Approaches to the mitigation of ammonia inhibition during anaerobic digestion – a review

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Abstract

The digestion process of organic waste rich in high ammonia content has always been a gridlock during the methanogenesis process. The free ammonia may increase inhibition/toxicity, which in turn affects the microbial community in the digester and eventually leads to process failures. Substantial methods have been proposed and assessed for curtailing ammonia emissions in anaerobic digesters to attain a safe and steady process so that, along with high methane production, high quality effluents can also be recovered. There are several means for lowering the erratic ammonia in organic wastes that are in use currently, such as decrease of pH, which favours the formation of ammonium over ammonia in the equilibrium; for example, the use of chemical additives that attach ammonium-N. Ammonia can also be removed from nitrogen-rich substrates during anaerobic digestion through other methods such as struvite precipitation, membrane distillation, air stripping, ion exchange, and adsorption. A thorough survey of different articles has shown that ion exchange, adsorption and changing of the C/N ratio through the co-digestion technique are the most commonly studied methods for mitigating ammonia inhibition in wastewater during anaerobic digestion. A detailed review of these methods in the context of nitrogen-rich substrates will be discussed in this paper.

Key words: ammonia, ammonium, anaerobic digestion, methane, pH and temperature

Highlights

• Temperature and pH ranges for overcoming inhibition.
• Best C/N ratio.
• The use of cryogenics.

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INTRODUCTION

The current utilisation of alternative and non-petroleum based renewable energy sources has created attention among the public due to the ongoing depletion of fossil fuels, which have been regarded as the chief source of energy production. Apart from being depleted as time goes on, the burning of these fossil fuels has been unfriendly to the environment as it results in global warming. However, the biological process of organic waste occurring in the absence of oxygen (anaerobic digestion) can be regarded as a potential solution to global warming through biogas production (Andriani et al. 2014). Through biological and thermo-chemical routes, the biogas production process is considered as an alternative to fossil fuels and an affordable technology for energy production as a means of conserving the environment (Chandra et al. 2012).

Several organic wastes such as cow dung, pig manure, abattoir waste, municipal waste and agricultural waste can serve as sources of biogas production during anaerobic digestion (AD). The biogas technology has gained extreme importance recently since it can produce an alternative source of energy through the biological treatment of organic wastes with different characteristics (Yenigün & Demirel 2013). The main products produced during anaerobic digestion of organic waste are methane and carbon dioxide, though the concentration of ammonia may be contained in the digestate. Therefore, there would be an accumulation of ammonia and recirculation of the effluent in the digester during the breakdown of the feedstock (Sheng et al. 2013). A high concentration of ammonia can affect the methanogenesis process and lower the quantity of methane produced during anaerobic digestion. The recommended level of total ammonia nitrogen (TAN) for a suitable and conducive environment for methanogens in the reactor is below 200 mg/L during the anaerobic digestion process (Liu & Sung 2002). Numerous technologies for removing ammonia have been developed and reported such as chemical precipitation, air stripping, ion exchange and adsorption (Ahn 2006; Han et al. 2008; Qiao et al. 2010; Zhang et al. 2011). Inhibitors in AD processes include organics such as chlorophenols, halogenated aliphatics, N-substituted aromatics, or inorganics such as ammonia, sulfide and light metal ions in nature or a combination thereof (Anjum et al. 2016).

NITROGEN-RICH SUBSTRATES

Microorganisms present in the reaction undergoing anaerobic digestion require a balanced ratio of fermentable carbohydrate, nitrogen, phosphorous and other elemental nutrients for their normal growth (Ghasimi et al. 2009). For instance, research that was done in Salta, Argentina, revealed that the organic fractions of C:N:P found in municipal solid waste (MSW) had an optimum ratio of 126:7:1 (Plaza et al. 1996).
However, high nitrogen fractions in the substrate are not suitable as they result in an accumulation of ammonia during the AD process. This phenomenon inhibits further growth of methanogens, which leads to reduced biogas quality and quantity. Many kinds of literature have reported a very high ammonia concentration in wastewater ranging from 1,700 mg/L to 14,000 mg/L (Anjum et al. 2017). In most cases, organic nitrogen in the digester can be presented as uric acids, amino acids and proteins, which is then hydrolysed to inorganic ammonia during the AD process. The released ammonia tends to accumulate during protein degradation, a process happening very slowly in the digester (Karthikeyan & Visvanathan 2012). Substrates known to have high nitrogen contents are animal wastes, municipal wastes (bio-wastes), meat processing wastes and dairy wastes. Besides, being an inhibitor in the AD process, free ammonia is also an environmental pollutant. Free ammonia and increased eutrophication, respectively, are noxious for fish species, lowering the dissolved oxygen, being highly corrosive and elevating infections (Lauterböck et al. 2012). Many possibilities to control ammonia inhibition have been studied and reported in the literature. Some methods were practical and applicable at large scale, while some are still in research at lab scale. However, each method has its pros and cons, depending on the inoculum, type, and characteristics of the substrate, reactor configuration, environmental and operational conditions.

MECHANISM OF AMMONIA INHIBITION

During the AD process, a small amount of the organic nitrogen is biologically broken down to inorganic ammonia (NH$_4^+$–N/NH$_3$–N). From the experiment done by Gallert and Winter in 1997 (Gallert & Winter 1997), it was reported that only about 1/3 and 1/2 of the total Kjeldahl nitrogen was converted to ammonia during mesophilic and thermophilic degradation, respectively. In the liquid phase, total ammonia occurs in two principal forms: the ionised form of the ammonia ion (NH$_4^+$) and the free, un-ionised gaseous form of ammonia (NH$_3$). The dissociation equilibrium of ammonia in aqueous solutions (Equation (1)) depends on pH and temperature. With a rise in pH and temperature the equilibrium shifts to NH$_3$.

$$\text{NH}_4^{+}\text{(aq)} \leftrightarrow \text{NH}_3\text{(aq)} + \text{H}^+\text{(aq)} \quad (1)$$

The free ammonia (NH$_3$) and ammonium species (NH$_4^+$) form an equilibrium. The NH$_3$ species, which is toxic and vulnerable to the cell membrane of bacteria and archaea, can affect the intracellular pH, and concentrations of ions once it has entered the cell. Among the anaerobic degrading microorganisms, methanogens (Euryarchaeota) are reported to be the groups most affected by elevated ammonia levels (>1,800 mg/L) and the first to be inhibited (Krakat et al. 2017). However, the toxicity of free ammonia that can be tolerated by microorganisms described in literature differed significantly, with concentrations ranging between 50 to 1,500 mg NH$_3$–N/L (Hansen et al. 1998; Bujoczek et al. 2000; Siles et al. 2010).

