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ABSTRACT

The organic matter and nitrogen contents of swine wastewater (SW) can be reduced and, at the same time, a fertiliser as ammonium salt can be recovered by wastewater treatments. One of the most promising technique is air stripping (AS). However, the operational parameters (pH, temperature and air flow rate) of AS must be optimised, in order to maximise the ammonia recovery and reduce the requirement of chemicals and energy.

In this study 27 batch tests at laboratory scale were carried out on real SW, varying (individually or simultaneously) the pH (not adjusted, 8 and 10), temperature (ambient, 40 and 60 °C) and flow rate (0, 1 and 5 L_{air} L_{SW}^{-1} min^{-1}) of AS; the changes in soluble COD (sCOD) and total ammonia nitrogen (TAN) concentrations were evaluated in response to the parameters adjustments. For the tests including AS, the ammonium sulphate recovered was also measured.

In general (about 50% of the tests), more than 80% of TAN was removed. Most of these tests were carried out with pH and temperature control and AS at the highest flow rate; the highest efficiency was found for a combination of chemical, thermal and aeration treatments. For a few tests with the same process control, an increase (up to 50%) or a very limited (less than 10%) decrease of sCOD were detected; therefore, these treatments can be adopted prior of anaerobic digestion of SW. A high flow rate, which increases the removal efficiency of both sCOD and TAN, should be adopted, when AS is used as pre-treatment of activated sludge or lagooning plants. Very high amounts (over 80% of the theoretical yield) of ammonium sulphate were recovered by AS at the maximum air flow rate (5 L_{air} L_{SW}^{-1} min^{-1}), which would provide a nitrogen fertiliser at a sustainable cost.

KEYWORDS: air stripping; ammonium sulphate; anaerobic digestion; lagooning; pre-treatment; swine wastewater.

1. INTRODUCTION

Swine wastewater (SW) is composed of a mixture of urine, feces, water spillage, residues of undigested food, antibiotic residues and pathogenic microrganisms (Viancelli et al., 2013). The direct disposal of SW can release into the environment high amounts of nutrients (mainly nitrogen), salts and organic pollutants (Motteran et al., 2013) and thus severe environmental pollution is possible.

To face the environmental and economic constraints of SW management, several systems have been proposed (e.g. electrocoagulation (Mores et al., 2016), multi-stage treatment systems (Motteran et al., 2013), aerobic biological treatment (Kim et al., 2004), struvite precipitation (D. Zhang et al., 2012), lagooning (e.g. Loughrin et al., 2012; Trias et al., 2004), anaerobic lagooning (Zema et al., 2016)), buttheir efficiency and sustainability are still questionable, mainly due to the high costs (Yang et al., 2016), the complexity and, in some cases, the high instability and duration of the treatments. Anaerobic digestion (AD) is a promising management system for SW, since this system, beside wastewater depuration, allows energy recovery as bio-methane (Zema et al., 2019, 2018) . However, the methane production in the anaerobic digestion of SW is limited by the high ammonia content (often over 4.0 g L^{-1}) that inhibits the activity of methanogenic bacteria (Hansen et al., 1998; Zhang et al., 2012).

Moreover, the high nitrogen concentration (mainly organic and ammonium) of SW nitrogen is an issue for all the proposed treatments. However, the high presence of ammonium in SW pushes for recovery, since it is a natural source of nitrogen. The latter is an essential fertiliser for plants and crops , but it is often expensive to produce. In addition, the nitrogen recovery from SW reduces at the same time the ammonia toxicity in the anaerobic process (thus increasing the methane yield) and the cost of aerobic treatments (due to lower aeration requirements).

Ammonia is commonly removed from wastewater of animal origin by air stripping (AS). AS generally consists of the aeration of wastewater, which is generally previously mixed with alkali (since ammonia stripping is easier at pH over 8.5). Ammonia is then recovered as ammonium sulphate (which can be directly used as a fertilizer); after the AS, pH of wastewater is adjusted at its optimal value before the anaerobic digestion. The removal efficiency of AS mainly depends on four parameters: (i) pH; (ii) temperature; (iii) air flow rate per unit volume of wastewater; and (iv)

characteristics of the raw wastewater (Bonmatı and Flotats, 2003; Lei et al., 2007; Zhang and Jahng, 2010).

The influence of some of these parameters on ammonia removal efficiency has been widely studied. From the literature, the highest rates of ammonia removal have been achieved at high temperatures and/or alkali doses (Bonmatı and Flotats, 2003; Lei et al., 2007), which, however, make the treatment expensive, also considering the high reaction time (up to 48 hours, Zhang et al., 2012). Moreover, the characteristics of the treated slurry influence the efficiency of the subsequent AD, since an excessive removal of ammonia often reduces methane yield (Zhang and Jahng, 2010), due to the unbalanced C/N ratio. These difficulties can be overcome by optimizing the recovery process, properly adjusting the pH by chemical additives, the temperature by heating SW and the AS by increasing the flow rates.

This study aims at optimising the SW treatments, whose performance is compared under variable operational conditions. More specifically, the removal efficiency of soluble Chimical Oxygen Demand (sCOD) and Total Ammonia Nitrogen (TAN) from SW have been evaluated in batch tests by varying the pH, temperature and flow rate of AS. Since the ammonium salt recovery process can be applied as pre-treatment before the AD or the aerobic treatments (activated sludge or lagooning), the process conditions allowing either simultaneous TAN stripping and sCOD preservation (optimal for the AD), or maximum TAN stripping coupled with sCOD removal (which is beneficial for the aerobic treatments) have been identified. Moreover, the production of ammonium salts has been quantified.

2. MATERIALS AND METHODS

2.1. Wastewater characterization

Samples of wastewater were collected in several operations from the pond of a swine breeding farm located in Calabria (Southern Italy) and stored at 4 °C until use for a maximum of 2 weeks. The main average chemical-physical properties of SW samples (Table 1) were measured in duplicate using standard methods on each collected sample (APHA, 2012).

Soluble Chimical Oxygen Demand (sCOD) and Total Ammonia Nitrogen (TAN) were evaluated in the liquid phase of the sample after centrifugation at 10000 rpm for 20 minutes. TAN was evaluated by the Kjeldhal method (Total Kjeldhal Nitrogen, TKN, the sum of organic nitrogen, un-ionised ammonia and ammonium ion). It had been hypothesized that TAN in liquid phase was equal to

TKN, since the ammonia nitrogen is highly soluble for almost neutral pH (Bonmatı and Flotats, 2003), while organic nitrogen was mainly contained in the solid residue removed by centrifugation.

Table 1 – Average physico-chemical parameters of SW subjected to the batch tests.

Parameter	Value (mean ± std. dev.)
pH [-]	7.35 ± 0.19
TS [%]	1.89 ± 1.65
TVS [% TS]	57.49 ± 9.18
tCOD [mg L^{-1}]	27131 ± 15224
sCOD [mg L^{-1}]	5246 ± 1623
TAN [mg L^{-1}]	1308 ± 142

Notes: TS = Total Solids; TVS = Total Volatile Solids; tCOD, sCOD = total and soluble Chemical Oxygen Demand; TAN = Total Ammonia Nitrogen.

2.2. Ammonia stripping tests

Each treatment (individual or in combination with others) of SW was carried out for 24 hours in batches of 1-litre volume. The combination of pH (natural, 8 or 10) temperature (ambient, 40 or 60 °C) and air flow rate (no aeration, 1 or 5 L_{air} L_{SW}^{-1} min^{-1}) produced a total of 3 x 3 x 3 = 27 treatments (Table 2). The treatment with natural pH, ambient temperature and without aeration was assumed as control.

