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Effects of Ammonia Stripping and Other Physico-Chemical Pretreatments on Anaerobic Digestion of Swine Wastewater

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Abstract: In order to overcome anaerobic digestion (AD) inhibition due to the large nitrogen content of swine wastewater (SW), air stripping (AS) and other chemical and physical pretreatments were applied on raw SW before AD. The efficiency of these pretreatments on both ammonia removal—recovering ammonia salts to be used as fertilizers in agriculture—and the increase of methane production were assessed in batch tests. Since the pH, temperature, and air flow rate heavily influence AS efficiency and the composition of treated SW, these parameters were set individually or in combination. In more detail, the pH was increased from the natural value of SW to 8 or 10, temperature was increased from the room value to 40 °C, and the air flow rate was increased from zero to 5 $L_{air} L_{SW}^{-1} min^{-1}$. AS was generally more efficient at removing ammonia (up to 97%) from raw (non-treated) SW compared to the other treatments. However, the tested pretreatments were not as efficient as expected in increasing the biogas production, because the methane yields of all pretreated substrates were lower (by about 10–50%) to compared raw SW. The inhibitory effect on AD could have been due to the lack of nutrients and organic matter in the substrate (due to the excessive removal of the pretreatments), the concentration of toxic compounds (such as metal ions or furfural due to water evaporation), and an excess of alkali ions (used to increase the pH in AS). Overall, AS can be considered a sustainable process for the recovery of ammonium sulphate and the removal of other polluting compounds (e.g., organic matter) from SW. Conversely, the use of AS and other chemical and/or thermal processes tested in this study as pretreatments of SW before AD is not advised because these processes appear to reduce methane yields.

Keywords: air stripping; methane production; energy recovery; ammonium sulphate; ammonia removal efficiency; digestate; anaerobic digestion

1. Introduction

Swine wastewater (SW) consists of a blend of urine, feces, water, residues of undigested food and antibiotics, and pathogens [1–4]. The management of SW is an important problem for sustainable production in swine breeding farms. As a matter of fact, the direct disposal of SW would contaminate surface and ground waters, cause unpleasant odor emissions in air, and degrade soil quality.

Intensive treatments [5], as well as other chemical, physical, and biological systems [5–8], generally show low efficiency, high costs [9], and process instability due to the high content of organic matter and toxic compounds, such as ammonia nitrogen, in SW. Natural or semi-natural extensive systems, such as aerobic and/or anaerobic lagooning [10–12], offer a high environmental and economic sustainability

because these systems are cheaper, more reliable, and environmentally sound. However, the time required for reducing the pollutant load of SW can be very long (some weeks or even months) because the physico-chemical and biological depuration processes cannot be properly controlled [13–15]. Anaerobic digestion (AD) seems to be a viable alternative to both intensive and extensive treatment systems for SW. AD is able to degrade the high organic load of SW and, at the same time, to produce biogas, a biofuel mainly composed of methane and carbon dioxide and digestate. Carbon dioxide is used for the production of electric and/or thermal energy, while digestate, the liquid effluent of AD, is used as fertilizer). The substrates for AD—usually activated sludge, energy crops, residues of agro-industries, and animal breeding farms—should have a balanced C/N (carbon/nitrogen) ratio, a pH between 6.5 and 8.0, and a noticeable content of organic compounds for appreciable methane yields. However, the high ammonia concentration of the SW can inhibit the activity of methanogenic bacteria in AD plants, noticeably reducing methane yield [16,17]. The removal of nitrogen compounds before AD may enhance methane production, since it reduces the compounds' toxicity towards the microbial consortium [18,19]. Therefore, SW pre-treatments that are able to remove or convert its nitrogen content before AD are feasible for increasing digester efficiency.

Some physico-chemical treatments, such as chemical precipitation or air stripping (AS), can remove nitrogen compounds from SW. In addition, nutrients—e.g., struvite or ammonium sulphate [20,21]—can be recovered from these treatments and used as fertilizers in agriculture. Hence, these techniques are able to produce natural fertilizers and increase the methane yields of AD using SW as a substrate.

AS is a common system to treat wastewater of different sources, such as urine, digestate, manure, and municipal and industrial wastewater [22–26]. Briefly, AS consists of a desorption process of a gas dissolved in a liquid through a mass transfer. In the case of SW, which is the liquid phase, ammonia is used as gas. In the AS process, the wastewater is aerated after mixing with alkali at pH over 8.5, which allows for easier ammonia stripping. Ammonia is then recovered by an adsorbing unit, filled with a sulfuric acid solution, as ammonium sulphate. The latter can be directly spread on agricultural fields as a fertilizer. Air flow rate, pH, and temperature are the parameters that most influence the removal rates of ammonia from SW.

However, while the AD of raw SW has been widely studied, e.g., [27–32], the ammonia removal efficiency of AS applied to SW has been studied little (e.g., [33–35]), and much less research about integration of AS as pre-treatment and AD for SW treatment is available in the literature. Moreover, the results of these few studies are contrasting. Bonmati and Flotats [36] did not observe the better performance in the AD of treated SW, while Zhang et al. [2,16] reported a noticeable methane increase in the AD of air-stripped SW compared to untreated SW.

In order to advance knowledge about AS efficiency on raw SW, as well as the performance of the AD of SW previously subjected to AS, this study proposes an integrated system, AS and AD, for depurating SW and producing methane from this effluent; this system was compared to other integrated systems consisting of chemical and thermal pretreatments and AD. The preliminary treatment of SW by AS was aimed at recovering ammonia nitrogen as base for fertilizer and, at the same time, at reducing the inhibitory effects of nitrogen compounds in the subsequent AD. Overall, the study aimed to evaluate whether and by what extent the effects of pre-treatments weighed on the energy yields of the AD, or, in other words, how much the studied pre-treatment varies the methane yields of the combined process.

2. Materials and Methods

2.1. Effects of the Operational Parameters of AS on the Removal Efficiency of Ammonia Nitrogen

SW contains ammonia in the form of ammonium ions (the ionic form, NH_4^+) and gas (the molecular form, NH_3) [26]. The chemical equilibrium between the forward reaction rate and the reverse reaction rate is the following:



The distribution between molecular ammonia and ammonium ions, described by Equation (2), depends on pH and temperature, as explained by Equation (3):

$$[\text{NH}_3] = \frac{[\text{NH}_3 + \text{NH}_4^+]}{1 + [\text{H}^+]/K_a} \quad (2)$$

$$\text{p}K_a = 4 \times 10^{-8}T^3 + 9 \times 10^{-5}T^2 \times 0.0356 T + 10.072 \quad (3)$$

where:

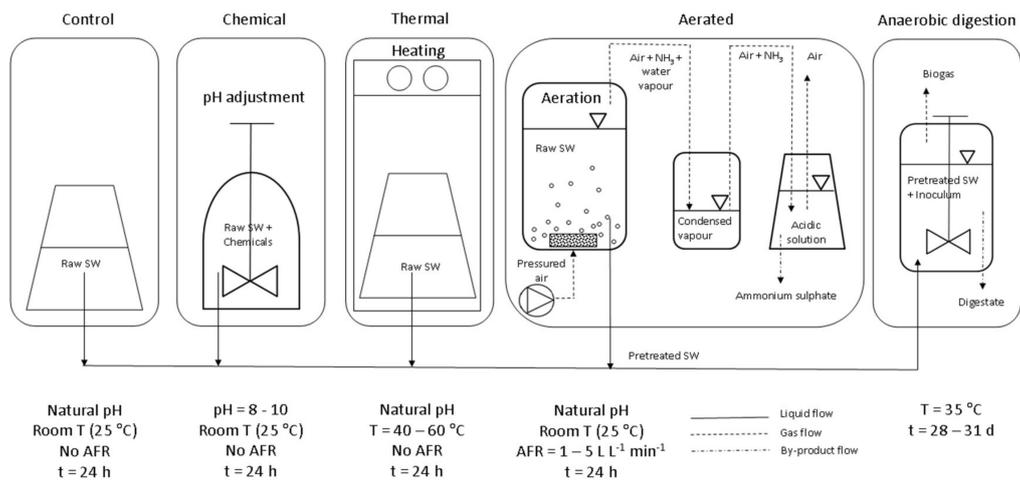
- $[\text{NH}_3]$ = molecular ammonia concentration (mol L^{-1}).
- $[\text{NH}_3 + \text{NH}_4^+]$ = total ammonia nitrogen (TAN, mol L^{-1}).
- $[\text{H}^+]$ = hydrogen ion concentration (mol L^{-1}).
- K_a = acid ionization constant (dimensionless).
- T = temperature (K) [37].