STRATEGIES TO OVERCOME AMMONIA INHIBITION

Recently, there have been several methods to reduce volatile ammonia, which include the reduction of pH, in which ammonium is highly favoured over ammonia during the process, application of chemical additives to adsorb nitrogen species. However, the use of physical covers, biofilters and scrubbers can also be employed for ammonia removal (Ndegwa et al. 2008). Breakpoint chlorination and membrane-based technologies have been less commonly used, unlike some studies based on the alteration of substrate C/N ratios to ensure optimal microbial growth (Kayhanian 1999; Siles et al. 2010; Karthikeyan & Visvanathan 2012). Meanwhile, stripping and chemical precipitation, which are physical-chemical processes, have also been in use for mitigation of ammonia. However, also,
the reduction of ammonia can either be done through a pretreatment step, during AD or as a post-treatment of the AD effluent (Serna-Maza et al. 2015).

The ongoing depletion of fossil fuels on earth has influenced the perspective of utilising organic waste with a low-cost process treatment to harvest biogas as renewable energy. In turn, this technology has triggered the desire to increase the performance and efficiency of the process. Through the process, various studies have been done to remedy the effect of ammonia inhibition. This paper highlights some of the strategies that have been recently in use to lower ammonia, and they have been categorised into three groups, namely optimisation of substrate parameters and properties, physical-chemical processes and application of various additives.

Optimisation of substrate parameters and properties

The performance of the digester can be improved through optimisation of some parameters, which can provide a conducive environment for microorganisms that are vulnerable to the unstable system of the reactor. In this case, ammonia inhibition can be reduced through optimisation of different properties and parameters following the substrate’s nature. For example, alteration of the C/N ratio, pH and temperature can be among the fundamental strategies to lower the ammonia inhibition level.

PH AND TEMPERATURE ADJUSTMENT

pH and temperature have been among the critical parameters that can be optimised to control the accumulation of ammonia in the digester during AD of wastewater (Wang et al. 2012). The effect of pH and temperature increase does not only retard the growth of methanogens but also affects the production rate of biogas during anaerobic digestion (Xie et al. 2015). For example, at pH range of 7.3–7.7 and TAN concentration of 2,000 mgNL⁻¹, it was observed that both NH₃ and NH₄⁺ induce the inhibition process largely as per both experimental and model results (Astals et al. 2018). Generally, during the thermophilic condition in which the operating temperature is above 40°C, there is an accumulation of fatty acids, which inhibits the growth of methanogens resulting into low biogas production (Jena et al. 2017). Different studies have suggested that there is a relationship between the biogas produced during the AD process with a range of temperature settings. These results revealed that there is a linear correlation between the biogas produced with temperature from 25°C to 44°C. Although higher temperature (thermophilic) influences rapid degradation of substrates, it is not recommended due to its low effect on biogas production rate, large energy input and operational complications, hence it is not economically feasible (Chae et al. 2008).

However, the variation of pH and temperature can influence the transition of ammonium ion (NH₄⁺) and free ammonia (NH₃) in the liquid phase (Zhang et al. 2005). Thus, this phenomenon is very crucial in determining the equilibrium shift between the two species since NH₄⁺ is not toxic to methanogens and is regarded as a potential fertiliser (Hunt & Boyd 1981). Furthermore, it is indicated from other researchers that biogas production can be reduced when there is an increase in temperature due to the free ammonia (NH₃) released in the reactor, which ultimately inhibits the methanogenesis process (Angelidaki & Ahring 1994; Hansen et al. 1999).

It is therefore recommended that in order to lower ammonia inhibition during AD of the substrate rich in nitrogen compounds, the digester should be operated at a pH below 7.4 and maintained at mesophilic condition (Siegrist et al. 2002).

CHANGING THE C/N RATIO

The carbon to nitrogen ratio is another important parameter that can determine the feasibility of microorganisms during the AD process (Kumar et al. 2010). Since carbon is used for energy production and
nitrogen is used for building cell structure, a combination of the two elements is a paramount factor determining the survival of microorganisms during the AD process. To ensure the sustainability of microorganisms in the reactor undergoing AD process, there is a need to balance the nutrients supplied from both carbon and nitrogen in a ratio in which the amount of carbon is higher than nitrogen. For example, Dai et al. (2016) reported that the adjustment of the C/N ratio to 17/1 during AD of waste activated sludge (WAS) and perennial ryegrass co-digestion enhanced high production of methane content in the biogas. However, from the study that was done by Xu et al. (2016), it was observed that heterotrophic bacteria in the AD system were actively playing a major role in removing ammonia when the C/N ratio was higher than 18/1. If the amount of nitrogen exceeds that of carbon (low C/N ratio), the excess amount of nitrogen is converted to ammonia, which becomes inhibitory for methanogens (Mata-Alvarez et al. 2011; Astals et al. 2012; Wang et al. 2012).

It is vital to control the C/N ratio during the AD process to reduce the possibility of ammonia accumulation in the digester when the nitrogen content exceeds carbon (Dai et al. 2016). Co-digestion is among the appropriate solutions to get a better carbon to nitrogen balance in which different organic materials are mixed to enhance the stability of the AD process (Mshandete et al. 2004; El-Mashad & Zhang 2010). However, there are several other benefits that can be obtained through the co-digestion process. Some of the benefits include the dilution of the potentially toxic compounds, both pH and moisture contents are adjusted, and the buffer capacity to the mixture content is maintained (Esposito et al. 2012).

