Doctoral Dissertation
Doctoral Program in Civil and Environmental Engineering (31th Cycle)

Effects of thermo-alkali pre-treatments on WAS and technical-economic assessment for their applicability in the largest Italian WWTP

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Politecnico di Torino
January, 2019

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Abstract

Methane production of waste activated sludge (WAS) is limited by poor and slow biodegradability when subjected to anaerobic digestion (AD).

In this dissertation alkali pre-treatments, low temperature (<100 °C) thermal pre-treatments and thermo-alkali pre-treatments (a combination of above-mentioned lysis techniques) were studied. In the research activity two experimental steps were carried out. The first step consisted in nine batch AD tests, the second step involved four pilot scale semi-continuous anaerobic tests.

In the first phase of the study, samples of WAS, collected from the Castiglione Torinese WWTP, were subjected to alkali, thermal and thermo-alkali pretreatments with NaOH and $Ca(OH)_2$ with dosage range from 0.04 to 0.20 g alkali/g TS, for 1.5 and 3 hours at 20, 70 and 90°C. The performance of each treatment processes was assessed first by determining the Disintegration Rate (DR) and later by performing a series of anaerobic digestion tests in batch modality 38 °C (Mesophilic conditions).

The aim of the second experimental step was to assess the impact of thermo-alkali pre-treatments of WAS (4g NaOH/100g TS, 90 min, 90°C) in a pilot scale-semi-continuous AD test (mesophilic condition 38 °C); this treatment was chosen because in the first experimental step it shown the best performance in term of methane production increase (+86.1%).

AD tests were carried out on raw and treated WAS in a 240-L semi-continuous reactor with an HRT equal to 20 days. At the same time 10 L-digester was employed for the semi-continuous anaerobic digestion test of primary sludge. The anaerobic biodegradability of tested substrates was assessed in terms of methane production increase (B_0) and hydrolysis rate constant (k). The couple of parameters for untreated WAS, treated WAS and primary sludge were estimated using a first order

kinetics model. Moreover, in this dissertation a revision of the first kinetic model applied to semi-continuous anaerobic digestion tests was proposed, used and validated.

Based on the data returned from the pilot-scale tests, it was observed that the thermo-alkali pre-treatment could increase B_0 by 61.3% and the k from 0.085 to 0.465 d^{-1}. The results of this study demonstrated that a thermo-alkali pre-treatment could increase the specific methane production of WAS in a full-scale, steady-state continuous stirred tank reactor (CSTR), with an HRT of 20 days, from 0.09 to 0.23 Nm^3/kgVS (+144 %). Conversely, by using the same working volume but in a two-stage AD configuration the methane production of WAS could increase of 167 %.

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Introduction

Primary (PS) and waste activated sludge (WAS) are the main by-products of wastewater treatment processes. In conventional Wastewater Treatment Plants (WWTPs) sludge disposal costs account up to 50% of the total operational costs (Li et al., 2012) (Ruffino et al., 2015). In medium and large WWTPs, Anaerobic Digestion (AD) is the worldwide most used technique to stabilize and reduce the sludge generated in WWTPs. Additionally, anaerobic digestion is the most cost-effective technique because of the high energy and resource recovery that is possible to obtain from sewage sludge. (Choi et al., 2018) (Ding et al., 2017). However, AD requires large volume reactors due to the long Hydraulic Retention Time (HRT) necessary for the process. During AD, a bio-chemical process, biodegradable substrates are converted into biogas. Biogas is a mixture of gases mainly constituted of methane and carbon dioxide. Methane is present with a volumetric concentration generally variable from 50 to 70 %. Because methane has a lower heating value (LHV) of 35,880 kJ/Nm^3, biogas is an important renewable energy source.

Biogas is commonly used as a fuel in Cogeneration Heat and Power engines (CHPs) or upgraded to biomethane. The electric energy produced in CHPs is used to reduce the total energy demand in the WWTPs. It is known from literature and managing experience that, in conventional WWTPs, about 25–40% of operating costs is due to energy consumption (Panepinto et al., 2016). Moreover, a new popular topic in the scientific community is the energy efficiency in WWTPs. The energy optimization can be achieved through a combination of energy saving and new energy recovery techniques. In the next years, the challenge of technicians, involved into wastewater treatment processes, will be to reach self-sustainable WWTPs from an energetic point of view or, in the best condition, to design and manage plants able to produce more energy than they need. Energy self-sustainable WWTPs are studied to reduce operation costs, energy consumption and achieve carbon neutrality (Gu et al, 2017).

The AD is a complex biological process. The AD pathway of organic matter degradation is a multi-steps process of series and parallel reactions. The anaerobic degradation of organic matter can be divided in four series stages: disintegration-hydrolysis, acidogenesis, acetogenesis and methanogenesis. During the first step (hydrolysis), the complex and particulate substrates are converted in soluble and easier biodegradable compounds. Hydrolysis is a physical-chemical phenomenon, and it is the only step where the microorganisms are not directly involved during the process. More in detail, hydrolysis is a surface phenomenon where the eso-enzymes have a crucial role (Vavilin et al, 2008). The eso-enzymes are produced by the totality of microorganisms involved in the AD process. Temperature strongly influences the activity of eso-enzymes. After hydrolysis, soluble matters can pass through the cell walls of fermentative microorganisms (val Lier et al., 2008).

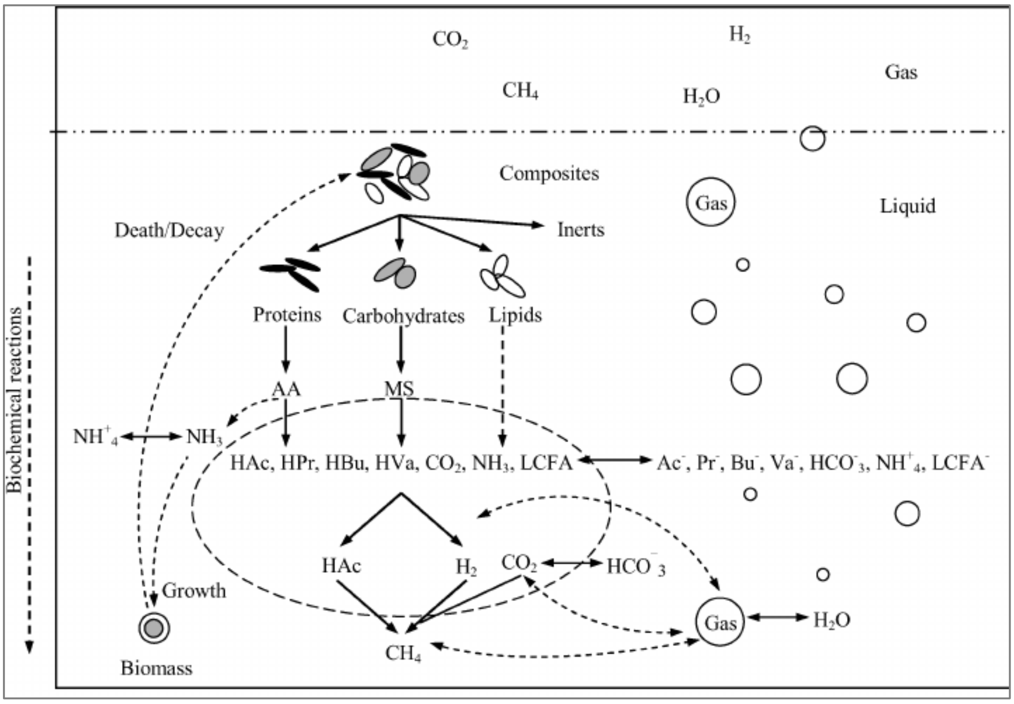

Figure 1 Physical-Chemical and biological processes involved during the AD (Batstone DJ et al, 2002)

In order to increase sludge biodegradability, hydrolysis rate, biogas/methane production, to reduce the total sludge amount that have to be disposed and the digesters volume necessary for a correct AD stabilization, in the last 30 years some researchers from both universities and private companies have developed different pre-treatment methods. Some of these methods are presented only in research papers and tested at a laboratory and pilot scales, others are fully implemented into industrial plants. Indeed, Science Direct website shows that the number of publications per year with sludge “pre-treatment” and “anaerobic digestion” as a keyword, has a sharp increase over the last twenty years (Zhen et al., 2017): only 134 papers published in 2000, over 500 papers per year since 2010 and up to 1500 papers in 2018.

Pre-treatment methods include mechanical, thermal, chemical, and biological processes. Hybrid pre-treatments are a combination of two or more of the lysis techniques previously mentioned. Recently, the study of single and hybrid WAS lysis processes has gained attention because those processes have been shown to be able to promote the hydrolysis effect onto substrates that are difficult to be biodegrades (Neumann et al., 2018).

Furthermore, different companies currently commercialize industrial hydrolysis systems such as Cambi, Turbotec, and Veolia (thermal hydrolysis), Ultrawave and Hielscher (ultrasound treatment) with worldwide applications of both (Neumann et al. , 2018).

A complete review of sludge lysis techniques is available in a rich scientific papers production. (Gonzales et al., 2018) (Zhen et al., 2017) (Carrère et al,, 2010) (Anjum et al., 2016).

Pre-treatments are more effectives to WAS than to primary sludge (PS). PS is generally easy to be anaerobically biodegraded, in contrast to WAS (called also secondary or biological sludge), that has a more complex structure. Indeed, microbial cells, cell walls, extracellular polymeric substances (EPS) and WAS membrane are strong barriers against the penetration of enzymes.

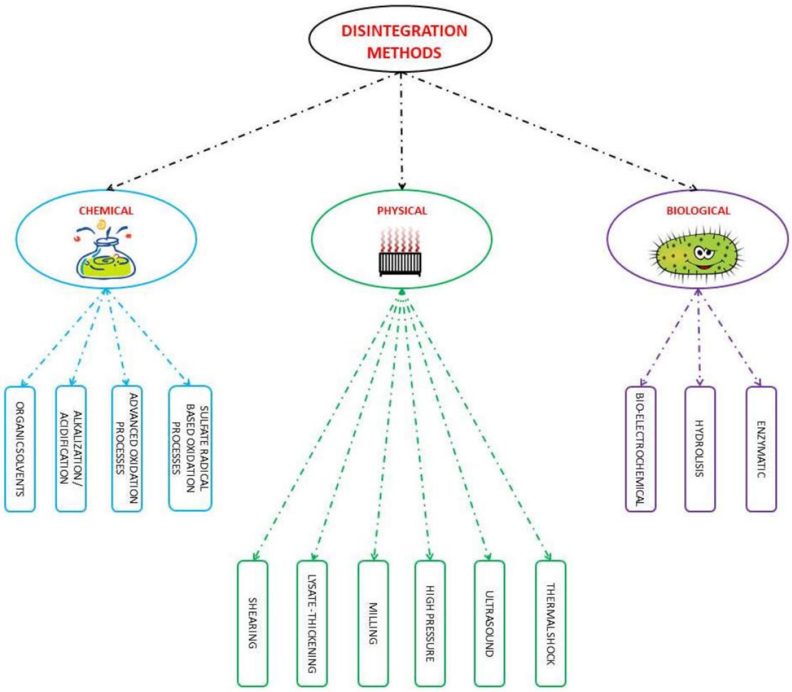

Figure 2 Avoidable disintegration methods for WAS (Wacławek et al., 2019)

"To comprehend the effects of the different pre-treatments on the anaerobic biodegradability of WAS, its composition should be identified. For instance, in term of % VS, it is composed of 10-24 % bacterial biomass, 7-19 % carbohydrates; 25-62.5 % proteins, 7.7 – 28 % humic substances and < 3.5% DNA.

The WAS is composed mostly of protein and humic acid substrates with some bacterial biomass and carbohydrate. Proteins, DNA and carbohydrates are anaerobically biodegradable compounds. However, when they are combined into an organized structure like WAS, the apparent biodegradability decreases.

Similarity, the presence of humic acid substrate is challenging for anaerobic digestion as they affect enzymatic activity by immobilizing enzymes, which, consequently lower biodegradability. In addition, humic acid substrates are difficult or impossible to degrade anaerobically." (Gonzales et al, 2018).

Therefore, the application of a lysis pre-treatment in a full WWTP not only decreases the amount of sludge that must be disposed but also increases the energy recovery from the treated substrate. The correct implementation of sewage sludge pre-treatment could drastically decrease the operational costs in wastewater treatment processes.

From the analysis of the published reviews it can be concluded that some pre-treatment techniques, such as thermal hydrolysis, thermal phased anaerobic digestion and ultra-wave hydrolysis are effective ways to increase energy production and to improve other sludge properties such as dewatering. However, these techniques require a high energy employment and both large capital expenditure (Capex) and operating expenditure (Opex). As a consequence, research on milder pre-treatment techniques is valuable (Gianico et al., 2013).

With the aim to overcome the above-mentioned problems, researching an easy implementable technique, in this dissertation a series of low thermal, chemical and hybrid (thermo-chemical) pre-treatments were studied at a laboratory scale. Moreover, the most promising pre-treatment, the thermo-chemical treatment (90 °C, 90 min.,4 gNaOH/100 gTS), was tested at pilot scale. The results obtained by the pilot-scale test were applied, to evaluate the feasibility of the proposed pre-treatment at the full-scale. The sludge used for all the experiments came from the Castiglione Torinese WWTP. Besides, all the technical and economic evaluations were done taking into account the technical data of the already mentioned WWTP.

The scientific activity, discussed in the thesis, is a part of a concluded research project in partnership between Politecnico di Torino and SMAT (Società Metropolitana Acque Torino). SMAT company is the owner and manager of Castiglione Torinese WWTP.

Chapter 1 Castiglione Torinese WWTP: a focus on the sludge line

SMAT Group, Società Metropolitana Acque Torino, is the water utility of the Turin metropolitan area. The company was founded by the union between Azienda Acque Metropolitane Torino S.p.A. and Po Sangone Company on 1st April 2001.

Currently, the SMAT Group manages the sources of water supply, one water treated plant (WTP), wastewater treatments plants (WWTPs), the distribution facilities and sewage collection networks for a catchment area of 286 Municipalities and over 4 million inhabitants served. Moreover, SMAT company manages the Castiglione Torinese WWTP.

The Castiglione Torinese WWTP is the largest Italian WWTP and treats municipal and industrial wastewater with a capacity of about 2,000,000 equivalent inhabitants. At the end of the treatment processes the water is discharged into Po river. (SMAT group, 2013)

Figure 1. 1 Castiglione Torinese WWTP. An overview

Castiglione Torinese WWTP consists of four parallel lines devoted to wastewater treatment and a sludge treatment line. Each wastewater line treats an average flow rate of about 25,000 m^3/h. The wastewater line is made up of the following processes: grid screens, grit and grease removal, primary sedimentation, pre-denitrification, biological oxidation, secondary sedimentation and final filtration. Phosphorous removal is carried out by chemical process and the dosed compound is ferric chloride. An extensive analysis of the wastewater treatment process in available in (Borzooei, 2018). The wastewater treatment process generates primary and secondary sludge that is sent to the sludge line.

1.1 Sludge line

The sludge line consists of the following treatments: pre-thickening, mesophilic anaerobic digestion, post-thickening, dewatering. Aa the end a portion of dewatered sludge is thermally dried. The pre-thickening process, carried out by means of gravity devices with the addition of polyelectrolyte for thickening of secondary sludge, reduces the volume of sludge to be treated by AD process. A flow rate of about 140 m^3/h, with an average TS content of 3.0 % for both primary and secondary sludge is anaerobically digested in six anaerobic digesters.

1.1.1 Pre- thickening Section

During the thickening of raw sludge, the sludge transferred from the water treatments modules under goes a first thickening process that increases its concentration. The raw sludge thickening section is composed of six covered sedimentation tanks in which sedimentation occurs, thus separating water from thickening sludge. The rotating bridge scraper inside each tank allows for sediment collection. The thickened sludge is removed from the bottom. The sludge is collected in a storage pit and from here it is pumped to the subsequent anaerobic digestion stage. The effluent, extracted through the top spillway of the raw sludge thickener tank, is collected, similarly to the water separated during the subsequent stage, into a storage tank and then sent to the plant inlet to be subjected to treatment in the WW line.

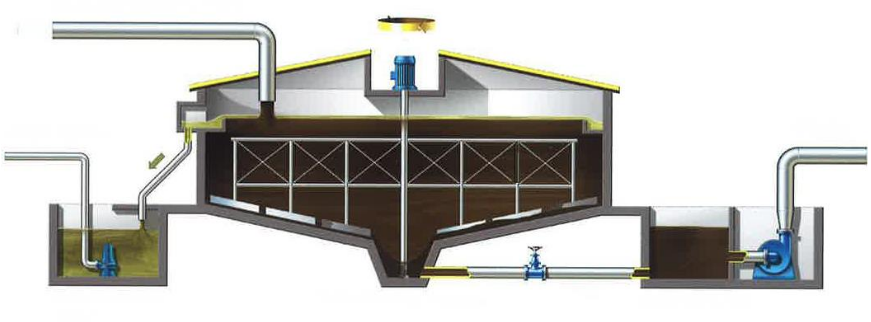

Figure 1. 2 Pre- thickener Castiglione Torinese WWTP (SMAT group, 2013)

Technical data		
Covered Circular Tanks	6	
Diameter	22	m
Total Volume	7,890	m^3
Total Area	2,300	m^2
Load	55	kg TS/m^3
Average Retention Time	6 / 24	h

Table 1. 1 Technical data –Pre-thickeners Castiglione Torinese WWTP (SMAT group, 2013)

1.1.2 Sludge Digestion

The digestion stage treats almost all the organic matter in the thickened sludge through the action of anaerobic microorganisms. The anaerobic digestion is conducted at mesophilic condition (34-40 °C). The thickened raw sludge, added to the recirculation sludge, are preheated inside of a section of a heat exchanger bundle.

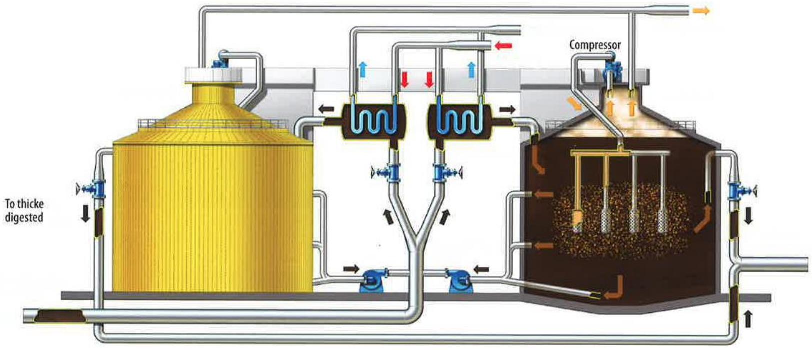

Figure 1. 3 Anaerobic Digesters. Castiglione Torinese WWTP (SMAT group, 2013)

Due to thermal conduction, the 80 °C process water yields the heat necessary to the sludge to raise its temperature.

The high temperature of the process water is guaranteed by heat recovery from the recovery of heat from engine generators, from dry section and from the direct combustion of natural gas in a boiler. The anaerobic digestion occurs inside if six digester tanks having a diameter of 26 m and height of 30 m that are equipped with a vane compressor agitation device. The biogas is filtered and stored in three gasholders having a total volume of 16,890 m^3. The gas is subsequently used for the combustion in the CHP unit.

The post-thickeners are used as storage tanks before the mechanical dewatering. During this stage the primary and secondary digestate sludge, coming from the AD process, are mixed.

Technical data		
Digesters	6	
Diameter	26	m
Height	30	m
Total Volume	72,000	m^3
Average Retention Time	15 / 20	d
Temperature	34 / 40	°C

Table 1. 2 Technical data –Anaerobic Reactors (SMAT group, 2013)

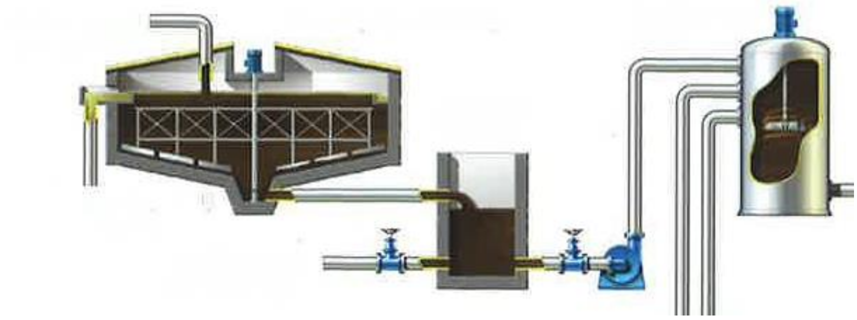

Figure 1. 4 Post- thickener Castglione Torinese WWTP (SMAT group, 2013)

1.1.3 Power station

The energy recovery station is constituted by four cogeneration engines (CHPs) coupled to alternators. The CHPs unit uses the biogas produced in the AD process as a fuel. The biogas storaged in the gasholder is compressed before the combustion in the CHPs. The engines produced heat and electricity. The heat recovered from the engine exhaust gases and cooling circuit is used to heat the process water.

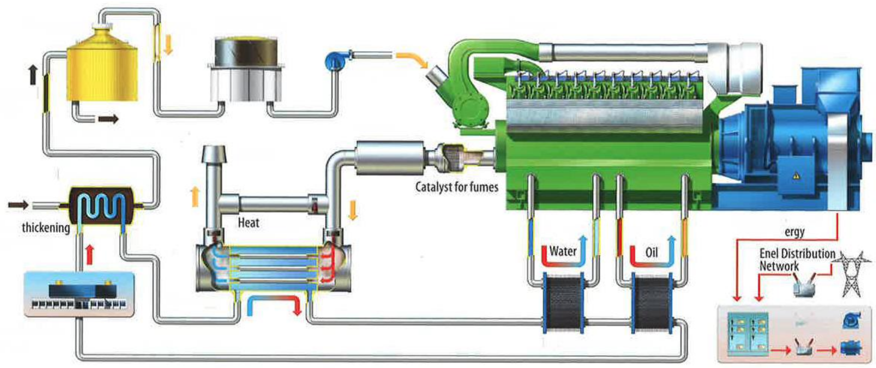

Figure 1. 5 Cogeneration Heat power unit and heat network scheme (SMAT group, 2013)

Technical Data		
Biogas Storage		
Gas-holders	3	
Total Volume	16,890	m^3
Energy recovery		
Cogeneration Heat Power Units (CHPs)	4	
Electric Efficiency	41.9	
Thermal Efficiency	42.2	

Table 1. 3 Technical data - Biogas Storage and CHPs electric and thermal efficinecies (SMAT group, 2013)

1.1.4 Dewatering

Dewatering normally takes place by means of four centrifuges. Polyelectrolyte is added to the sludge inlet flow. Polyelectrolyte is a polymeric organic reagent that allows to aggregate the organic matter contained in the sludge. The four centrifuges, having a capacity of 80 m^3/h each, receive the sludge conditioned with polyelectrolyte. Later, one part of the dewatered sludge can be sent to the subsequent drying treatment.

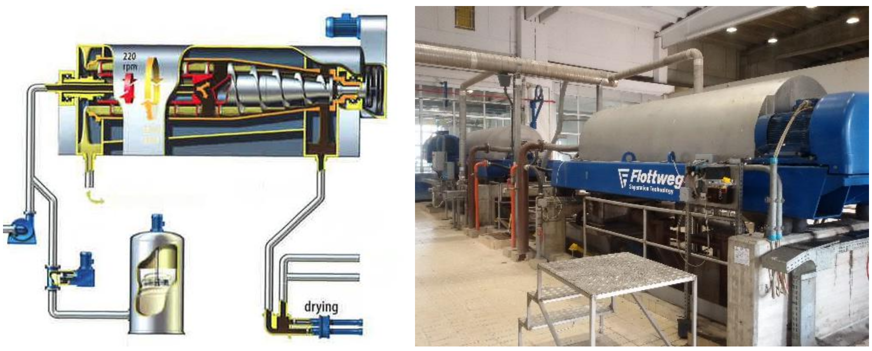

Figure 1. 6 Dewatering units (SMAT group, 2013)

Technical data		
Centrifuges	4	
Drum diameters	725	mm
Rotation speed	2,800	rpm
Centrifugal acceleration	3,160	G
Capacity (each)	80 (2 % TS)	m^3/h
Dewatered Sludge storage capacity	460	m^3

Table 1. 4 Technical data Dewatering units (SMAT group, 2013)

1.1.5 Drying Unites

The sludge drying section has two independent line with same characteristics. The dewatered sludge (after centrifuge dewatering) with a dry content of 26% is stored, for each line, in a silo having a capacity of 230 m^3. The sludge is fed to the dryer by means of a concrete piston pump. Here a list of the features of each dryer:

- Dryer puddle indirect heating;
- Heat carrier fluid: diathermic oil heated to 220 °C;
- Dryer body with diathermic oil heated jacketed
- Double shaft with diathermic oil heated hollow blades;

Each dry unit can treat 5,000 kg of sludge per hour. The inlet sludge, previously dewatered, has a total solid content equal to 26%. The dried sludge reached a total solid concentration equal to 91%. The thermal energy required by each line for the water evaporation is produced in a natural gas boiler with a power output of 3,488 kW.

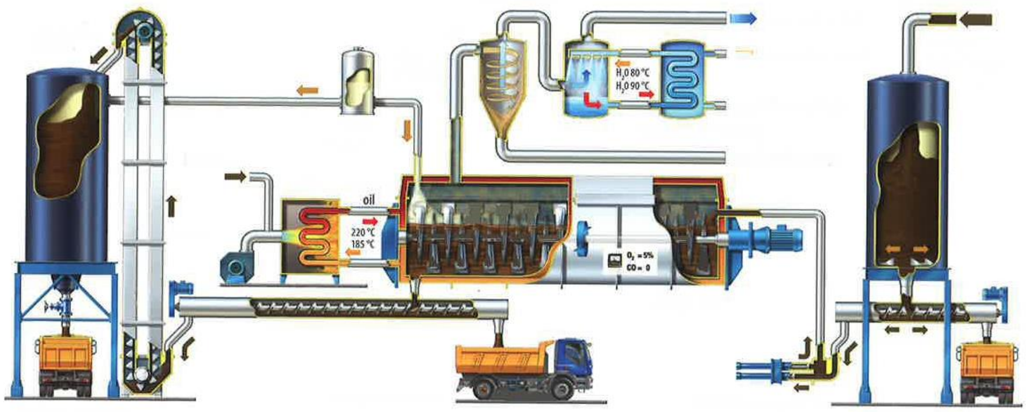

Figure 1. 7 Drying sludge Unit (SMAT group, 2013)

Technical data		
Sludge dryer system	2	
Feed (each)	5,000	kg/h
Intake Dry Content	26	%
Dry sludge productivity	1,428	kg/h
Output dry content	91	%
Output Temperature	105	°C
Evaporation capacity	3,572	kg H_2O/h
Thermal requirement (each)	2,636	kW
Thermal recovery (each)	1,750	kW
Natural gas consumption (each)	300	Nm^3/h
Electricity consumption (each)	160	kW
Process time	6	h
Dry sludge storage capacity	360	m^3
Total production	10,000	t/y

Table 1. 5 Technical data - Dry sludge unit

1.1.6 Deammonification unit

DEMON® is the deammonification process utilizing granular anaerobic ammonium oxidizing bacteria (anammox) biomass for aiding in reduction of high strength ammonia from side stream solids dewatering facilities reject flows. The true key to the success of the technology is the patented advanced biological process controls and the physical separation used to facilitate the growth and retention of the anammox bacteria.

Figure 1. 8 Deammobification Unit. Demon. Castiglione Torinese WWTP- Smat

The deammonification treatment consists in the following units:

- A pre-storage tank, it receives the centrate liquor from the dewatering unit;
- A lamella pack unit;
- A pre- equalization tank;
- A pumping section, it pumps the wastewater to the deammonification treatment unit;
- three sequencing batch reactors; where the deammonification process take place;
- a post equalization tank, where the treated water is storage before to be send to the wastewater line.

Technical data		
Average volumetric low treated	133	m^3/h
Max. volumetric low treated	90	m^3/h
Average Electric power consumption	32.7	kWe
Average N removed	48	Kg N/h
Demon unit - Capex	3,000,000	€
Demon unit – Opex	110,000	€/h

Table 1. 6 Technical data – Deammonification unit

Chapter 2 One year of monitoring of the sludge line in Catiglione Torinese WWTP

This Chapter shows the current performances of primary (PS) and secondary sludge (WAS) anaerobic digestion in Castiglione Torinese WWTP. The data analysis was carried out in order to evaluate the possible future full-scale application of the sludge pre-treatment tecniques discussed in the next Chapters. With the aim of comprehend the AD performances of the sludge line, one year of daily data were considered, from 25/10/2016 to 24/10/2017. In this study the two processes: pre-thickening and anaerobic digestion were taken into account. During the analyzed period data six pre-thickeners and six digesters were used. At the same time, four thickeners were adopted to increase the total solids content of primary sludge and two thickeners to treat the biological sludge. In the same way, four digesters were fed with primary sludge, the others two were loaded with WAS.

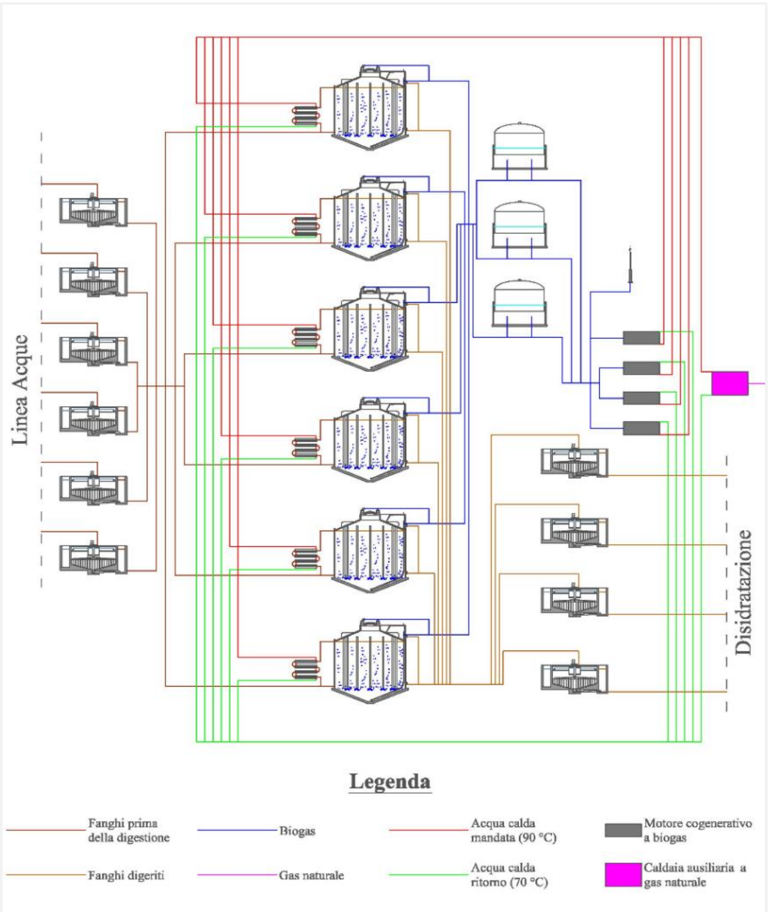

Figure 2. 1 Anaerobic Digestion, Castiglione Torinese WWTP. Flow scheme

2.1 Materials and methods

2.1.1 Analytical procedure

All the analytical parameters monitored in the Chapter, total solids concentration (TS) and volatile solids concentration (VS) were determined using Standard Methods (APHA, AWWA, WEF, 2012) and all the analysis were done in SMAT Chemical Laboratory. The gas volumes were referred to the standard condition (0 °C, 1 atm) and indicate as Nm^3. Finally, the Methane production (B) was calculated by considering the total volatile solids fed to the anaerobic reactors.

2.1.2 Data collection

All the data collected and processed were provided by SMAT company. The WWTP is equipped with a Supervisory Control and Data Acquisition (SCADA). The control system architecture is furnished of sensors, PIDs, computers, network data communications, graphical user interfaces and hardware for data storage. SCADA records the process values of the sludge line. The values used for the analysis were the daily average data processed and stored in SCADA. Both pre-thickeners and digesters are equipped with sensors. Examples of the graphical user interfaces are reported in Figure 2.2 and Figure 2.3.

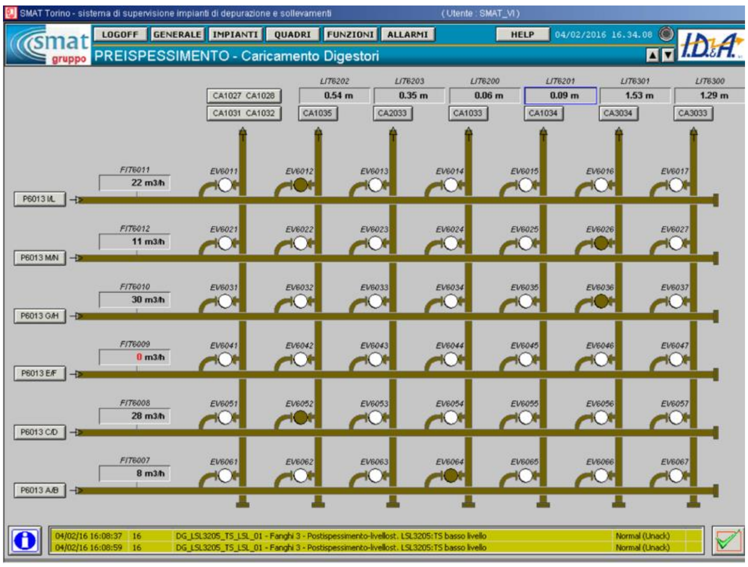

Figure 2. 2 Graphical user interfaces. Connections from pre-thickener outflow and digesters inflow

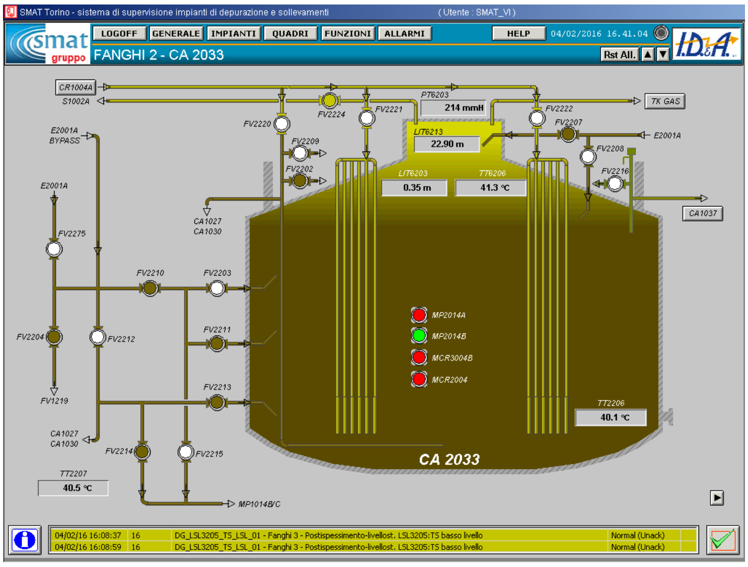

Figure 2. 3 Exempla of one SCADA digester graphical user interface

Three times a week, generally on Monday, Wednesday and Friday, a SMAT operator collected six samples, from each of the six pre-thickener outlet flows. Moreover, three times a week also digestate samples were collected; these samples came from the working anaerobic reactors.

