PRELIMINARY TECHNICAL AND ECONOMIC ANALYSIS OF ALKALI AND THERMO-ALKALI PRETREATMENTS FOR THE ANAEROBIC DIGESTION OF WASTE ACTIVATED SLUDGE

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Abstract

Waste activated sludge (WAS) contains various organic and inorganic substances that should be treated for safe disposal. Anaerobic digestion (AD) is the most widely accepted method for stabilizing WAS.

This work investigated the technical and economic feasibility of alkali and hybrid thermo-alkali pretreatments for the improvement of WAS anaerobic digestion. Chemicals used for pretreatments were NaOH and $Ca(OH)_2$, with doses in the range of 0.04-0.2 g alkali/g TS. The same substances were used for hybrid pretreatments at low temperature (70 and 90°C).

Test outcomes demonstrated that NaOH was a more performing chemical in sludge disintegration and COD liberation than $Ca(OH)_2$. NaOH showed good performances already at low doses (0.08 g NaOH/g TS) with disintegration rates in the order of 20%. The thermal effect improved alkali performance. Biogas yield increased of 13.2% and 26.8% when samples were treated respectively at room temperature and 70°C with 0.04 g NaOH/g TS for 90 minutes.

Until nowadays economic issues (mainly the cost of chemicals for alkali pretreatments and pH conditioning) have limited the real-world applications of alkali and hybrid pretreatments. The preliminary economic analysis performed in this work demonstrated that only an increase in the methane yield in the order of 60% could offset the cost of chemicals. On the other hand, if the alkali treatment was coupled to heat, increases in the methane yields in the order of 15-20% were sufficient.

Introduction

Waste activated sludge (WAS) is an important source of biological matter that is produced from the secondary treatment of wastewater treatment plants (WWTPs). Since it contains easily decomposable organic matter, pathogens and harmful insect eggs, it should be properly treated prior to final disposal. Handling and disposal of sludge is a costly operation that accounts for up to 50% of the total operating costs of a sewage treatment plant (Neyens et al., 2004; Kim et al., 2013).

Anaerobic digestion (AD) is a common and widely adopted process for WAS treatment and stabilization. AD can reduce the amount of WAS by approximately 40–50%, while producing clean energy in the form of biogas. Nevertheless, AD is not completely effective towards WAS because the complexity of the substrate limits the efficacy of the biological process. In fact microbial cells, cell walls and membrane in the WAS are strong barriers to the penetration of hydrolytic enzymes (Appels et al., 2008).

In order to improve the digestibility of sludge, with subsequent lower digester retention time and higher methane production rates, several types of pre-treatments have been tested (Carrère et al., 2010; Climent et al., 2007, Dhar et al., 2012; Ruffino et al., 2014, 2015). They have the purpose of reducing macromolecule dimensions, avoiding the presence of macro-flocks inside the sludge and breaking bacteria cell walls with the subsequent release of intracellular organic matter.

Among the various pretreatment technologies, alkaline and the combinations with other pretreatments (thermal, mechanic, ultrasonic, microwave) have been the most widely investigated due to their simplicity and high efficiency (Kim et al., 2013). Alkaline pretreatment breaks the flocs apart and induces the swelling of particulate organics (Kim et al., 2010), rendering the biopolymer substances more susceptible to the extracellular enzymes produced by anaerobic microflora (Zhen et al., 2014).

For the combination alkali-thermal hydrolysis, most literature has dealt with high-temperature (>100°C) conditions up to 270°C (Appels et al., 2010), and several studies reported that the optimum temperature is 170-200°C (Bougrier et al., 2006). However, high-temperature treatment requires large amounts of energy and the increased biogas production could even be offset by the extra energy consumption for sludge pretreatment. Pretreatments at low temperatures (<100°C), especially if assisted by alkali addition, can be a viable alternative (Climent et al., 2007).

However, little research has been carried out on low-temperature thermo-alkaline pretreatment of WAS, and limited information is available on the combined effects of alkali concentration and temperature. Moreover, most of the studies were aimed only to search for the best operating conditions to increase the hydrolyzed organic matter and the production of biogas and methane. Only a couple of studies made an attempt to perform assessments on the economic sustainability of the treatment (Kim et al., 2013; Cho et al., 2014). In fact, pretreatments at room temperature may be carried out with simple systems but substantial cost items are the alkali agent and the acid necessary to restore the pH to values compatible with the development of the AD process.

This paper aims to perform a preliminary technical and economic assessment of alkali and hybrid thermo-alkali pretreatments at low temperature values (70°C-90°C) for the improvement of the AD of sewage sludge.

2. Materials and Methods

2.1 WAS collection and characterization

Samples of WAS were collected from the WWTP located in Castiglione Torinese (NW Italy) owned by SMAT company (2,300,000 p.e., population equivalent). Raw WAS samples were firstly sieved at 0.295 mm (using a 48-mesh Tyler Standard sieve), in order to remove coarse particles and impurities, and then thickened from an initial TS content of about 0.8% (see Section 3.1) to a final TS content of 5-6%. Samples were stored at 4°C until utilization, in all cases no later than 48 hours from collection.

The following parameters: total solids (TS), volatile solids (VS), SCOD – that is the COD in the liquid phase after filtration on a 0.45 μm acetate-cellulose membrane - pH, electric conductivity (EC), elemental composition, that is C, H, N, S content, and soluble ammonium were determined according to standard methods (APHA, AWWA, WEF, 2005). The total COD of sludge (TCOD) was calculated from the outcomes of the elemental analysis as in van Lier et al. (2008).

