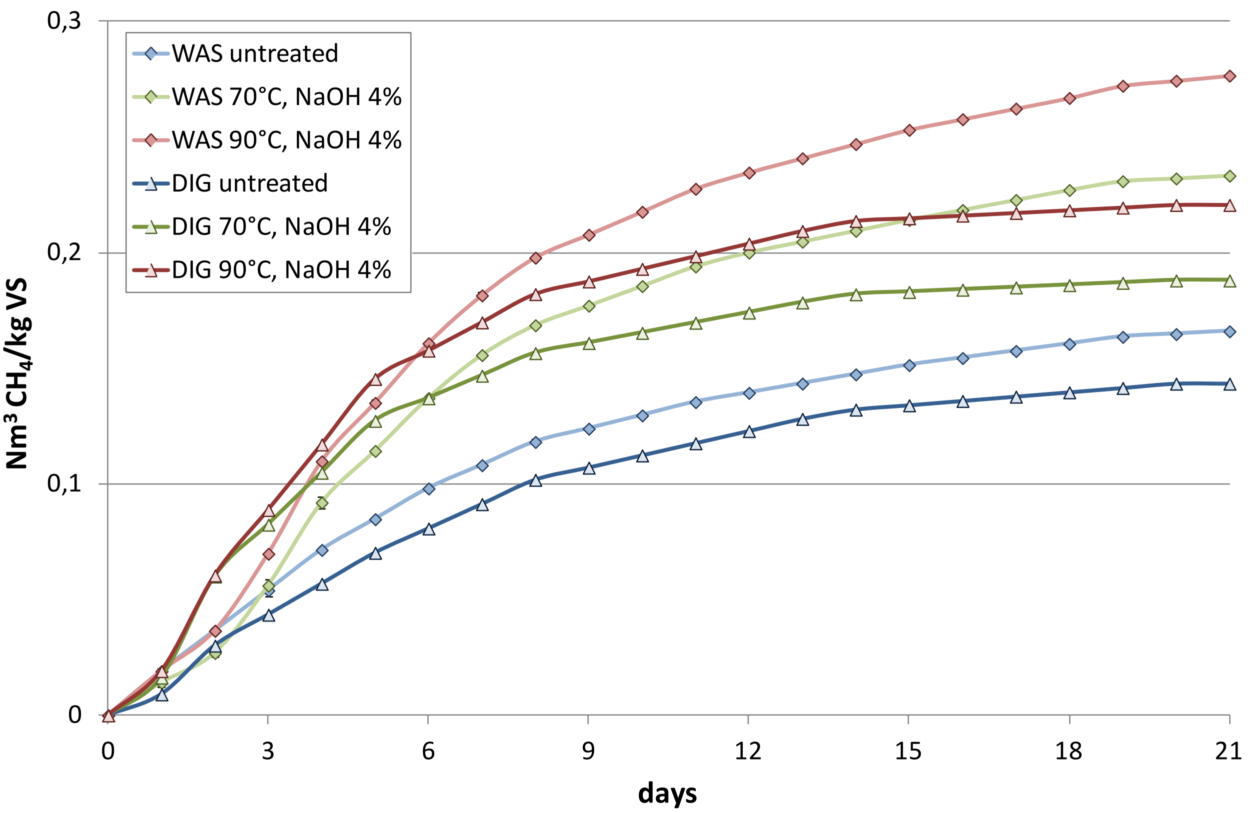

Figure 6. Evolution of the methane specific production for WAS and digestate samples treated with the same operating conditions.