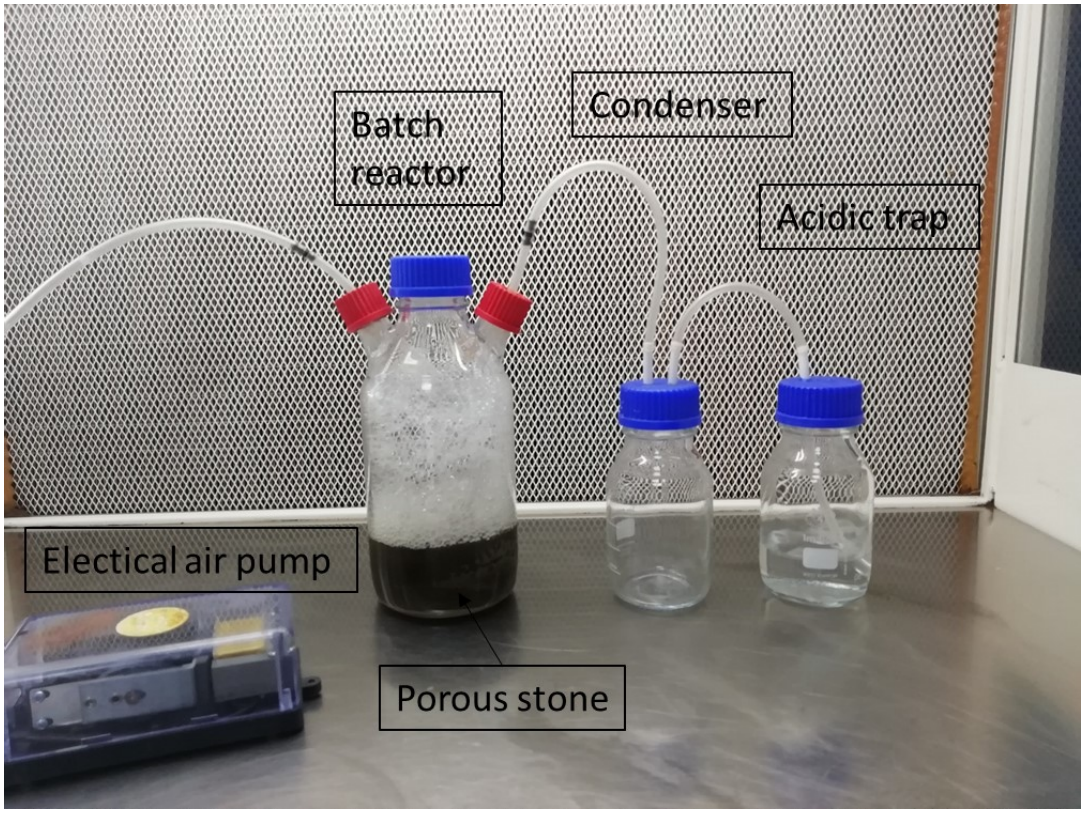
Table 2 - Experimental design of the tests and related operational parameters.

Test	Treatment	pH	Temperature	Air flow rate

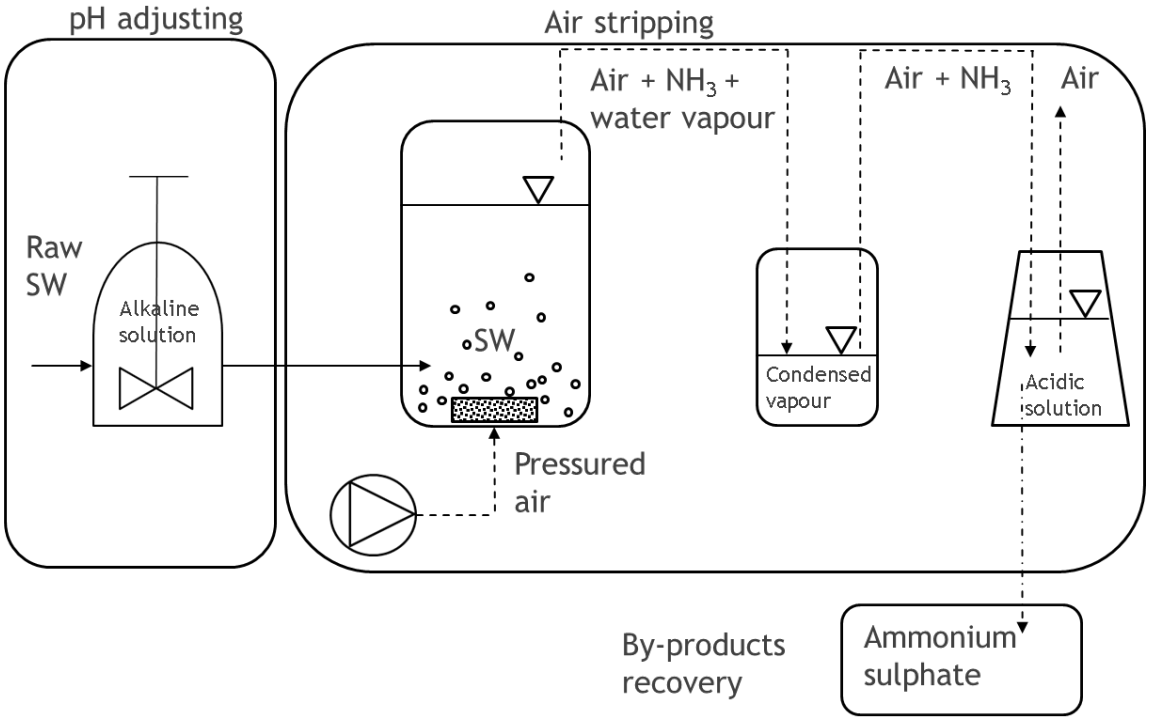
		[-]	[°C]	[L_{air} L_{SW}^{-1} min^{-1}]
Control	Control	Natural	Ambient	0
T_{n-40-0}	Thermal	Natural	40	0
T_{n-60-0}			60	
C_{8-25-0}	Chemical	8	Ambient	0
$C_{10-25-0}$		10		
A_{n-25-1}	Aerated	Natural	Ambient	1
A_{n-25-5}				5
CT_{8-40-0}	Chemical-Thermal	8	40	0
CT_{8-60-0}			60	
$CT_{10-40-0}$		10	40	
$CT_{10-60-0}$			60	
TA_{n-40-1}	Thermal-aerated	Natural	40	1
TA_{n-40-5}				5
TA_{n-60-1}			60	1
TA_{n-60-5}				5
CA_{8-25-1}	Chemical-aerated	8	Room	1
CA_{8-25-5}				5
$CA_{10-25-1}$		10		1
$CA_{10-25-5}$				5
CTA_{8-40-1}	Chemical-thermal-aerated	8	40	1
CTA_{8-40-5}				5
$CTA_{10-40-1}$		10		1
$CTA_{10-40-5}$				5
CTA_{8-60-1}		8	60	1
CTA_{8-60-5}				5
$CTA_{10-60-1}$		10		1
$CTA_{10-60-5}$				5

In more detail, the experiments included individual thermal (hereinafter indicated by the symbol T), chemical (C) and aerated (A) treatments as well as all the possible combinations: chemical-thermal (CT); thermal-aerated (TA); chemical-aerated (CA); and chemical-thermal-aerated (CTA) treatments (Table 2), hereinafter indicated as “combined treatments”.

In the C tests, a solution of $Ca(OH)_2$ (30% w/v) was used to adjust the pH at 8 and 10. The doses were 16 ± 9 $mL_{c_{a(OH)2sol}} L_{SW}^{-1}$ 40 ± 8 $mL_{c_{a(OH)2sol}} L_{SW}^{-1}$, respectively. The T tests were carried out by heating the batches in a thermostatic chamber. The A tests consisted of a batch with three units (Figure 1). In the first unit, SW was aerated by an electrical pump connected to a porous stone and submerged in SW. The porous stone was used to homogenise the air flow in the wastewater. Moreover, the electrical air pump was provided with a flowmeter to manually vary the required air flow. The vapour stripped by the air flow was collected in a second unit (condenser), while the gaseous ammonia flowed into a third unit (trap), containing an acidic solution (0.1 M H_2SO_4), where the ammonia nitrogen was recovered as salt. At the end of the treatment, the production of ammonium salts was quantified. When the A treatment was combined with the T treatment, the batches were placed in the thermostatic chamber, while the condenser and the acidic trap were kept at room temperature.