Therefore, the inhibitory effect of ammonia can be alleviated through anaerobic co-digestion of different organic substrates, provided that a C/N ratio ranging between 15 and 30 is obtained. This ratio is usually regarded as the optimum ratio after mixing the substrates and is considered to be perfect for a stable AD process (Li et al. 2009; Zhang et al. 2013).

Physical-chemical processes

Most of the protein-rich substrates are composed of nitrogen fragments and carbon, which determines the sequence of amino acids, which are regarded as building blocks of protein. The excess of nitrogen fragments in the digester can form various kinds of nitrogen groups such as NH₃, NH₄⁺ and NH₃⁻N, which induces the inhibitory effect to methanogens in the reactor (Chiu et al. 2007). However, ammonia's effect in the anaerobic digester can be removed by physical-chemical processes such as air ammonia stripping, the formation of struvite and membrane filtration (Guštin & Marinšek-Logar 2011).

**AIR STRIPPING**

Air stripping is the technology that separates the volatile organics from wastewater by increasing the surface area of wastewater exposed to air. The method involves the mass transfer of volatile contaminants from water to air (Gorre & Himabindu 2014). This method is sometimes accompanied by direct aeration treatment, which forces the air through a reactor; as a result, the volatile ammonia is released to the atmosphere. Recent studies show that both CO₂ and biogas produced during the AD process can be used for the stripping process because of their potentiality in adjusting the pH of the anaerobic digestion effluent (Lei et al. 2007; Laureni et al. 2013).

For example, Liao and other co-authors (Liao et al. 1995), from their study revealed that during the stripping method, there are three factors to take into consideration when removing ammonia in both forms, either as ammonium ion or volatile ammonia. These factors are temperature, pH and the ratio of air to wastewater flow rate. The method further revealed that the volatility of ammonia depends on temperature whereby the air temperatures must be upheld at appropriately steep levels. In addition, Georgiou et al. (2019), in their findings, concluded that a temperature above 45°C is mostly favoured
for air stripping. Moreover, when ammonia removal was considered for ammonia fermented swine manure, the efficiency was 90% and 85% for air stripped at pH of 8.8 and 10.2, respectively (Huang et al. 2019). However, the decrease in ammonia removal efficiency from 90% to 85% was due to the increase of pH from 8.8 to 10.2, which was adjusted with the addition of lime before the stripping process. Lime addition, such as calcium hydroxide (Ca(OH)₂), is usually done in order to elevate the pH for simplifying the volatilisation of ammonia and removal of heavy metals through co-precipitation of other organic macromolecules and particulate matters present in the substrate (Renou et al. 2009). Among the drawbacks of this method is the packed tower, which results in the formation of a suspension due to solid particles that are a result of slaked lime added in the wastewater for pH adjustment (Quan et al. 2009). However, Yuan et al. (2016) revealed that high mass transfer performance could be achieved when rotating packed beds (RPB) are used to enhance a continuous flow compared with packed towers, which demand stripping tanks. Generally, RPBs are very small in size, which improves the high efficiency and short retention time.

**PH EFFECTS**

Results from Table 1 concerning the experiment that was done by Liao et al. (1995) indicate that ammonia removal in swine wastewater was achieved at 90.5% removal efficiency, 22 °C, pH of 9.5 and airflow rate of 45 L/min for 55 hrs. However, the higher removal efficiency was achieved as the pH decreased below 10, while increasing the pH above 10 did not significantly induce ammonia removal efficiency. Through mass transfer, the stripping process is enhanced by elevating the pH, favouring the transition in the chemical equilibrium between NH₃ and NH₄⁺ (Equation (1)). This phenomenon suggests that the pH should be maintained in alkaline media, in which the equilibrium shift lies in the direction of ammonia, as it would be substantial for increased ammonia removal efficiency during the recovery process (Ferraz et al. 2013).

**Table 1** | Tower air-stripping experiments (Liao et al. 1995)

| Experiment no. | T.S(%) | NH₃-N (mg/l) | Air flow (l/min) | Liquid flow(l/min) | Air/liquid (ratio) | pH | T°C |
|----------------|--------|--------------|------------------|-------------------|-------------------|-----|-----|
| 1              | 0.659  | 1,951        | 45               | 0.830             | 54.2              | 9.4 | 22-25|
| 2              | 0.663  | 2,192        | 45               | 0.861             | 52.3              | 11.5| 22-24|
| 3              | 0.942  | 2,154        | 65               | 0.877             | 74.1              | 10.6| 21-23|
| 4              | 0.942  | 2,142        | 65               | 0.833             | 78.0              | 9.5 | 21-23|
| 5              | 0.942  | 2,072        | 65               | 0.870             | 74.7              | 11.9| 21-22|
| 6              | 1.953  | 838          | 65               | 1.172             | 55.5              | 10.6| 21-22|
| 7              | 1.953  | 819          | 90               | 1.171             | 76.9              | 11.5| 19-23|
| 8              | 2.963  | 706          | 90               | 1.062             | 84.7              | 10.6| 16-19|
| 9              | 2.963  | 694          | 90               | 1.034             | 87.0              | 9.6 | 17-22|
| 10             | 0.649  | 2,152        | 90               | 0.885             | 101.9             | 11.7| 13-18|
| 11             | 0.613  | 2,192        | 90               | 0.863             | 104.3             | 9.4 | 6-14 |
| 12             | 0.613  | 2,192        | 90               | 0.870             | 103.4             | 10.6| 8-15 |
| 13             | 0.651  | 1,812        | 90               | 0.851             | 105.8             | 10.7| 18-21|
| 14             | 0.651  | 2,031        | 90               | 0.845             | 106.5             | 11.7| 18-21|

**THE EFFECTS OF AIRFLOW RATE**

The stripping technique was aided by increasing the airflow ratio from 52 to 73 regardless of the pH change. However, the stripping efficiency increased when the airflow rate was kept constant at
65 L/min, but this increase did not influence the ammonia removal efficiency as this remained the same when the flow rate was increased to 90 L/min. Consequently, when the airflow rate increases so does the liquid – surface area, which makes the amount of NH₃ diffused in air easily controlled (Srinath & Loehr 1974). Nevertheless, it is recommended that the optimum airflow rate be 5 L/min for 1 L of wastewater because the increase in airflow rate influences a high demand for engineering operational cost with little increase in ammonia removal efficiency (Lei et al. 2007).

