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**INNOVATIVE TREATMENT SYSTEMS OF SWINE  
WASTEWATER FOR ENERGY VALORISATION  
AND RECOVERY OF BY-PRODUCTS**

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## Abstract

Unsuitable wastewater management in the animal breeding sector can lead to negative environmental and economical impacts. With regard to the swine breeding farms, the swine wastewater (SW) is characterised by high concentrations of organic matter and ammonia. These concentrations make difficult the SW treatment in the intensive depuration plants, commonly adopted by several farms. The feasibility of SW spreading on soil without any pre-treatments is limited by the possible polluting effects (such as the eutrophication of water bodies and the depletion of oxygen in soil). Moreover, these systems have a high requirement of both energy and/or chemical additives for guaranteeing an efficient treatment. Extensive systems, such as lagooning, are cheaper and environmentally more sustainable compared to the intensive plants. However, these systems require long retention time (weeks or even months) and large space for plants, which makes the treatment of large volumes of SW difficult or even impossible.

Anaerobic digestion (AD), although being more and more common for the treatment of agricultural residues, has been less used for depurating the SW, since the biochemical processes are very sensitive to the high concentration of ammonia. In addition to organic matter degradation and nitrogen removal, the AD produces a biogas that is rich in biomethane, a gaseous renewable biofuel, and the digestate, the liquid effluent that is commonly used as soil fertiliser.

The possibility to simultaneously recover energy and marketable by-products from the SW treatment is a good opportunity for swine breeding farms. Therefore, the AD could be a suitable alternative to the common treatments. However, the specific physico-chemical characteristics of the SW strongly limit the methane production. An AD pre-treatment could be necessary to remove the ammonia without reducing too much the organic content of SW. Air stripping (AS) is a simple but efficient system to reduce the amount of volatile compounds, using only air flow in the wastewater, and simultaneously recover nitrogen as ammonium sulphate (a soil fertiliser). The pre-treated SW, with a lower ammonia content compared to the raw SW, avoids or limits AD inhibition. Until now, in spite of a large body of literature about AS and AD of SW, few experiences have been carried out using AS as AD pre-treatment of SW. Moreover, the combined process is far from being optimised in terms of ammonium sulphate and biomethane yields.

To fill this gap, this thesis aims at optimising an integrated system consisting of AS and AD treatments applied in series, with the aims of depurating SW and, at the same time, producing biomethane and ammonium sulphate. The efficiency of AS for treating SW is compared to other physico-chemical treatments carried out on raw SW.

To summarise the results of the laboratory experiments, AS was able to remove over 80% of ammonia nitrogen, with increased efficiency when pH and temperature were adjusted to optimal values; the soluble organic matter increased up to 50% in a few tests. Higher air flows allowed the increase of the recovery of ammonium sulphate. However, regardless of the pre-treatments, the AD of treated SW produced less methane compared to raw SW. The ammonia concentration was always kept below the inhibition limit, and therefore this lower production could be due to the shortage of nutrient and organic matter as well as to other reasons, such as the presence of heavy metals and/or other toxic compounds (e.g., furfurals).

Overall, this study has highlighted the feasibility of AS as a pre-treatment of SW, because it removes significant amounts of pollutants and recover a marketable nutrient at the same time; on the other hand, the results have shown the importance of optimising the operational parameters of AS, to ensure a yielding substrate for the AD process. More research is needed to increase the energy yields of the combined AS+AD system, in order to ensure its environmental and economical sustainability for the SW valorisation.

**Keywords:** ammonium sulphate; environmental sustainability; air stripping; bio-chemical, anaerobic digestion, biomethane production.







## Riassunto

La gestione delle acque reflue nel settore dell'allevamento animale porta a impatti negativi dal punto di vista sia ambientale, sia economico. Le acque reflue degli allevamenti di suini sono caratterizzate da elevate concentrazioni di composti organici e dell'ammoniaca. Queste concentrazioni rendono difficile il trattamento delle acque suinicole negli impianti intensivi di depurazione comunemente adottati per tale tipologia di reflui. La fattibilità della somministrazione delle acque suinicole sul suolo senza alcun pretrattamento è limitata a causa dei possibili effetti inquinanti (come l'eutrofizzazione dei corpi idrici e il consumo di ossigeno nel suolo). Questi sistemi, inoltre, hanno un'elevata richiesta di energia e di additivi chimici, entrambi necessari per rendere efficienti i trattamenti. I sistemi estensivi, come il lagunaggio, sono meno costosi e più sostenibili dal punto di vista ambientale rispetto agli impianti intensivi. I sistemi estensivi, tuttavia, richiedono lunghi tempi di ritenzione (da settimane a mesi) ed elevati spazi per gli impianti, che rendono difficile, o persino impossibile, il trattamento di elevati volumi di acque suinicole.

La digestione anaerobica, nonostante sia sempre più diffusa per il trattamento dei residui agricoli, è stata meno utilizzata per la depurazione delle acque suinicole, poiché i processi biochimici sono molto sensibili alle alte concentrazioni di composti ammoniacali. Oltre alla degradazione della sostanza organica e alla rimozione dei nutrienti, la digestione anaerobica produce biogas ricco in biometano, un biocombustibile gassoso rinnovabile, e digestato, l'effluente liquido, comunemente utilizzato come fertilizzante per i suoli.

La possibilità di recuperare dai reflui suinicoli simultaneamente energia e sottoprodotti commerciabili è una buona opportunità per gli allevatori di suini. La digestione anaerobica, quindi, potrebbe essere una ottimale alternativa ai comuni trattamenti. Tuttavia, le specifiche caratteristiche fisico-chimiche delle acque suinicole limitano fortemente la produzione di metano. Allo scopo di rimuovere l'ammoniaca senza ridurre eccessivamente il contenuto organico nelle acque suinicole, potrebbe essere necessario un pretrattamento prima della digestione anaerobica. L'air stripping (AS) è un sistema semplice ma efficace per ridurre la quantità di composti volatili, sottoponendo il refluo ad un semplice flusso d'aria, e, allo stesso tempo, per recuperare l'azoto come solfato d'ammonio (un fertilizzante per il suolo). Le acque suinicole pretrattate, con un contenuto di ammoniaca più basso rispetto alle acque suinicole tal quali, evitano o limitano l'inibizione della digestione anaerobica. A tutt'oggi, nonostante la consistente letteratura sull'AS e la digestione anaerobica delle acque suinicole, sono state condotte poche esperienze usando l'AS come pretrattamento delle acque suinicole prima della digestione anaerobica; inoltre, il processo combinato non garantisce alte rese di biometano.

Per colmare questa lacuna, questa tesi si pone lo scopo di ottimizzare un sistema integrato composto da AS e digestione anaerobica in serie, per depurare e, allo stesso tempo, produrre biometano e solfato d'ammonio. L'efficienza dell'AS per il trattamento dei reflui suinicoli è confrontata con altri trattamenti fisico-chimici condotti sulle acque suinicole tal quali.

Sintetizzando i risultati degli esperimenti di laboratorio, l'AS è stata in grado di rimuovere oltre l'80% di azoto ammoniacale, con un incremento dell'efficienza se il pH e la temperatura vengono corretti a valori ottimali; in alcuni test la sostanza organica solubile è aumentata del 50%. Portate d'aria consistenti hanno consentito il recupero di maggiori quantità di solfato di ammonio. Tuttavia, indipendentemente dal pretrattamento, la digestione anaerobica delle acque suinicole pretrattate ha prodotto un volume di metano inferiore rispetto alle acque suinicole non trattate. La concentrazione di ammoniaca è sempre stata mantenuta sotto la soglia di inibizione e, quindi, tale bassa produzione potrebbe essere dovuta ad una carenza di nutrienti o ad altri fattori, come la presenza di metalli pesanti e/o altri composti tossici (come i furfurali).

Nel complesso, lo studio ha evidenziato la fattibilità dell'AS come pretrattamento delle acque suinicole, in quanto si riesce contemporaneamente a rimuovere una notevole quantità di inquinanti ed a recuperare nutrienti commerciabili; d'altro canto, i risultati hanno evidenziato l'importanza di ottimizzare i parametri operativi dell'AS per assicurare un substrato adatto al processo di digestione anaerobica. Sono necessarie ulteriori indagini per aumentare le rese energetiche del sistema combinato AS + digestione anaerobica, allo scopo di assicurare la sua sostenibilità ambientale ed economica per la valorizzazione delle acque reflue suinicole.





## General Introduction

The agricultural and industrial sectors are subjected to important changes towards a more sustainable economy, as required by the targets of the EU's Circular Economy Package (Directive 2018/851). The hierarchical system, previously illustrated in the Waste Framework Directive 2008/98/EC, proposes the following phases for the reduction and management of waste production: prevention, reuse, recycling, energy recovery and final disposal. Hence, particular attention is given to the possibility of waste conversion into by-products and/or recovered energy.

The agro-industrial and animal breeding sectors are some of the most pollutant activities with negative impacts on the environment. The management of the produced wastes (such as manure, citrus peel waste and wastewater, olive mill wastes) needs specific treatment systems based on their physico-chemical characteristics. Traditional systems are expensive and may not be efficient in the removal of pollutant compounds. For instance, chemical processes generally produce other pollutant effluents or waste, biological processes may be inhibited by the presence of toxic compounds while physical treatments are energy consuming and often inadequate to reach the treatment goals.

One of the main issues for swine breeding farms is the large production of wastewater (SW), mainly composed of a mixture of urine and feces as well as water spillage, residues of undigested food, antibiotic residues and pathogenic microorganisms (Viancelli et al., 2013). SW is characterized by a noticeable content of polluting compounds, mainly organic matter and ammonia nitrogen. These specific characteristics make difficult the SW treatment in conventional systems (e.g., activated sludge plants percolating filters) and the direct disposal on soil, often used for other agricultural wastewater, impossible. The management systems commonly used for SW depuration (chemical, physical, biological or combined processes) are generally not efficient to remove organic matter and nutrients (Hill, 2003; Mehta et al., 2015); moreover, the high concentration of nitrogen may be the cause of eutrophication of water bodies or soil pollution in case of disposal without adequate treatments (Motteran et al., 2013). The extensive treatments, such as lagooning in biological ponds or phyto-depuration in constructed wetlands, could be theoretically cheap and thus sustainable for the smallest swine-breeding farms. However, the long time required (2-3 weeks and even months) for the wastewater depuration may not be technically feasible (Andiloro et al., 2013; Zema et al., 2016, 2012).

All these issues lead to severe environmental and economic constrains in SW treatment for swine breeding farms, and therefore innovative systems for SW valorisation that should make the management of SW safer for the environment and cheap for the farmers must be suggested.

Anaerobic digestion (AD) is considered a viable option for the energy valorisation of several agro-industrial wastes, such as the olive mill wastewater or citrus peel waste and wastewater (Calabrò et al., 2018; Zema et al., 2019, 2018b). In addition to the wastewater depuration, the AD recovers renewable energy as bio-methane (Zema et al., 2019, 2018a), while the digestate (the liquid effluent of AD) can be used as soil conditioner. However, the anaerobic process is not always feasible for SW. The main reason is the high concentrations of organic matter (up to about 80 g per litre of COD) and ammonia nitrogen (generally over 4.0 g L<sup>-1</sup>). The latter inhibits the microorganisms' activity of biological processes (Hansen et al., 1998; L. Zhang et al., 2012), yielding an extremely low methane production, not over 200 mL per g of volatile solids (Browne et al., 2013; Hansen et al., 1998; L. Zhang et al., 2012; Zhang and Jahng, 2010).

On the other hand, the high content of nitrogen in SW can be recovered by physical and/or chemical processes to produce natural fertilisers, such as ammonium sulphate and struvite (Sengupta et al., 2015; D. Zhang et al., 2012; Zhang and Jahng, 2010), that are usually expensive to produce.

Air stripping (AS) is a common physical process used to remove volatile compounds and, in the case of nitrogen-rich wastewater, to recover ammonia. The main stripping effect is due to the air action, which is blown in the wastewater by an electric pump. Moreover, the addition of chemicals, specifically alkali (such as sodium or calcium hydroxide), shifts the chemical reaction equilibrium between free ammonia (NH<sub>3</sub>) and ammonium ions (NH<sub>4</sub><sup>+</sup>) towards the undissociated ammonia, which is a gas with a low water solubility. The stripped ammonia is then conveyed to an adsorbing unit, usually consisting of a solution of sulphuric acid, where the ammonia precipitates as ammonium sulphate.

Hence, the nitrogen removal from SW could be considered at the same time a process for fertiliser production and a pre-treatment for the AD. The reduction of nitrogen content in SW may increase the methane yield in anaerobic digestion. Moreover, the digestate of AD could be directly spread on soil without further chemical treatments.

Both processes of AS and AD have been individually studied for a wide range of treated substrates, such as kitchen manure (Chen et al., 2017; Fuchs et al., 2018), landfill leachate (Collivignarelli et al., 1998; Ozturk et al., 2003), digestate manure (Zeng et al., 2006), urine (Liu et al., 2015; Xu et al., 2017), in order to identify the optimal conditions of these processes for high nitrogen removal or methane production. However, the use of these processes as treatments for SW and the evaluation of the related efficiency have been rarely carried out. Moreover, studies on the effects of AS as pre-treatment of AD are scarce or even absent in literature.







## Objectives

To fill the gaps above mentioned, this PhD thesis evaluates the feasibility of the integrated process AS + AD as system for the treatment (i.e. depuration) and valorisation (i.e. simultaneous production of fertiliser and energy) of SW.

More specifically, the first phase (AS) is targeted to the ammonia nitrogen removal from SW and the removed nitrogen is recovered as ammonium sulphate to be used as fertiliser.

In the second phase of the integrated system the pre-treated SW is used as substrate for the AD process. Since the excess of ammonia has been partly removed in the stripping process, the methane yield of the treated SW is expected to increase compared to the digestion of untreated SW. However, the AS may excessively remove ammonia from the SW and since this nutrient is essential for microorganisms' metabolism, a drop in methane production may be possible. Moreover, the alkali used to adjust pH during AS can produce compounds that are toxic for microbial consortium (e.g. furfurals).



## Organisation

This PhD thesis is presented as a collection of three articles published in peer-reviewed, SCOPUS and ISI indexed, international journals and consists of the following chapters.

The Chapter 1 of the PhD thesis is the paper titled “Environmental and Economic Sustainability of Swine Wastewater Treatments Using Ammonia Stripping and Anaerobic Digestion: A Short Review”, published in July 2020 on Sustainability (Folino et al., 2020b). This article reports the state-of-the-art of the AS used as pre- and post-treatment for the AD process and compares the efficiency of the AS coupled with other processes for the treatment of SW.

The need for this review is the lack of comprehensive papers on this specific topic. More specifically, AS has been extensively discussed in reviews as a treatment for several types of wastewater, such as urine, municipal or industrial wastewater; however, no reviews have been published about ammonia removal and recovery from raw and digested SW by AS treatment. This paper fills this gap also discussing the application of AS to digested SW, when no treatment is applied to SW prior to AD. Moreover, the synergistic effects between AS and AD, that is consistent to this thesis are also evaluated. Finally, future research perspectives for the technical and environmental sustainability of AS of raw and digested SW are suggested.

Based on the knowledge acquired by writing the review article (Chapter 1), the Chapter 2 of the PhD thesis is the paper titled “Organic matter removal and ammonia recovery by optimised treatments of swine wastewater”, published on Journal of Environmental Management in March 2020 (Folino et al., 2020c). This article reports the results of an experiment about the treatment of SW using AS and other physical and/or chemical treatments.

As explained in the General Introduction section, the AS process has been chosen to both pre-treat SW before AD, in order to reduce the content of ammonia, and to recover it for fertiliser production.

As extensively explained in Chapter 1 (Folino et al., 2020b), the removal efficiency of AS mainly depends on four parameters: pH; temperature; air flow rate (AFR) per unit volume of wastewater; and characteristics of the raw wastewater.

In general, high AFR, heating and/or alkali addition (the latter to increase the pH at the desired value) lead to high ammonia removal efficiency, but they make the AS treatment expensive. The study of Chapter 2 therefore aims at optimising these operational parameters (pH, temperature and AFR) in the experimented SW treatments (AS and other physical and/or chemical). Since the treatment efficiency under extreme values of these parameters is known by previous literature

experiences, this study is targeted to obtain similar efficiencies in removing both organic matter and ammonia nitrogen using “mild” operational conditions for temperature, alkali dosages and AFR. The production of ammonium salts has been also qualitatively and quantitatively evaluated for the cases of AS application.

Moreover, the results of AS experiments were compared with the efficiency of other individual chemical and thermal treatments, where only pH or temperature were varied.

To summarise the results, more than 80% of TAN was removed in about 50% of the tests. 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 total ammonia nitrogen (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 ( $5 L_{\text{air}} LSW^{-1} \text{ min}^{-1}$ ), which would provide a nitrogen fertiliser at a sustainable cost.

The Chapter 3 of the PhD thesis is the paper titled “Effects of Ammonia Stripping and Other Physico-Chemical Pretreatments on Anaerobic Digestion of Swine Wastewater”, published on *Energies* in June 2020 (Folino et al., 2020a). Since the AD has been chosen as system for the energy valorisation of SW, Biochemical Methane Potential (BMP) tests were carried out on pre-treated SW. The experiments were carried out only on the pre-treated SW that showed the best characteristics for a yielding AD (such as the maximum removal of ammonia and increase of soluble chemical oxygen demand), using raw SW as control. Since the inhibitory compounds have been removed by the pre-treatments, the biogas production was expected to increase. However, the excessive removal of ammonia and organic matter could lead to the opposite result. Since few studies are available in literature about AD of air-stripped SW and, moreover, the results are contrasting, this study evaluates whether the integrated AS + AD system is a suitable system for the treatment of SW and the related depuration and energy valorisation efficiencies.

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%) compared to raw SW. The inhibitory effect on AD could have been due to the lack of nitrogen and organic matter in the substrate (due to the excessive removal of the pretreatments), the presence of

toxic compounds (such as metal ions or furfural formed during alkali addition), 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.

The findings of this research can advance the knowledge on the possible alternatives to traditional SW management systems.

The final section of the PhD thesis gives a summary and a critical overview of the results of the 3-year study together with some indications about the future perspectives towards an environmentally and economically sound integrated system AS + AD for SW valorisation.





# Chapter 1. Environmental and economic sustainability of swine wastewater treatments using ammonia stripping and anaerobic digestion. A short review

Source: Folino, A., Zema, D. A., & Calabrò, P. S. (2020). Environmental and Economic Sustainability of Swine Wastewater Treatments Using Ammonia Stripping and Anaerobic Digestion: A Short Review. *Sustainability*, 12 (12), 4971.



Review

## Environmental and Economic Sustainability of Swine Wastewater Treatments Using Ammonia Stripping and Anaerobic Digestion: A Short Review

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**Abstract:** One of the most promising systems to treat swine wastewater is air stripping. This system simultaneously recovers nitrogen salts, to be used as fertiliser, and reduces the organic pollutant load in the effluents of swine breeding farms. Several reviews have discussed the air stripping as a treatment for many types of industrial wastewater or nitrogen-rich digestate (the liquid effluent derived from the anaerobic digestion plants) for the stripping/recovery of nutrients. However, reviews about the use of air stripping as treatment for raw or anaerobically digested swine wastewater are not available in literature. To fill this gap, this study: (i) Summarises the experiences of air stripping for recovery of ammonium salts from both raw and digested swine wastewater; and (ii) compares air stripping efficiency under different operational conditions. Moreover, combined systems including air stripping (such as struvite crystallisation, chemical precipitation, microwave radiation) have been compared. These comparisons have shown that air stripping of raw and digested swine wastewater fits well the concept of bio-refinery, because this system allows the sustainable management of the piggery effluent by extracting value-added compounds, by-products, and/or energy from wastewater. On the other hand, air stripping of raw and digested swine wastewater has not been extensively studied and more investigations should be carried out.

**Keywords:** air stripping; ammonia removal efficiency; ammonium sulphate; digestate; nitrogen recovery; process conditions; struvite

One of the most promising systems to treat swine wastewater is air stripping. This system simultaneously recovers nitrogen salts, to be used as fertiliser, and reduces the organic pollutant load in the effluents of swine breeding farms. Several reviews have discussed the air stripping as a treatment for many types of industrial wastewater or nitrogen-rich digestate (the liquid effluent derived from the anaerobic digestion plants) for the stripping/recovery of nutrients. However, reviews about the use of air stripping as treatment for raw or anaerobically digested swine wastewater are not available in literature. To fill this gap, this study: (i) Summarises the experiences of air stripping for recovery of ammonium salts from both raw and digested swine wastewater; and (ii) compares air stripping efficiency under different operational conditions. Moreover, combined systems including air stripping (such as struvite crystallisation, chemical precipitation, microwave radiation) have been compared. These comparisons have shown that air stripping of raw and digested swine wastewater fits well the concept of bio-refinery, because this system allows the sustainable management of the piggery effluent by extracting value-added compounds, by-products, and/or energy from wastewater. On the other hand, air stripping of raw and digested swine wastewater has not been extensively studied and more investigations should be carried out.

**Keywords:** air stripping; ammonia removal efficiency; ammonium sulphate; digestate; nitrogen recovery; process conditions; struvite

## **1.1. Introduction**

The management of swine wastewater (hereinafter indicated as “SW”) is an important problem for swine breeding farms, as the large production and polluting content lead to several environmental and economic constraints and a generally low sustainability. Due to the high contents of organic and nitrogen compounds, improper disposal of SW causes pollution of surface and ground waters, unpleasant odour emission in atmosphere, and consumption of oxygen in soil and water bodies.

Intensive depuration plants are the most common systems for SW treatment (Kim et al., 2004). Other chemical (such as coagulation/flocculation, Hill, 2003; Mehta et al., 2015; Mores et al., 2016), physical (Safavi and Unnthorsson, 2017), or biological (multi-stage or aerobic treatment, Kim et al., 2004; Motteran et al., 2013) systems (Cai et al., 2015; Cheng et al., 2000; Motteran et al., 2013) have been proposed to ensure an environmentally and economically sound management of SW (Table 1.1). However, these treatments generally show low efficiency, high costs (Yang et al., 2016), and process instability, mainly due to the high concentration of ammonia nitrogen that inhibits the microorganisms’ activity. When chemicals are added to the processes (e.g., coagulation/flocculation), the resulting sludge/concentrate cannot be directly spread in agricultural fields, as it may contain undesired by-products of the chemical process or toxic compounds (e.g., heavy metals) (Hill, 2003; Mehta et al., 2015). Moreover, secondary pollution may occur (Cao et al., 2018) and other subsequent treatments may be necessary for the produced sludge/concentrate.

Often, most of these treatments are not sustainable for the smallest swine-breeding farms working in rural contexts. For these reasons, much attention has been recently paid to extensive systems for SW depuration, such as the aerobic and/or anaerobic lagooning plants (e.g., Craggs et al., 2008; Loughrin et al., 2012; Trias et al., 2004). These extensive systems allow a proper equalisation of the physico-chemical characteristics of wastewater and a reduction of its pollutant load, as for other agro-industrial effluents (Andiloro et al., 2013; Zema et al., 2016, 2012). However, the physico-chemical and biological processes of lagooning plants require a long time (weeks or even months) because the environmental conditions cannot be properly set up.