In order to understand the nature of the sludge (PS or WAS) fed to the digesters, it was necessary crossing the data from the outflows of thickeners with the inflows fed to the digesters. Periodically, technicians of SMAT plant recorded all the changing inflow to the digesters in a paper register. By processing the collected data, it was possible to know the nature of the sludge fed to the anaerobic reactors.

Finally, in order to estimate the unknown daily concentrations of total and volatile solids concentration of the influents to the digesters as well as the TS and VS concentrations present into each anaerobic reactor, a series of linear interpolations of the data were done. The linear interpolations were performed between the available analytical data. Two examples of linear interpolation are reported in figure 2.4.

Also, SMAT Company provided the required total electric energy for the Wastewater Treatment processes (The electric consumption is reported in table

2.1). In table 2.1 the costs of electric energy, natural gas, polyelectrolyte, and sludge disposal are also reported. Moreover, the GRIN incentive for the renewable electric energy produced is described.

Castiglione Torinese WWTP	
Total Electrical Energy Required	158.5 MWh/d
Electrical Energy Price	145 €/MWh
Natural Gas Price	0.32 €/Nm^3
Incentive GRIN	0.089 €/kWh
Cationic Polyelectrolyte Price (Solution 45%)	1.38 €/kg
Dewatered Sludge Disposal Cost	90 €/ton
Dry Sludge Disposal Cost	100 €/ton
Renewable Electric Energy Incentive GRIN	89 €/MWh
Dry sludge disposal (2017)	10.000 t

Table 2. 1 Technical Data- Energy, Gas and Disposal Sludge Costs, Incentive

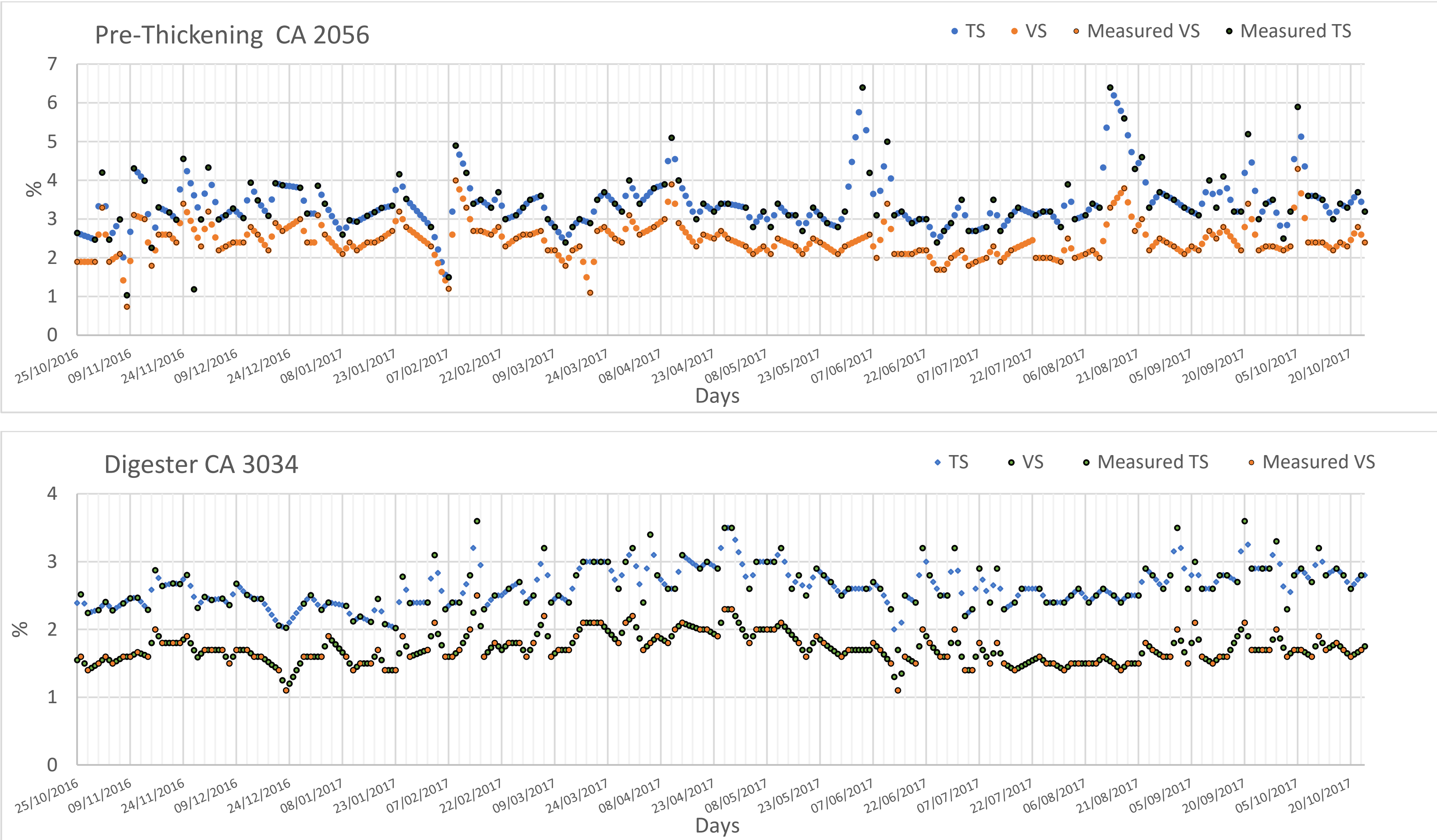

Figure 2. 4 Examples of linear interpolation. a) Pre-thickening (called Ca 2056). b) Digester (called Ca3034)

With reference to the "GRIN", it must be mentioned that in Italy the electric energy produced from renewable sources benefits from incentives. According to DM 6/07/2012, biogas from AD of sewage sludge that fuels endothermic engines is included in renewable sources. From 2017, the bonuses granted for the production of green energy are calculated by using GRIN application. According to this method, the incentive rate (I) is calculated by the following formula (GSE, 2018):

$$I = k \times (180 - Re) \times 0.78$$

Equation 2. 1

Where

- 180 is the reference value of a green certificate (equal to 180 €/MWh);
- Re is equal to the sale price of electricity defined by the Authority annually on the basis of the economic conditions recorded on the market in the previous year. For year 2017 Re was of 53,14 €/MWh;
- k is a constant, the value of which depends on the type of used renewable source; for the case considered in this study k was equal to 0.8.

Incentives are granted for a duration of 20 years, starting from the year in which they are required for the first time.

2.1.2 Energy Balance

The energy balance presented in this section is aimed to evaluate the performance of the primary and secondary sludge AD process. The study was carried out at the actual condition (no sludge pre-treatment implemented). In order to keep the process temperature at the constant value of 38°C (mesophilic condition) the heat exchangers must provide an amount of heat sufficient to warm the sludge and to offset the heat losses through the walls of digesters due to the exchange with the exterior environment. The heat necessary to the maintain the hot water circuit at the temperature of 80 °C is supplied by the cogeneration engines (CHPs) and a boiler.

The last one is fed by natural gas; the boiler is used in order to supply the thermal energy deficiency. The CHPs and the boiler have a thermal efficiency equal to 42 and 85 % respectively. The heat network is also fed to the thermal energy recovery by the sludge drying unites (see Chapter 1 - Table 1.5). However, the recovery heat linked with the dry units was not considered in the present work. In this dissertation the boundary of the system is the sludge line; consequently, the mass and energy balances of the dry unit ware not considered.

In order to keep the anaerobic digesters completely stirred conditions into the anaerobic digesters a continuous recirculation of biogas and digestate is adopted. Moreover, with the aim of obtain a good homogenization between the incoming sludge and the digestate present into the digesters, the incoming sludge is mixed with the digestate flow (average digestate flow rate is equal to 250 m^3/h) (Ruffino, 2014). The heat losses with the external ambient were evaluated by considering the materials employed for the construction and the digesters geometry. The temperature of fed sludge to the digester and soil were fixed to 15 °C. The outside temperature (exterior environment) was a monthly average as reported in UNI 10349 rule.

The following formula was used to calculate the heat losses to the exterior environment:

$$Q_{1i} = k_{Ti} \times S_i \times \Delta T$$

Equation 2. 2

Where:

- Q_{1i} is the heat losses by the generic *i-th* surface;
- S_i is the *i-th* surface
- k_{Ti} is the *i-th* surfaces global transmission coefficient. This parameter makes known all the conduction coefficients of the materials, placed in series and in the same direction of the thermal flow direction, which

constitute the digester walls and the h_{Ci} convection coefficients of the fluids present into the digester.

- ΔT is the gradient temperature between the inside and outside of the digester.

The equation used to calculate the k_{Ti} was the follow:

$$k_{Ti} = \left[\frac{1}{h_{C1}} + \sum\left(\frac{s_i}{k_{Ci}}\right) + \frac{1}{h_{C2}}\right]^{-1}$$

Equation 2. 3

- h_{C1} is the convection coefficient of the fluid in contact with the inner wall;
- h_{C2} is the convection coefficient of the fluid contact with the outer wall;
- s_i is the thickness of the i-th materials.

The energy necessary (Q_2) to heat the sludge to the prefixed temperature (38°C) was calculate as following:

$$Q_2 = qc_p(T_d - T_a)$$

Equation 2. 4

Where cp is the specific heat of sludge (assumed equal to 4,186 kJ/kg), q is the inflow rate to the digesters, Td is the digestion temperature and Ta is temperature of the inflow sludge.

Finally, the total required thermal energy is calculated as the sum of Q_1 and Q_2.

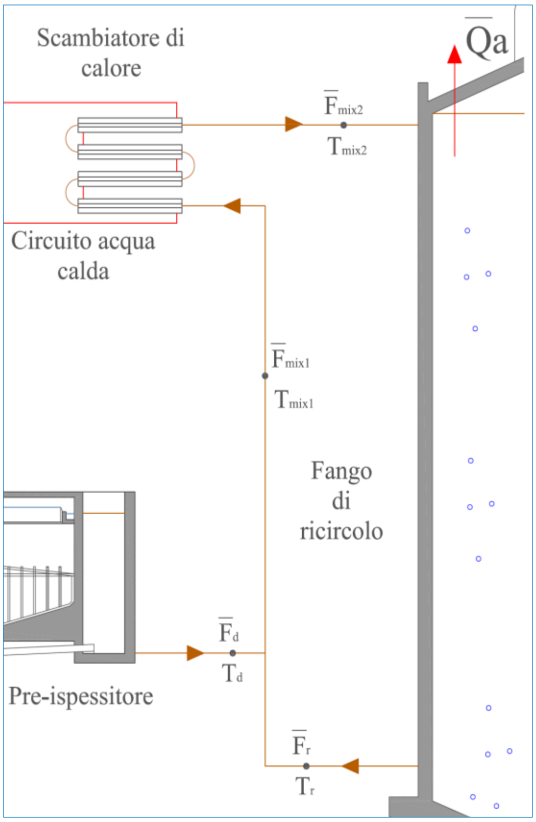

Figure 2. 5 Heat exchange system

2.2 Results

2.2.1 Mass balance and methane production

The total average mass flow rate of primary and secondary sludge sent to the digesters was equal to 4,317 kg TS/h. The substrate average VS/TS ratio was equal to 0.71. Consequently, the total average mass flow rate of volatile solids fed to the digesters was 3,051 kg/h. An amount of VS equal to 65% of VS came from primary sludge, the complementary from secondary sludge. The average concentration of TS was 3.2 % in primary sludge; this parameter was equal to 2.9 % in the WAS. The average total volumetric flow rate sent to the anaerobic reactors was 140 m^3/h. The primary sludge flow rate fed to the digesters was equal to 61,4% of the totality. The average flow rate of WAS and primary sludge fed to each digester were of 21.5 m^3/h and 27.0 m^3/h respectively.

Considering the previously reported results, the average hydraulic retention time (HRT) of all the digested sludge was equal to 17.1 days. Furthermore, known the numbers of employed digesters, the average HRTs of primary and secondary sludge were calculated; the results showed the following values: HRT 18.6 days (primary sludge); HRT 14.8 days (secondary sludge).

During one year of SCADA data monitoring, the recorded average digestion temperature values, inside the anaerobic reactors, was between 38 and 42 ° C in the case of primary sludge; while the average digestion temperature value of WAS was equal to 34 °C. The hourly average methane production in the sludge line was equal to 653 Nm^3/h. The average specific methane production (*B)* of primary sludge resulted equal to 0.288 Nm^3/VS, while the *B* of secondary sludge was 3.6 time smaller (0.09 Nm^3/VS).

The analysis of data concerning the digestate returned an average mass flow rate of discharged sludge from digesters of 3,259 kgTS/h. Therefore, the anaerobic digestion process was able to reduce the total solid production of the 25%. The percentage of reduction, taking into account the only volatile solids, increase to the 37 %. The anaerobic digestion was able to biodegrade the 44% of the primary sludge SV; indeed, the anaerobic biodegradability of secondary sludge decreased to only 16%.

Castiglione Torinese WWTP one year of monitoring		
TS_{fed}	4,317	kg/h
VS_{fed}	3,051	kg/h
$TS_{discharged}$	3,259	kg/h
$VS_{discharged}$	1,966	kg/h
Methane production	653	Nm^3/h
Primary Sludge TS_{fed}	2,755	kg/h
Primary Sludge VS_{fed}	1,975	kg/h
Primary Sludge $TS_{discharged}$	1,860	kg/h
Primary Sludge $VS_{discharged}$	1,005	kg/h
Secondary Sludge TS_{fed}	1,562	kg/h
Secondary Sludge VS_{fed}	1,076	kg/h
Secondary Sludge $TS_{discharged}$	1,399	kg/h
Secondary Sludge $VS_{discharged}$	907	kg/h
Digesters	6	
Secondary Sludge HRT	14.8	d
Primary Sludge HRT	18.6	d
$CH_{4(WAS)}$/ $CH_{4(Tot)}$	16	%
REE /EER *	44	%

*Table 2. 2 Anaerobic digestion of sewage sludge. One year of monitoring. * REE= Renewable Electric energy; EER = Electric Energy Required for the Wastewater treatment processes*

2.2.2 Thermal required energy

The required thermal power for the AD of sewage sludge in the worst condition was equal to 4,111 kW. The worst condition coincided with the month of January, when the average ambient temperature in Castiglione Torinese is the minimum in the year. The average thermal power produced from the CHPs, calculated starting from the thermal efficiency of the engines, was equal to 2,730 kW. In order to supply the necessary thermal power, the methane burnt in the boiler should be 163 Nm^3/h. The calculated values did not consider the thermal energy losses along the heat network present into the plant. Assuming that the thermal power lost by the heat water circuit was equal to 20 %, the required natural methane should be increased to 228 Nm^3/h.

2.3 Conclusions

The mass and energy balances presented in this Chapter aimed to evaluate the performances of the current sewage sludge AD process in Catiglione Torinese WWTP. The results show:

- the produced electric power by the CHPs units is equal to 2.7 MWe;
- the AD of secondary sludge contributed for only the 15 % to the total electric and thermal power production in CHPs unit. Moreover, without any treatment, the amount of WAS consumed in the AD process is equal only to 16 %; indeed, the methane specific production is equal to 0.09 $Nm^3/kgSV$;
- in the present condition the primary and secondary sludge AD process is not thermally auto-sustainable.

Therefore, the improvement actions could be the following:

- increase the dry solid content of the sludge;
- increase the methane production of WAS by using a pre-treatment before the AD;

- Increase the dry content of sludge and increase the methane productivity of WAS, a combination of the two solutions previously mentioned.

Chapter 3 Sludge Treatment Line, Castiglione Torinese WWTP. Improvement of pre-thickening sludge

The aim of the thickening process is to increase the concentration of solids in the sludge. Thickening is a solid-liquid mechanical separation and it is carried out in the sludge line in order to obtain a concentrated sludge as well as a clarified water. Thickening is achieved by subjecting sludge to thickening in special units called "thickeners".

The increase of total solids concentration should decrease the amount of thermal power necessary to keep the desired temperature for the AD process inside the digesters. By reducing the heat power necessity, the Anaerobic Digestion process should become energetic self-sustainability. The advantage should be the reduction or complete elimination of the natural gas consumption and at the same time the reduction of the number of operating digesters.

3.1 Technical introduction

The total solids content (TS) of primary sludge (PS), secondary sludge (WAS) as well as mixed sludge depend on their physical characteristics, the age of sludge, the sludge removal techniques, pumping facilities and operational methods (Metcalf & Eddy Aecom, 2014)

Thickening is a physical operation able to increase the solids content by removing a percentage of water fraction. As an example, if WAS that is commonly pumped from secondary settling tanks with a content of TS equal to 0.8 % is thickened to a concentration of 3.2 %, a four-fold reduction in total sludge flow rate is reached. Thickening is generally done by devices like: gravity settling tanks and dynamic thickeners. Centrifuges, gravity belts and rotary drums are the principal machines used as thickeners for primary, secondary and mixed sludge.

Method	*Type of sludge*	*Frequency of use and relative success*
Gravity, thickening in separate tank	Primary Sludge Waste activated Sludge Mixed Sludge	Commonly used with excellent results Seldom used: poor solid concentration (2 to 3 %) Other used.
Solid bowl centrifuge	Primary Sludge Waste activated Sludge Mixed Sludge	Often used in medium and large plants (4 to 9 TS%)
Gravity belt thickener	Primary Sludge Waste activated Sludge Mixed Sludge	Often used (4 to 9 TS%)
Rotary drum thickener	Primary Sludge Waste activated Sludge Mixed Sludge	Limited used; good results (4 to 6 TS %)

Table 3. 1 Dynamic and mechanized thickeners - Performance (Metcalf & Eddy Aecom, 2014)

The performance of gravity and dynamic pre-thickeners is typically quantified by the reached concentrations of total solids in the thickened sludge and in centate/ clarified liquor. The recovery parameter (R) is quantified by the following expression (WAF 2010, MetCalf &Eddy 2014):

$$R = \frac{TS_P \times (TS_F - TS_C)}{TS_F \times (TS_P - TS_C)}$$

Equation 3. 1

Where:

- R= recovery;
- TS_P=Total solid concentration in the thickened product;
- TS_F= Total solid concentration in the fed sludge;
- TS_F= Total solid concentration in the centrate.

In all the done considerations present in the dissertation, the recovery parameter (R) was considered constant (not improvable). Therefore, the future installation of one of the dynamic thickeners available in the market will not increase the sludge mass flow that have to be digested. Two commercial dynamic thickeners examples were reported int the following sections.

3.1.1 Rotary Screw Thickener

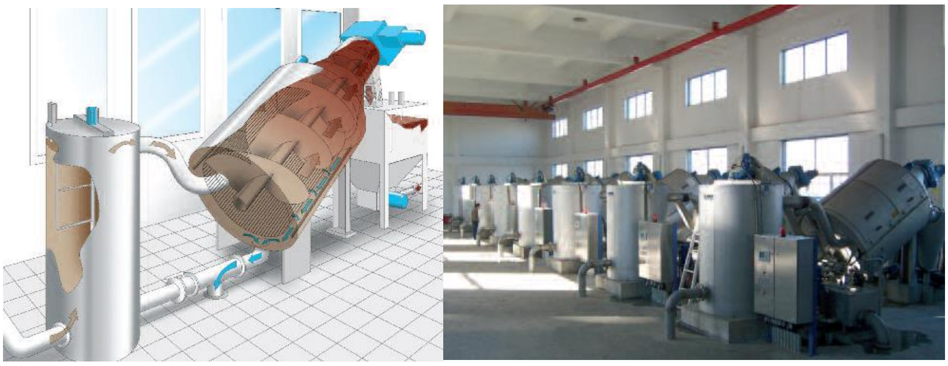

Figure 3. 1 Rotary Screw Thickener Huber

A screw thickener consists of a cylindrical section tank which retains the solids contained in the fed sludge. A screw, slowly rotating with variable speed, conveys the solids gently upward through the inclined basket. Water drains through the basket. The degree of thickening is adjustable by means of a height adjustable weir plate in the sludge discharge and the variable screw speed. A rotating spray bar cleans the wedge wire periodically from the outside during screw operation.

(Huber, s.d.)

Rotary Screw Thickener	
Typical thickening results	*> 6*
Polymer consumption	*2-3 g/kg TS*
Energy consumption	*0.03 kW/m³*

Table 3. 2 Technical Data (Huber, s.d.)

3.1.2 Belt Thickener

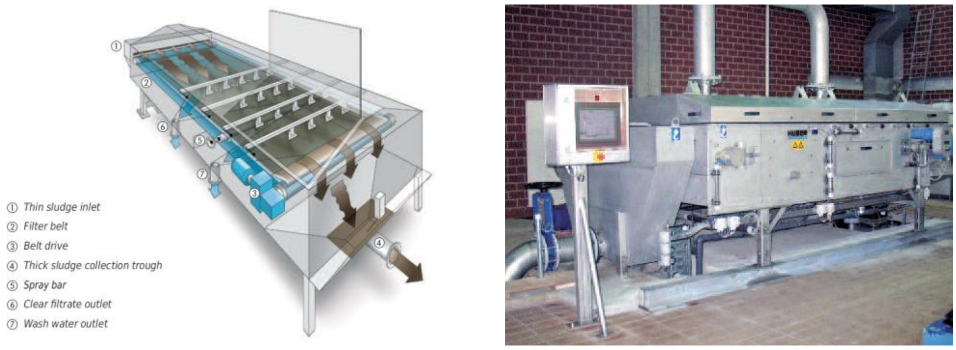

Figure 3. 2 Belt Thickener (Huber, s.d.)

The polyelectrolyte is added to the sludge and the sludge conditioned in a flocculation reactor prior to being distributed evenly over the full width of the continuously travelling filter belt. The water filtered through the belt filter cloth drains off into collection troughs whilst the solids are retained on the filter belt.

(Huber, s.d.)

Belt Thickener	
Typical thickening results	> 7
Polymer consumption	*3-5 g/kg TS*
Energy consumption	*0.035 kW/m^3*

Table 3. 3 Belt Thickener - Technical Data (Huber, s.d.)

3.2 Methods

The possible first solution to make Castiglione Torinese WWTP sludge line thermally self-sustainable is to increase the TS content of primary and secondary sludge. TS content of primary sludge ranging from 3.2 to 8.0 % was considered in the calculation. While, TS ranging from 2.9 to 8.0 % was considered for the WAS. 3.2 % and 2.9 % TS were respectively the average concentration of primary and secondary sludge fed to the digesters (see Chapter 2). In each calculation, the TS concentration of primary and secondary sludge was increased by steps of 0.1%.

In all the analyzed conditions, it was planned to mix primary and secondary sludge before the AD. Moreover, the minimum number of required digesters for the AD process was evaluated in order to maintain the HRT equal to one used in the current AD condition (HRT 17.1 days).

The research moved from the simplified hypothesis that the thermal losses through the whole heat network (HN) were equal to zero; in a second steps the thermal losses of HN were fixed equal to 20 %.

Other simplified hypotheses are the following:

- the increase of TS and VS concentration in the sludge does not affect the biogas/methane production;
- the dynamic pre-thickeners have the same recovery efficiency (*R*) of gravity pre-thickeners in terms of COD losses into the centrate (clarified water fed to the Wastewater line).

The economical assessment performed for the studied scenario in this section did not consider the costs for purchase and installation of the new dynamic thickeners, the electrical energy required for working by the new tools and the cost of the necessary polyelectrolyte.

3.3 Results

The results are summarized in figures 3.3, 3.4, 3.5 and 3.5.

The figure 3.3 shows the minimum number of employed digesters as a function of the TS content of primary and secondary sludge. The results were obtained having fixed the minimum Hydraulic Retention Time of the sludge equal to 17.1 days. Figure 3.3 displays that the sludge must be thickened at a solid concentration higher than 6 % in order to reduce to 3 the number of required digesters. In figure3.5 and figure 3.6 represent the thermal power required in order to heat the sludge to the prefixed temperature. In order to reach the thermal self-sustainable system both PS and WAS have to be overthickened. The system should be thermal self-sustainable if both primary and secondary sludge are thickened at a concentration higher than 6 %.

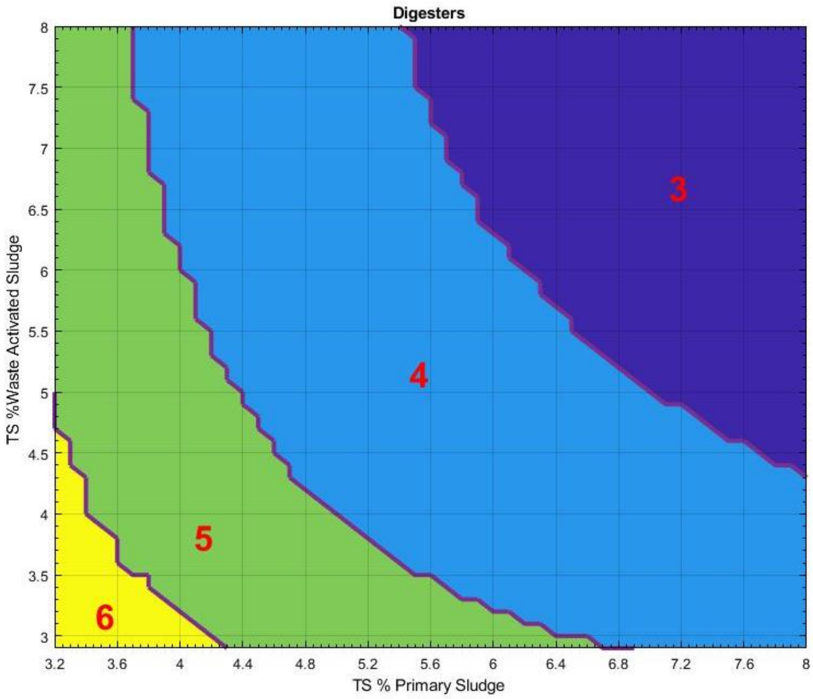

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Figure 3. 3 Number of required digesters

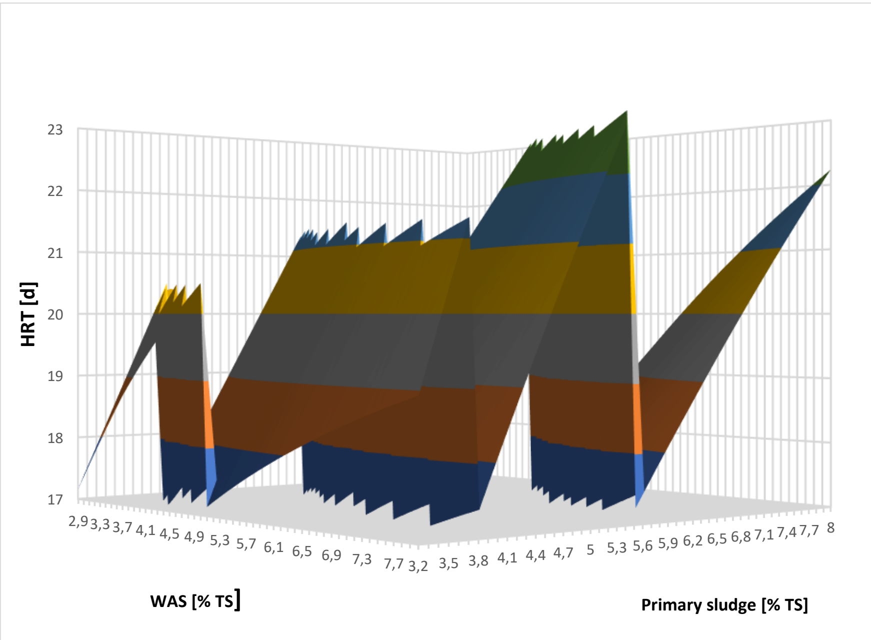

Figure 3. 4 Hydraulic Retention Time Vs % TS and Digesters used

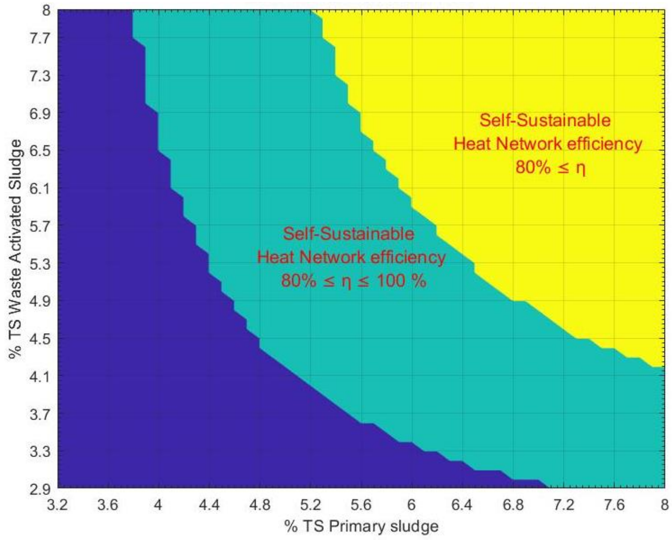

Figure 3. 5 Thermal self-sustainable

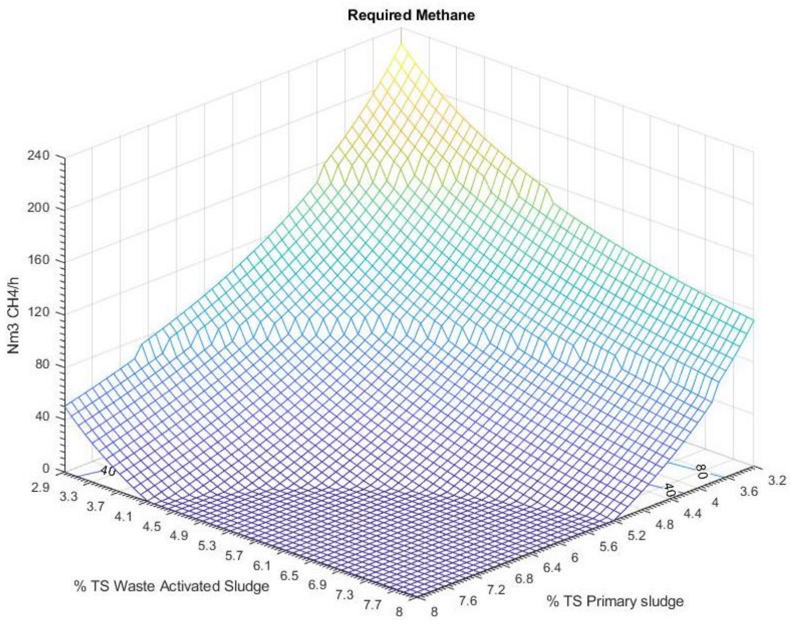

Figure 3. 6 Required Natural gas (Heat transfer efficiency equal to 80 %)

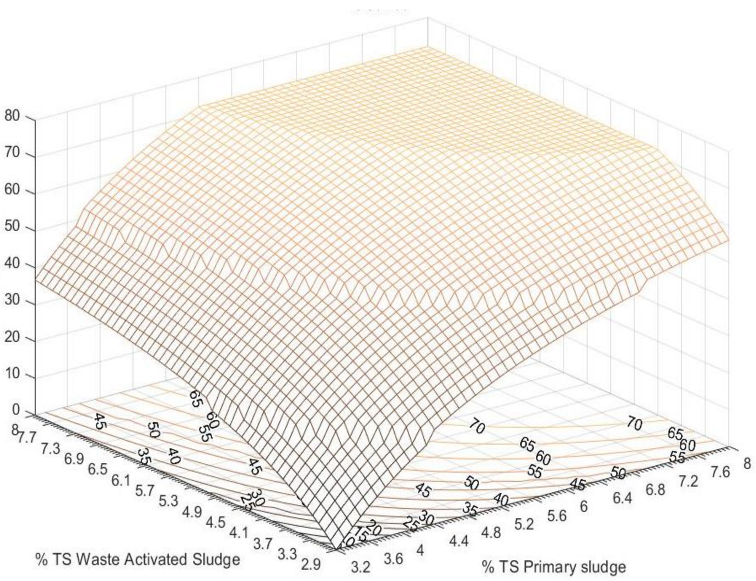

Figure 3. 7 Saved Money (Heat transfer efficiency equal to 80 %)

Chapter 4 Low-thermal, alkaline and thermo alkaline pre-treatments of WAS. Lab tests and preliminary technical-economic evaluation

Reformed and extended version of papers originally published in:

"Preliminary technical and Economic Analysis of Alkali Low temperature and Thermo-alkali pre-treatment for the anaerobic digestion of WAS" 2016.
Ruffino B., Campo G., Cerutti A., Zanetti M., Lorenzi E., Scibilia G., Genon.G.
Waste Biomass. Valor. (2016) 7, 667-675

"Pre-treatments and Intermediate Hybrid Treatments for the Improvement of the anaerobic Digestion of Sewage Sludge: Preliminary Results" 2018
Campo G., Cerutti A., Zanetti M., Scibilia G., Lorenzi E, Ruffino B.
J. Environ. Eng., 143, 1-7

"Enhancement of waste activated sludge (WAS) anaerobic digestion by means of pre and intermediate treatments. Technical and economic analysis at the full scale WWTP" 2018
Campo G., Cerutti A., Zanetti M., Scibilia G., Lorenzi E, Ruffino B.
J. Environ. Manag. (2018) 216, 372-382

"Thermo-alkali pretreatment for the improvement of the anaerobic digestion of waste activated sludge in the largest Italian WWTP" 2016
Campo G., Ruffino B., Zanetti M.C., Cerutti A., Scibilia G., Lorenzi E., Genon G.
SludgeTech 2016, London Uk

This Chapter presents the results of anaerobic lab tests and the preliminary technical and economic assessment of alkali, thermal and thermo-alkali pretreatments. The tested substrate was the Waste Activated Sludge (WAS) and all the thermal pre-treatments were conducted at low temperatures (below 100°C). The data employed for the preliminary technical and economic assessment come from the Castiglione Torinese WWTP are presented in Chapter 2.