2.2 Alkali and thermo-alkali pretreatments

Chemicals used for alkali pretreatments were NaOH and $Ca(OH)_2$. The same substances have also been used for thermo-alkali pretreatments at low temperature (70°C and 90°C). Test procedures (that is type and dose of the reagent, temperature and contact time) are summarized in Table 1.

Table 1. Operative parameters for alkali and thermo-alkali pretreatments

Series	Reagent	Dose g alkali/100 g TS	T (°C)	Contact time (min)
I	NaOH	4	Room (20)	90
		8	Room	90
		12	Room	90
		16	Room	90
		20	Room	90
II	$Ca(OH)_2$	4	Room	90
		8	Room	90
		12	Room	90
		16	Room	90
		20	Room	90
III	NaOH	4	70	90
		8	70	90
IV	$Ca(OH)_2$	4	70	90
		8	70	90
V	NaOH	4	Room	180
		4	70	180
		4	90	180

As shown in Table 1, five series of tests were performed. They were designed to investigate the effect of different parameters on the solubilization of COD (DR, disintegration ratio). In fact, the lysis effect on WAS samples of both alkali and thermo-alkali pretreatments was preliminarily assessed in terms of the disintegration rate (DR) parameter. DR is one of the most frequently employed indicators to compare the effectiveness of different WAS pre-treatments (Dohányos et al., 1997). The DR formula is the following:

$$DR = \frac{SCOD_l - SCOD_0}{TCOD \ \ - SCOD_0} \cdot 100\%$$

where the terms TCOD, $SCOD_0$ and $SCOD_l$ refer respectively to the total COD of sludge, the soluble COD before and after pretreatment.

The first two series of tests were carried out at room temperature, for a duration of 90 minutes with a dose of chemical (NaOH or $Ca(OH)_2$) between 0.04 and 0.2 g alkali/g TS. They aimed to investigate the effect of the alkali dose on the resulting DR. The third and fourth series of tests were intended to evaluate the combined effect of chemical agent and heat in sludge lysis. Low doses (0.04-0.08 g alkali/g TS) of NaOH or $Ca(OH)_2$ were employed in a 90-minute thermal treatment at low temperature (70°C). Finally, the fifth series of tests had the purpose of investigating the performance of longer (180 min) hybrid treatments (thermal + chemical) at low doses of alkali (0.04 gNaOH/g TS) and temperatures up to 90°C.

Pretreatment tests were carried out in pyrex glass bottles of 300 ml equipped with screw caps. A volume of 200 ml of thickened sludge was put in contact with 50 ml of a solution of NaOH or $Ca(OH)_2$. Alkali solutions that contained the dose of chemical chosen for the test were obtained starting from a 100 g/L alkali mother solution. Mixtures made of sludge and alkali solution were stirred by hand for 1 minute every 15 minutes. Hybrid pretreatments were carried out in a water bath. Bottles were dipped in a thermostatic bath preheated at the temperature value established for the test. Before and after pretreatment the measurement of pH and EC, other than SCOD, has been performed.

2.3 pH conditioning

The pH values resulting from alkali and thermo-alkali treatments (>10) are incompatible with an AD process. It was therefore necessary to restore the pH values close to neutrality. For pH correction 1M HCl solutions were employed. Doses of HCl necessary to restore pH to values suitable for AD were firstly determined on a lab scale using samples of small volumes (50 mL). Aliquots of decreasing volume (500-100-50 μl) of a 1M solution of HCl were added to one of the systems subjected to alkali pretreatment (NaOH dose 0.08 g/g TS, room temperature, 90 minutes, resulting pH 11.45). From the addition of a volume of HCl solution to the subsequent addition, pH was waited to reach a stable value.

In order to upscale the alkali or thermo-alkali pretreatment process to the industrial scale, the dose of HCl to be introduced for the correction of the pH must be precisely known. The dose firstly determined on a lab scale using samples of small volumes (50 mL) was subsequently verified on the samples of larger volume (1000 mL) subjected to the same pretreatment and employed in the digestibility tests (see Section 2.4).

2.4. Digestibility batch tests

Some of the pretreated systems considered most promising for the upscale of the process have been subjected to digestibility tests in 6 batch reactors of the volume of 6 liters each. Batch tests were performed in order to assess the effect of the different pretreatment conditions on WAS digestibility and verify the correspondence between the increase in soluble COD and the increase in biogas and methane production.

Due to the limited availability of pilot-scale digesters (6), two series of tests were performed. Each series consisted of two untreated samples (control), two samples subjected to a type of pretreatment and two samples subjected to a different type of pretreatment. Following the outcomes found in the alkali and thermo-alkali pretreatment tests (see Section 3), among the 17 tested systems, four were chosen to undergo digestibility tests in batch mode.

The first series of tests involved samples of sludge chemically pretreated with NaOH (dose of chemical equal to 0.08 g NaOH/g TS) for 90 minutes at room temperature. Before subjecting samples to AD, the pH was corrected with HCl (as described in Section 2.3) and brought from the initial value of approximately 11.5 to 8.5 and 7.5 respectively. Correction of pH value was necessary to prevent the inhibition of the digestion process.