TEMPERATURE EFFECTS

The liquid and air temperatures are the factors that seem to be influencing the ammonia removal efficiency at a pH below 10.5, as described elsewhere. Nevertheless, the ammonia removal efficiency was not significant above pH 10.5 as the temperature was increasing. From these observations of temperature influence, it was recommended that the ammonia stripping processes should be done during warm weather (Liao et al. 1995).

From the study of Bonmati & Flotats (2003), it was observed that a combination of air stripping and absorption could be applied to eliminate and restore ammonia from pig slurry whereby sulfuric acid was used to absorb ammonia transferred in the air from waste. The experiment was done based on pH and temperature as the factors in assessing the feasibility of the process and it was found that an initial pH of 11.5 was significant for removing ammonia regardless of the temperature, which was increased up to 80 °C.

Since the ammonia stripping method involves the transition of ammonium ion (NH₄⁺) and ammonia gas (NH₃) in the liquid phase (Deublein & Steinhauser 2011), the shift of the equilibrium towards ammonia gas (NH₃) (Lei et al. 2007) can be achieved through variations of the two parameters, pH and temperature, of the medium. The coexistence of both ammonium and ammonia in the liquid phase can be described in the equation below:

\[
[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+] / K_a}
\]  

(2)

For instance, Guštin & Marinšek-Logar (2011) examined the pH and temperature parameters for the feasibility of biogas plant operating conditions. The findings of ammonium exclusion were correlated with tentatively determined values of free ammonia in the same conditions. Through the stripping method, ammonium ions were removed by 92%, whereby total nitrogen from the anaerobic effluent was also removed by 88.5%. It was observed that the high pH was profoundly influencing the stripping process, favouring the change in ammonia/ammonium ratio over free ammonia. Moreover, the quantity of air that was outflowing through the stripping bench impacted the conversion of ammonia from the liquid phase to the gaseous phase with little effect of the temperature.

For this case, air stripping seems to be a convenient method for the wastewater treatment process, particularly in the recovery of valuable ammonia and other nitrogen species. To maximise the efficiency of the process, air stripping must be operated in a packed tower to provide a large mass transfer area (Djebbar & Narbaitz 1998).

AMMONIA RECOVERY PROCESS

Since ammonia gas is released to the environment during the stripping process, there should be a mechanism to prevent the direct release of the ammonia gas to the environment, as it can affect the ecosystem due to its toxicity. Many kinds of literature consider an ammonia stripping process coupled with absorption as an alternative method for ammonia removal in the final stage of the
process (Bonmati & Flotats 2003). In most cases, sulfuric acid (H₂SO₄) is used as an absorbent in which free ammonia (NH₃) reacts with H₂SO₄ to form ammonia salt (NH₄)₂SO₄ that can be used as a fertiliser (Lei et al. 2007).

**STRUVITE PRECIPITATION METHOD**

Struvite precipitation is among persistent efforts made so far to lessen the loss of ammonia in the composting operation by generating struvite crystallisation in the compost mixed with the addition of water-soluble Mg and P salts (Huang et al. 2014). The gaseous loss of ammonia was lowered by the growth of struvite crystals, which caused a massive increase in the ammonia content in the compost of up to 1.5%. The other findings by Jeong & Hwang (2005) tried to scrutinise how the overall behaviour of nitrogenous materials could be changed by the aggregation of ammonia into struvite crystals.

This approach has been applied to numerous wastewaters, including swine waste (Burns et al. 2001; Nelson et al. 2003), agro-industrial effluents (Altinbas et al. 2002), landfill leachate (Li et al. 1999; Altinbaş et al. 2002), calf manure (Schuiling & Andrade 1999), coke manufacturing (Zdybiewska & Kula 1991), leather tanning (Tünay et al. 1997) and anaerobic digester sidestreams (Fujimoto et al. 1991; Battistoni et al. 1997). The removal of (NH₄⁺), phosphate (PO₄³⁻) or both from wastewater by struvite precipitation is usually done by the addition of Mg²⁺ ion, which is specifically meant for changing the solubility product equilibrium and triggering precipitation. Different sources of Mg²⁺ ion, for example Mg(OH)₂, MgO, MgCl₂·6H₂O, etc., have been in use for ammonia removal by struvite precipitation (Uludag-Demirer et al. 2005).

**FORMATION OF STRUVITE**

According to Kim et al. (2007), the equation below shows how the white crystalline solid of struvite forms:

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} \]  \hspace{1cm} (3)

The formation of struvite in a solution is a pH-based reaction because the precipitating ions are all pH-dependent.

Subsequently, struvite precipitation is primarily based on the thermodynamic equilibrium of constituent ions in the solution. Kim et al. (2007) conducted a study in which the feeding of chemicals such as magnesium, orthophosphate and buffering reagent were studied to affirm the performance variation of struvite precipitation rendering to the feeding sequence. In this study, magnesium chloride and potassium phosphate solutions were used at different concentrations in the molar ratio of Mg:PO₄ 1:1.2:1.2 for NH₄⁻–N removal (Ohlinger et al. 1998). The NH₄⁻–N removal capability was found to be less than 50% as a result of the high accumulation of PO₄³⁻ and Mg²⁺ ions, which eventually dropped the pH to 6. The decrease in pH affected the crystallisation and precipitation of the solution that resulted from the dissolution of the struvite. Furthermore, the efficiency in removing NH₄⁻–N was increased to 78% when the pH was increased to 9.2 and decreased when the pH was increased above 9.4 (Ryu et al. 2008). On the other hand, magnesium and orthophosphate dosage were examined and it was found that the molar ratio affected the removal efficiency in which the NH₄⁻–N removal was greatly affected by the concentration of orthophosphate in the solution much more than that of magnesium ions (Escudero et al. 2015).