(a)



(b)

Figure 1 – Photo of the equipment (a) and scheme of the experimental design (b) for the AS treatments.

Each test was carried out in duplicate. The main physico-chemical parameters of the SW were measured (in duplicate) at the start and at the end (after 24 hours) of the test. The removal efficiencies for total COD (tCOD), sCOD and TAN were respectively evaluated by a mass balance between the initial (before pH adjustment, when applied) and final contents, in order to take into account the mass reduction (MR) of the liquid sample that mainly occurs in T and/or A treatments. Hereinafter, each test will be indicated by one to three capital letters followed by three letters/numbers identifying the value of the operational parameter. For example, $TA_{n\text{-}40\text{-}1}$ is a thermal-aerated (T+A) test with no pH adjustment (n), temperature of 40 °C (40) and air flow rate of 1 $L_{air}\ L_{SW}^{-1}\ min^{-1}$ (1).

2.3. Production of ammonium salts

From the TAN concentration (known at the start and at the end of the tests) the theoretical recoverable ammonium sulphate (RAS) was evaluated. The theoretical amount of ammonium sulphate produced was calculated using the following stoichiometric equation:

$$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad (1)$$

It was hypothesized that the ammonium ions in the SW sample were totally converted to ammonia gas.

At the end of each test including AS, the acidic solution containing the precipitated ammonium salts was dried in oven at a temperature of 40 °C until weight stabilization, in order to obtain the salt crystals. In order to evaluate whether the chemical treatment has affected the crystalline structure and the composition of the salts, two samples of crystals were analysed using a scanning electron microscope (SEM). The two samples were selected among the samples produced in the tests ($TA_{n\text{-}60\text{-}5}$ and $CTA_{10\text{-}60\text{-}5}$). These tests yielded a TAN removal efficiency higher than 90% and were carried out at the same temperature (60 °C) and air flow rate (5 L_{air} L_{SW}^{-1} min^{-1}), but SW in the first test was subject to the chemical treatment and in the second test pH of SW was not controlled.

2.4. Statistical analysis

First, the statistical significance of changes in the operational parameters before and after each treatment was investigated using t-test (at $p < 0.05$). Then, three-way ANOVA were separately applied to the sCOD and TAN removal as well as to RAS (assumed as response variables), using pH, temperature and air flow rate as factors (explanatory variables); the interactions among these factors were considered. In order to satisfy the assumptions of the statistical tests (equality of variance and normal distribution), the data were subjected to normality test or were transformed whenever necessary. Statistical analysis of samples was carried out by the XLSTAT (release 2019) software.

3. RESULTS

3.1. Effects of the treatments on SW characteristics

Due to the intrinsic variability of SW that, as previously mentioned, was collected in several sampling times, the characteristics of the wastewater used in the test were not equal. For this reason, rather than showing the actual concentrations, the removal efficiency of sCOD and TAN (i.e. the difference on mass balance between the initial and final values divided by the initial value) were calculated and reported. The TS and TVS variations were both on the average close to 7%. Much of the initial concentration of organic matter was contained in the settling solids, the sCOD being on average about 30% of the tCOD. A mean MR of about 10% and a maximum value of 46% were observed in the treatments. As expected, for the samples with the same pH value, MR increased in

212 the treatments with the highest temperature and air flow rate, due to a more effective evaporation
213 (Table 3).
214 At the end of the treatments (t = 24h), pH increased, respect to the value at the beginning of the test
215 in all treatments with no adjustment or pH adjusted to 8, and decreased in the treatments with the
216 pH adjusted to 10. The variation of pH was relatively high - but not statistically significant - in T
217 and/or A treatments under extreme conditions (60 °C and 5 L_{air} L_{SW}^{-1} min^{-1}) (Table 3).
218
219
220 Table 3 – Differences in physico-chemical parameters of the SW (mean ± std. dev. in %) before and
221 after the batch tests.
222

Test	TS	TVS	pH	MR
Control	-10.44 ± 15.42	0.76 ± 5.35	0.47 ± 0.10	0.67 ± 0.05
$T_{n\text{-}40\text{-}0}$	-0.36 ± 0.40	6.68 ± 1.58	7.09 ± 0.48	2.14 ± 0.10
$T_{n\text{-}60\text{-}0}$	8.22 ± 5.09	-6.25 ± 3.78	11.62 ± 0.38	11.43 ± 0.01
$C_{8\text{-}25\text{-}0}$	-12.07 ± 11.06	-2.05 ± 6.28	0.12 ± 0.18	0.81 ± 0.05
$C_{10\text{-}25\text{-}0}$	-5.39 ± 0.76	-11.00 ± 26.55	-6.21 ± 0.79	0.43 ± 0.61
$A_{n\text{-}25\text{-}1}$	-9.07 ± 3.59	0.66 ± 0.49	25.96 ± 3.00	2.47 ± 0.47
$A_{n\text{-}25\text{-}5}$	-4.71 ± 3.21	-6.60 ± 0.97	21.08 ± 3.54	8.61 ± 6.80
$CT_{8\text{-}40\text{-}0}$	-7.04 ± 9.93	-13.08 ± 0.90	1.37 ± 0.00	2.09 ± 0.16
$CT_{8\text{-}60\text{-}0}$	-14.82 ± 0.73	-20.40 ± 2.32	0.50 ± 0.18	5.85 ± 0.28
$CT_{10\text{-}40\text{-}0}$	9.01 ± 3.99	3.80 ± 4.78	-10.43 ± 0.19	1.51 ± 0.24
$CT_{10\text{-}60\text{-}0}$	18.29 ± 5.17	-12.71 ± 25.20	-20.60 ± 0.16	12.27 ± 0.78
$TA_{n\text{-}40\text{-}1}$	-2.68 ± 3.30	-0.46 ± 1.64	20.79 ± 3.63	4.47 ± 4.06
$TA_{n\text{-}40\text{-}5}$	10.59 ± 8.32	-13.82 ± 0.20	19.90 ± 3.78	15.22 ± 1.06
$TA_{n\text{-}60\text{-}1}$	-0.54 ± 6.30	-4.45 ± 1.28	25.46 ± 6.01	5.37 ± 0.15
$TA_{n\text{-}60\text{-}5}$	142.43 ± 26.34	-7.65 ± 5.40	24.88 ± 1.61	46.42 ± 13.90
$CA_{8\text{-}25\text{-}1}$	-11.64 ± 1.49	3.39 ± 0.61	6.17 ± 0.68	2.29 ± 0.99
$CA_{8\text{-}25\text{-}5}$	-3.92 ± 3.15	-6.61 ± 5.80	8.25 ± 5.80	6.07 ± 2.94
$CA_{10\text{-}25\text{-}1}$	-5.61 ± 3.82	-3.42 ± 18.92	-9.04 ± 1.15	1.52 ± 0.28
$CA_{10\text{-}25\text{-}5}$	-10.02 ± 5.90	-10.92 ± 8.47	-14.79 ± 8.85	8.58 ± 5.07
$CTA_{8\text{-}40\text{-}1}$	-1.24 ± 10.63	-0.17 ± 6.69	11.67 ± 0.15	3.64 ± 2.43
$CTA_{8\text{-}40\text{-}5}$	19.89 ± 26.55	-4.57 ± 2.56	8.78 ± 2.42	21.46 ± 2.61
$CTA_{10\text{-}40\text{-}1}$	-12.21 ± 6.33	-12.73 ± 7.11	-8.11 ± 2.14	4.25 ± 1.31
$CTA_{10\text{-}40\text{-}5}$	7.85 ± 13.34	-10.41 ± 5.53	-23.20 0.65	19.60 ± 2.33
$CTA_{8\text{-}60\text{-}1}$	22.53 ± 31.06	-10.49 ± 6.73	13.61 ± 1.83	15.88 ± 1.62
$CTA_{8\text{-}60\text{-}5}$	35.16 ± 60.14	-14.91 ± 3.20	10.68 ± 6.42	33.06 ± 14.87
$CTA_{10\text{-}60\text{-}1}$	28.80 ± 27.84	-9.25 ± 2.14	-16.25 ± 3.49	7.90 ± 1.46
$CTA_{10\text{-}60\text{-}5}$	7.09 ± 38.15	-13.64 ± 5.69	-13.41 ± 8.71	25.42 ± 11.75
Mean	7.34 ± 12.30	6.68 ± 5.93	3.57 ± 2.46	9.98 ± 2.83

223 Notes: TS = Total Solids; TVS = Total Volatile Solids; MR = Mass reduction after 24 hours.
224

The addition of the alkaline solution also affected the variations in sCOD of the SW immediately after pH conditioning. After the addition of chemicals, in the treatment $CTA_{10\text{-}60\text{-}5}$ the mean sCOD variation, which shows a high standard deviation, almost doubled compared to raw SW. In general, a pH value adjusted to 8 led on the average to a higher sCOD, presumably due to chemical hydrolysis. At pH set to 10, this effect was lower, presumably due to flocculation and subsequent removal by centrifugation (Figure 2).

