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Nitrogen recovery from wastewater using gas-permeable membranes: Impact of inorganic carbon content and natural organic matter

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ABSTRACT

Gas-permeable membranes coupled with low-rate aeration is useful to recover ammonia (NH$_4^+$) from livestock effluents. In this study, the role of inorganic carbon (bicarbonate, HCO$_3^-$) to enhance the N recovery process was evaluated using synthetic effluents with various NH$_4^+$ to HCO$_3^-$ molar ratios of 0.5, 1.0, 1.5 and 2.0. The study also evaluated the effect of increased organic matter on the NH$_4^+$ recovery using humic acids (3000 to 6000 mg L$^{-1}$), and the N recovery from high-strength swine manure. The release of hydroxide from the HCO$_3^-$ with aeration increased the wastewater pH and promoted gaseous ammonia formation and membrane uptake. At the same time, the recovery of gaseous ammonia (NH$_3$) through the membrane acidified the wastewater. Therefore, an abundant inorganic carbon supply in balance with the NH$_4^+$ is needed for a successful operation of the technology. NH$_4^+$ removal efficiencies > 96% were obtained with NH$_4^+$ to HCO$_3^-$ ratios ≤ 1. However, higher molar ratios inhibited the N recovery process resulting in lower efficiencies (< 65%). Fortunately, most swine manures contain ample supply of endogenous inorganic carbon and the process can be used to more economically recover the ammonia using the natural inorganic carbon instead of expensive alkali chemicals. In 4 days, the recovered NH$_4^+$ from swine manure contained 48,000 mg L$^{-1}$. Finally, it was found the process was not inhibited by the increasing levels of organic matter in the wastewater evaluated.

Keywords: ammonia recovery, ammonia capture, gas-permeable membranes, livestock wastewater, ammonia emissions control.
1. Introduction

Ammoniacal nitrogen is one of the main contaminants of domestic and industrial waste. The concentration of ammoniacal nitrogen varies from 10 to 200 mg L\(^{-1}\) in urban wastewater, from 5 to 1,000 mg L\(^{-1}\) in industrial wastewater, such as those generated by the production of chemical fertilizers, and from about 400 to 5,000 mg L\(^{-1}\) in livestock effluents (Lema and Suarez, 2017; USDA, 2008). Some of the environmental problems that have been cited from ammoniacal nitrogen in wastewater and liquid wastes include the reduction of the dissolved oxygen concentration, the toxic effects on fish, the reduction of disinfection efficiencies, and metal corrosion (Lauterböck et al., 2012). Hence, its removal is necessary in order to protect both natural resources and public health.

Traditionally, organic waste from livestock production has been a source of nutrients which was added to agricultural soils. Intensive livestock farming in certain geographical areas in Europe has made this type of waste a problem since it has caused the contamination of aquifers and soils. Furthermore, in 2015, the EU-28 agricultural sector emitted into the air a total of 3,751 kilotonnes of ammonia, and was responsible for 94% of total ammonia emissions across the region; they mainly occur as a result of volatilisation from livestock excreta (EEA, 2017). While this happens, the global consumption of synthetic fertilizers grows (Heffer and Prud’homme, 2013). Therefore, the capture and recovery of ammonia from livestock farming and its transfer to areas suffering shortages is necessary, in this way reducing the environmental impact while at the same time replacing commercial fertilizers and opening new economic perspectives (Keyzer, 2010; Szogi et al., 2015; Vanotti et al., 2017).

The different techniques to remove the nitrogen content can be classified into biological, chemical and physical processes. The biological processes include nitrification-
denitrification (Vanotti et al., 2009), anammox (Magri et al., 2012a) or microbial fuel cells (Kuntke et al., 2012). The chemical and physical processes include struvite precipitation (Nelson et al., 2003), ammonia stripping (Bonmatí and Flotats, 2003), reverse osmosis (Masse et al., 2010), nanofiltration (Kertesz et al., 2010), ion exchange (Milan et al., 1997), evaporation (Fuchs and Drogs, 2013) and, recently, the treatment using gas-permeable membranes (Vanotti and Szogi, 2015; García-González and Vanotti, 2015).