**Table 1.1.** Advantages and drawbacks of the main systems for the treatment of swine wastewater.

<b>Treatment</b>	<b>Type</b>	<b>Advantages</b>	<b>Limitations</b>
<b>Chemical</b>	Coagulation— Flocculation— Disinfection (possible)	<u>Water disinfection</u> Microbes and solids can be removed by sedimentation or filtration after flocculation by the addition of coagulants (Hill, 2003) <u>Chemical accumulation of nutrients</u> Soluble nutrients bound to colloids precipitate as solids and separated by settling in clarifiers (Mehta et al., 2015) <u>Removal of organic matter and other inorganic species</u> , such as arsenic and fluoride (Mehta et al., 2015) <u>Flexibility of the operational process.</u> The use of simultaneous chemical precipitation in modified activated sludge systems (De Haas et al., 2001) <u>Low capital cost</u> for reducing phosphorous concentration in the effluent (De Haas et al., 2001)	<u>Possible undesired by-products</u> , such as trihalomethanes and chlorites in case of chlorination (Hill, 2003) <u>Variability of process conditions</u> depending on the level of disinfection required (Hill, 2003) <u>Operating costs</u> (De Haas et al., 2001) <u>Sludge production and possible presence of heavy metals</u> (De Haas et al., 2001) <u>Possible inhibitory effects in the following biological treatment</u> (Liu et al., 2011) <u>Low nutrients availability and agronomic utilisation</u> , particularly with aluminium and iron coagulation (Cox et al., 1997)
<b>Physical</b>	Sedimentation	<u>Fertiliser production</u> by bio-solid recovery (Hill, 2003) <u>Pathogens reduction</u> , such as <i>Salmonella typhimurium</i> , <i>E. coli</i> , <i>Streptococcus faecalis</i> (Hill, 2003) <u>Reduction of the organic load</u> for the following treatments (Hill, 2003)	<u>Energy costs</u> of filtration membranes (Mehta et al., 2015) <u>Not suitable direct use of the concentrate</u> due to the accumulation of undesired contaminants (Mehta et al., 2015) <u>Pre-treatment needed</u> to prevent membrane fouling (Mehta et al., 2015)
	Membrane filtration	<u>Selective separation of the constituents from waste streams</u> based on the membrane used (Mehta et al., 2015)	High cost for membrane replacement due to fouling

<b>Treatment</b>	<b>Type</b>	<b>Advantages</b>	<b>Limitations</b>
<b>Biological System</b>	Activated sludge process	<u>Odour control, nitrogen management, and biodegradation of organic waste</u> (Hill, 2003)  <u>Pathogens inactivation and/or removal</u> (Hill, 2003)	<u>Possible inhibition due to the presence of toxic compounds</u> (such as resistant pathogens, heavy metals, other organic compounds)  <u>Process sensitivity</u> to environmental conditions (pH, temperature, organic load)

Another viable system for SW treatment is the anaerobic digestion, which allows an easier control of the main operational parameters of the depuration process. The anaerobic digestion systems are used for depurating several agro-industrial waste and wastewater, such as the olive mill wastewater or citrus peel waste and wastewater (Calabrò et al., 2018; Zema et al., 2019, 2018b). However, the methane production in the anaerobic digestion plants treating SW is often reduced or even inhibited by the high ammonia content (often over  $4.0 \text{ g L}^{-1}$ ) that hampers the activity of the methanogenic bacteria (Hansen et al., 1998; L. Zhang et al., 2012). As a consequence, the methane yield of raw SW is about  $50 \text{ mL gCOD}^{-1}$  (L. Zhang et al., 2012; Zhang and Jahng, 2010) or  $100\text{--}200 \text{ mL gVS}^{-1}$  (Browne et al., 2013; Hansen et al., 1998). As the SW has a high organic and nutrient loads, the treatment efficiency is not always high and the limits for discharging the treated effluents into water bodies are very strict in some countries (such as Italy), the depurated SW very often is spread on soil for agronomic purposes or sent to further treatments, such as lagooning and constructed wetlands.

On the other hand, the high presence of ammonium and phosphorus compounds has suggested the recovery of natural fertilisers from SW using physico-chemical treatments. Examples of these recovered compounds are struvite (either in magnesium,  $\text{MgNH}_4\text{PO}_4$ , or potassium,  $\text{KNH}_4\text{PO}_4$ , form) (Sengupta et al., 2015; D. Zhang et al., 2012) and ammonium sulphate (Zhang and Jahng, 2010). Nitrogen and phosphorus are essential nutrients for plant growth and crop cultivation, but their production is often expensive. The removal of these compounds from SW not only allows their recovery, but also makes the following treatments easier, leading to a more efficient depuration in lagooning plants and to an increase of the methane yield in anaerobic digestion systems.

The most common system for ammonia recovery is air stripping. This system consists of blowing air in wastewater, which is also chemically pre-treated by adding alkali - such as  $\text{NaOH}$ ,  $\text{Ca(OH)}_2$ , or  $\text{CaO}$  - in order to optimise its pH before aeration. The stripped ammonia is recovered by an adsorbing unit as ammonium sulphate, an inorganic salt that can be directly used as a fertiliser. Moreover, when air stripping is used as a pre-treatment for the SW, the risk of ammonia inhibition is lower; for the

direct use of the digestate in agriculture, a simple solid–liquid separation without other chemical treatments is only required.

An alternative plant scheme is the air stripping of digested wastewater. The effluents of anaerobic digestion, if influent SW is not pre-treated, usually show a high nitrogen content even after the anaerobic digestion. Moreover, the high water content and the possible presence of contaminants (such as heavy metals and organic matter) often makes the digestate not suitable for direct spreading on land (Mehta et al., 2015). In these cases, air stripping is also applied to reduce the ammonia nitrogen content, in order to allow the valorisation of the digestate as soil conditioner, thus increasing the sustainability of the whole management processes.

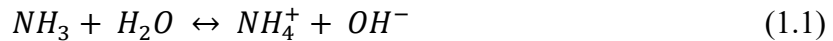
The literature reports several reviews on AS of wastewater of different sources, such as municipal or industrial wastewater (Karri et al., 2018; Kinidi et al., 2018; Mehta et al., 2015; Perera et al., 2019; Sagberg and Berg, 2000; Sengupta et al., 2015) as well as of urine (Maurer et al., 2006) and manure (Zarebska et al., 2015), and about recovery of nutrients from digestate (Macura et al., 2019; Vaneeckhaute et al., 2017). However, no reviews have been published on ammonia removal from raw or digested SW by air stripping. In order to fill this gap, this review analyses the AS techniques and their performances on both raw and digested SW. Based on the most important studies found in literature, the state of the art is outlined and the future research directions are suggested, to further improve the technical, economic, and environmental sustainability of AS of raw SW and digested SW.

## 1.2. Air Stripping

Air stripping is one of the most common systems for removing volatile pollutants, especially ammonia, from aqueous solution (Karri et al., 2018), because it is a relatively simple and cost-effective process (Kinidi et al., 2018; Ozturk et al., 2003). However, the industrial application of air stripping is still in its preliminary phase (Karri et al., 2018). Thus, more research is needed to consolidate its practical use (Mehta et al., 2015). The removal efficiency of air stripping mainly depends on four parameters: (i) pH; (ii) temperature; (iii) air flow per unit volume of wastewater (hereinafter “air flow rate”, AFR); and (iv) characteristics of the raw wastewater (Bonmatí and Flotats, 2003; Lei et al., 2007; Zhang and Jahng, 2010). The following sub-sections explain the effects of the operational parameters (pH, temperature, and AFR) on the removal efficiency of ammonia nitrogen and the main drawbacks in air stripping application; then, the processes of nutrient recovery and the alternative schemes of air stripping in literature are discussed.

*1.2.1. Effects of the Operational Parameters on the Removal Efficiency of Ammonia Nitrogen and Main Drawbacks of Air Stripping Application*

Basically, air stripping consists of a mass transfer based on a desorption process, which transfers a gas from the liquid to a gas phase. For SW (the liquid phase), ammonia can be found as ammonium ions (the ionic form,  $NH_4^+$ ) and ammonia gas (the molecular form,  $NH_3$ ) (Kinidi et al., 2018), which are in equilibrium according to the following reaction (Equation (1.1)) (Kinidi et al., 2018):



The distribution between molecular ammonia and ammonium ions, described by Equation (1.2) (Lei et al., 2007), depends on pH and temperature, as explained by Equation (1.3) (Bonmatí and Flotats, 2003):

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+]/K_a} \quad (1.2)$$

$$pK_a = 4 \cdot 10^{-8} T^3 + 9 \cdot 10^{-5} T^2 + 0.0356 T + 10.072 \quad (1.3)$$

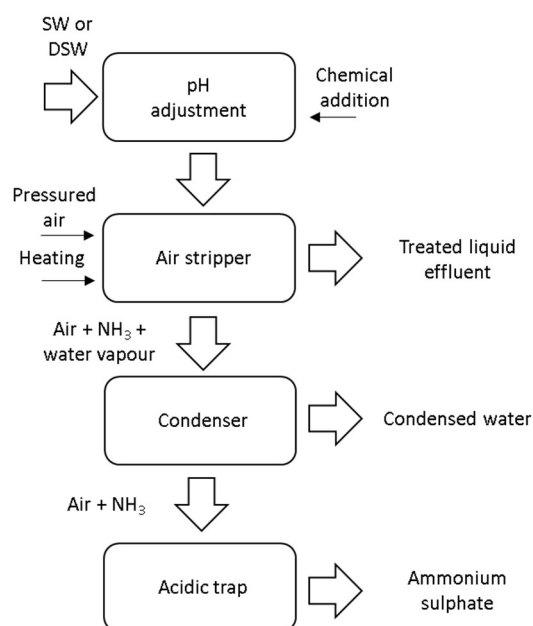
where  $[NH_3]$  is the molecular ammonia concentration [ $mol L^{-1}$ ],  $[NH_3 + NH_4^+]$  is the total ammonia nitrogen (TAN) concentration [ $mol L^{-1}$ ],  $[H^+]$  is the hydrogen ion concentration [ $mol L^{-1}$ ],  $K_a$  is the acid ionization constant, and  $T$  is the temperature [ $^{\circ}C$ ] (Tchobanoglous and Burton, 2003);  $pK_a$  is equal to  $-\log_{10}(K_a)$  [dimensionless]. If the pH is acidic, neutral, or slightly alkaline ( $< 8.0-8.5$ ), the equilibrium reaction shown in the Equation (1.1) is displaced to the right, while, if pH increases ( $> 8.5$ ), the formation of molecular ammonia is enhanced (Table 1.2) (El-Gohary and Kamel, 2016; Guštin and Marinšek-Logar, 2011; Karri et al., 2018; Tchobanoglous and Burton, 2003).

**Table 1.2.** Effects of variations of parameters on air stripping system.

Parameter	Variation	Effect on Air Stripping
pH	↑	↑
Temperature	↑	↑
Air flow rate	↑	↑

A scheme of the air stripping process is shown in Figure 1.1. As the aim of the treatment is the removal of ammonia nitrogen compounds (both the ionic and molecular forms) from the SW, the pH

increase over a certain threshold allows the conversion of almost all the content of  $\text{NH}_4^+$  into the gaseous form,  $\text{NH}_3$ . Hence, the first step of the process generally consists of the addition of an alkali solution to the raw SW, in order to increase its pH. Then, in the second unit, the mass transfer of  $\text{NH}_3$  from SW is enhanced by the aeration that alters the air–liquid boundary (Karri et al., 2018). Temperature plays an important effect on the removal of molecular ammonia from wastewater, since the solubility of ammonia in water, according to Henry’s law, is governed by the temperature as well as by solute and solvent amounts (Kinidi et al., 2018; Quan et al., 2009; Sengupta et al., 2015; Tchobanoglous and Burton, 2003). Heating wastewater enhances the diffusion of the ammonia molecules to the surface of the solution, and then to the atmosphere (Karri et al., 2018). In the case of air stripping, the  $\text{NH}_3$  transfer from wastewater to the air is facilitated by the air bubbles. Besides the pH and temperature, the AFR is another important parameter that influences the removal rates (mass transfer) of ammonia from SW, as it establishes a high gradient of ammonia concentration between the liquid and air phases (Bonmatí and Flotats, 2003; Kinidi et al., 2018). This process is known as ‘diffusion’: the molecules (free ammonia in this case) spontaneously mix an, moving from regions of relatively high concentration into regions of lower concentration (Cussler, 2007), blowing air in the SW. Therefore, the transfer of ammonia from the wastewater is strongly improved by the air flow. The water vapour stripped by the air flow is generally collected into a third unit (condenser), while the gaseous ammonia flows into the last unit (trap), containing an acidic solution (generally  $\text{H}_2\text{SO}_4$ ), where the ammonia nitrogen is recovered as salt.



**Figure 1.1.** Scheme of the air stripping process and recovery of ammonium sulphate as by-product (SW = swine wastewater; DSW = digested swine wastewater).



Typical literature values of the parameters influencing air stripping are pH between 10.0 and 11.0, temperature up to 80 °C, and air flow rate from 0.5 to 10 L L<sup>-1</sup> min<sup>-1</sup>.

### *1.2.2. Processes of Nutrient Recovery and Alternative Schemes of Air Stripping Although*

Although air stripping theoretically is an efficient method to remove ammonia from wastewater, this process shows some drawbacks, such as the fouling of the ammonia stripping tower, production of sludge, and release of ammonia gas (Kinidi et al., 2018). Fouling of stripping tower is usually due to the to the formation of salts (e.g., calcium carbonate) that scale the surface of the packing materials (Kinidi et al., 2018), but also to the presence of suspended solids. The preliminary phase of solid–liquid separation is extremely important to avoid this problem, as most of the suspended solids can be retained in the solid fraction after separation (Vaneekhaute et al., 2017). Moreover, the high cost of the air stripping process may limit its application in the future (Mehta et al., 2015).

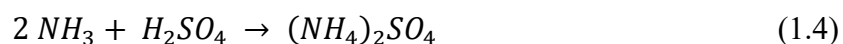
Chemicals, such as alkalis for raising up the pH of the treated wastewater over 9.5 (Mehta et al., 2015) and acids for lowering the pH of the post-stripping sludge, are needed during air stripping. This need is another issue of the process (Sengupta et al., 2015), since alkalis (such as lime, NaOH, or Ca(OH)<sub>2</sub>) are quite cheap, but high doses can increase the overall cost of air stripping (Hidalgo et al., 2016). For this reason, the pH optimisation is advised to balance the efficiency and cost of the process (Kinidi et al., 2018). On the other hand, the effect of the different alkali type on the ammonia removal efficiency is not significant (Markou et al., 2017). The pH adjustment may be necessary to meet the required limits for the disposal of the treated wastewater in sewage or water bodies, thus increasing the treatment costs (Kinidi et al., 2018). The latter can be increased, when pre-heating (in the case of high-temperature process, sometime close to 80 °C (Saracco and Genon, 1994)) and/or high aeration rates (up to 10 L<sub>air</sub> L<sub>wastewater</sub><sup>-1</sup> min<sup>-1</sup>) are required, to fasten the process (Mehta et al., 2015).

Besides the process cost, the emission of the stripped ammonia to the atmosphere is a serious environmental issue (Kinidi et al., 2018). For this reason, the ammonia adsorption after air stripping allows its conversion in the form of salt and this prevents the direct release of the ammonia into the environment (Kinidi et al., 2018). This is a sustainable option for the valorisation of nitrogen in wastewater (Laureni et al., 2013), since, as mentioned above, the recovered ammonium sulphate is marketable as fertiliser in agriculture. This option is one of the main advantages of air stripping, as detailed below. However, the ammonia concentration in the wastewater is another important factor affecting air stripping efficiency. In order to ensure a high concentration gradient for ammonia diffusion, aeration should be increased with increasingly high ammonia concentration (Karri et al., 2018) (thus increasing the energy cost). Air stripping of wastewater with low ammonia concentration

(less than  $2 \text{ g L}^{-1}$ ) is not economically sustainable (Mehta et al., 2015; Perera et al., 2019). The production of the fertiliser obtained by air stripping (ammonium sulphate) strictly depends on the concentration of ammonia in wastewater (the recovery of the ammonia salt is explained in the following Subsection 1.2.2.1.). Therefore, a limited production of marketable fertiliser makes the process not economically convenient.

#### 1.2.2.1. Ammonium Sulphate Recovery by Air Stripping Ammonium

Ammonium sulphate can be simply recovered by an adsorbing unit (acidic trap) immediately after the gas stripping phase (Desloover et al., 2012; Luther et al., 2015; Perera et al., 2019; Saracco and Genon, 1994) (Figure 1.1). The amount of ammonium sulphate recovered can be determined by the stoichiometric Equation (1.4):



In this equation, it is hypothesized that the ammonium ions in the wastewater sample are totally converted to ammonia gas. The Gibbs' free energy of formation ( $\Delta_f G^0$ ) under standard conditions (pH = 7 and  $25 \text{ }^\circ\text{C}$ ) of the ammonium sulphate is  $-596.52 \text{ kJ mol}^{-1}$ . Since the Gibbs' free energy is negative, the product formation in the Equation (1.4) is spontaneous. The production of the ammonium sulphate not only allows the recovery of nitrogen, but also makes sulphur available as macronutrient. The products recovered by the acidic trap generally include ammonium sulphate, concentrated ammonia solution, or other ammonia salts, such as ammonium nitrate (Mehta et al., 2015). Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) results from the reaction between  $\text{NH}_3$  and nitric acid and  $\text{HNO}_3$  (Sigurnjak et al., 2019), according to the following reaction (Equation (1.5)) (Speight, 2017):



As for the ammonium sulphate, this is a spontaneous reaction ( $\Delta_f G^0 = -53.88 \text{ kJ mol}^{-1}$ ).

High quality and/or purity of these products should be ensured for reaching the market standards (Vaneckhaute et al., 2017). In the case of nitrogen recovery by air stripping, the use of sulphuric acid of high quality is sufficient to recover high purity by-products (Vaneckhaute et al., 2017). The amount of sulphuric acid required affects the S concentration in the salt; salt pH can largely vary from about 3.0 to 7.5 (Sigurnjak et al., 2019). In general, low values of pH may lead to corrosion of

machinery, leaf burning, and soil acidification in case of long-term application (Vaneekhaute et al., 2013), while high pH may cause  $\text{NH}_3$  volatilisation during the fertilisation (Sigurnjak et al., 2019).

The acidic trap usually consists of a packed tower, in which the acid is sprayed by nozzles over the packing material and ammonia-enriched air is blown into the tower in counter current. At the real scale, the result is a concentrated solution of ammonium sulphate (with salt concentration of about 30%) marketed as liquid fertiliser at 90 to 120 €  $\text{ton}^{-1}$  (Vaneekhaute, 2015; Vaneekhaute et al., 2017, 2013). This price is lower compared to the cost of crystallised ammonium sulphate (about 140 €  $\text{ton}^{-1}$  (“Ammonium Sulfate Prices | Historical & Current | Intratec.us,” 2020, “SE Asia Ammonium Sulphate | Fertilizerworks.com,” 2020)), since the market price mainly depends on the particle size of the salt (GEA Messo PT, 2010; Vaneekhaute et al., 2017). The difficulty to obtain large-sized ammonium sulphate is mainly due to the construction, operational, and maintenance costs of the crystalliser vessel. Producing small-sized (about 0.4–1.0 mm) crystals of ammonium sulphate is more sustainable, compared to higher sizes (up to 2.6 mm), in terms of initial capital cost, energy requirement, and plant management (GEA Messo PT, 2010). In order to evaluate the purity of the produced ammonium sulphate, some physico-chemical analyses are required. In particular, the melting point of the salt should be equal to 240 °C and the nitrogen and sulphur content should be equal to 20% and 24%, respectively (Kandil et al., 2017). Nitrogen is determined by Kjeldahl method, while sulphur by gravimetric determination. However, ammonium sulphate produced from wastewater may show organic contamination (impurities), which affects the quality and the value as fertiliser (Laureni et al., 2013). In this case, biofilters can be used as a supplementary treatment to control volatile organic matter presence (Bonmatí and Flotats, 2003). On the other hand, impurities (such as aluminium sulphate) were found to increase the crystallisation kinetics and size of the produced ammonium sulphate (Rauls et al., 2000). This was probably due to the different adsorption equilibria of the impurities on the crystal. Hence, the control of impurity concentrations may lead to the optimisation of crystal size and quality (Rauls et al., 2000). Also the concentrated ammonia solution (under non-crystallised form) is marketed, because the technical and economic sustainability of ammonium sulphate production under granular form has not been extensively investigated (Vaneekhaute et al., 2017). On the other hand, the higher nitrogen concentration in the salt reduces the transport costs of these products compared to the animal manure (Sigurnjak et al., 2019).

The ammonium sulphate can replace the synthetic fertilisers, since it is rich in nitrogen and sulphur, which are crop macronutrients (Vaneekhaute et al., 2017, 2013); this compound is particularly recommended for soils with alkaline or neutral reaction (Kinidi et al., 2018; Macura et

al., 2019). However, nitrogen recovery by air stripping or other treatments is more expensive than the production of synthetic ammonia fertiliser. The latter product is obtained by the well-consolidated Haber–Bosch process (Mehta et al., 2015). The energy requirement of this process is around 10 kWh kg<sup>-1</sup> (Luther et al., 2015; Maurer et al., 2003), which is practically equal to the value of the air stripping process (9 kWh kg<sup>-1</sup> of nitrogen) (Desloover et al., 2012; Maurer et al., 2003; Perera et al., 2019).

The ammonium sulphate can be recovered from raw wastewater and digestate from anaerobic digestion, thanks to the release of nutrients in soluble form (e.g., N–NH<sub>4</sub><sup>+</sup>, P–PO<sub>4</sub><sup>3-</sup>, and K–K<sup>+</sup>) during the anaerobic biodegradation (Mehta et al., 2015). However, the digestate from animal manure can be subjected to the strict regulation for fertilisers issued by some countries, such as the European Union. Under this point of view, processing of digestate for nutrient recovery can comply with these regulation constraints, and this turns the SW disposal problem into an economic opportunity (Vaneckhaute et al., 2017). It must be pointed out that the utilisation of ammonium sulphate from animal manure is also often officially regulated (e.g., 170 kg of nitrogen ha<sup>-1</sup> yr<sup>-1</sup>) according to the “Nitrate Directive” for the EU’s countries (91/676/CEE) (European Union, 1991; Sigurnjak et al., 2019).

In the United States, the standards for agricultural waste management are reported in the National Handbook of Conservation Practice Standards (CNMPs)(USDA-NRCS, 2020), drafted in accordance with the conservation planning policies of the US Natural Resources Conservation Service (NRCS) and the guidance of the Environmental Protection Agency (EPA). Moreover, the following important standards Conservation Practice Standards (CPS), that define the minimum level of quality by which these practices are planned, operated, and maintained, are shown in the Agricultural Waste Management Field Handbook (USDA-NRCS, 2009): Nutrient Management (Code 590); Amendments for the Treatment of Agricultural Waste (Code 591); Waste Treatment (Code 629); Waste Utilization (Code 633).