More specifically, an acidic pH enhances the formation of ammonium ions—the equilibrium reaction shown in Equation (1) is displaced to the right—while at strong alkaline pH values > 8.5 , molecular ammonia prevails and the equilibrium is displaced to the left [37–40]. As the aim of the treatment is the removal of ammonia nitrogen compounds (both under the ionic and molecular forms) from the SW, the increase of pH over a certain limit in wastewater allows for the conversion of almost all the NH_4^+ content into the gaseous form: NH_3 . Temperature has a noticeable influence on the molecular ammonia removal from wastewater, since ammonia solubility in water follows Henry's law and depends on the temperature, as well as solute and solvent amounts [20,26,37,41]. Heating wastewater enhances diffusion of the ammonia molecules to the liquid surface and subsequently to the atmosphere [38]. Moreover, the mass transfer of NH_3 from the liquid is enhanced by the aeration of the AS process that bubbles air in the solution and alters the air–liquid boundary [38]. The air flow rate (AFR), that is the air flow per volume of wastewater, establishes a higher gradient in ammonia concentration between the liquid and air phases [26,36].

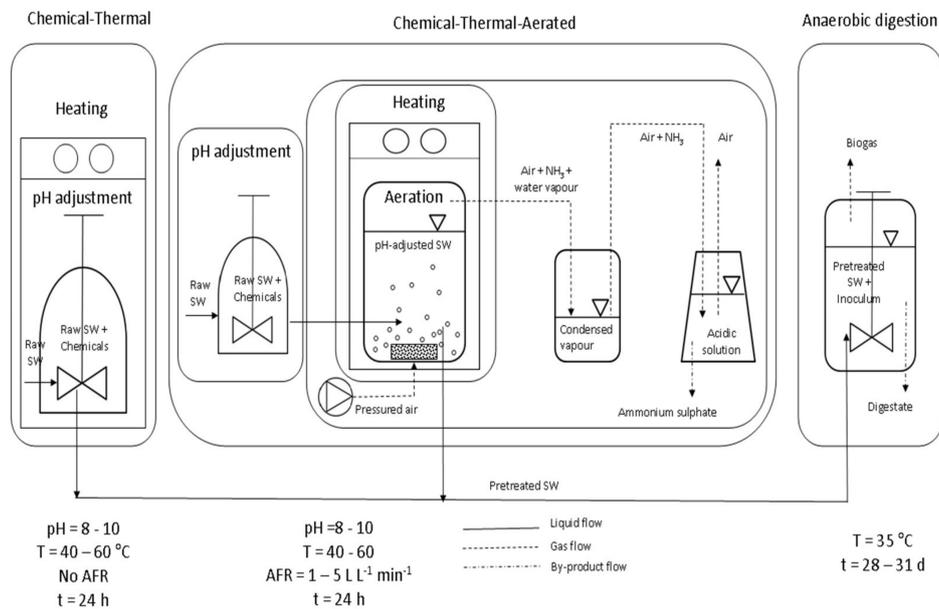
2.2. Experimental Setup

Figure 1 shows the scheme of the experimental setup used for the tests on the systems treating SW. First, the raw SW is subjected to AS and/or other chemical and physical treatments under different environmental conditions (i.e., temperature and/or pH) to reduce the ammonia nitrogen content; if air is supplied, ammonium salt recovery is also possible. Then, the treated SW is used as substrate to evaluate the methane production in AD through biochemical methane potential (BMP) tests.

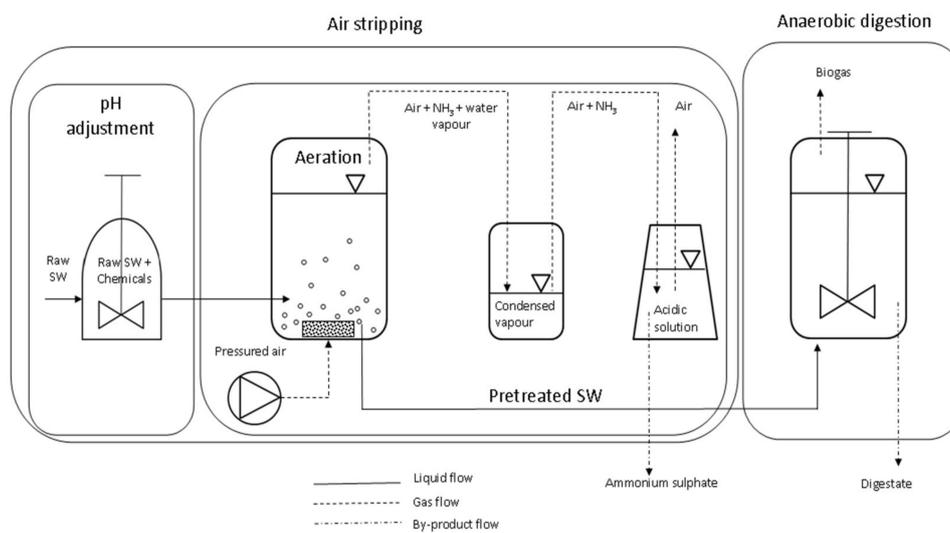
The removal efficiency of nitrogen compounds is mainly influenced by the initial pH of the SW, as well as AFR and temperature of the process. Therefore, in this study, SW was subjected to pretreatments, individually controlling each parameter. These experiments were the individual thermal (henceforth referred as “T” treatment), chemical (C), and aerated (A) treatments. The A treatment was AS. A combination of chemical–thermal–aerated (CTA) treatments was also tested. Moreover, a SW treatment by chemical and thermal processes (CT treatment) was also tested to disentangle the beneficial effect of the aeration of the CTA treatment. Overall, the choice of these individual (C, T, or A) and “combined” (CT and CTA) treatments was aimed at comparing ammonia removal efficiencies in terms of the TAN and the AD performances of the treated SW in terms of increased methane production with and without air supply. A control treatment was carried out on SW with natural pH and under room temperature without aeration. Table 1 summarizes the treatments adopted for SW. Henceforth, one to three capital letters followed by three letters or numbers (the value of the operational parameter) indicates each treatment. For example, $\text{CT}_{10-40-0}$ is a chemical–thermal (C and T) test with pH adjusted to 10 (10), a temperature of 40°C (40), and without aeration (0). The treatment including aeration is indicated with “A” as the letter and a number as third subscript indicating the value of the AFR (in $\text{L L}^{-1} \text{min}^{-1}$).



(a)



(b)



(c)

Figure 1. Experimental design of the systems treating swine wastewater (SW): (a) individual treatments, (b) combined treatments, and (c) air stripping and anaerobic digestion.

Table 1. Experimental design of the tests on SW and related operational parameters.

Test	pH	Temperature [°C]	Air Flow Rate [L _{air} L _{SW} ⁻¹ min ⁻¹]
Control	Natural	Room	0
T _{n-40-0}	Natural	40	0
C ₈₋₂₅₋₀	8	Room	0
C ₁₀₋₂₅₋₀	10		
A _{n-25-5}	Natural	Room	5
CT ₁₀₋₄₀₋₀	10	40	0
CTA ₁₀₋₄₀₋₅	10	40	5

The capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; and natural = without external control. pH varied between 7.03 ± 0.03 and 10.07 ± 0.04 ; the room temperature was 20 ± 3 °C.

