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A modelling approach for the assessment of energy recovery and impact on the water line of sludge pre-treatments

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Abstract

A simple, easy-to-use, first-order model was elaborated to predict the methane production and the release of ammoniacal nitrogen ($N\text{-}NH_3$) to the digestate in full-scale anaerobic digestion (AD) processes. The study used long-term, semi-continuous AD tests, carried out with samples of primary sludge (PS), raw waste activated sludge (WAS), WAS after a thermo-alkali pre-treatment (90°C, 90 min, 4 g NaOH/100 g TS) and mixed sludge (PS/treated WAS), to calibrate and validate the model. The results of both the experimental activities and the phase of model tuning demonstrated that the proposed model was capable to provide reliable information to completely characterize the AD process, thus overcoming the limitations due to discontinuity of experimental tests. Furthermore, it was demonstrated that low-temperature thermo-alkali pre-treatments could increase the values of the model parameters, namely methane production after an infinite time (B_0, +70%) and hydrolysis constant (k, +450%), and made them comparable to those obtained by the application of commercial, high-energy demanding treatments (e.g. Cambi). Finally, the issue concerning the release of $N\text{-}NH_3$ to digestate was deemed to be very worthy to being investigated because, after pre-treatments, the cost for nitrogen removal in the water line, through the traditional processes of nitrification – denitrification, could increase even by 140%.

Keywords: anaerobic digestion; ammonia; primary sludge; waste activated sludge; energy analysis; hydrolysis rate

Highlights

- Traditional WWTPs must increase their capacity in recovering resources
- Hybrid pre-treatments increase both methane production and nitrogen release
- Nitrogen release must be controlled in the application of sludge pre-treatments
- A simple, first-order model was validated to predict nitrogen release to the digestate
- Extra nitrogen in the water line due to pre-treatments raises treatments costs by 140%

1. Introduction

According to the circular economy roadmap, wastewater treatment plants (WWTPs) have to become "ecologically sustainable" technological systems in the near future [1], that means more efficient, less energy demanding and capable to support resource recovery [2]. At the same time, WWTPs must remain effective in maintaining their fundamental task, i.e. to provide a constant and adequate water pollution control, so as to protect human health and the environmental quality against conventional and emerging contaminants. In the framework of the broad spectrum of strategies for resource and energy recovery, anaerobic digestion (AD) processes, still frequently seen just as a profitable way to stabilize sludge, will have to become a cornerstone. In fact, AD processes offer lots of advantages for the transition of traditional WWTPs to water resource recovery facilities (WRRFs), such as: very high energy efficiency [3], versatility in terms of feed [4], medium to high pathogens inactivation [5], potentiality for nutrients (N, P and K) recovery [6] and for carbon-based building blocks production through fermentation to VFAs [7], effectiveness in degrading compounds that are recalcitrant to aerobic biodegradation [8].

The AD of primary and secondary sludge produced in a WWTP is a mature technology. However, the energy recovery from secondary sludge (also known as waste activated sludge, WAS) still remains at quite low values, at most up to 7% of the energy available in the wastewater [9]. Those low values depend on the nature of WAS, in fact, the presence of protective extracellular polymeric substances and the rigid structure of the microbial cell walls determine low hydrolysis rate and poor bio-methane productivity [10]. In order to enhance the energy recovery, WAS pre-treatment technologies, such as physical, thermal, and chemical treatments, or a combination of them, could be required before AD [11].

In the direction of the fulfillment of the circular economy package's objectives, the sludge line of existing WWTPs must be revamped through the introduction of interventions aimed at improving the efficiency of the AD process in each of its phases, from the thickening of sludge to the final treatment of digestate. However, such interventions are expensive and can be justified only on the basis of reliable results coming from extensive experimental campaigns [12]. The gap between the results obtained at a lab or pilot scale and a WWTP running at the full scale can be filled with a modelling approach, capable of describing the complexity of a system influenced by a number of operational parameters [13]. Several mathematical models and, more recently, machine learning applications have been developed, with the fundamental aim of understanding and optimizing the implementation of AD processes, thus eventually achieving more efficient functioning in WWTPs [14]. Quantitative models can support the designer not only in the reactor design and scale-up, but also in evaluating energy balance and economic sustainability, through the assessment of the dynamic behavior of key-process variables in a wide range of experimental conditions [15]. In 2002 the IWA Task Group for the Mathematical Modelling Processes published the Anaerobic Digestion Model No.1 (ADM1) [16]. ADM1 was aimed at providing a complete modelling of the fundamental AD mechanisms, through the description of the dynamics of 24 species which are involved in 19 conversion processes of both physico-chemical (namely disintegration-hydrolysis) and biological (namely acidogenesis, acetogenesis and methanogenesis) nature. However, the complexity of ADM1 and the large number of input parameters required by the model, such as COD fractionation or VFAs, the latter arising from the process intermediate stages, which are not routinely measured in a WWTP, significantly reduces its application [17]. If these measurements are not available, it is crucial to make significant reductions to the model, which can make the validity of AD simulations questionable [18]. For example, Tolessa et al. [19] had to resort to an extensive literature survey, combined with Monte Carlo analysis and a Gaussian Mixture Model approach, to account for parameter variability, leading to a probabilistic estimate of steady-state biogas production from agricultural residue substrates. Surrogate models, containing a limited number of parameters, have been developed, calibrated and validated [20]. However, calibration and validation processes of such models have often been carried out by using the results of BMP essays [21], which present evident differences with continuous, full-scale processes, for what concerns, among others, the representativity of the tested substrate and the evolution of the AD process. Other empirical models have been developed using a set of statistical and mathematical techniques, known as response surface methodology (RSM), artificial neural network (ANN) [22] or a combination of the two above-mentioned approaches [23]. Recently, Parthiban et al. [24] developed a second order model where the output neurons were biogas and biomethane, while the input neurons were thermophilic temperature, organic loading rate (OLR), pH, agitation time, and hydraulic retention time (HRT). However, calibration and validation of RSM or ANN models is based on the output of a large number of bench-scale tests and the mathematical form of the obtained response variable does not have a direct relationship with the dynamics of an AD process.

In this framework, in order to shorten the calculation procedure and make biogas production estimates easier, a simple model for the description of the production of methane in time, B(t), was proposed [25]. The model was based on a first-order kinetic rate reaction, such as that shown in Equation (1)

$$B(t) = B_0\,(1-e^{-kt}) \qquad (1)$$

The model proved to be capable to adequately capture the overall performance of mesophilic and thermophilic AD processes through the two parameters namely B_0 and k. B_0 was the specific methane production after an infinite HRT, that is the theoretical amount of methane produced by the whole amount of biodegradable VS in the substrate, and k was the hydrolysis constant. Differently from other experiences reported in literature (see, for example, the recent study of Tamang et al. [26]), that used biochemical methane potential (BMP) tests to assess B_0 and k parameters, in the above-mentioned study the two model's parameters were quantified by making use of long-term semi-continuous AD tests. That kind of tests was deemed more reliable than BMP tests for model calibration. The data obtained from the tests allowed the determination of the optimal sets of values of the two parameters (B_0, k) by using the best fit algorithms as done by Wei et al. [27].

On the grounds of above, the present study contributes to the current literature by further validating the already proposed model, in order to make it a simple, easy-to-use tool useful to provide information concerning not only the bio-methane productivity of organic substrates, but also the impact of the release of ammoniacal nitrogen ($N\text{-}NH_3$) following to the application of pre-treatments. Specifically, the present study had a two-fold aim: firstly, to definitely verify the goodness of the already proposed model through the digestion of pure and mixed sludge and, secondly, to assess if a similar approach could be used to predict the release of ($N\text{-}NH_3$), from a substrate to the digestate, during an AD process. For what concerns the first aim, long-term, semi-continuous AD tests were carried out on samples of primary sludge (PS), raw WAS and WAS after a thermo-alkali pre-treatment (90°C, 90 min, 4 g NaOH/100 g TS) with the aim of obtaining B_0 and k for each substrate. The model's parameters were validated with an AD test involving a mixture of PS and treated WAS. With reference to the second aim, it is well known that ammonia (NH_3), which is produced during the anaerobic degradation of nitrogenous organic matter (e.g. proteins, amino acids, urea and nucleic acids), is a common inhibitor of AD processes [28]. Furthermore, sludge pre-treatments boost the release of $N\text{-}NH_3$ to digestate, with possible technical and economic impacts onto the removal of nitrogen from wastewater, when the liquid fraction of the digestate is recirculated back to the water line. Except for the study of Alejo et al. [29], this topic has not been broadly addressed by the scientific literature. The study wants to fill this gap, thus proposing a model for the quantification of the amount of $N\text{-}NH_3$ released to the digestate and providing a rough, preliminary estimate of the costs that a WWTP must bear to cope with the increase of nitrogen loads in the water line.