With regards to Latin America, every country establishes its own regulations. For instance, prevention for water pollution in Bolivia is regulated by the Law 1333 (Latin American Energy Policies, 1992), while in Argentina, the protection of water quality and control of pollution are regulated by the Decree 674/89 and 776/92. In general, most of the countries of Latin America adopt regulations based on the EPA’s guidelines (Hernández-Padilla et al., 2017).

In Asian countries, e.g., China, the development of intensive farming required supply of nutrients in livestock manure; the uncontrolled discharge of manure waste, including SW, into the environment

was facilitated by the diversity of regulations adopted by the different cities (Q. Wang et al., 2017). The allowed ammonium concentration discharge is regulated by the Discharge Standard of Water Pollutant for Ammonia Industry (GB 13458–2001) (Li et al., 2012; Ministry of Ecology and Environment and The People's Republic of China, 2013). However, economic aspects may limit the diffusion of these technologies (Li et al., 2012).

The agronomic effects of the ammonium sulphate produced by air stripping and used as soil fertiliser must be compared to the same product synthesised by the industry. In this regard, the literature complains unsatisfactory results, as more attention has been paid to the recovery technologies (Sigurnjak et al., 2019) than to the quality and agronomic effects of recovered nutrients. Szymanska et al. (Szymanska et al., 2019) carried out an experiment in pots on maize and grass in silty loam and loamy sand soils. Compared to soil without fertilisation, these authors found crop yields under the recovered fertiliser (88% and 73% for maize and grass, respectively) that were similar as the yields under the commercial products (125% and 94%, respectively) regardless of the type of soil. Similar results were obtained by Sigurnjak et al. (2019) in terms of fertilising effects of ammonium sulphate compared to the synthetic nitrogen fertilisers. Moreover, this study showed that the nitrogen in the recovered ammonium sulphate is entirely under the mineral form (100% as  $\text{NH}_4^+$ -N), such as the synthetic nitrogen fertiliser. The absence of phosphorous in ammonium sulphate can be considered a positive aspect, because the nitrogen requirements of crops can be satisfied without exceeding the phosphorous application rates (Sigurnjak et al., 2019). The results obtained in the literature suggest that the ammonium sulphate recovered in bio-refinery can replace the industrial ammonium sulphate used as fertiliser in crop cultivation with evident economic and environmental benefits (Sigurnjak et al., 2019; Szymanska et al., 2019).

#### 1.2.2.2. Air Stripping Applications in Literature

Some applications of air stripping at full scale have been found in the literature (Table 1.3). The systems shown in Table 1.3 were applied to different waste streams (such as digestate, industrial wastewater, manure) and with different schemes for ammonia nitrogen recovery. Air stripping columns and packed tower are the most common configurations used for the treatment of air streams (such as acidic gases, alcohols, or solvents). In EU countries, companies propose their own patented systems that are more specifically addressed to the treatment of digestate from anaerobic digestion plant and to the recovery of ammonia as fertiliser. For instance, the AMFER® system has been used as pre-treatment of N-rich manure before the anaerobic digestion, thus increasing the capacity of feeding co-substrates to digesters; RECOV'AMMONIA™ ensures removal efficiencies over 90%.

Nitrogen removal systems in Asian countries (e.g., China) are rarely implemented, in spite of the continuous growth of animal farms (especially chicken) and anaerobic digestion plants for treating manure (Fuchs et al., 2018).

Full-scale stripping processes (extensively described in Vaneckhaute et al., 2017) have been also developed without internal packing. Some of these technologies can even work with relatively high suspended solids or without chemicals addition, giving a higher sustainability under both economic and environmental points of view (Vaneckhaute et al., 2017). The removal efficiency of these systems generally does not exceed 90% (although they are theoretically designed for a total removal), to reduce the operating costs (Vaneckhaute et al., 2017). On the other hand, a value of 90% of ammonia reduction in the effluent is generally considered acceptable.

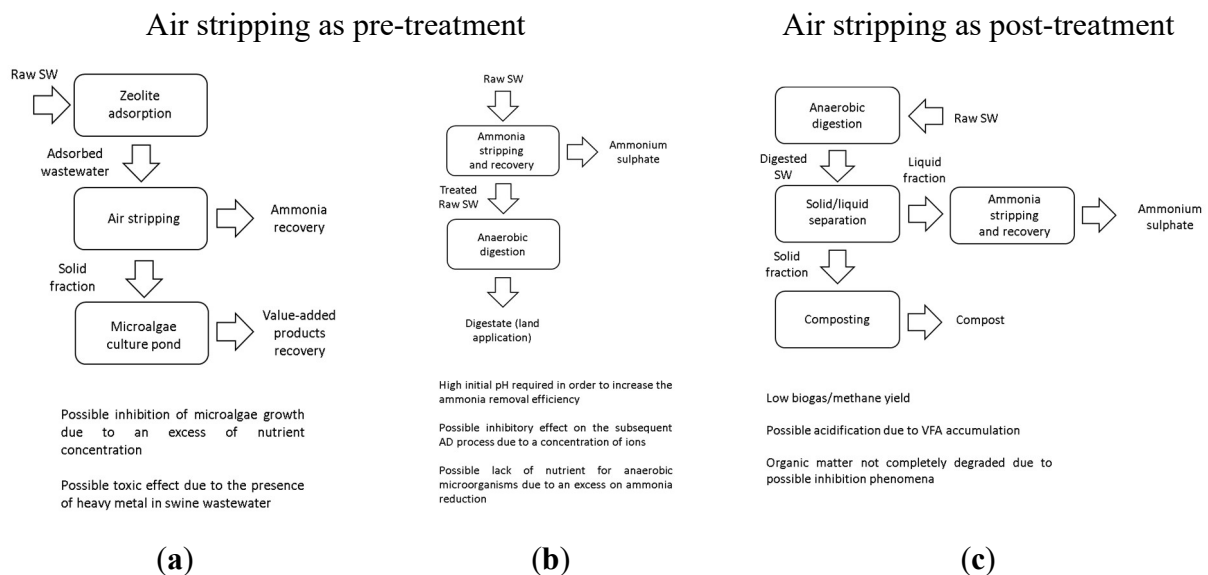
Several experiences with advanced air stripping have been carried out at the laboratory scale, employing schemes and technologies that could be used in future full-scale applications. The volume of the stripping unit at lab-scale ranges from 0.75 to 5 L (Ata et al., 2016; Bonmatí and Flotats, 2003; Cao et al., 2019b). Complex air stripping schemes have been developed, in order to overcome the operational problems previously mentioned and increase the ammonia removal efficiency. For example, the use of vacuum can facilitate the gas stripping (Ippersiel et al., 2012; Tao et al., 2018; Ukwuani and Tao, 2016), as vacuum lowers the boiling point of the liquid.

Different schemes have been developed to overcome the fouling problems of the packed towers for large-scale wastewater treatment (Sengupta et al., 2015). A water-sparged aerocyclone was proposed by Quan et al. (2009); the aerocyclone was more efficient compared to the traditional system in terms of energy saving and removal efficiency. A jet loop reactor configuration was used by Değermenci et al. (2012) to minimise the aeration energy requirement, since the mass transfer capability of this reactor was higher than other reactor types, even if less air was supplied, due to the high internal mixing and larger contact area. Yuan et al. (2016) used a continuous-flow rotating packed bed at lab- and pilot-scale at room temperature; this system was able to maximise the ammonia removal efficiency and reduce the treatment time.

**Table 1.3.** Examples of full-scale applications or constructors of air stripping systems in EU, USA, and Asia.

Country	Constructor/ Plant Site	Type of Wastewater	Systems/Applications
USA	Branch Environmental Corporation (Branch Environmentl Corp.)	Industrial wastewater	<u>Closed loop system</u> The discharged air is treated with an acid wash to form a salt from the ammonia and the air is reused in the stripper. Capacities up to 681 m <sup>3</sup> h <sup>-1</sup>
			<u>Air Stripping Columns</u> Used for relatively highly volatile organic compounds (VOC) in a liquid stream. VOCs evaporate by flowing and mixing the water using an air flow.
			<u>Packed Towers</u> Used for the absorption of a variety of gases and solvents, such as acidic gas, alcohol and ammonia.
EU	Colsen (The Netherlands) (Colsen)	Digestate Manure Highly polluted wastewater	<u>AMFER<sup>®</sup></u> Nitrogen recovery from waste and wastewater flows with high levels of ammonium. No need of de-watering or of pre-treatment of the waste flow. It consists of just one process step. CO <sub>2</sub> and NH <sub>3</sub> are successively removed from the substrate in a stripping column. The stripping air is passed through a gas scrubber, where ammonium sulphate or ammonium nitrate is produced.
	GNS (Röblingen am See, DE) (GNS)	Digestate	<u>ANAStrip<sup>®</sup> plant</u> Removal equal to 65% of the total nitrogen in the mineral fertilisers; recovery of calcium carbonate; recovery of heat from the process. Technical operational process: Digestate input [m <sup>3</sup> h <sup>-1</sup> ]: 5.5–12.6; NH <sub>4</sub> <sup>+</sup> -N [g L <sup>-1</sup> ]: 3–6; Ammonium sulphate output [t d <sup>-1</sup> ]: 13–27; Calcium carbonate output [t d <sup>-1</sup> ]: 4–8
	CMI Europe Environnement (France) (CMI Europe Environnement)	Digestate Polluted liquid waste	<u>RECOV'AMMONIA<sup>TM</sup></u> Removal efficiency: > 92%; Technical operational process: Pollutants: NH <sub>4</sub> <sup>+</sup> at 2,4 g L <sup>-1</sup> for a 102 kg h <sup>-1</sup> flow; Liquid flow: 42 m <sup>3</sup> h <sup>-1</sup> at 60°C and pH = 9; Process gas flow: 80,000 m <sup>3</sup> h <sup>-1</sup>
Asia	DQY biogas project (Beijing, China)	Raw manure	Recovery of ammonia before anaerobic digestion plant treating 100% chicken manure (Chen et al., 2017)

Biological treatments are often used in combination with air stripping (Figure 1.2). An aerobic treatment was used by Alitalo et al. (2012) to increase the pH of pig slurry without chemical addition, and the combined process removed over 30% of ammonia. The temperature was in the mesophilic range (35–37 °C) and chemicals (MgO and Ca(OH)<sub>2</sub>) were added in the subsequent stripping cycles, raising the ammonia removal efficiency up to 86%. Aerobic species generally able to treat swine wastewater are *Bacillus amyloliquefaciens*, *Bacillus cereus*, *Pseudomonas sp.*, *Paenibacillus sp.*, and uncultured *Actinobacteria* bacterium (Cai et al., 2015). In a study of Yang et al. (2004), the air stripping was used to increase acidogenesis as first stage for the subsequent methanogenesis in a two-stage anaerobic digestion system. In fact, acidogens play the primary role in producing major substrates for methanogens (Yang et al., 2004).



**Figure 1.2.** Schemes and limitations of air stripping (a) coupled with microalgae cultivation system (adapted from Cao et al., 2018), (b) as pre-treatment and (c) as post-treatment of anaerobic digestion (SW = swine wastewater; AD = anaerobic digestion).

Air stripping has been well integrated in bio-energy production systems, as this process can be applied on digestate after biogas production (thus for biofuel and/or heat production) from organic waste or as treatment prior to the anaerobic digestion (Figure 1.2). As a matter of fact, air stripping enhances methane yield, apart from being cost-effective for ammonia removal (Kinidi et al., 2018). When air stripping is used as pre-treatment of anaerobic digestion, the main purpose is the removal of ammonia compounds that can inhibit the methanogenic activity. In this case, the dose and type of alkalis for initial pH adjustment of SW should be appropriately evaluated, in order to avoid possible inhibition of the anaerobic digestion due to cationic toxicity (Zhang and Jahng, 2010) or to an

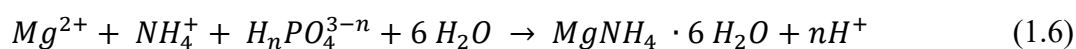


excessive nitrogen removal. The anaerobic digestion of raw SW, in addition to the difficulties mentioned above, may lead to the production of a digestate containing organic residues and ammonia compounds. Hence, a further biological (aerated) process is generally required to allow the use of the digestate as soil conditioner. To overcome this issue, air stripping can also be applied as post-treatment of anaerobic digestion to reduce the nitrogen and organic concentrations in the digestate. The stripped ammonia from both configurations (that is, from raw and digested SW) can be recovered as ammonium sulphate.

Moreover, anaerobic digestion is another way to recover carbon (generally expressed in terms of chemical oxygen demand, COD) from swine wastewater, since the biodegradable carbon can be decomposed by microorganisms (Cheng et al., 2020). However, as previously mentioned, the theoretical methane yield (about 380 mL gCOD<sup>-1</sup>, Heidrich et al. (2011), corresponding to a complete conversion of COD), cannot be achieved due to the presence of inhibiting ammonia compounds. When air stripping is coupled with anaerobic digestion (Figure 1.2b,c), relatively high temperatures (up to 60 °C) can be more easily achieved using the excess heat of the combined heat and power plant (Bousek et al., 2016) or recovering heat from flue gas in conventional schemes of electric generation. The reduction of the area required for the application of nitrogen-rich digestate after the biogas production and the possibility to treat the air stripped digestate in the wastewater plant are other advantages of the combined system AS/AD (Guštin and Marinšek-Logar, 2011). The main bacteria in the anaerobic process are hydrogenotrophic *Methanocorpusculum*, acetoclastic *Methanosaeta* (Jiang et al., 2020), *Methanobacteria*, and *Methanocorpusculum* (Wang et al., 2019). *Clostridia* are generally the most abundant bacteria for hydrolysis and fermentation as they can tolerate high concentrations of volatile fatty acids (Jiang et al., 2019; Wang et al., 2019), while the *Bacilli* class easily produces acetate and lactate (Jiang et al., 2020). Schröder et al. (2007) used the liquid fraction of the digestate to recover phosphorous and nitrogen by struvite precipitation; then, the effluent was used for the production of ammonium sulphate by air stripping. These combined systems allowed the nearly total recovery of nutrients. By struvite precipitation, up to 90% of soluble phosphates was removed, but only less than 30% of ammonia was recovered (Le Corre et al., 2009), due to the equimolar stoichiometry required for the chemical precipitation of struvite (Mehta et al., 2015). The residual ammonia in soluble form can be potentially recovered by subsequent air stripping.

Struvite (magnesium ammonium phosphate hexahydrate, MgNH<sub>4</sub>PO<sub>4</sub>) can be produced by chemical precipitation, which is a common method to recover phosphorous from wastewater. To facilitate the precipitation of struvite, the addition of Mg compounds (such as MgO or MgCl<sub>2</sub>) and

caustic soda (to increase the pH up to 10) is needed (Vaneekhaute et al., 2017). Struvite precipitates in a 1:1:1 molar ratio following the general Equation (1.6) (Le Corre et al., 2009):



with  $n = 0, 1, \text{ or } 2$ . Gibbs' free energy of formation is about  $3060.74 \text{ kJ mol}^{-1}$  (Iglesia, 2009). By the crystallisation process, over 90% of the phosphorous in wastewater can be recovered as struvite and approximately half as much nitrogen (Rahman et al., 2014), because struvite contains approximately 0.5 kg of nitrogen per kg of phosphorous (Macura et al., 2019).

The scheme generally used for struvite crystallisation consists of fluidized bed or continuously stirred tank reactors (Vaneekhaute et al., 2017). Stirring facilitates the mixing of the solution and the formation of crystals (Le Corre et al., 2009). However, the presence of other inorganic ions, such as  $Ca^{2+}$  and  $CO_3^{2-}$ , naturally present in SW, may complicate the precipitation of struvite by producing various mineral species (Ye et al., 2011). Calcium ions can interact with carbonate ions to form calcite ( $CaCO_3$ ) according to the Equation (1.7) (Le Corre et al., 2009):



Gibbs' free energy is equal to  $-1129.1 \text{ kJ mol}^{-1}$ . The chemical composition of struvite derives from its stoichiometric formula and thus its chemical characteristics are always the same. However, its production—with particular regard to purity and cristallisation operation—is influenced by the process conditions, such as the raw magnesium compounds added (such as MgO or  $MgCl_2$ ), temperature as well as other inorganic ions (e.g., calcium and sodium) and caustic soda present in the alkalis used to increase pH. Microwave radiation technique is also able to improve the ammonia removal during air stripping, by decreasing the reaction time and activation energy. In a study carried out by Ata et al. (2016), the ammonia removal efficiency of microwave-assisted air stripping was 25% higher compared to the conventional heating in air stripping; microwave radiation allows high mass transfer rate of ammonia. Conversely, the effect of aeration was less significant in ammonia removal, while pH, radiation time, and power value strongly affected the overall efficiency of the system (La et al., 2014).

### **1.3. Effect of Air Stripping on Raw SW**

#### *1.3.1. Characteristics of Swine Wastewater Swine*

Swine wastewater consists of a mixture of urine, faeces, water spillage, residues of undigested food, antibiotic residues, and pathogenic microorganisms (Cheng et al., 2017; Viancelli et al., 2013; Wu et al., 2015; Zhang and Jahng, 2010). Total solids (TS), volatile solids (VS), and chemical oxygen demand (COD) are generally much lower than in raw manure, due to the slurry dilution with washing water (Cai et al., 2015). The physico-chemical parameters of SW show large fluctuations (Table 1.4), mainly due to the variability of the pigpen management practices (Cheng et al., 2000; Kim et al., 2004). Raw SW is generally alkaline (pH of 7.0–7.5), less often slightly acidic. TS content is usually in the range 2–8 g L<sup>-1</sup>, despite some outliers (Table 1.4). Ammonia nitrogen is generally high (2–10 g L<sup>-1</sup>), while phosphorous content is usually low (0.05–0.13 PO<sub>4</sub><sup>3-</sup> - P g L<sup>-1</sup> (D. Zhang et al., 2012)).

Prior to its direct discharge into the environment or common depuration treatments, SW is generally subjected to physical processes, to reduce its polluting potential.

These physical processes mainly consist of:

- homogeneous mixing (Deng et al., 2014; Huang et al., 2016; Kim et al., 2013, 2012; Yang et al., 2004);
- solid–liquid separation by settlement (Cattaneo et al., 2019; Laurenzi et al., 2013; Yang et al., 2016; Zhai et al., 2017);
- sieving and filtration using filters with variable mesh, from 30 µm to 8 mm, to remove straw, coarse particles, suspended solids, or large-sized materials (e.g., stones, bedding material) (Cao et al., 2018, 2019b; Girault et al., 2011; Huang et al., 2015, 2017; Laurenzi et al., 2013; Safavi and Unnthorsson, 2017; Wu et al., 2015; Yang et al., 2004; Zhang and Jahng, 2010).

However, despite these preliminary treatments, SW still contains high concentrations of ammonia compounds and COD, very often over the limits for wastewater disposal (D. Zhang et al., 2012). In particular, the ammonia nitrogen is soluble and, as a consequence, its concentration in the liquid fraction may increase after filtration (Bonmatí and Flotats, 2003). As mentioned above, the very high concentrations of nitrogen and COD in SW have negative impacts on the environment in the case of disposal without proper treatments.

**Table 1.4.** Summary of the main physico-chemical characteristics of raw swine wastewater (SW) studied in literature.

SW	pH [-]	TS [%]	VS [%TS]	NH <sub>4</sub> <sup>+</sup> -N [gN L <sup>-1</sup> ]	NH <sub>3</sub> -N [gN L <sup>-1</sup> ]	TAN [gN L <sup>-1</sup> ]	TN [gN L <sup>-1</sup> ]	COD <sub>t</sub> [g L <sup>-1</sup> ]	COD <sub>s</sub> [g L <sup>-1</sup> ]	TP [g L <sup>-1</sup> ]	PO <sub>4</sub> <sup>3-</sup> - P [g L <sup>-1</sup> ]	Ref.	
Raw	7.4 ± 0.5	-	-	-	-	-	3.8 ± 0.2	50.9 ± 5.5	18.3 ± 3.0	-	-	Girault et al. (2011)	
	8.0 ± 0.1	4.2 ± 0.5 *	2.7 ± 0.3 *,**	-	2.2 ± 0.0	-	5.4 ± 0.0	69.4 ± 4.2	31.8 ± 2.4	-	-	Kim et al. (2012)	
	7.7 ± 0.1	7.9 ± 0.4 *	5.3 ± 0.3	-	6.6 ± 0.1	-	9.4 ± 0.2	155.5 ± 9.5	62.4 ± 5.7	-	-	Kim et al. (2013)	
	7.1 ± 0.1	-	-	0.892 ± 0.003	-	-	-	-	-	-	-	Zhai et al. (2017)	
	7.2 ± 0.1	-	-	0.599 ± 0.006	-	-	-	-	-	-	-	Zhai et al. (2017)	
	7.1 ± 0.0	-	-	0.346 ± 0.014	-	-	-	-	-	-	-	Zhai et al. (2017)	
	7.2	18.82 *	14.69 *	-	-	-	6.5	181.1	19.1	-	-	Auphimai et al. (2014)	
	7.3	-	0.50	-	1.8–2.0	0.004–	-	10.593	6.129–	-	-	Ho and Ho (2012)	
	7.7	-	0.52 *,**	-	-	0.01	-	13.220	7.010	-	-		
	7.8 ± 0.4	5.52 ± 1.47 *	3.62 ± 0.86 *,**	3.6 ± 1.7	-	-	7.3 ± 1.9	86.4 ± 18.6	-	-	-	Kim et al. (2012)	
	-	-	-	-	1.207 ± 0.111	±	2.023 ± 0.154	22.929 ± 889	-	0.358 ± 0.033	-	-	Viancelli et al. (2013)
	-	-	-	-	0.603 ± 0.008	±	0.958 ± 0.005	8.375 ± 0.152	-	0.216 ± 0.004	-	-	Yang et al. (2016)
	6.18	7.21 ± 0.39	86.39 ± 0.24	1.021 ± 0.038	-	-	-	63.724 ± 6.061	-	-	-	-	Córdoba et al. (2016)

*Environmental and economic sustainability of swine wastewater treatments using ammonia stripping and anaerobic digestion. A short review*