Each individual or combined treatment of SW was carried out at batch scale in a 1 liter bottle for 24 h. The values of initial pH (natural, 8, or 10), temperature (room or 40 °C) and AFR (none or 5 L L⁻¹ min⁻¹) were chosen based on the results of previous studies [16,36]. In particular, the optimal pH value for the efficient and fast removal of ammonia from raw SW was found to be in the range 9.5–10.0 [2,36]. A temperature of 40 °C can be easily reached in AD plants by biogas combustion (without external energy requirement) or solar panels, and it allows for a pre-heating of the substrate before the AD. An AFR of 5 L L⁻¹ min⁻¹ was an intermediate value among commonly used AFRs, from 0.05 to 10 L L⁻¹ min⁻¹ [16,36].

In the C tests, the pH was set up at 8 or 10 using a solution of Ca(OH)₂ (30% w/v). In the T tests, SW was heated in a thermostatic chamber. Three batch units were used for the A tests (Figure 1). In the first unit, SW was aerated using a submerged electrical pump (Ferplast model Airfizz 50) and a porous stone. The latter allowed for a more efficient air diffusion in the SW. The air volume supplied by the pump was manually set up by a flow meter. A second unit (condenser) collected the vapor stripped by the air flow. The gaseous ammonia flowed in a third unit (trap), which contained an acidic solution (0.1 M H₂SO₄); here, ammonia was recovered as salt (i.e., ammonium sulphate). In the combined TA treatment (thermal–aerated test), each batch was kept in the thermostatic chamber; the condenser and the acidic trap were instead left at room temperature. Each test was carried out in duplicate.

SW was characterized before each test and after 24 h, with the main physico-chemical parameters being measured in duplicate. The soluble chemical oxygen demand (sCOD) and TAN were evaluated by a mass balance to measure the removal efficiency of each treatment. The mass balance was performed considering the initial—before pH adjustment, when applied—and final contents of sCOD and TAN. This allowed for the estimation of the SW mass reduction (MR) mainly occurring in T and/or A treatments.

At the end of the treatment, the production of ammonium salts was quantified. Since the TAN concentration was known before and after the test, the ammonium sulphate that could be theoretically recovered from SW was estimated. The recovery of ammonium sulphate (RAS) in each test was calculated according the stoichiometric Equation (4):



The ammonium ions of SW were considered to be totally converted to ammonia gas.

After the pretreatments, two series of BMP tests, indicated as Run 1 and Run 2, were performed using pretreated SW as the substrate (Figure 1). Raw samples of SW were used as the control—c1 and c2 for Run 1 and Run 2 tests, respectively. Table 2 reports the main characteristics of the blends subjected to AD.

Table 2. Main characteristics of the biochemical methane potential (BMP) tests on pretreated SW.

Parameter		Run 1					Run 2				
		Blank	c1	T _{n-40-0}	C ₈₋₂₅₋₀	C ₁₀₋₂₅₋₀	Blank	c2	A _{n-25-5}	CT ₁₀₋₄₀₋₀	CTA ₁₀₋₄₀₋₅
V _{inoculum}	mL	150	150	150	150	150	150	150	150	150	150
V _{substrate}	mL	-	66	62	61	73	-	76	130	80	110
F/M	g _{VS} g _{VS} ⁻¹	-	0.16	0.16	0.17	0.23	-	0.06	0.10	0.17	0.34
TAN	mg L ⁻¹	-	352	354	351	353	-	346	50	31	24
sCOD	g	-	0.391	0.417	0.380	0.398	-	0.206	0.115	0.230	0.125
tCOD	g	-	0.441	0.447	0.499	0.442	-	0.554	0.747	0.586	0.726
tCOD/TAN	g g ⁻¹	-	5.22	5.27	5.92	5.22	-	6.69	49.87	77.48	109.66
Ca	g L ⁻¹	-	-	-	0.65	1.96	-	-	-	2.28	4.37
TS _{mix}	[%]	1.41	1.67	1.67	1.71	2.02	2.32	2.58	2.16	2.78	2.82

F/M = food/microorganisms ratio; TAN = total ammonia nitrogen; sCOD and tCOD = soluble and total COD; Ca = calcium; TS_{mix} = tenure of total solids of the mixture inoculum and substrate; VS = volatile solids; the capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; c = control; and c1 and c2 = raw SW used as control of the tests in Runs 1 and 2, respectively.

BMP experiments were carried out in duplicate at mesophilic temperature (35 ± 2 °C). Blends, consisting of inoculum and substrate, were prepared according to the Italian norm UNI/TS (Italian Authority of Standardization/Technical Specification) 11703:2018 and to the work of [42]. The inoculum was the liquid digestate of a full-scale biogas plant fed with manure and other agro-industrial residues, while the substrate was the SW of each pretreatment. According to the norm, three different solutions (henceforth solutions A, B, and C) were used to provide micro- and macro-nutrients for the microorganisms' growth in the digested blend. Amounts of KH₂PO₄, Na₂HPO₄·12H₂O, and NH₄Cl (solution A); CaCl₂·2H₂O, MgCl₂·6H₂O, and FeCl₂·4H₂O (solution B), and MnCl₂·4H₂O, H₃BO₃, ZnCl₂, CuCl₂, Na₂MoO₄·2H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, and Na₂SeO₃ (solution C) were dosed following the norm. Blanks, that is batches with inoculum only, were used in both runs to evaluate the endogenous methane production. Biogas volume was measured three times a week, and the methane content was evaluated by the fluid displacement method [43–45] using a three-neck bottle that contained an alkaline trap (3M NaOH) that captured the CO₂ in the biogas. The biogas was transferred to the alkaline solution from one neck; through the second neck, the increased trap pressure displaced a corresponding volume of the alkaline solution into a graduated cylinder. As the alkaline solution trapped the CO₂, the methane volume of biogas was assumed to be equal to alkaline solution displaced in the cylinder. The average methane yield of each test at standard pressure and temperature conditions was depurated from the methane production of the inoculum (blank). The specific methane yield of the test was expressed in NmL of methane per gram of tCOD of the substrate added, NmL g_{tCODadded}⁻¹. The specific cumulative methane production throughout the BMP tests was also calculated (hereinafter "BMP value"). Based on the stoichiometric formulas of AD, the amount of tCOD converted to methane was assessed.

The modified Gompertz model was used to simulate the kinetics of the methane yields [46,47] (Equation (5)):

$$M = P \times \exp \left\{ - \exp \left[\frac{R_m \times \theta}{P} \times (\lambda - t) + 1 \right] \right\} a = 1 \quad (5)$$

where:

- M = cumulative methane production [L per gram of tCOD added, L g_{tCODadded}⁻¹].
- P = methane potential [L per gram of tCOD added, L g_{tCODadded}⁻¹].
- R_m = maximum production rate of methane [L per g of tCOD added and per day, L g_{tCODadded}⁻¹ d⁻¹].
- λ = lag phase period or the minimum time required to produce biogas [d].
- t = time for digestion [d].

The methane yields of the BMP tests were regressed to the values provided by Equation (5) using the least square methods. For this, the routine 'Solver' of Microsoft Excel was applied.

Run 1 of BMP was carried out on the following pretreated SW as substrate: T_{n-40-0}, C₈₋₂₅₋₀, and C₁₀₋₂₅₋₀. Raw SW (c1) was used as a control (Table 2). In this run, the TAN concentration was kept at about 0.35 g L⁻¹ in each batch. The TAN (free ammonia plus ammonium) concentration was found to inhibit the methanogenic activity of different substrates at levels ranging from 0.1 to 4.5 g L⁻¹ [48–50]. The major contributor to digestion inhibition was free ammonia, which is cell-membrane-permeable [51], at concentration from 0.04 to 1.1 g L⁻¹ [17,52–54]. The high variability in the inhibition concentration was due to several factors, such as the pH of the wastewater, the temperature of the AD process (mesophilic or thermophilic conditions), the characteristics of the substrates, and the adaptation of the inoculum [17,21,30,51]. For these reasons, TAN in Run 1 was kept at a quite low concentration, about 13% of the mean value of the range 0.1–4.5 g L⁻¹, in order to avoid an inhibitory effect on AD. However, the supplied nitrogen was above the minimum concentration required for microorganisms' growth (0.14 g L⁻¹) according to the norm UNI/TS 11703:2018. For the same reason, nutrient Solution A, which was the solution that provided nitrogen addition suggested by this norm, was not added to the batch because nitrogen was naturally supplied by the substrate.