TAN reduction was on the average about 3% of its initial content, except for the tests $CTA_{10\text{-}40\text{-}5}$ and $CTA_{10\text{-}60\text{-}1}$, which showed a concentration lower by 60% and 32%, compared to the raw SW, immediately after alkali addition (Figure 2).

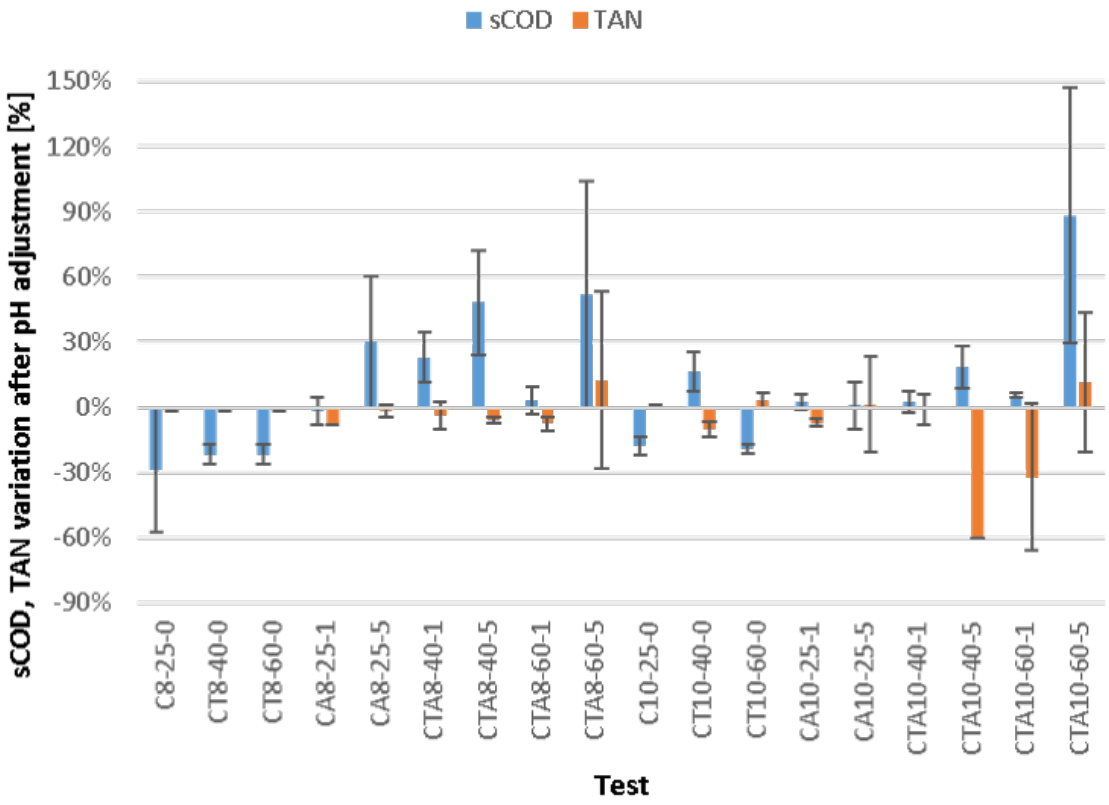


Figure 2 - Effect of pH adjustment on the variations of sCOD and TAN concentrations in SW immediately after alkali addition (T = 0 hours).

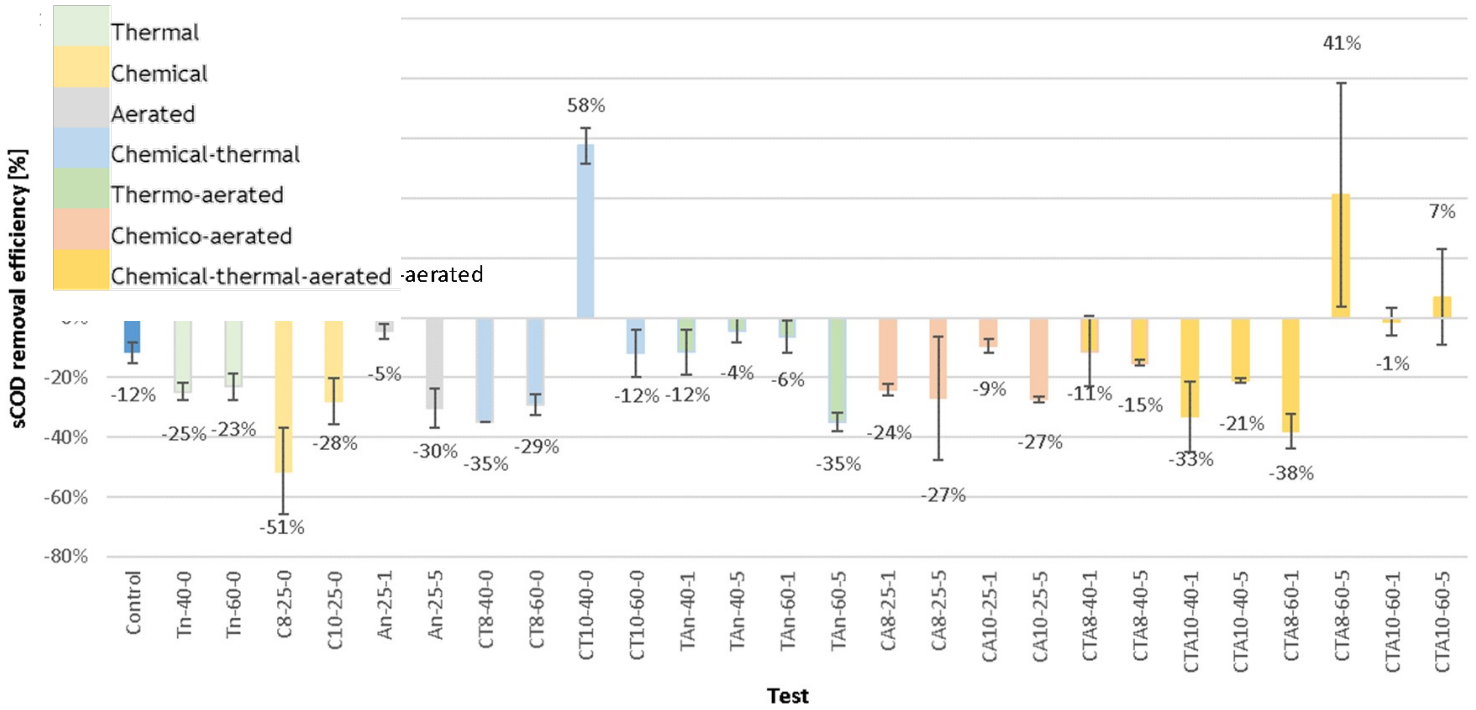
3.1.1. Effects of the treatments on the sCOD removal

The control test showed an average sCOD reduction of 12%. Almost all treatments reduced the sCOD, with the exception of the $CTA_{10\text{-}60\text{-}5}$, $CTA_{8\text{-}60\text{-}5}$ and $CT_{10\text{-}40\text{-}0}$, which showed on average a sCOD increase of 6.8 ± 16.0%, 41.2 ± 37.4% and 57.6 ± 5.9%, respectively. In the tests $CTA_{10\text{-}60\text{-}5}$ and $CTA_{8\text{-}60\text{-}5}$ a high standard deviation was noticed, indicating a certain process instability (Figure 3a).