SW	pH [-]	TS [%]	VS [%TS]	NH <sub>4</sub> <sup>+</sup> -N [gN L <sup>-1</sup> ]	NH <sub>3</sub> -N [gN L <sup>-1</sup> ]	TAN [gN L <sup>-1</sup> ]	TN [gN L <sup>-1</sup> ]	COD <sub>t</sub> [g L <sup>-1</sup> ]	COD <sub>s</sub> [g L <sup>-1</sup> ]	TP [g L <sup>-1</sup> ]	PO <sub>4</sub> <sup>3-</sup> -P [g L <sup>-1</sup> ]	Ref.
	6.15	5.57 ± 0.66	4.60 ± 0.66	-	-	1.959 ± 0.05	-	56.109 ± 3.794	-	-	-	Córdoba et al. (2018)
	7.5	5.29 *	3.52 *,**	3.39 *	-	-	5.63 *	70.59*	-	-	-	Bonmatí and Flotats (2003)
	6.64	5.95 *	3.89 *,**	4.95	-	-	7.6	94.2	54.2	-	-	L. Zhang et al. (2012)
	6.75 ± 0.18	2.5 ± 0.18	63.0 ± 2.28	2.26 *	-	-	3.93 *	-	-	0.371 ± 0.043*	-	Cattaneo et al. (2019)
	7.60 ± 0.15	-	-	0.599 ± 0.014	-	-	0.798 ± 0.023	2.383 ± 0.065	-	0.043 ± 0.00031	-	Cao et al. (2018)
	7.3 ± 0.5	2.04 ± 0.29 *	1.46 ± 0.17 *,**	2.7 ± 0.1	-	-	3.2 ± 0.1 2.7	25.2 ± 4.1	-	-	-	Belmonte et al. (2011)
	8.6 ± 0.1	37.1 ± 0.2	77.6 ± 0.2	-	-	10.6 ± 0.3 ***	29.8 ± 1.5 *****	-	-	-	-	Huang et al. (2016)
	6.64	5.95	3.89 **	-	4.95	-	7.6	94.2	54.2	-	-	Zhang and Jahng (2010)
	7.57 ± 0.03	-	-	0.612 ± 0.00814	-	-	0.724 ± 0.009	4.960 ± 0.106	-	0.0614 ± 0.00065	-	Cao et al. (2019b)
	8.11– 8.27	-	-	1.013– 1.426	-	-	1.381– 2.001	5.338– 7.065	-	0.0893– 0.1894	0.0551– 0.1397	D. Zhang et al. (2012)
	8.02 ± 0.11	-	-	-	2.74 ± 0.017	-	3.054 ± 0.019	23.82 ± 2.59	10.87 ± 0.41	0.527 ± 0.067	-	La et al. (2014)
	7.7 ± 0.05	-	-	-	-	0.730 ± 0.051	-	3.532 ± 0.231	-	-	-	Huang et al. (2017)
<b>Filtered</b>	7.66	0.54	55	0.993	-	-	1.180	3.625	-	-	-	Laureni et al. (2013)

SW	pH [-]	TS [%]	VS [%TS]	NH <sub>4</sub> <sup>+</sup> -N [gN L <sup>-1</sup> ]	NH <sub>3</sub> -N [gN L <sup>-1</sup> ]	TAN [gN L <sup>-1</sup> ]	TN [gN L <sup>-1</sup> ]	COD <sub>t</sub> [g L <sup>-1</sup> ]	COD <sub>s</sub> [g L <sup>-1</sup> ]	TP [g L <sup>-1</sup> ]	PO <sub>4</sub> <sup>3-</sup> - P [g L <sup>-1</sup> ]	Ref.
	7.65	1.06	55	1.298	-	-	1.636	9.579	-	-	-	Laureni et al. (2013)
	7.6	5.04	70	4.197	-	-	5.564	86.569	-	-	-	Laureni et al. (2013)
	7.61	5.19	61	6.708	-	-	8.349	77.886	-	-	-	Laureni et al. (2013)
	-	-	-	-	-	4.0	-	-	-	-	-	Yang et al. (2004)
	7.7 ± 0.2	-	-	-	-	0.378 ± 0.024	-	2.756 ± 0.184	-	0.105 ± 0.0084	-	Huang et al. (2015)
	6.6– 7.3	-	-	0.400– 0.600	-	-	-	3.500– 6.000	-	0.080– 0.110	-	Wu et al. (2015)
	-	3.93	73.62	-	-	-	-	28.000	-	-	-	Safavi and Unnthorsson (2017)

Notes: TS, VS = total and volatile solids, respectively; TAN = total ammonia nitrogen, TN = total nitrogen; COD<sub>t</sub>, COD<sub>s</sub> = total and soluble chemical oxygen demand, respectively; TP = total phosphorous; \* adapted data; \*\* on wet basis; \*\*\* g kg<sup>-1</sup> of VS.

### *1.3.2. Efficiency of Air Stripping on Raw SW*

A summary of literature data on AS of SW and the related conditions is reported in Table 1.5, while the ammonia removal efficiency for the different air stripping schemes used for SW is summarised in Figure 1.3. The effects of the operational parameters of air stripping on the ammonia removal efficiency are highly variable. In general, the highest rates of ammonia removal (over 90%) have been found at high temperatures (up to 80 °C) and/or pH (over 10.0) (Bonmatí and Flotats, 2003; Lei et al., 2007; Van der Heyden et al., 2015). The control of these parameters, however, makes the treatment expensive, also considering the high reaction time adopted (up to 48 h, L. Zhang et al., 2012).

Lime, caustic soda, and calcium hydroxide are commonly used for increasing pH, generally up to 10.0 or even more, since, starting from around 9.3, the dissolved ammonium is quantitatively transformed to ammonia gas (Sengupta et al., 2015). When pH was increased to 9.5, no significant differences in ammonia removal rates were found by Bonmatí and Flotats (2003) compared to the test without pH control; instead, higher removal efficiencies (in terms of nitrogen and COD) were detected when pH was corrected to 11.5. At this pH, high ammonia removal can be obtained even at lower temperatures (about 20 °C), but operational drawbacks are expected, due to the excess of alkalis (Liao et al., 1995). On the other hand, at lower pH values (typical of raw SW) ammonia can be completely removed, provided that air stripping is carried out at high temperature (80 °C) (Bonmatí and Flotats, 2003). The influence of the initial pH values on ammonia removal efficiency has been also reported by other studies: Zhang and Jahng (2010) obtained a removal efficiency of about 70% at mild temperature (37 °C) and air flow rate ( $1 L_{\text{air}} L_{\text{SW}}^{-1} \text{min}^{-1}$ ) and pH set at 10.0 in 24 h; increasing reaction time to 48 h and pH to 11, L. Zhang et al. (2012) showed a removal efficiency of 80%.

However, the highest ammonia reduction (92%) was observed at the highest air flow rate ( $10 L_{\text{air}} L_{\text{SW}}^{-1} \text{min}^{-1}$ ) and pH adjusted to 9.0. These results confirm the influence of the aeration rate on the ammonia removal rate (L. Zhang et al., 2012). Moreover, higher pH values improve the process kinetics, reducing the reaction time needed for a pre-set ammonia removal (Laureni et al., 2013).

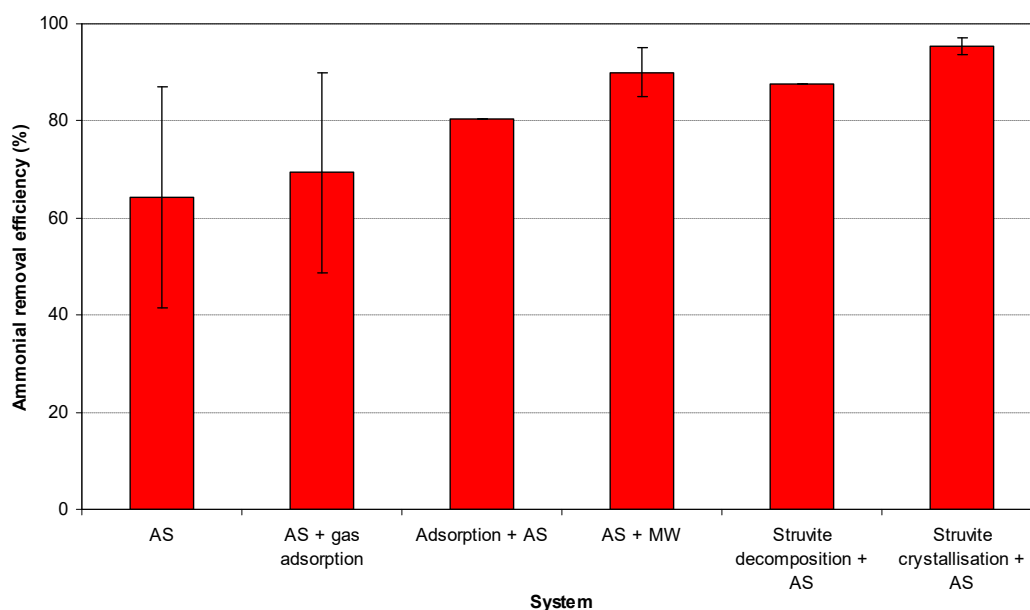
**Table 1.5.** Literature data about experimental tests of swine wastewater (SW) treatment using air stripping.

System	Notes	Chemical Addition	Adjusted pH	Temperature [°C]	Time [h]	Air Flow Rate [ $L_{air} L_{SW}^{-1} min^{-1}$ ]	Ammonia Removal Efficiency [%]	Ammonium Sulphate Recovery	Ref.	
AS	-	n.a.	11.5	22	7	30 *	90.3	No	Liao et al. (1995)	
			9.5	22	55	15 *	91.0			
			10.5	22	10	30 *	90.0			
			9.5	22	30	30 *	90.0			
	VFA production	NaOH	10.5	Room	1			25.0	No	Yang et al. (2004)
					2			40.0		
					6	15		62.5		
					24			70.0		
					48			77.5		
					96			80.0		
AS + AD	AD	NaOH	9.5				49.3*	No	Zhang and Jahng, (2010)	
			10.0				70.5 *			
			9.5	37	24	1.0 *	40.4 *			
	-	Ca(OH) <sub>2</sub>	None	10.0				71.3 *	No	Zhang and Jahng (2010)
				9.5				30.5 *		
				10.0				49.1 *		
				7.7				65		
-	Ca(OH) <sub>2</sub>	None	9.5	80	4	0.05 *	69	Yes	Bonmatí and Flotats (2003)	
			11.5				98.8			
-	-	NaOH	7.2	37	48	1.0	28.0	No		



System	Notes	Chemical Addition	Adjusted pH	Temperature [°C]	Time [h]	Air Flow Rate [L <sub>air</sub> L <sub>sw</sub> <sup>-1</sup> min <sup>-1</sup> ]	Ammonia Removal Efficiency [%]	Ammonium Sulphate Recovery	Ref.
AS + gas adsorption	-	(40% w/w) NaOH	9.0	37	48	1.0	47.0	No	L. Zhang et al. (2012)
			10.0				80.0		
			11.0				88.1		
	COD > 27 g L <sup>-1</sup>	None	-	50	3.75	10 *	46.0	Yes	L. Zhang et al. (2012)
							62.2		
							77.9		
COD < 10 g L <sup>-1</sup>	None	-	50	3.75	10 *	92.0	Yes	Laureni et al. (2013)	
						43.2–50.0			
AS + MW	Power = 700 W	NaOH	9.5	50	3.75	10 *	> 90	Yes	La et al. (2014)
							> 80		
Struvite decomposition + AS	97% phosphorous removal efficiency	NaOH	11.0	Not controlled	0.06 *	0	88.2	Yes	Huang et al. (2015)
						0.5 *	90.3		
Struvite crystallisation + AS	-	MgO	8.0–10.5	40–80	n.a.	800–4400 **	91.6	Yes	Huang et al. (2017)
							94.3		
Adsorption AS	Used for biomass production	n.a.	11.0	25	3	5	96.7	Yes	Cao et al. (2018)
							94.3		
Adsorption AS	+	n.a.	11.0	30	1	18.2 *	80.5	Yes	Cao et al. (2018)
							80.5		

Notes: AS = air stripping; AD = anaerobic digestion; MW = microwave radiation; VFA = very fatty acids; n.a. = not available; \* = adapted data; \*\* = gas – liquid volume ratio.



**Figure 1.3.** Summary of the ammonia removal efficiency (mean  $\pm$  std. dev.) data of the air stripping systems for raw swine wastewater (SW) reported in literature (AS = air stripping; MW = microwave radiation; AD = anaerobic digestion).

Increasing the pH from the natural value (about 7.0) to 11.0, the rate of ammonia removal increases nearly 8-fold (L. Zhang et al., 2012). At pH over 10.5, the ammonia removal efficiency is directly dependent upon the temperatures of the influent air and liquid (Bonmatí and Flotats, 2003; Liao et al., 1995). At this pH level (over 10.0) and room temperature, in a study by Yang et al. (Yang et al., 2004), more than 90 h were required to achieve 80% of ammonia removal with a high flow rate ( $15 \text{ L L}^{-1} \text{ min}^{-1}$ ). Conversely, about 65–70% of ammonia recovery was obtained at a lower pH (7.7–9.5) and temperature of  $80 \text{ }^\circ\text{C}$ , using a very low air flow rate ( $0.05 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$ ) in 4 h only (Bonmatí and Flotats, 2003).

The alkali type affects the process efficiency; in particular, sodium and potassium hydroxides allow higher ammonia removal rates compared to lime (Zhang and Jahng, 2010). The choice of the alkali type is particularly important when air stripping is used as a pre-treatment for SW before AD, as the excess of light metals ions (i.e., Ca or Na due to the solubilisation of salts) can inhibit the process. Changes in pH during air stripping are expected, because the temperature drives the chemical equilibrium among the reagents leading to a pH modification; for instance, the formation and accumulation of very fatty acids (VFA) can lead to a pH reduction (Bonmatí and Flotats, 2003). Moreover, pH can increase due to concentration of alkali solution caused by water evaporation (Bonmatí and Flotats, 2003).

As mentioned in Section 1.2.2.2., air stripping can be integrated with other processes, such as microwave radiation or chemical precipitation for recovering struvite. However, La et al. (2014) found that, in the integrated system air stripping plus microwave radiation, the effect of aeration was not significant in the removal efficiency of nitrogen, while the initial pH of the SW, radiation time, and applied power noticeably influenced this efficiency. Chemical precipitation is more often coupled with air stripping for the simultaneous recovery of nitrogen and phosphorous, allowing a high removal of nutrients. Huang et al. (2015) removed over 90% of total ammonia nitrogen and approximately 97% of total phosphorous by an integrated reactor. In a study of Huang et al. (2017), phosphate was first recovered by chemical precipitation, then the supernatant was subjected to air stripping for ammonia recovery. The best conditions allowing a reduction in ammonia of 94% in 3 h, consisted of an air flow rate of  $5 \text{ L L}^{-1} \text{ min}^{-1}$ , a dose of  $8 \text{ g L}^{-1}$  of MgO for pH adjustment (over 10.0), and a temperature of  $25 \text{ }^\circ\text{C}$ .

Cao et al. (2018) used an adsorbing-stripping stage that efficiently removed nutrients (about 80% of ammonia) and heavy metals from SW, while obtaining the maximum amount of biomass to obtain various bio-products. The produced biomass was *Chlorella vulgaris*, an unicellular and autotrophic photosynthetic green algae, which can synthesise lipids, carbohydrates, and protein with water, nitrogen, phosphorus, sun-light, and  $\text{CO}_2$  through photosynthesis (Cao et al., 2018). In this case, air stripping acts as a pre-treatment (Figure 1.2), since the excessive nutrient concentration in swine wastewater inhibits microalgae growth. In this study, the treatment of SW using the combined system N-adsorption plus air stripping plus microalgae cultivation was proposed as an alternative to the common anaerobic digestion process of raw SW.

Microalgae cultivation would be, indeed, a sustainable technology to recover the carbon from swine wastewater (Cheng et al., 2020). Microalgae can uptake both inorganic carbon (autotrophic metabolism) in the presence of light or organic carbon (heterotrophic metabolism) when light is absent (Cheng et al., 2020). A combined system ammonia removal plus anaerobic digestion plus microalgae growth was developed by Zhang et al. (2017), with methane and biomass production from the organic matter fed to anaerobic digestion. Several cultivations of microalgae were used for the treatment of SW (Cheng et al., 2020), mainly *Chlorella vulgaris* (Wang et al., 2015), *Neochloris aquatica CL-MI* (Y. Wang et al., 2017), *Parachlorella kessleri QWY28* (Qu et al., 2019), *Coelastrella sp. QY01* (Luo et al., 2016), or blooms of *Chlorella vulgaris*, *Scenedesmus obliquus*, and *Pseudokirchneriella subcapitata* with the fungus *Ganoderma lucidum* (Guo et al., 2017). The efficiency in COD reduction was in the range of 63–88%. The removal efficiency as well as the

quality of the ammonia solution recovered by air stripping are also influenced by the SW characteristics. More specifically, air stripping of SW with low organic matter ( $< 10 \text{ g}_{\text{COD}} \text{ L}^{-1}$ ) and without pH modification showed a removal efficiency over 90%, while higher organic matter content ( $> 27.0 \text{ g}_{\text{COD}} \text{ L}^{-1}$ ) reduced the nitrogen removal efficiency down to 50% or less (Laureni et al., 2013). Increasing pH to 9.5 significantly improved air stripping with removal efficiencies over 80% for COD below  $40 \text{ g}_{\text{COD}} \text{ L}^{-1}$  after a treatment of about 4 h (Laureni et al., 2013). The organic compounds stripped from the SW by air stripping could affect the quality of the recovered ammonium sulphate. For this reason, an alkaline trap (pH of the solution over 12) before the acidic trap can be used to absorb the stripped volatile compounds (retention of over 60% of the stripped organics) to avoid salt contamination (Laureni et al., 2013).

Although the air stripping is primarily used to remove ammonia compounds, this process is also effective to reduce the organic matter load of wastewater. In the studies reported in Table 1.3, the COD removal efficiency varied from less than 10% to 30%. The main reasons of the reduction in organic compounds by air stripping process were the stripping of volatile compounds, such as VFA, and the aerobic biological degradation (Bonmatí and Flotats, 2003; L. Zhang et al., 2012; Zhang and Jahng, 2010).

## 1.4. Effect of Air Stripping on Digested SW

### 1.4.1. Characteristics of Digested SW Although

Although being the product of a biochemical treatment (Figure 1.2c), anaerobically digested SW is still characterised by a high concentration of nitrogen compounds (Sui et al., 2015; Zhang et al., 2013) (Table 1.6). In more detail, almost all organic phosphorous and nitrogen in the SW are transformed into phosphate and ammonia through the anaerobic process (Song et al., 2011), due to the low conversion into biomass compared to the aerobic processes. It follows that, in spite of the biogas production, the anaerobic digestion cannot effectively reduce the nutrient load (Lin et al., 2018) and especially ammonia accumulates in digesters (usual concentrations range between  $300 \text{ mg L}^{-1}$  and  $3000 \text{ mg L}^{-1}$  or even more, Ashrafizadeh and Khorasani, 2010). As a consequence, as happens for raw SW, digested SW requires further treatments before its release into the environment (Cao et al., 2018, 2019a; Lin et al., 2018) (Figure 1.2).

**Table 1.6.** Summary of the main physico-chemical characteristics of digested swine wastewater (SW) studied in literature experiences.

Digestate Type	pH [-]	TS [%]	VS [%TS]	NH <sub>4</sub> <sup>+</sup> -N [gN L <sup>-1</sup> ]	NH <sub>3</sub> -N [gN L <sup>-1</sup> ]	TAN [gN L <sup>-1</sup> ]	TN [gN L <sup>-1</sup> ]	COD <sub>t</sub> [g L <sup>-1</sup> ]	COD <sub>s</sub> [g L <sup>-1</sup> ]	TP [g L <sup>-1</sup> ]	PO <sub>4</sub> <sup>3-</sup> -P [g L <sup>-1</sup> ]	Ref.	
DSW	8.2–8.5	-	0.36–0.42 *,**	2.104–2.111	0.916–0.920	-	-	7.134–7.924	3.138–4.889	-	-	Ho and Ho (2012)	
	8.4	3.172 *	1.717 *,**	3.68 *	-	-	4.73 *	-	41.23 *	-	-	Bonmatí and Flotats (2003)	
	8.1 ± 0.08	4.2 ± 0.44	58.2 ± 0.89	3.4 *	-	-	4.6 *	-	-	1.137 ± 0.355 *	-	Cattaneo et al. (2019)	
	8.17	1.48	51	3.013	-	-	3.415	14.943	-	-	-	Laureni et al. (2013)	
	8.75	1.13	48	2.686	-	-	3.353	9.790	-	-	-	Laureni et al. (2013)	
	7.63 ± 0.04	1.149 ± 0.0724 *	0.0461 ± 0.0012 *,**	0.298 ± 0.0024	-	-	0.460 ± 0.0092	1.602 ± 0.032	-	-	1.14.9 ± 0.00724	-	Cao et al. (2019a)
	7.18 ± 0.18	-	-	0.706 ± 0.216	-	-	-	2.108 ± 0.479	-	-	-	0.0403 ± 0.0095	Song et al. (2011)
	7.3–8.0	-	-	-	> 0.160	-	-	0.150–0.500	-	-	> 0.03	-	Quan et al. (2010)
	7.76 ± 0.09	-	-	-	-	-	0.874 ± 0.112	0.968 ± 0.123	1.595 ± 0.361	-	-	-	Sui et al. (2015)
	7.94	0.070 *	0.032 *,**	2.2	-	-	-	5.4	-	-	-	-	Guštin and Marinšek-Logar (2011)
7.50	-	-	1.510	0.034	-	1.770	2.290	-	0.432	0.227	-	Lei et al. (2007)	

Notes: TS = Total Solids; VS = Volatile Solids; TAN = Total Ammonia Nitrogen; TN = Total Nitrogen; COD, COD<sub>t</sub> = total and soluble COD; TP = Total Phosphorous; DSW = digested swine wastewater; Co-DSW = Co-Digested swine wastewater.

Air stripping is considered as a more sustainable treatment for digested SW to remove nitrogen compared to other systems, due to (i) the waste heat produced by on-site biogas combustion that is usable to increase the temperature during air stripping, (ii) lower alkali requirement for pH adjustment, and (iii) more sustainable investment costs (Bonmatí and Flotats, 2003; Guštin and Marinšek-Logar, 2011). On the other hand, the digestate stripping is limited by specific constraints, such as the high content of solids, which causes clogging or scaling of the equipment and limits the application of the commonly used packed bed columns (Bousek et al., 2016). For this reason, digested SW is generally subjected to solid–liquid separation by settling (Sui et al., 2015) or filtration to remove solids (Cao et al., 2019a), before being processed by air stripping.

#### *1.4.2. Efficiency of Air Stripping on Digested SW*

A summary of literature data on air stripping of digested SW and the related process conditions is reported in Table 1.7, while the ammonia removal efficiency of the different air stripping schemes used for digested SW is summarised in Figure 1.4. Before discussing the efficiency of the studied systems, it may be worth to mention that the digestate used in the experiments was often derived from the co-digestion of SW with other substrates, such as glycerin, exhausted oil, food processing or slaughterhouse waste (Guštin and Marinšek-Logar, 2011), pig manure, maize silage, sugar and pig fodder (Bousek et al., 2016), pig excreta and kitchen waste (Lei et al., 2007), manure, and flushing water of a swine farm (Sui et al., 2015). Less commonly, the analysed digested SW derives from the anaerobic digestion of SW only (e.g., Cao et al., 2019a; Quan et al., 2010).

The effects of air stripping on digested SW are different from those observed in raw SW. In general, a lower reaction time (less than 24 h) was required to achieve a higher ammonia removal efficiency (over 90%); moreover, pH seems to influence less the overall treatment efficiency, although higher pH values were effective in improving the process kinetics (Laureni et al., 2013).