The second series of tests involved samples that underwent pretreatments with a low dose of NaOH at room temperature and 70°C. The pretreatment was carried out with 0.04 g NaOH/g TS for 90 minutes. The pH of the resulting systems has been corrected to the final value of 8.5 with a 1M HCl solution.

Digestibility tests were performed in batch mode, under mesophilic conditions (35°C), using 6-L poly methyl methacrylate (PMMA) digesters placed in a thermostatic bath. The anaerobic environment inside the digesters was prepared by filling them with water, then replacing water with nitrogen. This procedure also ensured that the reactors were leak free. In order to simulate real digestion conditions, pH value was not adjusted and no nutrients were added.

For digestibility tests in batch mode, 1000 ml of on-purpose treated WAS (or an equal volume of the control) were put in contact with an inoculum, according to a VS feedstock/VS inoculum ratio of 0.9 and a digester volume filling level of 80%. The inoculum was prepared from 1,000 mL of sludge collected from the anaerobic digesters of the WWTP of Castiglione Torinese. The inoculum was progressively fed with amounts of primary sludge, coming from the same WWTP, to reach a total volume of 2,400 ml. The inoculum was considered ready to start digestibility tests when its daily biogas production was of less than 0.5% of the total production registered throughout the whole period of preparation. The inoculum had a TS content of 1.74 ± 0.04%, a VS/TS ratio of 57.4 ± 1.5% and a pH value of 7.31 ± 0.02 (average value on 6 replicates ± standard deviation).

For each replicate, the produced biogas 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 normal conditions.

The parameters TS, VS/TS ratio, SCOD and soluble ammonium were determined according to standard methods (APHA, AWWA, WEF, 2005) to all the samples involved in the digestibility tests, before and after digestion.

3. Results and Discussion

3.1 WAS characterization

Sludge samples, as collected from the secondary clarifiers of the WWTP (i.e. before thickening), had an average TS content of approximately 0.8% and a VS/TS ratio of 70%. The soluble COD (SCOD) was of 30 mg/L, the pH value in the neutral range (6.5-7.5), the EC value of approximately 1200 µS/cm and the soluble ammonium (NH_4^+) content of 40 mg/L.

The elemental composition of the sludge (on dry basis) was equal to C 48.0%, H 16.9%, N 7.1%, O 37.2% by weight. From this composition a brute formula CaHbOcNd could be assumed, where the values of subscripts were respectively equal to a = 7.94; b = 13.61; c = 4.60; d = 1.00. Consequently, for this sludge, the relationship between VS content and total COD resulted of 1.35 g TCOD/g VS.

3.2. Effect of alkali and thermo-alkali pre-treatments on COD solubilization

The treatment of WAS samples with alkali inevitably causes the increase of the pH, that reached also strongly basic values (>12), and EC, as shown in Figure 1. For example, the electrical conductivity of samples treated at room temperature with NaOH increased by 10 times (from 2.66 to 22.4 mS/cm) when the dose of hydroxide increased from 0.04 to 0.2 g NaOH/g TS.