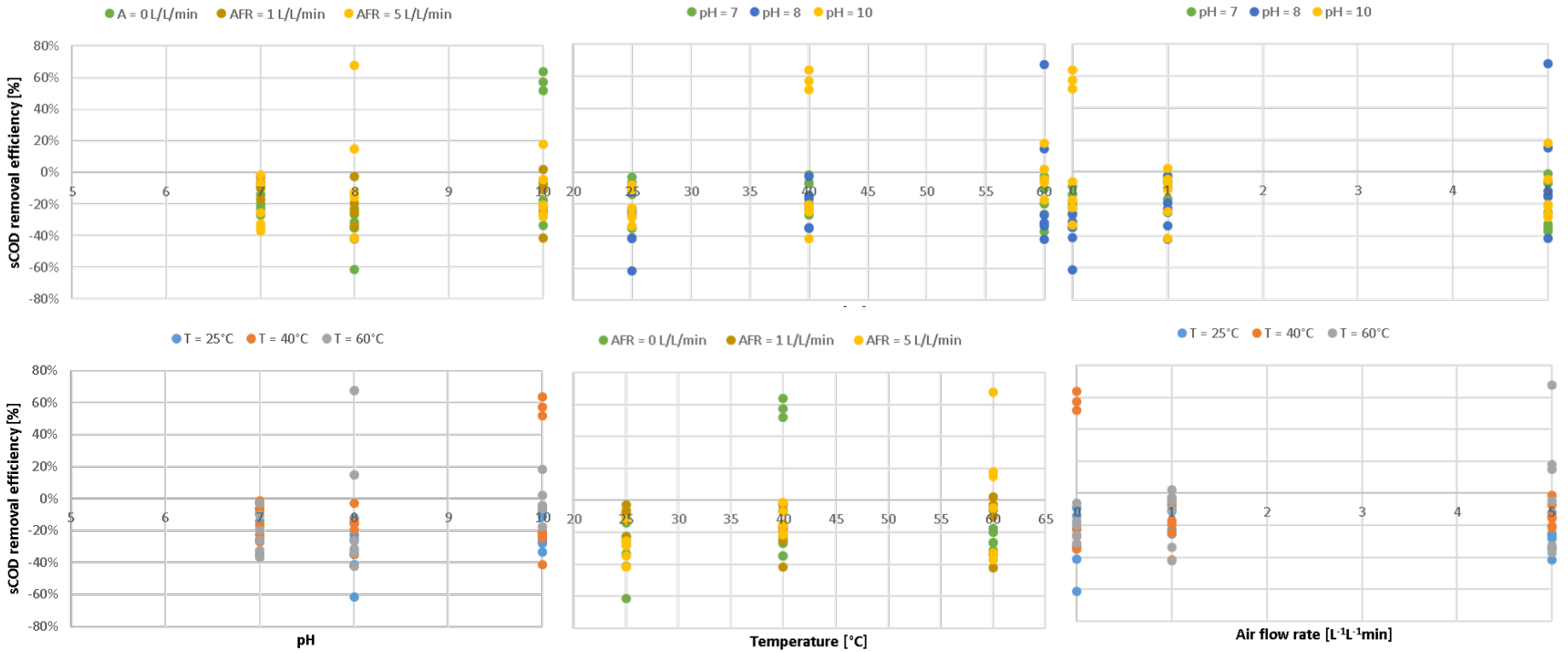
As a general tendency, lower pH and higher temperature seem to enhance sCOD removal efficiency. Instead, the influence of the aeration is much lower, although a slightly higher removal for lower aeration rates is evident (Figures 3b, 3c and 3d).

Among the individual treatments (C, T and A), the C tests have showed the highest reduction of sCOD (from -28% of $C_{10\text{-}25\text{-}0}$ to -51% of $C_{8\text{-}25\text{-}0}$). For the treatments $CTA_{10\text{-}40\text{-}1}$ and $CTA_{8\text{-}60\text{-}1}$ the highest sCOD removal efficiencies (-33.1 ± 11.8% and -37.9 ± 5.9% of sCOD removed, respectively) were found, while only the treatments $CT_{8\text{-}40\text{-}0}$ and $TA_{n\text{-}60\text{-}5}$ removed over 30% of sCOD; the minimum reduction (-1.3 ± 4.7%) was observed in the treatment $CTA_{10\text{-}60\text{-}1}$. Overall, the treatments $C_{8\text{-}25\text{-}0}$, $CT_{8\text{-}40\text{-}0}$, $CT_{8\text{-}60\text{-}0}$, $TA_{n\text{-}60\text{-}5}$, $CTA_{10\text{-}40\text{-}1}$ and $CTA_{8\text{-}60\text{-}1}$ showed sCOD removal efficiency over 30% (Figure 3a).

According to the 3-way ANOVA, nor the operational parameters neither their interactions had a statistically significant (at $p < 0.05$) influence the sCOD removal efficiency. However, it should be precised that the statistical model explains only 19% of the variance of the factors.


Thermal
Chemical
Aerated
Chemical-thermal
Thermo-aerated
Chemico-aerated
Chemical-thermal-aerated
sCOD removal efficiency [%]
-20%
-40%
-60%
-80%
-12%
-25%
-23%
-51%
-28%
-5%
-30%
-35%
-29%
58%
-12%
-12%
-4%
-6%
-35%
-24%
-27%
-9%
-27%
-11%
-15%
-33%
-21%
-38%
41%
-1%
7%
Control
Tn-40-0
Tn-60-0
C8-25-0
C10-25-0
An-25-1
An-25-5
CT8-40-0
CT8-60-0
CT10-40-0
CT10-60-0
TAn-40-1
TAn-40-5
TAn-60-1
TAn-60-5
CA8-25-1
CA8-25-5
CA10-25-1
CA10-25-5
CTA8-40-1
CTA8-40-5
CTA10-40-1
CTA10-40-5
CTA8-60-1
CTA8-60-5
CTA10-60-1
CTA10-60-5
Test

(a)



(b) (c) (d)

Figure 3 – Variations of sCOD removal efficiency throughout the tests (a, all treatments), (b, treatments with the same pH), (c, treatments with the same temperature), (d, treatments with the same air flow rate).

3.1.2. Effects of the treatments on TAN removal

The TAN removal efficiency in the control test was 5.4 ± 4.4%. In general, TAN stripping was enhanced mainly by higher air flow rates, but also by increases in pH and temperature (Figure 4a, 4b and 4c).

Among the individual tests, the treatments $A_{n\text{-}25\text{-}1}$ and $A_{n\text{-}25\text{-}5}$ were more efficient (TAN removal efficiency of 36.1 ± 5.7% and 79.7 ± 16.8%, respectively) compared to $T_{n\text{-}40\text{-}0}$ (2.1 ± 1.6%), $T_{n\text{-}60\text{-}0}$ (22.8 ± 4.3%), $C_{8\text{-}25\text{-}0}$ and $C_{10\text{-}25\text{-}0}$ (7.1 ± 0.3 %). The treatment $T_{n\text{-}40\text{-}0}$ showed instead a slight increase (2.1 ± 1.6%) of TAN concentration (Figure 4a).