An almost complete ammonia removal was achieved by Bonmatí and Flotats (2003), by setting the initial pH at 9.5, but no further increases were reported when the initial pH was set at 11.5. This showed that, at a temperature of 80 °C, the process requires a pH higher than 9.5. Lowering the temperature at 50 °C leads to an ammonia removal of 75% (Guštin and Marinšek-Logar, 2011). Similar results were found by Hidalgo et al. (2016), who reported that a pH over 10.5 did not affect the balance between molecular ammonia and ionic ammonium (Kinidi et al., 2018).

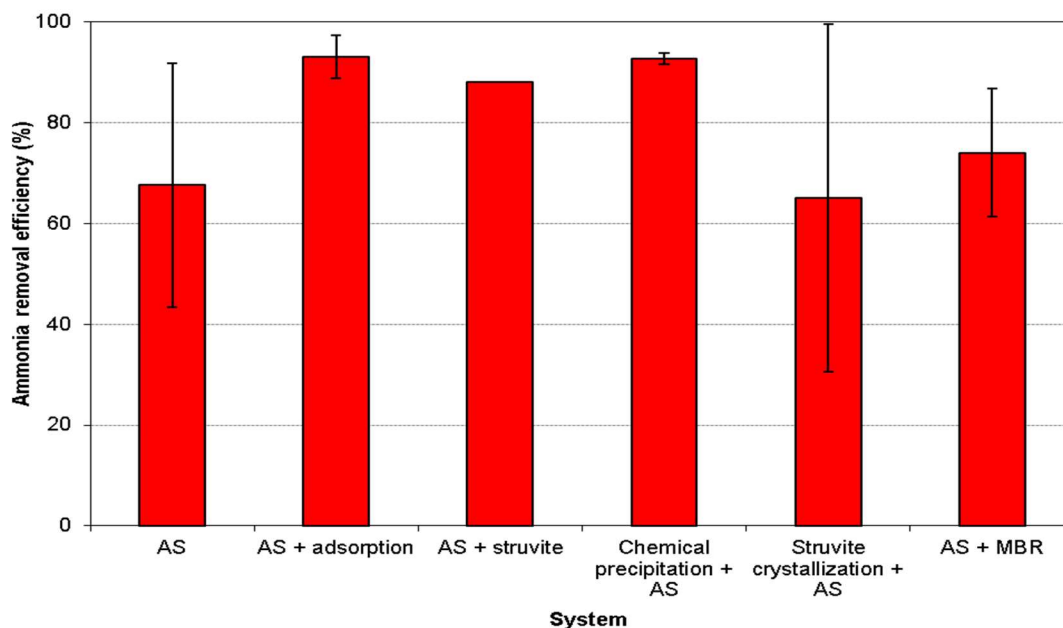
**Table 1.7.** Literature data about experimental tests of digested swine wastewater (SW) treatment using air stripping.

System	Notes	Chemical Addition	Adjusted pH	Temperature [°C]	Time [h]	Air Flow Rate [ $L_{air} \text{ min}^{-1}$ ]	Rate $L_{SW}^{-1}$	Ammonia Removal Efficiency [%]	Ammonium Sulphate/Nutrient Recovery	Ref.	
AS	Continuous bench plant spraying DSW	NaOH	8.5	50	n.a.	1875 ***		27	Yes	Guštin and Marinšek-Logar (2011)	
			10.5					30			93
			10.0	70				30			
			10.0	50				92			
	CO <sub>2</sub> stripping + AS + Biogas purification	Ca(OH) <sub>2</sub>	12.0	15	24	0		25	Yes	Lei et al. (2007)	
			12.0					12			72
			12.0	15				5			90
			12.0	15				10			95
	Biogas flow Flue gas flow	None	> 7.5	65	4	5		47	No	Bousek et al. (2016)	
								86			
-	NaOH	10.5	30	2	2000		67	Yes	Zou et al. (2019)		
		11.0					69				
		11.5					71				
		12.0					74				
AS adsorption	+ Filtration before AS	None	8.5	80	4	0.05 *		> 96	Yes	Bonmatí and Flotats (2003)	
			9.5					> 96			
	COD < 10 g L <sup>-1</sup>	None	> 8.0	50	3.75	10 *		>90	Yes	Laureni et al. (2013)	
			NaOH					9.5			50

System	Notes	Chemical Addition	Adjusted pH	Temperature [°C]	Time [h]	Air Flow Rate [L <sub>air</sub> min <sup>-1</sup> L <sub>SW</sub> <sup>-1</sup> ]	Ammonia Removal Efficiency [%]	Ammonium Sulphate/Nutrient Recovery	Ref.
AS + struvite	-	MgO	9–10	40	3	8	88 **	Yes	Cao et al. (2019a)
Chemical precipitation + AS	Simultaneous removal of N, P and COD by a WSA	Ca(OH) <sub>2</sub>	> 11.0	28–30	1	13 *,***	94	Yes	Quan et al. (2010)
		Ca(OH) <sub>2</sub>	> 11.0	28–30	1	39 *,***	> 92		
		Ca(OH) <sub>2</sub>	> 11.0	28–30	1	9 *,***	> 92 *		
Struvite crystallization + AS	CO <sub>2</sub> stripping—SBR	None	-	0–20	1–4	0.25 *	40–90	Yes	Song et al. (2011)
	Continuous flow—HRT = 6–15 h	None	-	0–30	-	0.42 *	40–90		
AS + MBR	Continuous process	NaOH	10.0–	30	n.a.	2800 ***	83	No	Sui et al. (2015)
			10.5 9.0–9.5	30	n.a.	2800 ***	65		

Notes: \* Adapted/extrapolated data; \*\* Ammonium recovery in phosphoric acid and struvite precipitation; \*\*\* air to liquid ratio [L<sub>air</sub> min<sup>-1</sup> : L<sub>DSW</sub> min<sup>-1</sup> or m sec<sup>-1</sup> : m sec<sup>-1</sup>]; AS = air stripping; WSA = water sparged aerocyclone; SBR = sequencing batch reactor; MBR = membrane bioreactor; DSW = digested swine wastewater; HRT = hydraulic retention time.





**Figure 1.4.** Summary of the ammonia removal efficiency (mean  $\pm$  std. dev.) of the air stripping systems for digested swine wastewater (SW) reported in literature (AS = air stripping; MBR = membrane bioreactor).

Conversely, Guštin and Marinšek-Logar (2011) reported that pH had the strongest effect on stripping, with an ammonium removal up to 93%, while the temperature had the least significant effect. In general, the pH adjustments in the chemical treatments increases the alkalinity of digested SW (over 9.0–10.0), which requires further treatments before disposal or reuse, such as extensive depuration (e.g., lagooning) or neutralisation.

Lei et al. (2007) obtained similar results (95% of removal efficiency) at room temperature but adopting very high pH (up to 12.0) and AFR (up to  $10 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$  for 12 h). These results indicate that, at the same pH conditions, the ammonia removal increases with the AFR. However, a lower AFR (e.g., 1 or  $5 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$ ) still ensured high removal efficiencies (up to 90%), resulting in a more feasible process (Kinidi et al., 2018; Lei et al., 2007). The same conclusions were reported by Guštin and Marinšek-Logar (2011), who did not observe any increases in ammonia removal efficiency raising the air-to-liquid ratio from 1875 up to 2100.

Struvite precipitation is the most used physico-chemical process in combination with air stripping for the simultaneous removal of ammonia nitrogen and phosphate from digested SW (as for raw SW, see Section 3.2). Cao et al. (2019a) used MgO as chemical additive for both struvite precipitation and pH adjustment for air stripping of the residual ammonia. The optimal process conditions, allowing an ammonia removal efficiency of about 90%, were a temperature of 40 °C, an AFR of  $8 \text{ L L}^{-1} \text{ min}^{-1}$ , a reaction time of 3 h, and a dose of MgO equal to  $0.75 \text{ g L}^{-1}$ . Quan et al. (2010) used a water-sparged aerocyclone reactor for air stripping after struvite precipitation.  $\text{Ca}(\text{OH})_2$  was used as precipitant for

$\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and organic phosphorous compounds and as pH conditioner for the air stripping of residual ammonia; an ammonia removal over 90% was achieved in less than 3 h. Another air stripping system used in combination with a membrane bioreactor allowed a nitrogen removal from digested SW higher than 80% (Sui et al., 2015).

In order to avoid or at least reduce the need for chemicals as much as possible, a method to adjust pH may be the use of the biogas and/or the flue gas derived from biogas combustion. Before air stripping, the pH of water increases, when the amount of  $\text{CO}_2$  dissolved in the wastewater decreases. Therefore, Lei et al. (2007) increased the pH of the digested effluent (from 7.4 up to 9.3) by  $\text{CO}_2$  stripping (at the rate of  $2.5 \text{ L}_{\text{air}} \text{ L}_{\text{DSW}}^{-1} \text{ min}^{-1}$  for one day), thus reducing the required dose of alkalis. After air stripping, the effluent was subjected to biogas injection, in order to decrease the pH of the treated digested SW for the subsequent biological treatment or the disposal into water bodies, and at the same time to purify the biogas. The pH of the effluent was reduced from 11.0 to 7.0 in less than 0.5 h (biogas flow rate equal to  $1 \text{ L L}^{-1} \text{ min}^{-1}$ ) and the methane content in the biogas was increased up to about 75%. Song et al. (2011) recovered up to 85% of phosphate as struvite and removed up to 90% of ammonia nitrogen by air stripping without adding any chemicals, as the wastewater pH was increased by  $\text{CO}_2$  stripping. Moreover, Bousek et al. (2016) found that the flue gas (on average 82% of nitrogen and 18% of carbon dioxide) cannot replace the air in air stripping, since the ammonia removal efficiency was lower than 50% compared to a value of 86% using air. As for raw SW, Laurení et al. (2013) evaluated the quality of the ammonium sulphate solution from air stripping of digested SW. It was found that, although the total organic carbon concentrations were below the detection limit, the organic matter contamination of the solution strongly depends on the initial organic matter content and pH. It was suggested that a higher pH could also limit the contamination of the recovered product. Air stripping of digested SW with an initial organic matter content below  $10 \text{ g}_{\text{COD}} \text{ L}^{-1}$  showed over 90% of ammonia removal (in less than 4 h at an initial pH of 9.5, Laurení et al., 2013).

The COD reduction in digested SW after air stripping was in the range 20–70% according to the studies of Bonmatí and Flotats (2003), Quan et al. (2010), and Cao et al. (2019a). In the study of Bonmatí and Flotats (2003), the high removal of organic matter may be attributed to the high biomass content in the digested SW, which can adsorb suspended solids, subsequently removed by filtration.

### 1.5. Future Perspectives

Air stripping of raw and digested swine wastewater can be well integrated in the concept of bio-refinery, because this system allows a more sustainable management of the piggery effluent by

turning wastewater into new added-value compounds, by-products, and/or bioenergy. Moreover, the combination of air stripping with other technologies seems to be sustainable from both the environmental and economic aspects. The common combined systems include struvite precipitation and air stripping as pre- or post-treatment of the anaerobic digestion. Less commonly, air stripping was used in combination with biomass (e.g., microalgae) production.

The recovery of phosphorous by chemical precipitation of struvite, and the subsequent production of ammonia salts by air stripping is a sustainable option for the recovery of both nutrients, although usually phosphorus concentration in swine wastewater is moderate. Regarding the anaerobic digestion, the application of the air stripping as pre-treatment can increase the methane yield by reducing the inhibitory ammonia compounds. When applied on the digestate (as post-treatment of the anaerobic digestion), the recovery of nitrogen makes the digestate more suitable for direct land application; however, this opportunity needs a deeper insight. A possible solution could be the recovery of both struvite (before the anaerobic digestion) and nitrogen (on the struvite-pretreated swine wastewater subjected to anaerobic digestion). However, many other solutions can be developed since air stripping offers flexible and simple opportunities of implementation.

Beside the common parameters (pH, temperature, and air flow rate), the presence of organic matter of swine wastewater plays an important role on ammonia removal efficiency (for both raw and digested swine wastewater). However, the influence of the organic matter on this process has not been extensively studied. Thus, further research should evaluate the impact of the stripped organic volatile compounds on the quality of the ammonia salt produced by the air stripping as well as the agronomic effects of land application of the recovered by-products as fertilisers.

Overall, this review has demonstrated that the air stripping process as a treatment of raw and digested swine wastewater has not been exhaustively investigated. For instance, few experiments were found on the coupled system air stripping–biomass growth and optimized air stripping–anaerobic digestion as well as on the use of other technologies (e.g., microwave radiation). The possible nutrient recovery and biomass harvest (to obtain energy or by-products) would be of great interest on a circular economy approach. Under this aspect, a special effort is required to demonstrate the overall competitiveness on the market of fertilisers of the recovered ammonia salts.

## **1.6. Conclusions**

This review has analysed and summarised the main studies of air stripping carried out on raw and digested swine wastewater. The related experiments were performed under a large variety of

operational conditions: Natural (uncontrolled) or adjusted pH (up to 12), room temperature or wastewater heating up to 80 °C, air flow rate from 0.5 to 10 L L<sup>-1</sup> min<sup>-1</sup>, and initial ammonia content from 1.0 to 7.0 g L<sup>-1</sup>. The combination of these environmental conditions led to ammonia removal efficiencies from about 20% to nearly 100%. These results and the comparisons of literature experiences on raw (Section 3.2) and digested (Section 4.2) swine wastewater suggested the following indications, which could help the optimization of the air stripping treatment. The initial pH value of the wastewater before air stripping is the most influencing parameter, whose optimal value (9.5–10.0) allows an efficient and quick ammonia removal. At pH under 9.5, temperatures over 50 °C and/or air flow rates up to 5 L<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup> are needed for an efficient process. An excess of alkali, although causing drawbacks (e.g., membrane fouling), noticeably reduce the costs of aeration and heating. Moreover, no pH adjustment of the air stripping treated wastewater is needed when anaerobic digestion follows air stripping, since the pH of the pre-treated wastewater is generally optimal for an efficient anaerobic digestion. Digested swine wastewater is instead less influenced by the initial pH value.





## Chapter 2. Organic matter removal and ammonia recovery by optimised treatments of swine wastewater

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**Organic matter removal and ammonia recovery by optimised treatments of swine wastewater**

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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<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>) 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 pre or 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<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>), which would provide a nitrogen fertiliser at a sustainable cost.

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  $L_{\text{air}} L_{\text{SW}}^{-1} \text{min}^{-1}$ ) 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  $L_{\text{air}} L_{\text{SW}}^{-1} \text{min}^{-1}$ ), which would provide a nitrogen fertiliser at a sustainable cost.

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



## **2.1. Introduction**

Swine wastewater (SW) is composed of a mixture of urine, feces, water spillage, residues of undigested food, antibiotic residues and pathogenic microorganisms (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), but their 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, 2018a). However, the methane production in the anaerobic digestion of SW is limited by the high ammonia content (often over  $4.0 \text{ g L}^{-1}$ ) 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 (Bonmatí 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 (Bonmatí 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 Chemical 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.

## 2.2. Materials and methods

### 2.2.1. Wastewater characterization Samples

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 2.1) were measured in duplicate using standard methods on each collected sample (APHA, 2012).

Soluble Chemical 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 (Bonmatí and Flotats, 2003), while organic nitrogen was mainly contained in the solid residue removed by centrifugation.

**Table 2.1.** Average physico-chemical parameters of SW subjected to the batch tests.

<b>Parameter</b>	<b>Value (mean <math>\pm</math> std. dev.)</b>
<b>pH [-]</b>	7.35 $\pm$ 0.19
<b>TS [%]</b>	1.89 $\pm$ 1.65
<b>TVS [% TS]</b>	57.49 $\pm$ 9.18
<b>tCOD [mg L<sup>-1</sup>]</b>	27131 $\pm$ 15224
<b>sCOD [mg L<sup>-1</sup>]</b>	5246 $\pm$ 1623
<b>TAN [mg L<sup>-1</sup>]</b>	1308 $\pm$ 142

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

### *2.2.2. Ammonia stripping tests*

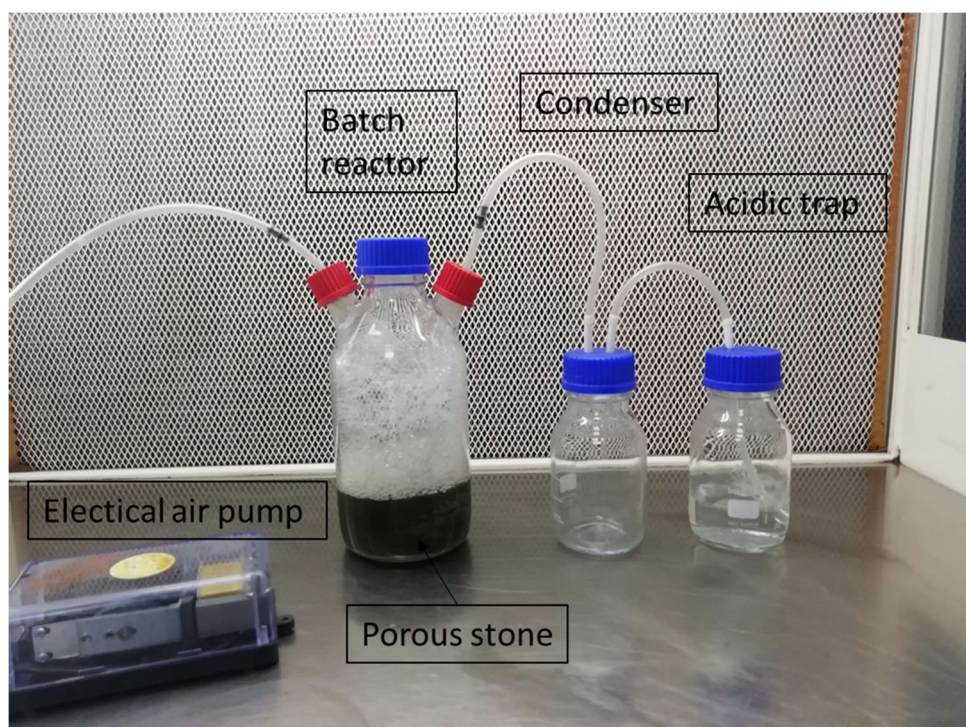
Each treatment (individual or in combination with others) of SW was carried out for 24 hours in batches of 1-litre volume. The combination of pH (natural, 8 or 10) temperature (ambient, 40 or 60 °C) and air flow rate (no aeration, 1 or 5 L<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>) produced a total of 3 x 3 x 3 = 27 treatments (Table 2.2). The treatment with natural pH, ambient temperature and without aeration was assumed as control.

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 2.2), hereinafter indicated as “combined treatments”.

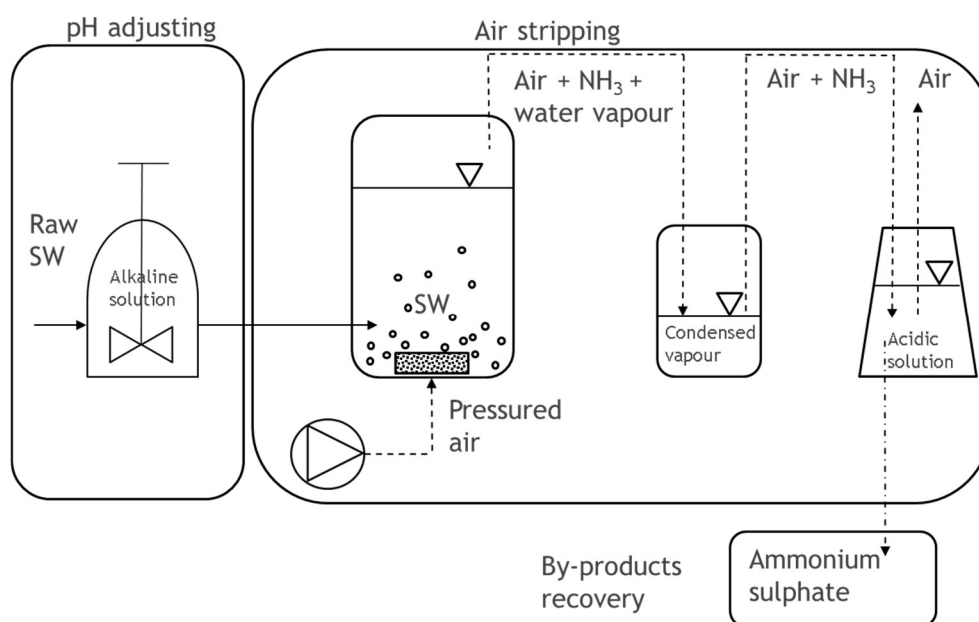
In the C tests, a solution of Ca(OH)<sub>2</sub> (30% w/v) was used to adjust the pH at 8 and 10. The doses were 16  $\pm$  9 mL<sub>Ca(OH)<sub>2</sub>sol</sub> L<sub>SW</sub><sup>-1</sup> 40  $\pm$  8 mL<sub>Ca(OH)<sub>2</sub>sol</sub> L<sub>SW</sub><sup>-1</sup>, respectively. The T tests were carried out by heating the batches in a thermostatic chamber. The A tests consisted of a batch with three units (Figure 2.1).

**Table 2.2.** Experimental design of the tests and related operational parameters.

<b>Test</b>	<b>Treatment</b>	<b>pH</b> [-]	<b>Temperature</b> [°C]	<b>Air flow rate</b> [L <sub>air</sub> L <sub>SW</sub> <sup>-1</sup> min <sup>-1</sup> ]
<b>Control</b>	Control	Natural	Ambient	0
<b>T<sub>n-40-0</sub></b> <b>T<sub>n-60-0</sub></b>	Thermal	Natural	40 60	0
<b>C<sub>8-25-0</sub></b> <b>C<sub>10-25-0</sub></b>	Chemical	8 10	Ambient	0
<b>A<sub>n-25-1</sub></b> <b>A<sub>n-25-5</sub></b>	Aerated	Natural	Ambient	1 5
<b>CT<sub>8-40-0</sub></b> <b>CT<sub>8-60-0</sub></b> <b>CT<sub>10-40-0</sub></b> <b>CT<sub>10-60-0</sub></b>	Chemical-Thermal	8 10	40 60 40 60	0
<b>TA<sub>n-40-1</sub></b> <b>TA<sub>n-40-5</sub></b> <b>TA<sub>n-60-1</sub></b> <b>TA<sub>n-60-5</sub></b>	Thermal-aerated	Natural	40 60	1 5 1 5
<b>CA<sub>8-25-1</sub></b> <b>CA<sub>8-25-5</sub></b> <b>CA<sub>10-25-1</sub></b> <b>CA<sub>10-25-5</sub></b>	Chemical-aerated	8 10	Room	1 5 1 5
<b>CTA<sub>8-40-1</sub></b> <b>CTA<sub>8-40-5</sub></b> <b>CTA<sub>10-40-1</sub></b> <b>CTA<sub>10-40-5</sub></b> <b>CTA<sub>8-60-1</sub></b> <b>CTA<sub>8-60-5</sub></b> <b>CTA<sub>10-60-1</sub></b> <b>CTA<sub>10-60-5</sub></b>	Chemical- thermal-aerated	8 10 8 10	40 60	1 5 1 5 1 5 1 5



(a)



(b)

**Figure 2.1.** 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 h) 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<sub>n-40-1</sub> is a thermal-aerated (T+A) test with no pH adjustment (n), temperature of 40 °C (40) and air flow rate of 1 L<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup> (1).