Waste activated sludge samples were collected from the WWTP and subjected to pretreatments. The doses of NaOH and $Ca(OH)_2$ were included in the range between 0.04 and 0.20 g alkali/g TS; the tested contact times were 1.5 and 3.0 h; finally the tests were conducted at the following temperatures 20, 70 and 90°C. The performance of each treatment process was assessed first by determining the Disintegration Rate (DR) and then by undergoing the treated WAS were submitted to batch mode anaerobic digestion tests (mesophilic conditions, 38 °C).

The results of the methane anaerobic tests revealed that the methane yield increase of 28.0, 44.8 and 68.1%, in comparison to the untreated sample, if WAS samples were treated with a NaOH dose of 0.04 g/g TS at respectively 20, 70 and 90°C. The 1.5 hour of 0.04gNaOH/100 kgTS alkali treatment at 70 and 90 °C can respectively add +146 €/h and 195 €/h thus increasing the financial benefit of whole process.

4.1 Materials and methods

4.1.1. Waste Activated Sludge

The waste activated sludge used in this study was collected from one of the secondary settling tanks in the Castiglione Torinese WWTP. Raw WAS samples were firstly sieved by a 48-mesh Tyler Standard sieve, in order to remove coarse particles and impurities (larger than 0.295 mm). Subsequently they were thickened from an initial total solid (TS) content of about 0.8% 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 (soluble COD) which is the COD in the liquid phase after filtration on a 0.45 µm acetate-cellulose membrane, pH, electrical conductivity (EC), elemental composition that is C, H, N, S content, and soluble ammonium were determined according to standard methods (APHA, 2012) (APHA, AWWA, WEF, 2012) The total COD of sludge (tCOD) was calculated from the outcomes of the elemental analysis as in van Lier et al 2008 (val Lier J.B., 2008).

4.1.2 Thermo, alkali and thermo-alkali pretreatments

The hydrolysis techniques employed in this study were:

- Low thermal treatment (70°C and 90°C)
- Alkali pretreatment (NaOH and $Ca(OH)_2$) with different dosage between 0.02 and 0.4 g hydroxide/g TS;
- Thermo-alkali pre-treatment, a combination of the above-mentioned processes;

In all cases, the duration of pretreatments was fixed to 1.5 or 3.0 hours. All the pretreatments were performed at laboratory scale. The pretreatments were carried out on WAS samples in 500mL DURAN® laboratory bottle equipped with screw caps. The thermal pretreatments were conducted on 250 mL of sludge; conversely, for alkali and thermo-alkali pre-treatments only 200 mL of raw sludge with 50 mL of alkaline solutions were used. Alkali solutions that contained the dose of chemical chosen for the test were obtained starting from a 100 g/L alkali mother solution.

The bottles were immersed in a thermo-static bath, the water inside was preheated at the temperature decided for the tests. In the case of thermal and thermo-chemical pretreatment at the end of the treatment the bottles were cooled to room temperature using tap water.

Figure 4. 1 Employed thermo-static batch reactor

Before and after pretreatment the measurement of pH, EC and sCOD, was performed. At the end of the treatment, the sludge liquid phase was separated from the corpuscolate phase by means of centrifugation (4000 rpm, 15 min). The supernatant was subsequently filtrated on 0.45 μm acetate-cellulose membranes. Seven series of tests were conducted. They were designed to investigate the effect of different parameters on the solubilization of COD. DR is one of the most commonly used indicators to compare the effectiveness of different WAS pre-treatments (Dohányos M. et al., 1997). The employed formula for DR calculation was the following:

$$DR = \frac{sCOD_i - sCOD_0}{tCOD - sCOD_0}$$

Equation 4 1

Where: the parameters tCOD, $sCOD_0$ and $sCOD_i$ refer to the total COD of sludge and the soluble COD before and after pretreatment respectively.

4.1.3 Laboratory methane production test

Digestibility tests, carried out in duplicate, were performed in order to assess the effect of the different pretreatment conditions on WAS anaerobic biodegradability and to verify the correspondence between the increase of soluble COD and methane production.

After the lysis tests, only the techniques considered more suitable for future application at the full scale were anaerobically tested. The treatments considered were:

- Low temperature thermal pretreatments:
    1. 70°C, 1.5 h;
    2. 90 °C, 1.5 h;
- Alkali pretreatments:
    1. 0.08g NaOH/gTS 1.5 h, 20 °C, pH 7.5;
    2. 0.08g NaOH/gTS 1.5 h, 20 °C, pH 8.5;
    3. 0.04g NaOH/gTS 1.5 h, 20 °C, pH 7.5;
    4. 0.04g NaOH/gTS 1.5 h, 20 °C, pH 8.5;
- Thermo-alkali pretreatments:
    1. 0.04g NaOH/gTS, 1.5 h, 70 °C, pH 8.5;
    2. 0.04g NaOH/gTS, 1.5 h, 90 °C, pH 8.5;

Lab anaerobic digestion tests (LADT) were performed in batch mode and in mesophilic condition (38°C). Due to the limited availability of lab-scale digesters, four series of tests were performed. Each series consisted of two inoculum samples, two untreated samples (control), two pairs of samples, each one subjected to different pretreatment method. For each series of tests 8 lab digesters were used. All the anaerobic reactors were immersed in a controlled temperature water bath. Six digesters each one with a total volume of 6 L (Working Volume 4 L) each were used. Moreover, for each series of tests other two batch reactors were used (Total volume 2.8 L). The 2,8 L lab-reactors were used to evaluate the residual methane production of the inoculum. The working volume of the two reactors was equal to 2.0 L.

For each reactor, the produced biogas was collected in one or two 5 L Tedlar bags connected to each other. The characterization and measurement of the volume of the produced biogas was carried out daily, throughout the whole duration of the tests. The characterization, which is the volumetric composition of the biogas in terms of CH_4, CO_2, O_2 was obtained by analyzing 500 mL of biogas with a biogas analyzer (Biogas Check 3000, Geotechnical Instruments Ltd). The residual volume of the biogas after characterization was measured by replacing volumes of water with the residual gas. Daily, the temperature of laboratory was recorded. The produced volumes of biogas and methane were referred to the standard condition (0°C, 1 atm).

The substrate inoculum ratio S/I was fixed to 1.5 g VS added/g VS inoculum. The chosen ratio is higher than the optimal values suggested by the literature (Angelidaki at. al, 2004), (Angelidaki and Sanders 2008), (Angelidaki et al. 2009) (S/I equal to 0.5 g VS added/g VS inoculum). This choice was dictated by the limits of the used biogas analyzer and by the low anaerobic biodegradability of the tested substrates. A good characterization of the produced biogas is possible only with a considerable volumetric production of gas.

The inoculum employed during the anaerobic digestion tests was collected in one of the six digesters of the WWTP of Castiglione Torinese. The characterization of the used inoculums for the tests is shown in table 1. In order to deplete the residual biodegradable organic material present in the inoculum, a "degassing" phase has been carried out as suggested by Angelidaki el al. 2009. The pre-incubation of inoculum was done at the same temperature values at which the consequent anaerobic digestion tests. Degassing duration was prolonged until no significant biogas volumes were produced (approximately 4-6 days of incubation). The batch digesters were checked for any leakage and flushed with 100% pure nitrogen for approximately 3 min to ensure anaerobic conditions. The tests were considered concluded when the cumulative biogas curve reached an asymptotic trend (observed variation in the cumulative production was below 1%) as normed by VDI Standard (2006).

Figure 4. 2 Batch AD tests. Lab reactors

4.1.4 pH adjustment after alkali and thermo-alkali pretreatment

The pH values resulting from alkali and thermo-alkali treatments (pH>10) were incompatible with an AD process. It was therefore necessary to restore the pH values close to neutrality. For pH correction 1M HCl solution was employed. Doses of HCl necessary to restore pH to values suitable for the AD were firstly determined on a lab scale using samples of small volumes (50 mL). 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 large volume.

4.2 Result and discussion

4.2.1 WAS analysis before pre-treatments

The elemental composition of the sludge (on volatile dry basis) used in the tests was equal to C 48.0%, H 16.9%, N 7.1%, O 37.2% by weight. Assuming the chemical formula of $C_aH_bO_cN_d$ for volatile dry sludge, the a,b,c d values can be identified as follow: a = 7.94; b = 13.61; c = 4.60; d = 1.00.

Consequently, the ratio between COD and VS has been calculated as 1.35.

4.2.2 Effect of pretreatment DR ad pH

All the results of the sludge treatment method tested in this study were reported in figures 4.3, 4.4, 4.5 4.6 and 4.7.

Figure 4.3 shows the effect of the alkali dosage (0-0.2 g alkali/g TS) at 20 °C in terms of DR and pH values. It is clear that the effect of the alkali treatment with NaOH, in all tested dosages, was stronger than that of the $Ca(OH)_2$ treatments. The treated sludge with NaOH (0.2 g /g TS) reached a DR value close to 30%. For the dosage of 0.2 g NaOH/g TS, the DR value was approximately 3.5 times higher than the maximum value obtained with $Ca(OH)_2$. As results of adding alkali solution, the pH of all pre-treated samples sludge increased. The result of the addition of alkali solution was a pH increase in all the pre-treated sludge samples. As expected, the highest pH values were recorded for the sludge treated with 0.2 g NaOH/g TS.

The results of a comparison of the effect of alkaline treatments at room (20 °C) and 70°C temperature values can be seen in the figures 4.4, 4.5 and 4.6. The DR values reported in figure 1.1b show the low capacity of the $Ca(OH)_2$ treatment in COD solubilizing.The effect of applying heat and $Ca(OH)_2$ in the same treatment was almost the same as the effect of only thermal treatment. Moreover, the pH values of sludge after thermo-alkaline pre-treatments were lower compared to those samples from only alkaline pre-treatments. The pH values were equal to 7.74 and 8.91 respectively. Figure 4.6 shows the DR values obtained from thermal, alkali and thermo-alkali pretreatments for a 0.04 g/g TS dosage of NaOH and contact times of 90 and 180 minutes. It can be seen that the thermo-alkali treatment carried out at 90°C for 90 minutes led to a DR close to 40%. With an increase of the duration of the pre-treatment to 3 hours, the DR value was also increased to approximately 45%, slightly less than two times the result obtained with the only thermal treatment at 90°C. The DR value resulted from combination of thermal and alkali pretreatment, with a dosage of 0.04 g alkali/g TS, is approximately equal to the sum of the DR values for each pre-treatment methods. For example, DR value for the sludge treated for 90 min. at 70 °C was close to 12%, the same sludge alkali-treated for the same time at 20 °C reached a DR equal to 11.8%, the combined effect of alkali and thermal treatment generated a DR equal to approximately 24 %.

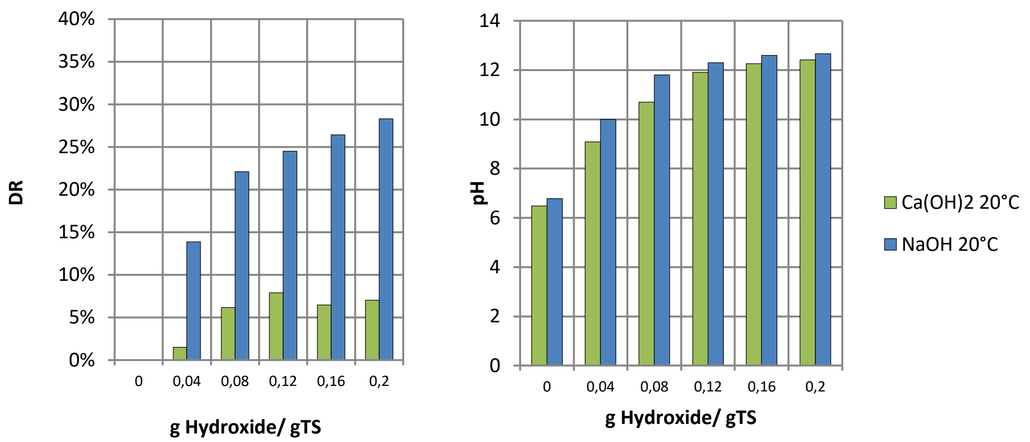

Figure 4. 3 Alkaline tratments

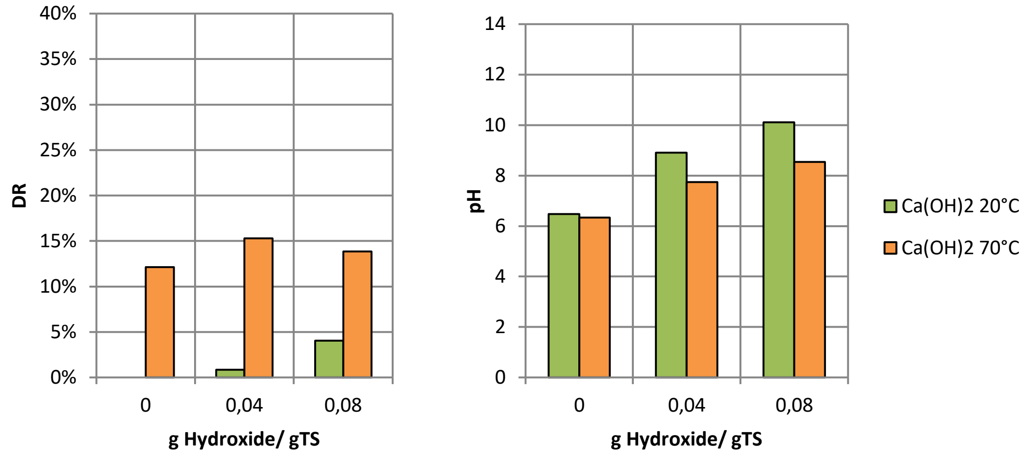

Figure 4. 4 Thermo alkali treatments

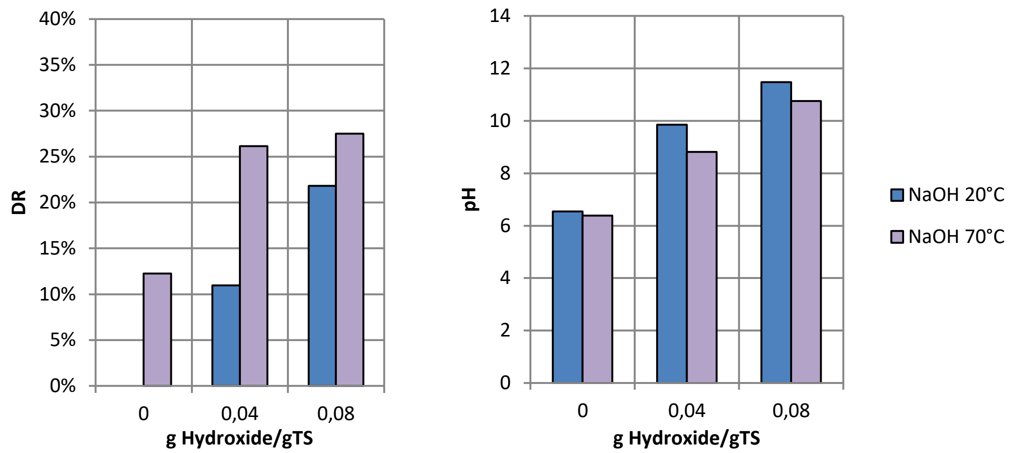

Figure 4. 5 Thermo-alkali treatments

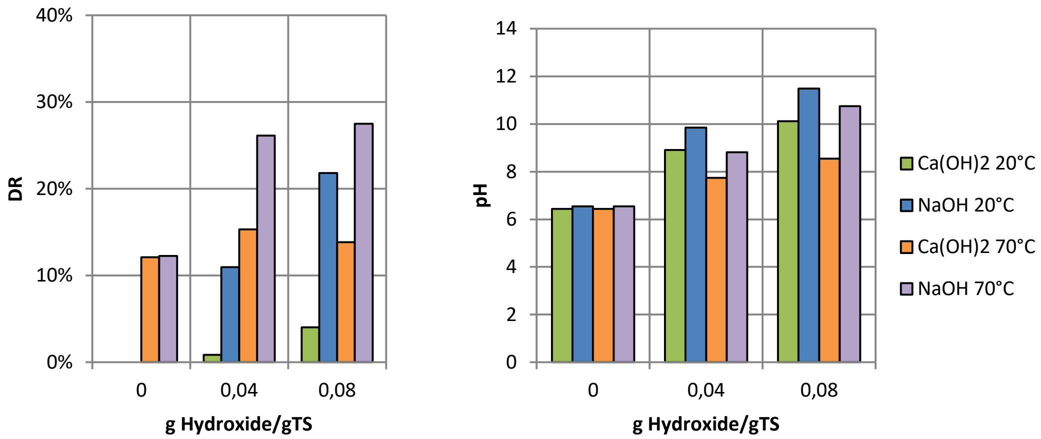

Figure 4. 6 Thermo-alkali treatments

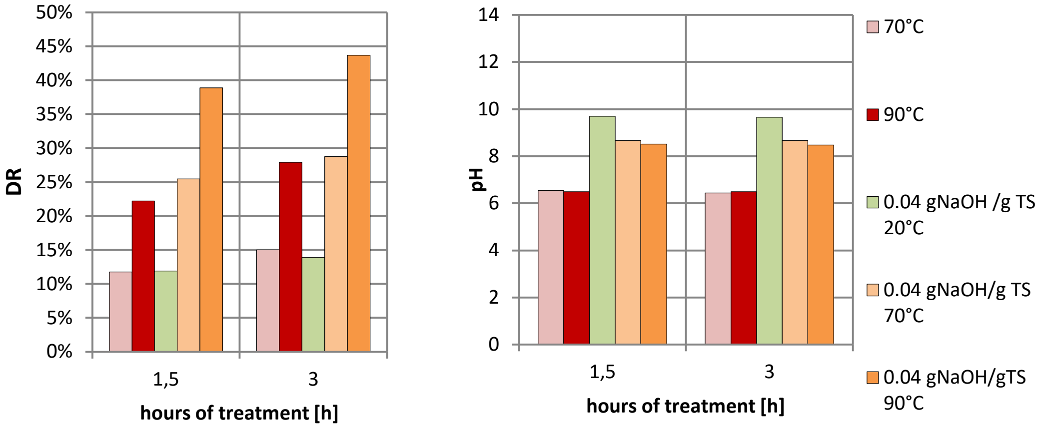

Figure 4. 7 Thermal vs thermo-alkaline treatments

Temperature [°C]	Pre-treatments alkali dose	Time [h]	pH	DR
20	0.04 gNaOH/gST	1.5	10.0	14%
20	0.08 gNaOH/gST	1.5	11.8	22%
20	0.12 gNaOH/gST	1.5	12.3	25%
20	0.16 gNaOH/gST	1.5	12.6	26%
20	0.20 gNaOH/gST	1.5	12.7	28%
20	0.04 $gCa(OH)_2/gST$	1.5	9.1	1%
20	0.08 $gCa(OH)_2/gST$	1.5	10.7	1%
20	0.12 $gCa(OH)_2/gST$	1.5	11.9	3%
20	0.16 $gCa(OH)_2/gST$	1.5	12.3	6%
20	0.20 $gCa(OH)_2/gST$	1.5	12.4	7%
20	0.04 gNaOH/gST	1.5	9.9	11%
20	0.08 gNaOH/gST	1.5	11.5	22%
70		1.5	6.4	12%
70	0.04 gNaOH/gST	1.5	8.8	26%
70	0.08 gNaOH/gST	1.5	10.7	27%
20	0.04 $gCa(OH)_2/gST$	1.5	8.9	1%
20	0.08 $gCa(OH)_2/gST$	1.5	1011	4%
70	0.04 $gCa(OH)_2/gST$	1.5	7.7	17%
70	0.08 $gCa(OH)_2/gST$	1.5	8.5	16%
20	0.04 gNaOH/gST	1.5	9.7	12%
20	0.04 gNaOH/gST	3.0	9.7	14%
70		1.5	6.6	12%
70		3.0	6.4	15%
70	0.04 gNaOH/gST	1.5	8.7	25%
70	0.04 gNaOH/gST	3.0	8.7	29%
90		1.5	6.5	22%
90		3.0	6.5	28%
90	0.04 gNaOH/gST	1.5	8.5	39%
90	0.04 gNaOH/gST	3.0	8.6	44%

Table 4. 1 Disintegration Rate tests. Results

4.2.3 Anaerobic digestion

Not all the pretreatments condition tested in order to assess the COD release were evaluated in terms of biogas and methane potential increases. Indeed, only eight treatment condition considered the most suitable for future applicability at the full scale were anaerobically tested at laboratory scale. Pre-treatment conditions for AD lab tests and the relative results are reposted in table 4.1 and 4.2.

Substrate	Series of tests	Test durations [d]	Bo [Nm^3 CH_4/kg VS]	Standard Deviation
Un-treated WAS	4	19-21	0.132	± 0.05

Table 4. 2 Anaerobic digestion tests. Raw WAS results

Pre-treatment	*Test duration [d]*	*Added acid [g HCl/100g TS]*	*Increase in Biogas yield [%]*	*Increase in CH_4 yield [%]*
70 °C 1.5h	19		11.6	13.1
90 °C 1.5h	19		18.7	19.3
8g NaOH/100 g ST- pH 7.5 - 20 °C, 1.5h	20	4.73	18.4	18.4
8g NaOH/100 g ST- pH 8.5- 20 °C, 1.5h	20	3.78	16.4	16.4
4g NaOH/100 g ST -pH 7.5 - 20 °C, 1.5h	21	2.56	4.6	0.9
4g NaOH/100 g ST - pH 8.5- 20 °C, 1.5h	21	1.52	19.2	28.0
4g NaOH/100 g ST- pH 8.5- 70 °C, 1.5h	20	0.00	26.8	46.8
4g NaOH/100 g ST - pH 8.5 -90 °C, 1.5h	20	0.00	56.2	86.1

Table 4. 3 Thermal, alkaline and thermo-alkaline WAS pre-treatments. Lab anaerobic digestion tests results

The only thermal pretreatments (<100°C) were the first techniques anaerobically tested. Thermal treatments at 70 and 90°C for 90 min have been studied. The results show an increase in biogas yields equal to 11.6 (13.1% methane) and 18.7% (19.3% methane) at 70 and 90 °C respectively and compared to the untreated sample.

The WAS pre-treated with 0.08 NaOH/g TS, for 1.5h and at room temperature (20°C) was the second pretreatment technique anaerobically digested. The sludge after pretreatment had a pH value equal to 11.58, it was not suitable for the success of an AD process. Consequently, in order to make this parameter compatible with the development of a biological process, avoiding inhibition phenomena, the final pH value of the systems was corrected to neutral conditions with HCl solutions. In the performed tests the doses of 1M HCl solution required to bring the pretreated sample, respectively, at pH 8.5 and 7.5, resulted of 0.038 g HCl/g TS and 0.047 g HCl/g TS respectively. The results of these BMPs show that the biogas/methane yields of the two conditions taken into account were approximately equal. The details of the production are shown in table 4.2.

The third pre-treated sludge system subjected to anaerobic digestion was 0.04 g NaOH/g TS, 1.5h and at 20°C. The sludge after alkaline pretreatment presented a pH value equal to 9.81. As in a previous case, also in these tests the pH value was corrected to reach the value of 8.5 and 7.5. The results of this digestion experiences (reported in table 4.2) show no big difference with the sludge treated with the double dosage of NaOH.

The fourth series of tests, involved samples treated with 0.04 g NaOH/g TS at 70 and 90 °C for 90 min. The biogas production registered an increase of 30.7 %, respect to control sample, for the sample treated at 70°C; also, the sample treated at 90°C showed an increase of the same parameter equal to 46.2%.

Better results were obtained if specific production of methane is considered. In detail the results show an increase of methane yield equal to 46.8% and 86.1% at 70 and 90 °C respectively.

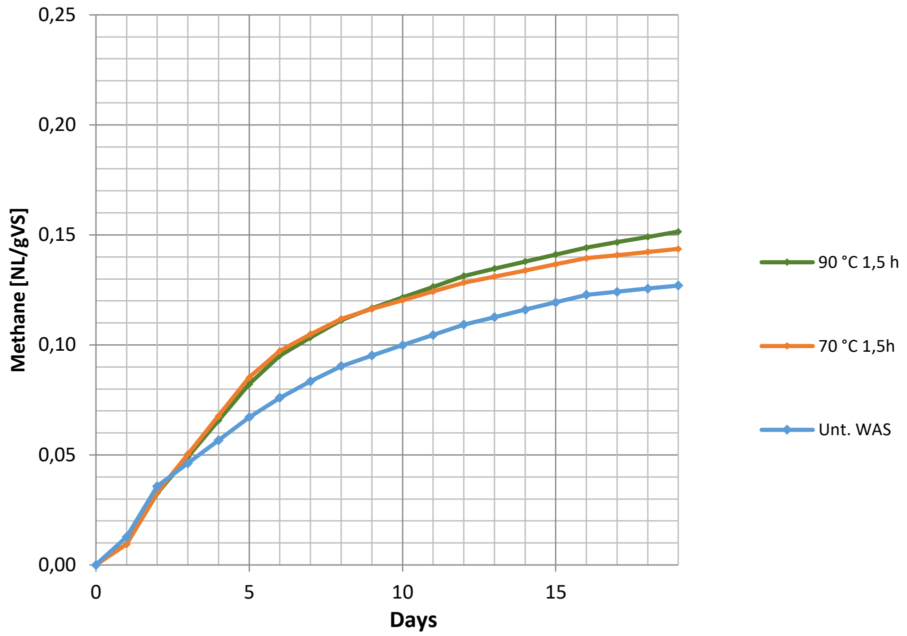

Figure 4. 8 Low temperature thermal treatments. Methane production

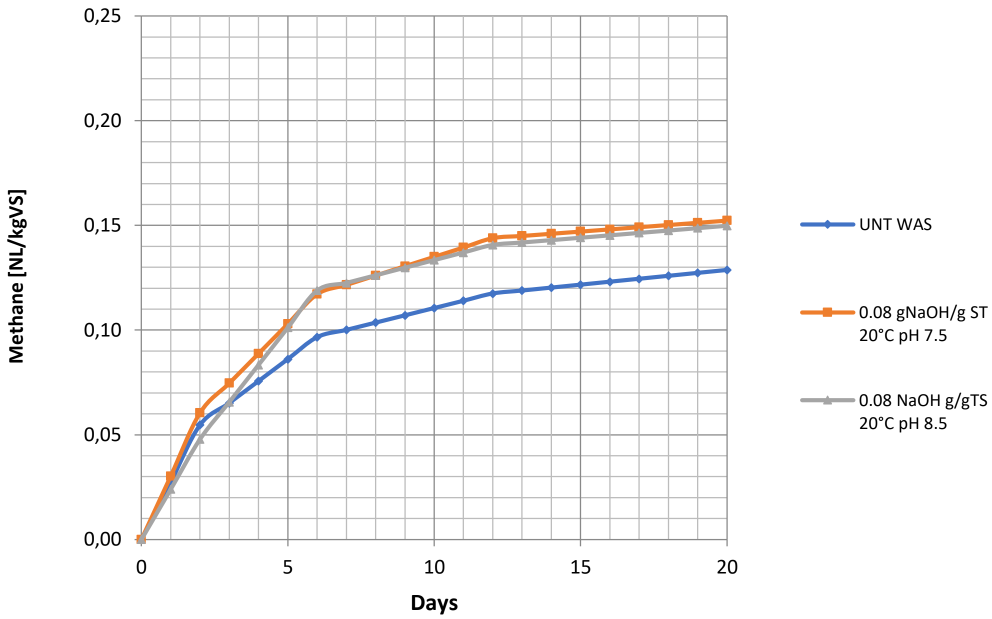

Figure 4. 9 Alkali treatments (8 g NaOH/100 gTS). Methane production

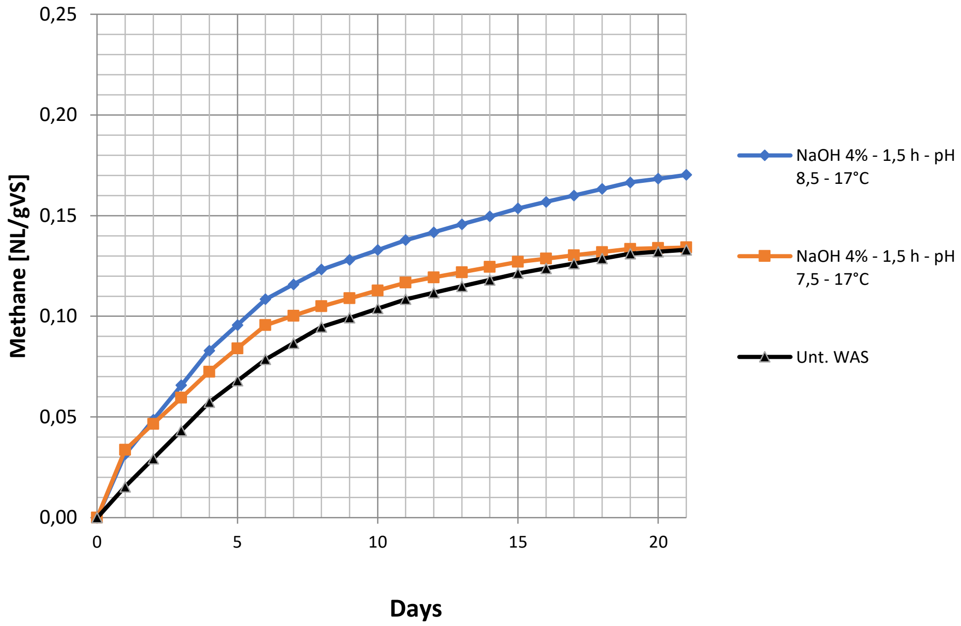

Figure 4. 10 Alkali treatments (4g NaOH/100 gTS). Methane production

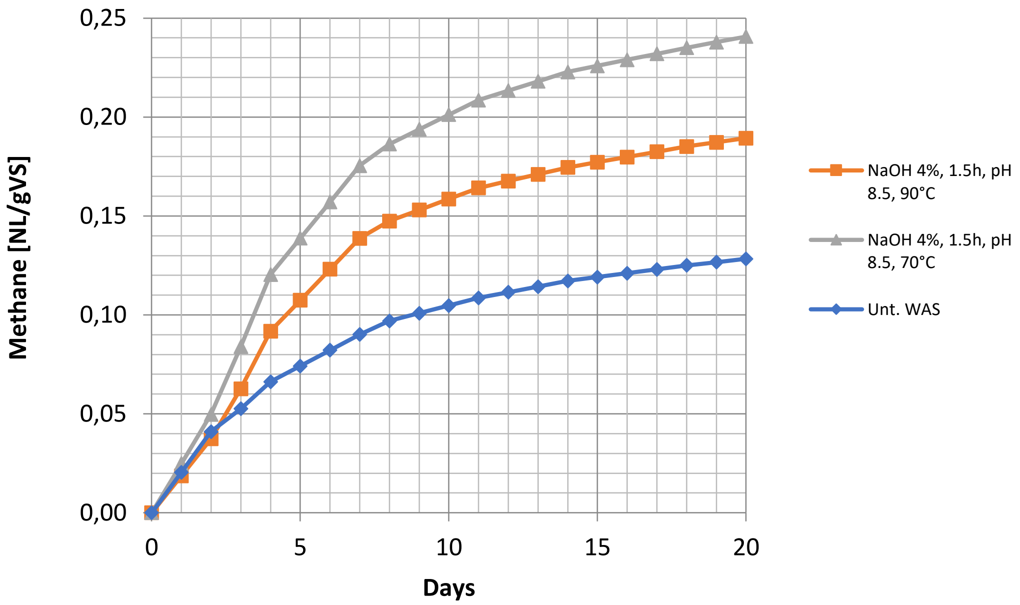

Figure 4. 11 Thermo-alkali pre-treatments. Methane production

The results of the AD tests can be compared with those from the studies of Kim et al. 2003 (Kim J, 2013) and Cho et al. (Chao S.K, 2014) , who performed alkali and thermo-alkali pretreatments on WAS. As mentioned before, Kim et al. 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 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 et al. (30 % of the TS content) was 7.5 times higher than the dose employed in the second series of tests of this work.

On the other hand, Cho et al. examined the technical and economic performance of an alkali-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. These last results were very surprising and went from the very low methane yield of the control (0.034 Nm^3CH_4/kg VS compared to 0.132 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 in the tests. As discussed in ‘‘pH Conditioning’’ section, the type and the amount of substances (organic acids) released during a pretreatment strongly affect the final pH value of sludge and no direct correlation between alkali dose and pH value may be found.

4.2.4 Preliminary cost-benefit analysis

In order to evaluate the performance of the pretreatments and its applicability at the full scale, not only the benefices associated with the increase in the methane yield but also the costs of thermal power and the necessary reagents for the treatment must be considered.

The results obtained throughout the overall experimentation (thermal, alkali and thermo-alkali pretreatments, neutralizing trials and digestibility tests) were used to evaluate the economic feasibility of the treatments. However, in this work only the operating costs were considered and not investments, maintenance and manpower costs concerning needful equipment, installations and procedures.

With reference to the costs necessary to perform the pre-treatment, the costs of reagents, amounting to 0.45 €/kg for NaOH and 0.6 €/kg for HCl (Solvay, s.d.), were considered. As reported in Chapter 3, in the situation evaluated (from 25/10/2016 to 24/10/2017) the thermal balance of primary and secondary sludge digestion in the studied WWTP was negative because, the AD process required an average consumption of auxiliary methane of about 228 Sm^3/h.

All the graphical results of preliminary cost-benefit analysis relative to nine studied Scenarios were reported in figures 4.12, 4.13, 4.14, 4.15, 4.16, 4.17, 4.18 4.19 and 4.20.

Table 4.3 presents the results of the preliminary analysis of economic feasibility of the thermal, alkali and thermal-alkali pretreatments tested with lab scale digesters. The assessment of the economic sustainability is a balance between the costs that are necessary to support the pretreatments and the economic value of the surplus products (only electricity) obtained after anaerobic digestion. The analysis was aimed to seek the value of percentage increase of methane that must be achieved in order to balance the costs of pretreatment (see table 4.4).