$CT_{10\text{-}60\text{-}0}$ was the most efficient among the CT treatments, yielding a TAN removal efficiency of 97.4 ± 2.0%. Among the TA treatments, $TA_{n\text{-}40\text{-}5}$ and $TA_{n\text{-}60\text{-}5}$ showed the highest removal efficiencies (98.8 ± 1.7% and 95.9 ± 5.7%, respectively). High performances were deteced also for the CA treatments, which gave TAN removal efficiencies over 57%, with a maximum value of 85.6 ± 9.1% ($CA_{10\text{-}25\text{-}5}$). Overall, the CTA treatments resulted to be the most efficient, since the TAN removal efficiency was always over 90%, except for $CTA_{8\text{-}40\text{-}1}$ and $CTA_{10\text{-}40\text{-}1}$ that showed lower performances (50.5 ± 25.8% and 79.3 ± 3.3%, respectively) (Figure 4a).

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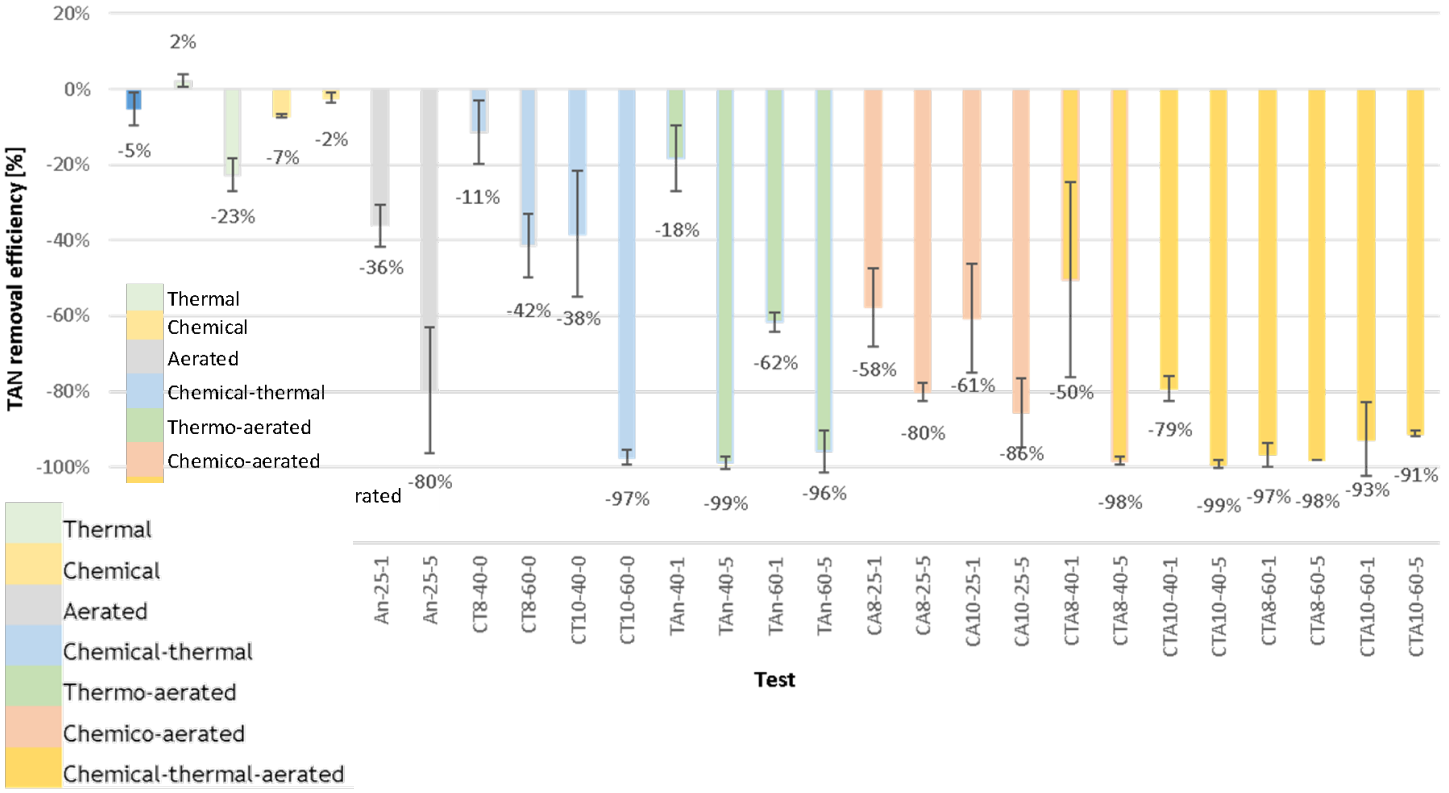
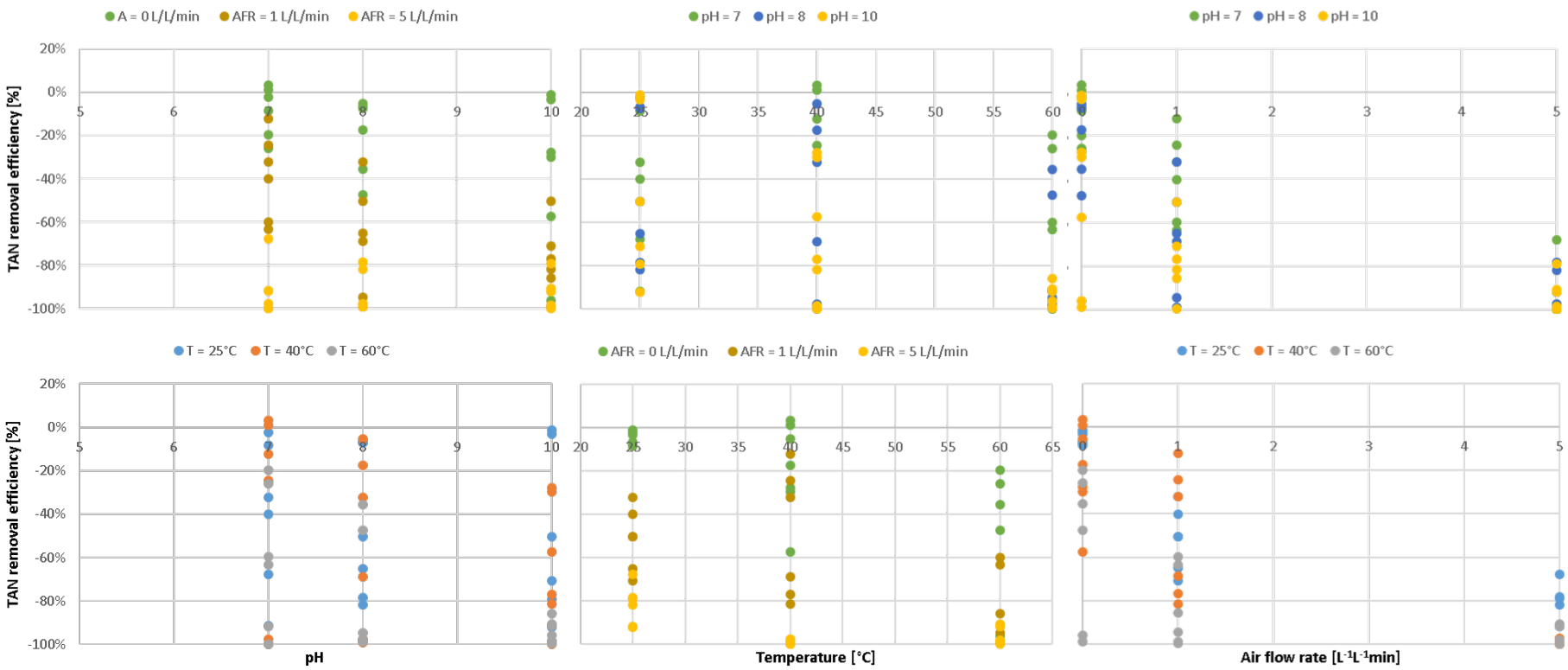

20%
0%
-20%
-40%
-60%
-80%
-100%
TAN removal efficiency [%]
2%
-5%
-23%
-7%
-2%
-36%
-80%
-11%
-42%
-38%
-97%
-18%
-99%
-62%
-96%
-58%
-80%
-61%
-86%
-50%
-98%
-79%
-99%
-97%
-98%
-93%
-91%
rated
Thermal
Chemical
Aerated
Chemical-thermal
Thermo-aerated
Chemico-aerated
Chemical-thermal-aerated
An-25-1
An-25-5
CT8-40-0
CT8-60-0
CT10-40-0
CT10-60-0
TAn-40-1
TAn-40-5
TAn-60-1
TAn-60-5
CA8-25-1
CA8-25-5
CA10-25-1
CA10-25-5
CTA8-40-1
CTA8-40-5
CTA10-40-1
CTA10-40-5
CTA8-60-1
CTA8-60-5
CTA10-60-1
CTA10-60-5
Test

283 (a)

284



(b) (c) (d)

Figure 4 - Variations of TAN removal efficiency throughout the tests (a, all treatments) (b, treatments with the same pH), (c, treatments with the same temperature), (d, treatments with the same air flow rate).