Run 2 was carried out using SW pretreated by the A_{n-25-5}, CT₁₀₋₄₀₋₀, and CTA₁₀₋₄₀₋₅ treatments; c2 was a BMP applied to raw SW (Table 2). In this case, the initial TAN concentration was set at 0.35 g L⁻¹, as in Run 1, but this setting was only possible for c2. In the remaining tests, the TAN concentration was very low, at less than 50 mg L⁻¹, due to the efficient ammonia removal during pretreatments. Additionally for the tests of Run 2, although nitrogen concentration was below the minimum limit for efficient methanogenic activity, Solution A was not added. This choice was justified by the specific aim of the study, which was to evaluate the effect of a possible nitrogen deficiency, due to its previous removal, on the methane yield of AD.

Finally, the BMP test efficiency—the percent difference compared to the respective control test—was calculated and compared separately among the tests of each run, since the control and pretreated SW samples were different for the two runs.

2.3. Physico-Chemical Characteristics of Inoculum and SW

Samples of both raw SW and inoculum were collected at two sampling dates (July 2019 and November 2019), and this explained the different initial physico-chemical characteristics of the substrates (Table 3).

Table 3. Main physico-chemical characteristics of the inoculum and raw SW used for the integrated air stripping and anaerobic digestion (AS and AD) system tests.

Description	TS [%]	VS [%TS]	pH	sCOD [g L ⁻¹]	tCOD [g L ⁻¹]	TAN [gN L ⁻¹]
i1	2.26 ± 0.18	70.12 ± 0.17	8.13 ± 0.02	-	-	-
i2	3.87 ± 0.10	67.83 ± 0.47	8.16 ± 0.03	-	-	-
c1	1.02 ± 0.01	65.16 ± 2.65	7.04 ± 0.03	6675 ± 601	8063 ± 880	1280 ± 42
c2	0.48 ± 0.00	55.33 ± 0.57	7.61 ± 0.01	2708 ± 18	8593 ± 1798	970 ± 0

Mean ± standard deviation; i1 and i2 = inoculum of the tests in Runs 1 and 2, respectively; c1, c2 = raw SW used as control of the tests in Runs 1 and 2, respectively; TS = total solids; VS = volatile solids; sCOD and tCOD = soluble and total COD; and TAN = total ammonia nitrogen. The experiments were carried out in duplicate.

The liquid digestate of the full-scale plant, used as inoculum in the BMP experiments, was first sieved to eliminate straw and small stones. Then, the digestate was placed in an oven under anaerobic conditions at 35 °C for 7 d before the experiments. This allowed for the maximum reduction of the non-specific biogas production, that is the biogas produced by the inoculum. The main physico-chemical properties of the inoculum (hereinafter indicated as i1 and i2) used in the BMP tests are reported in Table 3.

Samples of raw SW were collected from a swine breeding farm located in Calabria (Southern Italy). Before the pretreatments, SW samples were sieved to remove possible residues (e.g., wheat or

grass) and used as fresh biomass. Sieved samples of raw SW, of which the main physico-chemical properties are reported in Table 2, were used controls for the two runs of pretreatments and BMP tests.

2.4. Analytical Methods

The following physico-chemical properties of inoculum and raw samples, as well as treated SW, were measured in duplicate using standard methods [55]:

- Total solids (TS), on oven-dried biomass at 70 °C (until weight stabilization).
- Total volatile solids (VS), on calcinated dried matter.
- pH, by a portable pH-meter from XS Instruments.

Moreover, the sCOD and TAN were evaluated on raw and pretreated SW. The liquid phase of the samples was obtained by centrifugation at 10,000 revolutions per minute of the rotor, equal to 0.559 g, for 20 min. The sCOD and TAN were evaluated by cuvette cap tests (WTW, code 1.14555, photometer WTW, PhotoLab S12) and the Kjeldhal method (Total Kjeldhal Nitrogen: TKN), respectively. The TKN is the sum of organic nitrogen, un-ionized ammonia, and ammonium ions. The TAN of the liquid phase was hypothesized to be equal to the TKN, because the ammonia nitrogen is highly soluble at pH values close to neutrality [36], whereas the organic nitrogen is mainly present in solid residue, which was removed by centrifugation.

3. Results and Discussions

3.1. Effect of SW Pretreatments on TAN and COD Removal Efficiencies

In the SW pretreatments, the MR of the control tests was always under 4%, mainly due to water evaporation. MR was higher for the A_{n-25-5} and $CTA_{10-40-5}$ treatments at $12.01\% \pm 10.27\%$ and $42.00\% \pm 0.35\%$, respectively, due to the higher water evaporation (Table 4 and Figure 2) that was enhanced by the air supply and temperature.

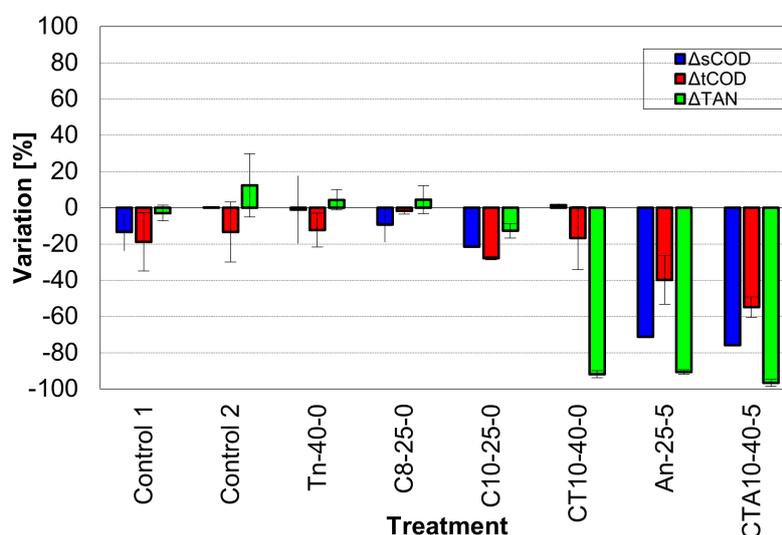


Figure 2. Variation of sCOD, tCOD, and TAN concentrations compared to the raw swine wastewater (SW) used at the end of the treatment. TAN = Total ammonia nitrogen; sCOD and tCOD = soluble and total COD; Δ sCOD, Δ tCOD, and Δ TAN = variations of sCOD, tCOD, and TAN throughout the treatment; the capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; and c = control. The error bars represent the standard deviations. The experiments were carried out in duplicate.

Table 4. Physico-chemical characteristics of pretreated SW and variations compared to raw SW.

Treatment	pH _i	pH _f	sCOD [mg L ⁻¹]	ΔsCOD [%]	tCOD [mg L ⁻¹]	ΔtCOD [%]	TAN [mg L ⁻¹]	ΔTAN [%]	MR [%]	Average Conversion of Added COD to Methane [%]
c1	7.03 ± 0.03	7.16 ± 0.01	5925 ± 177	-13.40 ± 10.37	6675 ± 601	-18.78 ± 16.10	1280 ± 14	-2.89 ± 4.29	-2.96 ± 0.05	94
T _{n-40-0}	7.08 ± 0.04	7.50 ± 0.28	6725 ± 672	-0.98 ± 18.72	7215 ± 21	-12.29 ± 9.32	1370 ± 28	4.39 ± 5.61	-2.56 ± 0.10	85
C ₈₋₂₅₋₀	8.03 ± 0.03	8.14 ± 0.01	6225 ± 106	-9.27 ± 9.71	8173 ± 746	-1.77 ± 1.77	1380 ± 57	4.51 ± 7.74	-3.18 ± 0.03	66
C ₁₀₋₂₅₋₀	10.07 ± 0.04	10.19 ± 0.27	5450 ± 495	-21.48 ± 0.06	6051 ± 576	-27.77 ± 1.01	1160 ± 14	-12.77 ± 3.95	-3.82 ± 0.2	45
c2	7.61 ± 0.01	7.95 ± 0.02	2713 ± 25	0.18 ± 0.26	7295 ± 134	-13.37 ± 16.56	1090 ± 170	12.37	0.00 ± 0.00	149
A _{n-25-5}	7.98 ± 0.59	8.92 ± 0.01	883 ± 18	-71.32 ± 0.39	5748 ± 81	-39.74 ± 13.44	115 ± 2	-90.60	-12.01 ± 10.27	95
CT ₁₀₋₄₀₋₀	8.86 ± 0.91	9.91 ± 0.64	2875 ± 7	1.48 ± 0.91	7330 ± 0	-16.66 ± 17.44	95 ± 36	-91.86	-4.44 ± 0.00	95
CTA ₁₀₋₄₀₋₅	9.96 ± 0.01	9.30 ± 0.03	1135 ± 21	-75.69 ± 0.30	6603 ± 562	-54.84 ± 5.65	60 ± 27	-96.64	-42.00 ± 0.35	93