Scenario	1*	2	3	4	5	6	7	8	9
Dose [g NaOH/100 gTS]		0	0	8	8	4	4	4	4
Pre-treatment temperature [°C]		70	90	20	20	20	20	70	90
Target pH before AD				7.5	8.5	7.5	8.5	8.5	8.5
Acid treatment, HCl dose				4.73%	3.78%	2.57%	1.52%	0	0
Cost of the alkali pretreatment €/kgTS				0.024	0.024	0.012	0.012	0.012	0.012
Cost of the acid treatment €/kgTS				0.028	0.023	0.015	0.009	0	0
Total cost of the pretreatment €/kgTS				0.052	0.047	0.027	0.021	0.012	0.012
Total cost of the pretreatment €/kgVS				0.074	0.066	0.039	0.030	0.017	0.017
Increase in CH4 yield		13.1	19.3	18.4	16.4	0.9	28.0	44.8	86.1
Increase in CH4 yield – target				68.2	60.8	27.7	21.4	11.8	11.8

Table 4. 4 Preliminary economic analysis fasibility of the pre-treatments tested

The first scenario considered the condition for the energetic self-sustainability of the AD process without any pre-treatment. This scenario differed that presented in the Chapter 2 because the methane production B_o of secondary sludge was fixed equal to the average values obtained in the lab tests, that is 0.132 Nm^3/kg VS (Chapter 2 the biomethane returned from field observations was equal to 0.088 Nm^3/kg VS).

The second and third Scenarios referred to tests that involved low-temperature thermal treatments. Low thermal treatments do not require chemical reagents, therefore the increase of methane necessary to balance the cost of chemicals is equal to zero.

With reference to the second session of anaerobic digestion tests (4^{th}-5^{th} scenarios), the increases in the production of methane necessary to offset the costs of reagents (HCl and NaOH) were equal to 68.2% and 60.8% for the sludge digested at a pH values of 7.5 and 8.5. Moreover, the costs of acidification were higher or equal to the cost of alkaline treatment.

The results from 6th and 7th scenarios proved that the dose of 0.04g/gTS was the most suitable from an economic point of view. Indeed, the necessary increase the methane production to offset the costs of reagents (HCl and NaOH) decreased. Moreover, while the increase in methane production of the sludge digested at a pH of 7.5 was neglected, the increase of the same parameter of the WAS treated with the same amount of NaOH but digested with a pH equal to 8.5 increase of about 28 %. In these conditions the electric energy that can be produced should be able to cover the cost of the employed alkali and acid reagents. The last two scenarios reported in table 4 list the economical applicability of thermo-alkaline pretreatment with NaOH at 70 and 90 °C. With reference to the conditions tested in the last two series of digestibility tests (scenarios 8 and 9 in Table 4) the increases in methane production necessary to offset the costs of reagents (only NaOH) was for both 11.8 %. The percentages of increase in methane production recorded after BPTs were equal to 44.8 and 86.1 % respectively. Those values were 3.1 and 4.8 time higher compared to the target value (14.2 %). In all cases, with the aim to reach anaerobic digestion thermally self-sustainable it is necessary to thicken the sludge to a dry content higher than the current conditions. The minimum concentration of TS b.w. for each scenario is reported in table 5. Starting from the experimental results it was possible to evaluate what should be the profits concerning the increase of methane and consequently extra producible electrical energy. The graphical results for each pre-treatment were reported in figures 4.12, 4.13, 4.14, 4.15, 4.16, 4.17, 4.18,4.19 and 4.20. The preliminary economic assessment results are listed in table 4.4. The most suitable treatment from an economic point of view should be the thermo alkali treatment 0.04g NaOH/gST 90°C 1.5h recording a money saving of 195.1 €/h.

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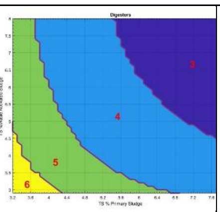
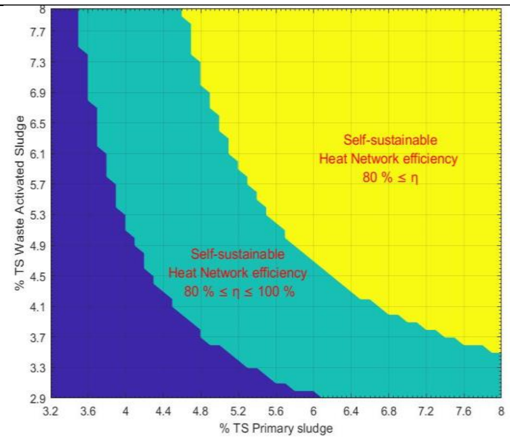
<tr><td>Required digester
</td><td>Un-treated WAS
B_o 0.132 Nm^3CH_4/kg VS
Primary Sludge
B_o 0.288 Nm^3CH_4/kg VS</td></tr>
<tr><td>Self-Sustainable
Thermal power</td><td>
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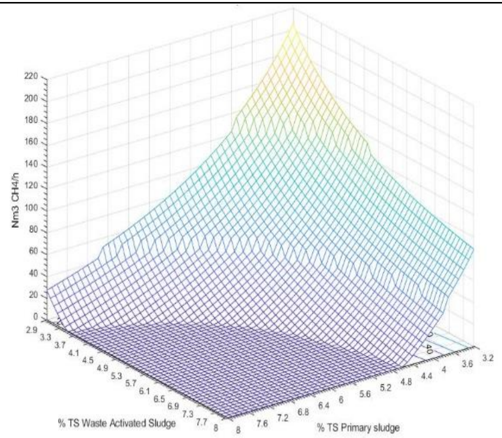
<tr><td>Required natural gas
Heat transfer efficiency 80 %</td><td>
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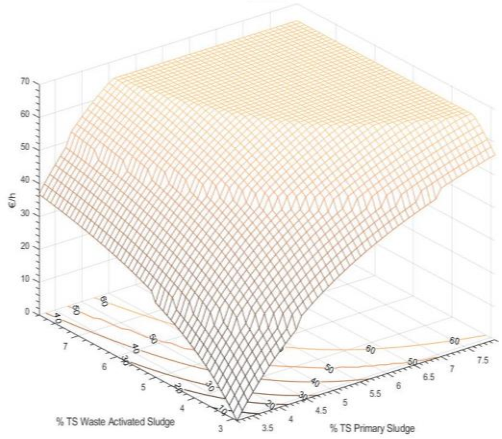
<tr><td>Saved Money</td><td>
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Figure 4. 12 No pre-treatment. Cost analysis

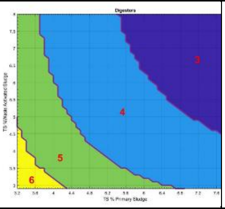
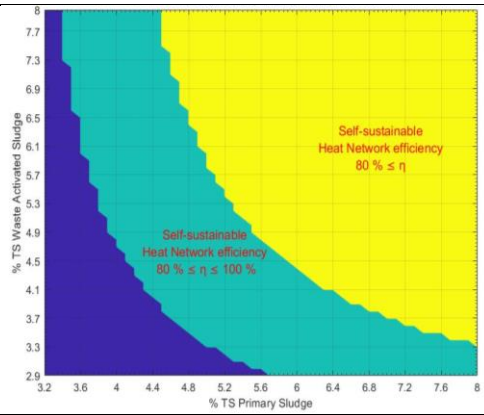
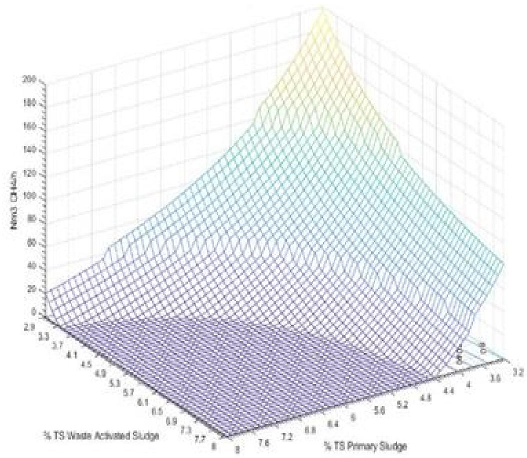
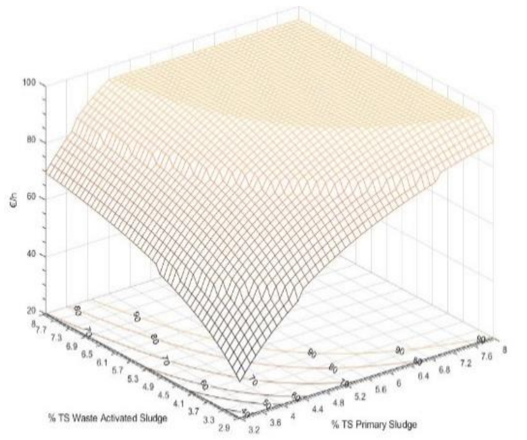
Required digester 	*Treated WAS-70 °C, 90 min.* *B_o 0.149 Nm^3CH_4/kg VS* Primary Sludge B_o 0.288 Nm^3CH_4/kg VS
S Self-Sustainable Thermal power	
Required natural gas Heat transfer efficiency 80 %	
Saved Money	

Figure 4. 13 Thermal Treatment (70°C, 90 min.). Preliminary cost-benefit analysis

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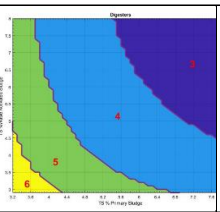</td>
<td>Treated WAS-90 °C, 90 min.
B_o 0.157 Nm^3CH_4/kg VS
Primary Sludge
B_o 0.288 Nm^3CH_4/kg VS</td>
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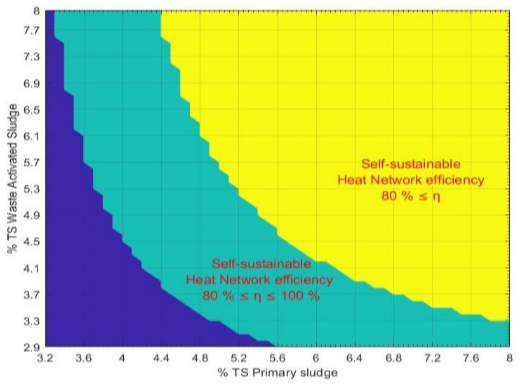
Thermal power</td>
<td>
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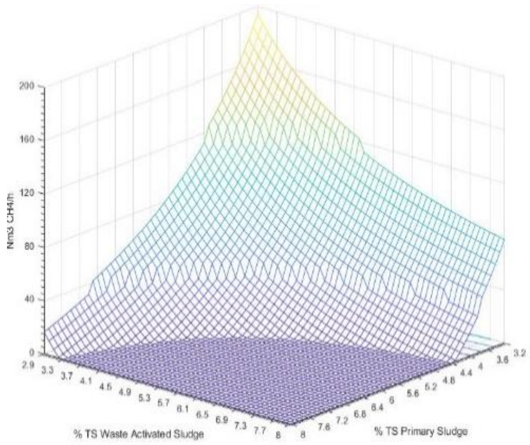
Heat transfer efficiency 80 %</td>
<td>
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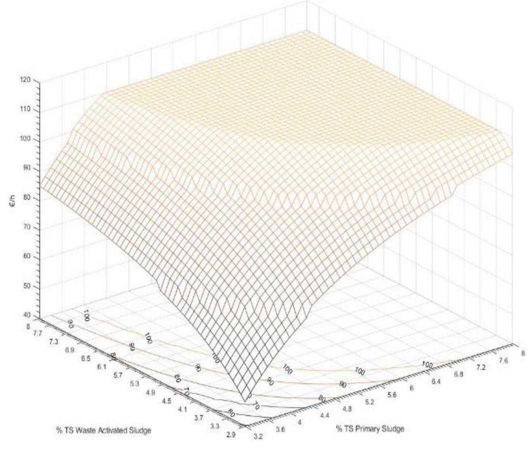
<td>
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Figure 4. 14 Thermal Treatment (90°C, 90 min.). Preliminary cost-benefit analysis

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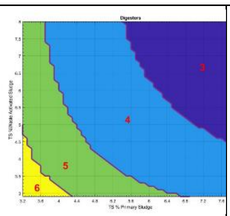
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<td>Treated WAS- 20 °C
8 g NaOH/100 g TS, pH 7.5, 90 min.
B_o 0.156 Nm^3CH_4/kg VS
Primary Sludge
B_o 0.288 Nm^3CH_4/kg VS</td>
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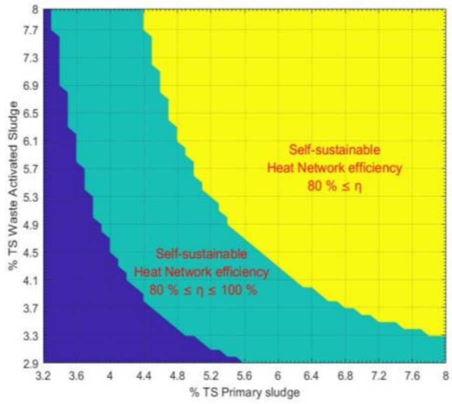
<tr>
<td>Self-Sustainable
Thermal power</td>
<td>
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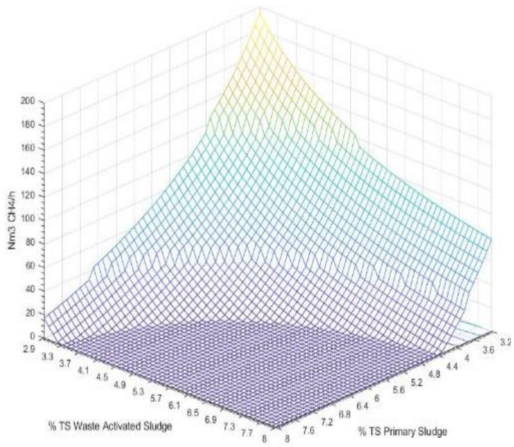
<td>Required natural gas
Heat transfer efficiency 80 %</td>
<td>
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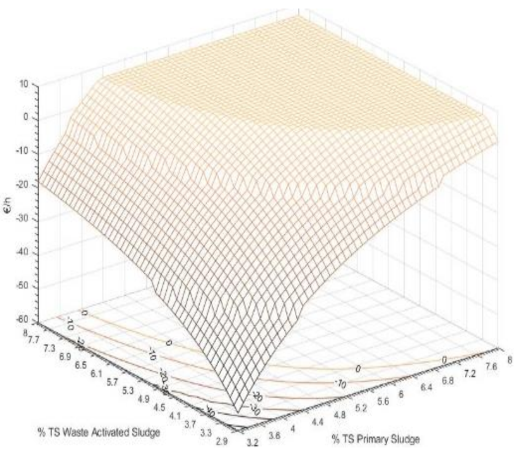
<td>
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Figure 4. 15 Alkali treatment (8 g/100g TS, pH 7.5, 90 min). Preliminary cost-benefit analysis

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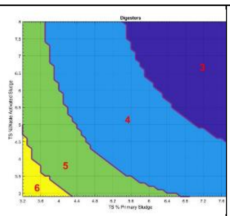
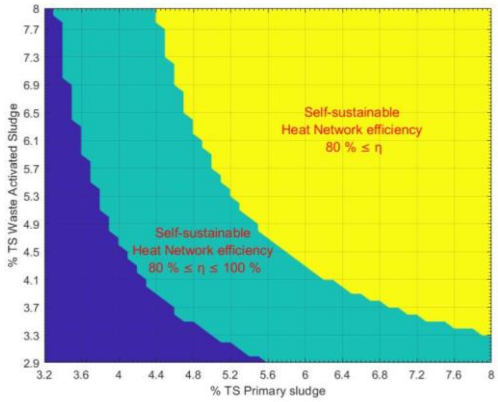
</td><td>Treated WAS-20 °C
8 g NaOH/100 g TS, pH 8.5, 90 min.
B_o 0.154 Nm^3CH_4/kg VS
Primary Sludge
B_o 0.288 Nm^3CH_4/kg VS</td></tr>
<tr><td>Self-Sustainable
Thermal Power</td><td></td></tr>
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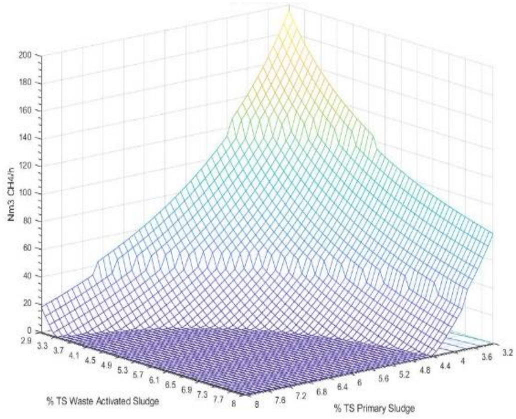
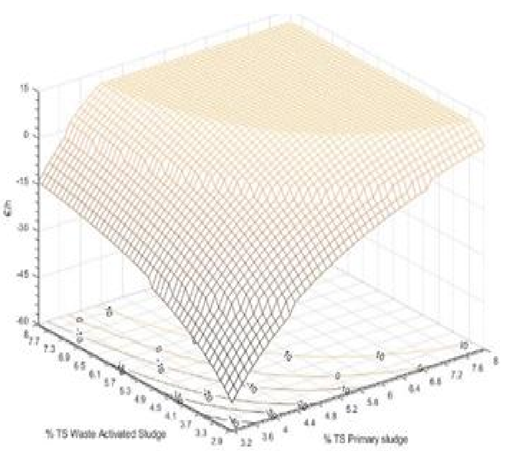
Heat transfer efficiency 80 %</td><td></td></tr>
<tr><td>Saved Money</td><td></td></tr>
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Figure 4. 16 Alkali treatment (8 g/100g TS, pH 8.5, 90 min). Preliminary cost-benefit analysis

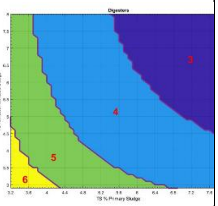
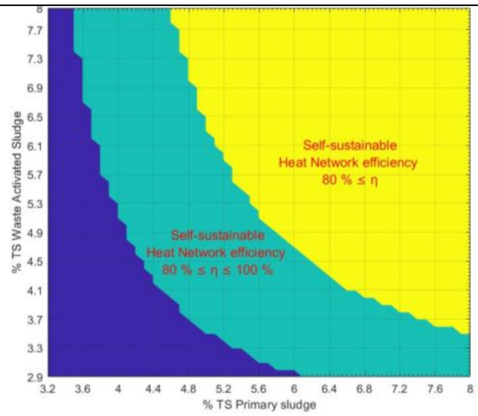
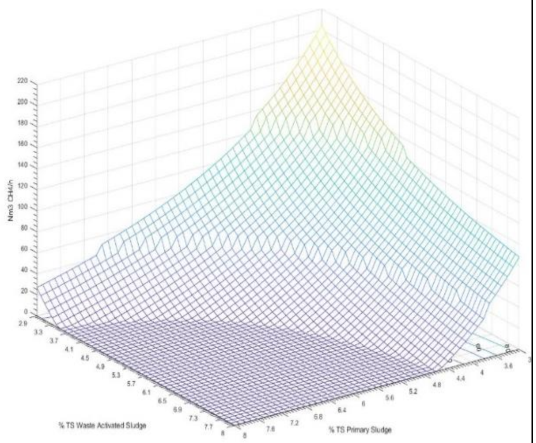
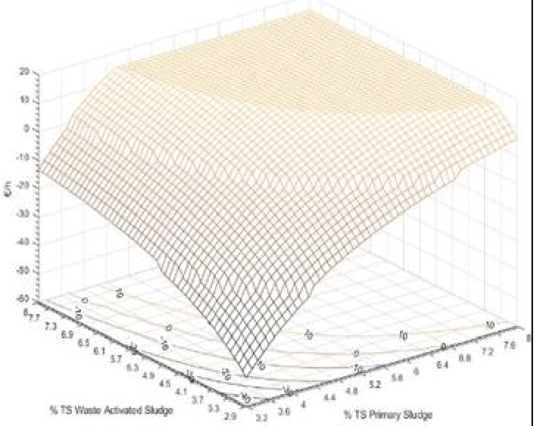
Required digester 	*Treated WAS- 20°C* *4 g NaOH/100 g TS, pH 7.5, 90 min.* *B_o 0.133 Nm^3CH_4/kg VS* Primary Sludge B_o 0.288 Nm^3CH_4/kg VS
Self-Sustainable Thermal Power	
Required natural gas Heat transfer efficiency 80 %	
Saved Money	

Figure 4. 17 Alkali treatment (4 g/100g TS, pH 7.5, 90 min). Preliminary cost-benefit analysis

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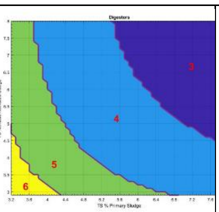
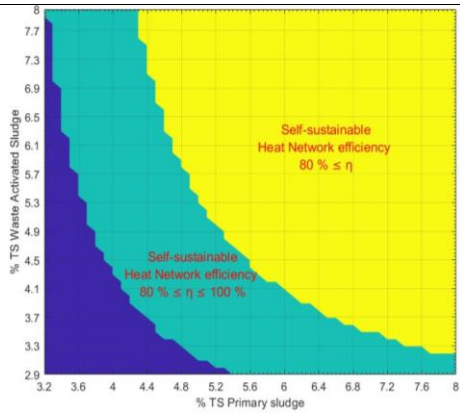
</td><td>Treated WAS- 20°C
4 g NaOH/100 g TS, pH 8.5, 90 min.
B_o 0.168 Nm^3CH_4/kg VS
Primary Sludge
B_o 0.288 Nm^3CH_4/kg VS</td></tr>
<tr><td>Self-Sustainable Thermal Power</td><td></td></tr>
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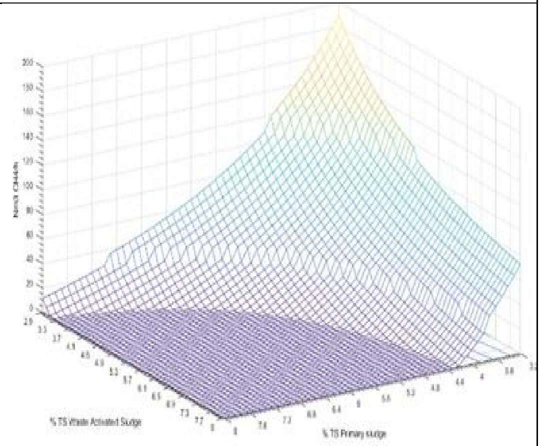
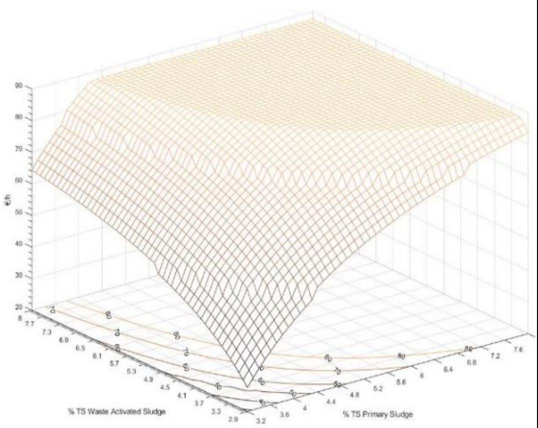
Heat transfer efficiency 80 %</td><td></td></tr>
<tr><td>Saved Money</td><td></td></tr>
</table>

Figure 4. 18 Alkali treatment (4 g/100g TS, pH 8.5, 90 min). Preliminary cost-benefit analysis

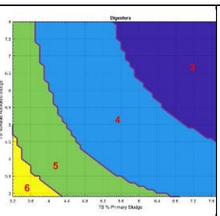
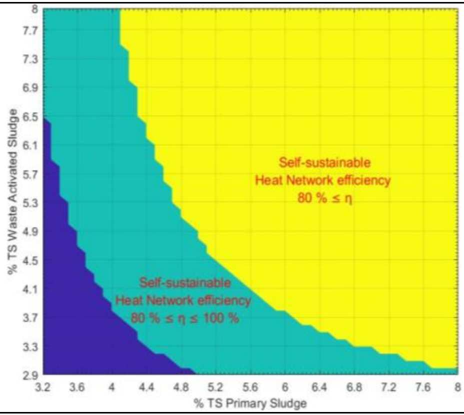
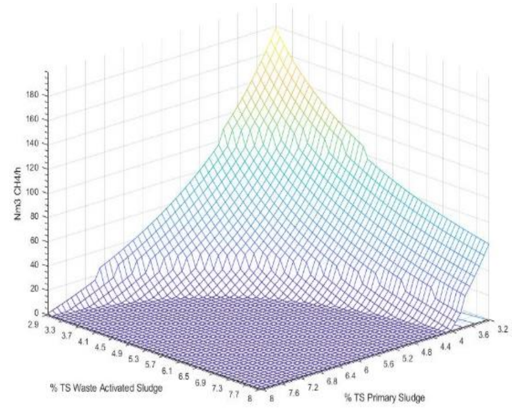
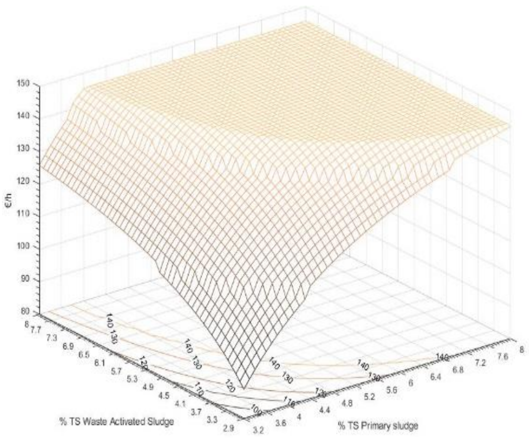
Required digester 	*Treated WAS- 70°C* *4 g NaOH/100 g TS, pH 8.5, 90 min.* *B_o 0.194 Nm^3CH_4/kg VS* Primary Sludge B_o 0.288 Nm^3CH_4/kg VS
Self-Sustainable Thermal Power	
Required natural gas Heat transfer efficiency 80 %	
Saved Money	

Figure 4. 19 Thermo-Alkali treatment (4 g/100g TS, pH 8.5, 70°C, 90 min). Preliminary cost-benefit analysis

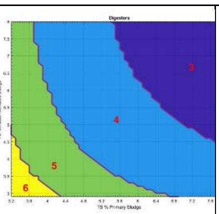
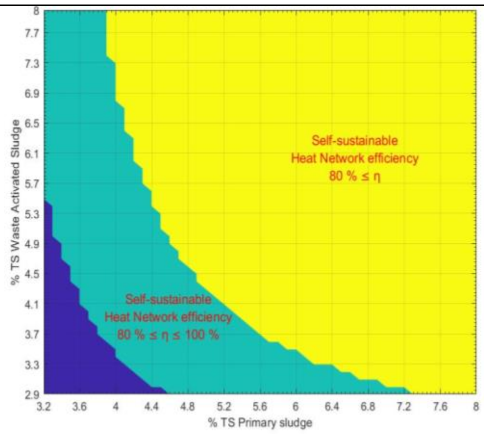
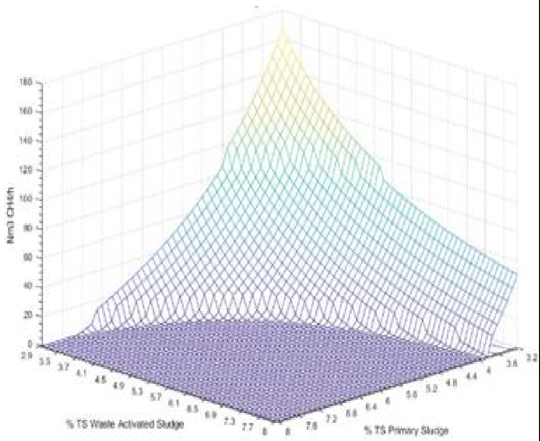
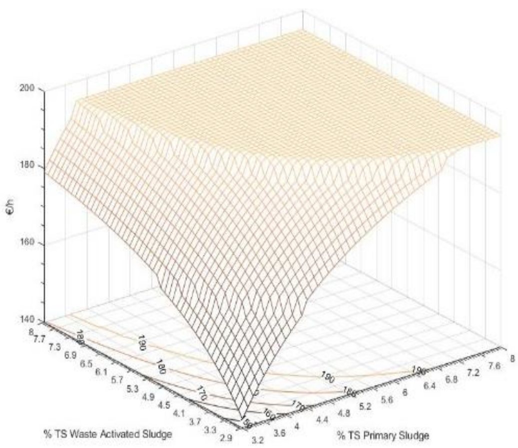
Required digester 	*Treated WAS- 90°C* *4 g NaOH/100 g TS, pH 8.5, 90 min.* *B_o 0.247 Nm^3CH_4/kg VS* Primary Sludge B_o 0.288 Nm^3CH_4/kg VS
Self-Sustainable Thermal Power	
Required natural gas Heat transfer efficiency 80 %	
Saved Money	

Figure 4. 20 Thermo-Alkali treatment (4 g/100g TS, pH 8.5, 90°C, 90 min). Preliminary cost-benefit analysis

	Money Saving Worst condition (No dynamic pre-thickener installed)	*If Self-Sustainable Thermal Power*	*Money Saving Best condition*
Present situation	0	TS primary sludge 3,2 % TS WAS sludge 2.9 % auxiliary methane need	0
Scenario 1	0	No auxiliary natural gas need	+64,9 €/h
Scenario 2, 70°C-1.5h	+ 32.8 €/h	No auxiliary natural gas need	+95.4 €/h
Scenario 3, 90°C-1.5 h	+ 48.3 €/h	No auxiliary natural gas need	+ 109.8€/h
Scenario 4, 0.08 gNaOH/gTS 1.5h pH 7.5- 20°C	- 54.8 €/h	No auxiliary natural gas need	+ 6.8€/h
Scenario 5, 0.08 gNaOH/gTS 1.5h pH 8.5 – 20°C	- 50.9 €/h	No auxiliary natural gas need	+11.1€/h
Scenario 6, 0.04 gNaOH/gTS 1.5h pH 7.5- 20°C	- 50.0 €/h	No auxiliary natural gas need	+14.7 €/h
Scenario 7, 0.04 gNaOH/gTS 1.5h pH 8.5- 20°C	+ 27.6 €/h	No auxiliary natural gas need	+ 87.5 €/h
Scenario 8, 0.04 gNaOH/gTS 1.5h pH 8.5- 70°C	+ 89.0 €/h	No auxiliary natural gas need	+ 146.0 €/h
Scenario 9, 0.04 gNaOH/gTS 1.5h pH 8.5- 90°C	+ 142.4 €/h	No auxiliary natural gas need	+ 195.1 €/h

Table 4. 5 Preliminary Cost-effect analysis

5 Conclusions

This Chapter reposts an assessment of the investigated the technical and economic feasibility of thermal, alkali and hybrid thermo-alkali pretreatments for the improvement of WAS anaerobic digestion in the largest WWTP in Italy.

Test results proved a higher efficiency of NaOH compared to $Ca(OH)_2$ in sludge disintegration and consequently in the soluble COD release. The combined effect of the chemical reactant and the temperature at 90°C made possible to obtain DR values in the order of 40%.

Alkali, thermal and thermo alkali pre-treatments on WAS may actually improve the performances of the AD process. Methane specific production increased by 13.1 %

and 19.0 % for samples WAS treated for 1.5 h at 70 and 90 °C. Waste activated sludge pretreated with a dose of 0.04 gNaOH/gST for 1.5 h at 20° C, 70 °C and 90°C showed a methane yields increase by 28.0 44.8 and 86.1% respectively.

The profits increase by 108.8 €/h if the sludge is treated at 90 °C for 1.5 h, this value decreases by 15 €/h if the thermal treatment was carried out 70°C. Moreover, if the thermal treatment was made by adding 0.04 gNaOH/gTS the revenues increased by approximately 146 and 195 €/h at temperatures of treatment of 70 and 90 °C respectively.

Finally, was verified that the achievement of a TS content of 6%.in both primary and secondary sludge is sufficient to make the AD process self-sustainable. It is necessary to point out that these results consider a global heat efficiency transfer of 80%.

Chapter 5 Process performance assessment of semi-continuous Anaerobic Digestion pilot test of thermo-alkaline pre-treated WAS. Thermo-Alkaline pre-treatment (4 g NaOH/100 g TS, 90 min, 90 °C)

Reformed and extended version of conference paper originally published:

"Pilot-scale study of enhanced methane production during anaerobic digestion of waste activated sludge after combination of low thermal (90 °C, 1.5 h) and alkaline (NaOH) pretreatment" 2018
Campo G., A. Cerutti A., Zanetti M.C, Scibilia G., Lorenzi E., Ruffino B.
SMICE Sludge Management in Circular Economy. Rome 23th -25th May

Reformed and extended version of conference paper under revision:

"Thermo-alkaline pre-treatment of WAS: Application of pilot semi-continuous AD test to assess biochemical methane potential and hydrolysis rate" 2019
Campo G., A. Cerutti A., Zanetti M.C, Scibilia G., Lorenzi E., Ruffino B.
16th IWA World Conference on anaerobic Digestion Delft (The Netherlands)
23^{th} – 26^{th} June 2019

The aim of Chapter 5 is to assess the impact of thermo-alkali pre-treatments of WAS (4g NaOH/100g TS, 90 min, 90°C) in a pilot scale - semi-continuous AD test (mesophilic condition - 38 °C).

This pre-treatment technique was studied in Chapter 4 in laboratory batch-scale anaerobic digestion test. Batch tests carried out in Chapter 4 demonstrated that, among several conditions, the pre-treatment technique (4g NaOH/100g TS, 90 min, 90°C) had the best performance in term of methane production increase (+86,1%); moreover, a preliminary technical-economic analysis showed an economic advantage (+195 €/h).

In order to accurately compare the results of thermo-alkali treatment proposed here with the different hydrolysis techniques reported in scientific papers and technical reports the only biogas/methane production increase is not sufficient.

In fact, the anaerobic biodegradability of treated sludge assessed in lab and batch scale depends on the duration of the process, activity of inoculum, possible partial and temporary inhibition, inoculum substrate ratio and hydrolysis rate.

Consequently, with the purpose to understand if the thermo-alkali pre-treatment has only the effect on the increase of anaerobic biodegradability or also on the hydrolysis constant increase the couple of parameters biochemical methane potential (Bo) and hydrolysis rate constant (*k)* had be evaluated. *Bo* is the maximum amount of methane that a substrate can produce after an infinite time of AD process; the *k* is a first order kinetic constant able to model the disintegration process.

Two AD and semi-continuous tests were done; during the first anaerobic digestion test, the biodegradability of raw secondary sludge was assessed; after, the effects of thermo-alkali treatment of WAS, submitted to a semi-continuous and completely stirred anaerobic digestion, was studied.

The methane production, the VS reduction and the HN_4^{+} release, regarding the particular conditions (HRT, OLR) of digestion tests, were evaluated.