Among numerous applications, the treatment with gas-permeable membranes has been used to retrieve ammonium from liquid manures (García-González et al., 2015; García and Vanotti, 2015). This process requires augmenting the pH of the solution to be treated so as to favor the transformation of ammoniacal nitrogen (NH$_4^+$) into the un-ionized, gaseous ammonia (NH$_3(g)$) (Eq.(1)) enabling it to cross a microporous hydrophobic membrane where an acidic solution circulates (Figure 1). With a pH < 2, the acidic solution dissolves the NH$_3$ in the form of ammonium.

\[ \text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3(g) + \text{H}_2\text{O} \] (1)

The studies of García-González et al. (2015) and Vanotti and Szogi (2015) have proposed using nitrification inhibitors and introducing low-rate aeration to obtain a higher pH without the need of adding alkaline chemical elements, in this way reducing the economic and environmental costs of ammonia treatment. During aeration of the manure, carbonate alkalinity is consumed and OH$^-$ is instantly released, increasing the pH and reducing the bicarbonate in the wastewater environment according to Eq. (2) and enhancing both the formation of NH$_3$ as defined in Eq. (1) and the NH$_3$ uptake via the gas-permeable membrane (Vanotti et al., 2017). For the purpose of the enhancement of the recovery of NH$_3$ N recovery using gas-permeable membranes, the term “low-rate aeration”
was defined as an aeration rate that is less than about 5\% of the aeration rate used for biological ammonia removal/nitrification (Vanotti et al., 2017).

\[ \text{HCO}_3^- + \text{air} \rightarrow \text{CO}_2 + \text{OH}^- \]  

(2)

However, according to Eq. (3), the recovery of \( \text{NH}_3(g) \) through the gas-permeable membrane causes an increase of acidity in the wastewater environment being treated as the \( \text{H}^+ \) does not permeate the hydrophobic membrane. Therefore, it is necessary to continually raise the pH levels in order to maintain the efficiency of the recovery (Garcia-Gonzalez and Vanotti, 2015).

\[ \text{NH}_4^+ \rightarrow \text{NH}_3(g) + \text{H}^+ \]  

(3)

The aeration effect is double, on one hand, the increase in pH and, on the other hand, the increase in the concentration of free ammonia which allows active permeation of \( \text{NH}_3 \) through the membrane (García-González et al., 2015). The implementation of this type of physical-chemical treatment versus other types of nitrogen recovery systems has been discussed in several essays, such as those of García-González et al. (2015), Zarebska et al. (2015) and Dube et al. (2016). Zarebska et al. (2015) indicated that the energy consumption of recovering the nitrogen is among the lowest (0.18 kW·h·kg\(^{-1}\)\( \text{NH}_3 \)), compared in a review of six methods; it was also noted that the main economic drawback from gas-permeable membrane systems was the addition of reactive alkaline chemical elements. García-González et al. (2015) demonstrated the positive effect of low-rate aeration on the use of gas-permeable membranes for the purpose of \( \text{NH}_4^+ \) recovery. With the aeration approach applied to waste effluents from raw liquid swine manures, the \( \text{NH}_4^+ \) recovered was 98\% of the quantity initially present, the ammonia emission losses were less than 1.5\%, and the operational cost of ammonia recovery was reduced by 57\% with respect to the alternative approach using NaOH addition to increase pH (García-González et al., 2015).
The study of Dube et al. (2016) showed that the \( \text{NH}_4^+ \) recovery with the low-rate aeration was between 5 and 6 times faster than the treatment without aeration, reducing treatment costs by 70% in swine manure anaerobic digester effluent. Although the process was proven to work in several experiments with livestock effluents, the mechanism is difficult to understand when working with complex effluents with total alkalinites that may be comprised of inorganic carbon (carbonate/bicarbonate) plus hydroxide and phosphate compounds. For this reason, there is a need to reconstruct the process using simple solutions to understand the role of the inorganic carbon in this N recovery process.

The objective of this research was to determine the role of inorganic carbon (bicarbonate) on the effectiveness of ammonia removal using gas-permeable membranes and low—rate aeration. A series of experiments were carried out using synthetic solutions containing various carbonate to ammonia ratios on the efficiency of the process. Further, the effect of organic matter content on ammonia capture was assessed using humic acids. Lastly, the technology was applied to liquid swine manures from farm areas for fattening pigs with various high-solids strengths to evaluate the behavior of the variables in the study and their impact on the efficiency of ammonium removal and recovery.