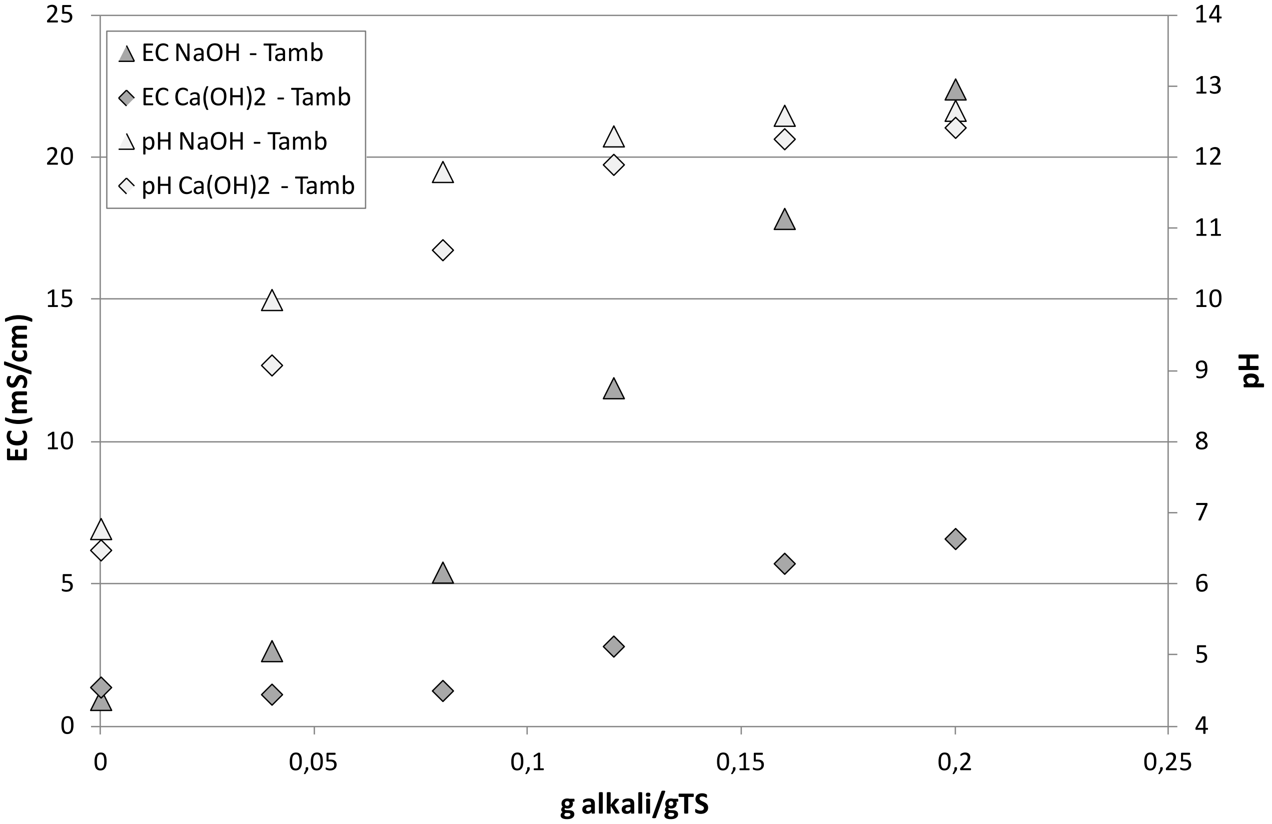

Figure 1. Effect of the alkali dose (0-0.2 g alkali/g TS) on EC and pH value – room temperature

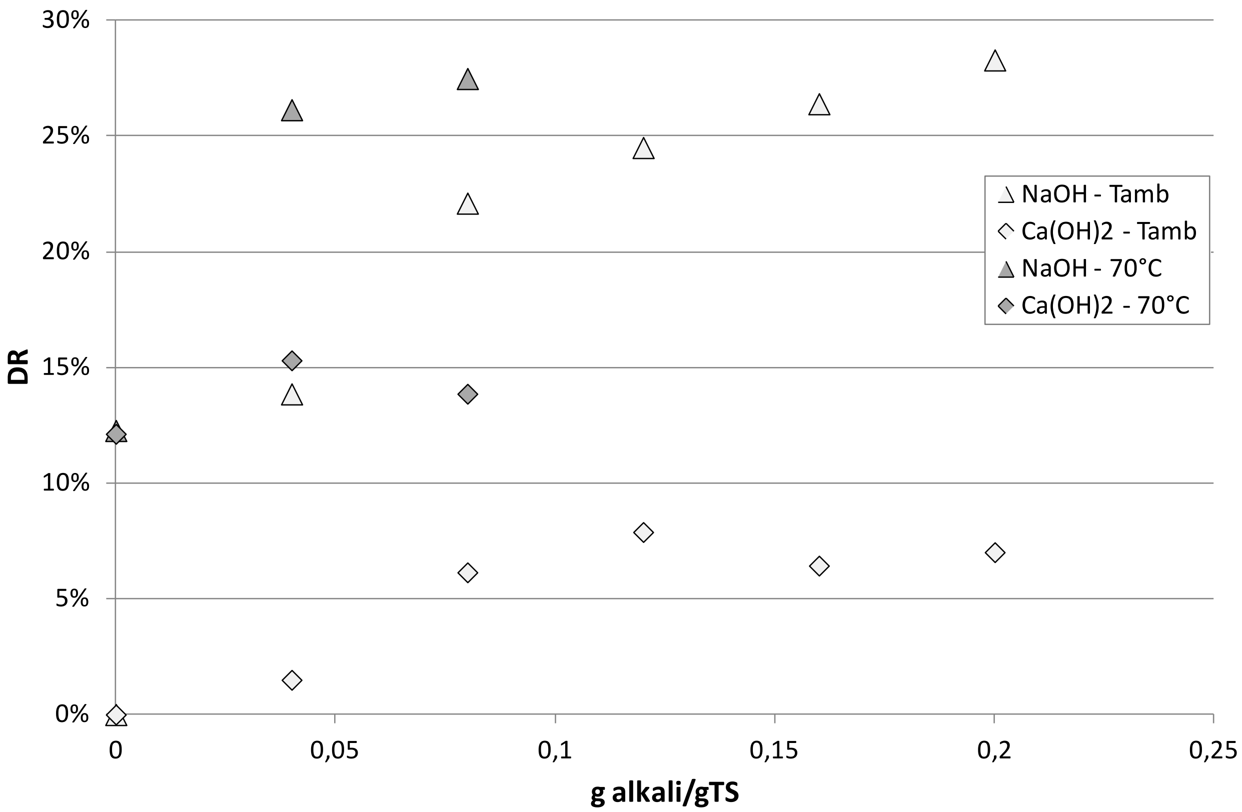

Figure 2. Effect of alkali dose (0-0.2 g alkali/g TS) and temperature value (room, 70°C) on sludge solubilization (DR)

Figure 2 shows the effect of the alkali dose (0-0.2 g alkali/g TS) and temperature value (room, 70°C) on the DR parameter. DR values did not exceed 8% when sludge samples were treated with $Ca(OH)_2$ at room temperature. DR value increased to approximately 15% when the alkali treatment with $Ca(OH)_2$ was aided by the thermal effect (70°C, 90 min). On the other hand, systems treated with NaOH reached a DR value close to 30% for the dose of 0.2 g NaOH/g TS. This value was approximately 3.5 times higher than that obtained with $Ca(OH)_2$ in the same conditions. NaOH treatments aided by the thermal effect at 70°C determined the achievement of DR values in the order of 26-27%, already for doses of 0.04 and 0.08 g NaOH/g TS. Similar values were obtained at room temperature with the dose of 0.2 g NaOH/g TS.