In this dissertation the biochemical methane potential (Bo) and the hydrolysis rate (k) were evaluated using the data obtained during the semi-continuous AD tests.

Based on the data returned from the pilot-scale tests, the thermo-alkali pre-treatment could increase B_0 by 61.3% and the k from 0.085 to 0.465 d^{-1}. The results of this study demonstrated that a thermo-alkali pre-treatment could increase the specific methane production of WAS in a full-scale, steady-state continuous stirred tank reactor (CSTR), with an HRT of 20 days, from 0.09 to 0.23 $Nm^3/kgVS$ (+142 %).

5.1 Materials and methods

5.1.1 Waste Activated Sludge

Samples of WAS were weekly collected from the outlet of the two gravity pre-thickeners used in Castiglione Torinese Plant. The pre-thickeners are used in the ordinary operation of the plant to increase the density of WAS before the AD process. In Castiglione Torinese WWTP, the performance of the thickening process is improved by the aid of a cationic polyelectrolyte that is added to the WAS at the inlet of the pre-thickeners. The used polyelectrolyte dosage is equal to 5 g/100 gTS.

5.1.2 Sludge pretreatment reactor

All the pretreatments were carried out by means of a cylindrical batch reactor with a working volume of 35 L (See Figure 5.1). The reactor was mechanically completely mixed using an electric propelled shaker. The mixing inside the reactor worked for all the duration of the treatments. The heat was transferred to the sludge by using three electrical band resistances, each one with an electric power of 2.6 kW. These resistances were placed on the lateral surface of the reactor. The temperature inside the reactor was controlled by an open source single-board microcontroller (Arduino).

The pretreatment was done twice a week, both pre-treatment sessions were carried out in the same day, generally Tuesday. The sludge used for the treatment was an untreated WAS; it was previously characterized in terms of TS concentration and sCOD (soluble COD). The sludge (storage at a temperature equal to 4°C) and the relative amount of NaOH were added to the lysis reactor at the beginning of the operation. The pre-treatment time counting started when the sludge into the reactor reached 20 °C. The sludge reached 90°C after 30 min. . At the end of the pretreatments, after 90 min, the sludge left to the lysis reactor and it was stored in four 10 L-tanks equipped with a cap. Subsequently, the full tanks containing the treated sludge have been cooled in a tap water bath. In order to maintain a constant temperature inside the cooling bath a continuous flow of tap water was flushed. After 30 min, the cold tanks were stored in a refrigerator at 4°C for at maximum one week.

Figure 5. 1 Sludge pre-treatment. Employed Reactor and operation activity

5.1.3 Anaerobic digester

The AD tests were performed in a 300 L reactor (240 L working volume), equipped with an 80 L gasometer and an electronic system to monitor the produced biogas. The digester was a completely stirred tank reactor. The mixing inside the reactor was guaranteed through a biogas recirculation (5 min. on/5 min off).

Figure 5. 2 Employed pilot anaerobic digester

Two pilot-scale AD tests were run in mesophilic condition (38°C). The details of the tests are shown in Table 5.1.

AD tests	Days[d]		HRT [d]	OLR [kg VS m^{-3} d^{-1})]
WAS	*158*	*112*	*15*	*1.43 ± 0.31*
		46	*20*	*1.22 ± 0.36*
tWAS	*119*	*29*	*20*	*1.28 ± 0.32*
		90	*20*	*0.56 ± 0.15*

Table 5. 1 Pilot anaerobic digestion tests. Days, HRTs and OLRs

The digester was used to test firstly the untreated sludge and later the thermo-alkali treated WAS (tWAS). During the first digestion test, two hydraulic retention times (HRT) were applied: at first the HRT was equal to 15 days, after 112 days it was increased to 20 days.

In the treated WAS digestion test two Organic Loading Rates (OLR) were used. During the first 29 days of AD test, the average OLR was equal to 1.28 kg VS/(m^3 d); later, the average OLR was reduced by 50 %. During the second phase, the sludge fed to the AD reactor was composed of 50% b.v. tap water and the 50% treated sludge. The reasons of this choice are discussed in the results session.

Sludge was fed in a semi-continuous mode only during the working days, generally five days per week from Monday to Friday. Biogas production was daily recorded, and the gas was characterized in terms of CH_4, CO_2, O_2 and "balance" (i.e. all the gases that are different from the first three) through a GA5000 Range Gas Analyzer, Geotechnical Instruments Ltd. The biogas/methane daily production were referred to the standard condition (0°C and 1 atm.). Digestate was analysed daily. The analysed parameters were pH, TS, VS. FOS/TAC. FOS/TAC is the ratio between Organic Acids Concentration (FOS, expressed as mg/L of equivalents of acetic acid) and Total Alkalinity (TAC, expressed as mg/L of $CaCO_3$).

5.1.4 Analytical methods

All the analytical monitored parameters in the lysis tests (TS, VS, pH, NH_4^+ electric conductivity (EC), sCOD) were determined using Standard Methods (APHA, 2012). The elemental analysis was performed by means of a CHNS-O Thermo Fischer Flash 2000 Analyzer EA 1112. The oxygen content was assumed as the complementary fraction of the sum of all the other detected components. The elemental composition of VS was calculated as the ponderal difference between the elemental composition of total solids and the elemental composition of non-volatile solids. The total COD was determined starting from the elemental analysis of VS as proposed by van Lier et al. 2008 (val Lier J.B. et al., 2008) . Given the ponderal formula of a generic compound ($C_aH_bO_cN_d$), the tCOD was calculated as in Equation 5.1:

$$tCOD = \frac{8 \times (4a + b - 2c - 3d)}{(12a + b + 16c + 14d)} \left[\frac{gCOD}{gVS}\right]$$

Equation 5 1

Buswell and Mueller (1952) developed a molar stoichiometric relationship between carbon, hydrogen and oxygen in an organic compound and the volumes of methane and carbon dioxide that can be produced in an anaerobic digestion process. Their relationship was further modified to include the nitrogen. (Metcalf & Eddy Aecom, 2014) The formula was reported in equations 5.2, 5.3, 5.4 and 5.5:

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right) H_2O \rightarrow \left(\frac{4a + b - 2c - 3d}{8}\right) CH_4 + \left(\frac{4a - b + 2c + 3d}{8}\right) CO_2 + dNH_3$$

Equation 5 2

$$Biogas_{th}\left[\frac{Nm^3}{kg_{VS}}\right] = \frac{\left[\left(\frac{4a + b - 2c - 3d}{8}\right) + \left(\frac{4a - b + 2c + 3d}{8}\right)\right]}{12a + b + 16c + 14d} 22{,}415 = \frac{22{,}415a}{12a + b + 16c + 14d}$$

Equation 5 3

$$f_{CH_4} = \frac{CH_{4th}}{Biogas_{th}} = \frac{4a + b - 2c - 3d}{8a} = \frac{1}{2} + \frac{b}{8a} - \frac{1}{4}\frac{c}{a} - \frac{3}{8}\frac{d}{a}$$

Equation 5 4

$$CH_{th}\left[\frac{Nm^3}{kg_{VS}}\right] = f_{CH_4} \times PSB$$

Equation 5 5

5.1.5 Semi-continuous anaerobic digestion test, Proposed Mathematical Model

The anaerobic biodegradability of raw and treated sludge was assessed in terms of biochemical methane potential *(Bo)* and hydrolysis rate *(k)*. The biochemical methane potential (*Bo*) is the maximum amount of methane that a substrate can produce after an infinite time of AD; the hydrolysis rate constant (*k*) is a first order kinetic constant able to model the disintegration process. The anaerobic digestion consists of four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The hydrolysis is the first step, and it is the only one where the microorganisms are not directly involved. This process is merely a surface phenomenon in which the particulate and polymeric matters are degraded through the action of eso-enzymes. After hydrolysis, the produced smaller molecules by the process can cross to the cell barriers (val Lier J.B., 2008). The disintegration-hydrolysis phase is generally the rate-limiting step during the AD of particulate/complex substrates (Zhen G. L. X., 2017). WAS is a typically particulate and complex matter hard to biodegrade.

If hydrolysis is assumed to be the limiting step of AD, and no other inhibition phenomena occur, the methane production can be modelled through a first order kinetic. In a batch reactor the equations used to predict the methane production and the substrate degradation are described by Equation 5.6 and 5.7 respectively (Angelidaki I. et al.., 2009):

$$B(t) = V \times VS_{b_0} \times CH_{4_{th}} \times (1 - e^{-kt})$$

Equation 5 6

$$VS_b(t) = V \times VS_{b_0} e^{-kt \cdot}$$

Equation 5 7

Where *B(t)* is the cumulative methane production at a given time, *V* is the working volume of batch reactor, CH_{4th} is the theoretical biochemical methane potential, k is the hydrolysis rate, VS_{b_0} is the concentration of biodegradable substrate at $t=0$ and $VS_b(t)$ is the concentration of biodegradable substrate at time t. Hence, once CH_{4th} and *k* are known, it is possible to predict the behaviour of a batch reactor at the generic time t (both VS reduction and methane production).

In this dissertation a revision of the first kinetic model applied to semi-continuous anaerobic digestion tests was proposed, used and validated. With the developed model it is possible to estimate the *Bo* (biomethane potential) and *k* (first order hydrolysis constant) of the particulate substrates tested in a continuous/semi-continuous stirred digester.

A series of protocols to perform biomethane potential tests (BMP) were proposed and published in the last years Angelidaki and Sanders 2004, Angelidaki et al 2009, Holliger et al, 2016). These protocols had the aim to standardize the AD lab tests in order to research the couple of values Bo and k. Unfortunately, the drawback of this approach is that k values change depending on the time used to estimate it (Astals S, et al. 2013). Moreover, in 2002 the IWA Task Group for the Mathematical Modelling Processes published a mathematical model called ADM no. 1 (Batstone DJ. et al., 2002) . The model ADM no. 1 is able to describe all the steps of the anaerobic digestion process, both the chemical-physical processes (disintegration-hydrolysis) and the biological steps (acidification, acetification and methane production). The last three steps are biological, and they were modelled on the basis of the Monod kinetic. Unfortunately, the ADM no.1 is not easy to be implemented and used. Indeed, if the goal is to estimate the disintegration first order kinetic constant in a continuous/semi-continuous anaerobic digestion process, the use of ADM no.1 could be too much data expensive and time consuming. It seems to be licit deriving robust values of the first order (*k)* constant and biochemical methane potential (Bo) from the methane cumulative production obtained during the semi-continuous AD tests.

The complete system of equations necessary to describe the AD process in a CST digester (if the disintegration is assumed to be limiting step and the substrate is made of particulate matter) is reported in equations 5.8, 5.9, 5.10 and 5.11.

$$\frac{dVS_b(t)}{dt} = \frac{q(t) \times VS_{b_{in}}(t)}{V} - \frac{q(t) \times VS_b(t)}{V} - k \times VS_b(t)$$

Equation 5 8

$$B_d(t) = VS_b(t) \times k \times CH_{4_{th}} \times V$$

Equation 5 9

$$\frac{dVS_{nb}(t)}{dt} = \frac{q(t) \times VS_{nb_{in}}(t)}{V} - \frac{q(t) \times VS_{bn}(t)}{V}$$

Equation 5 10

$$\frac{dNVS(t)}{dt} = \frac{q(t) \times NVS_{in}(t)}{V} - \frac{q(t) \times NVS(t)}{V}$$

Equation 5 11

Where the parameters represent:

- $q(t)$ = in and out flow rate fed/discharged to the digester [L^3/t];
- V.= working volume of the digester [L^3]
- $B_d(t)$ = daily methane production [L^3/t]
- $VS_{b_{in}}$= concentration of biodegradable volatile solid substrate fed to the digester [M/L^3]
- VS_b = concentration of biodegradable volatile solid substrate into the digester [M/L^3]
- k = hydrolysis rate of the substrate [1/t]
- $CH_{4_{th}}$=Theoretical biochemical methane potential of volatile solid fed to the digester [L^3/M]
- $VS_{nb_{in}}$= concentration of non-biodegradable volatile solid substrate fed to the digester [M/L^3]
- VS_{nb} = concentration of non-biodegradable volatile solid substrate into the digester [M/L^3]
- $VS_{nb_{in}}$= concentration of non-biodegradable volatile solid substrate fed to the digester [M/L^3]
- VS_{nb} = concentration of non-biodegradable volatile solid substrate into the digester [M/L^3]
- NVS_{in}= concentration of non-biodegradable volatile solid substrate fed to the digester [M/L^3]

- NVS = concentration of non-biodegradable volatile solid substrate into the digester [M/L^3]

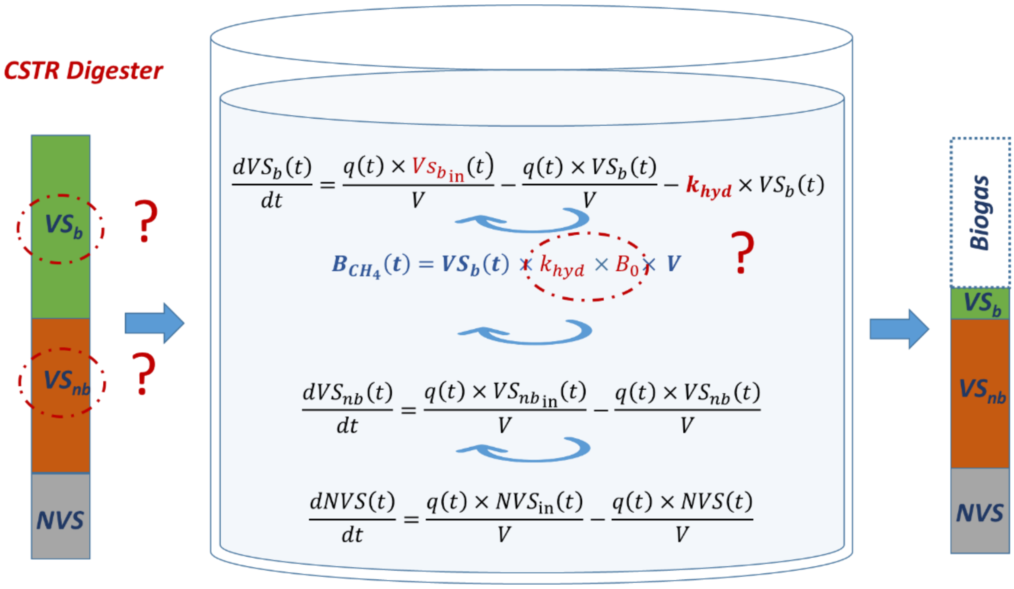


Figure 5. 3 CSRT. Anaerobic Digestion. Differential equations

However, generally it is not possible to know, before AD test, the total amount of anaerobically biodegradable VS. Therefore, the unknown parameters, mentioned above are: the ratio of VS_b/VS, $CH_{4_{th}}$ and the first order constant k.

For this reason, the previously first two equations (5.8 and 5.9) were modified as following:

$$\frac{daVS_b(t)}{dt} = \frac{q(t) \times VS_{in}(t)}{V} - \frac{q(t) \times aVS_b(t)}{V} - k \times aVS_b(t)$$

Equation 5 12

$$B_d(t) = aVS_b(t) \times k \times B_o \times V$$

Equation 5 13

Where the parameters not yet defined represent:

- B_o = the Biochemical methane potential [L^3/M]. It is the maximum amount of methane that a substrate can produce after an infinite time. The parameter B_o is always minor or equal to $CH_{4_{th}}$. The two parameters are equal to the same value only if all the fed volatile solids in the anaerobic reactor are anaerobically biodegradable.
- VS_{in}= the concentration of volatile solid fed to the digester [M/L^3];
- aVS_b= the artefact concentration of volatile solid inside the reactor [M/L^3]. This value is an artefact parameter; it is equal to zero when all the biodegradable volatile solids VS_b are transformed into biogas/methane.

If B_o is calculated by using Equations 5.12 and 5.13, it is also possible to estimate the absolute biodegradation (Y) , it is defined in equation 5.14 (Gonzalez et al., 2018):

$$Y = \frac{B_0}{SV_{in} \times \frac{COD_{in}}{SV_{in}} \times 0.350 \left[\frac{Sm^3}{kg\ COD}\right]}\ [\%]$$

Equation 5 14

Where $COD_{in}$is the concentration of the fed substrate in terms of chemical oxygen demand and 0.350 is the maximum theoretical conversion of COD to methane at standard condition (Mottet et al., 2009) .This parameter (Y) does not consider that COD is also necessary for microorganism cell growth and their maintenance. Moreover, during the AD process, the COD is consumed due to the presence of other electron accepters like in presence of sulfate-reducing microorganisms (Gonzalez et al., 2018). As reported in literature (Angelidaki et al., 2004) the biodegradable COD consuming during the growth and maintenance of microorganisms is 5-10 % of the degraded substrate. Consequently, the absolute biodegradation parameter (Y) is a consistent value from a technical point of view. In effect, the real biodegradability of a substrate is a little bit higher (+ 5-10 %) than Y. Therefore, the absolute biodegradability of the substrate takes into account also the biodegradable COD used from microorganisms during the anabolic metabolism; nevertheless, 5-10 % of the biodegradable COD, during the AD process ,is transformed into new particulate matter (new cells).

Recognizing:

- the definition of Y;
- the elemental analysis of the total volatile substrate submitted to AD;

and hypothesizing that the ponderal formula ($C_aH_bO_cN_d$) of the raw and treated substrate is the same for both biodegradable and not biodegradable, is also possible to predict the VS concentration in the digestate during an AD process. The three following equations are necessary:

$$\frac{dVS_{nb}(t)}{dt} = \frac{q(t) \times VS_{nb_{in}}(t)}{V} - \frac{q(t) \times VS_{bn}(t)}{V}$$

Equation 5 15

$$\frac{dVS_b(t)}{dt} = \frac{q(t) \times Y \times VS_{in}(t)}{V} - \frac{q(t) \times VS_b(t)}{V} - k \times VS_b(t)$$

Equation 5 16

$$VS(t) = VS_{nb}(t) + VS_b(t)$$

Equation 5 17

The biochemical methane potential and first order hydrolysis rate constant of untreated and treated WAS were evaluated using the first order kinetic model described in equations 5.12 and 5.13. All the numerical simulations were carried out by using Matlab2017b – academic use (ode 15 solver). The model was used to fit the cumulative methane production data observed during the semi-continuous AD tests.

After having estimated of the two first order model parameters (*Bo* and *k*), the equations 5.14, 5.15, 5.16 and 5.17 were used to validate the model. The validation consists in the prediction of concentration of VS in the effluent from the anaerobic reactor.

5.1.5.1 Proposed Mathematical Model. Ammonia release

With the aim to estimate the ammonia release in the digestate, during the anaerobic digestion of untreated and treated sludge, another first order kinetic model was proposed. The ammonia release is linked to proteins hydrolysis, the subsequent amino acids (AA) production, and the final transformation of AA to volatile fatty acids (VFAs). NH_3 is released during the VFAs production.

Therefore, if the hydrolysis is the limiting step, also the ammonia production could be modelled using the first order kinetic model. Ammonia release is expressed as the mass ratio between the potential maximum ammonia release and the VS fed to the digester. The differential equation is defined as in equation 5.18:

$$\frac{dNH_4{}^+(t)}{dt} = \frac{q \times NH_4{}^+{}_{in}(t)}{V} - \frac{q \times NH_4{}^+(t)}{V} + perNH_4{}^+ \times k \times \ aVS_b(t)$$

Equation 5 18

The three parameters not yet defined represent:

- $NH_4{}^+{}_{in}$= concentration of ammonia in the influent [M/L^3];
- $NH_4{}^+$= concentration of ammonia in the effluent [M/L^3];
- $perNH_4{}^+$= represents the mass ratio between the maximum available release of ammonia of the tested substrate [M/L^3] and the concentration of VS fed to the digester [M/L^3].

The model was used to fit the concentration of ammonia in the effluent observed during the semi-continuous AD tests and the expected concentration from the model.

5.1.5.2 Steady state AD process modelling

Subsequently, known the searched parameters (*B_o, k and per $NH_4{}^+$)* it is possible to predict the behaviour of a completely stirred anaerobic reactor, working in steady state conditions. The steady state conditions, generally rarely to reach at the industrial scale, is used to make an easy comparison among different considered scenarios.

The employed formulas are:

$$aVS_b = \frac{1}{1 + k \times HRT} \times VS_{in}$$

Equation 5 19

$$VS_b = \frac{1}{1 + k \times HRT} \times Y \times VS_{in} = \frac{1}{1 + k \times HRT} \times VS_{b_{in}}$$

Equation 5 20

$$VS_{nb} = (1 - Y) \times VS_{in}$$

Equation 5 21

$$VS = VS_b + VS_{nb}$$

Equation 5 22

$$B = \left(1 - \frac{1}{1 + k \times HRT}\right) \times B_0$$

Equation 5 23

$$NH_4{}^+(t) = NH_4{}^+{}_{in} + perNH_4{}^+ \times \frac{k \times HRT}{1 + k \times HRT} \times VS_{in}$$

Equation 5 24

5.1.5.3 Uncertainty analysis

Residual sum of squares (RSS) between the measured data and model predicted data is the objective function (J). The optimal couple of Bo and k parameters will be the one under which the RSS is minimized (J_{min}). Moreover, the parameters surface is used to estimate the uncertainty of the searched values. The parameters surface can be described by a $J_{crit} > J_{min}$ using the F distribution by assuming that the residual errors are normally distributed (Wei W. et al., 2017) (Batstone D.J. et al., 2003). The couple of values (B_o and k) as well as the $perNH_4{}^+$value, that give a J value minor of J_{crit}, are considerate acceptable.

$$J_{crit} = J_{min} \times \left(\frac{p}{(N_{data} - p)} \times F_{(\alpha,p,N_{data-p})}\right)$$

Equation 5 25

Where p is the number of parameters, N_{data} are the number of measured points, and α is the confidence limit fixed equal to 0.95.

	p	*WAS*		*tWAS*	
		N° days	N_{data}	N° days	N_{data}
Bo and k	2	158	120	120	80
per NH_4^+	1	120	5	120	16

Table 5. 2 Uncertainty analysis. Used parameters

5.2 Results

5.2.1 Sludge Characterization

The results of the elemental analysis of Waste Activated Sludge were used to calculate the VS raw WAS ponderal formula ($C_{6.8}H_{11.8}O_{3.2}N$). In the table 5.3 COD/VS ratio and the theoretical biogas/methane potential production calculated by the Buswell relationship as shown (Equations 5.2, 5.5).

Substrate	*N/VS [gN/100g VS]*	*COD/VS [gO₂/gVS]*	*Biogas* $_{th}$ *[Nm³/kg VS]*	$CH_{4\ th}$ *[Nm³/kg VS]*
WAS	8.6	1.49	0.96	0.52

Table 5. 3 WAS. Sludge Characterization

5.2.2 Anaerobic digestion tests

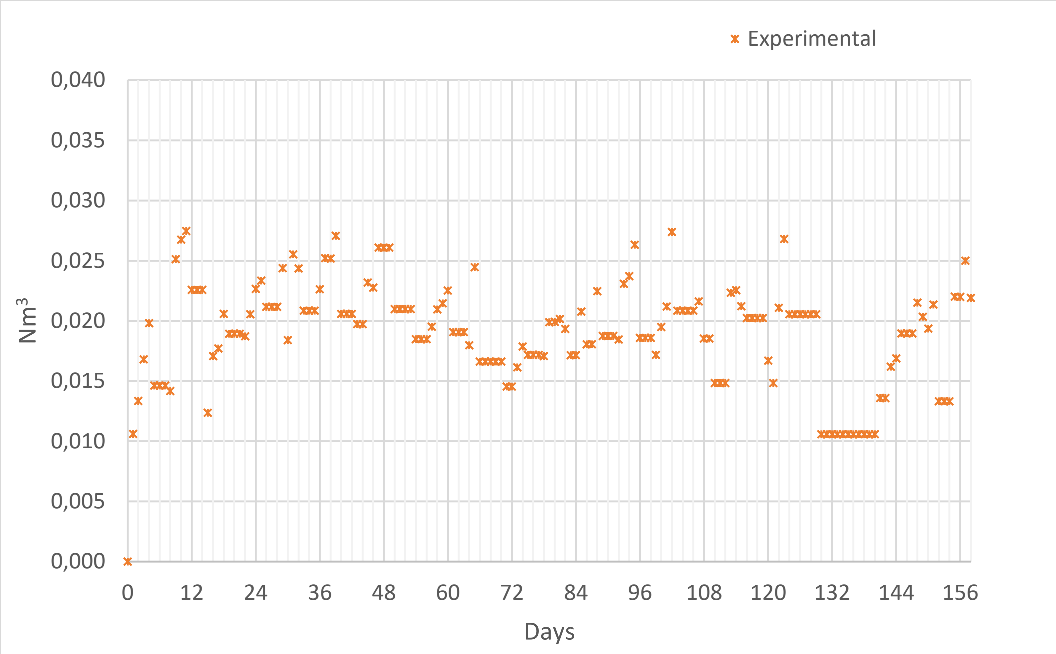


Figure 5. 4 Was digestion test. Daily methane production

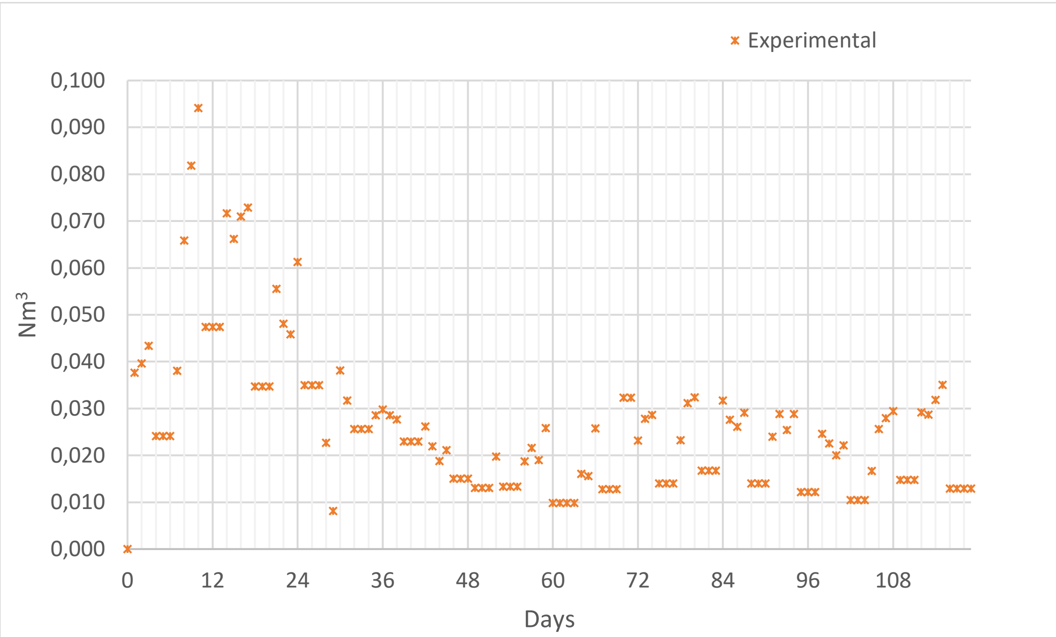


Figure 5. 5 tWAS digestion test. Daily methane production

The daily methane production values obtained from the two semi continuous anaerobic digestion tests are shown in figures 5.4 and 5.5.

As well shown in figure 5.6 the anaerobic digestion test of treated WAS after three weeks of started experimentation presented a biological instability phenomenon. After the firsts 21 day of experimentation the daily methane production significantly decreased. At the sometime the concentration of total acidity grew. The increased acidity is an indicator of biological instability. VFAs as valeric acid, butyric acid, propionic acid as well as acetic acid are the main intermediate products of AD. If the total acidity is accumulated in the digester liquor and the biogas/methane production significantly decrease, one or more of the biological AD steps are inadequate to treat the total amount of fed substrate. The causes of the problems previously mentioned should be researched in a possible inhibitor concentrations growth, like free ammonia, or in a drastic increase of OLR; the two cited causes generally are linked. In our experimentation both the phenomena occurred. The total ammonia augmented from 1.1 g/L (pH 7.5), measured at the first day of experimentation, to 1.5 g/L (pH 7.8) recorded in the effluent digestate at 21^{st} day of AD test. The OLR was 0.90 kg SV/(m^3 d) during the first week of test, it was doubled after the second week of AD test. In order to solve the biological instability from the 29^{th} day of experimentation to the end it was decided to reduce the OLR of 50 % while the HRT was unchanged. The new fed was composed of 50 % by volume of tWAS and 50 % by volume of tap water. Also, in this case the same first order model was used (developed for continuous/semi-continuous CST AD reactor).

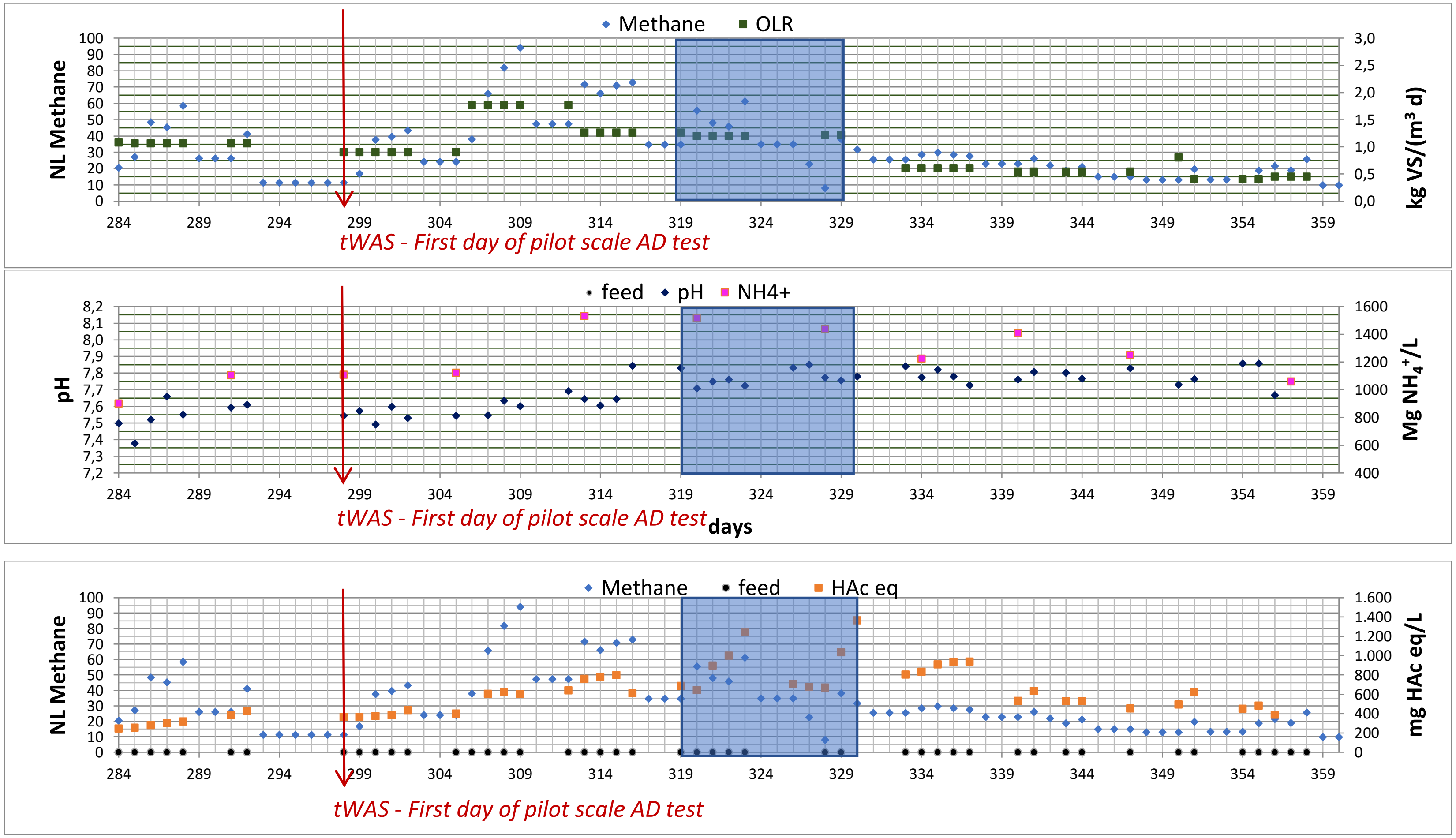


Figure 5. 6 Pilot and Semi-continuous Anaerobic digestion of tWAS. Inibition phenome