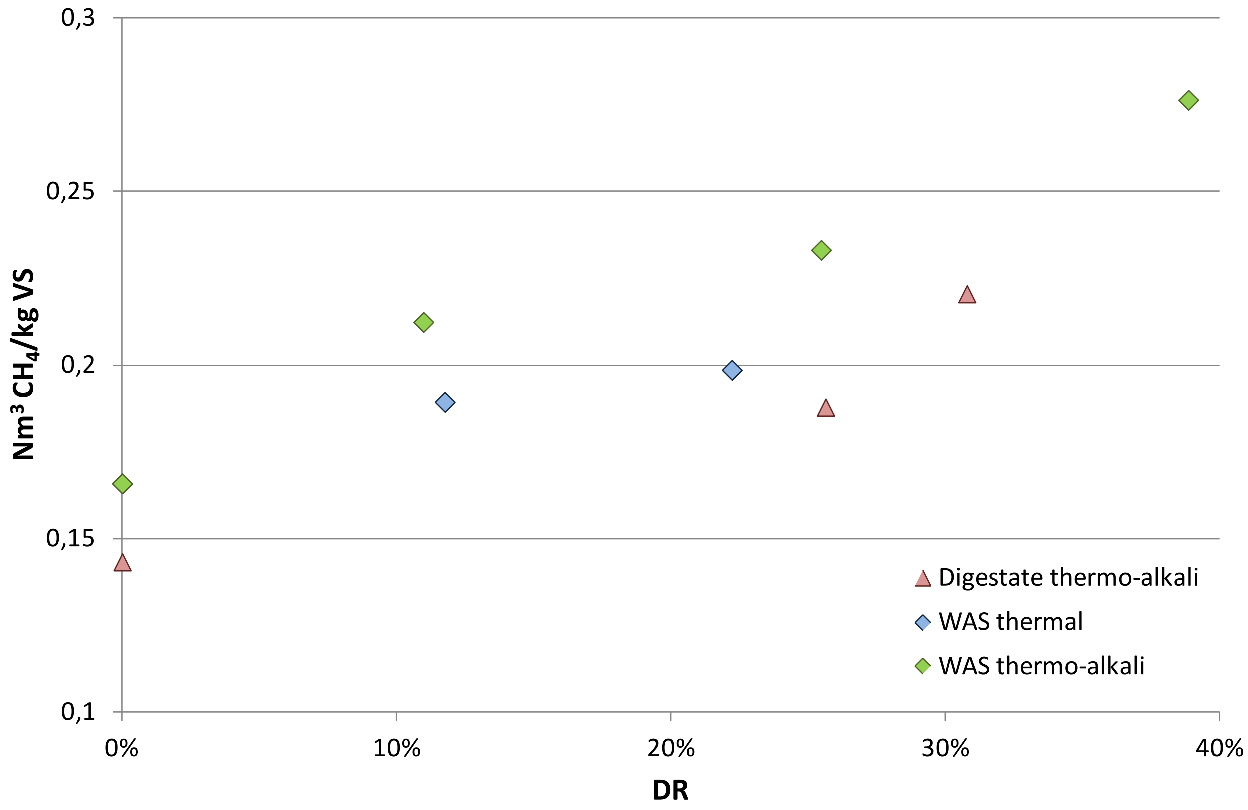

Figure 7. Methane specific yields vs. DR values for all treatment conditions.

The sample of untreated digestate showed a specific methane yield of 0.143 Nm^3/kg VS, approximately 14% less than the raw WAS. With the hybrid treatment the capacity of producing methane of the digestate increased by 31%, at the temperature of 70 °C, and by 54% at 90 °C. Also in this case, the percentage of methane in the biogas generated by digestate samples ranged between 60% and 70%. The digestate employed in the tests was collected from SMAT digesters after a residence time of 10 days. The residence time in normal operating condition is of 17 days, this is the reason why the sample had a significant residual capacity in producing biogas and methane.

Figure 7 relates DR values with methane specific yields for samples of WAS subjected to only-thermal and hybrid pretreatments and for samples of digestate subjected to intermediate treatments. An overall trend between the two parameter was difficult to identify but a nearly linear relation can be found for the two groups of WAS subjected to thermal (R^2 = 0.96) and hybrid (R^2 = 0.97) pre-treatments.

Curves of Figures 5 and 6 show that a sample of untreated WAS was able to produce approximately 78% of the overall potential methane production (i.e. the specific yield recorded when the digestion process was completed), after a digestion process of 10 days (0.130 Nm^3 CH_4/kg VS vs. 0.166 Nm^3 CH_4/kg VS). The product of this digestion process is the digestate that underwent the hybrid intermediate treatments. We can then hypothesize that the overall AD process could develop though two phases:

1. The first phase has a duration of 10 days and involves the untreated WAS. In this phase 0.130 Nm^3 CH_4/kg VS are produced.
2. The sludge digested in phase 1 undergoes hybrid intermediate treatments. Then, it is involved in a second AD process with a duration of 10 days.