Mean ± standard deviation, values measured after 24 h; the capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; pH_i, pH_f = pH values at the beginning and the end of the treatment; sCOD and tCOD = soluble and total COD; TAN = total ammonia nitrogen; ΔsCOD, ΔtCOD, and ΔTAN = variation (in percentage) compared to raw SW; MR = mass reduction of the sample after 24 h of treatment; c1 and c2 = raw SW used as control of the tests in Runs 1 and 2, respectively; C = chemical; T = thermal; and A = aerated. The experiments were carried out in duplicate.

The highest reductions in sCOD, tCOD, and TAN, ($75.69\% \pm 0.3\%$, $54.84\% \pm 5.65\%$ and $96.64\% \pm 1.95\%$, respectively) were measured in the CTA₁₀₋₄₀₋₅ treatment. The A_{n-25-5} treatment showed similar sCOD and TAN removal efficiencies of $71.32\% \pm 0.36\%$ and $90.60\% \pm 1.27\%$, respectively, and, at the same time, a lower but noticeable tCOD reduction of $39.74\% \pm 13.44\%$. This result was in accordance to the findings of [16], who reported that a high TAN removal can be achieved at a high AFR, between 4 and 10 L_{air} L_{SW}⁻¹ min⁻¹, without any influence of the initial pH of the wastewater. According to Equation (4), the ammonium sulphate recovered by the A_{n-25-5} and CTA₁₀₋₄₀₋₅ treatments was equal to 4.67 ± 0.79 and 4.98 ± 0.87 g L_{SW}⁻¹, respectively.

Among the treatments without aeration, CT₁₀₋₄₀₋₀ showed the highest TAN removal efficiency of $91.86\% \pm 1.96\%$, followed by C₁₀₋₂₅₋₀ of $12.77\% \pm 3.95\%$. The TAN reduction in CT₁₀₋₄₀₋₀ was comparable to the other aerated treatments, thus showing that the combined effect of alkali addition and temperature was beneficial for the ammonia removal (also without air supply). However, tCOD reduction was less than 20% and sCOD removal efficiency was negligible. Unexpectedly, the C₁₀₋₂₅₋₀ treatment, carried out at the same initial pH as CT₁₀₋₄₀₋₀, but room temperature (25°C), showed a higher sCOD removal efficiency of $27.77\% \pm 1.01\%$. The other treatments, T_{n-40-0} and C₈₋₂₅₋₀, showed a slight increase in TAN content of about 4.5%, probably due to the degradation of complex molecules, and low sCOD and tCOD reductions of about 10% (Table 4 and Figure 2).

3.2. Effect of Pretreatments on Methane Yields of AD

3.2.1. Run 1 (BMP Tests at the Same TAN Concentration)

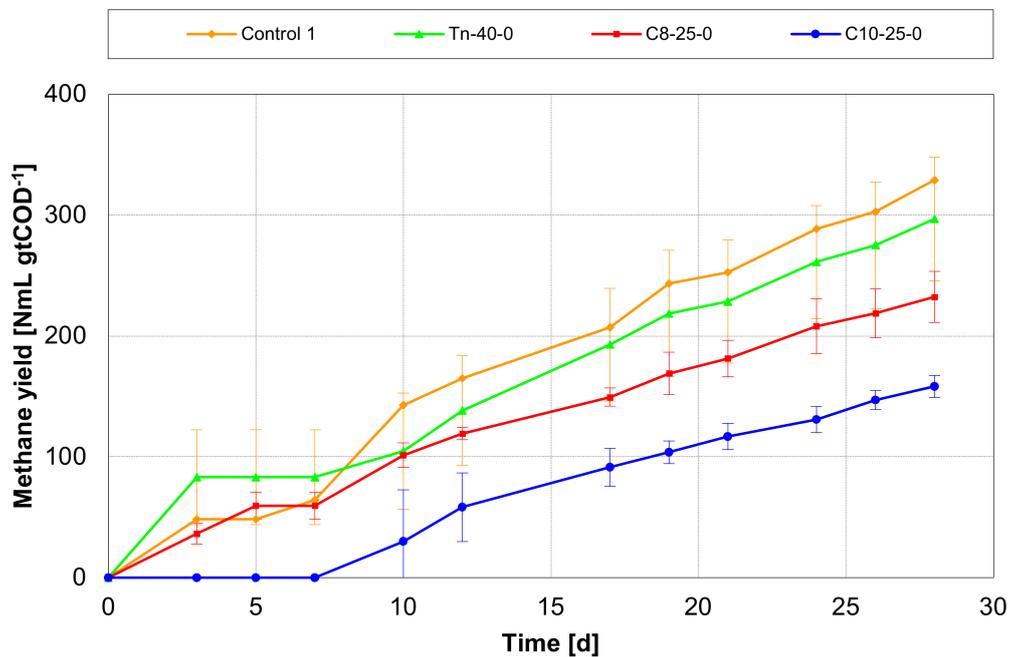
The control 1 test produced the highest methane yield of 329 ± 18 NmL g_{tCOD}⁻¹ at 70% of the biogas volume, and it showed the highest degradability of the raw SW; this yield converted a tCOD equal to 94% of the initial value (Table 4). All the other tests showed a lower methane production compared to c1, corresponding to a tCOD conversion lower than 85%. In more detail, the samples subjected to chemical treatment, C₈₋₂₅₋₀ and C₁₀₋₂₅₋₀, produced less methane, 232 ± 21 and 158 ± 9 NmL g_{tCOD}⁻¹, which comprised 67% and 75% of average methane content in biogas, respectively, compared to the T_{n-40-0} treatment without chemical adjustment, which produced 297 ± 51 NmL g_{tCOD}⁻¹/62% of methane in biogas (Figure 3a). Since all blends were prepared at the same TAN concentration, the differences in methane production can be attributed to the different SW pretreatments.

The addition of Ca(OH)₂ to adjust the pH required for the treatment may have partially inhibited the AD process. The pH increase after the addition of calcium compounds was found to be slightly inhibitory if its concentration was in the range of 2.4–4 g L⁻¹, with a 50% inhibition of methanogenic activity at about 5.0 g L⁻¹ and a strong inhibition at 8 g L⁻¹ [32,56,57]. Moreover, when calcium concentration was increased up to 3 g L⁻¹, the authors of [32] noticed a positive effect of lipid-rich SW on AD, in which the lag phase of the process decreased and the methane production increased. The authors of [30] also reported negative effects for calcium concentration over 5 g L⁻¹.