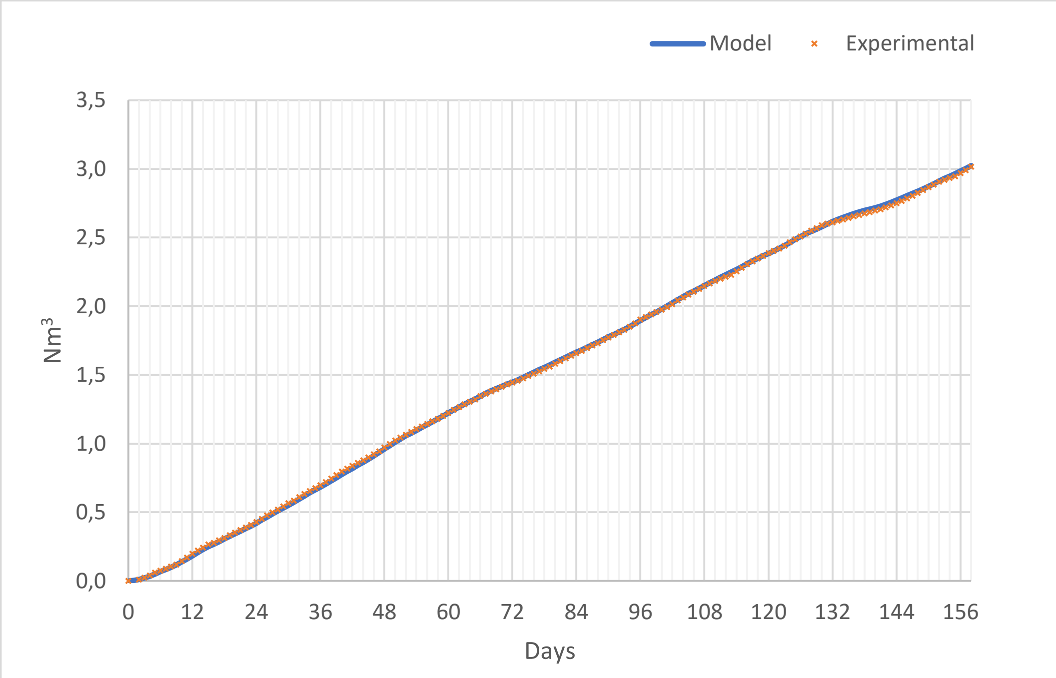


Figure 5. 7 Was AD test. Cumulative methane production. Model Calibration

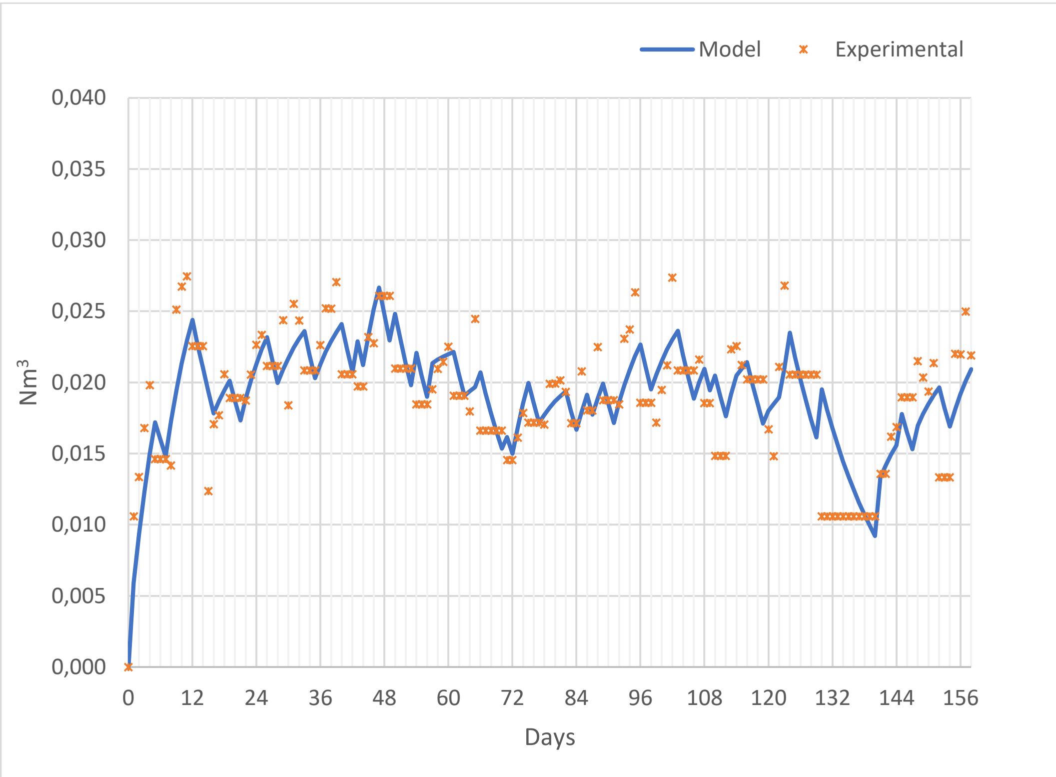


Figure 5. 8 WAS AD test. Experimental daily methane production vs Model daily methane production

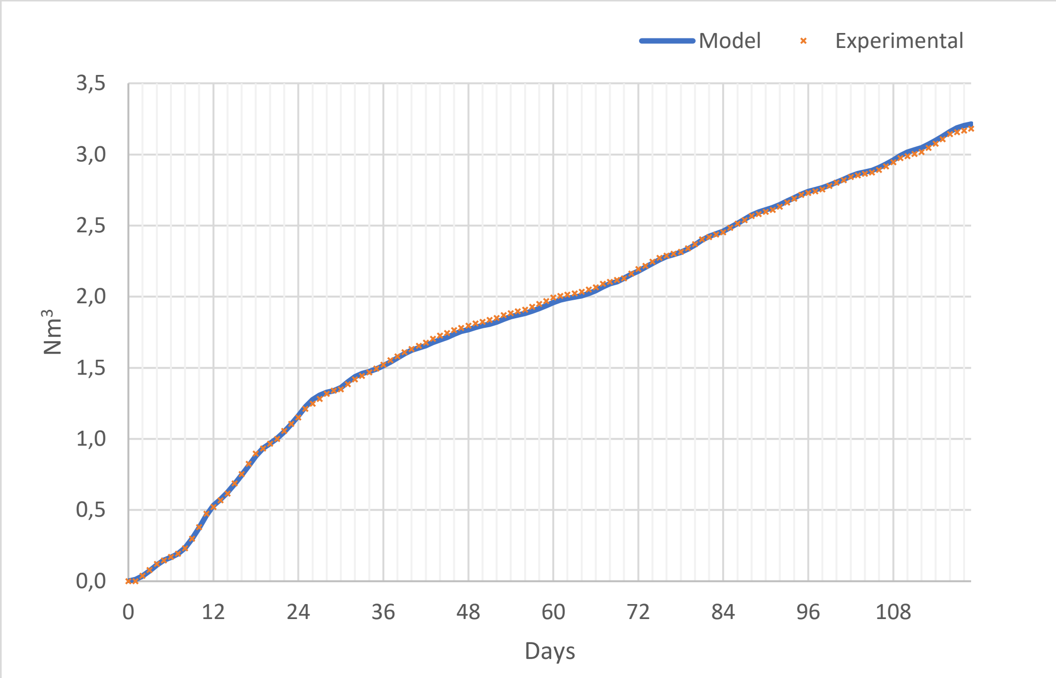


Figure 5. 9 tWas AD test. Cumulative methane production. Model Calibration

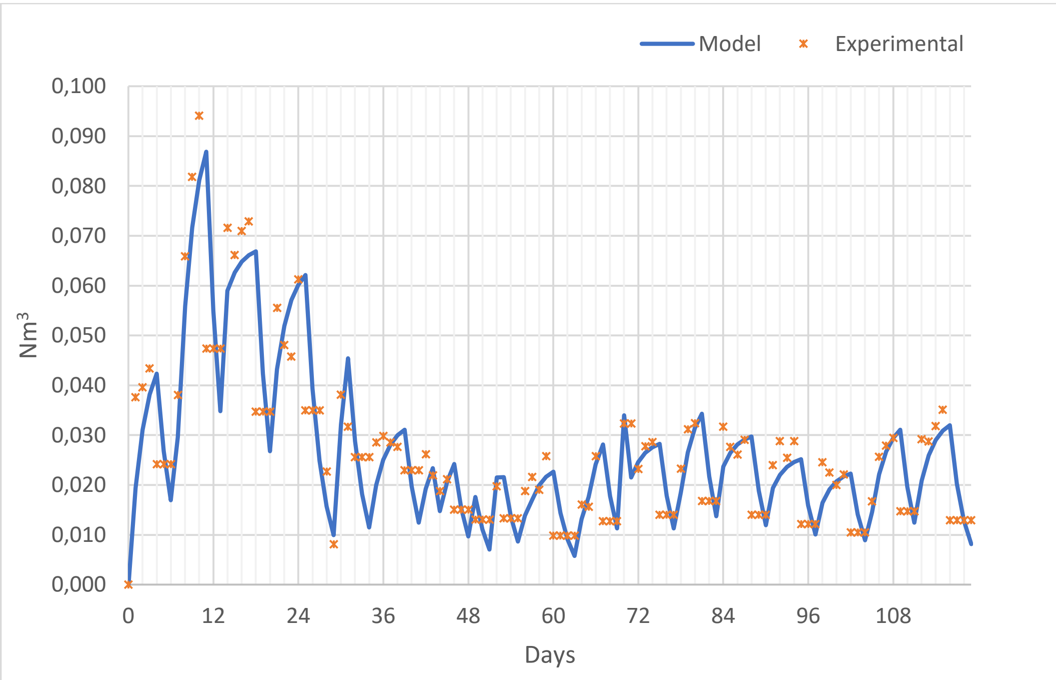


Figure 5. 10 tWAS AD test. Experimental daily methane production vs Model daily methane production

The fitting of experimental data of cumulative methane production (see figures 5.7 and 5.9), obtained from the semi-continuous pilot-scale tests, returned B_0 and k parameters for raw WAS and thermo-alkali treated WAS. The results are synthetically reported in Table 5.4. In table 5.4, the values of Absolute Biodegradation (Y) also are reported (Y was calculated as shown in equation 5.14).

Figure 5. 11 Left un-treated WAS, Right treated WAS

Sludge	*AD test*	B_o $[Nm^3/kg\ VS]$	*k* *[1/d]*	*Biodegradability* *Y [%]*
WAS	1	0.147 ±0.000	0.085±0.000	0.28 ± 0.000
Treated WAS	2	0.250 ±0.000	0.465±0.020	0.48 ± 0.000

Table 5. 4 Raw WAS and thermo-alkaline pre-treated WAS. Biochemical Methane Potential (B_o), hydrolysis rates(k) and biodegradability (Y).

The proposed model was used to fit the cumulative methane production data observed during the semi-continuous AD tests. Residual sum of squares (RSS) between the measured data and the model predicted data was the objective function (J). The optimal set of Bo and k was the one under which the RSS is minimized (J_{min}). The range of data used to estimate the searched parameters are reported in table 5.5.

	Number of measured data points	*Bo [Nm³ CH₄/kg VS]*	*k [1/d]*	*N° couple tested*
WAS	120	0.05-0.20 (step 0.0025)	0.05-0.20 (step 0.0025)	3721
tWAS	80	0.20-0.30 (step 0.0025)	0.35-0.50 (step 0.0025)	2501

Table 5. 5 Range of data used to estimate the searched parameters

Moreover, the surface parameters of treated and untreated sludge were achieved. The graphic results are reposted in figure 5.12 (raw WAS) and figure 5.14 (tWAS).

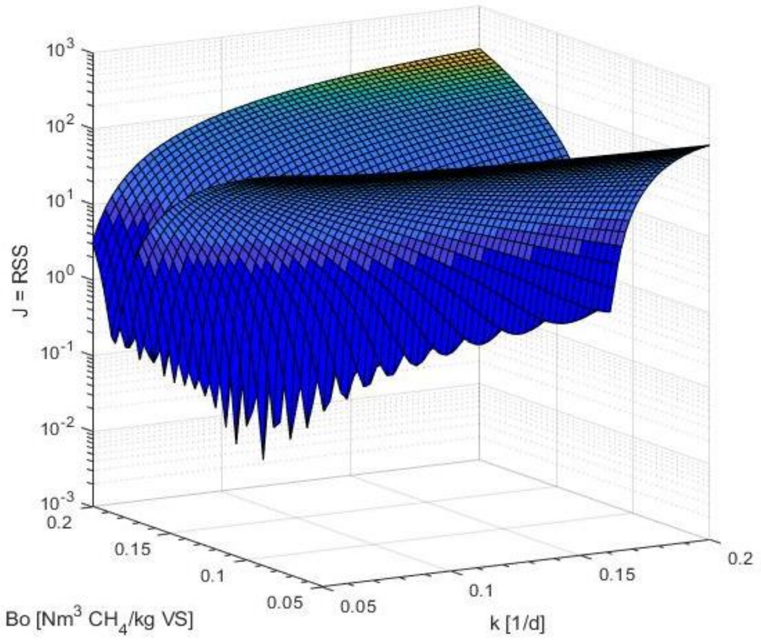


Figure 5. 12 WAS Residual sum of square matrix

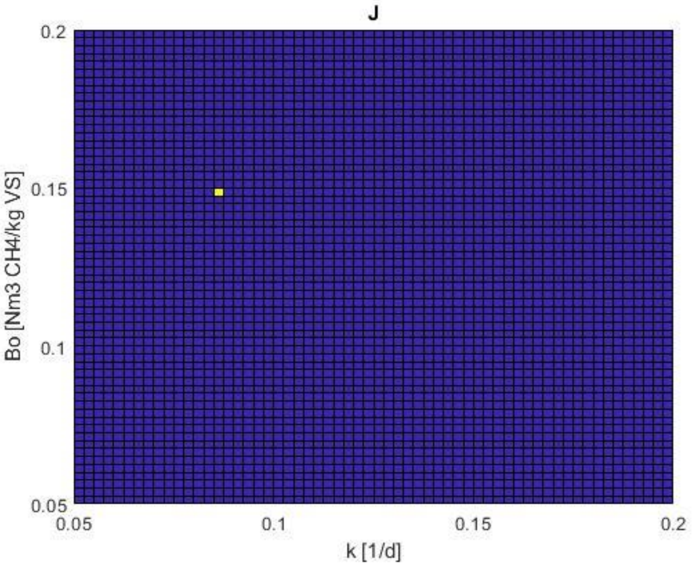


Figure 5. 13 WAS. Uncertainty analysis

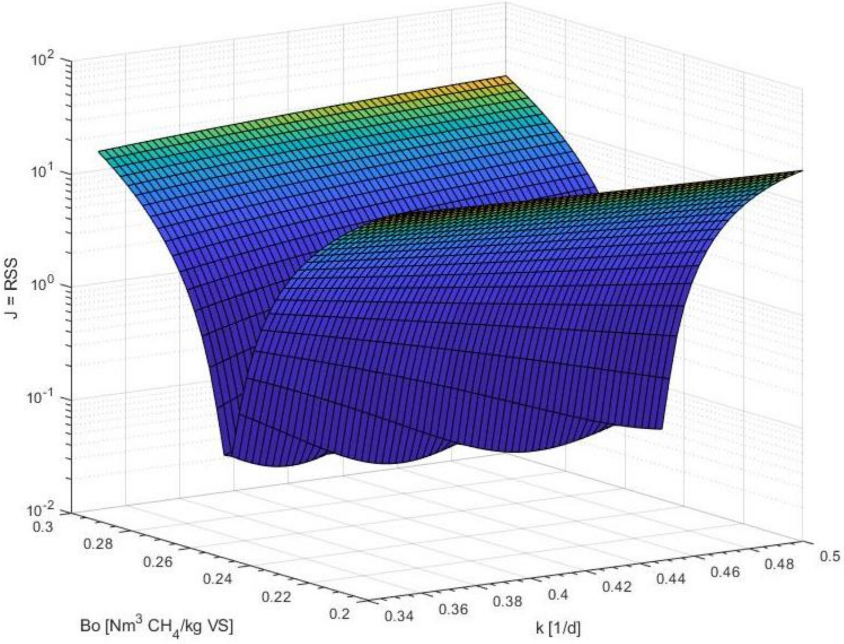


Figure 5. 14 tWAS. Residual sum of square matrix

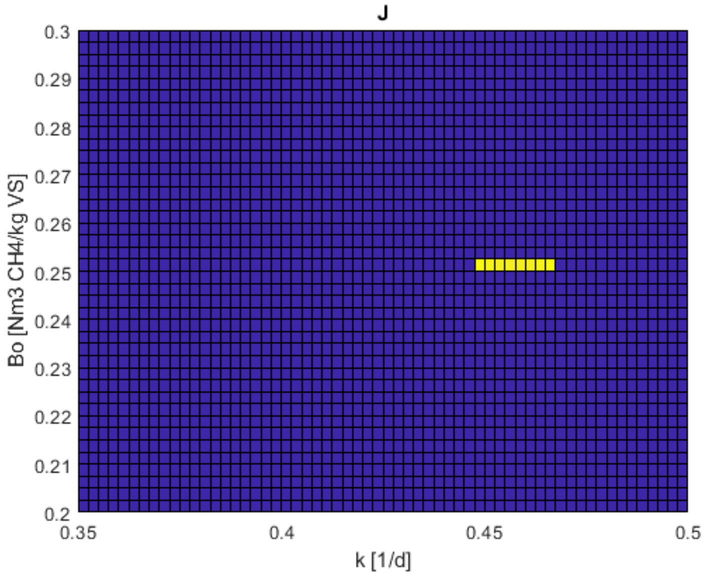


Figure 5. 15 tWAS. Uncertainty analysis

The thermo-alkali treatment of WAS determined an increase in the B_0 parameter of 70.1%. In fact, it passed from 0.147 Nm^3/kgVS of WAS to 0.250 Nm^3/kgVS of treated WAS.

Moreover, both the reported biomethane potentials parameters are in agree with the results obtained during the batch tests; these results are shown in the Chapter 4 (Batch anaerobic digestion tests). In detail, a comparison between the found results obtained in batch tests and semi-continuous AD experience are reposted in Table 5.6. The comparison was done using the equation 5.6. The equation was employed in order predict the methane production in a batch AD process by using the found Bo e k parameters. The first order kinetic model was used to extimate the methane production of both raw and treated sludge.

Sludge	*Batch AD tests [Nm^3/kg VS] (21 days) **	*Simulated Batch AD processes (Bo **, k **, 21 days)*
WAS	0.132	0.126
tWAS	0.247	0.250

*Table 5. 6 Results comparison - Batch AD test vs Simulated Batch AD Processes. The simulations were done by using the first order kinetic model. * Results reported in Chapter 4. **Main results of semi-continuous anaerobic digestion tests (See table 5.4)*

Values of the k parameter resulted of 0.085 and 0.465 d^{-1} for untreated WAS and treated WAS respectively. The increase of 447 % demonstrated that the thermo-alkali pre-treatment carried out on WAS has had a strong effect not only at the overall production of methane (testified by the increase on Bo) but especially in the hydrolysis phase, making the substrate readier degradable and shortening the duration of the process.

The validation of the model results was carried out. One strong hypothesis done was: the nature of biodegradable and non-biodegradable VS is similar; therefore, the COD/VS ratio of both degradable and non-degradable matter is the same. The validation consisted in the comparison of the cumulative amount of volatile solid extracted from the semi-continuous reactor with the amount of volatile solids in the digestate expected by the model. The graphical result of the raw WAS AD test is reported in figure 5.16 and figure 5.17. The graphical result of the tWAS AD test is reported in figure 5.18 and figure 5.119. The applied model was able to predict the concentration of volatile solid in the discharged digestate for both tested raw and treated sludge. The error between the experimental data and data predict by the model concerning the cumulative VS discharged at the end of the semi-continuous AD tests was equal to 1.3% and 1.8 % for WAS and tWAS respectively.

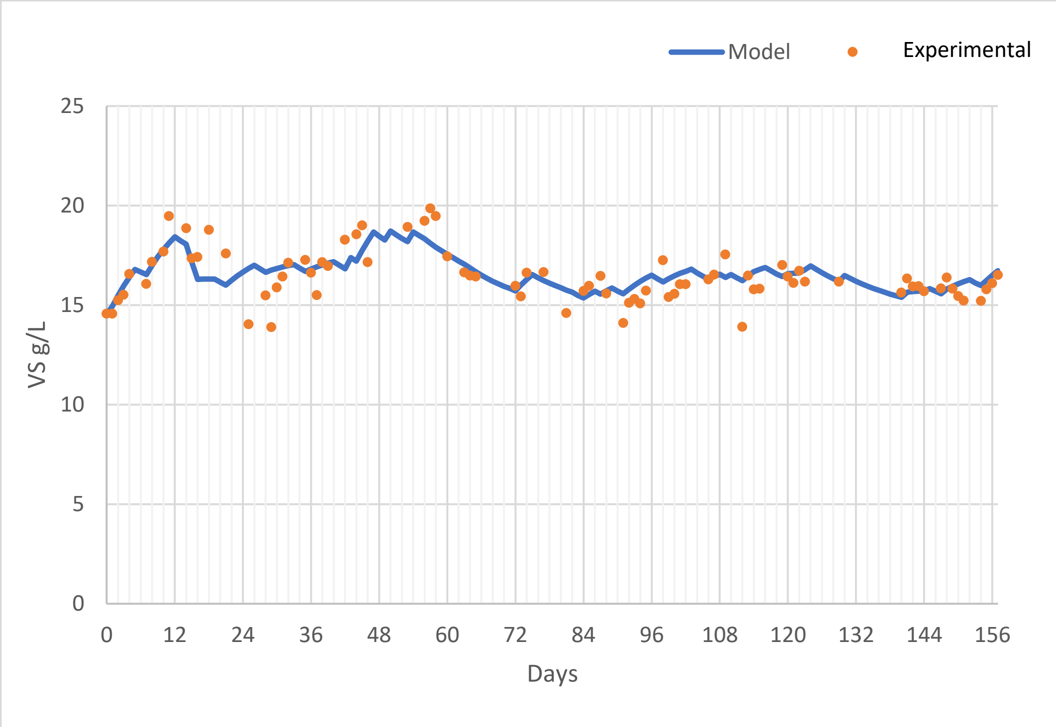


Figure 5. 16 WAS digestion test. Daily Volatile Solids concentration discharged from the digester in time

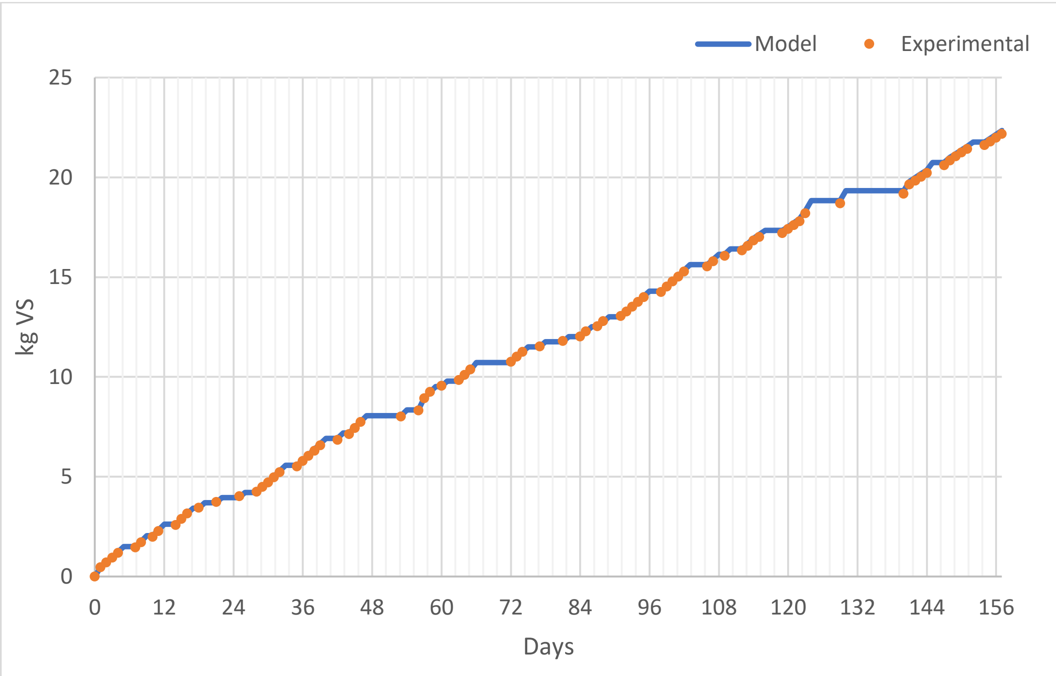


Figure 5. 17 Was digestion test. Cumulative Volatile Solids discharged from the digester in time

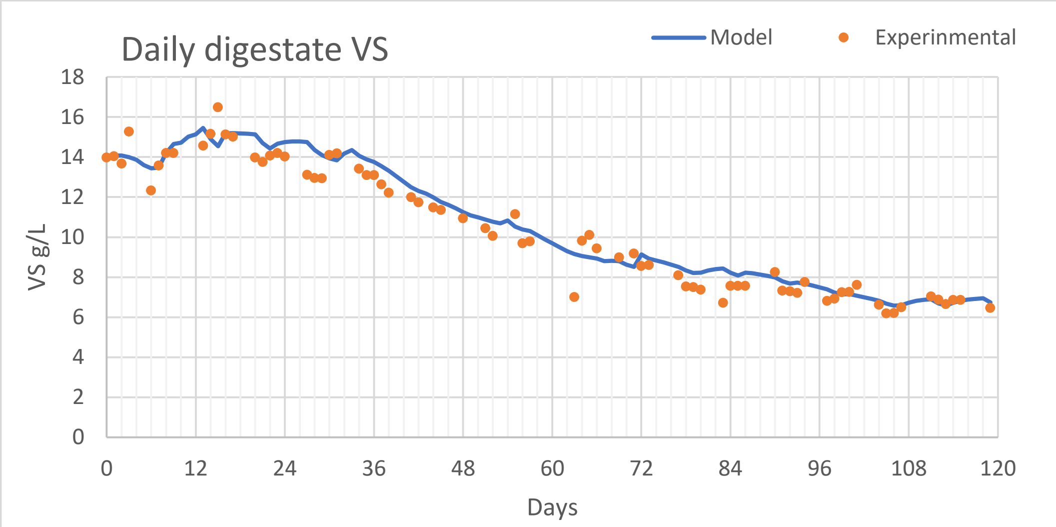


Figure 5. 18 tWAS digestion test. Daily Volatile Solids concentration discharged from the digester in time

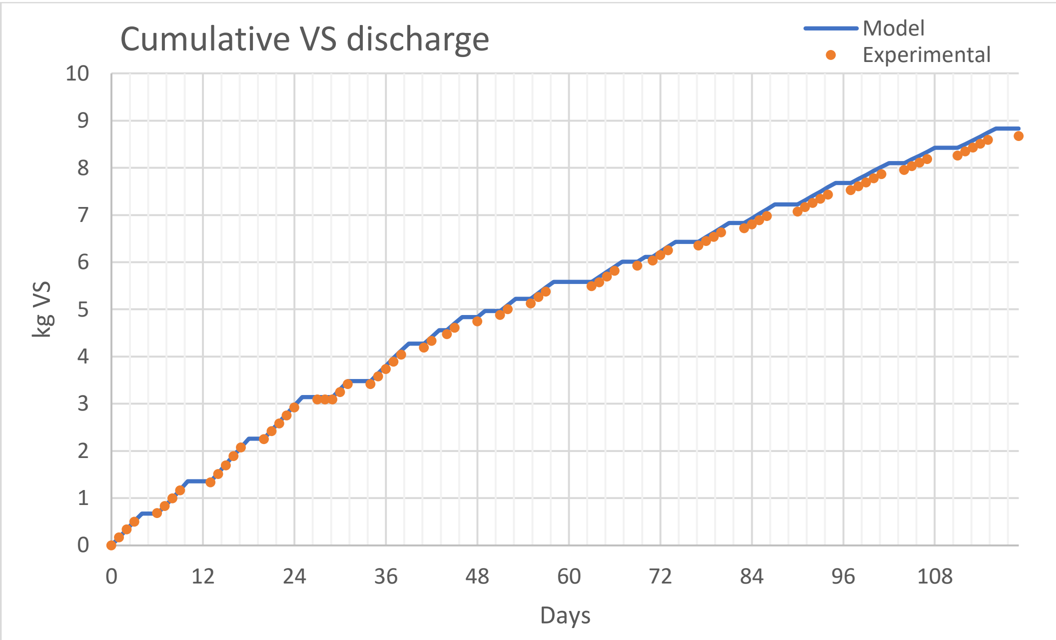


Figure 5. 19 Was digestion test. Cumulative Volatile Solids discharged from the digester in time

The $perNH_4^+$parameter was also evaluated for both the two tested substrates. The searched value represents the maximum amount of ammonia releasable per unit of volatile solid fed to the anaerobic reactor. Table 5.7 shows the parameter used to estimated $perNH_4^+$. Figure 5.21 shows the concentration of ammonia during the anaerobic digestion of raw WAS, as well as the figure 5.23 shows the concentration of ammonia during the anaerobic digestion of tWAS. In the figures 5.21 and 5.22 also the values of ammonia predicted by the model are shown. Also, in this case the optimal $perNH_4^+$was the one under which the RSS was minimized (J_{min}).

Moreover, the parameters surface was used to estimate the uncertainty of the searched value. However, in this case the unknown parameter to search is only one $perNH_4^+$. Therefore, the parameter surface becomes a line. The accepted parameters were those with J (the residual sum of squares) values lower than J_{crit}. values. The results were reported in table 5.7.

	Number of Experimental data	*Range* perNH$_4^+$ *[g NH$_4^+$/g VS$_{fed}$]*	perNH$_4^+$ *[g NH$_4^+$/g VS$_{fed}$]*
WAS	5	0.0-0.1 (step 0.0005)	0.0475 ± 0.0025
tWAS	16	0.0-0.1 (step 0.0005)	0.0655 ± 0.0025

Table 5. 7 Ammonia release. Results

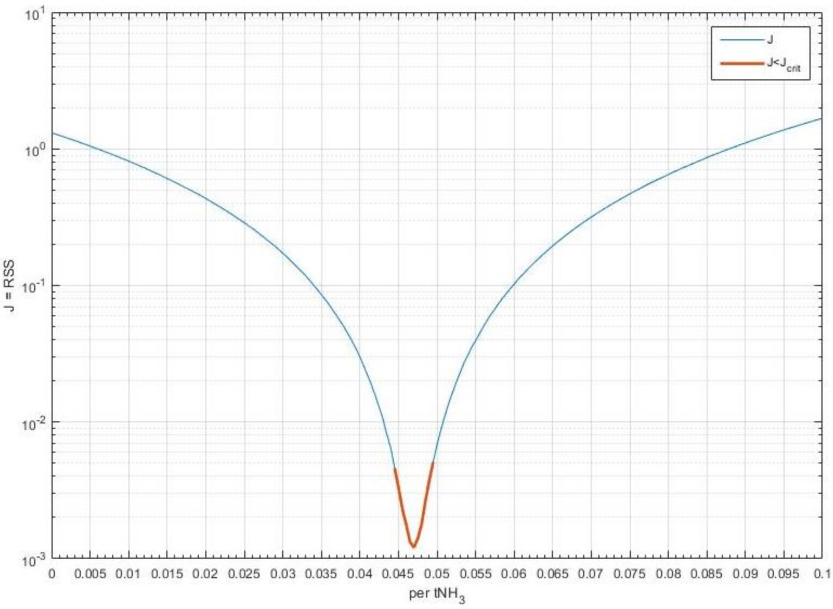


Figure 5. 20 Raw WAS digestion test. Residual Sum of Squares and uncertainty analysis

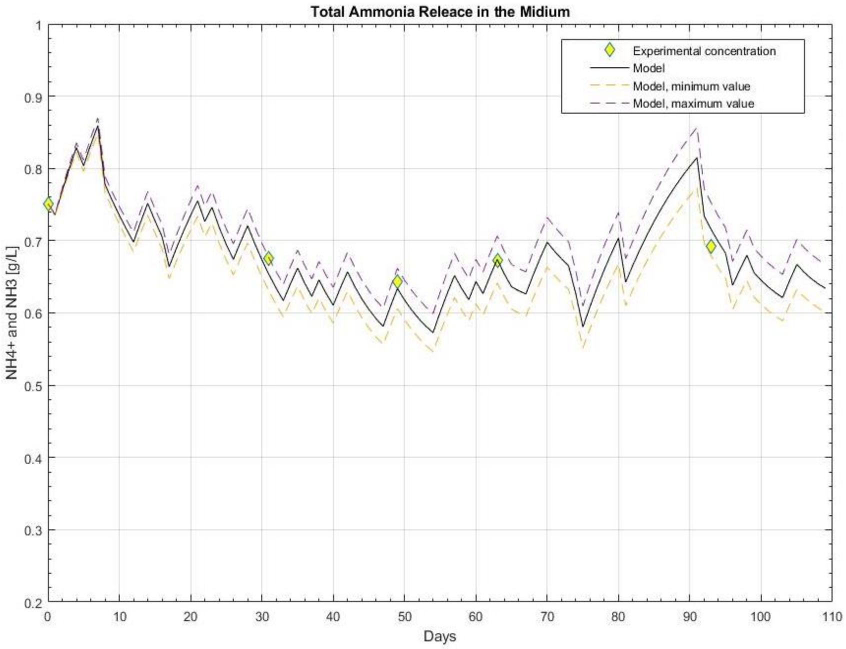


Figure 5. 21. Raw WAS digestion test. Ammonia in the liquor. Experimental concentration vs Model concentration

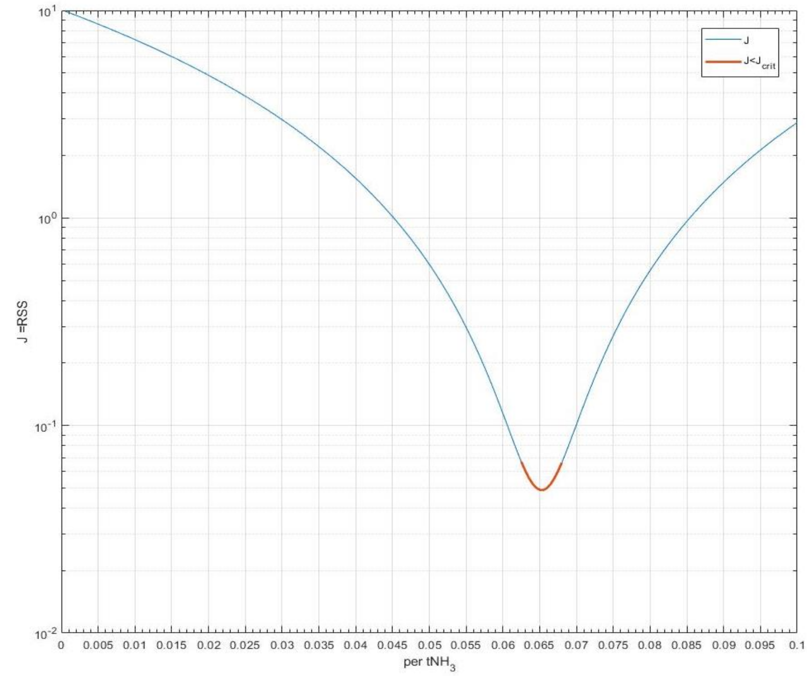


Figure 5. 22 Treated WAS digestion test . Residual Sum of Squares and uncertainty analysis

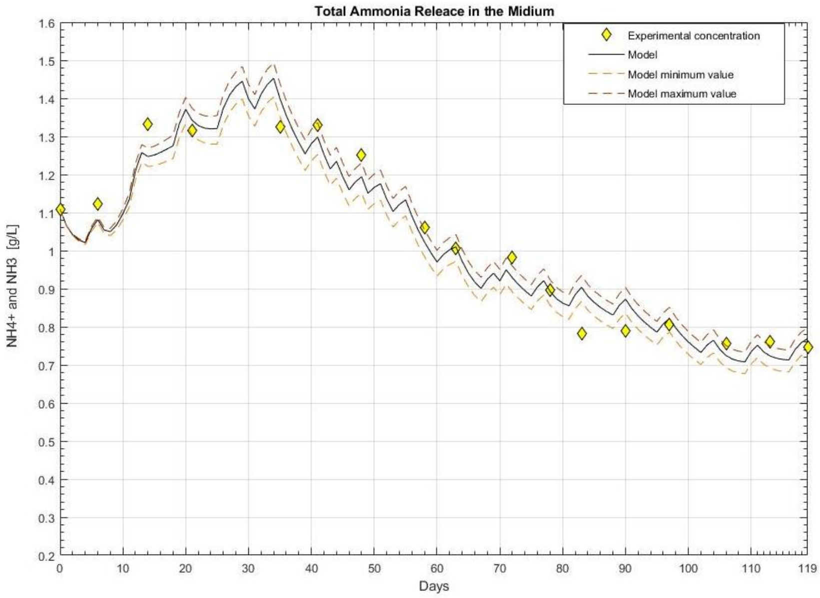


Figure 5. 23 Treated WAS digestion test. Ammonia in the liquor. Experimental concentration vs Model concentration

Starting from the results of the experimentation, the biomethane production, the VS reduction and the ammonia release during the steady state process were calculated. In table 5.8 the results of two steady state conditions were reported.