2. Materials and methods

2.1. Analytical Methods

Total solids, volatile solids and ammoniacal nitrogen determinations were performed according to APHA Standard Methods (1998). Total solids (TS) were determined after drying to constant weight at 105°C (2540B method) and volatile solids (VS) were determined after further ignition at 550°C for one hour (2540E method). The ammonium analysis was performed with distillation (2100 Kjeltec Distillation Unit), capture of distillate in borate
buffer and subsequent titration with 0.10N H$_2$SO$_4$ (4500B and C methods). In experiment 2, the ammonium analysis was done by colorimetry (4500-NH$_3$ G). Alkalinity was determined with an automatic titrator (TitroLine easy, Schott Instruments) by measuring the amount of 0.01 M hydrochloric acid required to reach an end-point pH of 4.5 and was reported as mg CaCO$_3$ L$^{-1}$ (total alkalinity, 2320 B method). Total carbon and inorganic carbon were measured with a Total Organic Carbon analyzer (Shimadzu brand, TOC5000 model).

Density of the semi-solid manure was measured gravimetrically using buckets of known volume, and density of the diluted manures was measured with a Bouyoucos hydrometer.

The concentrations of free ammonia, NH$_3$ (FA) were calculated using the equations given by Anthonisen et al. (1976) based on wastewater temperature (°C), pH, and total NH$_4$-N concentration (mg L$^{-1}$) values:

$$FA \text{ as } NH_3 \text{ (mg L}^{-1}) = \left(\frac{17}{14}\right) \times \left\{\left(\frac{NH_4-N \times 10^{pH}}{[K_b/K_w]+10^{pH}}\right)\right\}$$

where $K_b$ and $K_w$ are ionization constants for NH$_3$ and H$_2$O and the ratio $(K_b/K_w) = \exp \left[\frac{6344}{(273 + T)}\right]$.

### 2.2. Ammonia separation reactor

Batch experiments were performed using the ammonium separation reactor and protocol of Dube et al. (2016) (Fig. 2). It consisted of wastewater vessels made of PET with an effective volume of 2 L fitted with a submerged gas-permeable membrane connected with a stripping solution reservoir that contained 200 mL acidic solution made with 0.5 M H$_2$SO$_4$. The acidic solution was recirculated with a peristaltic pump (Watson Marlow brand, 120S model) at a rate of 5.8 L day$^{-1}$. This solution flowed inside the tubular membranes and returned to the stripping solution reservoir, completing a closed loop. The gas-permeable membrane used to capture NH$_3$ was tubular and made of expanded...
polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock Hill, SC). The length of the tubular membrane was of 0.6 m and its characteristics are shown in Table 1. Aeration was performed with aquarium pumps (Sera brand, air 110 plus model) and porous plate that provided fine bubbles. The aeration rate was 0.24 L air per L of wastewater per minute (Garcia-González et al., 2015); it was about 4 times lower than aeration rates used by Magri et al. (2012) that greatly inhibited nitrite production activity in experiments of partial nitritation of swine wastewater (0.9 L-air L-liquid$^{-1}$min$^{-1}$). Even so, 10 mg L$^{-1}$ of N- Allylthiourea (98%) were added as a nitrification inhibitor, following strategies presented in other essays (Vanotti and Szogi, 2015).