2. Materials and Methods

2.1 Substrates

Samples of primary sludge (PS) and waste activated sludge (WAS) were collected from the outlet of the gravity pre-thickeners of the Castiglione Torinese WWTP (located 20 km from Turin, NW Italy) once a week. The inoculum used for the start-up of the long-term AD tests, described in Section 2.2, was obtained from one of the anaerobic digesters fed with WAS in the same WWTP.

The Castiglione Torinese WWTP is one of the facilities run by SMAT (Società Metropolitana Acque Torino), the company that manages the integrated water service in the Metropolitan City of Turin. The WWTP has a treatment load of approximately 2,000,000 population equivalent (p.e.). The AD process is carried out in six digesters with average HRTs of 14.8 and 18.6 days for WAS and PS respectively.

Details of the water and sludge line of the Castiglione Torinese WWTP were provided in a previous paper [30]. Shortly, the WWTP has a standard configuration that includes the following treatment phases: preliminary treatments (grating and sand/oil removal), primary settling, pre-denitrification, biological oxidation with a solids retention time (SRT) of approx. 30-35 days, secondary settling and final filtration on a dual media, sand – anthracite, bed.

A total of 2 plus 4 gravity pre-thickeners are used in the ordinary operation of the WWTP with the aim of increasing the TS content of WAS and PS, respectively, before AD. WAS has a final TS content, before AD, in the order of 3%, obtained with the addition of 0.5 g of a cationic polyelectrolyte / 100 g TS. PS and WAS account for 64% and 36%, by weight (b.w.), on a TS basis, of the overall amount of sewage sludge produced in the WWTP.

After being screened using a 40-mesh sieve to remove large particles, the sludge samples were stored in 10 L polypropylene tanks at 4 °C prior to AD tests. Table 1 shows the average characteristics of the two substrates, namely PS and WAS, averaged over the duration of the AD tests.

Table 1. Average characteristics of the two substrates, PS and WAS, used in the tests

	Primary sludge	Waste activated sludge
Total solids (TS, %)	2.56	3.05
Volatile solids (VS, %)	1.86	2.04
pH	6.11	7.20

Total and volatile solids were obtained as described in Section 2.3.

2.2 Reactors set up and experimental tests

WAS was used in the AD tests as a raw or thermo-alkali pretreated substrate. The thermo-alkali pre-treatment (4 g NaOH/100 g TS, 90°C, 90 min) was carried out in a batch reactor. The operating conditions for pre-treatments were fixed on the basis of the results obtained in a previous work [31], that compared the performance of thermal, alkali and thermo-alkali pre-treatments for the enhancement of methane production from WAS. The reactor used for the pre-treatment had a working volume of 35 L and was completely stirred with an electric propelled shaker. The heat was transferred to the sludge through three electrical band resistances, placed on the lateral surface of the reactor, with an electric power of 2.6 kW each. The temperature inside the reactor was controlled by an open source single-board microcontroller (Arduino).

The digestion tests were performed with two apparatus. The first digester was a continuous stirred reactor (CSR) with a total volume of 12 L (operating volume, 10 L), equipped with a water jacket, for the temperature control, and gasometers and systems for on-line monitoring of the volume and composition of the biogas (see details in [25]). Mixing inside the digester was obtained through biogas recirculation for 15 min every hour.

The second digester was a CSR with a total volume of 300 L (operating volume, 240 L), equipped with an 80 L gasometer and an electronic system for on-line monitoring of the biogas volume and composition (see details in [32]). Mixing inside the digester was obtained through an alternate biogas recirculation (15 min on / 15 min off).

A total of four long-term, semi-continuous digestion tests were carried out. Details of the tests are reported in Table 2. The substrate used in test n.4 was a mixture (50/50 by volume, b.v.) of PS and thermo-alkali pre-treated WAS. In all tests the operations of substrate supply and digestate extraction were carried out five days a week, from Monday to Friday.

Table 2. Details of the AD tests

Test number	Substrate	Reactor	Temperature regime	HRT (d)	Duration (d)	OLR $kgVS/m^3{\cdot}d$
1	PS	CSR 10-L	Mesophilic, 38°C	20	158	0.93±0.13
2a	WAS	CSR 240-L	Mesophilic, 38°C	15	112	1.43±0.31
2b	WAS	CSR 240-L	Mesophilic, 38°C	20	46	1.22±0.36
3a	Treated WAS	CSR 240-L	Mesophilic, 38°C	20	29	1.28±0.32
3b	Treated WAS	CSR 240-L	Mesophilic, 38°C	20	90	0.56±0.15
4	Mixed sludge	CSR 240-L	Mesophilic, 38°C	20	108	1.03±0.08

2.3 Analytical methods

Total and volatile solids (TS, VS) were determined according to the Standard Methods [33]. The total volatile fatty acid (tVFA) concentration, as acetic acid (CH_3COOH) equivalent, and the total alkalinity (TA) were obtained by a potentiometric titration, according to the Nordmann method, by using a SI Analytics automatic titrator. Specifically, a sample of 20 mL of digestate was titrated with a 0.1 N sulfuric acid (H_2SO_4) solution up to pH 5.0, so as to calculate the TA value, expressed in mg/L of calcium carbonate ($CaCO_3$). Then the tVFA value was obtained after a second titration step from pH 5.0 to pH 4.4.

The soluble COD (sCOD) and ammonium ion (NH_4^+) were determined according to the Standard Methods [33] on the liquid phase of the substrates (raw and pre-treated sludge) or digestate. The liquid phase was obtained after an initial centrifugation at 15,000 rpm for 10 min and a subsequent filtration of the supernatant on a 0.45 μm nylon membrane filter, as recommended by Roeleveld and van Loosdrecht [34].

The elemental composition analysis was carried out on samples of PS and WAS dried at 105 °C and on the residual ashes after combustion at 600 °C. A Flash 2000 ThermoFisher Scientific CHNS analyzer was used for the elemental analysis, assuming that the oxygen content of the substrate was the complementary fraction towards C, H, N, S contents. The results of the elemental analysis were used to calculate the theoretical COD and the theoretical methane production (B_{th}), according to the Buswell model, of the two substrates.

2.4 The mathematical model to predict the methane production in an AD process

Interventions on the sludge line of existing WWTPs, such as the introduction of pre-treatments or change of the digestion scheme, from one-stage to two-stage, can be justified only on the basis of reliable results coming from extensive experimental campaigns. Mathematical models can help in filling the gap between the results of tests carried out at a lab or pilot scale and the operation of the WWTP at a full scale. In a previous work [25], a simple model was proposed and validated through a series of AD tests carried out in mesophilic and thermophilic conditions. The above-mentioned model was based on a first-order rate reaction, such as that shown in Equation (1), and contained two parameters, namely the biochemical methane potential (B_0) and the hydrolysis rate (k). B_0 is the maximum amount of methane that a substrate can produce after an AD process of infinite duration; k is the first-order kinetic constant that describes the velocity at which the substrate is made available for the AD process.

$$B(t) = B_0 \left(1-e^{-kt}\right) \qquad (1)$$

As it is well-known, an AD process consists of the four steps namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the only step in which microorganisms are not directly involved. In fact, that process is merely a surface phenomenon, in which particulate and polymeric matters are degraded through the action of eso-enzymes. After hydrolysis, the produced smaller molecules can cross the cell barriers and be used by microorganisms for the production of intermediate and final AD products [35]. The hydrolysis phase is generally the rate-limiting step during an AD process of particulate substrates [36]. WAS is a typical particulate and complex substrate 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 rate reaction, such as that shown in Equation 1.

Equations 2-5 represent the complete set of equations necessary to describe an AD process in a CSR, when hydrolysis is assumed to be the limiting step and the substrate is made of particulate matter.

$$B(t) = VS(t) \cdot k \cdot B_0 \cdot V \quad (2a)$$

$$B(t) = VS_b(t) \cdot k \cdot Y \cdot B_{th} \cdot V \quad (2b)$$

$$\frac{dVS_b(t)}{dt} = \frac{q(t) \cdot VS_{b,in}(t)}{V} - \frac{q(t) \cdot VS_b}{V} - k \cdot VS_b(t) \quad (3)$$

$$\frac{dVS_{nb}(t)}{dt} = \frac{q(t) \cdot VS_{nb,in}(t)}{V} - \frac{q(t) \cdot VS_{nb}}{V} \quad (4)$$

$$\frac{dNVS(t)}{dt} = \frac{q(t) \cdot NVS_{in}(t)}{V} - \frac{q(t) \cdot NVS}{V} \quad (5)$$

In Equation 2a the daily methane production, at the time t, B(t), is related with the amount of volatile solids, VS, at the same time frame, the hydrolysis rate constant (k), the biochemical methane potential (B_0) and the volume of the reactor (V). With reference to Equation 2a, it is important to keep in mind that the substrate fed to the digester is made of volatile (VS) and non-volatile solids (NVS or fixed solids) and that not all the VS are degradable in an AD process, even after an infinite time. Equations (3-5) describes the mass balance of biodegradable VS (VS_b), non-biodegradable VS (VS_{nb}) and NVS as a sum of (i) the input of fresh substrate, (ii) the output of the digested product and (iii) the degradation term where applicable. The time-change of the three kind of solids is a function of both volumetric flow rate (q) and volume (V).