Figure 3 shows the DR values obtained from alkali, thermo-alkali and thermal pretreatments for a dose of NaOH of 0.04 g/g TS and contact time of 90 and 180 minutes. The results of Figure 3 demonstrate that a thermo-alkali treatment carried out at 90°C for 90 minutes led to a COD solubilization degree close to 40%. If the duration of the treatment was increased up to 3 hours, the DR value reached approximately 45%, slightly less than twice the result obtained with the only thermal treatment at 90°C or with the hybrid pretreatment carried out at 70°C. Figure 3 shows the equivalence of DRs (for both values of contact time) for the couples (alkali room temperature and only thermal 70°C) and (70°C alkali – only thermal 90°C).

The values of DR obtained in the five series of tests of this study were in line with those showed in Kim et al. (2013). Kim and coauthors performed thermo-alkali pretreatments with NaOH at low temperature values (60-75-90°C) using doses of reagent in the order of 30-60% of the TS content (concentration values of NaOH solutions of 0.1-0.2 M, sludge TS content of 1.24%). The treatments carried out by Kim and coauthors had a total duration of 6 hours. From the obtained results, Kim and coauthors built a 3D model capable of predicting the DR value as a function of the dose of chemical and temperature of treatment. There was a good agreement between the results of this study and the results returned from the model of Kim and coauthors for NaOH concentrations in the range of 5-10%. However, Kim and coauthors did not report the amount of HCl required to return pretreated samples to pH values suitable for AD.

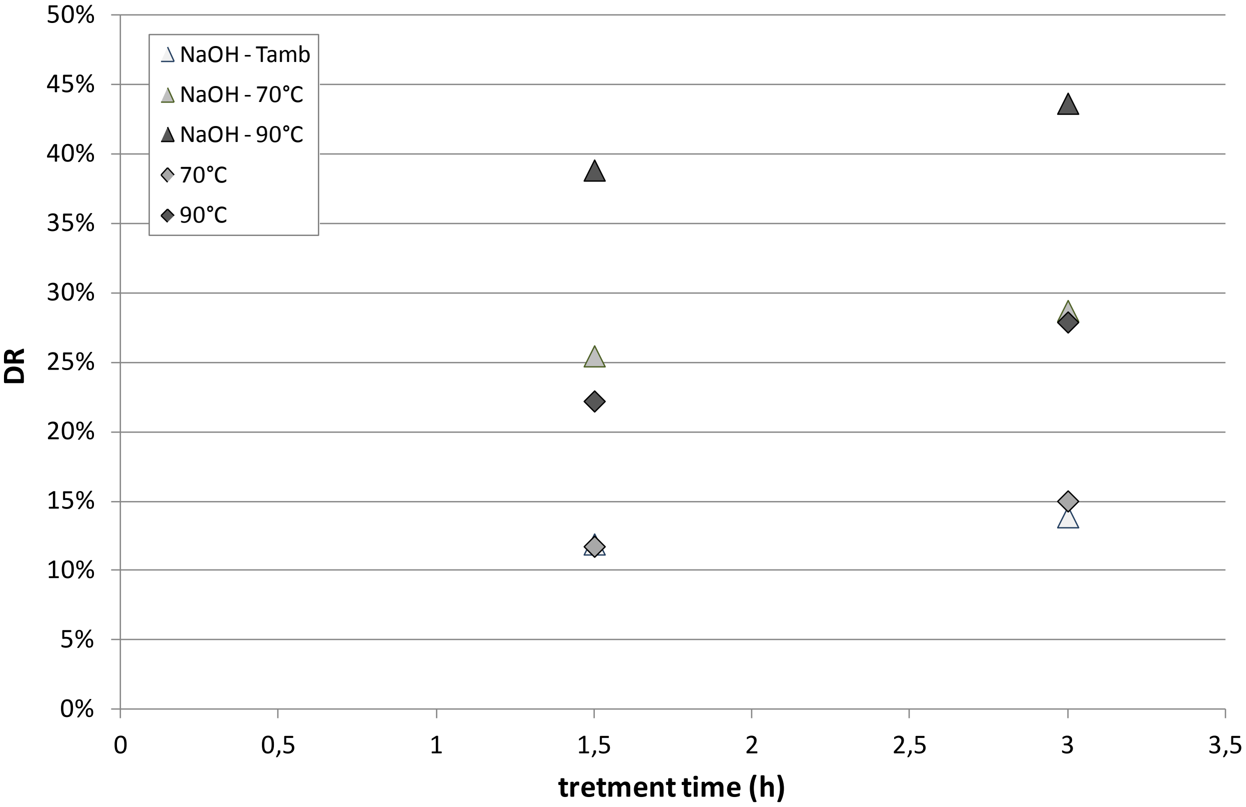

Figure 3. Effect of treatment time and temperature value on sludge solubilization (DR) – alkali dose 0.04 g NaOH/g TS

3.3. pH conditioning

The values of pH that sludge samples reached after the alkali treatment are not suitable for the success of an AD process. Consequently, in order to assess the improvement of AD performances of WAS due to alkali or thermo-alkali pretreatments, the final pH value of the systems has to be corrected to neutral conditions with HCl solutions. In the test performed on a lab scale the doses of 1M HCl solution required to bring the pretreated sample, respectively, at pH 8.5 and 7.5, resulted of 0.030 g HCl/g TS and 0.039 g HCl/g TS.