It can be concluded that pH is also among important parameters to consider besides the dosage of orthophosphate and magnesium ions when this approach is applied.
MEMBRANE DISTILLATION METHOD

The MD method is a thermally determining operation in which a mixture across a hydrophobic microporous membrane is separated by physical means. The membrane operates as a boundary to isolate a heated solution from a more cooling chamber that encompasses either a liquid or a gas phase (Banat & Simandl 1998). Recently, the technology has been used considerably for volatile compounds removal such as ammonia due to its hypothetically low energy prerequisite. It is most likely for recovering and reuse precisely, which can be an advantageous approach for wastewater treatment having a relatively low level of volatile compounds but operating under high temperature. The simulation experiment that was done by Xie and other co-authors in 2009 (Xie et al. 2009), on wastewater encompassing low concentration of ammonia (100 mg/L) with sweep gas membrane distillation at pH 11.5, showed the ammonia removal was achieved by 97% at the highest temperature and fastest gas flow. The feed rate and gas flow were also investigated, in which from 59 to 100 mL/min, the removal efficiency increased from 67 to 77% after two hours. A further increase of the feed rate from 100 to 250 mL/min had a trivial impact on the removal rate contrary to the feed temperature, which increased the ammonia removal rate. On the other hand, the increase in temperature (about 40 °C) influenced the diffusion of ammonia in the membrane pores due to a higher mass transfer coefficient (Lin et al. 2018). This phenomenon is regulated by the endothermic nature of the feed solution, which enables the volatility and dissociation of ammonium ions.

Nevertheless, the ammonia removal efficiency was investigated using a modified direct contact membrane distillation (MDCMD) in the aqueous solution, which was compared with a hollow fibre membrane contractor (HFMC). In line with this experimentation, the effect of controlling parameters such as pH, temperature and contact time was also examined, in which the experimental results showed a higher ammonia removal efficiency of 99.5% for MDCMD compared to 52% and 88% for DCMD and HMC within 105 min, respectively. The best feed pH of 12.20 was proved to be the main factor in the modified direct contact membrane distillation (MDCMD). The increase in feed temperature and flow rate influenced the higher ammonia mass transfer coefficient, ammonia removal efficiency and permeate flux within the examined range. Considering different MD configurations, the findings in 2013 and 2015 (Duong et al. 2013; Fang et al. 2015), focused on the application of sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) for eliminating the little amount of ammonia in the liquid phase. The study involved the investigation of the effects of feed flow rate, feed temperature, sweep gas flow rate and vacuum degree as operating parameters for ammonia removal and separation performance. The impact of different factors, such as the feed temperature, the feed flow rate, airflow rate and vacuum degree, inside the membrane module on ammonia overall mass transfer coefficient, ammonia flux and separation factor were examined.

From Table 2, it is evident that the increase in sweep flow rate from 0.4 to 5.0 L/min influenced the increase in overall mass transfer from $0.86 \times 10^{-5}$ to $3.21 \times 10^{-5}$ m/s. Meanwhile, the VMD had great

| SGMD | VMD |
|------|-----|
| Feed temperature (°C) | 65 |
| Feed flow rate (L/min) | 0.3 |
| Sweep gas flow rate (L/min) | 0.4 |
| $K_{ov}$ (10^{-5} m/s) | 0.86 |
| Vacuum degree (torrs) | 300 |
| $K_{ov}$ (10^{-5} m/s) | 1.00 |
| 2.0 | 2.02 |
| 200 | 2.25 |
| 3.0 | 2.58 |
| 130 | 5.58 |
| 5.0 | 3.21 |
| 100 | 10.97 |
dependence on pressure variations in the vacuum membrane, which as the pressure decreased from 300 to 100 torrs influenced the overall mass transfer increase from $1.00 \times 10^{-5}$ to $10.97 \times 10^{-5}$ m/s. However, a related tendency was reported in earlier studies (Lawson & Lloyd 1997; Ding et al. 2006; El-Bourawi et al. 2007). Apart from other factors such as feed rate, airflow rate, vacuum degree and feed temperature, which affect the separation process and mass transfer coefficients calculated ($K_v$), the results show that $K_v$ for VMD is higher than that for SGMD when the process is treated in the same conditions. These results suggest that the ammonia removal efficiency was improved by increasing sweep gas flow rate or by decreasing downstream pressure.

Application of various additives to lower ammonia inhibition level

Various additives have been used to reduce the NH$_3$ volatilisation, predominantly with acidifying and adsorbent additives. The acidifying additives have been potentially used to shift the equilibrium between NH$_3$ and NH$_4^+$ in which the pH reduction favours the formation of more ammonium ion (NH$_4^+$) species in the equilibrium (Hansen et al. 1998), which is less toxic to methanogens when compared to free ammonia (NH$_3$) species (Zhang et al. 2014). In this paper, the role of additives in removing ammonia has been categorised under ion exchange and adsorption methods.

ION EXCHANGE METHOD

Ion-exchange is among several approaches that are commonly used in removing ammonia from water. This process generally incorporates capturing species of interest (ammonia) through ion exchange and adsorption technique. These ion exchangers are usually either natural or artificial. In most cases, minerals that are crystalline, hydrated, aluminosilicate of alkali, or alkaline earth ions provide ion exchangers with high adsorption capacity (Adam et al. 2018).