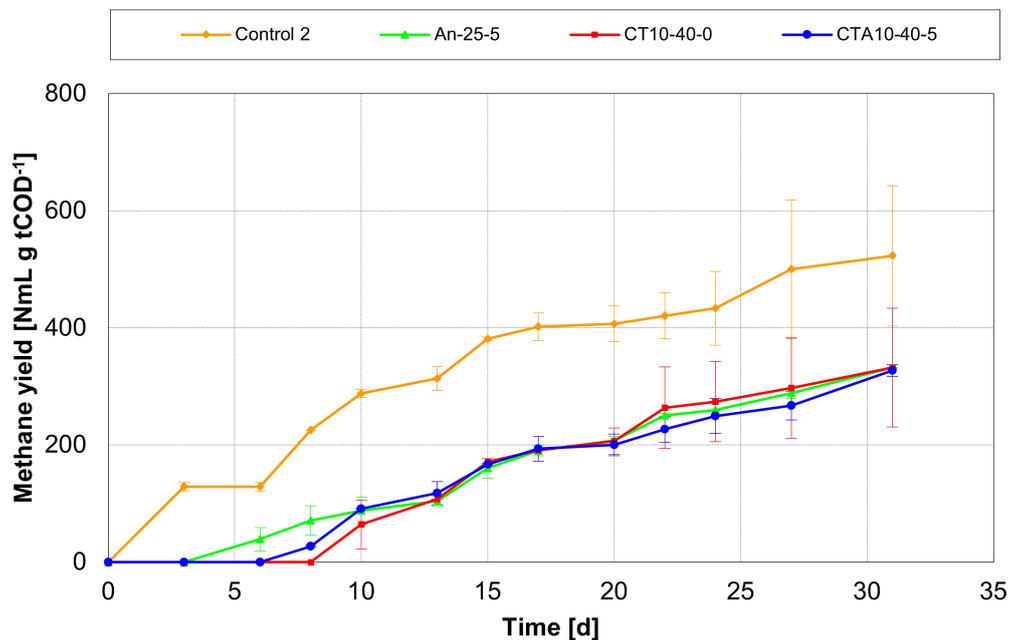
Conversely, the authors of [2] observed a slight decrease (by about 10%) of the methanogenic activity when calcium ions were added up to 7.2 g L⁻¹. The calcium concentration may have played a role in reducing the AD efficiency of the substrates subjected to C pretreatments, although it was lower—below 2 g L⁻¹—than the inhibitory limits mentioned above (Table 3). Another possibility is that alkaline pretreatment caused the generation of inhibitory compounds (e.g., furfurals), as reported in [58–61]. In fact, the alkali addition did not increase the methane production of the C₈₋₂₅₋₀ and C₁₀₋₂₅₋₀ tests, which were lower by 29.4% and 51.9%, respectively, compared to c1. The fact that there was certain proportionality between higher alkali dosage and lower methane supports the possible inhibition due to the factors mentioned above.

Moreover, the treatment T_{n-40-0}, without pH adjustment, showed the highest methane production—which was reduced by about 10% compared to the control—among the pretreated substrates. In comparison to the chemically-treated substrates, the higher methane yield of T_{n-40-0} may

have been due to the lower reduction in sCOD (Table 4), although Δ sCOD showed a high variability and the sCOD/TAN ratio was kept constant for all blends (Table 3).



(a)



(b)

Figure 3. Specific methane production recorded in (a) Run 1 and (b) Run 2 of the BMP tests performed on pretreated SW. The capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; c = control; and tCOD = total COD. The error bars represent the standard deviations. The experiments were carried out in duplicate.

Except for C₁₀₋₂₅₋₀, whose methane production was characterized by a lag-phase of about 7 d and a time needed to reach 50% of the production at the end of the test (t_{50}) of 15 d, the biogas production immediately started in all the other tests of Run 1, and t_{50} was achieved in about 12 d (Table 5 and Figure 4).

Table 5. Kinetic parameters of the Gompertz modified Equation (5).

BMP Test	t_{50}	Parameters of Gompertz Equation (5)		
	[d]	P	Λ	R_m
c1	12.0	0.390	1.2	0.014
T _{n-40-0}	12.9	0.769	0.0	0.011
C ₈₋₂₅₋₀	11.7	0.297	0.0	0.009
C ₁₀₋₂₅₋₀	15.2	0.174	7.0	0.009
c2	9.2	0.510	0.0	0.026
A _{n-25-5}	15.4	0.399	4.4	0.014
CT ₁₀₋₄₀₋₀	14.8	0.339	7.7	0.020
CTA ₁₀₋₄₀₋₅	14.7	0.330	5.8	0.016

The capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; c1 and c2 = raw SW used as control of the tests in Runs 1 and 2, respectively; BMP = biochemical methane potential; t_{50} = time needed to reach 50% of the production at the end of the test; P = methane potential [$L\ g_{tCODadded}^{-1}$]; R_m = maximum production rate of methane [$L\ g_{tCODadded}^{-1}\ d^{-1}$]; and λ = lag phase period or the minimum time required to produce biogas [d].

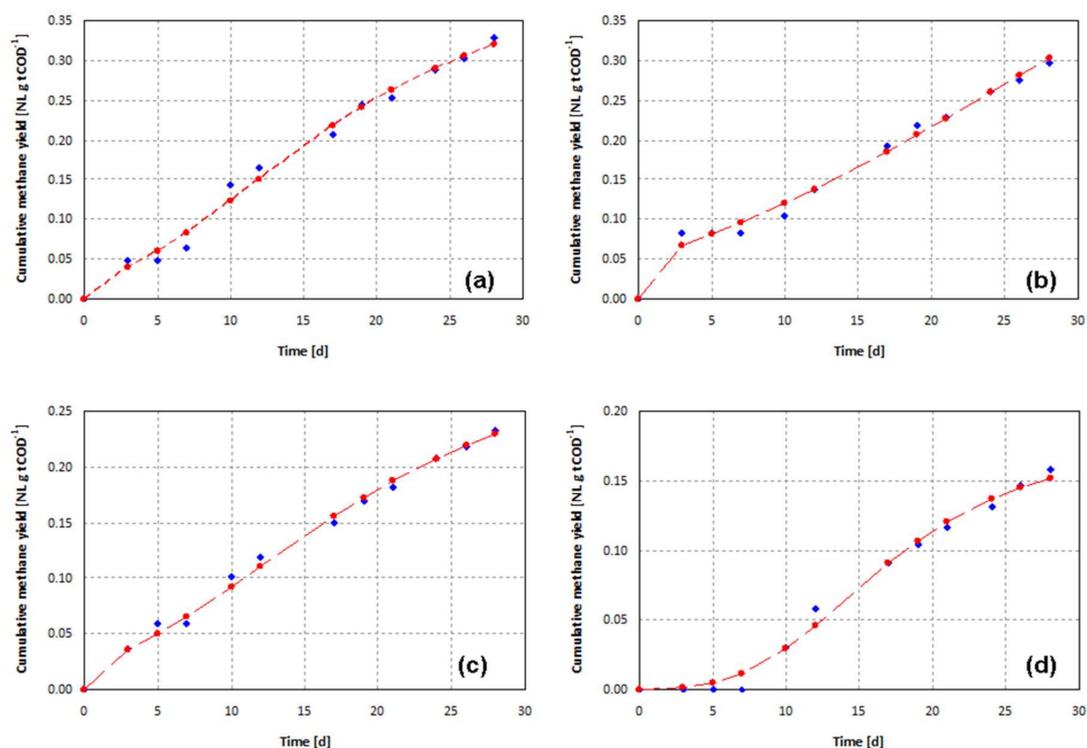


Figure 4. Measured and modeled (using the modified Gompertz Equation (5)) cumulative methane production of (a) c1, (b) T_{n-25-0}, (c) C₈₋₂₅₋₀, and (d) C₁₀₋₂₅₋₀. The capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature and air flow rate; C = chemical; T = thermal; c1 = raw SW used as control; and tCOD = total COD. The experiments were carried out in duplicate.

A very close agreement, shown by a correlation of about 99%, between the measured methane production and the corresponding values modeled using the modified Gompertz Equation (5) was found for all the BMP tests of Run 1 (Figure 4 and Table 5).