The obtained HCl doses were verified using a 1L-sample that had to be subsequently subjected to digestibility tests. The test was carried out as described in Figure 4. The HCl dose determined in the test at a lab scale was added to the alkali pretreated sludge sample. A period of 120 minutes was waited because the pH of the system reached a steady value. The value recorded for that time (still far from the target value) was corrected by the addition of further small amounts of acid solution to reach the target pH value. In both cases (pH target of 8.5 or 7.5), the expected dose of acid solution was underestimated by 25%. In the case of the target value of 8.5, an actual dose of 0.038 g HCl/g TS was necessary instead of 0.030 g HCl/g TS determined in a lab test. On the other hand, in the case of the target value of 7.5, the required dose was of 0.047 g HCl/g TS instead of 0.039 g HCl/g TS.

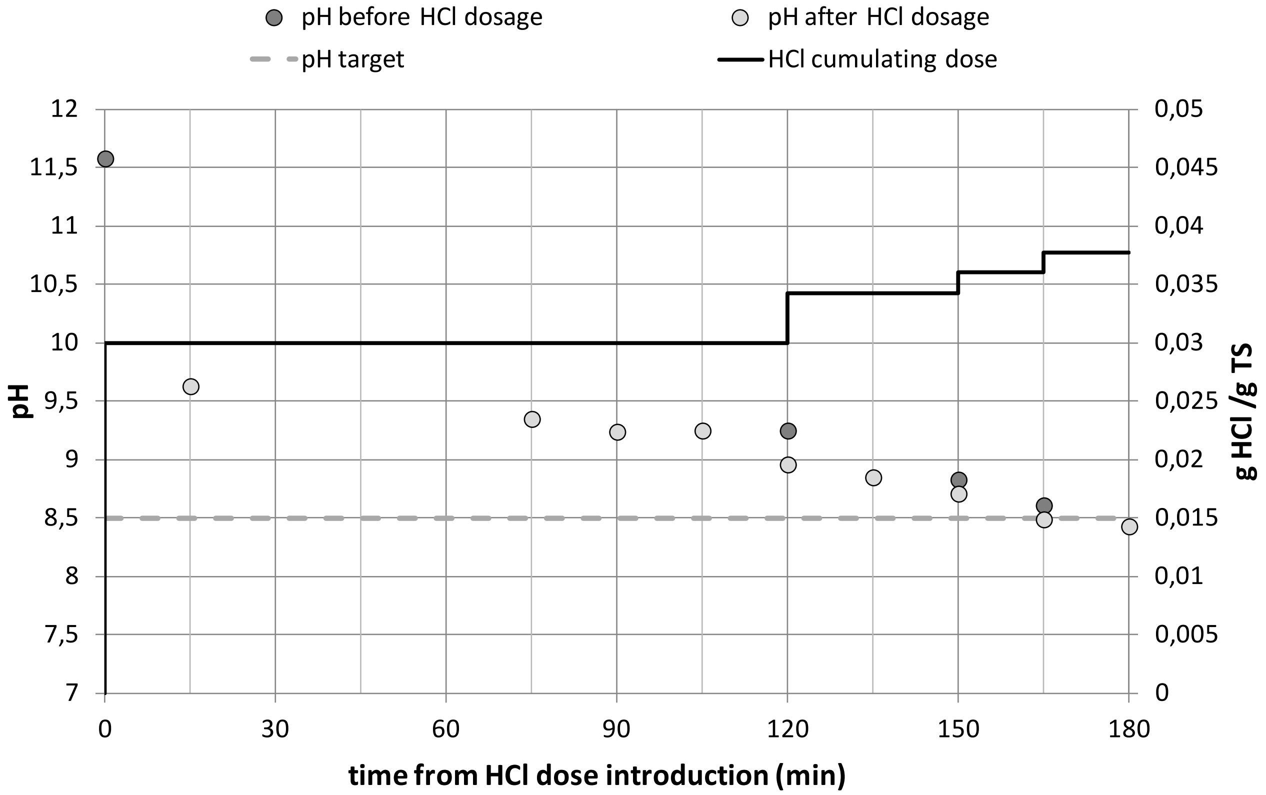

Figure 4. Test development and final result of pH correction on 1-L pretreated WAS sample (0.08 g NaOH/g TS, room temperature, 90 minutes, 8.5 pH target)

In order to estimate the dose of acid necessary for the pH adjustment to the range of neutrality, it is not possible to use predictions based on stoichiometric calculations. In fact, with reference to the sample treated with 0.08 g NaOH/g TS at room temperature, the dose of alkali used in the pre-treatment (0.1 M) should have caused a pH increase to a final value of 13. The value experimentally found was instead of approximately 11.5. This happened because the organic acids released in the alkali pretreatment buffered the free pH raise. Moreover, the final pH value also depends on the initial value of the sludge sample. Similarly, the dose of acid experimentally determined (about 0.04 g HCl/g TS) for the correction towards neutral pH values of the systems subjected to pretreatment, differed by about two orders of magnitude from the dose obtained by stoichiometric calculations (0.55 M against $2\text{-}3\cdot10^{-3}$ M).