It is this condition that brings about the ion exchange process as an alternative method for ammonia removal, specifically the ammonium ion (NH$_4^+$) (Jorgensen & Weatherley 2003; Romero-Güiza et al. 2016). Ion exchangers are advantageous over biological treatment since their performance is not pH and temperature-dependent, conditions which are necessary for biological removal of ammonia. For this case, ion exchangers can still work in the presence of antimicrobial compounds (Jorgensen & Weatherley 2006). Clinoptilolite and zeolites, which occur naturally, are among several ion exchangers reported in the literature for effective ammonia removal from wastewater (Jorgensen & Weatherley 2003). The equilibrium mechanism between the ion exchanger and ammonia is given below (Heisler et al. 2008):

\[
(M^-A^+)_{(s)} + (Ammonium^+)_{(aq)} \leftrightarrow (M^-Ammonium^+)_{(s)} + (A^+)_{(aq)}
\]  

Jorgensen and Weatherley in 2006 (Jorgensen & Weatherley 2006), examined the performance of fixed beds of exchanger resin consisting of clinoptilolite (natural zeolite), Dowex50w-x8 (gel resin), and Purolite MN-500 (macronet resin) for comparison of ammonium ion removal efficiency. Secondly, the influence of two contaminants, citric acid and whey protein isolate, for ammonium ion breakthrough was determined. Thirdly, the breakthrough performance of the exchanger resin after regeneration was determined. Finally, the effect of the pollutants upon regeneration performance was examined and it was revealed that the occurrence of organic compounds had a varying impact on ammonium ion adsorption. In the case of clinoptilolite, it was found that the presence of protein seemed to have less effect upon ion exchange capacity. However, when the clinoptilolite was mixed with the MN-500, a significant improvement in the reduction of ammonium ion capacity was noticed in the presence of citric acid. Regardless of acetic acid being a weak acid, the effect of its presence on
the ion exchanger signifies its role for competing with protons in the cationic sites on the exchanger. After cycles of exhaustion and regeneration, clinoptilolite was very superior over synthetic resins, which displayed a reliable performance in each run.

However, apart from resin, there are other materials that can be used for the ion exchange process in removing NH₄⁺–N. For example, the work done by Liu and other co-authors in 2011 (Liu et al. 2011), to test ammonia removal efficiency by calcinated kaolin, showed that the extruded powder material of 1–2 mm grain size was superior for the ammonia removal process. Results indicated that ion exchange capacity, which was studied by Cation Exchange Capacity (CEC), was above the concentration of 70 mg NH₄⁺–N /g for the material prepared. In wastewater treatment, 90% of the ammonia nitrogen could be removed using this material.

The other study involved the use of ion exchange materials for ammonia removal (Tao et al. 2017) and assessing the effect of pH reduction on the digesters’ performance, particularly the features of the microbial community. The extended removal of NH₄⁺–N was completed over ion-exchanging at both temperatures (thermophilic and mesophilic), with ordinary removals of 50 and 70% for the clinoptilolite and resin-dosed reactors, respectively. The pH reduction was approximately done at the unit of 0.2–0.5 dosages in the reactors, which eventually decreased the free NH₃ concentration in the range between 600 and 90 mg/L at 43 °C. In these conditions, methane yield was increased by 54% due to alleviation of ammonia inhibition. Some criteria, such as flow rates and pH, were examined (Wirthensohn et al. 2009) to evaluate the ability of acidic gel cation exchange resins and clinoptilolite in column experiments to remove ammonium ions. It was found that the quality of the effluent was very reasonable (NH₄⁺–N <2 mg/l) and ammonium ion removal efficiency was nearly 99%.

Ammonia – ammonium equilibrium in the aqueous phase is principally pH-dependent (Hedström 2001) whereby ion exchange can be used to remove the ionised form from a solution. The performance of MesoLite for ion exchange in the liquid phase was investigated (Thornton et al. 2007). In this experiment, 100 ml of NH₄⁺–N solution was used to equilibrate with 0.5 g of MesoLite grain size ranging from 0.1–0.6 mm. Different concentrations were varied when the sample of MesoLite was equilibrated with (0–2,000 mg/l NH₄⁺–N) at 20 °C for 24 h. Consequently, 15% of sodium silicate was added in the mixture as a binding agent, which was mixed in the same proportion as the crushed sample. The effect of contact time on the equilibrium capacity based on kinetic experiments was studied at different intervals of 5, 10, 15, 30, 45, 60, 120, 180 and 240 min to examine the adsorption properties of the material. Langmuir and Freundlich isotherm models fitted adequately with the results obtained as well as providing a better explanation of the mechanism. A maximum equilibrium capacity of 49 g NH₄⁺–N kg⁻¹ was obtained, indicating that the increase in solution concentration and contact time provided the best performance at an optimum pH between 6 and 7. Through this study, it was concluded that the capacity of the MesoLite material is greatly influenced by solution concentration and pH between 6 and 7.

**ADSORPTION METHOD**

The most preferred adsorbents are those with high surface area and small pores for efficient removal of contaminants. Ammonia adsorption using these porous materials has been progressively discussed for their applications (Helminen et al. 2001; Furtado et al. 2011; Johnson et al. 2012). Recently, conventional inorganic adsorbents such as activated carbon, alumina, silica gel, and 13X zeolite, have been in use; nevertheless; they exhibit low adsorption capacities in the range from 2.5 to 12.0 mol/kg (37 to 192 mg/g) (Helminen et al. 2001). For purposes such as adsorbing ammonia, the adsorbents must have a higher surface area with small pore sizes to enhance the chemical interaction between the surface of the adsorbent and the adsorbate. Several inorganic nanoporous materials have been used as an alternative to zeolites and activated carbon for gaseous adsorption
Activated carbon seems to have more advantages over other porous solids due to its larger surface area, extremely established porous structure and the ability of the porous structure to be modified further for special applications (Marsh & Reinoso 2006). Since the activated carbon generally consists of non-polar surfaces, both pre and post-synthesis treatment as a means of modifications are crucial when adsorbing polar gases (e.g. NH₃). The removal of ammonia in wastewater using activated carbon is affected by many factors such as textural properties but also the chemical nature of its surface and the nature of oxygen-containing functional groups (Faria et al. 2004). By considering the role of surface modification for proper adsorption of NH₃ (Gonçalves et al. 2011), the impact of functional groups in the exclusion of ammonia using an improved resin-based activated carbon was studied. The results indicated that the activated carbon, which was modified by nitric acid, had improved the adsorption capacity at room temperature. Supposedly, there is a correlation between the total adsorption capacity and the amount of supplementary acidic and fewer stable oxygen surface groups. Related researches show that there is a relationship between the humidity and surface chemistry of the carbon used, in which the moisture enhances the adsorption capacity of the adsorbents due to the dissolution behaviour between ammonia and water. However, the presence of moisture at the surface of the carbon material has little effect on the adsorption process since both Brønsted and Lewis acid centres offer more adsorption pathways from the carbon surface. The formation of both NH₄⁺ and NH₃ species was confirmed by FTIR analyses of the exhausted oxidised samples. The interaction between lone pair electrons of NH₃ species with graphene layers through Lewis acid sites is in agreement with the conclusion that total surface area, interior porous structure and the existence of functional groups on the pore surface of activated carbon are very crucial for determining the adsorption capacity (Ahmedna et al. 2000).