### 2.2.3. 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:



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<sub>n-60-5</sub> and CTA<sub>10-60-5</sub>). 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<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>), but SW in the first test was subject to the chemical treatment and in the second test pH of SW was not controlled.

### 2.2.4. 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.

## **2.3. Results**

### *2.3.1. 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 the treatments with the highest temperature and air flow rate, due to a more effective evaporation (Table 2.3).

At the end of the treatments ( $t = 24\text{h}$ ), pH increased, respect to the value at the beginning of the test in all treatments with no adjustment or pH adjusted to 8, and decreased in the treatments with the pH adjusted to 10. The variation of pH was relatively high - but not statistically significant - in T and/or A treatments under extreme conditions ( $60\text{ }^{\circ}\text{C}$  and  $5\text{ L}_{\text{air}}\text{ L}_{\text{SW}}^{-1}\text{ min}^{-1}$ ) (Table 2.3).

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 CTA10-60-5 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 2.2).

TAN reduction was on the average about 3% of its initial content, except for the tests CTA<sub>10-40-5</sub> and CTA<sub>10-60-1</sub>, which showed a concentration lower by 60% and 32%, compared to the raw SW, immediately after alkali addition (Figure 2.2).

**Table 2.3.** Differences in physico-chemical parameters of the SW (mean  $\pm$  std. dev. in %) before and after the batch tests.

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

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



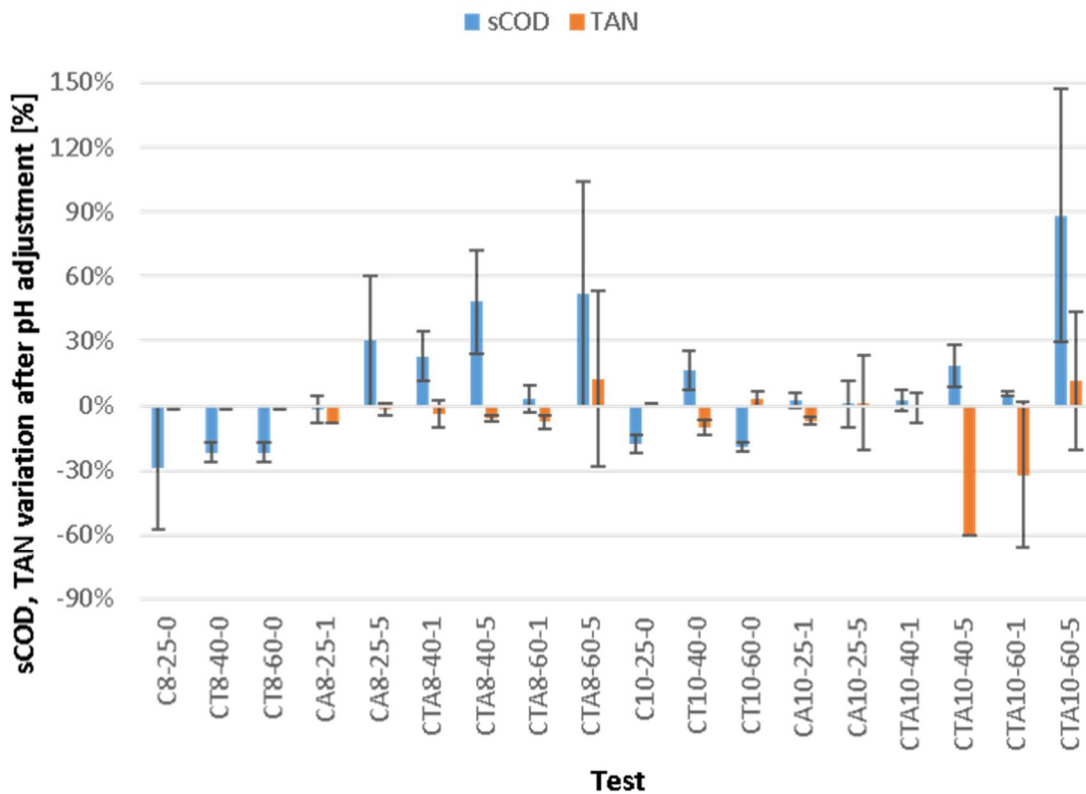


Figure 2.2. Effect of pH adjustment on the variations of sCOD and TAN concentrations in SW immediately after alkali addition ( $t = 0$  hours).

### 2.3.1.1. Effects of the treatments on the sCOD removal

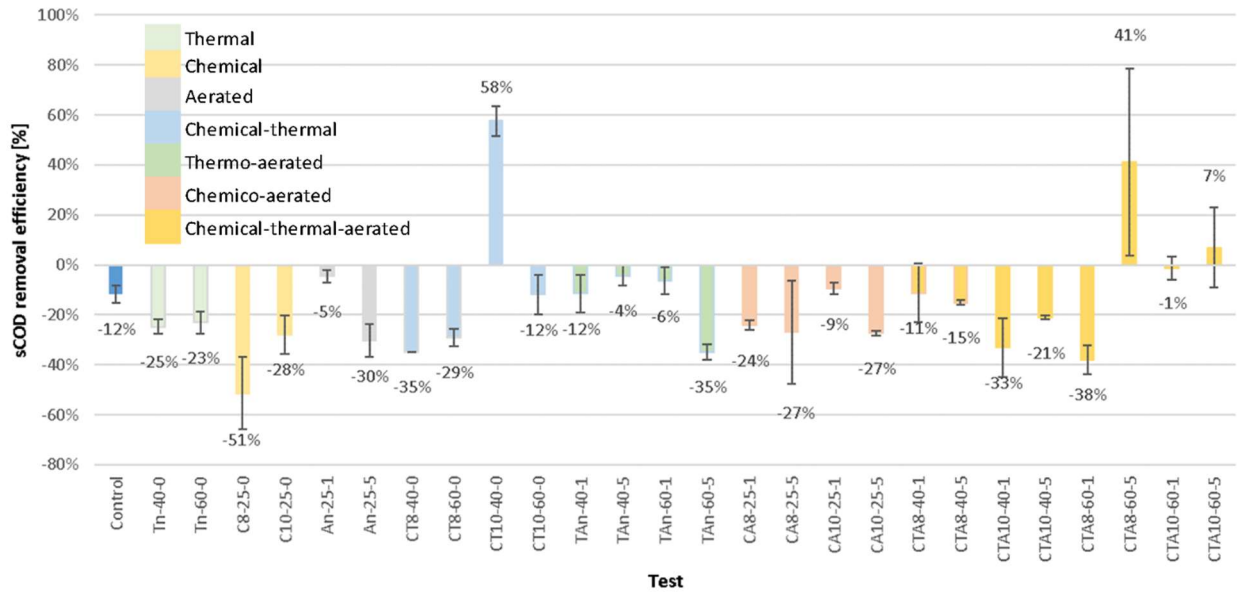
The control test showed an average sCOD reduction of 12%. Almost all treatments reduced the sCOD, with the exception of the  $CTA_{10-60-5}$ ,  $CTA_{8-60-5}$  and  $CT_{10-40-0}$ , which showed on average a sCOD increase of  $6.8 \pm 16.0\%$ ,  $41.2 \pm 37.4\%$  and  $57.6 \pm 5.9\%$ , respectively. In the tests  $CTA_{10-60-5}$  and  $CTA_{8-60-5}$  a high standard deviation was noticed, indicating a certain process instability (Figure 2.3a).

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 2.3b, 2.3c and 2.3d).

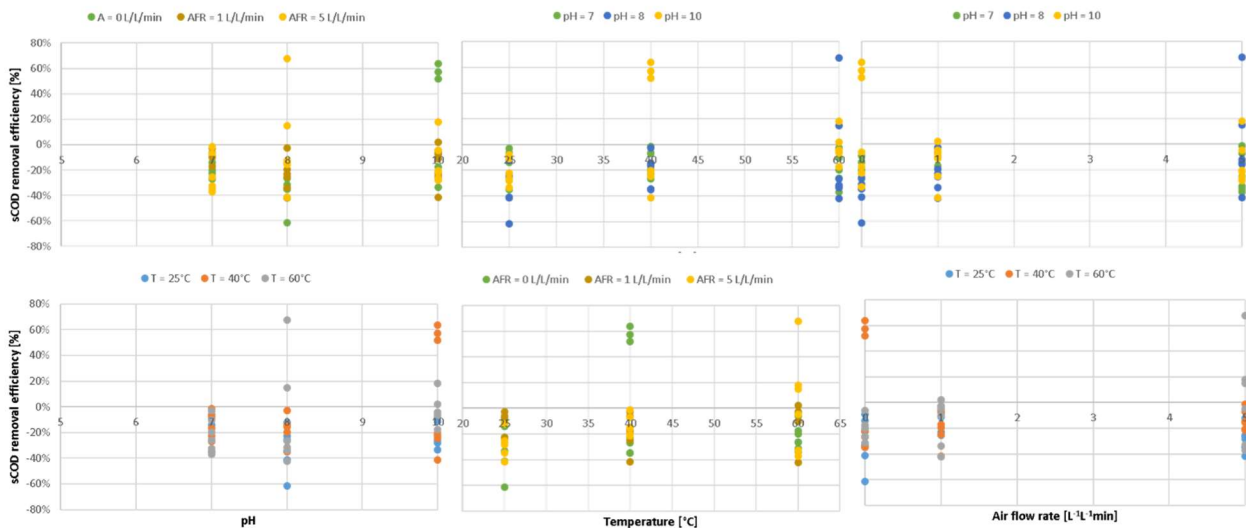
Among the individual treatments (C, T and A), the C tests have showed the highest reduction of sCOD (from -28% of  $C_{10-25-0}$  to -51% of  $C_{8-25-0}$ ). For the treatments  $CTA_{10-40-1}$  and  $CTA_{8-60-1}$  the highest sCOD removal efficiencies ( $-33.1 \pm 11.8\%$  and  $-37.9 \pm 5.9\%$  of sCOD removed, respectively) were found, while only the treatments  $CT_{8-40-0}$  and  $TA_{n-60-5}$  removed over 30% of sCOD; the

minimum reduction ( $-1.3 \pm 4.7\%$ ) was observed in the treatment CTA<sub>10-60-1</sub>. Overall, the treatments C<sub>8-25-0</sub>, CT<sub>8-40-0</sub>, CT<sub>8-60-0</sub>, TA<sub>n-60-5</sub>, CTA<sub>10-40-1</sub> and CTA<sub>8-60-1</sub> showed sCOD removal efficiency over 30% (Figure 2.3a).

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.



(a)



(b)

(c)

(d)

**Figure 2.3.** 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).

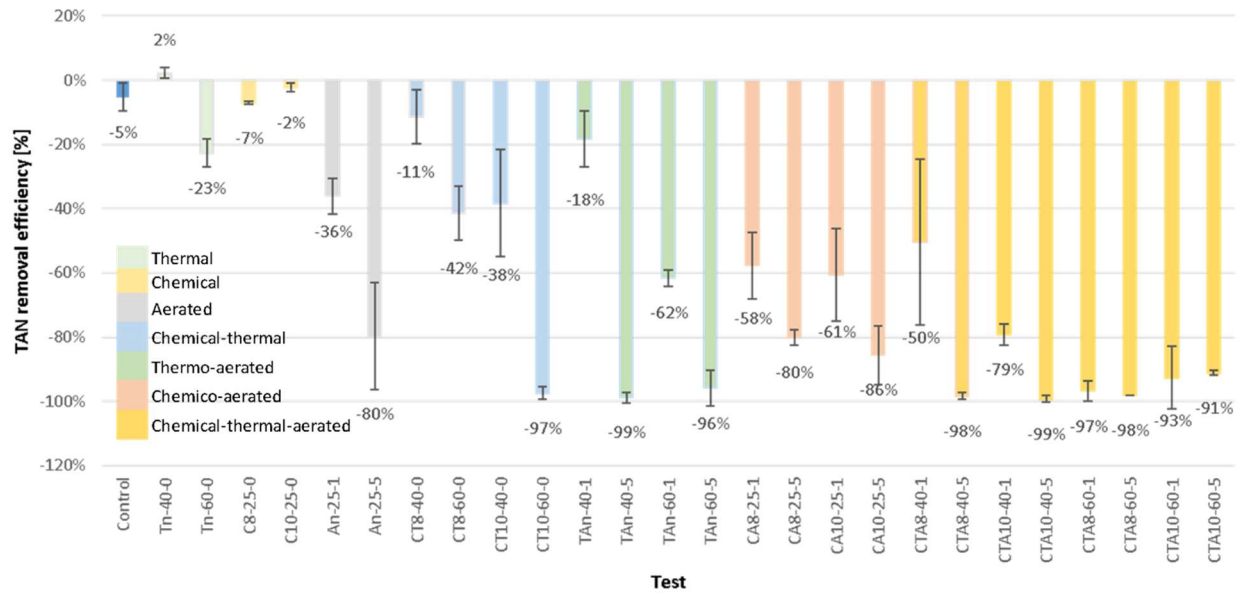
### 2.3.1.2. Effects of the treatments on TAN removal

The TAN removal efficiency in the control test was  $5.4 \pm 4.4\%$ . In general, TAN stripping was enhanced mainly by higher air flow rates, but also by increases in pH and temperature (Figure 2.4a, 2.4b and 2.4c).

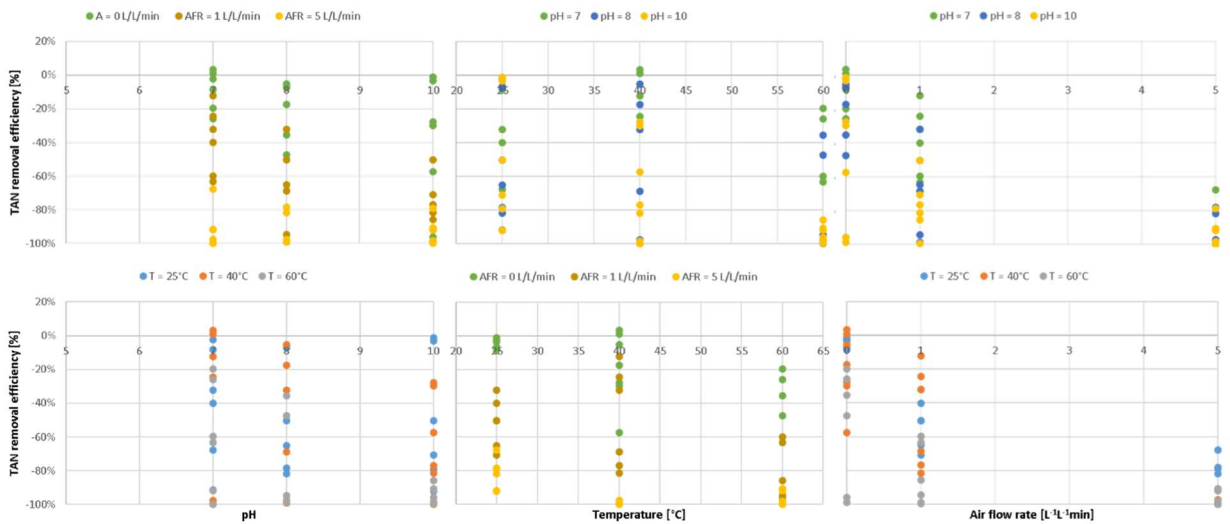
Among the individual tests, the treatments  $A_{n-25-1}$  and  $A_{n-25-5}$  were more efficient (TAN removal efficiency of  $36.1 \pm 5.7\%$  and  $79.7 \pm 16.8\%$ , respectively) compared to  $T_{n-40-0}$  ( $2.1 \pm 1.6\%$ ),  $T_{n-60-0}$  ( $22.8 \pm 4.3\%$ ),  $C_{8-25-0}$  and  $C_{10-25-0}$  ( $7.1 \pm 0.3\%$ ). The treatment  $T_{n-40-0}$  showed instead a slight increase ( $2.1 \pm 1.6\%$ ) of TAN concentration (Figure 2.4a).

$CT_{10-60-0}$  was the most efficient among the CT treatments, yielding a TAN removal efficiency of  $97.4 \pm 2.0\%$ . Among the TA treatments,  $TA_{n-40-5}$  and  $TA_{n-60-5}$  showed the highest removal efficiencies ( $98.8 \pm 1.7\%$  and  $95.9 \pm 5.7\%$ , respectively). High performances were detected also for the CA treatments, which gave TAN removal efficiencies over 57%, with a maximum value of  $85.6 \pm 9.1\%$  ( $CA_{10-25-5}$ ). Overall, the CTA treatments resulted to be the most efficient, since the TAN removal efficiency was always over 90%, except for  $CTA_{8-40-1}$  and  $CTA_{10-40-1}$  that showed lower performances ( $50.5 \pm 25.8\%$  and  $79.3 \pm 3.3\%$ , respectively) (Figure 2.4a).

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.



(a)



(b)

(c)

(d)

**Figure 2.4.** 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).

### 2.3.2. 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 ( $5 L_{\text{air}} L_{\text{SW}}^{-1} \text{ min}^{-1}$ , treatments  $TA_{n-40-5}$ ,  $CTA_{8-40-5}$ ,  $CTA_{10-40-5}$ ,  $CTA_{8-60-5}$ ) (Table 2.4).

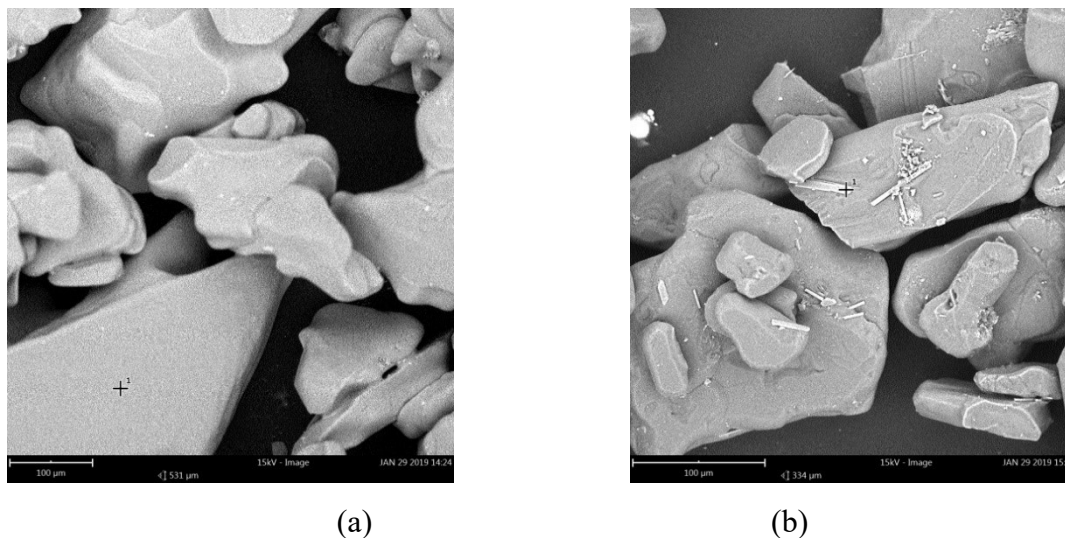
**Table 2.4.** Ammonium sulphate recovered by the AS aerated treatments of SW.

Test	Recovered ammonium sulphate	
	[g L <sup>-1</sup> ]	[%]
$A_{n-25-1}$	$2.20 \pm 0.07$	$36.1 \pm 5.7$
$A_{n-25-5}$	$5.53 \pm 0.17$	$79.7 \pm 16.8$
$TA_{n-40-1}$	$0.97 \pm 0.35$	$18.3 \pm 8.7$
$TA_{n-40-5}$	$7.99 \pm 0.78$	$98.8 \pm 1.7$
$TA_{n-60-1}$	$3.67 \pm 0.15$	$61.6 \pm 2.5$
$TA_{n-60-5}$	$6.56 \pm 2.49$	$95.9 \pm 5.7$
$CA_{8-25-1}$	$3.75 \pm 0.64$	$57.7 \pm 10.3$
$CA_{8-25-5}$	$5.55 \pm 1.25$	$80.1 \pm 2.5$
$CA_{10-25-1}$	$3.44 \pm 0.78$	$60.6 \pm 14.4$
$CA_{10-25-5}$	$5.75 \pm 1.83$	$85.6 \pm 9.1$
$CTA_{8-40-1}$	$2.85 \pm 1.26$	$50.5 \pm 25.8$
$CTA_{8-40-5}$	$7.52 \pm 1.18$	$98.3 \pm 1.0$
$CTA_{10-40-1}$	$4.71 \pm 0.51$	$79.3 \pm 3.3$
$CTA_{10-40-5}$	$7.20 \pm 0.13$	$99.3 \pm 1.0$
$CTA_{8-60-1}$	$5.28 \pm 0.16$	$96.8 \pm 3.1$
$CTA_{8-60-5}$	$6.26 \pm 2.18$	$98.2 \pm 0.1$
$CTA_{10-60-1}$	$6.11 \pm 1.25$	$92.6 \pm 9.7$
$CTA_{10-60-5}$	$6.20 \pm 1.88$	$91.1 \pm 0.6$

The 3-way ANOVA, which explains 67% of the variance of the original variables, shows that pH, temperature and air flow rate (the latter being the most influential factor) as well as the interaction between the air flow rate and pH had a significant (at  $p < 0.05$ ) effect on the amount of ammonium sulphate recovered from SW; conversely, the interactions of temperature with pH and air flow rate were not influential factors.

The qualitative analysis of the recovered salt shows that the structure of the salts produced by the treatment  $TA_{n-60-5}$  is clearer and the crystals are well defined compared to  $CTA_{10-60-5}$ . The salts

produced by this batch show instead a dispersed structure. Moreover, thin lines among the crystal salts are evident. These impurities are composed of the calcium used for pH correction, although these precipitates were found in traces (Figure 2.5).



**Figure 2.5.** Samples of ammonium salts recovered by AS treatments of SW and analysed by SEM: a) test  $TA_{n-60-5}$ ; b) test  $CTA_{10-60-5}$ .

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

## 2.4. Discussions

According to the literature, the operational parameters of the batch tests are influential factors with different levels (Bonmatí 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 (Bonmatí 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<sub>8-25-0</sub> 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<sub>8-25-0</sub>) 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)<sub>2</sub> at a dose of  $16 \pm 9 \text{ mL}_{\text{Ca(OH)}_2\text{sol}} \text{ L}_{\text{SW}}^{-1}$ . 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 Bonmatí 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)<sub>2</sub> 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  $5 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$  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 2.5 compares the sCOD and TAN removal efficiency detected in this study with the experiments about AS of SW reported in the literature. Bonmatí and Flotats (2003) recovered almost all the ammonia in a short reaction time (four hours) using a very low air flow rate ( $0.05 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$ ), 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  $10 \text{ L}_{\text{air}} \text{ L}_{\text{SW}}^{-1} \text{ min}^{-1}$ ) 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 ( $37\text{ }^{\circ}\text{C}$ ) and air flow rate ( $1\text{ L}_{\text{air}}\text{ L}_{\text{SW}}^{-1}\text{ min}^{-1}$ ) at  $\text{pH} = 10$  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  $\text{pH} = 9$  and air flow rate of  $10\text{ L}_{\text{air}}\text{ L}_{\text{SW}}^{-1}\text{ min}^{-1}$ . In these studies, the highest concentration of total nitrogen was over  $7\text{ g L}^{-1}$ .