The developed model, with its characteristic parameters were determined as described in the 5.1.2 section, was used to predict the behaviour of the steady state-AD process characterized by the HRTs of 14.8 and 20.0 days.

A value of 14.8 days was selected because it was the average WAS hydraulic retention time in Castiglione Torinese WWTP digesters. This average HRT was calculated after one year of full scale WWTP monitoring (See Chapter 2).

After the WAS thermo-alkaline treatment (4g NaOH/100 gTS, 90 °C, 90 min.), and passing from an HRT of 14.8 d to 20 d the methane production should increase by 174.7% and the SV reduction should increase from 16 % to 43%. However, the ammonia release will increase by 126%; therefore, before implementing the lysis technique the problem relative to the ammonia increase in digestate liquor have to be considered. Surely, the thermochemical pre-treatment if implemented at the full-scale increases the methane production and decrease the digested sludge volume to manage. However, the increase of ammonia should be accurately evaluated in order to understand if the wastewater treatment line or the side-stream anammox process would be able to treat the produced ammonia overload.

Finally, a new scheme of the sludge line should be proposed in order to recover the thermal energy spent during the pre-treatment before the anaerobic digestion.

		WAS		*tWAS*	
HRT [d]		*14.8*	*20.0*	*14.8*	*20.0*
B [Nm^3 CH_4/ kgVS]		*0.082*	*0.093*	*0.218*	*0.226*
	WAS tWAS				
Results	*HRT 14.8 - HRT 14.8*			*165.6%*	
	HRT 20.0 - HRT 20.0				*143.1%*
	HRT 14.8 - HRT 20.0				*174.7%*
$VS_{effluent}$/VS_{fed}		*0.84*	*0.82*	*0.58*	*0.57*
Results	*HRT 14.8 - HRT 14.8*	*-16 %*	*-18%*	*-31.0%*	
	HRT 20.0 - HRT 20.0				*-31.0%*
	HRT14.8 - HRT 20.0				*-32.7%*
$NVS_{effluent}$/NVS_{fed}		*1.0*	*1.0*	*1.0*	*1.0*
g $NH_4^+$$_{effluent}$/kg$SV_{fed}$		*26.3*	*30.0*	*61.4*	*63.6*
Results	*HRT 14.8 - HRT 14.8*			*118.4%*	
	HRT 20.0 - HRT 20.0				*99.8%*
	HRT 14.8- HRT 20.0				*125.9%*

Table 5. 8 Steady state conditions. Results

5.3 Conclusions

The feasibility to improve the methane production during anaerobic digestion of WAS after a thermo-alkaline pretreatment was evaluated by a semi-continuous anaerobic digestion test. A comparison among the results here reported and some others present in the literature review is reported in table 5.9.

Oosterhuis M. et al. (2014) studied a thermal hydrolysis process (THP); the treatments were carried out by mean a THP-pilot reactor (Cambi process) and the test was done in cooperation with Cambi A.S. The adopted pre-treatment conditions were: temperature 165 °C, treatment time 20 min. and pressure 6 bar. The average absolute biodegradability (Y) of the control and treated sludge were 26 % and 42

% respectively. Oosterhuis's biodegradability values are in agreement with the results of thermo alkali treatment and AD test discussed in this Chapter (Y_{was} = 28 %, $Y_{t\ was}$=48%).

Gianico et al tested a WAS high temperature thermal pre-treatment. However, the conditions of the studied thermal treatment lysis technique were milder than those of a typical THP process. The treatment was done at a temperature values of 134 °C and under a pressure values of 3 bar. Both biomethane potentials and biodegradability of control and treated WAS were similar to those achieved in this research activity.

Finally, as reported in table 5.9, Wei and co-authors are the only who evaluated the hydrolysis kinetic constant. Wei at al. studied the free ammonia WAS pre-treatment under environment temperature. The free ammonia was used in the range between 0.085 and 0.680 mg NH_3/L. The recorded maximum value of k was equal to 0.53 d^{-1} (pre-treatment condition 680 mg NH_3/L); while, the kinetic constant of the untreated sludge was equal to 0.22 d^{-1}.

The following conclusions can be drawn from this study:

- The thermo-alkali treatment improves the biochemical methane potential by 70.1 %;
- The thermo-alkali treatment is strongly effective to increase the hydrolysis constant. The raw WAS is slowly biodegradable (k =0.085 d^{-1}), after thermo alkali pre-treatment the k values increases by 447%;
- Due to the thermo-alkaline treatment; the WAS biodegradability increased from 28 to 48% (increase of 71.4 %);
- The improved efficiency of WAS anaerobic digestion, after the thermo-alkali treatment, is comparable with the performance of other treatments present into the market or reported in scientific literature;
- The thermo-alkali treatment increases the ammonia release in the digestate liquor.

- The proposed first order kinetic model can be used as a tool in order to obtain the *Bo* and *k* couple of parameters.

Pre-treatment conditions	*Bo [Nm^3/kg VS]*		*hydrolysis rate [1/d]*		*Y biodegradation [%]*		*Reference*
	Control	tWAS	Control	tWAS	Control	tWAS	
Temperature 135 °C *Treatment time 30 min.*	0.261	0.292			49	55	(Bougrier et al., 2007)
Temperature 190 °C *Treatment time 15 min.*	0.261	0.327			49	62	(Bougrier et al., 2007)
Temperature 134 °C *Treatment time 20 min.* *Pressure 312 kPa*	0.154	0.223			31	46	(Gianico et al., 2013)
Temperature 134 °C *Treatment time 20 min.*	0.128	0.228					(Valo et al., 2004)
Temperature 150°C *Treatment time 5 min.*	0.220	0.312					(Sapkaite et al., 2017)
Temperature 180°C *Treatment time 50 min.*	0.220	0.340					(Sapkaite et. al, 2017)
Temperature 165 °C *Treatment time 20 min.* *Pressure 6 bar*					26	42	(Oosterhuis et al., 2014)
Temperature: ambient *Free ammonia 85 mg/L* *Treatment time 24 h*	0.160	0.163	0.22	0.41	30	30	(Wei et al., 2017)
Temperature: ambient *Free ammonia 250 mg/L* *Treatment time 24 h*	0.160	0.181	0.22	0.41	30	34	(Wei et al., 2017)
Temperature: ambient *Free ammonia 420 mg/L* *Treatment time 24 h*	0.160	0.195	0.22	0.42	30	36	(Wei et al., 2017)
Temperature: ambient *Free ammonia 680 mg/L* *Treatment time 24 h*	0.160	0.183	0.22	0.53	30	34	(Wei et al., 2017)
Temperature:90 °C *4 gNaOH/100 g TS* *Treatment time 90 min.*	0.148	0.250	0.085	0.465	28	48	This research activity

Table 5. 9 Literature review. Biomethane potential, hydrolysis rate and biodegradability values of treated WAS

Chapter 6 Full scale applicability of thermo-alkali pre-treatment of WAS. Technical and Economic Analysis

Reformed and extended version of conference paper originally published:

"Pilot-scale study of enhanced methane production during anaerobic digestion of waste activated sludge after combination of low thermal (90 °C, 1.5 h) and alkaline (NaOH) pretreatment" 2018
Campo G., A. Cerutti A., Zanetti M.C, Scibilia G., Lorenzi E., Ruffino B.
SMICE Sludge Management in Circular Economy. Rome 23th -25th May

Reformed and extended version of conference paper under revision in:

"Thermo-alkaline pre-treatment of WAS: Application of pilot semi-continuous AD test to assess biochemical methane potential and hydrolysis rate" 2019
Campo G., A. Cerutti A., Zanetti M.C, Scibilia G., Lorenzi E., Ruffino B.
16th IWA World Conference on anaerobic Digestion Delft (The Netherlands)
23^{th} – 26^{th} June 2019

This Chapter presents the results of two semi-continuous anaerobic digestion tests and the preliminary technical and economic assessment of the thermo-alkali treatment of WAS (90 °C, 4 g NaOH/100 g TS, 90 min.) for its full-scale applicability in Castiglione Torinese WWTP.

First, the anaerobic biodegradability of primary sludge (PS) produced in Castiglione Torinese WWTP was evaluated. In the same way as already done for raw and treated WAS AD tests, presented in Chapter 5, the couple of parameters (biomethane potential and B_o hydrolysis first order kinetic k) for PS was estimated.

Secondly, the anaerobic digestion of a mixed sludge (PS and thermo-alkali treated WAS) in a pilot and semi-continuous anaerobic reactor was carried out. The previously estimated B_o and k parameters, relative to treated WAS and raw PS, were used to predict the daily and cumulative methane production from an AD test carried out with mixed sludge at a pilot scale.

At last, the techno-economic analysis of the applicability of the thermo-alkali pre-treatment at the full scale was assessed. Two new configurations in sludge line, that include the thermos-alkali pre-treatment of WAS, were proposed. In all cases the gravity thickening of primary and secondary sludge was substituted by dynamic thickening; moreover, the treated WAS was mixed with the raw PS in order to recovery the thermal energy spent during the pre-treatment. The two proposed configurations differ because the first one involves a single stage digestion process and the second one a two-stages process. In both cases HRT was fixed equal to 17.1 days (the HRT recorded during one year of sludge line full scale monitoring Chapter 2).

The results shown that the anaerobic biodegradability of PS was equal to 49 %, while the hydrolysis first order kinetic constant of primary sludge was equal to 0.52 d^{-1}. The estimated parameters for PS and tWAS were able to well predict the anaerobic digestion of the mixed sludge. Indeed, since no inhibition phenomena occurred, the anaerobic digestion process of mixed sludge was modelled as a linear combination of the two substrates separately digested. Finally, if in Castiglione Torinese WWTP the thermo-alkali pre-treatment is applied, and the mixed sludge is digested in a two stages reactor, each one with an hydraulic retention time (HRT) equal to 8.55 days, the total increase in the methane production will be equal to 34 %.

6.1 Materials and methods

All the analytical parameters monitored in the lysis and AD tests (TS, VS, pH, electric conductivity (EC), soluble COD (sCOD) were determined using Standard Methods (APHA, 2012). Details were presented in paragraph 5.1.1.

6.1.1 Sludge

Samples of PS and WAS were collected from the outlet of gravity pre-thickeners used in Castiglione Torinese WWTP. In the plant two pre-thickeners were used to increase the total solids content of WAS, while the other four were used to treat the primary sludge.

6.1.2 Anaerobic digesters test

Two semi-continuous anaerobic digesters were used. The AD test with untreated primary sludge was performed in a 12 L anaerobic reactor (working volume equal to 10 L). The temperature in the digester was kept at 38°C (mesophilic conditions) by a temperature-controlled water jacket.

Figure 6. 1 - 12 L Anaerobic Reactor

The feeding was performed in a semi-continuous mode. The anaerobic reactor was fed only during the working days, generally five days per week from Monday to Friday. The applied HRT was equal to 20 days. The reactor had been working for 158 days and the number of sludge feeding was equal to 104.

The reactor was a cylindrical CST reactor, mechanically mixed by a coaxial and electric propelled shaker. The produced biogas was collected in two gas bags (each bag with a maximum volume of 5 L). The volume of the gas was quantified and characterized daily. The volumetric composition of the biogas in terms of CH_4, CO_2, O_2 was obtained by flushing 500 mL of biogas through a biogas analyser (Biogas Check, Geotechnical Instruments Ltd). The residual volume of the biogas after characterization was measured by displacing volumes of water with the residual gas and referring the obtained value to the normal conditions (273.15 K and 1 atm).

The second pilot and semi-continuous anaerobic reactor had a working volume of 240 L. Details of the reactor are found in Chapter 5 (See Paragraph 5.1.4). The anaerobic reactor was fed only during the working days, generally five days for week from Monday to Friday.

The second digester was used to test the anaerobic digestion of the mixed sludge and to validate the results of tWAS and PS digestion test. The composition of mixed sludge was the following:

- 50 % by volume of PS;
- 50 % by volume thermo-alkaline treated WAS.

The employed lysis reactor, and the operative phases of the pre-treatment were the same of those ones previously listed in Chapter 5 (See Paragraph 5.1.3). The trend of daily volatile solid fed to the anaerobic reactor, distinguished in PS and tWAS, was reported in figure 6.2. The anaerobic digestion test lasted 108 days and the number of daily feeding was equal to 73.

The volume of the gas was quantified and characterized daily. The volumetric composition of the biogas in terms of CH_4, CO_2, O_2 was obtained by flushing 500 mL of biogas through a biogas analyser (Biogas Check, Geotechnical Instruments Ltd).

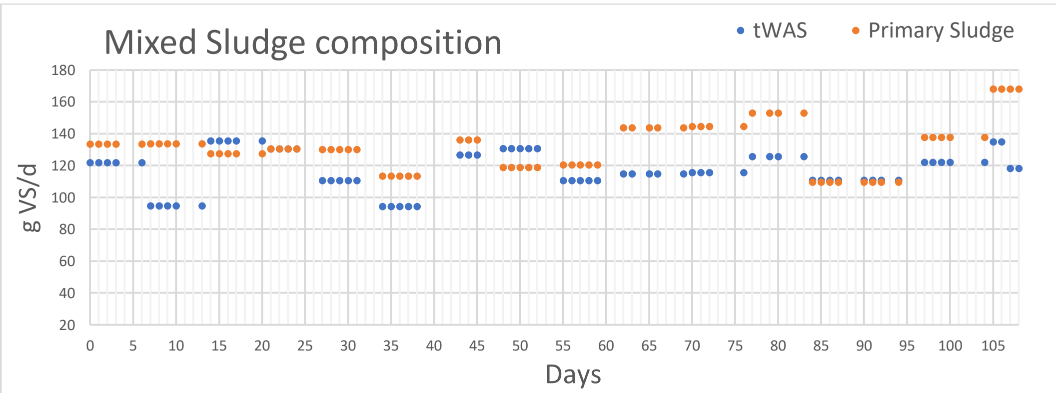


Figure 6. 2 Daily mixed sludge composition

6.1.3 Mathematical Model

The mathematical model used to determine the couple of parameters B_o and k for primary sludge is the same described in Chapter 5 - Section 5.1.5. The same model was used to predict the behaviour, in terms of methane production, of the mixed sludge in the anaerobic digestion test.

6.1.4 Preliminary Technical Assessment

The thermal energy necessary to heat the secondary sludge from the environment temperature to the treatment temperature (90 °C) was calculated as in the Equation 6.1:

$$Q = q_{WAS} \times c_p \times (T_p - T_1)$$

Equation 6. 1

Where the parameters represent:

- q_{WAS} = secondary sludge flow rate;
- c_p=specific heat capacity of sludge;
- T_p = temperature of pre-treatment;
- T_1= temperature of secondary sludge;

In order to design a self-sustainable thermo-alkali WAS pre-treatment, in the Casglione Torinese WWTP sludge line, the thermal power required to heat the secondary sludge, from the ambient temperature to the treatment temperature value, should be at maximum equal to the thermal energy produced by the CHPs unit. Known the thermal power available in sludge line, the maximum WAS flow rate and the consequent minimum TS of WAS concentration were calculated as in Equations 6.2 and 6.3:

$$q_{WAS} = \frac{Q_1 \eta_1}{c_p \times (T_p - T_1)}$$

Equation 6. 2

$$TS_{WAS}\% = \frac{M_{WAS}}{q_{WAS} \times 1000}$$

Equation 6. 3

Where the parameters represent:

- Q_1= thermal power available to heat sludge;
- q_{WAS} = secondary sludge flow rate;
- c_p=specific heat capacity of sludge;
- T_p = temperature of pre-treatment;
- T_1= temperature of secondary sludge;
- M_{WAS} = secondary sludge mass flow rate;
- $TS_{WAS}\%$ = TS concentration in WAS;
- η_1= heat transfer system efficiency

The heat transfer system has an efficiency (η) lower than 100 %. Therefore, five condition were considered. The five heat transfer system efficiencies taken in account were: 100, 90, 80, 70, 60 %.

Furthermore, the thermal energy required to digest primary and secondary sludge should be calculated as follows:

$$Q_2\eta = (q_{WAS} + q_{PS}) \times c_p \times (T_2 - T_1) + n \times Q_a$$

Equation 6. 4

Where the parameters are listed in the follow

- Q_1 = thermal power required to to heat sludge;
- η_2= Heat network efficiency;
- q_{PS} = primary sludge flow rate;
- q_{WAS} = secondary sludge flow rate;
- c_p=specific heat capacity of sludge;
- T_2 = temperature of digestion process;

- T_1= temperature of primary and secondary sludge;
- n = number of employed digesters;
- Q_a = thermal power loss towards the outside from each one digester.

Moreover, in order to design a self-sustainable system, the required thermal energy to digest primary and secondary sludge should be generated from the burned biogas. The maximum flow rate of mixed sludge to be fed into the digesters should be calculated with the aim to recovery the thermal energy spent during the WAS pre-treatment. In this condition Q_1 should be equal to Q_2. Known the thermal power available in sludge line, the maximum flow rate of WAS and PS can be calculated solving the following system of equations:

$$\begin{cases} Q_1 = q_{WAS} \times c_p \times \left(T_p - T_1\right) \\ Q_1\eta = (q_{WAS} + q_{PS}) \times c_p \times (T_2 - T_1) + n \times Q_a \end{cases}$$

Equation 6. 5

Therefor knowing the maximum available WAS flow rate, the PS flow rate that can be heat using the thermal power spent during the WAS pre-treatment can be calculated as follows:

$$q_{PS} = \frac{1}{(T_2 - T_1)} \times \left\{ q_{WAS} \times \left[\eta T_p + T_1(1-\eta) - T_2\right] - \frac{nQ_a}{c_p} \right\}$$

Equation 6. 6

Known the average primary and secondary sludge mass flows produced in the WWTP, the minimum concentrations of TS of PS and WAS were calculated:

$$TS_{WAS}\% = \frac{M_{WAS}}{q_{WAS} \times 1000}$$

Equation 6. 7

$$TS_{PS}\% = \frac{M_{PS}}{q_{PS} \times 1000}$$

Equation 6. 8

6.1.5 Preliminary Economic assessment

From the final outcome of the energy balance, a preliminary economical assessment of the whole AD process was performed. This assessment took into account the items listed here:

- the price of employed natural gas as an auxiliary fuel;
- the money saved from the self-production of renewable electrical energy,
- the State incentive, called "GRIN", for the renewable electric energy production;
- the price of polyelectrolyte;
- the price of sludge disposal;
- the price of consumed electrical energy for the dynamic thickening of WAS and PS.

For the economic assessment, the amount of NaOH used in the pre-treatment was precautionary counted as non-volatile solid NVS into the digestate. Therefore, all the employed sodium hydroxide for the WAS pre-treatment have to be disposal as digestate sludge. Then, it was assumed that the dewaterability properties of digested and mixed sludge did not change after the pre-treatment implementation. Moreover, the analysis did not consider the maintenance of the new pieces of pre-treatment equipment that have to be implemented in the sludge line as well as it did not contemplate the labour cost. The detail of each cost is listed in table 6.1.

Castiglione Torinese WWTP	
Total Electrical Energy Required	158.5 MWh/d
Electrical Energy Price	145 €/MWh
Natural Gas Price	0.32 €/Nm^3
Incentive GRIN	0.089 €&kWh
Cationic Polyelectrolyte Price (Solution 45%)	1.38 €/kg
Dewatered Sludge Disposal Cost	90 €/ton
Dry Sludge Disposal Cost	100 €/ton
Polyelectrolyte consumption (pre-thickening PS and WAS)	5 g/ kgTS
Polyelectrolyte consumption (dewatering digestate Sludge)	15 g/ kgTS
Pre-thickening of PS and WAS (Electric Energy consumption)	0.03 KWh/m^3
Dry sludge disposal (2017)	10.000 t

Table 6. 1 Technical and economic data used for the preliminary economic assessments

Starting from the Opex (operating expense) previously listed a preliminary range of Capex (Capital Expenditures) was evaluated. In order to calculate a range of Capex four pay-back times were fixed. The considered pay-back times were: 2, 3, 4, and 5 years. The formula of Net Present Value (NPV) was used. NPV is the sum of the present value of a series of present and future cash flows.

$$NPV = -I_0 + \sum_{n=1}^{n} \frac{R_i}{(1+i)^n}$$

Where:

- Io is the total cost at time zero; it is the total costs for the implementation of the dynamic thickening of PS and WAS sludge and the WAS pre-treatment;
- R_i is the net cash flow;
- i is the annual interest rate;
- n is the time of the cash flow;

Fort this assessment, *n* and *i* parameters were fixed to 20 years and 0.05 respectively. Moreover, it is was planned to implement the WAS pre-treatment in the Castiglione Torinese WWTP in the year 2020; from the first working year to the 2023 SMAT company will receive the State incentive for the produced renewable electric energy; from the year 2024 to the end of life time (2039) of the machines used for the pre-treatments, the renewable electric energy incentive will not be granted.

6.2 Results

6.2.1 Primary Sludge Elemental Analysis

The results of the elemental analysis of Primary Sludge were used to calculate the VS ponderal formula ($C_{10.6}H_{18.2}O_{4.1}N$). In the table Table 6.2 the COD/VS ratio and the theoretical biogas/methane potential production (calculated by the Buswell relationship) are shown.

	N/VS [gN/gVS]	COD/VS [gO_2/gVS]	Biogas $_{th}$ [Nm^3/kg VS]	$CH_{4\ th}$ [Nm^3/kg VS]
PS	6.2 %	1.76	1.06	0.62

Table 6. 2 Primary Sludge characterization and theoretical biogas and methane specific productions

6.2.2 Anaerobic digestion

6.2.2.1 Primary sludge

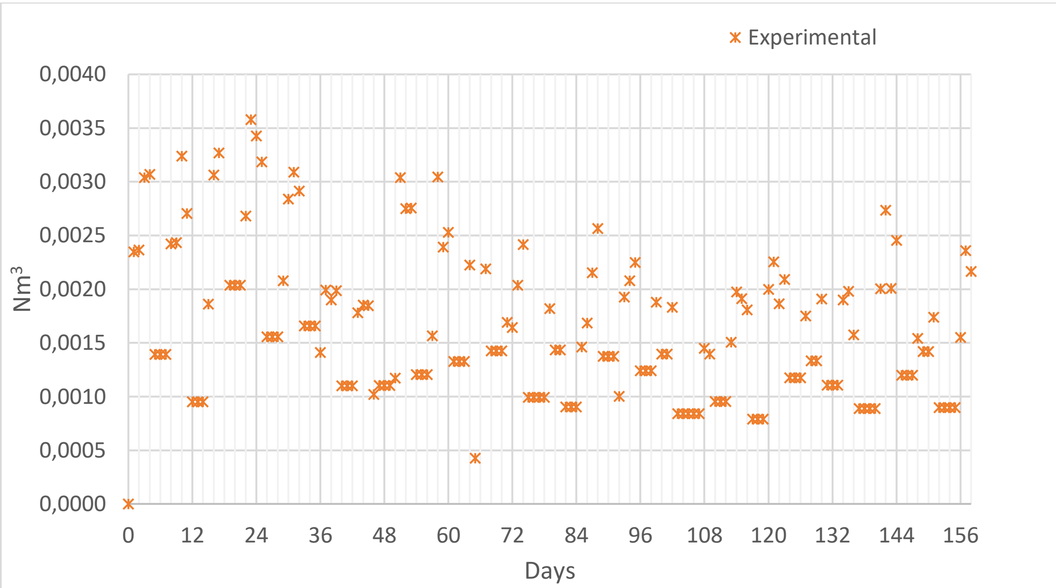


Figure 6. 3 PS digestion test. Daily methane production

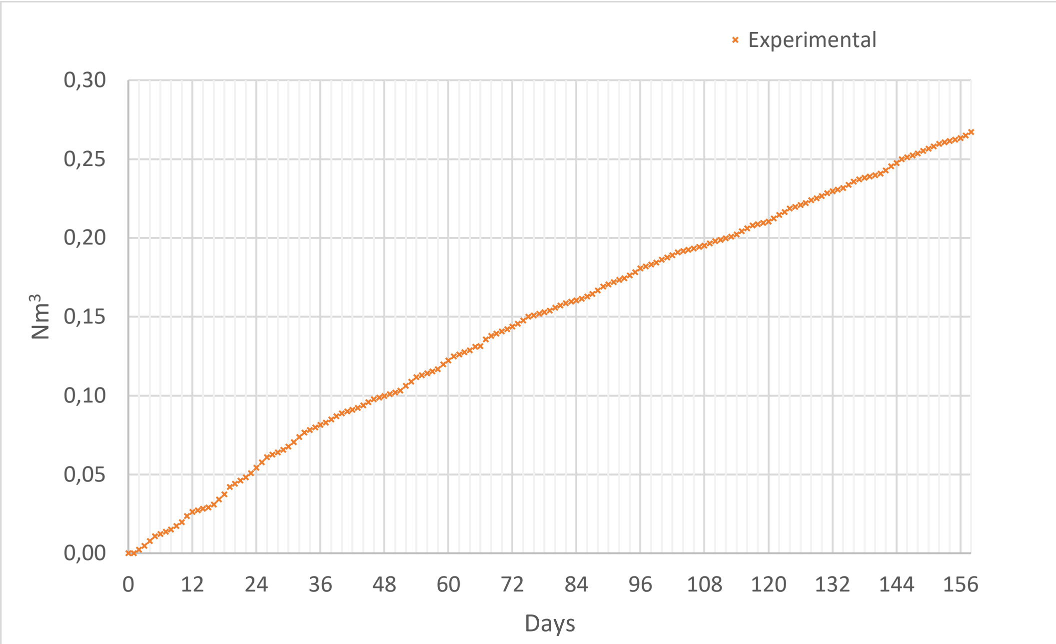


Figure 6. 4 PS digestion test. Cumulative methane production

The daily and cumulative methane production values obtained from the semi-continuous anaerobic digestion tests are shown in figures 6.3 and 6.4.

The fitting of experimental data of cumulative methane production (figure 6.4), obtained from the semi-continuous pilot-scale test, returned B_0 and k parameters for PS. The results are synthetically reported in table 6.3. It also reports the values of Absolute Biodegradation (Y).

Sludge	*AD test*	*B_o [Nm^3/kg VS]*	*k [1/d]*	*Y [%]*
Primary	3	0.30 ±0.00	0.52±0.04	0.49

Table 6. 3 Biochemical Methane Potential (B_o), hydrolysis rate constant (k) and biodegradability (Y) values of primary sludge.

Residual sum of square (RSS) between the measured data and model predicted data was the objective function (J). The optimal set of Bo and k was the one under which the RSS is minimized (J_{min}). The range of data used to estimate the searched parameters were reported in table 6.4.

	Number of measured data	Bo [Nm^3 CH_4/kg VS]	k [1/d]
PS	104	0.20-0.40 (step 0.01)	0.40-0.40 (step 0.01)

Table 6. 4 Range of data used to estimate the searched parameters

Moreover, the surface parameters uncertainty of Primary Sludge was calculated by using the Equation 5.25. The graphic results were reported in figures 6.5 and 6.6. The biomethane potential and first order hydrolysis kinetic parameters of PS were respectively equal to 0.300 Nm^3/kg VS and 0.52 d^{-1} respectively.

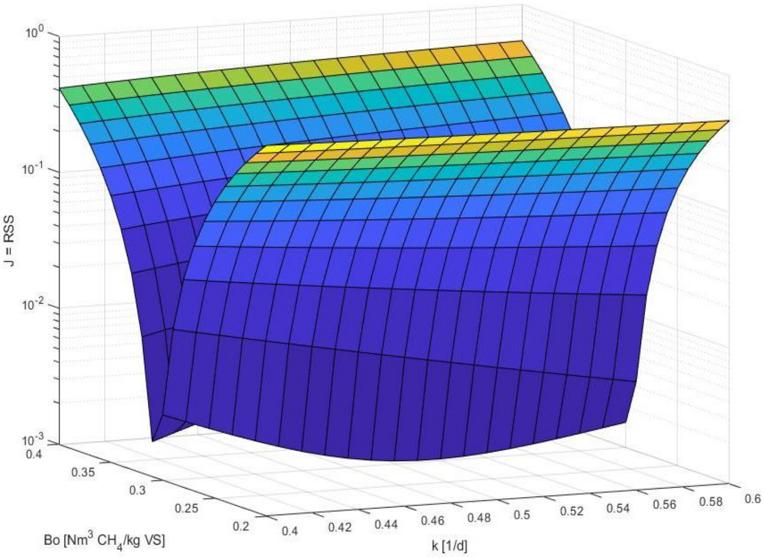


Figure 6. 5 PS. Residual sum of square matrix

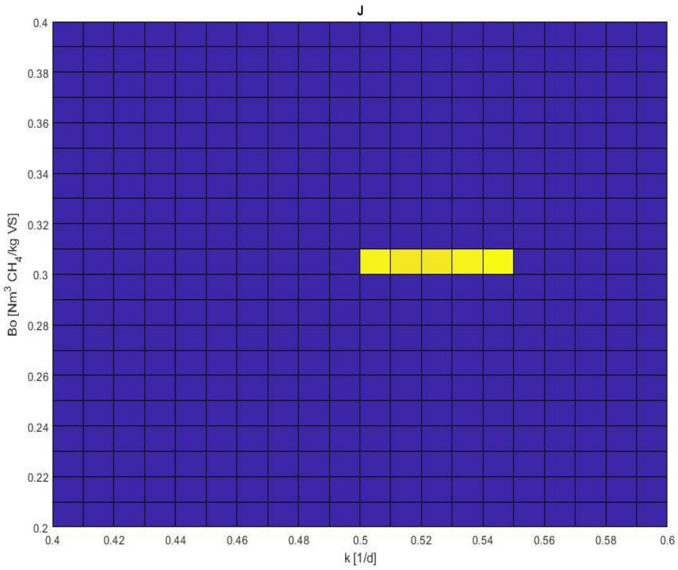


Figure 6. 6 PS. Uncertainty analysis

The comparison between the experimental and modelled values of cumulative methane production during the anaerobic digestion test are reposted in figure 6.7. Furthermore, Figure 6.8 shows the comparison between the experimental and modelled values of daily methane production during the Primary sludge AD test. The daily and cumulative values of the VS discharged from the digester are reported in Figures 6.7 and 6.8.