The 3-way ANOVA, which explains 78% of the variance of the independent variables, shows that all the factors and their interactions (except pH x temperature) had a significant (at $p < 0.05$) effect on the TAN removal; the most influential variables were the air flow rate and temperature.

3.2. Ammonium sulphate recovery

The RAS percentage from AS of SW was equal to the TAN removed, since, as expected, the removed un-ionized ammonia totally reacted with the acidic solution to form the ammonium sulphate. For this reason, the highest RAS values (up to 99%) were found for almost all the treatments with the highest air flow rate (5 L_{air} L_{SW}^{-1} min^{-1}, treatments $TA_{n\text{-}40\text{-}5}$, $CTA_{8\text{-}40\text{-}5}$, $CTA_{10\text{-}40\text{-}5}$, $CTA_{8\text{-}60\text{-}5}$) (Table 4).

Table 4 - Ammonium sulphate recovered by the AS aerated treatments of SW.

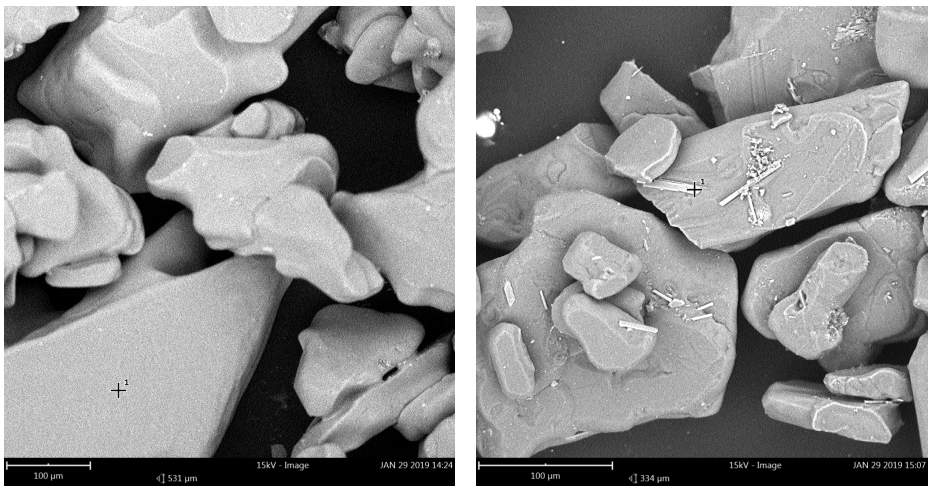
Test	Recovered ammonium sulphate	
	[g L^{-1}]	[%]
$A_{n\text{-}25\text{-}1}$	2.20 ± 0.07	36.1 ± 5.7
$A_{n\text{-}25\text{-}5}$	5.53 ± 0.17	79.7 ± 16.8
$TA_{n\text{-}40\text{-}1}$	0.97 ± 0.35	18.3 ± 8.7
$TA_{n\text{-}40\text{-}5}$	7.99 ± 0.78	98.8 ± 1.7
$TA_{n\text{-}60\text{-}1}$	3.67 ± 0.15	61.6 ± 2.5
$TA_{n\text{-}60\text{-}5}$	6.56 ± 2.49	95.9 ± 5.7
$CA_{8\text{-}25\text{-}1}$	3.75 ± 0.64	57.7 ± 10.3
$CA_{8\text{-}25\text{-}5}$	5.55 ± 1.25	80.1 ± 2.5
$CA_{10\text{-}25\text{-}1}$	3.44 ± 0.78	60.6 ± 14.4
$CA_{10\text{-}25\text{-}5}$	5.75 ± 1.83	85.6 ± 9.1
$CTA_{8\text{-}40\text{-}1}$	2.85 ± 1.26	50.5 ± 25.8
$CTA_{8\text{-}40\text{-}5}$	7.52 ± 1.18	98.3 ± 1.0
$CTA_{10\text{-}40\text{-}1}$	4.71 ± 0.51	79.3 ± 3.3
$CTA_{10\text{-}40\text{-}5}$	7.20 ± 0.13	99.3 ± 1.0
$CTA_{8\text{-}60\text{-}1}$	5.28 ± 0.16	96.8 ± 3.1
$CTA_{8\text{-}60\text{-}5}$	6.26 ± 2.18	98.2 ± 0.1

$CTA_{10\text{-}60\text{-}1}$	6.11 ± 1.25	92.6 ± 9.7
$CTA_{10\text{-}60\text{-}5}$	6.20 ± 1.88	91.1 ± 0.6

304

305

306 The 3-way ANOVA, which explains 67% of the variance of the original variables, shows that pH,
307 temperature and air flow rate (the latter being the most influential factor) as well as the interaction
308 between the air flow rate and pH had a significant (at $p < 0.05$) effect on the amount of ammonium
309 sulphate recovered from SW; conversely, the interactions of temperature with pH and air flow rate
310 were not influential factors.
311 The qualitative analysis of the recovered salt shows that the structure of the salts produced by the
312 treatment$TA_{n\text{-}60\text{-}5}$ is clearer and the crystals are well defined compared to $CTA_{10\text{-}60\text{-}5}$. The salts
313 produced by this batch show instead a dispersed structure. Moreover, thin lines among the crystal
314 salts are evident. These impurities are composed of the calcium used for pH correction, although
315 these precipitates were found in traces (Figure 5).
316



317

318 (a) (b)

319 Figure 5 - Samples of ammonium salts recovered by AS treatments of SW and analysed by SEM: a)
320 test $TA_{n\text{-}60\text{-}5}$; b) test $CTA_{10\text{-}60\text{-}5}$.

321

322 The acidic trap was selective towards ammonia, since the main elements, detected using the
323 elemental analysis, are S, O and N (18.9 ± 0.9%, 67 ± 1.8% and 14.1 ± 3.3% in weight,
324 respectively) for the treatment $TA_{n\text{-}60\text{-}5}$; S, Ca and N (35.4 ± 1.3%, 11.5 ± 2.7% and 54.0 ± 4.9%,
325 respectively) for $CTA_{10\text{-}60\text{-}5}$.

326

4. DISCUSSIONS

According to the literature, the operational parameters of the batch tests are influential factors with different levels (Bonmatı and Flotats, 2003; Lei et al., 2007; D. Zhang et al., 2012; Zhang and Jahng, 2010). In this study, all treatments modified the physico-chemical characteristics of the SW, although the differences in the analysed parameters were not statistically significant.

The pH varied throughout the experiments and this could be due to the new chemical equilibrium, which is the effect of the temperature variation. The pH increase could have been enhanced by the concentrating alkali solution due to water evaporation (Bonmatı and Flotats, 2003).