On the basis of the elemental composition of the VS, it is possible to calculate the theoretical methane production of the substrate, B_{th}, (see Equation 2b) by referring to Equation 6:

$$B_{th} = VS_{in} \cdot \frac{COD_{in}}{VS_{in}} \cdot 0.350 \, \frac{Nm^3 CH_4}{kg\ COD} \quad (6)$$

B_0 is always smaller than B_{th}, because not all the VSs are biodegradable (i.e presence of VS_{nb} into the substrate fed to digester) and, in minor measure, because of the anabolic activity of anaerobic microorganisms. Furthermore, in a real case, the specific methane production (SMP) of a substrate is smaller than B_0, because, as in Equation 7, both the hydrolysis process (the rate of which is quantified by the kinetic constant, k) and the duration (HRT) of the AD process limit the methane production. Equation 7 provides the solution at steady condition of Equation 2a.

$$SMP = B_d(t) = \left(1 - \frac{1}{1+k\cdot HRT}\right) B_0 \quad (7)$$

The Y parameter, reported in Equation 2b, is the absolute biodegradation (or degradation extent), that is the ratio between B_0 and B_{th}, an intrinsic characteristic of the substrate. Because of the relationship between B_0 and VS_b, and between B_{th} and VS, Y can also be defined as the ratio between VS_b and total VS, as in Equation 8.

$$Y = \frac{B_0}{B_{th}} = \frac{VS_b}{VS} \quad (8)$$

The optimal set of B_0 and k values, capable of describing the trend of the SMP observed in the experimental tests carried out in a continuous mode, was obtained by minimizing the objective function (J). Function J is the residual sum of squares (RSS) between the measured data and the data predicted by the model, as stated in Batstone et al. [37]. If the RSS are normally distributed, a critical value (J_{crit}), that defines the surface of the parameter uncertainty region, can be defined by using the F distribution, as in Equation 9 [27].

$$J_{crit} = J_{min}\left(1 + \frac{p}{N_{data}-p} \cdot F_{\alpha,p,Ndata-p}\right) \quad (9)$$

where N_{data} is the number of measured data, p is the number of parameters, and $F_{\alpha,p,Ndata-p}$ is the value of the F distribution for α, p, and N_{data-p}. An α value of 0.05 was used to estimate the 95% confidence regions.

2.5 The mathematical model to predict the ammonia release from the substrate to the digestate

A new first-order kinetic model was proposed with the aim to predict the amount of $N\text{-}NH_3$ released to the digestate. During an AD process, nitrogen is released to the digestate, as a consequence of hydrolytic processes, under the two forms of ammonia (NH_3) and ammonium ion (NH_4^+), collectively called ammonia nitrogen (AN). The relative abundance of each of the two forms is regulated by a pH and temperature depending equilibrium (pKa = 9.25 at 25 °C, see Supplementary Materials, Section 1, SM1). The assessment of the $N\text{-}NH_3$ amount into the digestate is of capital importance for two main reasons. Firstly, concentrations of $N\text{-}NH_3$ higher than 1800 – 2000 mg/L into the digesting material have an adverse effect on the activity of the acetoclastic methanogenic microorganisms, that reduce the production of methane [38]. In the ADM1 the inhibition of methanogens due to free NH_3 is modeled as a non-competitive inhibition process [16]. Details concerning the equation and the default value of the inhibition parameter K_{INH3} are reported in SM2. Secondly, the liquid phase of the digestate, after solid – liquid separation, is often recirculated back to the water line, with an evident impact of the residual AN forms on the mass and energy balances of the biological processes, namely nitrification and denitrification.

The release of AN (and, depending on the pH, of the $N\text{-}NH_3$ fraction) to the digestate is limited by the hydrolysis process, that transforms the feedstock's proteins, firstly, into amino-acids and, finally, into AN and VFAs. The "per$N\text{-}NH_3$" parameter was introduced to indicate the ratio between the maximum amount of $N\text{-}NH_3$ that the AD substrate can potentially release to the digestate, and the amount of VS fed to the digester. A correspondence can be identified between B_0, that is the maximum amount of producible methane, and "per$N\text{-}NH_3$", that is the maximum amount of releasable $N\text{-}NH_3$. The model is described by Equation 10:

$$\frac{dN-NH_3(t)}{dt} = \frac{q \cdot N-NH_{3(in)}(t)}{V} - \frac{q \cdot N-NH_3(t)}{V} + perN - NH_3 \cdot k \cdot VS \quad (10)$$

Where

$N\text{-}NH_{3(in)}$, is the concentration (g/m^3) of ammoniacal nitrogen into the substrate fed to the digester

$N\text{-}NH_3$ is the concentration (g/m^3) of ammoniacal nitrogen into the digesting material

The solution of Equation 10 at steady state (SS) is that described by Equation 11:

$$N - NH_3(SS) = N - NH_{3(in)} + perN - NH_3 \cdot \frac{k \cdot HRT}{1 + k \cdot HRT} \cdot VS_{in} \quad (11)$$

All the mathematical models used to predict methane production (as in Section 2.4) and NH_3 release from the substrate, were implemented into the graphical programming environment Simulink-Matlab® (Simulink 9.2, solver method ode23t).

2.6 Energy analysis of future scenarios

The values of B_0 and k parameters, obtained from the model application (see Section 2.4), were used to compare two possible future configurations of the WWTP sludge line (see Figure 1). The energy balances reported in this section were written with reference to a WWTP's configuration where the produced biogas is combusted in combined heat and power (CHP) units with a thermal and electrical efficiency of 42.4% and 41.9% respectively. However, it should be emphasized that, at the time the experimentations were carried out, the produced biogas was burned in the CHP engines. Today, 2023, the biogas produced from the AD is sent to an upgrading and purification unit, which was designed for biomethane generation.

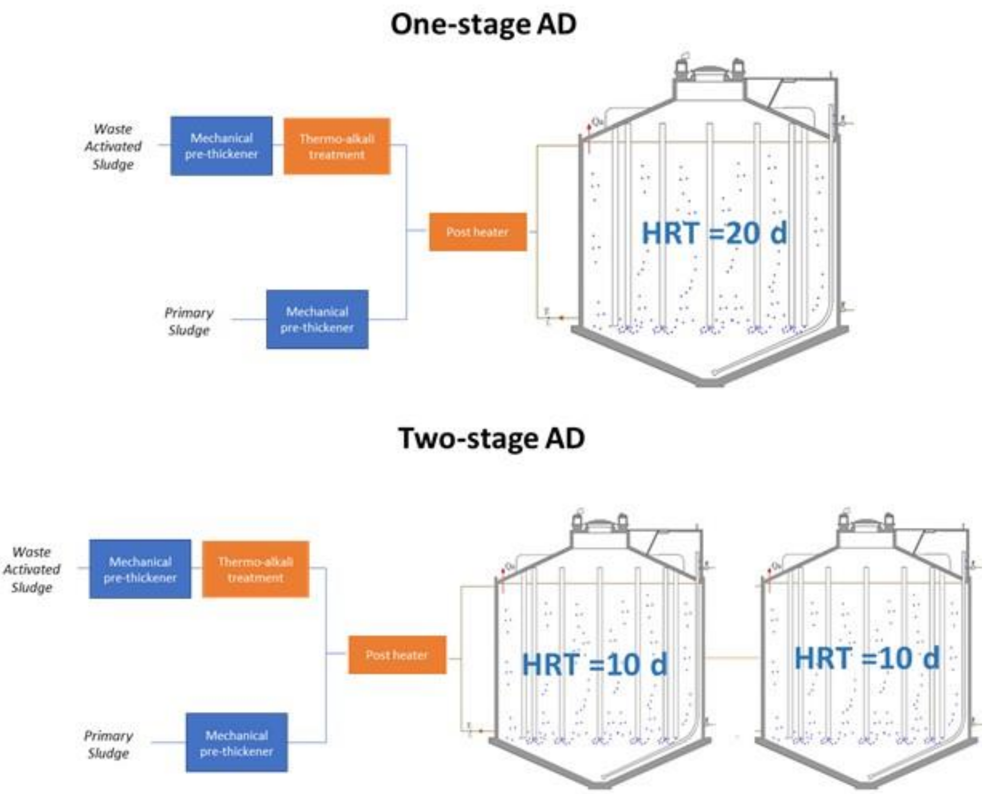


Figure 1. One-stage and two-stage AD sludge treatment line configuration

In the first scenario, thermo-alkali pre-treatments (90°C, 90 min, 4 g NaOH/100 g TS) were introduced for WAS and the AD process of PS and WAS was carried out in traditional one-stage digesters. In the second scenario, other than the introduction of the thermo-alkali pre-treatment for WAS, the AD process was carried out according to a two-stage scheme. The HRT of the modelled digesters was assumed equal to 20 and 10+10 days for the first and second scenario, respectively. For both scenarios, the thickening of PS and WAS was considered to be obtained with dynamic thickeners, that would substitute the gravity thickeners presently used in the WWTP. The heat recovered from the thermo-alkali pre-treated WAS was used to pre-heat the PS.
Equations 12 and 13 were used to calculate the SMP for the one-stage and two-stage process respectively.

$$SMP = \left(1 - \frac{1}{1+k \cdot HRT}\right) B_0 \qquad (12)$$

$$SMP = \left[1 - \frac{1}{1+kHRT_1}\frac{1}{1+kHRT_2}\right]B_0 \qquad (13)$$

The heat amounts involved in the energy analysis of the two scenarios were calculated as in the follow.