3.4. Digestibility batch tests

With reference to the first series of AD tests, the sample at pH 8.5 registered an increase of 16.4%, with respect to control, in the biogas production. For sample at pH 7.5 the increase was of 18.4%. The specific biogas production amounted to 0.204 Nm^3/kgVS for the untreated sample (deviation of 0.7% between the replicates), 0.242 Nm^3/kgVS for the sample at pH 7.5 (deviation of 3.0%) and 0.238 Nm^3/kgVS for the sample at pH 8.5 (deviation of 0.8%). The concentration of methane of pretreated samples stood on values in the order of 60%.

In the second series of tests, that involved samples treated with 0.04 g NaOH/g TS at room temperature and 70°C, the biogas production registered an increase of 13.2%, with respect to control, for the sample treated at room temperature and of 26.8% for the sample treated at 70°C. In this series of tests the specific production of biogas amounted to 0.236 Nm^3/kgVS for the untreated samples (deviation of 0.7% between the replicates), 0.267 Nm^3/kgVS for the sample treated with NaOH at room temperature (deviation of 3.4%) and 0.299 Nm^3/kgVS for the sample that underwent the thermal-alkali treatment (deviation of 4.4%). Also for this set of tests, the concentration of methane of pretreated samples stood on values in the order of 60%.

The results of the AD tests may be compared with those from the studies of Kim et al. (2013) and Cho et al. (2014), who performed alkali and thermo-alkali pretreatments on WAS. As mentioned before, Kim et al. (2013) studied low-temperature thermo-alkali pretreatment of WAS, within the range of 0–0.2 M NaOH and 60–90°C, to investigate the effects of NaOH concentration and temperature process on sludge degradability in AD. Kim and coauthors observed an increase of approximately 70% in the methane production (191.4 ml vs. 112.2 ml for the control) for the system treated at 75°C with a 0.1 M NaOH solution and of 57% for the system treated at 90°C with the same alkali dose. However, it has to be taken into account that the lowest dose of alkali employed by Kim and coauthors (30% of the TS content) is 7.5 times the dose employed in the second series of tests of this work.

On the other hand, Cho and coauthors (2014) examined the technical and economic performance of an alkaline-mechanical process carried out with a novel mechanical crushing device for thickened WAS. The pretreatment at 40 g TS/L, pH 13, and 90 min reaction time achieved 64% of solubilization efficiency and a methane yield 8.3 times higher than the control. This last results is very surprisingly and comes from the very low methane yield of the control (0.034 Nm^3CH_4/kg VS compared to 0.122 – 0.142 Nm^3CH_4/kg VS of this study). Moreover, it was quite difficult to make a comparison on the solubilization efficiency, because the authors reported only the pH value (11-12-13) at which the pretreatment was carried out but they did not mention the dose of alkali employed. As discussed in Section 3.3, the type and the amount of substances (organic acids) released during pretreatment strongly affect the final pH value of sludge and no direct correlation between alkali dose and pH value may be found.

3.5 Preliminary cost-benefit analysis of alkali and thermo-alkali pretreatments

The results obtained throughout the overall experimentation (alkali or thermo-alkali pretreatments, neutralizing trials and digestibility tests) were used to evaluate the economic feasibility of the treatment. For this assessment it was assumed that the heat produced by the combustion of methane fed a cogeneration engine (CHP, combined heat and power) that produced electricity and thermal energy. The electricity was distributed to the national grid and could therefore take advantage of public subsidies provided for the production of electricity from renewable sources. The thermal energy was instead used to sustain the process of AD and replaces part or all of the heat generated by an auxiliary fuel (natural gas).

Table 2 lists the assumptions which were employed for the analysis. The engine had an electrical and thermal efficiency of 0.4 electrical or thermal kWh per kWh of heat produced from the combustion of methane.

Table 2. Assumptions employed for the economic assessment

Methane LHV (kJ/Nm^3)	35880	
Methane LHV (kWh/Nm^3)	9.97	
	Electrical energy	Thermal energy
CHP efficiency (kWh/kWhCH_4)	0.4	0.4
Energy from one Nm^3CH_4 (kWh/Nm^3CH_4)	3.99	3.99
Total electrical energy price (base + public subsidy, €/kWhe)	0.222	-
Economic value of energy from methane (€/Nm^3)	0.885	0.170

LHV, lower heating value

The electricity produced could be sold at the price of 0.222 €/kWh. This value resulted from the sum of the economic value of electricity (0.145 €/kWh) and public subsidy (0.077 €/kWh). Therefore, the economic value of methane for the production of electricity was equal to 0.885 €/Nm^3 CH_4.

On the other hand, the thermal energy produced by the cogeneration engine was used to heat the digesters and sustain the AD process. So, thermal energy may save a part or all of the auxiliary fuel employed for digesters heating. The auxiliary fuel employed by the WWTP for the production of thermal energy is natural gas that has a cost of € 0.37/Nm^3. Natural gas, when burned in a boiler with a yield of 0.85%, produces 8.47 kWht/Nm^3. Consequently, the thermal energy so produced has a unit cost of 0.044 €/kWht. Taking into account the amount of thermal energy produced from the AD (equal to 3.99 kWht/Nm^3CH_4, see Table 2) and the economic value of this energy (0.044 €/kWht, amount of money avoided for the production of thermal energy from an auxiliary source), the value of the thermal energy produced from AD was then equal to 0.17 €/Nm^3 CH_4.