In the experimental tests, the organic matter degradation/oxidation level was shown by the reduction of TVS, tCOD and sCOD (the latter often noticeable) in many treatments. The treatment $C_{8\text{-}25\text{-}0}$ showed the highest sCOD removal efficiency (over 50%), which was about 4-fold the value of the control test. The sCOD reduction shown by the combined tests was lower compared to the most efficient individual treatment ($C_{8\text{-}25\text{-}0}$) and, in some cases, lower than the control test. This means that, at least to maximise the organic matter removal, it is convenient to adjust only the pH at 8 by adding $Ca(OH)_2$ at a dose of 16 ± 9 $mL_{Ca(OH)2sol}\ L_{SW}^{-1}$. SW heating can be evaluated, if energy is available at low cost (e.g. surplus heat in combined heat and power, CHP, schemes).AS can be avoided, if sCOD removal is an objective of the pretreatment. The share of the produced energy (generally heating), not sold as electricity at market price, can be used for SW heating without buying (or using the produced) electricity. A decrease of both tCOD and sCOD during air stripping was also observed by Bonmatı and Flotats (2003), who explained that aerobic biological degradation and stripping of volatile compounds occur during the process. The increases of sCOD measured in two CTA treatments and in one CT treatment were probably due to some forms of hydrolysis of complex organic compounds. Presumably, the sCOD concentration is influenced by a combination of two concurrent factors driven by $Ca(OH)_2$ addition: the alkali-induced hydrolysis of complex organic matter and the flocculation of non-settling solids removed by centrifugation.

In regard to the TAN removal, the combined treatments were more efficient compared to the individual tests, especially when aeration was applied at the higher flow rates. The combined treatments enhance ammonia stripping thanks to the joint beneficial effect of AS, heating (which influences both ammonia-ammonium equilibrium towards ammonia and decreases its solubility), and pH increase (which shifts ammonia/ammonium equilibrium towards gaseous ammonia). The CTA treatments have produced the highest TAN removal efficiency (up to more than 99% of the initial content) with two exceptions (both with TAN removal efficiency rate over 50%). However, since the energy requirement of the T treatment is generally higher than AS, a treatment with

temperature of 40 °C, air flow rate of 5 L_{air} L_{SW}^{-1} min^{-1} and moderate alkali addition (pH = 8) can assure TAN up to 98%. More severe T treatments (i.e., at T = 60 °C) can be considered only if surplus heat from CHP systems is available.

Table 5 compares the sCOD and TAN removal efficiency detected in this study with the experiments about AS of SW reported in the literature. Bonmatı and Flotats (2003) recovered almost all the ammonia in a short reaction time (four hours) using a very low air flow rate (0.05 L_{air} L_{SW}^{-1} min^{-1}), but at high temperature (80 °C) and pH (11.5); when pH was adjusted to 9.5, the ammonia removal efficiency (69%) was similar to those without pH adjustment. Lei et al. (2007) used even more extreme conditions (pH adjusted to 12 and air flow rate up to 10 L_{air} L_{SW}^{-1} min^{-1}) to obtain a removal efficiency over than 70% from the anaerobically digested SW; their results indicated that, at the same pH conditions, the ammonia removal increases with the air flow rate. Zhang and Jahng (2010) obtained high ammonia removal efficiency (> 70%) at mild temperature (37 °C) and air flow rate (1 L_{air} L_{SW}^{-1} min^{-1}) at pH = 10 in a 24-hour reaction time. The same authors detected a sCOD reduction when the alkali solutions were added. Increasing the time to 48 hours and the pH to 11, Zhang et al. (2012) showed a removal efficiency of 80%; the maximum ammonia reduction (92%) was observed at pH = 9 and air flow rate of 10 L_{air} L_{SW}^{-1} min^{-1}. In these studies, the highest concentration of total nitrogen was over 7 g L^{-1}.

When simultaneous removal of sCOD and TAN are required (e.g., before conventional activated sludge or aerobic lagooning treatments), the treatments with efficiency higher than 30% for sCOD and 80% for TAN were: $A_{n\text{-}25\text{-}5}$ (-30% for sCOD and -80 for TAN), $TA_{n\text{-}60\text{-}5}$ (-35% and -96%), $CTA_{10\text{-}40\text{-}1}$ (-30% and -80%) and $CTA_{8\text{-}60\text{-}1}$ (-38% and -97%). This indicates that a treatment at pH of 8, T set at 40 or 60 °C (the temperature can be set up as a function of surplus heat availability, as above mentioned) and air flow rate at 5 L_{air} L_{SW}^{-1} min^{-1} would be a highly performing solution. If heating is not technically or economically feasible, the performance would be always acceptable (sCOD removal efficiency of about 25-30% and TAN removal of about 80%)

When the preservation of sCOD is advisable (i.e. in the case of AD following the pretreatment), pH adjustment to 10 combined with thermal treatment at 60 °C and aeration give high and stable performances. However, the issue of heating is crucial and must be carefully evaluated under an economical point of view.

As regards the fertiliser recovery from AS, it has been highlighted that all the aerated treatments produce very large amounts of ammonium sulphate (recovery rate over 80% of the theoretical yield) at the maximum air flow rate (5 L_{air} L_{SW}^{-1} min^{-1}). The addition of the $Ca(OH)_2$ solution influences the structure of the ammonium sulphate and some traces of the alkali were detected in the salts. In

some cases, the colour of the salts can be modified by the large amount of removed COD, although it could not be fixed in the high acid solution used in the tests (Bonmatı and Flotats, 2003).

The presence of calcium sulphate is however not detrimental for the proposed agricultural use of the recovered salts. In fact, this compound is routinely used in agriculture for soil amendment/fertilisation.

399 Table 5 - Literature data about experimental tests of SW treatment by AS.

400

Authors	Chemical addition	Adjusted pH	Temperature [°C]	Time [h]	Air flow rate [L_{air} L_{SW}^{-1} min^{-1}]	TKN [g L^{-1}]	NH^{+}_{4}-N [g L^{-1}]	Ammonia removal efficiency [%]	sCOD [mg L^{-1}]	sCOD removal efficiency [%]
Bonmatı and Flotats, 2003	None	7.7	80	4	0.05*	5.63	3.39	65	n.a.	n.a.
	$Ca(OH)_2$	9.5						69		
		11.5						98.8		
Lei et al., 2007**	$Ca(OH)_2$	12	15	12	3	1.77	1.51	72.1	n.a.	n.a.
					5			89.9		
					10			95.3		
Zhang and Jahng, 2010	NaOH	9.5	37	24	1.0*	7.60	4.95	49.3*	54200	4.8*
		10						70.5*		1.7*
	KOH	9.5						40.4*		10.0*
		10						71.3*		7.7*
	CaO	9.5						30.5*		14.9*
		10						49.1*		78.4*
Zhang et al., 2012	NaOH (40% w/w)	7.2	37	48	1.0	7.60	4.95	28.0	54200	n.a.
		9.0						47.0		
		10.0						80.0		
		11.0						88.1		
	NaOH (40% w/w)	9.0	37	48	1.0	7.60	4.95	46.0		
					2.0			62.2		
					4.0			77.9		
					10.0			92.0		

401 Notes: TKN = Total Kjeldahl Nitrogen; *estimated data; **study on anaerobic digested effluent; n.a. = not available.

5. CONCLUSIONS

In 27 batch tests the pH, temperature and air flow rate were adjusted, in order to optimise the ammonia nitrogen recovery from swine wastewater and the characteristics of treated SW destined to further treatments. While TAN reduction is always advisable, sCOD preservation is recommended if pretreated SW must be used as substrate for AD. On the contrary, if the pre-treatment is applied before an aerobic treatment, the maximum sCOD removal efficiency is required.

The fifty percent of the treatments of this study allowed a TAN removal efficiency of about 80% or higher. A combination of chemical, thermal and aeration treatment seems to give the best TAN removal efficiency. Minimum sCOD losses (< 10%) were observed in combined treatments including chemical (pH = 10) and thermal (T = 60 °C) conditioning. Treatments at 40 °C could also be effective. The best choice should be based on the energy balance (surplus energy for SW heating due to methane over-production and/or CHP schemes). If sCOD removal is needed, the chemical conditioning and aeration seem to be the most efficient choice, since, in this case, low-cost energy is usually not available.

Very high amounts (over 80% of the theoretical yield) of ammonium sulphate were recovered by AS at the maximum air flow rate (5 L_{air} L_{SW}^{-1} min^{-1}), which would provide a nitrogen fertiliser at a sustainable cost.

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