The overall amount of heat, recovered from the biogas combustion in the CHP units, was calculated as in Equation 14

$$Q_1 = (q_{PS} \cdot \%VS_{PS} \cdot SMP_{PS} + q_{WAS} \cdot \%VS_{WAS} \cdot SMP_{WAS}) \cdot LHV_{CH4} \cdot \eta_1 \qquad (14)$$

where:

q_{PS} = volumetric flow rate of PS, m^3/d

$\%VS_{PS}$ = concentration of VS into the PS, kg VS/m^3 PS

SMP_{PS} = specific methane production of PS, Nm^3 CH_4/kg VS

q_{WAS} = volumetric flow rate of the WAS, m^3/d;

$\%VS_{WAS}$ = concentration of VS into the WAS, kg VS/m^3 WAS

SMP_{WAS} = specific methane production of WAS, Nm^3 CH_4/kg VS

LHV_{CH4} = lower heating value of methane, 35.259 MJ/Nm^3

η_1 = efficiency of heat generation of the CHP unit

The generated heat can be used for the thermo-alkali pre-treatment of the WAS, as in Equation 15

$$Q_2 = \frac{q_{WAS} \cdot c_p \cdot (T_p - T_1)}{\eta_2} \qquad (15)$$

where:

c_p = specific heat capacity of sludge, $kJ/m^3 \cdot °C$

T_p = temperature of the pre-treatment, °C

T_1 = temperature of the environment, °C

η_2 = efficiency of heat transfer from the CHP unit to the cold, raw WAS

The heat transferred to the WAS in the pre-treatment process could be efficiently used to support the AD process, that is to heat the cold PS and compensate the heat losses across the walls and roof of the digesters. The heat necessary to support the temperature-controlled AD process was calculated as in Equation 16:

$$Q_3 = \frac{(q_{PS} + q_{WAS}) \cdot c_p \cdot (T_2 - T_1) + n \cdot Q_a}{\eta_3} \qquad (16)$$

where:

T_2 = temperature of the digestion process, 38°C

n = number of reactors

Q_a = heat losses across the walls and roof of digester(s)

η_3 = efficiency of the heat transfer from the pre-treated WAS to the cold PS;

The system is energy self-sustainable provided that (i) the heat generated from the biogas combustion (Q_1) is sufficient to support the pre-treatment of WAS and (ii) the heat recovered from the pre-treated WAS (Q_2) is sufficient to support the AD of PS and WAS (Q_3). The combination of Equations (15) and (16) allows to calculate the volumetric flow rate of PS that makes the AD process energy self-sustainable Equation (17):

$$q_{PS} = \frac{1}{(T_2 - T_1)} \cdot \left\{ q_{WAS} \cdot \left[\eta T_p + T_1(1-\eta) - T_2 \right] - \frac{n \cdot Q_a}{c_p} \right\} \quad (17)$$

3. Results and Discussion

3.1 Validation of the mathematical model to predict the methane production in an AD process

Four long-term, semi-continuous tests were carried out with the aim of validating the mathematical model proposed in Ruffino et al. [25] and recalled in Section 2.4 of this paper. From the data of methane production recorded in the first three tests, that involved PS, raw WAS and pre-treated WAS, the B_0 and k parameters were obtained for each substrate. After the calibration phase, the couple of parameters obtained for each substrate was validated by referring to the trend of VS into the digestate. Finally, the model was completely validated by using the results of the fourth AD test, that was carried out with the mixed sludge (PS – pre-treated WAS, 50/50 b.v.).

3.1.1 Tests and model calibration for the single substrates (PS, WAS, pre-treated WAS)

The raw formula of the VS of the two substrates (PS and WAS), the COD/VS ratio and the theoretical biogas and methane production according to the Buswell equation were calculated from the results of the elemental composition analysis (C, H, N and O content). The values of the above-mentioned parameters are reported in Table 3. It can be seen that the theoretical methane production of the two substrates, B_{th}, was equal to 0.62 and 0.52 Nm^3/kg VS for PS and WAS, respectively.

Table 3. PS and WAS parameters obtained from the elemental composition analysis

	PS	WAS
VS raw formula	$C_{10.6}H_{18.2}O_{4.1}N$	$C_{6.8}H_{11.8}O_{3.2}N$
COD/VS (g O_2/g VS)	1.76	1.49
Theoretical biogas production (Nm^3/kg VS)	1.06	0.96
Theoretical methane production (Nm^3/kg VS)	0.62	0.52

Figure 2 shows the evolution of the SMP during the approx. 160-day lasting digestion test that involved the PS. It can be seen that after approximately 35-40 days a steady value of SMP equal to 0.280 Nm^3/kg VS was reached. These findings confirmed the results obtained in a previous work [39].

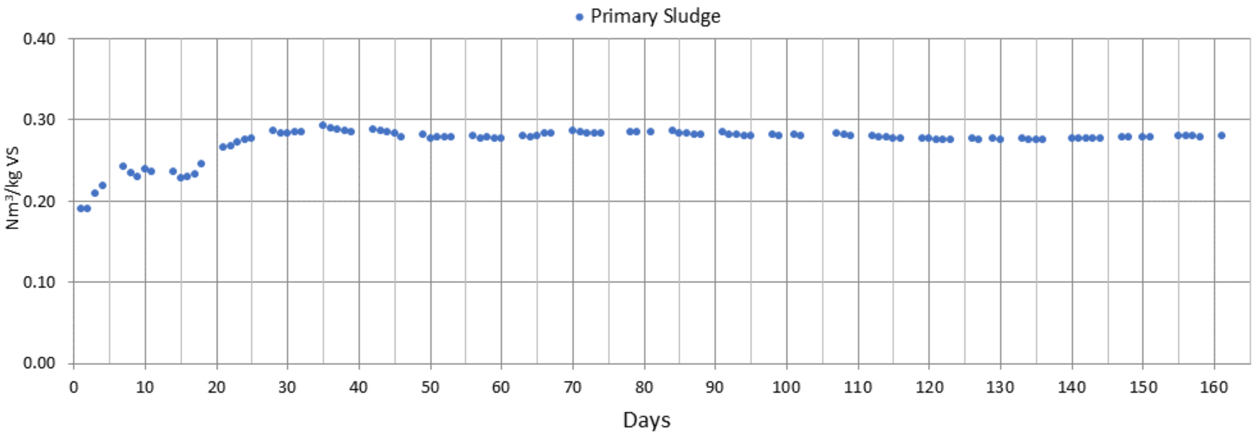


Figure 2. Trend of the SMP for PS (test n.1)

Figure 3 shows the combination of the results obtained in the two tests involving raw and thermo-alkali pre-treated WAS (test n. 2 and n.3, respectively). The whole study had been lasted for approx. one year. Figure 3 shows that, after a start-up phase lasting approximately two months, the SMP of the raw WAS reached the steady value of 0.110 Nm^3/kg VS (HRT = 15 days). That SMP value had been maintained for approx. 200 days, with an only moderate change in SMP (+ 9%) due to the increase in the HRT, from 15 to 20 days, that intervened after 169 days from the beginning of the test.