3.2.2. Run 2 (BMP Tests with Low TAN Concentration)

The cumulative methane production of c2 was $523 \pm 120 \text{ NmL g}_{\text{tCOD}}^{-1}$, which was 57% of average methane content in the biogas volume. This production was 150% of the value ($350 \text{ NmL g}_{\text{tCOD}}^{-1}$) reported in the UNI/TS 11703:2018 and corresponded to a tCOD conversion to methane of 149% (Figure 3b and Table 4), considering that 1 mol of formed CH_4 corresponded to 48 g of consumed COD, according to stoichiometry. This high production was similar to the maximum methane production obtained by the complete degradation of proteins of about 500 mL gVS^{-1} , UNI/TS 11703:2018 (corresponding to approximately $420 \text{ NmL g}_{\text{tCOD}}^{-1}$ [62]), suggesting the presence of more complex organic compounds in the raw substrate. Another possible explanation could be an anomalous methane overproduction from inoculum, presumably due to an enhanced hydrolysis in the specific batch [43,63,64].

For all the other tests, regardless of the pretreated substrate, the cumulative methane production was, on average, $330 \text{ NmL g}_{\text{tCOD}}^{-1}$ (70% of methane content in biogas) (Figure 3b), corresponding to a reduction of about 37% compared to the raw SW. The lower methane production in the A_{n-25-5} , $CT_{10-40-0}$, and $CTA_{10-40-5}$ tests, compared to c2, may be explained by a lack of nitrogen needed for microorganisms' activity, because the TAN concentration in the blends was very low (from 24 to 50 mg L^{-1}). Nutrient deficiency in Run 2 could also be observed considering the very high values of the sCOD/TAN ratios of the pretreated substrates (from 6.7 for the raw SW up to 110 for $CTA_{10-40-5}$, which was the blend with the lowest TAN concentration; see Table 3). Overall, the share of the initial tCOD converted to methane by AD and pretreatments was less than 95% of the initial value (Table 4). The methane production of SW subjected to the $CT_{10-40-0}$ and $CTA_{10-40-5}$ treatments was similar to A_{n-25-5} without chemical adjustment. However, the calcium concentration in the $CTA_{10-40-5}$ treatment was above 4 g L^{-1} , showing that the alkali addition may have different effects on the AD of SW [2], as discussed above. Moreover, since the three pretreatments showed different sCOD and tCOD reductions, the similar methane yields could not be related to the organic matter variation. It should be also noticed that the high AFR in the A_{n-25-5} and $CTA_{10-40-5}$ treatments led to noticeable aerobic degradation and organic loss of up to about 55% and 75% of tCOD and sCOD, respectively (Table 4). A long-lasting AS process would even oxidize a large amount of organic compounds, which would have reduced the methane yields of AD; thus, a longer process should be excluded. Apart from c2, whose biogas production immediately started at the beginning of the experiment, the other tests showed a lag-phase of 4–7 d (Table 5). Raw SW also produced methane faster, with a t_{50} of less than 10 d, while the other tests reached 50% of their maximum production after about 15 d (Table 5 and Figure 5). Additionally for the BMP tests of Run 2, the modified Gompertz Equation (5) showed a very good accuracy, $R^2 = 99\%$, in modeling the measured cumulative methane production (Figure 5).

3.3. Comparisons of BMP Values with Literature Experiments

All pretreated substrates showed a lower methane production compared to the respective controls, and this was somewhat expected, considering that aeration or the other physico-chemical treatments may have disturbed the growth of methanogenic bacteria; with specific reference to AS, compared to the control SW, a larger amount of organic compounds were oxidized by the air flow and could not be converted to methane. The microbiological aspects of the pretreatment effects on AD methane yield, which went beyond the main goal of this study, should be studied with a comparative analysis between aerated and control treatments. The best performance of AD was obtained by T_{n-40-0} , which showed a methane reduction of less than 10%, while the chemically-pretreated SW ($C_{10-25-0}$) showed the highest methane reduction at above 50%. In all the other pretreated substrates (C_{8-25-0} , A_{n-25-5} , $CT_{10-40-0}$, and $CTA_{10-40-5}$), the methane reduction was in the range of 30–37%.

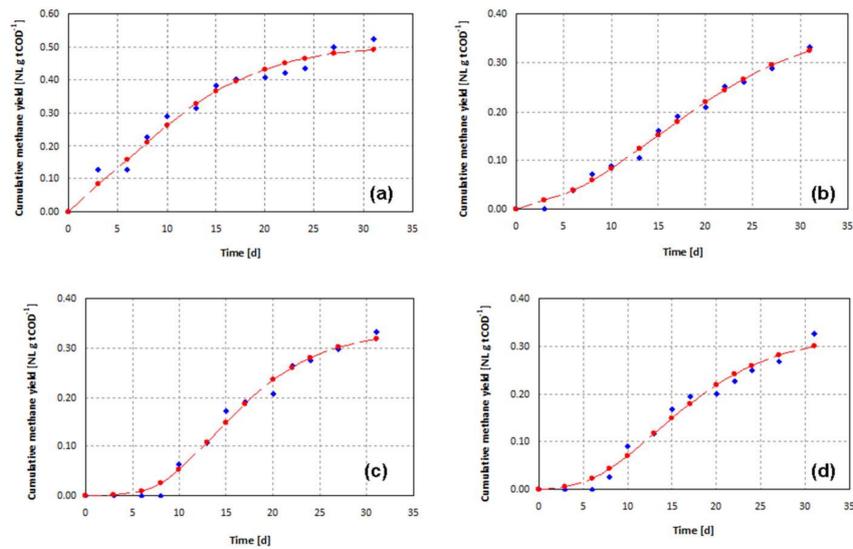


Figure 5. Measured and modeled (using the modified Gompertz Equation (5)) cumulative methane production of (a) c2, (b) A_{n-25-5} , (c) $CT_{10-40-0}$, and (d) $CTA_{10-40-0}$. The capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; C = chemical; T = thermal; A = aerated; c2 = raw SW used as control; and tCOD = total COD. The experiments were carried out in duplicate.

In the first run, where the TAN concentration was kept constant and below the limit in all blends, so any inhibitory effect due to nitrogen compounds can be excluded. Conversely, the alkali addition affected the methane production, although the calcium concentration was always under the lower limit reported in literature for possible inhibition. However, a negative effect of other by-products of the alkaline pretreatment cannot be excluded. Calcium is needed [65] for the precipitation of the long-chain fatty acids in SW as a calcium salt. However, calcium may be toxic to methanogenic bacteria (Jackson-Moss et al., 1989), thus inhibiting the AD process. The effect of calcium may be an inhibitor on the anaerobic treatment of wastewater at high concentrations over $2.5\text{--}4.0\text{ g L}^{-1}$ according to Parkin and Owen [56], although Jackson et al. [65] reported that concentration up to 7 g L^{-1} can be tolerated by anaerobic processes. However, this inhibition mechanism is still not clearly understood [32].

The most likely cause of inhibition is the presence of furfurals (not analyzed in this study because the related effects on AD were beyond its specific aim), produced by the degradation of hemicellulosic feedstock [66], which commonly used for animal feed. Moreover, their concentration may be increased by AS and/or water evaporation during T treatments since they are non-volatile compounds [36].

In the second run, no differences were detected in the methane yields of A_{n-25-5} , $CT_{10-40-0}$, and $CTA_{10-40-5}$ treatments, although in $CTA_{10-40-5}$, the calcium concentration was above the inhibitory limit. This result suggests that, in the case of lack of nutrients, the influence of the alkaline pretreatment was secondary.

In regard to the other literature experiments, a negative effect of AS on AD was reported only by the authors of [36]. Raw SW showed the highest methane production, followed by the air-stripped SW, with a methane reduction of about 47%, and the air-stripped SW with pH adjusted to 9.5 and 11.5, with a methane reductions of about 53% and 74%, respectively. These findings are similar to the results of the BMP tests in Run 1, since the methane production decreased with increasing alkali doses. However, the same authors suggested that the process inhibition could be attributed to the high free ammonia concentration and other toxic compounds, such as heavy metals concentrated by AS. Conversely, the studies of [2] and [16] demonstrated that the AS of SW is able to increase the methane yield of pretreated SW. Additionally in these experiments, an excessive addition of alkali reduced the methane production, although the pretreated substrates always showed a methane yield higher than the raw SW. Moreover, the lower and slower methane production recorded in the SW treated with the highest air flow rate, $10.0\text{ L L}^{-1}\text{ min}^{-1}$, was attributed to the aerobic degradation and organic loss due to air stripping [16] (Table 6).