Meanwhile, Yeom & Kim (2017) did a study on inorganic nanoporous materials such as mesoporous alumina (MA), which were investigated to replace the role of zeolite and activated carbon for NH₃ adsorption. The characterisation of MA showed a uniform pore size distribution and interlinked pore system, properties that were superior to other commercial adsorbents (activated carbon, zeolite, and silica powder). The free hydroxyl groups in MA serve as useful adsorption locations for NH₃ connected with the interlinked adsorbent pore system, which is an important feature to enhance adsorption.

In addition to that, the ammonia inhibition level was studied by investigating the appropriateness of a mixture of activated carbon and limestone in reducing ammoniacal nitrogen, which exists in a considerable quantity (between 429 and 1,909 mg L⁻¹) in one of the disposal areas in Malaysia (Aziz et al. 2004). It was observed that either activated carbon or a mixture of both activated carbon and limestone in a ratio of 5:35 could remove 40% of ammoniacal nitrogen present in a landfill. Therefore, from the study and results obtained, it can be concluded that limestone is theoretically suitable as a substitute material to replace activated carbon at an affordable cost.

### OPERATING CONDITIONS TO IMPROVE AMMONIA REMOVAL IN THE AD SYSTEM

From the above explained strategies on how to remove ammonia in substrates rich in nitrogen during the AD process, there are some parameters that play a vital role for the effective removal of ammonia during the AD process, as summarized in Table 3. In fact, parameters such as pH level, amount of air, C/N ratio and temperature are considered to be economically viable operating conditions in a biogas reactor (Güstin & Marinšek-Logar 2011). For example, when the pH is adjusted to an alkaline level it affects the stripping process, in which the ratio of ammonia/ammonium is altered, favouring ammonia removal efficiency due to the equilibrium shift as shown in Equation (1). However, ammonia removal efficiency may be improved by air passing through the stripping bench plant, which compresses the ammonia in the liquid phase and hence vapourises the liquid ammonia, which is then
transformed to the gas phase (Georgiou et al. 2019). Generally, a pH between 7.0–7.4 is regarded as a convenient condition for reducing ammonia inhibition. At this range of pH, NH$_4^+$ concentration, which is less toxic, is more highly favoured than NH$_3$ concentration (Siegrist et al. 2002). Meanwhile, the C/N ratio is also among the vital parameters to lower ammonia inhibition since, when adjusted, it can favour the growth of microorganisms and maximise the production of methane. The C/N ratio may be increased by the addition of carbohydrate substrates, into which the level from 20/1 to 30/1 is considered to be appropriate for metabolic activities of microorganisms and VFA production (Li et al. 2019). Nevertheless, the temperature is also regarded as a potential operating condition during AD for ensuring process stability and overwhelming inhibition progression. It has been observed that setting the digester temperature above 40°C (thermophilic condition), is not an effective way to improve the digestion process due to accumulation of excess fatty acids, which in turn affects the growth of methanogens though high-temperature influences rapid degradation (Zinatizadeh & Mirghorayshi 2019). In practice, for better performance of the digester during biogas production, it is recommended that the mesophilic condition (30 °C–40 °C) should be adopted, especially when treating agricultural organic waste for AD process (Wang et al. 2019).

**Table 3** | Summary of methods and their appropriate conditions for the operation of the AD system in controlling ammonia inhibition

| Method/technique          | Appropriate condition(s)                                                                 | Reference                                      |
|---------------------------|------------------------------------------------------------------------------------------|------------------------------------------------|
| pH and temperature adjustment | – Alkaline pH range between 7.0–7.4.  
– Mesophilic temperature (35°C – 45°C). | Astals et al. (2018); Wang et al. (2019); Zinatizadeh & Mirghorayshi (2019); Mpolu et al. (2020) |
| C/N ratio adjustment      | – C/N ratio ranging between 15/1 and 30/1 is convenient for reducing ammonia inhibition.  | Xu et al. (2016); Li et al. (2019)              |
| Air stripping             | – Temperature above 45°C for volatilisation of ammonia.  
– pH range between 8.8–10.2.  
– High stripping tower to facilitate air temperature for volatilisation of ammonia. | Georgiou et al. (2019); Huang et al. (2019); Li et al. (2020) |
| Struvite precipitation    | – 1.5% compost mixture of water-soluble Mg and P salts.  
– Molar ratio of 1.5:1:1.5 of Mg/N/P and pH of 9.5. | Huang et al. (2014); Hu et al. (2020a, 2020b) |
| Membrane distillation     | – High feed temperature (>40°C) and low downstream pressures influence diffusion of ammonia in the membrane pores.  
– Ammonia removal efficiency is increased as water pH is raised to 10. | He et al. (2018); Lin et al. (2018) |
| Ion exchange              | – Acidic medium for facilitating ion exchange through protons which competes with cationic sites.  
– Extruded powder materials of 1–2 mm grain size are superior for the ammonia removal process.  
– Optimum pH between 6 and 7. | Thornton et al. (2007); Ham et al. (2018) |
| Adsorption                | – High surface area and small pores for sufficient chemical interaction between the surface of the adsorbent and the adsorbate.  
– Adsorption capacity is favoured most at high adsorbent dosage.  
– pH range between 3–8. | Huang et al. (2018); Al-Sheikh et al. (2020) |
### Table 4 | Advantages and disadvantages of current methods for ammonia removal