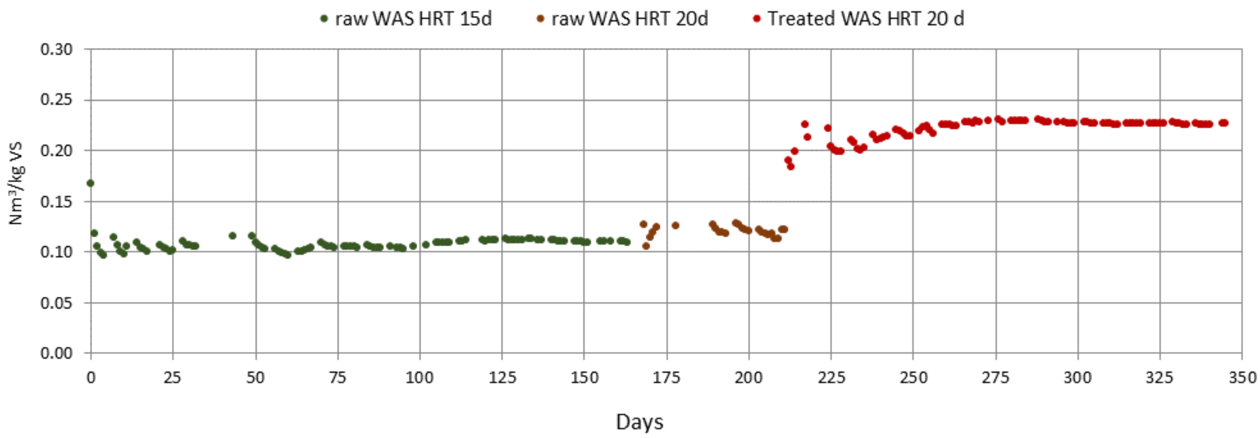


Figure 3. Trend of the SMP for raw and thermo-alkali pre-treated WAS (tests n.2 and 3)

As expected, the thermo-alkali pre-treatment (90°C, 90 min, 4 g NaOH/100 g TS) of the WAS promoted the solubilization of particulate organic matters [40], thus determining an increase in the sCOD [10]. The observed disintegration rate was in the order of 40% (data not shown), in line with the values found in the tests carried out at a smaller scale [31]. The pH of the WAS after the pre-treatment was in the order of 8.5.

Figure 4 shows the detail of the results of the digestion test involving the thermo-alkali pre-treated WAS (test n.3).

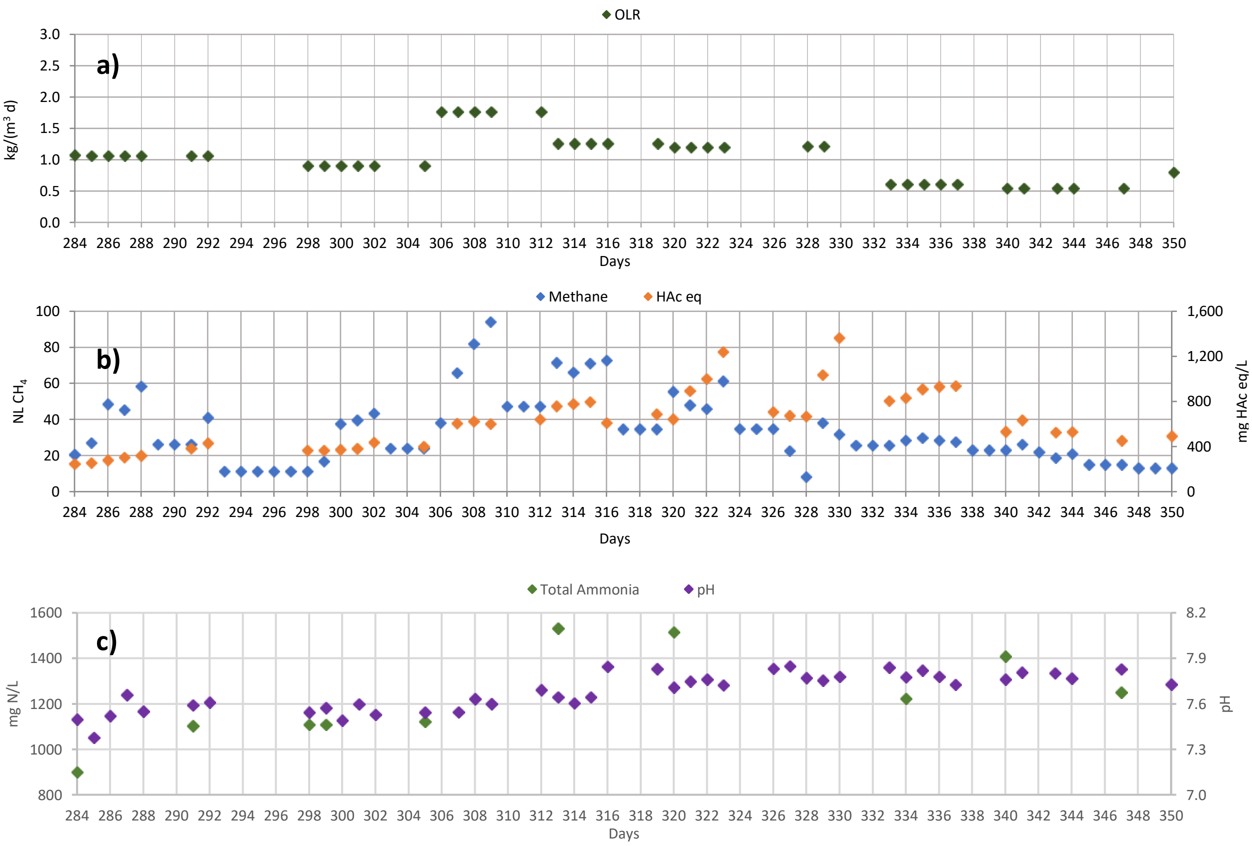


Figure 4. Details of the digestion test (n.3) involving the thermo-alkali pre-treated WAS: trend of (a) daily organic loading rate (OLR) (b) daily methane production and total acidity concentration; (c) $N\text{-}NH_3$ and pH.

It can be seen from Figures 4a and 4b that the substrate fed at an OLR value of approx. 1.3 kg $VS/m^3{\cdot}d$ (phase "a" of test n.3) determined an evident instability of the system already after 20 days from the beginning of the test. The daily methane production dropped from 50-60 NL to less than 20 NL. The instability was due to an increase of the concentration of $N\text{-}NH_3$ into the digestate, from 1000 mg/L (the first day of the test) to 1500 mg/L (the 21st day, Figure 4c), that inhibited methanogens thus determining a reduction in the methane production and an evident accumulation of acidic species (total VFAs) as observed, for example, in Capson-Tojo et al. [41]. Figure 4a shows that the concentration of total VFAs rose from approx. 400 mg acetic acid equivalent/L to values of more

1000 mg acetic acid equivalent/L. Consequently, in order to avoid that the digestion process was completely compromised, the OLR was decreased by 50%, by mixing the feedstock with an equal volume of tap water (50:50 by volume). As it can be seen from Figure 3, the digestion process had been carried out with the dilute feedstock for approx. 100 days, and it evidenced a SMP of 0.230 Nm^3/kg VS, approx. 110% more than the value observed for the raw WAS.

As shown by the Figures provided in SM3, the daily production of methane of the three substrates was heavily affected by the frequency of the digester feeding. In fact, it was not possible to keep the HRT at a constant value, because the digester was fed only five days per week. Consequently, it was verified whether, with the aid of the first order kinetic model described in Section 2.4, the raw data collected from the experimentation could be used to provide a complete description of the AD process, in terms of B_0 and k. In fact, the raw data alone cannot be considered sufficient to quantify the substrate production at a fixed HRT.

The data of methane production obtained from the long-term, semi continuous tests were fit with the first order kinetic model described in Section 2.4. In the phase of model calibration, the optimal set of B_0 and k values were found by minimizing the objective function J. Details concerning the calculus of the two parameters, namely the number of experimental data used for the model calibration and the range of the values into which the optimal values of B_0 and k were searched for are reported in SM4. A very good agreement between the experimental and the calculated data was obtained, as shown in Figure 5a, 5b and 5c for the PS, raw and pre-treated WAS.