2.3. Experimental Design

Four sets of experiments were carried out using the experimental device for NH$_4^+$ capture shown in Fig. 2. Experiments 1, 3 and 4 were done in Alicante, Spain and experiment 2 in South Carolina, USA. In the first experiment, the effect of NH$_4^+$/HCO$_3^-$ molar ratios on N removal was evaluated. The pH evolution and NH$_4^+$ elimination were determined using synthetic wastewaters that were prepared with four different ratios of NH$_4^+$/$\text{HCO}_3^-$ (four treatments) by varying the NH$_4^+$ concentration and keeping the HCO$_3^-$ concentration constant. Four complete experimental reactor modules were tested simultaneously using the ammonia separator reactor described in section 2.2. The trials were carried out in single reactors. Target NH$_4^+$/$\text{HCO}_3^-$ molar ratios were 0.5, 1.0, 1.5 and 2. The synthetic wastewaters were prepared with the addition of NH$_4$NO$_3$ chemical to reach concentrations of 1000, 2000, 3000 and 4000 mg NH$_4^+$ L$^{-1}$ (56, 111, 167 and 222 mmol NH$_4^+$ L$^{-1}$), and the same addition of 9660 mg L$^{-1}$ NaHCO$_3$ in all treatments (115 mmol L$^{-1}$ of bicarbonate or 5750 mg L$^{-1}$ carbonate alkalinity).
The second experiment evaluated the effect of inorganic carbon on N recovery from synthetic wastewaters by varying the amounts of HCO$_3^-$ while keeping the NH$_4^+$ concentration constant. The experiment included three treatments based on results of the first experiment regarding NH$_4^+$/HCO$_3^-$ ratios and N removal. The first treatment was an ideal synthetic solution in terms of the balance of inorganic carbon and NH$_4^+$: it contained about 15% more HCO$_3^-$ than the amount needed to remove all the NH$_4^+$ by the gas-permeable membrane process (NH$_4^+$/HCO$_3^-$ molar ratio = 0.87). The second treatment was a deficient synthetic solution also made of NH$_4^+$ and inorganic carbon but containing half the HCO$_3^-$ used in treatment 1 (NH$_4^+$/HCO$_3^-$ molar ratio = 1.74). The third treatment was a control made only with NH$_4^+$ without the inorganic carbon. The synthetic wastewaters in treatments 1, 2 and 3 were prepared with the addition of 6,900, 3450 and 0 mg L$^{-1}$ NaHCO$_3$, respectively (82, 41, and 0 mmol L$^{-1}$ bicarbonate or 4100, 2050, and 0 mg L$^{-1}$ carbonate alkalinity), and the same amount of NH$_4$Cl (3,820 mg L$^{-1}$) in all cases that provided a constant NH$_4$-N concentration across treatments (1000 mg/L NH$_4$-N or 71.4 mmol NH$_4^+$ L$^{-1}$).

The pH of the freshly made control solution (NH$_4$Cl without inorganic carbon) was lower (pH = 5.2) than the initial pH of treatments 1 and 2 (pH = 7.8-7.9) and for this reason it was adjusted from 5.2 to 7.8 with the addition of a small amount of NaOH (1.5 mmol NaOH L$^{-1}$).

The experiment used the set-up of Dube et al., (2016) with aeration rate of 0.12 L air per L of wastewater per minute, 1.5 L effective reactor volume, 60 cm tubular membrane length (same membrane described in section 2.2), 4 mL min acid circulation rate, and 250 mL 0.5 M H$_2$SO$_4$ in the acid tank. The room temperature was constant (20.9 ± 1.0°C). The trials were carried out in duplicate reactors. Results of treatment 1 were compared in regards to alkalinity consumption and NH$_4^+$ removal with results obtained by other authors using a variety of digested and raw manures.
The third experiment evaluated the effect that organic matter content in wastewater could have on the flow of NH$_3$ through the membrane and the N recovery. Three synthetic wastewaters were prepared containing different concentrations of humic acids (three treatments): 3000, 4500 and 6000 mg L$^{-1}$ (added humic acid sodium salt, Sigma Aldrich, ref H16752). All treatments contained 1000 mg L$^{-1}$ of NH$_4^+$ (778 mg NH$_4$-N L$^{-1}$) using NH$_4$NO$_3$ chemical and 9660 mg L$^{-1}$ NaHCO$_3$ (NH$_4^+$/HCO$_3^-$ molar ratio = 0.5) that provided a non-limited inorganic carbon supply. The trials were carried out in single reactors using the ammonia separator reactor and conditions described in section 2.2.