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:  $\text{A}_{\text{n-25-5}}$  (-30% for sCOD and -80 for TAN),  $\text{TA}_{\text{n-60-5}}$  (-35% and -96%),  $\text{CTA}_{10-40-1}$  (-30% and -80%) and  $\text{CTA}_{8-60-1}$  (-38% and -97%). This indicates that a treatment at pH of 8, T set at 40 or 60  $^{\circ}\text{C}$  (the temperature can be set up as a function of surplus heat availability, as above mentioned) and air flow rate at  $5\text{ L}_{\text{air}}\text{ L}_{\text{SW}}^{-1}\text{ min}^{-1}$  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  $^{\circ}\text{C}$  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 ( $5\text{ L}_{\text{air}}\text{ L}_{\text{SW}}^{-1}\text{ min}^{-1}$ ). The addition of the  $\text{Ca}(\text{OH})_2$  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 (Bonmatí 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.



**Table 2.5.** Literature data about experimental tests of SW treatment by AS.

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 [%]
Bonmatí and Flotats (2003)	None Ca(OH) <sub>2</sub>	7.7	80	4	0.05*	5.63	3.39	65	n.a.	n.a.
		9.5						69		
		11.5						98.8		
Lei et al. (2007)**	Ca(OH) <sub>2</sub>	12	15	12	5	1.77	1.51	72.1	n.a.	n.a.
		10		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		
	NaOH (40% w/w)	11.0	88.1							
		9.0	46.0	62.2						
		9.0	77.9							
		10.0	92.0							

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

## 2.5. 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 ( $5 L_{\text{air}} L_{\text{SW}}^{-1} \text{ min}^{-1}$ ), which would provide a nitrogen fertiliser at a sustainable cost.





## Chapter 3. Effects of ammonia stripping and other physico-chemical pretreatments on anaerobic digestion of swine wastewater

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Article

### 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<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>. 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

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<sub>air</sub> L<sub>SW</sub><sup>-1</sup> min<sup>-1</sup>. 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.

### **3.1. Introduction**

Swine wastewater (SW) consists of a blend of urine, feces, water, residues of undigested food and antibiotics, and pathogens (Cheng et al., 2017; Viancelli et al., 2013; Wu et al., 2015; Zhang and Jahng, 2010). 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 (Kim et al., 2004), as well as other chemical, physical, and biological systems (Cai et al., 2015; Kim et al., 2004; Mehta et al., 2015; Safavi and Unnthorsson, 2017), generally show low efficiency, high costs (Yang et al., 2016), 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 (Craggs et al., 2008; Loughrin et al., 2012; Trias et al., 2004), 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 (Andiloro et al., 2013; Zema et al., 2016, 2012). 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 (Hansen et al., 1998; L. Zhang et al., 2012). The removal of nitrogen compounds before AD may enhance methane production, since it reduces the compounds' toxicity towards the microbial consortium (Noike et al., 2004; Uludag-Demirer et al., 2008). 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 (Huang et al., 2019; Sengupta et al., 2015)—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 (Kinidi et al., 2018; Macura et al., 2019; Maurer et al., 2006; Perera et al., 2019; Zarebska et al., 2015). 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., Ahn et al., 2006; Belmonte et al., 2011; Córdoba et al., 2016; Deng et al., 2014; Jiang et al., 2020; Zeng et al., 2019), the ammonia removal efficiency of AS applied to SW has been studied little (e.g., Cao et al., 2019b; Laurení et al., 2013; Liao et al., 1995), 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. Bonmatí and Flotats (2003) did not observe the better performance in the AD of treated SW, while Zhang and Jahng (2010) and L. Zhang et al. (2012) reported a noticeable methane increase in the AD of air-stripped SW compared to untreated SW.

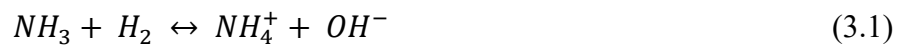
In order to advance knowledge about AS efficiency on raw SW, as well as the performance of the AD of SW previously subjected to AS, this study proposes an integrated system, AS and AD, for depurating SW and producing methane from this effluent; this system was compared to other integrated systems consisting 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.



### **3.2. Materials and Methods**

#### *3.2.1. Effects of the Operational Parameters of AS on the Removal Efficiency of Ammonia Nitrogen SW contains*

SW contains ammonia in the form of ammonium ions (the ionic form,  $\text{NH}_4^+$ ) and gas (the molecular form,  $\text{NH}_3$ ) (Kinidi et al., 2018). 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 (3.2), depends on pH and temperature, as explained by Equation (3.3):

$$[\text{NH}_3] = \frac{[\text{NH}_3 + \text{NH}_4^+]}{1 + [\text{H}^+]/K_a} \quad (3.2)$$

$$pK_a = 4 \cdot 10^{-8} T^3 + 9 \cdot 10^{-5} T^2 + 0.0356 T + 10.072 \quad (3.3)$$

where:

$[\text{NH}_3]$  = molecular ammonia concentration ( $\text{mol L}^{-1}$ ).

$[\text{NH}_3 + \text{NH}_4^+]$  = total ammonia nitrogen (TAN,  $\text{mol L}^{-1}$ ).

$[\text{H}^+]$  = hydrogen ion concentration ( $\text{mol L}^{-1}$ ).

$K_a$  = acid ionization constant (dimensionless).

T = temperature (K) (Tchobanoglous and Burton, 2003).

More specifically, an acidic pH enhances the formation of ammonium ions—the equilibrium reaction shown in Equation (3.1) is displaced to the right—while at strong alkaline pH values  $> 8.5$ , molecular ammonia prevails and the equilibrium is displaced to the left (El-Gohary and Kamel, 2016; Guštin and Marinšek-Logar, 2011; Karri et al., 2018; Tchobanoglous and Burton, 2003). 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  $\text{NH}_4^+$  content into the gaseous form:  $\text{NH}_3$ . 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 (Kinidi et al.,

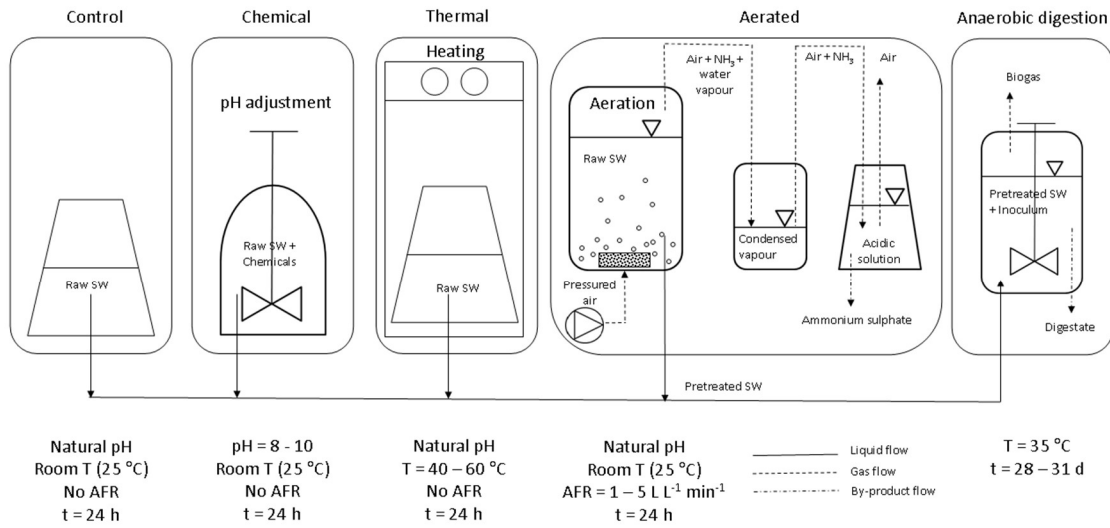
2018; Quan et al., 2009; Sengupta et al., 2015; Tchobanoglous and Burton, 2003). Heating wastewater enhances diffusion of the ammonia molecules to the liquid surface and subsequently to the atmosphere (Karri et al., 2018). Moreover, the mass transfer of  $\text{NH}_3$  from the liquid is enhanced by the aeration of the AS process that bubbles air in the solution and alters the air–liquid boundary (Karri et al., 2018). 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 (Bonmatí and Flotats, 2003; Kinidi et al., 2018).

### 3.2.2. Experimental Setup

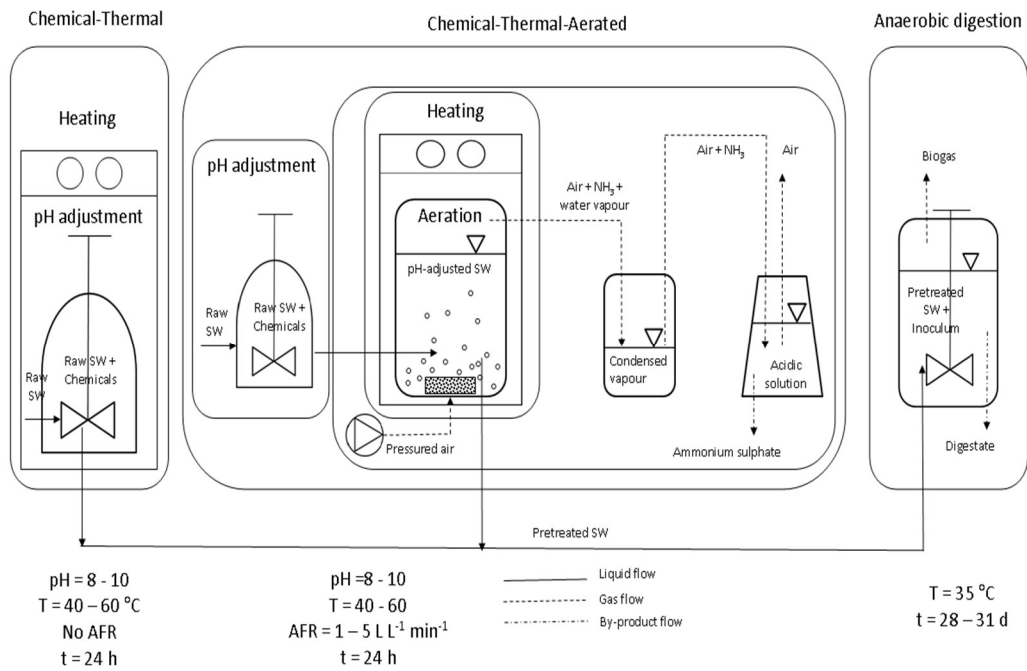
Figure 3.1 shows the scheme of the experimental setup used for the tests on the systems treating SW. First, the raw SW is subjected to AS and/or other chemical and physical treatments under different environmental conditions (i.e., temperature and/or pH) to reduce the ammonia nitrogen content; if air 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.

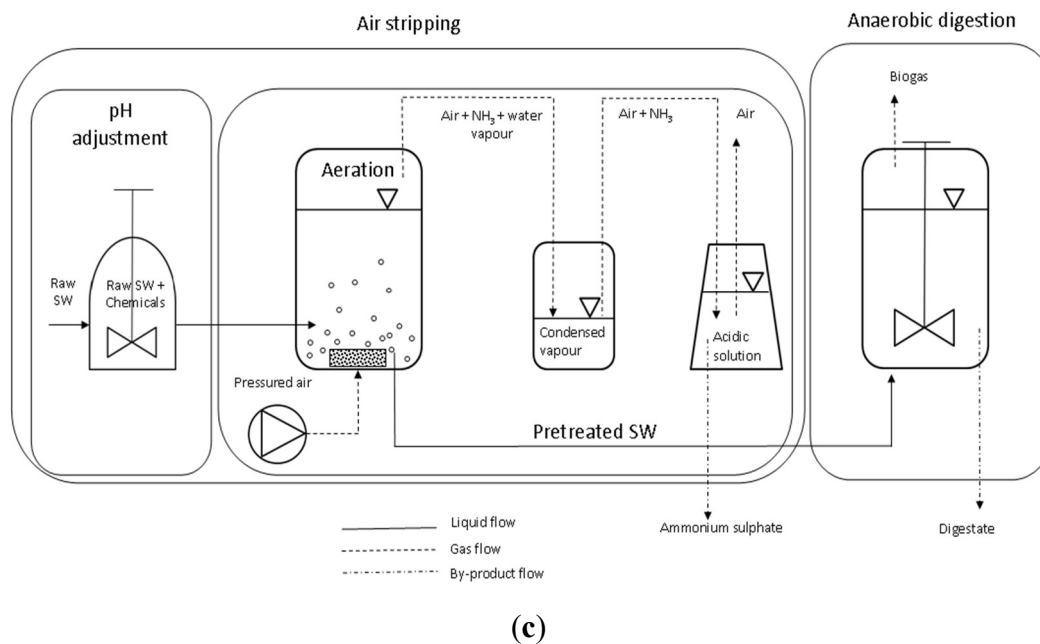
*Effects of ammonia stripping and other physico-chemical pretreatments on anaerobic digestion of swine wastewater*



(a)



(b)



**Figure 3.1.** Experimental design of the systems treating swine wastewater (SW): (a) individual treatments, (b) combined treatments, and (c) air stripping and anaerobic digestion.

Table 3.1 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, CT<sub>10-40-0</sub> 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 L L<sup>-1</sup> min<sup>-1</sup>).

**Table 3.1.** Experimental design of the tests on SW and related operational parameters.

Test	pH	Temperature [°C]	Air Flow Rate [L <sub>air</sub> L <sub>SW</sub> <sup>-1</sup> min <sup>-1</sup> ]
Control	Natural	Room	0
T <sub>n-40-0</sub>	Natural	40	0
C <sub>8-25-0</sub>	8	Room	0
C <sub>10-25-0</sub>	10		
A <sub>n-25-5</sub>	Natural	Room	5
CT <sub>10-40-0</sub>	10	40	0
CTA <sub>10-40-5</sub>	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  $7.03 \pm 0.03$  and  $10.07 \pm 0.04$ ; the room temperature was  $20 \pm 3$  °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<sup>-1</sup> min<sup>-1</sup>) were chosen based on the results of previous studies (Bonmatí and Flotats, 2003; L. Zhang et al., 2012). 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 (Bonmatí and Flotats, 2003; Zhang and Jahng, 2010). 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<sup>-1</sup> min<sup>-1</sup> was an intermediate value among commonly used AFRs, from 0.05 to 10 L L<sup>-1</sup> min<sup>-1</sup> (Bonmatí and Flotats, 2003; L. Zhang et al., 2012).

In the C tests, the pH was set up at 8 or 10 using a solution of Ca(OH)<sub>2</sub> (30% w/v). In the T tests, SW was heated in a thermostatic chamber. Three batch units were used for the A tests (Figure 3.1). 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 H<sub>2</sub>SO<sub>4</sub>); 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 (3.4):



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 3.1). Raw samples of SW were used as the control—c1 and c2 for Run 1 and Run 2 tests, respectively. Table 3.2 reports the main characteristics of the blends subjected to AD.

**Table 3.2.** Main characteristics of the biochemical methane potential (BMP) tests on pretreated SW.

Parameter		Run 1					Run 2				
		Blank c1		T <sub>n-40-0</sub>	C <sub>8-25-0</sub>	C <sub>10-25-0</sub>	Blank c2		A <sub>n-25-5</sub>	CT <sub>10-40-0</sub>	CTA <sub>10-40-5</sub>
V <sub>inoculum</sub>	mL	150	150	150	150	150	150	150	150	150	150
V <sub>substrate</sub>	mL	-	66	62	61	73	-	76	130	80	110
F/M	g <sub>VS</sub> g <sub>VS</sub> <sup>-1</sup>	-	0.16	0.16	0.17	0.23	-	0.06	0.10	0.17	0.34
TAN	mg L <sup>-1</sup>	-	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 <sup>-1</sup>	-	5.22	5.27	5.92	5.22	-	6.69	49.87	77.48	109.66
Ca	g L <sup>-1</sup>	-	-	-	0.65	1.96	-	-	-	2.28	4.37
TS <sub>mix</sub>	[%]	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<sub>mix</sub> = 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 ( $35 \pm 2$  °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 Holliger et al. (2016). 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 KH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, and NH<sub>4</sub>Cl (solution A); CaCl<sub>2</sub>·2H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, and FeCl<sub>2</sub>·4H<sub>2</sub>O (solution B), and MnCl<sub>2</sub>·4H<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub>, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, and Na<sub>2</sub>SeO<sub>3</sub> (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 (Calabrò et al., 2019, 2018, 2016) using a three-neck bottle that contained an alkaline trap (3M NaOH) that

captured the CO<sub>2</sub> 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 CO<sub>2</sub>, 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<sub>tCODadded</sub><sup>-1</sup>. 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 (Equation (3.5)) was used to simulate the kinetics of the methane yields (Donoso-Bravo et al., 2010; Ghatak and Mahanta, 2014):

$$M = P \cdot \left\{ -\exp \left[ \frac{R_m \cdot \Theta}{P} \cdot (\lambda - t) + 1 \right] \right\} \quad (3.5)$$

where:

M = cumulative methane production [L per gram of tCOD added, L g<sub>tCODadded</sub><sup>-1</sup>].

P = methane potential [L per gram of tCOD added, L g<sub>tCODadded</sub><sup>-1</sup>].

Θ = Euler's constant.

R<sub>m</sub> = maximum production rate of methane [L per g of tCOD added and per day, L g<sub>tCODadded</sub><sup>-1</sup>d<sup>-1</sup>].

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 (3.5) 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<sub>n-40-0</sub>, C<sub>8-25-0</sub>, and C<sub>10-25-0</sub>. Raw SW (c1) was used as a control (Table 3.2). In this run, the TAN concentration was kept at about 0.35 g L<sup>-1</sup> 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<sup>-1</sup> (Chen et al., 2008; McCarty, 1964; Nie et al., 2015). The major contributor to digestion inhibition was free ammonia, which is cell-membrane-permeable (Ho and Ho, 2012), at concentration from 0.04 to 1.1 g L<sup>-1</sup> (Angelidaki and Ahring, 1994; Gallert and Winter, 1997; Hansen et al., 1998; Ortner et al., 2014). 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 (Belmonte et al., 2011; Hansen et al., 1998; Ho and Ho, 2012; Huang et al., 2019). 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<sup>-1</sup>, 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<sup>-1</sup>) 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<sub>n-25-5</sub>, CT<sub>10-40-0</sub>, and CTA<sub>10-40-5</sub> treatments; c2 was a BMP applied to raw SW (Table 3.2). In this case, the initial TAN concentration was set at 0.35 g L<sup>-1</sup>, 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<sup>-1</sup>, 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.

### 3.2.3. 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 3.3).

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 3.3.



**Table 3.3.** 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 <sup>-1</sup> ]	tCOD [g L <sup>-1</sup> ]	TAN [gN L <sup>-1</sup> ]
<b>i1</b>	2.26 0.18	± 70.12 0.17	± 8.13 ± 0.02	-	-	-
<b>i2</b>	3.87 0.10	± 67.83 0.47	± 8.16 ± 0.03	-	-	-
<b>c1</b>	1.02 0.01	± 65.16 2.65	± 7.04 ± 0.03	6675 ± 601	8063 ± 880	1280 ± 42
<b>c2</b>	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.

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 3.2, were used controls for the two runs of pretreatments and BMP tests.

#### 3.2.4. Analytical Methods

The following physico-chemical properties of inoculum and raw samples, as well as treated SW, were measured in duplicate using standard methods (APHA et al., 2012):

- 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.

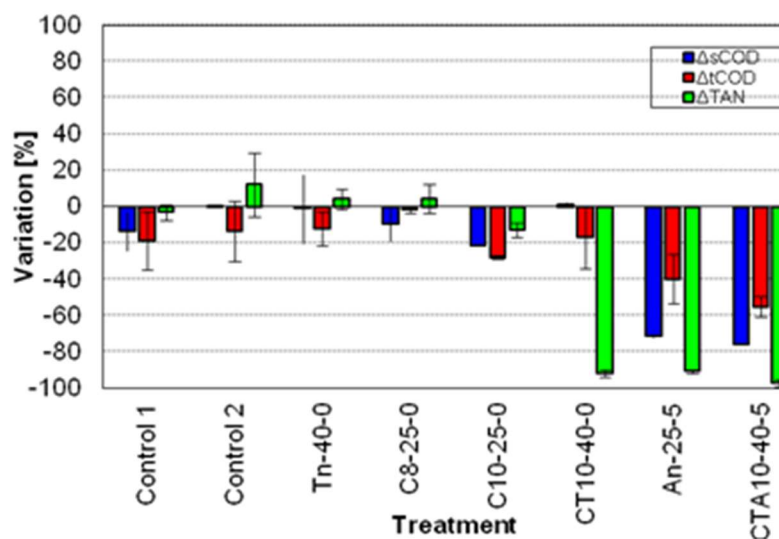
Moreover, the sCOD and TAN were evaluated on raw and pretreated SW. The liquid phase of the samples was obtained by centrifugation at 10,000 revolutions per minute of the rotor, equal to 0.559 g, for 20 min. The sCOD and TAN were evaluated by cuvette cap tests (WTW, code 1.14555, photometer WTW, PhotoLab 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 (Bonmatí and Flotats, 2003), whereas the organic nitrogen is mainly present in solid residue, which was removed by centrifugation.

### 3.3. Results and Discussions

#### 3.3.1. 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 3.4 and Figure 3.2) that was enhanced by the air supply and temperature.

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  $CTA_{10-40-5}$  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 (L. Zhang et al., 2012), 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 (3.4), the ammonium sulphate recovered by the  $A_{n-25-5}$  and  $CTA_{10-40-5}$  treatments was equal to  $4.67 \pm 0.79$  and  $4.98 \pm 0.87 g L_{SW}^{-1}$ , respectively.



**Figure 3.2.** 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;  $\Delta sCOD$ ,  $\Delta tCOD$ , and  $\Delta TAN$  = 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 3.4.** Physico-chemical characteristics of pretreated SW and variations compared to raw SW.