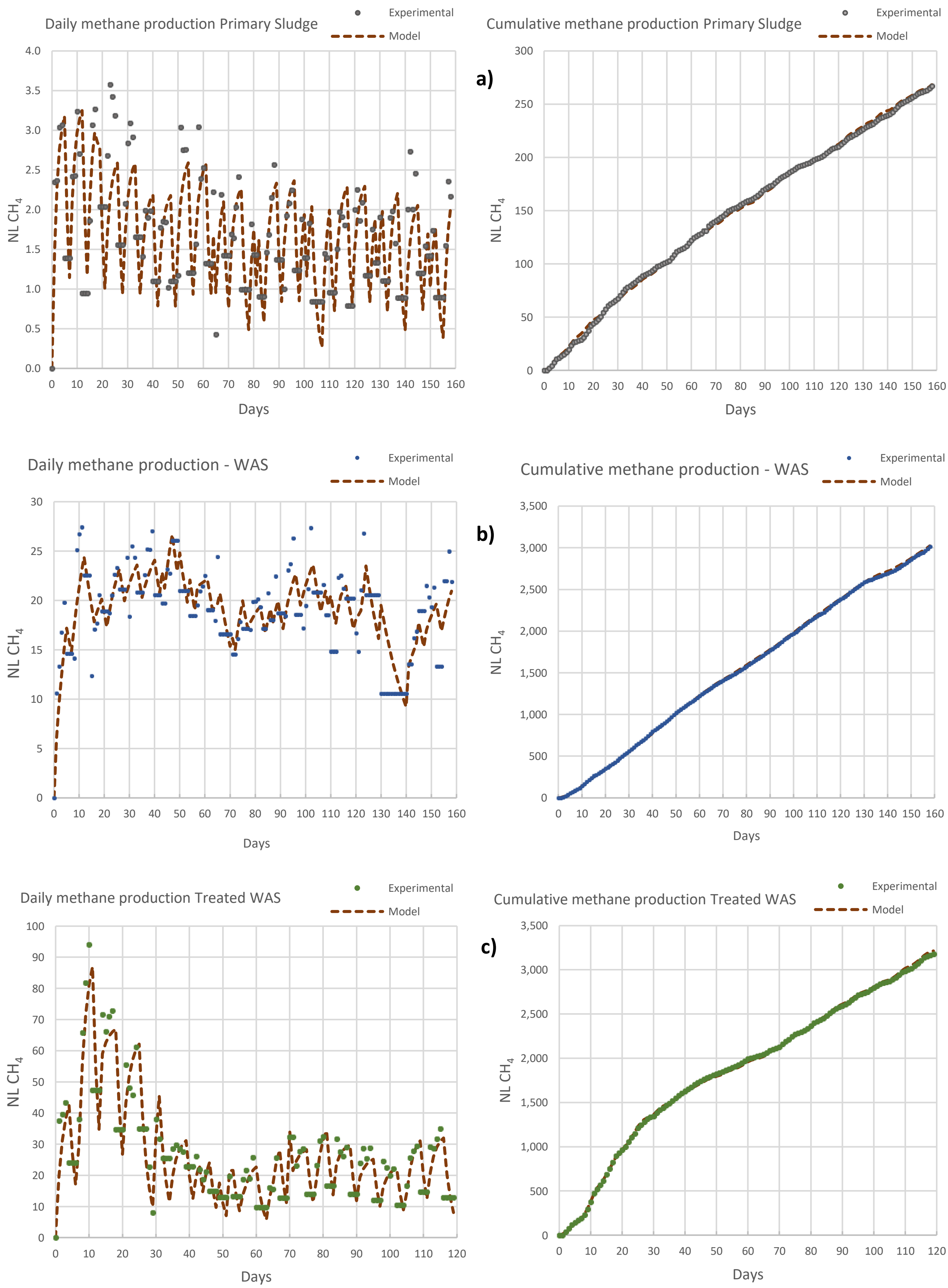


Figure 5. Daily and cumulative volumes of methane produced during the AD test involving the PS (a, test n. 1), the raw WAS (b, test n. 2) and the pre-treated WAS (c, test n. 3)

The model parameters that characterized the three substrates, PS, WAS and thermo-alkali treated WAS, namely B_0, k and biodegradability (Y) are reported in Table 4.

Table 4. Values of the B_0 and k parameters and biodegradability (Y) for the three substrates, PS, WAS and thermo-alkali treated WAS

Substrate	B_0 (Nm^3 CH_4/kgVS)	k (1/d)	Y (%)
Primary sludge	0.300 ± 0.000	0.520 ± 0.040	49 ± 0
Raw WAS	0.147 ± 0.000	0.085 ± 0.000	28 ± 0
Pre-treated WAS	0.250 ± 0.000	0.465 ± 0.020	48 ± 0

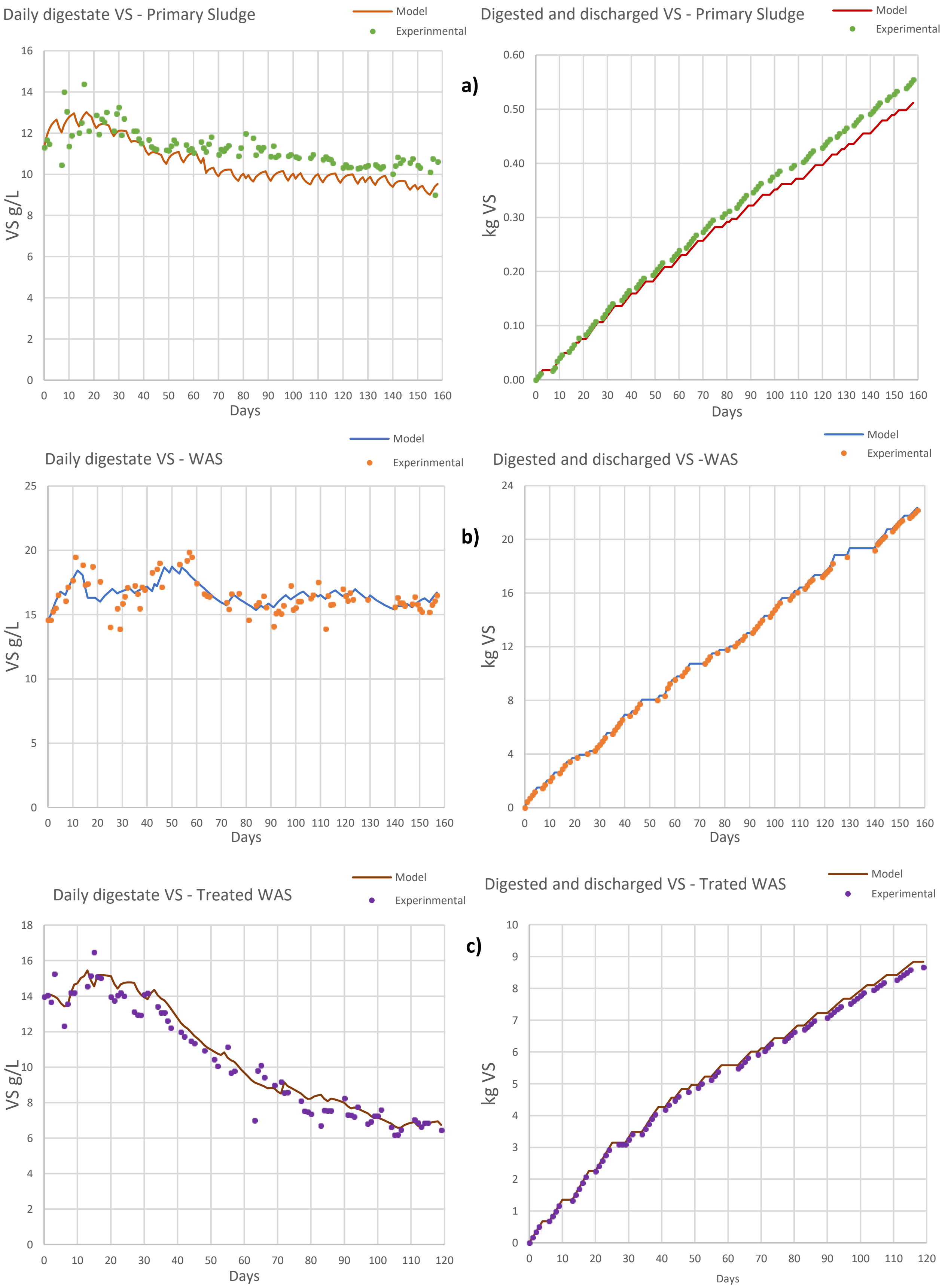
It can be seen from the figures of Table 4 that, the SMP obtained in the experimental test for the PS, equal to 0.280 Nm^3/kg VS, approached the value obtainable from an AD process of infinite duration, being the difference between the experimental SMP and B_0 of only 7%. The biodegradability was in the order of 50%. The effect of the thermo-alkali pre-treatment on WAS was not only an increase in the amount of biodegradable organic matter, from 28% to 48%, and, consequently, in the produced methane (B_0, + 70%), but, above all, an increase in the rate at which the substrate was made available for the digestion process (k, + 447%). An increase in the k allows the AD process to be performed with shorter HRTs and, consequently, with smaller reactors [42]. It was evident that the thermo-alkali pretreatment modified the behavior of the WAS in an AD process, thus making it quite similar to that of PS, in terms of biodegradability and biogas potential production.