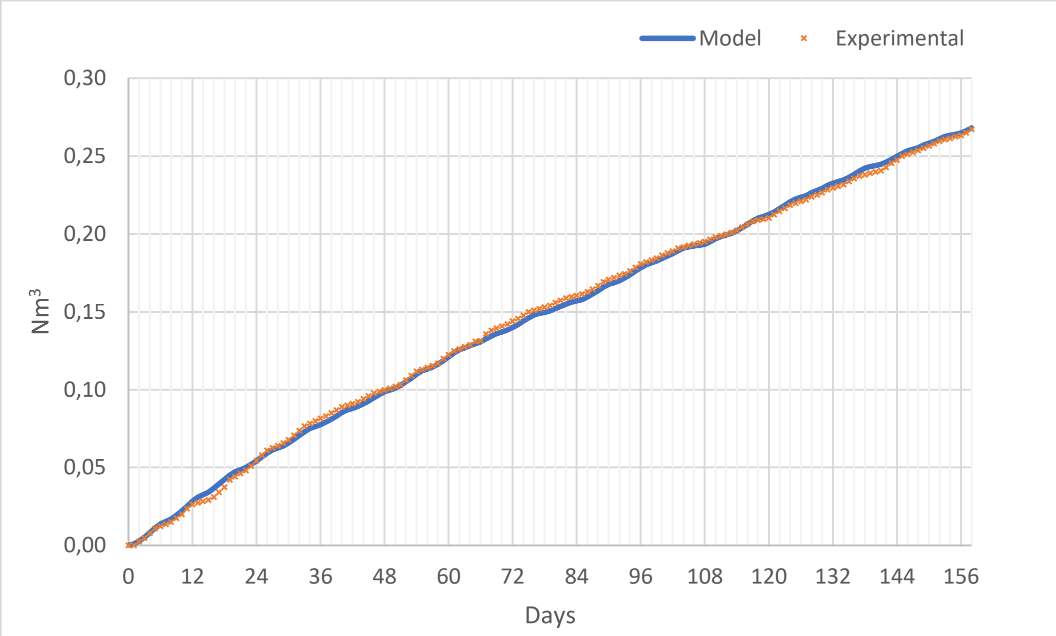


Figure 6. 7. Primary sludge AD test. Cumulative methane production

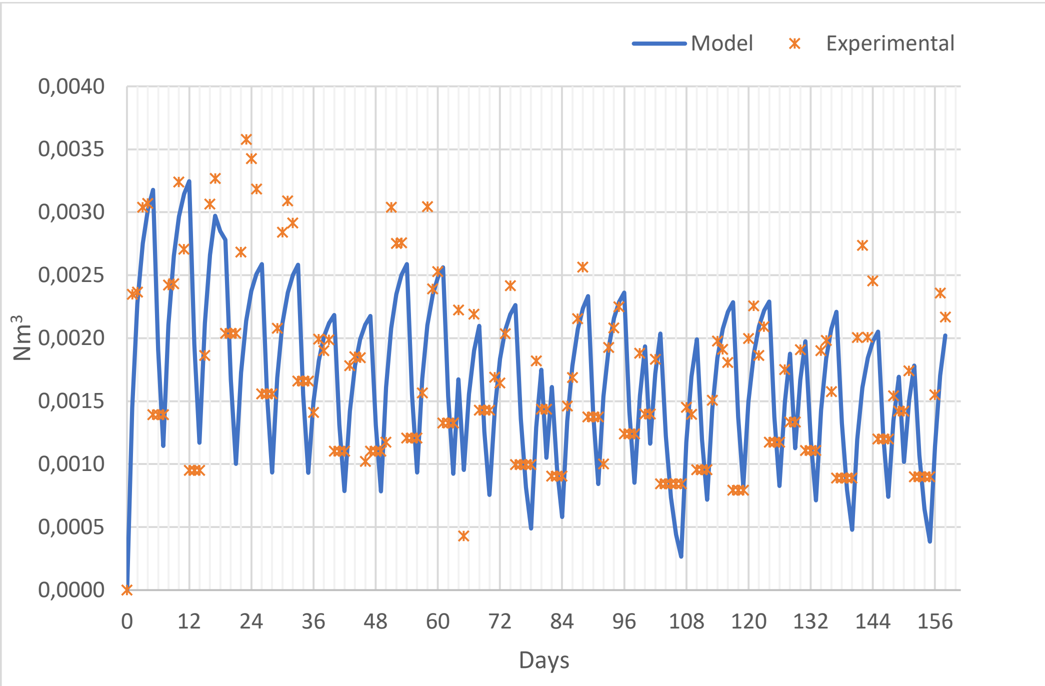


Figure 6. 8 Primary sludge AD test. Daily methane production

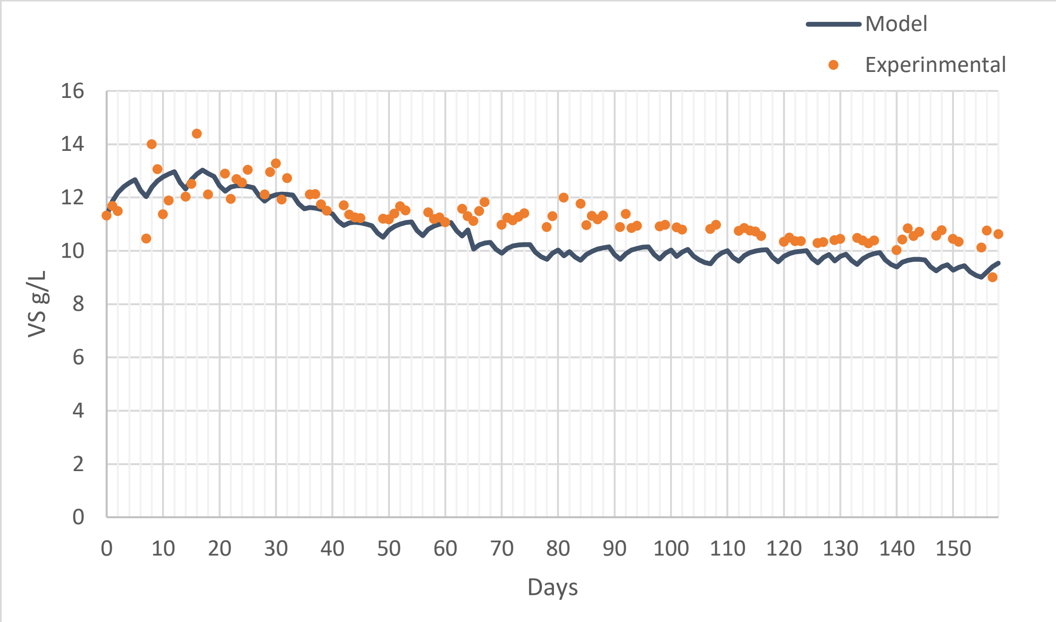


Figure 6. 9 Primary sludge AD test. Daily Volatile Solids concentration discharged from the digester in time

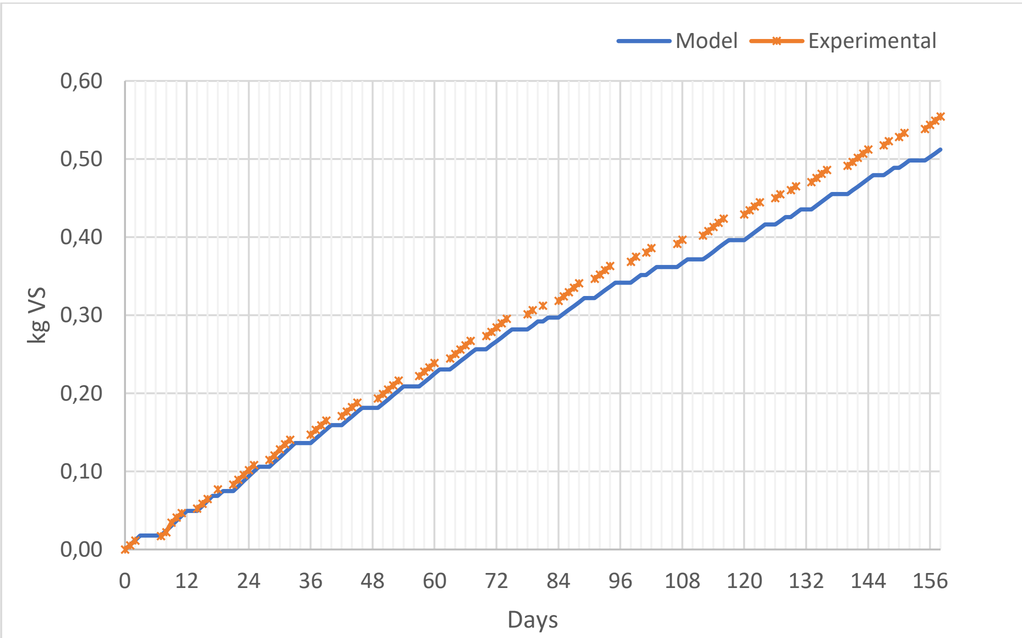


Figure 6. 10 Primary sludge AD test. Cumulative Volatile Solids discharged from the digester in time

6.2.2.2 Mixed sludge anaerobic digestion

The graphical results of the semi-continuous anaerobic digestion test that involved the mixed sludge are reported in figures 6.11 and 6.12.

The four parameters found for PS and tWAS (the couple B_o and k for each substrate) were used to predict the daily and cumulative methane production from the AD of the MIX substrate. The error between the experimental and modelled data of cumulative methane production, at the end of the test, was only of 1.1%.

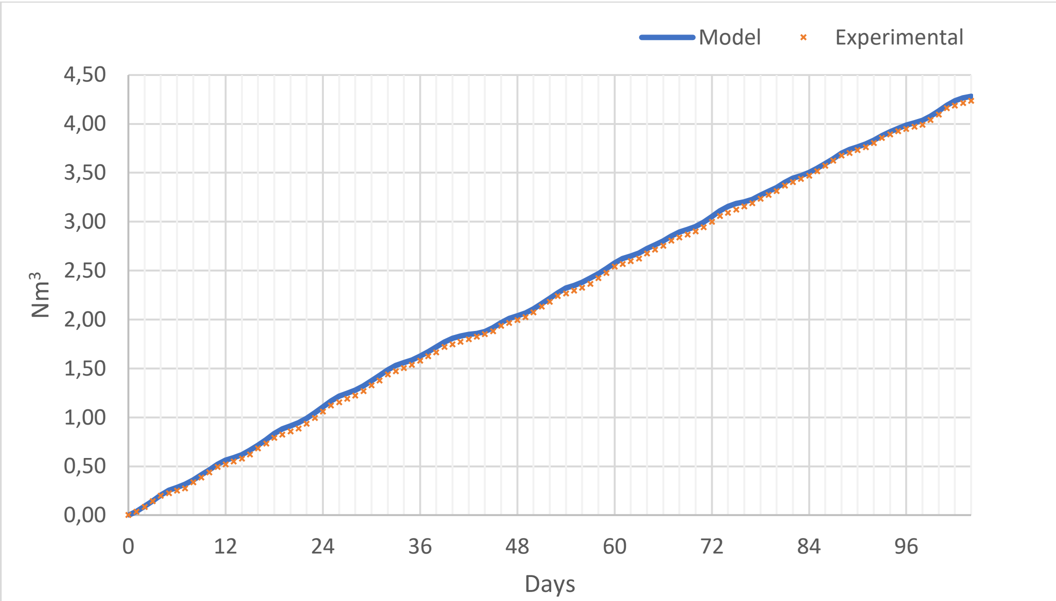


Figure 6. 11 AD Mixed Sludge. Cumulative methane production

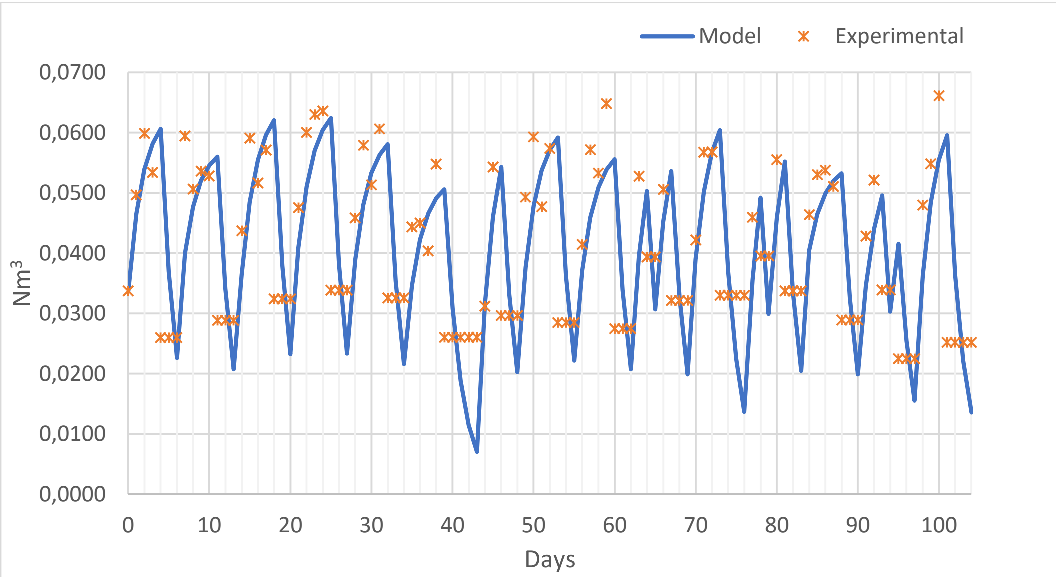


Figure 6. 12 AD Mixed Sludge. Daily methane production

6.2.3 The proposed two configurations

Two new configurations in the sludge line, that include the thermo-alkaline pre-treatment of WAS, were proposed. The configurations are reported in figures 6.13 and 6.14. In all cases the gravity thickening of primary and secondary sludge was substituted by a dynamic thickening process ((Electric Energy consumption 0.03 kWh/m^3). Moreover, the treated and undigested WAS was mixed to the raw PS in order to recover the thermal energy spent during the pre-treatment. It is also necessary to a recall the effect of a thermo-alkali pre-treatment on ammonia release (see table 5.8). The mixing of WAS with primary sludge helps in controlling ammonia concentration, adjusts pH to neutral values and dilutes the load of sodium ions introduced with the NaOH used for the treatment (Ruffino 2015, Ruffino 2016, Pinto et al., 2016; Sarwar et al., 2018).

The two proposed configurations differ because the first involves a single-stage digestion process and the second a two-stages process. In both cases the HRT was set equal to 17.1 day. This HRT was selected in order to easy compare the present situation (Chapter 2) and with the possible advantage to implement the thermo-alkaline treatment in the sludge line of Castiglione Torinese WWTP. In fact, during one year of full-scale AD process monitoring, the average HRT was equal to 17.1 days.

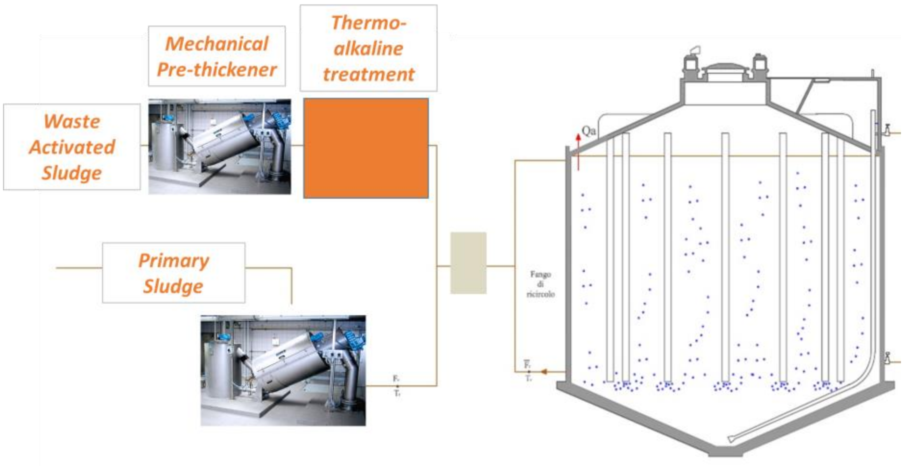


Figure 6. 13 One-stage anaerobic digestion system

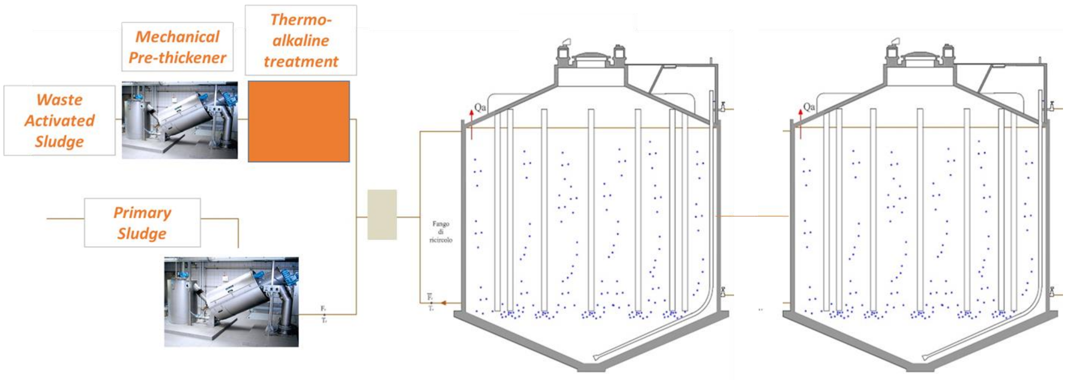


Figure 6. 14 Two stages anaerobic digestion

In the table 6.5 the principal results of all the semi-continuous anaerobic digestion tests were summarized.

Sludge	*AD test*	*B_o [Nm^3/kg VS]*	*k [1/d]*	*Biodegradability [%]*
WAS	1	0.148	0.08	0.28
Treated WAS	2	0.250	0.46	0.48
Primary	3	0.300	0.52	0.49

Table 6. 5 Biochemical Methane Potential (B_o), hydrolysis rates and biodegradability k of raw WAS, thermo-alkaline pre-treated WAS and primary sludge.

The parameters concerning PS and tWAS, listed in Table 6.5, were used in order to predict the effects of the thermo-alkaline treatment of WAS on the Castiglione Torinese WWTP.

To assess the economic feasibility of the tested thermo-alkaline treatment, raw and treated WAS as well as PS were assumed to go through CSTR steady state anaerobic reactor. The studied HRTs were 14.8[1], 17.1[2] and 20 days during the WAS and tWAS simulation; while the simulations of PS digestion were done using the following HRTs: 17.1, 18.6[3] and 20 days. The full-scale WWTP by a technical assessment was done both for one stage and two stage anaerobic digestion configurations.

One stage digestion:

$$B = \left(1 - \frac{1}{1 + k \times HRT}\right) \times B_0 \times SV$$

Equation 6. 9

$$VS_{nb} = (1 - Y) \times VS_{in}$$

Equation 6. 10

$$VS_b = \frac{1}{1 + k \times HRT} \times Y \times VS_{in}$$

Equation 6. 11

$$VS = VS_b + VS_{nb}$$

Equation 6. 12

$$NH_4^{\ +}(t) = NH_4^{\ +}{}_{in} + perNH_4^{\ +} \times \frac{k \times HRT}{1 + k \times HRT} \times VS_{in}$$

Equation 6. 13

[1] WAS Average HRT value in Castiglione Torinese WWTP. One year of full monitoring (See Chapter 2).
[2] Total Sludge Average HRT value in Castiglione Torinese WWTP. One year of full monitoring (See Chapter 2).
[3] PS Average HRT value in Castiglione Torinese WWTP. One year of full monitoring (See Chapter 2).

Two stages digestion:

$$B = \left[1 - \frac{1}{(1 + k \times HRT_1)(1 + k \times HRT_2)}\right] \times B_0 \times SV_{in}$$

Equation 6. 14

$$VS_{nb} = (1 - Y) \times \ VS_{in}$$

Equation 6. 15

$$VS_b = \frac{1}{1 + k \times HRT_1} \times \frac{1}{1 + k \times HRT_2} \times Y \times VS_{in}$$

Equation 6. 16

$$VS = VS_b + VS_{nb}$$

Equation 6. 17

$$NH_4{}^+(t) = NH_4{}^+{}_{in} + perNH_4{}^+ \times \frac{k \times HRT_1}{1 + k \times HRT_1} \times VS_{in} + perNH_4{}^+ \times \frac{k \times HRT_2}{(1 + k \times HRT_1)(1 + k \times HRT_2)} VS_{in}$$

According to the results of the simulation, the introduction of the thermo-alkali pre-treatment of WAS in sludge line of Castiglione Torinese WWTP determined an increase in methane production of 144% and 167% in a mono-stage or a two-stage AD process respectively. While, the total increase of methane production grew from 25 to 34% for one stage and two stages respectively. The complete results are reported in table 6.6.

AD Process		PS + WAS		PS + tWAS	
		One stage	Two stage	One stage	Two stage
HRT 17.1 [d]		17.1	17.1	17.1	17.1
B [Nm^3 CH_4/ kgVS]		0.205	0.222	0.253	0.272
VS reduction [%]		34 %	37 %	43 %	46 %
HRT 20.0 [d]		20.0	20.0	20.0	20.0
B [Nm^3 CH_4/ kgVS]		0.210	0.226	0.257	0.275
VS reduction [%]		35 %	38 %	44 %	47 %
NH_4^+[kg/h] – only WAS AD		26.3	30.0	66.8	68.3
HRT: WAS 14.8 [d]- PS 18.6 [d]					
B [Nm3 CH4/ kgVS]		0.205	0.221	0.257	0.275
VS reduction [%]		34 %	37 %	44 %	47 %
Results: Methane increase	HRT 14.8 -18.6		8%	23%	33%
	HRT 20 - HRT 20.0		8%	22%	31%
	HRT 14.8 - HRT 20		8%	25%	34%
	Current condition - HRT 20		10 %	25%	34%
Results: VS Reduction increase	HRT 14.8 - HRT 14.8		8%	27%	36%
	HRT 20.0 - HRT 20.0		10%	29%	38%
	HRT17.1 - HRT 20.0		7 %	29%	38%
$NVS_{effluent}/NVS_{fed}$		1.0	1.0	1.0	1.0

Table 6. 6 Proposed configurations. Steady State condition results

6.2.4 Preliminary Technical and Economic Assessment

The results of the system of equations (equation 6.5) written for the two new proposed configurations are reported in figure 6.15. The mono-stage digestion of mixed sludge was called Scenario 1, the two-stages digestion was called Scenario 2.

In the Scenario 1, under the hypothesis of heat transfer efficiency equal to 80%, the AD system is thermally self-sustainable only if both primary and secondary sludge were thickened to a minimum TS concentration of 5%. Conversely, the Scenario 2, assuming the same TS concentration in primary and secondary sludge, the AD system reached the complete heat self-sustainability with a total heat thermal transfer efficiency of only 70 %.

The results of the preliminary economical assessment are reported in Tables 67 and table 6.8. All the results were obtained under the simplified assumption that the efficiency of the global heat transfer system in future configurations of the sludge line was the same of the present condition. Taken into account the Scenario 2 (the configuration with the maximum increase in production of methane (+34%) and the minimum production of digested sludge (-38%)) the starting investment of 5.83 M€ was recovered after only two years (global heat transfer efficiency 60 %, worst considered condition). Moreover, from table 6.8 it can be observed that SMAT company could regain an investment of 12.52 M€ in 5 years (global heat transfer efficiency 60 %, worst considered condition).

Finally, by implementing the thermo-alkaline treatment, the ratio between the renewable electric energy produced by CHPs units and the total electric energy required for the wastewater treatment process increased from 44 % to 55% and 59 %, in one-stage and two-stage configuration respectively (HRT 20 d).

Pay-back period		2 years	3 years	4 years	5 years
Global AD system heat transfer efficiency		Starting Investment M€			
	100%	3.60	5.28	6.48	7.63
	90%	3.76	5.51	6.78	8.00
	80%	3.92	5.74	7.09	8.37
	70%	4.08	5.97	7.39	8-74
	60%	4.28	6.21	7.68	9.11

Table 6. 7-Economic Assessment. Pay-back period and Starting investiments. One Stage AD process

Pay-back period		2 years	3 years	4 years	5 years
Global AD system heat transfer efficiency		Starting Investment M€			
	100%	5.20	7.61	9.43	11.17
	90%	5.35	7.84	9.67	11.41
	80%	5.51	8.07	9.97	12.78
	70%	5.67	8.31	10. 27	12.15
	60%	5.83	8.54	10.58	12.52

Table 6. 8 Economic Assessment. Pay-back period and Starting investiments. Two stage Stage AD process

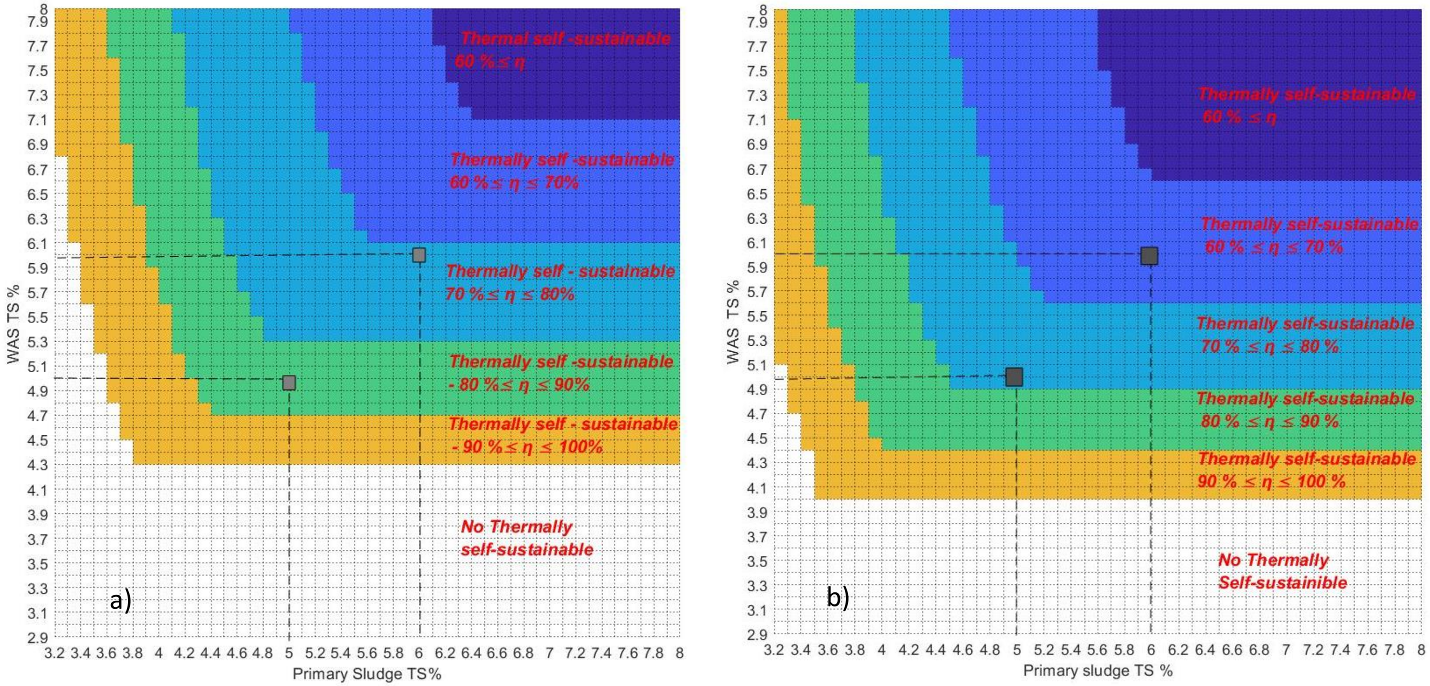


Figure 6. 15 Thermally self-sustainable vs TS concentration of WAS and PS a) one-stage AD reactor; b) two-stages AD reactor

6.3 Conclusion

The thermo-alkali pre-treatment (4 gNaOH/100 gVS, 90 °C, 90min.) of WAS sludge produced in Castiglione Torinese WWTP is effective in methane yield increase during the Anaerobic Digestion. The results of this study demonstrated that a thermo-alkali pre-treatment implemented in The Castiglione Torinese WWTP could increase the methane production of WAS (+167 %).

The modeling of a process that applies the proposed thermo-alkali pre-treatment in a CSTR, fed with a mixture of PS and tWAS, in steady-state condition in a single-stage and with an HRT of 17.1 days, returned an increase in the total methane production of 25% more than the identical AD process carried out with a mixture of PS and raw WAS.

Conversely, by using the same working volume but in a two-stage AD configuration (with an HRT for each digester equal to 8.55 days), the methane production could increase of 34%. Moreover, with reference to the last Scenario 2, SMAT company could bear an investment of 12.52 M€ with a payback period time of 5 years. Definitely, the results are consistent and comparable with the performance of Cambi process applied in the same WWTP (+24 % methane production, Acri M. et al 2018).

Conclusions

The study wanted to analyse the effects of thermo-alkali (4g NaOH/100g TS, 90 min, 90°C) pre-treatment of WAS and its full applicability in Castiglione Torinese WWTP. The research started with one-year monitoring of sludge line Castiglione Torinese performance and it was concluded with the technical and economic feasibility assessment of thermo-alkali pre-treatment of WAS.

During the year of monitoring, the average total solids content of primary and secondary sludge was equal to 3.2% and 2.9 % respectively. The total sludge flow rate fed to the six digesters was equal to 140 m^3/h; moreover, the primary sludge flow rate was equal to 61.5 % of the sludge average total flow.

In the present condition, the electric power produced by the CHPs units is equal to 2.70 MWe; this value is 44 % of the total electric power necessary in WWTP. Moreover, the AD process is not thermally self-sustainable. The average thermal power produced by the CHPs, calculated starting from the thermal efficiency of the engines, is equal to 2.73 MW; conversely, the required thermal power is equal to 4.11 MW. Therefore, assuming that the thermal power lost by the heat water circuit and heat exchange equipment was equal to 20 %, the required natural methane employed in the auxiliary boiler is equal to 228 Nm^3/h. The AD of secondary sludge contributed for only 15 % to the total electric and thermal power production in CHPs unit. The methane specific production of digested WAS is equal to 0.09 $Nm^3/kgSV$. Furthermore, without any treatment, the amount of WAS consumed in the AD process is equal to only 16 %.

In order to reach the system thermally self-sustainable, the efficiency of the thickening process for both PS and WAS have to be enhanced. The system will be thermally self-sustainable if both primary and secondary sludge are thickened to a concentration higher than 6 %.

Hydrolysis lab tests proved a higher efficiency of NaOH compared to $Ca(OH)_2$ in sludge disintegration and consequently in soluble COD release. The combined effect of the chemical and temperature at 90°C made possible to obtain DR values in the order of 40%. The AD lab tests carried out in batch mode and mesophilic conditions revealed that the studied thermo-alkali pre-treatment techniques (4 gNaOH/100 g TS per 90 min) at both temperature values of 70 °C and 90 °C increased the methane production by 46.8% and 86.1% respectively.

Later, the feasibility of improving the methane production during anaerobic digestion of WAS after a thermo-alkaline pre-treatment (4 gNaOH/100 g TS, 90 min, 90 °C) was evaluated by a semi-continuous anaerobic digestion test. The couple of parameters (biochemical methane potential *Bo*, and hydrolysis constant k) for raw WAS, treated WAS and primary sludge were estimated using the data obtained during the semi- continuous AD tests. In this dissertation a revision of the first kinetic model applied to semi-continuous anaerobic digestion tests was proposed, used and validated.
The results of the tests carried out on treated WAS showed an increase of the biochemical methane potential parameter by 70.1 % and increase the first order hydrolysis constant by 447%, compared with the same values of untreated secondary sludge. The used model succeeded in predicting the volatile solids concentration of digestate. The error between the experimental data and data predict by the model concerning the cumulative VS discharged at the end of the semi-continuous AD tests 1.8 %.

Sludge	*AD test*	*B_o [Nm^3/kg VS]*	*k [1/d]*	*Biodegradability [%]*
WAS	1	0.148	0.08	0.28
Treated WAS	2	0.250	0.46	0.48
PS	3	0.300	0.52	0.49

Table conclusions 1. Semi continuous AD tests. Principal results

The couple of parameters (B_o, k) obtained for tWAS and PS were used to predict the daily and cumulative methane production from the semi-continuous AD of a substrate attained by mixing PS and tWAS (named Mix). The error between the experimental and modelled data of cumulative methane production, at the end of the test, was only of 1.1%, thus demonstrating that the first kinetic model succeeded in predicting the daily and cumulative methane production of the mixed sludge. Therefore, the co-digestion of primary and treated sludge can be modelled as a linear sum of the two substrates anaerobic digested in two separated systems.

Two new configurations in the sludge line, that include the thermo-alkaline pre-treatment of WAS, were proposed. The two proposed configurations differ because the first involves a single-stage digestion process and the second a two-stages process. In the two-stage configuration, two CRT reactors with the same volume were employed.

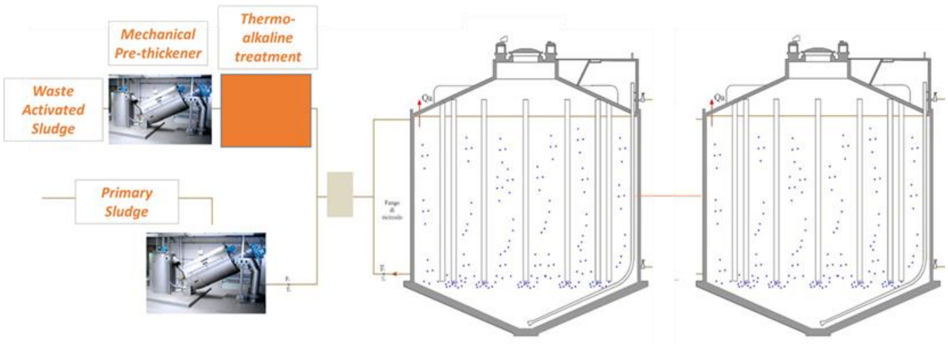


Figure conclusion. Two-stages reactor configuration

In all cases the gravity thickening of primary and secondary sludge was substituted by a dynamic thickening process. Moreover, the treated and undigested WAS were mixed to the raw PS in order to recover the thermal energy spent during the pre-treatment.

With reference to the two stage reactors configuration, the starting investment of 12.52 M€ was recovered after only five years (global heat transfer efficiency 60 %, worst considered condition). Also, in this new configuration, the thickening efficiency of PS and Was bust be improved in order to make the system thermally self-sustainable. The system will be thermally self-sustainable if primary and secondary sludge are thickened to a minimum concentration of 6% and 7 % respectively.

Finally, by implementing the thermo-alkali treatment, the ratio between the renewable electric energy produced by CHPs units and the required total electric energy for the wastewater treatment process increased from 44 % (actual condition – no WAS pretreatment) to 55% and 59 %, in one-stage and two-stages configuration (HRT 20 d).

However, before applying the proposed pretreatment to the full scale, further considerations should be deepened. In particular, the critical aspects that have be accounted include: the dewaterability of digested sludge, the biodegradability of organic matter and the higher ammonia load in the recycled water flow from sludge treatment line to the wastewater treatment line.

According to the present knowledge, it is impossible to have information about:

- The organic matter biodegradability, contained into the centrate, obtained after WAS pretreatment and AD process;
- the dewaterability of digested sludge.

While, some preliminary economic considerations can be evaluated about the higher ammonia release.

As shown in table 1 the thermo-alkali pre-treatment improve the WAS biodegradability. The treated WAS subjected to the mesophilic Anaerobic Digestion (HRT 20 d) increase the methane production of 143 %. Unfortunately, the AD of tWAS increases also the ammonia release (see table 2).

The amount of NH_4^+ discharges after the anaerobic digestion of WAS passes from 26.2 kg NH_4^+ /h (actual condition HRT =14.8 d and untreated sludge) to 68.2 NH_4^+/h (thermo-alkali treated WAS, HRT 20 d and two stages AD configuration process). Consequently, the ammonia loading rate, deriving from the WAS anaerobic digestion, increases by 160 %.

In order to estimate the increased energy demand due to the overloading ammonia, some points can be considered. Implementing, the nitrogen removal specific energy consumption in Castiglione Torinese WWTP line reported in Panepinto et al. (2016), the growth of electric power consumption can be estimated. To this end, the 14.66 kWh was considered as a required electric energy to remove 1 kg of nitrogen. Therefore, after implementing the thermo-alkali WAS pre-treatment, the required electric power grows from the current 300 kWe to 778 kWe.

Additionally, further considerations can be assessed on the techno-economic applicability of an Anammax process (anaerobic ammonium oxidation) in the side-stream treatment of recycled flow. The advantage of anammox process is the reduction of electric energy consumption, as shown in table 2. The required electric power should decrease of more than 20 times. As exemplum, in the worst condition (pretreatment od WAS, HRT 20 d, two stages AD) the electric power should decrease from 778 kWe to 36 kWe. Details of Annamox Unit implemented in Castiglione Torinese line are reported in Chapter 1.

In table 2 the overproductions of methane and the consequent renewable electric energy as well as the electric energy required to remove the higher ammonia load relative to the proposed different configurations are listed.

HRT	One stage AD		Two stages AD	
	WAS	tWAS	WAS	tWAS
[Nm^3/h]				
14.8 20.0	83.8 95.5	234.5 242.6	93.4 107.2	255.1 260.4
CHP unit - produced electric power [kWe]				
14.8 20.0	351 400	982 1016	391 449	1068 1090
NH_4^+ Release [kg/h]				
14.8 20.0	26.3 30.0	61.5 63.6	29.3 33.7	66.8 68.2
N Release [kg/h]				
14.8 20.0	20.5 23.3	47.8 49.4	22.8 26.2	52.0 53.1
N removal- Required Electric Power [kWe](Conventional Activated Sludge System Denitrification/Nitrification)				
14.8 20.0	300 342	701 725	335 384	762 778
N removal- Required Electric Power [kWe](DEMON ®- Smat Anammox process)				
14.8 20.0	14 16	33 34	16 18	35 36

Table conclusions 2
Electric Power Overproduction VS N-overload Removal Electric Power Consumption

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