According to the results shown in Figure 6, a digestion process of 10 days was able to extract approximately 88% of the overall potential methane production, as detailed in Table 4.

Table 4. Specific CH_4 yields after a 10-day digestion process

Treatment	Specific methane yield (Nm^3 CH_4/kg VS)	% Recovery
Hybrid, 70°C	0.165	88.0
Hybrid, 90°C	0.193	87.5

The third column of the table reports the amount of methane that can be extracted, after 10 days of digestion, with respect to the overall potential methane production. Then, a digestate sample subjected to thermo-alkali intermediate treatment at a temperature of 70 °C will give rise to a specific methane yield of 0.295 Nm^3 CH_4/kg VS against 0.233 Nm^3 CH_4/kg VS of the WAS sample pretreated in the same modality (+26.6%). For the temperature of 90°C, the intermediate treatment will lead to a specific methane yield of 0.323 Nm^3 CH_4/kg VS against 0.276 Nm^3 CH_4/kg VS (+17.0%) obtained with the pre-treatment applied on raw WAS. It can be concluded that the use of an intermediate treatment made possible to better exploit the production of methane, even working at a low temperature (70 °C).

These results are in line with the outcomes of two experiences that compared the performances of pre- and inter-stage treatments carried out at the same operating condition and on the same sludge. Unfortunately only a few works investigated the performances of intermediate treatments and, among them, very few studies compared pre- and intermediate processes carried out in the same operating conditions. Nielsen and coauthors (2011) compared three typologies of pre-treatments with inter-stage treatments carried out under the same operating conditions (moderate thermal, 80 °C; high thermal, 130–170 °C; and thermo-chemical, 170 °C/pH 10, KOH). They found that treatment of WAS were more effective when applied as an inter-stage treatment rather than a pre-treatment. The pre- treatment carried out at 80 °C had no effect on methane yield while the inter-stage treatment gave a 20% increase. Tests of Shana and coauthors (Shana et al., 2011; 2013) on samples of raw sludge and digestate were carried out at very hard operating conditions (165 °C, 7 bar, 30 min). They demonstrated that the intermediate thermal hydrolysis process (ITHP) configuration produced 20% more biogas compared to the THP configuration with around 62% methane content.

Conclusions

Several works have demonstrated the efficiency of different typologies of pre-treatments in liberating the intra-cellular organic substances contained in WAS and make them more available for AD. However, during an AD process, the production of new EPS partially neutralizes the benefit generated by pre-treatments. This work presents a preliminary comparison of the efficiency of only-thermal and hybrid (alkali-low temperature) treatments performed as a pre-treatment or intermediate treatments. The main results obtained in the experimentation demonstrated that:

- only thermal and hybrid treatments were, on average, more effective on WAS than on digestate, if the DR parameter is used to evaluate the performance of the treatment;
- for the treatment of both WAS and digestate NaOH had to be preferred to $Ca(OH)_2$. The combination with the thermal effect increased the amount of sCOD released;
- the results of the digestibility tests carried out on the WAS samples pre-treated with an hybrid process (NaOH 4%, 70 °C or 90 °C) showed an increase in the methane specific production of approximately 40% for the sample treated at 70 °C and of more than 66% for the sample treated at 90 °C, compared with the untreated sample;
- the only-thermal pre-treatment determined very low increases in the methane specific yield if compared to performances of hybrid pre-treatments. Increases were of respectively 14% for the temperature of 70 °C and of 20% for 90 °C. These findings were in line with the results of a previous study carried out on the same WAS sample;
- the sample of untreated digestate showed a specific methane yield of 0.143 Nm^3/kg VS, approximately 14% less than the raw WAS. With the hybrid treatment the capacity of producing methane of the digestate increased by 31%, at the temperature of 70 °C, and by 54% at 90 °C;
- a comparison between the two scenarios revealed that the substrate treated with an intermediate treatment carried out at 70 °C produces 27% more methane than the same substrate treated with a pre-treatment carried out in the same conditions.

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