The results predicted by the model for the pre-treated WAS make the introduction of the thermo-alkali pre-treatment in the sludge line of the Castiglione Torinese WWTP a promising and beneficial option. Oosterhuis et al. [43] obtained similar results after the introduction of a pilot-scale Cambi thermo-hydrolysis process, running at 165°C and 6 bars for 20 minutes, at the Hengelo WWTP (The Netherlands). They observed an increase in the Y parameter from 26% to 42% after WAS pre-treatment. In the present study, the pre-treatment carried out in less severe conditions (90°C, 30 min, in the presence of NaOH) determined an increase in the substrate biodegradability (Y) from 28% to 48%. Gianico et al. [44] observed values of the maximum methane production parameter (B_0) of 0.154 Nm^3 CH_4/kgVS, for raw WAS, and of 0.223 Nm^3 CH_4/kgVS for the WAS after a thermal lysis process (134°C, 3 bars, 30 min). Gianico et al. [44] carried out the pre-treatment under conditions that were milder than those of a typical thermo-hydrolysis process. It can be seen that the values by Gianico et al. [44] were very similar to those found in this study. Recently, Guerrero Calderon et al. [42] demonstrated that a free nitrous ammonia pre-treatment could increase the rate of hydrolysis (k) of WAS from 22-33% to 54-66%, depending on the presence of primary treatments in the water line of a WWTP. They observed k values of 0.20 d^{-1} for raw WAS and of 0.28 – 0.34 d^{-1} for treated WAS.

The thermo-alkali pre-treatment carried out in this study seemed to have a larger /more intense impact on the rate at which the organic substrate was made available for the AD process. He et al. [45] tested a pre-treatment method based on the reflux of the digestion liquid back to the WAS digestion unit (pH 9.5 for 24 h). The extent of the maximum methane production parameter (B_0) found by He et al. [45] (282.5 mL/gVS) was quite close to that of this study (0.250 NmL/g VS). Finally, Kim et al. [46] evaluated the potential of a series of lower (< 100°C) and higher (> 100°C) thermal pre-treatments applied to samples of dewatered sludge collected from a municipal WWTP and a brewery WWTP in Hongcheon, South Korea. The study demonstrated that thermal pre-treatments (mainly carried out at high temperatures) had a very good capacity in improving the methane production of the substrate (+81% with respect the control), but their potentiality was in general lower than that of the combination of milder temperatures and alkali substances.

3.1.2 Model validation for the single substrates (PS, WAS, pre-treated WAS)

After the calibration, the model was validated for each of the three substrates by using the VS remaining into the digestate after the digestion process. The phase of model validation made use of a strong hypothesis, that is that the nature and composition of the biodegradable VS was the same of non-biodegradable VS. Therefore, also the COD/VS ratio for both biodegradable and non-biodegradable organic matter was the same. The model validation consisted in the comparison of the daily amount of VS found in the digestate with the daily amount of VS predicted by the model. Figure 6 shows a very good agreement between the experimental and calculated data. The error values between the sets of experimental and predicted data were equal to 7.3 %, 1.3% and 1.8% for PS, raw WAS and thermo-alkali WAS respectively.



Daily digestate VS - Primary Sludge
Model
Experimental
VS g/L
Days
Digested and discharged VS - Primary Sludge
Model
Experimental
kg VS
Days
a)
Daily digestate VS - WAS
Model
Experimental
VS g/L
Days
Digested and discharged VS -WAS
Model
Experimental
kg VS
Days
b)
Daily digestate VS - Treated WAS
Model
Experimental
VS g/L
Days
Digested and discharged VS - Trated WAS
Model
Experimental
kg VS
Days
c)

Figure 6. Daily digestate VS concentrations and cumulative discharged VS during the semi-continuous AD tests involving the PS (a, test n.1), raw WAS (b, tests n.2) and treated WAS (c, tests n.3).

3.1.3 Model validation for the mixed sludge and assessment of WWTP's new configurations

The model, calibrated and preliminary validated as described in Sections 3.1.1 and 3.1.2, was further validated by using the results of the fourth AD test, carried out with the mixed sludge, 50/50 b.v. PS and pre-treated WAS. Figure 7 shows the daily and cumulative volumes of methane produced during the AD test.

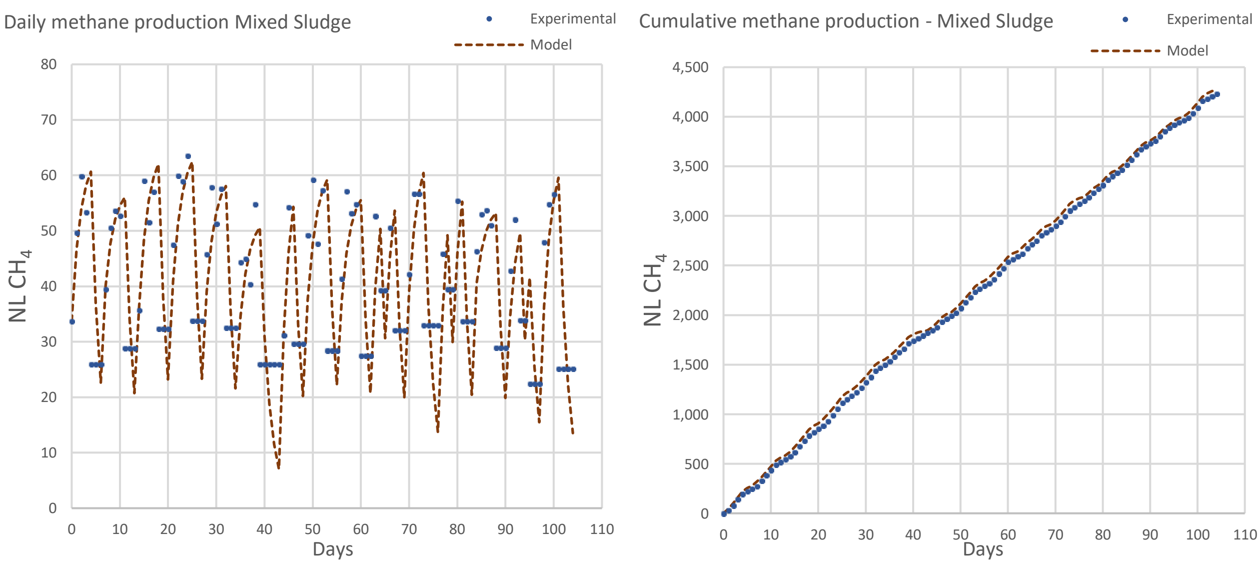


Figure 7. Daily and cumulative volumes of methane produced during the AD test involving the mixed sludge (test n. 4)

Values of B_0 and k found individually for the PS and the pre-treated WAS were used to predict the methane production of a digester with an HRT of 20 days fed with the mixed sludge. The error values of only 1.1% between the sets of experimental and predicted data, as in Figure 7, demonstrated that the proposed model was robust and could be successfully used even to predict the production of methane from an AD process where the feedstock was a mixture of substrates.

The model, with the key parameters B_0 and k, obtained as described in Sections 3.1.1 and 3.1.2 and listed in Table 4, was used to compare the two possible future configurations of the WWTP sludge line described in Section 2.6. The two novel configurations include the introduction of the thermo-alkali pre-treatment on WAS and a one-stage or two-stage digestion scheme.

The results of the calculations demonstrated that the introduction of the thermo-alkali pre-treatment determined an increase in the methane production from the digestion of WAS of 144% and 167%, for the one-stage and two-stage plant's configuration, respectively. Considering that WAS represents only 36% of the TS fed to the WWTP digesters, the increase in the total methane production from the AD process was of 25% and 34% for the one-stage and two-stage configuration respectively.

The data reported in Figure 8 were calculated by referring to the energy analysis carried out as described in Section 2.6. Figure 8 shows the ranges of TS concentration in PS and WAS that make the digestion processes carried out at the WWTP under one-stage (left) or two-stage (right) scheme self-sustainable on a thermal point of view. The position and the amplitude of each zone depends on the TS content of the two sludge and on the efficiency in heat transfer from the CHPs to the WAS. As expected, low TS contents for both sludges, in the order of 4%, require a high heat transfer efficiency. Conversely, high thickening performances, capable to produce substrates with a TS content of 7% or more, can tolerate/admit lower heat transfer efficiencies.