Table 3. Summary of the economic analysis performed on the four systems subjected to AD test verification

Scenario		1	2	3	4
Target pH before AD		7.5	8.5	8.5	8.5
Alkaline pretreatment, NaOH dose	g/gTS	0.08	0.08	0.04	0.04
pH resulting from alkali pretreatment		11.6	11.6	10.1	9.17
Acid treatment, HCl dose	g/gTS	0.0473	0.0378	0.0146	0.0067
Cost of the alkaline pretreatment	€/kg TS	0.024	0.024	0.012	0.012
Cost of the acid treatment	€/kg TS	0.028	0.023	0.009	0.004
Total cost of the pretreatment (TS basis)	€/kg TS	0.052	0.047	0.021	0.016
Total cost of the pretreatment (VS basis)	€/kg VS	0.074	0.066	0.029	0.022
Increase in CH4 yield	%	18.4	16.4	13.2	**26.8**
Economic value of the electricity increment	€/kg VS	0.024	0.021	0.019	0.042
Economic value of the thermal energy increment	€/kg VS	0.005	0.004	0.004	0.008
Economic value of the total energy increment	€/kg VS	0.029	0.025	0.023	0.051
Increase in CH4 yield – target – electricity only	%	68.2	60.8	22.8	**17.6**
Increase in CH4 yield – target	%	57.0	50.8	19.0	**14.7**

Table 3 shows the results of an analysis of economic sustainability of alkali or thermo-alkali pretreatments carried out on the four systems subsequently tested for AD. The analysis of economic sustainability is a balance between the costs that are necessary to support pretreatments and the economic value of the products (electricity and heat) of AD. The analysis aimed to seek the value of percentage increase of methane production that must be achieved in order to equalize the costs of pretreatment.

With reference to the costs that is necessary to bear for pretreatment, only the costs of reagents, amounting to 0.3 €/kg for NaOH and 0.6 €/kg for HCl (Solvay, 2015), were taken into account. The unit cost (per kg of VS) of the alkali treatment (pretreatment) depends on the employed dose of chemical. On the other hand, the unit cost of the treatment of acidification (pH conditioning before AD) depends on the pH value that results from the basification and on the target pH value (i.e. the pH value allowable to begin the process of AD).

By assuming to refer to the conditions tested in the first series of digestibility tests (scenarios 1 and 2 in Table 3), that is room temperature, dose of chemical of 0.08 gNaOH/g TS and pH target of 7.5 and 8.5, the increase in the production of methane necessary to offset the costs of reagents (HCl and NaOH) was respectively:

- 68.2% for the system at pH 7.5, and 60.8% for the system at pH 8.5, in the case of considering only the increase in the production of electricity;
- 57.0% for the system at pH 7.5, and 50.8% for the system at pH 8.5, in the case of considering other than the increase in the of production of electrical energy, also the increase in the production of thermal energy.

With reference to the conditions tested in the second series of digestibility tests (scenarios 3 and 4 in Table 3), that is dose of chemical of 0.04 gNaOH/g TS, pH target of 8.5, temperature of 20 or 70°C, the increase in the production of methane necessary to offset the costs of reagents (HCl and NaOH) was respectively:

- 22.8% for the system treated at room temperature, and 17.6% for the system at 70°C, in the case of considering only the increase in the production of electricity;
- 19.0% for the system treated at room temperature, and 14.7% for the system at 70°C, in the case of considering other than the increase in the of production of electrical energy, also the increase in the production of thermal energy.

These figures point out that the economic feasibility of the treatment could only be achieved using low doses of alkali and acid. Better results could be obtained if the alkali pretreatment was coupled with the thermal effect already at low temperature values (70°C). However, a more complete analysis, other than the economic balance between the cost of chemicals and the value of products, must take into account also the thermal sustainability of the process. As discussed in Ruffino et al. (2015) in detail, an increase in the specific biogas yield of 20-25% was sufficient to sustain both the 70°C pretreatment process and subsequent mesophilic AD, provided that the sludge TS content was at least of 4%.

4. Conclusions

This work investigated the technical and economic feasibility of alkali and hybrid thermo-alkali pretreatments for the improvement of WAS anaerobic digestion in the largest WWTP in Italy.

Here a list of the main outcomes that came from the experimentation:

- the comparison between NaOH and $Ca(OH)_2$ revealed that NaOH was a more performing chemical in sludge disintegration and COD liberation;
- NaOH showed good performances already at low doses (0.08 gNaOH/g TS) with DR values in the order of 20%;

- the thermal effect improved the alkali performance. DR values (for an alkali dose of 0.04 g NaOH/g TS) doubled if the temperature value raised from 20 to 70°C, and increased of approximately four times if temperature raised to 90°C;
- biogas yield increased of 13.2% and 26.8% when WAS samples were treated respectively at room temperature and 70°C with 0.04 gNaOH/g TS for 90 minutes.

However, until nowadays several economic issues (mainly related to alkali and acid costs) have limited the real-world applications of alkali and hybrid WAS pretreatments. The preliminary economic analysis performed in this work demonstrated that only an increase in the methane yield in the order of 60% could offset the cost of reagents for alkali pretreatments and pH conditioning. On the other hand, if the alkali effect is coupled to heat (and lower alkali and acid doses are required to obtain the same final effect), increases in the methane yields in the order of 15-20% were sufficient. Consequently, the system described in the scenario 4 was economically sustainable.

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