Treatment	pH <sub>i</sub>	pH <sub>f</sub>	sCOD [mg L <sup>-1</sup> ]	ΔsCOD [%]	tCOD [mg L <sup>-1</sup> ]	ΔtCOD [%]	TAN [mg L <sup>-1</sup> ]	ΔTAN [%]	MR [%]	Average Conversion of Added COD to Methane [%]
<b>c1</b>	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
<b>T<sub>n-40-0</sub></b>	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
<b>C<sub>8-25-0</sub></b>	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
<b>C<sub>10-25-0</sub></b>	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
<b>c2</b>	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
<b>A<sub>n-25-5</sub></b>	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
<b>CT<sub>10-40-0</sub></b>	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
<b>CTA<sub>10-40-5</sub></b>	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

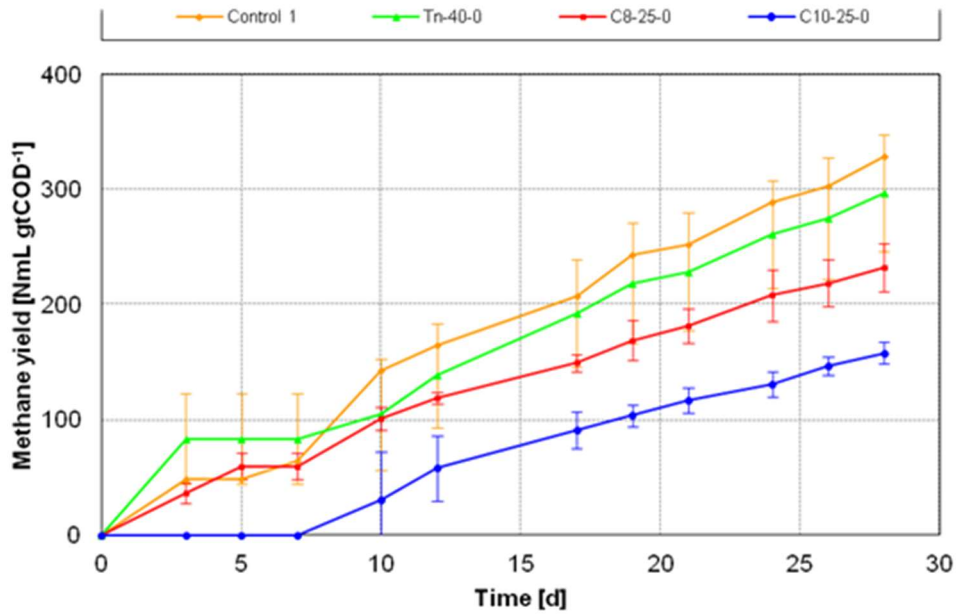
Mean ± standard deviation, values measured after 24 h; the capital letters of the tests indicate the treatment, and the three letters/numbers identify the value of the operational parameter, pH, temperature, and air flow rate; pH<sub>i</sub>, pH<sub>f</sub> = pH values at the beginning and the end of 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.

Among the treatments without aeration, CT<sub>10-40-0</sub> showed the highest TAN removal efficiency of 91.86% ± 1.96%, followed by C<sub>10-25-0</sub> of 12.77% ± 3.95%. The TAN reduction in CT<sub>10-40-0</sub> 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 C<sub>10-25-0</sub> treatment, carried out at the same initial pH as CT<sub>10-40-0</sub>, but room temperature (25°C), showed a higher sCOD removal efficiency of 27.77% ± 1.01%. The other treatments, T<sub>n-40-0</sub> and C<sub>8-25-0</sub>, 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 3.4 and Figure 3.2).

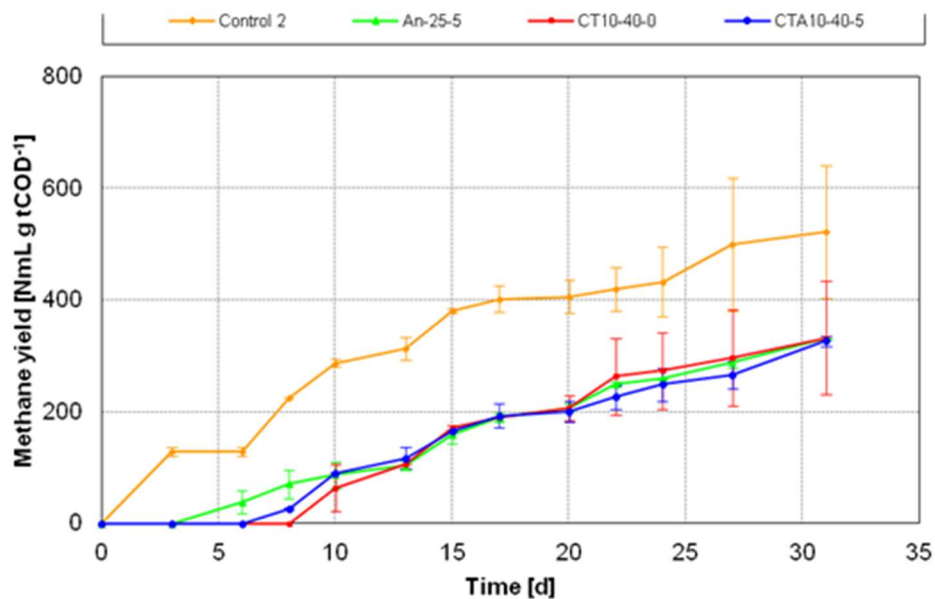
### 3.3.2. Effect of Pretreatments on Methane Yields of AD

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

The control 1 test produced the highest methane yield of 329 ± 18 NmL g<sub>tCOD</sub><sup>-1</sup> 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 3.4). 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, C<sub>8-25-0</sub> and C<sub>10-25-0</sub>, produced less methane, 232 ± 21 and 158 ± 9 NmL g<sub>tCOD</sub><sup>-1</sup>, which comprised 67% and 75% of average methane content in biogas, respectively, compared to the T<sub>n-40-0</sub> treatment without chemical adjustment, which produced 297 ± 51 NmL g<sub>tCOD</sub><sup>-1</sup>/62% of methane in biogas (Figure 3.3a). Since all blends were prepared at the same TAN concentration, the differences in methane production can be attributed to the different SW pretreatments.



(a)



(b)

**Figure 3.3.** 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.

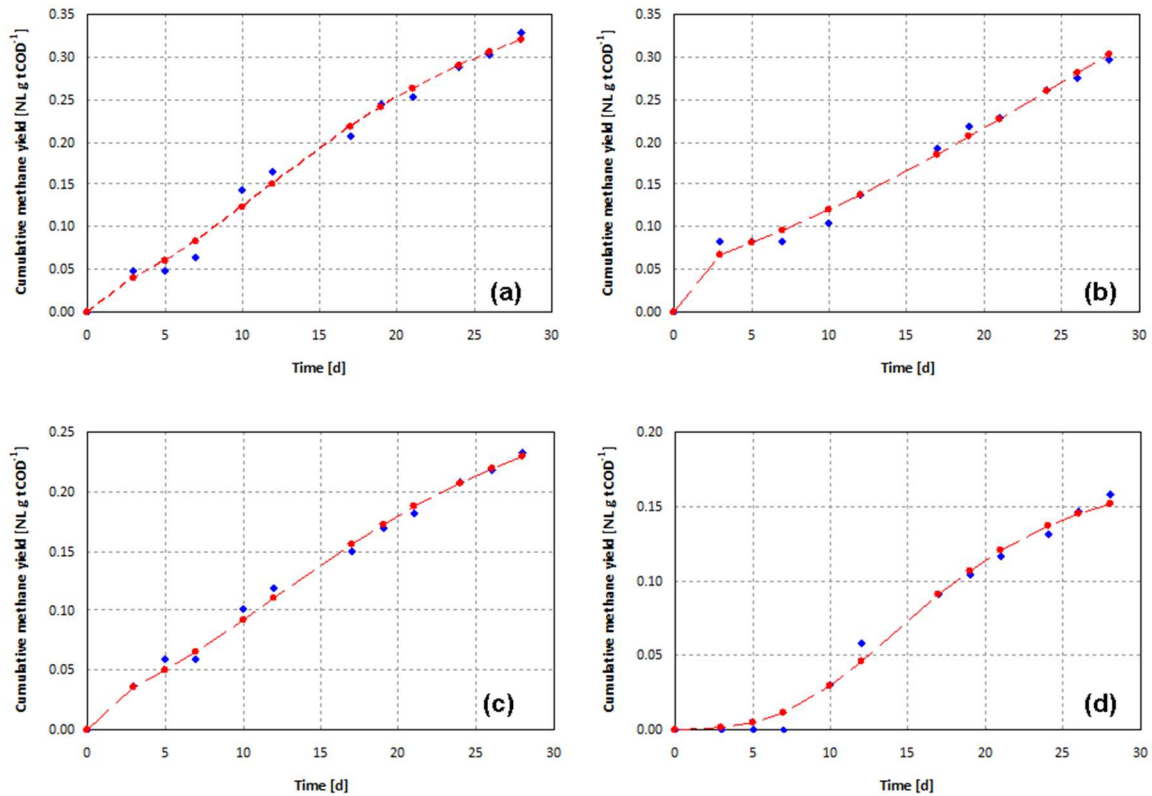
The addition of  $\text{Ca}(\text{OH})_2$  to adjust the pH required for the treatment may have partially inhibited the AD process. The pH increase after the addition of calcium compounds was found to be slightly inhibitory if its concentration was in the range of  $2.4\text{--}4\text{ g L}^{-1}$ , with a 50% inhibition of methanogenic activity at about  $5.0\text{ g L}^{-1}$  and a strong inhibition at  $8\text{ g L}^{-1}$  (Ahn et al., 2006; Kugelman and Chin, 1971; Parkin and Owen, 1986). Moreover, when calcium concentration was increased up to  $3\text{ g L}^{-1}$ , Ahn et al. (2006) noticed a positive effect of lipid-rich SW on AD, in which the lag phase of the process decreased and the methane production increased. Belmonte et al. (2011) also reported negative effects for calcium concentration over  $5\text{ g L}^{-1}$ .

Conversely, Zhang and Jahng (2010) observed a slight decrease (by about 10%) of the methanogenic activity when calcium ions were added up to  $7.2\text{ g L}^{-1}$ . 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  $2\text{ g L}^{-1}$ —than the inhibitory limits mentioned above (Table 3.3). Another possibility is that alkaline pretreatment caused the generation of inhibitory compounds (e.g., furfurals, as reported in Calabrò et al., 2015; Kumar et al., 2009; Monlau et al., 2012; Sambusiti et al., 2013). In fact, the alkali addition did not increase the methane production of the  $\text{C}_{8-25-0}$  and  $\text{C}_{10-25-0}$  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  $\text{T}_{n-40-0}$ , 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  $\text{T}_{n-40-0}$  may have been due to the lower reduction in sCOD (Table 3.4), although  $\Delta\text{sCOD}$  showed a high variability and the sCOD/TAN ratio was kept constant for all blends (Table 3.3).

Except for  $\text{C}_{10-25-0}$ , 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 3.5 and Figure 3.4).

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 (3.5) was found for all the BMP tests of Run 1 (Figure 3.4 and Table 3.5).



**Figure 3.4.** Measured and modeled (using the modified Gompertz Equation (3.5)) cumulative methane production of (a) c1, (b)  $T_{n-25-0}$ , (c)  $C_{8-25-0}$ , and (d)  $C_{10-25-0}$ . 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.

**Table 3.5.** Kinetic parameters of the Gompertz modified Equation (3.5).

BMP Test	$t_{50}$ [d]	Parameters of Gompertz Equation (5)		
		P	$\Lambda$	$R_m$
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 [ $L_{g_{tCOD_{added}}^{-1}}$ ];  $R_m$  = maximum production rate of methane [ $L_{g_{tCOD_{added}}^{-1} d^{-1}}$ ]; and  $\lambda$  = lag phase period or the minimum time required to produce biogas [d].

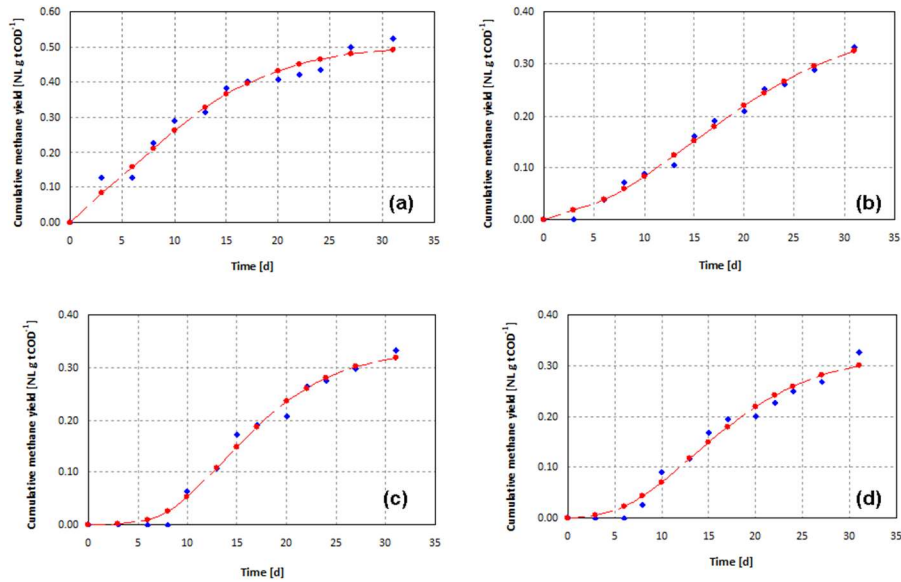
### 3.3.2.2. Run 2 (BMP Tests with Low TAN Concentration)

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 3.3b and Table 3.4), considering that 1 mol of formed  $\text{CH}_4$  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  $500 \text{ mL gVS}^{-1}$ , UNI/TS 11703:2018 (corresponding to approximately  $420 \text{ NmL g}_{\text{tCOD}}^{-1}$  (Bullock et al., 1996)), 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 (Calabrò et al., 2018; P. S. Calabrò et al., 2018; Yoon et al., 2014).

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 3.3b), 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  $50 \text{ mg L}^{-1}$ ). 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 3.3). Overall, the share of the initial tCOD converted to methane by AD and pretreatments was less than 95% of the initial value (Table 3.4). 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  $4 \text{ g L}^{-1}$ , showing that the alkali addition may have different effects on the AD of SW (Zhang and Jahng, 2010), 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 3.4). 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 3.5). 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 3.5 and Figure 3.5). Additionally, for the BMP tests of Run 2, the modified Gompertz Equation (3.5) showed a very good accuracy,  $R^2 = 99\%$ , in modeling the measured cumulative methane production (Figure 3.5).



**Figure 3.5.** Measured and modelled (using the modified Gompertz Equation (3.5)) 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.

### 3.3.3. 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%.

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 (Jackson-Moss et al., 1989) 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 2.5–4.0 g L<sup>-1</sup> according to Parkin and Owen (1986), although Jackson-Moss et al. (1989) reported that concentration up to 7 g L<sup>-1</sup> can be tolerated by anaerobic processes. However, this inhibition mechanism is still not clearly understood (Ahn et al., 2006).

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 (Rivard and Grohmann, 1991), 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 (Bonmatí and Flotats, 2003).

In the second run, no differences were detected in the methane yields of A<sub>n-25-5</sub>, CT<sub>10-40-0</sub>, and CTA<sub>10-40-5</sub> treatments, although in CTA<sub>10-40-5</sub>, 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 Bonmatí and Flotats (2003). 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 Zhang and Jahng (2010) and L. Zhang et al. (2012) 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 L L<sup>-1</sup> min<sup>-1</sup>, was attributed to the aerobic degradation and organic loss due to air stripping (L. Zhang et al., 2012) (Table 3.6).

**Table 3.6.** 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 <sup>-1</sup> min <sup>-1</sup> ]	Ammonia Variation [%]	pH, i	T [°C] – Time [d]	TAN [g L <sup>-1</sup> ]	NH <sub>4</sub> <sup>+</sup> - N [g L <sup>-1</sup> ]	NH <sub>3</sub> [g L <sup>-1</sup> ]	pH, f	BMP [mL g <sub>CODadded</sub> <sup>-1</sup> ]	Efficiency [%]
Bonmati and Flotats (2003)	Raw SW	-	-	-	7.7		3.24*		0.16*	8.3	38.4	-
	AS-SW (-)	-		-65	8.5		2.40*		0.68*	8.0	20.5	-46.6*
	AS-SW (9.5)	Ca(OH) <sub>2</sub>	80 – 4 – 0.05*	-69	8.8	35 – 80	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*
Zhang and Jahng (2010)**	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
	AS-SW (9.5)	CaO		-30.5*	8.06 ± 0.10				0.258 ± 0.049		262.3 ± 12.0	± 386
	AS-SW (10)			-49.1*	8.00 ± 0.12				0.185 ± 0.039		258.9 ± 17.3	± 379
	L. Zhang et al. (2012)	Raw SW	-	-	-				4.801			3.5*
AS-SW (7.2)		NaOH	37 – 48 – 1.0	-28.0	n.a.	37 – 20	n.a.	3.272	n.a.		35*	900
AS-SW (9.0)					-47.0				2.314			90*

Reference	Sample (Adjusted pH)	Pre-Treatment Conditions			AD Conditions								
		Alkali type	T [°C] – t [h] – Q [L L <sup>-1</sup> min <sup>-1</sup> ]	Ammonia Variation [%]	pH, i	T [°C] – Time [d]	TAN [g L <sup>-1</sup> ]	NH <sub>4</sub> <sup>+</sup> - N [g L <sup>-1</sup> ]	NH <sub>3</sub> [g L <sup>-1</sup> ]	pH, f	BMP [mL gCOD <sub>added</sub> <sup>-1</sup> ]	Efficiency [%]	
	AS-SW (10.0)			-80.0				0.838			182*	5100	
	AS-SW (11.0)			-88.1				0.465			142*	3957	
L. Zhang et al. (2012)	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	
	AS-SW (10.0)		37 – 48 – 10.0	-92.0				0.359			122*	1120	
								6.30 ± 0.045			49.2 ± 16.6	-	
L. Zhang et al. (2012)**	AS-SW (9.5)							2.93 ± 0.054			170.3 ± 26.0	246	
	AS-SW (10.0)	NaOH	37 – 24 – 4.0	n.a.	8.0 ± 0.2	37 – 20	n.a.	1.85 ± 0.072	n.a.		132.6 ± 8.6	170	
	AS-SW (11.0)							0.86 ± 0.061			78.9 ± 17.9	60	
This study	c1	-	-	-2.89	7.9 ± 0.03			0.352			7.47 ± 0.01	329	-
	T <sub>n-40-0</sub>	-	40 – 24 – 0	+4.39	8.03 ± 0.01			0.354			7.48 ± 0.01	297 ± 51	-9.8
	C <sub>8-25-0</sub> (8)	Ca(OH) <sub>2</sub>	25 – 24 – 0	+4.51	8.13 ± 0.02	n.a.		0.351	n.a.	n.a.	7.50 ± 0.00	232 ± 21	-29.4
	C <sub>10-25-0</sub> (10)		25 – 24 – 0	-12.77	8.93 ± 0.01			0.353			7.80 ± 0.01	159 ± 9	-51.9

*Effects of ammonia stripping and other physico-chemical pretreatments on anaerobic digestion of swine wastewater*

Reference	Sample (Adjusted pH)	Pre-Treatment Conditions			AD Conditions							
		Alkali type	T [°C] – t [h] – Q [L L <sup>-1</sup> min <sup>-1</sup> ]	Ammonia Variation [%]	pH <sub>i</sub>	T [°C] – Time [d]	TAN [g L <sup>-1</sup> ]	NH <sub>4</sub> <sup>+</sup> - N [g L <sup>-1</sup> ]	NH <sub>3</sub> [g L <sup>-1</sup> ]	pH <sub>f</sub>	BMP [mL gCOD <sub>added</sub> <sup>-1</sup> ]	Efficiency [%]
c2	-	-	25 – 24 – 0	+12.37	8.02 ± 0.02		0.346			7.75 ± 0.03	523 ± 120	-
A <sub>n-25-5</sub>	-	-	25 – 24 – 5	-90.60	8.42 ± 0.02		0.050			7.66 ± 0.01	332 ± 1	-36.5
CT <sub>10-40-0</sub> (10)		Ca(OH) <sup>2</sup>	40 – 24 – 0	-91.86	8.65 ± 0.01	n.a.	0.031	n.a.	n.a.	7.72 ± 0.04	332 ± 102	-36.5
CTA <sub>10-40-5</sub> (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<sub>i</sub> and pH<sub>f</sub> = 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.

### 3.4. 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  $0.35 \text{ g L}^{-1}$  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<sub>2</sub>-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.





## Conclusions and Future Perspectives

This 3-year study with the related laboratory experiments has inspired three main considerations.

First, the experimental activity has proved that the air stripping can be considered a suitable system for the management of swine wastewater, especially when it is combined with other technologies (for instance, for the simultaneous recovery of phosphorous and nitrogen or for the production of biomass, such as microalgae, to be valorised by other processes). This is due to the extreme flexibility of the air stripping: by properly settings of the operational parameters, it is possible to maximise the ammonia nitrogen recovery from swine wastewater and improve the characteristics of the treated SW for other subsequent treatments. For example, the results of the optimisation of air stripping process have showed that high ammonia removal can be obtained also at low temperature, chemical addition and air flow rate avoiding extreme process conditions with possible negative impacts on the environment.

Second, this research has shown that the ammonium sulphate recovered using air stripping, also in combination with other chemical and/or thermal processes, may be a natural fertiliser produced at a sustainable cost. However, no investigations have been carried out on the quality of the obtained ammonium sulphate that is related to the presence of organic matter in the wastewater. This activity goes beyond the specific aim of this thesis that mainly focused on the ammonia removal efficiency of the process, although the effective possibility of using the produced salts as fertiliser, that could be affected by the presence of volatile organic compounds stripped from the wastewater and precipitated together with the ammonia, could be explored. Hence, further research should evaluate the quality of the salts produced and their agronomic effects.

Third, in the conceptualisation of this research, the application of air stripping before the anaerobic digestion process was thought to enhance the methane yield of the treated substrate compared to the raw swine wastewater. However, beyond the expectations, all the anaerobic tests carried out on pre-treated swine wastewater showed lower methane production compared to the anaerobic digestion of raw swine wastewater. The main reasons for these unexpected results could be the lack of nutrients and organic matter (that are necessary for microorganisms' growth) as the consequence of the pre-treatments and the possible accumulation of toxic compounds (such as furfurals). Since the ammonia nitrogen was always kept under the inhibitory threshold reported in literature, the decrease in methane production can not be due to it. A possibility is that the test method used (BMP – batch tests) is not adapt to highlight the real potential of AS pretreatment before AD and that continuous-semicontinuous tests should be used instead. This is another important finding of this research: the

feasibility and the efficiency of the anaerobic digestion of swine wastewater can not be only based on the ammonia nitrogen and organic matter concentrations. Other parameters (such as the presence of furfurals or heavy metals) must be therefore taken into account; more research is needed, in order to deepen the possible reasons for the reduced methane yields of treated swine wastewater. Therefore, the optimal operation parameters leading to a balanced content of nitrogen and organic matter should be identified in further experiments.

Overall, we have demonstrated that air stripping is a suitable system to recover ammonium sulphate and remove organic compounds compared to the common intensive treatments. Conversely, the use of the air stripping as pre-treatment of the anaerobic digestion can not be suggested, if the latent reasons of the unsatisfactory performances are not clarified. Further researches should focus on the comprehension of possible relations among the physico-chemical characteristics of the raw and pretreated swine wastewater and the related methane production. Other type of alkalis could be used in the pretreatment phase to evaluate and compare their effect of both the ammonia recovery and the anaerobic process. Moreover, the effect of alkali dosages should also be considered to evaluate whether possible inhibition process is related to the quality and quantity of the added chemicals. Finally, semicontinuous anaerobic digestion tests would allow to define the process parameters (e.g. the organic loading rate) to be adopted in full scale digesters.

This study is a contribution for the consolidation in the animal breeding sector of environmentally and economically sustainable systems for the management of wastewater and solid residues.





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