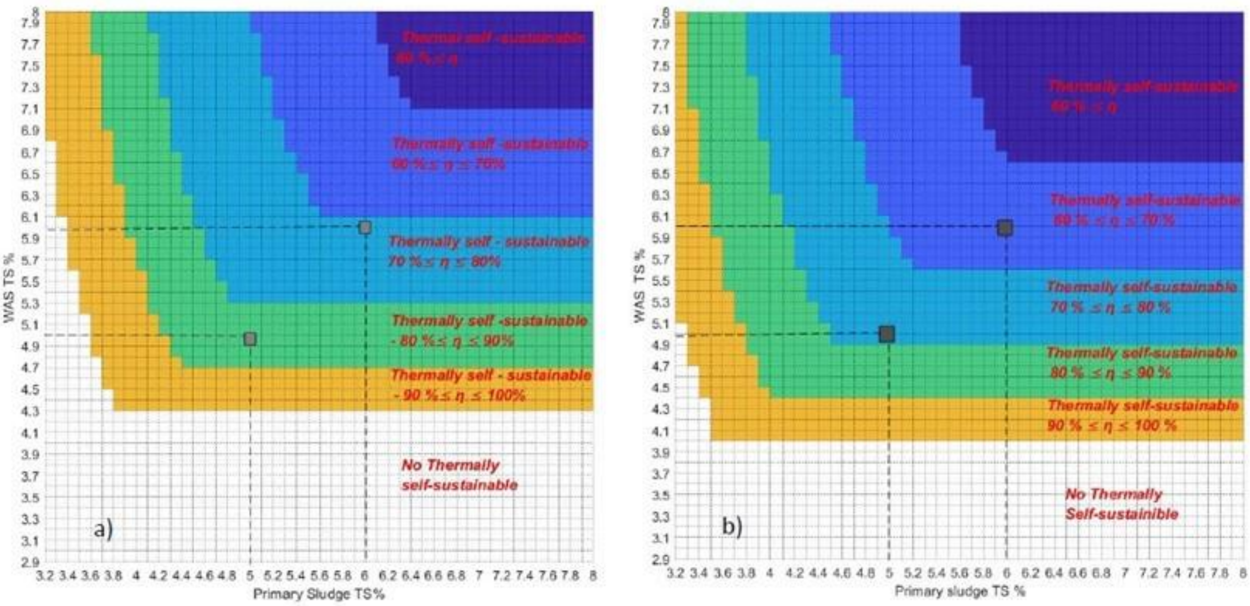


Figure 8. Ranges of TS concentration in PS and WAS that make the digestion processes carried out at the WWTP under one-stage (left) or two-stage (right) scheme thermally self-sustainable

3.2 Effect of the thermo-alkali pre-treatments on the ammoniacal nitrogen release

3.2.1 Validation of the mathematical model to predict the $N\text{-}NH_3$ release to the digestate

The concentration values of $N\text{-}NH_3$ into the digestate, coming from the two long-term digestion tests that involved the raw and pre-treated WAS, were used to calibrate the model presented in Section 2.5. The searched value for that model was the "perN-NH_3" parameter, that depends on both the composition of the substrate and the amount of VS fed to the digester. Details on the number of experimental data used for the model calibration and the range of the values into which the optimal value of "perNH$_3$" was searched for are reported in SM4. Table 5 lists the values found for the "perN-NH$_3$" parameter for the digestion tests involving either raw or pre-treated WAS.

Table 5. Parameters used to calibrate the model predicting the ammonia release to the digestate and values of the "perNH$_3$" parameter

	Number of experimental data	Range of "perN-NH$_3$" (g N-NH$_3$ / g VS$_{fed}$)	"perN-NH$_3$" (g N-NH$_3$ / g VS$_{fed}$)
WAS	5	0.0-0.1 (step 0.0005)	0.0475 ± 0.0025
Pre-treated WAS	16	0.0-0.1 (step 0.0005)	0.0655 ± 0.0025

The thermo-alkali pre-treatment, carried out on WAS, determined not only an increase in the B$_0$ and k parameters, as reported in Section 3.1.1, but also in the capacity of the substrate to release N-NH$_3$ to the digestate (see Table 5). In fact, the "perN-NH$_3$" parameter increased from 4.75% to 6.55% when the pre-treatment was applied. These findings are in line with the results of previous studies. Chen et al. [7] evidenced an increase in TN, in the supernatant of a pre-treated WAS, from 40.50 mg/L to 112.27 mg/L, 143.84 mg/L, and 248.94 mg/L after alkali, microwave irradiation and ultrasonication pre-treatment, respectively. Specifically, the addition of NaOH used in an alkali pre-treatment could determine a reaction of saponification between the alkali agent and phospholipids, that is the main component of cell membranes, thus disrupting the cell and determining the release of intracellular constituents such as proteins [7].

The developed model, calibrated with the parameters B$_0$, k and "perN-NH$_3$" found in the experimental tests, was used to predict (i) the production of methane (SMP, Nm^3/kg VS), (ii) the consumption of biodegradable solids (VS$_{effluent}$/VS$_{fed}$) and (iii) the release of ammonia ("perN-NH$_3$" gNH$_4^+$effluent/kg VS$_{fed}$) in full-scale AD processes, involving raw or pre-treated WAS. The HRT values considered in the AD processes were of 14.8 days, that is the value at which the digestion of WAS in the Castiglione Torinese WWTP was carried out during the experimental period, and 20.0 days, that is the value used for the tests of this study. Table 6 details the results obtained from the application of the model.

Table 6. Results obtained from the application of the model predicting the methane production and ammonia release to the digestate

	One-stage AD			Two-stage AD	
	Raw WAS	Raw WAS	tWAS	Raw WAS	tWAS
HRT (d)	14.8	20.0	20.0	10+10	10+10
SMP (Nm^3 CH_4/kg VS)	0.083	0.093	0.225	0.104	0.242
$VS_{effluent}/VS_{fed}$	0.84	0.82	0.55	0.80	0.54
$NVS_{effluent}/NVS_{fed}$	1.0	1.0	1.0	1.0	1.0
perN-NH_3 (gN-NH_4^+ /kg VS_{fed})	26.5	29.9	59.1	33.6	63.4

As it can be seen from the values of Table 6, the introduction of a thermo-alkali pre-treatment on the WAS in the sludge line of the Castiglione Torinese WWTP, at the present HRT value (14.8 days), could be of benefit for the methane production, that would increase by 175%. The results listed in Table 6 show that a larger amount of VS was consumed, with a decrease in the residual VS content of the digestate from 84% to 54% (two-stage AD scenario). It can also be seen that, especially for the scenario that considers the implementation of the pre-treatments, the increase of HRT from 14.8 to 20.0 days had a very limited impact on the SMP and VS consumption.

Furthermore, according to the data of Table 6, it can be seen that the pre-treatment determined an increase of the amount of N-NH_3 released to the digestate of more than 100% (123% at an HRT of 20 days and 139% at the same value of HRT but with a two-stage AD). As a consequence of that, the managers of the WWTP should carefully assess if the existing biological processes intended to nitrogen removal in the water line can cope with the increase in the AN load due to the implementation of pre-treatments in the sludge line. Otherwise, on-purpose made treatments for the reduction of the nitrogen load, such as a side-stream Anammox, should be considered.

It can be estimated that the electric energy necessary to remove the extra amount of AN, due to the introduction of the pre-treatment, in the water line through a nitrification – denitrification process increased from 129 kW to 254 kW, for the one-stage AD scenario (HRT = 20 days), and from 145 kW to 273 kW, for the two-stage AD scenario (HRT = 10+10 days). These values were obtained by referring to the unit electric power demand for nitrogen removal in the water line, equal 4.0 kWh/kg N, as reported in [47]. Whether it was possible to treat the AN in the liquid fraction of the digestate with a dedicated, side stream process, such as an Anammox process, the electric energy demand for the nitrogen removal would be in the order of 48 kW for the present situation, and of approx. 105-114 kW considering a future introduction of thermo-alkali pre-treatments. At Castiglione Torinese WWTP, SMAT recently introduced a DEMON process treating the reject water of sludge dewatering after AD. The process, based on partial nitritation and anaerobic ammonium oxidation carried out by anammox bacteria, is particularly efficient in treating high nitrogen load streams and less energy intensive than the traditional nitrification-denitrification scheme.

Conclusions

This study demonstrated that:

- first-order models could overcome the limitations due to discontinuity in experimentation and provide reliable parameters (B_0, k, "perN-NH_3") to describe the production of gas and the release of ammonia to the digestate when changes are introduced in existing WWTPs;
- secondly, low-temperature thermo-alkali pre-treatments could achieve comparable results, in terms of methane production (B_0) and velocity at which the substrate was made available for AD process (k), of some commercial, high-energy demanding treatments (e.g. Cambi). Specifically, the introduction of the thermo-alkali pre-treatment determined an increase in the methane production from WAS of 144% and 167%, for a one-stage and a two-stage digestion configuration respectively;
- finally, the issue concerning the ammonia release is very worthy to being investigated because, after pre-treatment, the cost for nitrogen removal in the water line, through traditional processes of nitrification – denitrification, could increase even by 139%.

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CRediT author statement

Giuseppe Campo: conceptualization, methodology, software, validation, formal analysis, investigation, writing – original draft, writing – review & editing, visualization; **Alberto Cerutti**: conceptualization, methodology, validation, investigation; **Mariachiara Zanetti**: conceptualization, writing – review & editing, supervision, project administration, funding acquisition; **Margherita De Ceglia**: investigation, resources, writing – review & editing; **Gerardo Scibilia**: conceptualization, validation, resources, writing – review & editing, supervision, project administration; **Barbara Ruffino**: conceptualization, methodology, validation, writing – original draft, writing – review & editing, supervision, project administration.

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