| Method                        | Advantages                                                                                           | Disadvantages                                                                                       | References                                      |
|-------------------------------|-------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| pH and temperature adjustment | The method influences the balance between NH₃ and NH₄⁻ species in the equilibrium; pH adjustment can improve both hydrolysis and acidogenesis; biogas production is maximised. The digestion process under thermophilic conditions enhances rapid degradation of substrates. pH regulation may strengthen the buffering system to improve methane production. | Low pH may increase the volatile fatty acids (VFA) production rate, which in turn inhibits the growth of methanogens and pH above 7 may induce inhibitory ammonia in the reactor. The high temperature can cause the metabolism rate of microorganisms to decline due to the denaturation of enzymes and ammonia volatilisation. | Angelidaki & Ahring (1994); Zhang et al. (2005); Chae et al. (2008); Gustin & Marinski-Logar (2011); Yang et al. (2015); Zhang et al. (2013); Latil et al. (2017); Astals et al. (2018); Meng et al. (2018); Wang et al. (2018); Algapani et al. (2019); Valentino et al. (2019); Mpofu et al. (2020) |
| Changing the C/N ratio        | Improves carbon to nitrogen balance; source of nutrients to microorganisms in the reactor; the higher the C/N ratio, the higher the amount of methane produced. | A high amount of nitrogen (low C/N ratio) can lead to ammonia inhibition; high C/N ratio affects the buffer capacity by accumulating more volatile fatty acids (VFA). | Puyuelo et al. (2011); Wang et al. (2012); Zeshan & Visvanathan (2012); Mao et al. (2017); Xu et al. (2018); Calcioglu & Demirer (2019); Choi et al. (2020) |
| Air stripping                 | The method is straightforward and usually cheap because it does not entail any of the construction facilities. | The stripping tower sometimes involves some construction costs in building the packed towers; the process is time-consuming especially when using traditional equipment; the method is inefficient to wastewater that contains ammonia concentrations above 100 mg/L. | Bonmati & Flotats (2003); Quan et al. (2009); Ferraz et al. (2013); Karri et al. (2018); Yin et al. (2018); Huang et al. (2019); Li et al. (2020) |
| Struvite precipitation        | The method is convenient for the removal of ammonium (NH₄⁺), phosphate (PO₄³⁻), or both, contained in wastewater. | pH, the chemical structure of the wastewater and temperature of the solution are the major factors affecting the method. | Uludag-Demirer et al. (2005); Kim et al. (2007); Cao et al. (2019); Hu et al. (2020a, 2020b); Vanotti et al. (2020) |
| Membrane distillation         | The large interfacial area of the membrane per unit volume offers high selectivity and efficiency of the method, whereby the flow rates of gas and liquid can easily be controlled. | The method is expensive; it requires chemicals for oxidation and regeneration as part of membrane maintenance; short lifespan due to membrane fouling. | Tan et al. (2006); El-Bourawi et al. (2007); Duong et al. (2013); Qu et al. (2013); Zarebska et al. (2014); Intrchom et al. (2020) |
| Ion exchange                  | Ion exchange materials can work under high temperature due to its high resistance to shock loadings; as a result, the time needed for regeneration can be shortened. | Frequent regeneration may incur some costs; ion exchangers are quickly saturated, leading to low performance. | Jorgensen & Weatherley (2003); Miladinovic & Weatherley (2008); Tao et al. (2017); Hu et al. (2020a, 2020b) |
| Adsorption                    | The method demands low energy and non-frequent maintenance; it is simple and most reliable; can be operated under minimum supervision when using carbon columns. Some additives such as iron (Ferric oxide) are considered as environmentally-friendly materials that can increase methane production. | The adsorbent needs to be replaced after a time because the number of cycles reduces the adsorption capacity. | Uludag-Demirer et al. (2005); Mazloomi & Jalali (2016); Novais et al. (2018); Fan et al. (2019); Lu et al. (2019); Al-Sheikh et al. (2020) |
CONCLUSIONS AND FUTURE PROSPECTS

To prevent process failures due to ammonia toxicity, different conventional strategies such as stripping, struvite precipitation, adjustment of C/N ratios, dilution of substrates and co-digestion of nitrogen-rich wastes have been suggested. Previous studies also reported using zeolite (both natural and synthetic) through the ion exchange and adsorption phenomenon, but the possibility of low adsorption in some cases and high costs for regeneration were the notable drawbacks. pH and temperature were also discussed as significant parameters that control the anaerobic digestion and determinants of proper technique during ammonia removal. For example, the effect of temperature, and the ratio of air to wastewater flow, were shown to have a positive effect on ammonia removal by the stripping method. Furthermore, it was found that struvite precipitation was efficiently progressed by an accumulation of additional magnesium and phosphate sources followed by addition of a buffering reagent for pH control. However, before magnesium and orthophosphate addition, the NH$_4^+$–N removal capacities were less than 50%.

From this review, the aforementioned approaches seem to have positive contributions towards ammonia removal in various wastes as a means to produce agricultural fertilisers as well as biomethane, a source of renewable energy. However, regarding the disadvantages of each method, as summarized in Table 4, I would recommend the use of cryogenics to liquefy nitrogen at a logical dividing line for most permanent gases including nitrogen, where the boiling temperature should not exceed –180 °C. Therefore, at this temperature range, nitrogen, which is the source of inhibitory ammonia, will liquefy and be discharged as liquid nitrogen.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest concerning the publication of this paper.

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