Table 6. Pretreatment conditions and AD performances obtained in this study and comparison with other experiments.

Reference	Sample (Adjusted pH)	Pre-Treatment Conditions				AD Conditions						
		Alkali type	T [°C]-t [h]-Q [L L ⁻¹ min ⁻¹]	Ammonia Variation [%]	pH _i	T [°C]-Time [d]	TAN [g L ⁻¹]	NH ₄ ⁺ -N [g L ⁻¹]	NH ₃ [g L ⁻¹]	pH _f	BMP [mL gCOD _{added} ⁻¹]	Efficiency [%]
[36]	Raw SW	-	-	-	7.7		3.24 *		0.16 *	8.3	38.4	-
	AS-SW (-)	-	-	-65	8.5	35-80	2.40 *		0.68 *	8.0	20.5	-46.6 *
	AS-SW (9.5)	Ca(OH) ₂	80-4 0.05 *	-69	8.8		2.15 *	n.a.	0.89 *	7.5	10.5	-72.6 *
	AS-SW (11.5)			-98.8	9.9		1.18 *		1.06 *	7.9	17.6	-54.2 *
[2] **	Raw SW	-	-	-	8.34 ± 0.10				0.877 ± 0.068		54.0 ± 14.5	-
	AS-SW (9.5)	NaOH		-49.3 *	8.20 ± 0.09				0.290 ± 0.035		182.3 ± 15.7	238
	AS-SW (10.0)			-70.5 *	8.20 ± 0.13				0.216 ± 0.030		165.7 ± 11.1	207
	AS-SW (9.5)	KOH	37-24-1.0 *	-40.4 *	8.30 ± 0.08	37-20	n.a.	n.a.	0.347 ± 0.062		155.3 ± 20.2	188
	AS-SW (10)			-71.3 *	8.49 ± 0.15				0.419 ± 0.044		69.3 ± 13.9	28
	AS-SW (9.5)			-30.5 *	8.06 ± 0.10				0.258 ± 0.049		262.3 ± 12.0	386
	AS-SW (10)	CaO		-49.1 *	8.00 ± 0.12				0.185 ± 0.039		258.9 ± 17.3	379
	Raw SW	-	-	-				4.801			3.5 *	-
[16]	AS-SW (7.2)			-28.0				3.272			35 *	900
	AS-SW (9.0)	NaOH	37-48-1.0	-47.0	n.a.	37-20	n.a.	2.314	n.a.		90 *	2471
	AS-SW (10.0)			-80.0				0.838			182 *	5100
	AS-SW (11.0)			-88.1				0.465			142 *	3957
[16]	Raw SW	-	37-48-0.0	-				4.495			10 *	-
			37-48-1.0	-46.0				2.314			75 *	650
	AS-SW(9.0)	NaOH	37-48-2.0	-62.2	n.a.	37-20	n.a.	1.702	n.a.		97 *	870
			37-48-4.0	-77.9				0.997			155 *	1450
[16] **	Raw SW	-	37-48-10.0	-92.0				0.359			122 *	1120
	AS-SW (9.5)			-				6.30 ± 0.045			49.2 ± 16.6	-
	AS-SW (10.0)	NaOH	37-24-4.0	n.a.	8.0 ± 0.2	37-20	n.a.	2.93 ± 0.054	n.a.		170.3 ± 26.0	246
	AS-SW (11.0)							1.85 ± 0.072			132.6 ± 8.6	170
This study	c1	-	-	-2.89	7.9 ± 0.03			0.352		7.47 ± 0.01	329	-
	T _{n-40-0}	-	40-24-0	+4.39	8.03 ± 0.01			0.354		7.48 ± 0.01	297 ± 51	-9.8
	C ₈₋₂₅₋₀ (8)		25-24-0	+4.51	8.13 ± 0.02	n.a.		0.351	n.a.	7.50 ± 0.00	232 ± 21	-29.4
	C ₁₀₋₂₅₋₀ (10)	Ca(OH) ₂	25-24-0	-12.77	8.93 ± 0.01			0.353		7.80 ± 0.01	159 ± 9	-51.9
	c2	-	25-24-0	+12.37	8.02 ± 0.02			0.346		7.75 ± 0.03	523 ± 120	-
	A _{n-25-5}	-	25-24-5	-90.60	8.42 ± 0.02			0.050		7.66 ± 0.01	332 ± 1	-36.5
	CT ₁₀₋₄₀₋₀ (10)	Ca(OH) ₂	40-24-0	-91.86	8.65 ± 0.01	n.a.		0.031	n.a.	7.72 ± 0.04	332 ± 102	-36.5
	CTA ₁₀₋₄₀₋₅ (10)		40-24-5	-96.64	8.22 ± 0.02			0.024		7.66 ± 0.00	327 ± 10	-37.4

The capital letters of the tests carried out in this study indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; BMP = biochemical methane potential; AS = air stripping; T = temperature; t = time; Q = air discharge; TAN = total ammonia removal; pH_i and pH_f = pH values at the beginning and the end of the treatment, respectively; AS-SW = air-stripped SW; * = adapted data; ** = refers to semi-continuous AD process; C = chemical; T = thermal; A = aerated; c1, and c2 = raw SW used as control of the tests in Runs 1 and 2, respectively; and n.a. = not available.

4. Conclusions

This study evaluated the feasibility of AS as a pretreatment for the AD of SW; moreover, the efficiency of the aeration process was compared with other C and T without air supply. The A treatments—specifically A_{n-25-5} and $CTA_{10-40-5}$ —showed the highest sCOD, tCOD, and TAN removal rates. The $CT_{10-40-0}$ treatment without air supply was as efficient in TAN removal as the A treatments due to the combined effects of the increased pH and temperature. However, this treatment did not allow for the recovery of ammonia sulphate, which was different from AS.

The SW pretreatments were not able to increase the biogas production of AD, as shown by the higher methane yields of the untreated SW. The AD processes well-tolerated TAN concentration over 0.35 g L^{-1} without inhibition effects due to nitrogen compounds. However, other SW characteristics and process operational parameters may explain these unexpected results: (i) the large variability of the physico-chemical characteristics of raw SW, which could not be easily controlled by setting the process conditions; (ii) the lack of positive effects of calcium addition as a pH adjuster of chemically pretreated SW; (iii) the lack of nutrients induced by the treatments, which reduced the methane yields of the pretreated SW; (iv) the noticeable reduction in tCOD and sCOD due to the A treatments, which limited the available organic matter for the anaerobic microorganisms; (v) other inhibitory processes during the AD of the pretreated SW, such as the accumulation of toxic compounds, such as furfurals; and (vi) the increase in the concentration of these inhibitory compounds due to the mass reduction for water evaporation during the pretreatments.

From this study, it can be seen AS is a viable process for the recovery of ammonium sulphate and the removal of other polluting compounds (e.g., organic matter) from SW; thus, AS is an alternative solution to intensive treatments that are often difficult and expensive. Conversely, the use of AS as well as other C and/or T processes suggested as pretreatments of SW before AD needs more research in order to identify the possible reasons for their reduced methane yields. An optimized integration of AS and AD could comprise the appropriate selection of pretreatment conditions as a function of the TAN concentration of the raw SW. Process duration and the alkali dose should be optimized in order to ensure a significant recovery, not only of the stripped ammonia but also of energy, by adjusting the concentration of nitrogen in the pretreated SW for microorganisms' growth and to reduce inhibitory compound presence. Replacing air with other gaseous streams in AS in order to avoid the aerobic removal of biodegradable COD, would be theoretically beneficial to increase the biomethane potential but is feasible only if N_2 is available as a by-product of other processes. In fact, CO_2 -rich gaseous streams (e.g., flue gas) cannot be an alternative since they would reduce the pH of SW and thus the ammonia stripping efficiency.

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