The fourth experiment used real manure samples of high to very-high strength, from a swine farm located in Santomera (Murcia, Spain) using the ammonia separator reactor described in section 2.2. Representative (composite) samples were taken from vessels containing a semisolid manure from the fattening production stage. Samples (10) were collected at 3 points of the vessel from the top 1.50-m depth using 5-L sampling jars and combined. The composite manure sample was transported to the laboratory. It was a semisolid material (14.6% TS). For the N recovery experiments, the thick manure was diluted with water 1:3 (liquid swine manure 1) and 1:5 (liquid swine manure 2) (Table 2). Water used for dilution was farm well water simulating the effect of cleaning as a usual farm practice. The farm water contained a high level of bicarbonate (249 mg HCO$_3^-$ L$^{-1}$ = 204 mg alkalinity L$^{-1}$). Other characteristics of the fam water were: pH = 8.0 ± 0.1; EC (mS/cm) = 0.80 ± 6%; calcium = 68.9 ± 13%; Ammonia N (mg L$^{-1}$) ≤0.05 ± 14%; CO$_3^{2-}$ ≤ 3 ± 12%. The strengths of swine manure have been classified based on TS concentration: low (0.4-0.8%), medium (0.8-1.7%) and high (1.7-3.2%) (Garcia-Gonzalez and Vanotti, 2015). Accordingly, the strength of liquid manure 1 having 3.65% TS was very-high and that of liquid manure 2 with 2.42% TS was high. The trials were carried out in duplicate reactors.
3. Results and discussion

3.1. Effect of the ratio NH$_4^+$ / HCO$_3^-$ on NH$_4^+$ removal and recovery

Figure 3 shows pH evolution in the four treatments in the first experiment using wastewater with varied NH$_4^+$ / HCO$_3^-$ molar ratios of 0.5, 1.0, 1.5 and 2. Measurements were performed approximately every 20 minutes during the first hour of the experiment and from that moment on, every 24 hours. In all the events, we observed an increase in the pH of about 0.5-0.6 in the first hour. The pH increase at 24 hours varied among treatment: in the two samples with lower NH$_4^+$ / HCO$_3^-$ ratios (0.5 and 1.0), the pH increases were 0.91 to 1.15 reaching pH levels between 8.8 and 9.1 units; this contrasted with the lower pH increases (about 0.6) in the other two samples with higher NH$_4^+$ / HCO$_3^-$ ratios (1.5 and 2) reaching pH levels at 24 hours of 8.3 to 8.5. Precisely, in all the cases and in this same 1-d period, the highest rates of NH$_4^+$ removal were attained (Fig. 4a). The pH increases obtained with synthetic solution and low rate aeration are consistent with pH increases of 1.1 (8.36 to 9.47) obtained by Vanotti et al. (2017) for anaerobically digested swine wastewater treated with the same technique.

Nevertheless, from the first day onwards, the pH decreased in all the treatments, except for the one with the lowest NH$_4^+$ / HCO$_3^-$ molar ratio of 0.5, where it rose, reaching a final value at day 4 of around 9.5 units and a net pH increase of 1.5; at the same time, the percentage of NH$_4^+$ removal grew to values of 98% (Table 3 and Fig. 4b). For the treatment with NH$_4^+$ / HCO$_3^-$ molar ratio of 1, the decrease in the pH level from day 1 to 4 was small, from 8.8 to 8.5 units, obtaining a net pH increase of 0.6 and a high NH$_4^+$ removal of 96% similar to the first treatment. Regarding the treatments where higher NH$_4^+$ / HCO$_3^-$ molar ratio were used (1.5 and 2), the pH fall was sharp after 1 day (Fig. 3), with final pH values...
averaging 4.5 units and percentages of NH$_4^+$ removal under 65% (Table 3). These results indicate that the applied Na$_2$CO$_3$, which provided a carbonate alkalinity concentration of 5750 mg L$^{-1}$ in each of the experiments, was enough for handling NH$_4^+$ concentrations not to exceed 2000 mg L$^{-1}$ (≤ 1556 mg NH$_4$-N L$^{-1}$). This suggested that, to obtain high removal efficiencies by this process, the carbonate alkalinity concentration initially present in wastewater should at least exceed 3.7 the initial NH$_4$-N concentration. With lower carbonate alkalinity to ammonia ratios (higher NH$_4^+$/HCO$_3^-$ molar ratio), the carbonate was used up quickly in the process of N recovery that generates acidity (eq. 3) and this caused a decrease in the pH of the wastewater environment, pushing the equilibrium of Eq. 1 towards the left, inhibiting NH$_4^+$ removal by the gas-permeable membrane system.

As observed in Fig. 4 by analyzing the four treatments, the maximum concentration of ammonium ion that was removed, approximately 106-115 mmol L$^{-1}$ of NH$_4^+$ (1800-1950 mg NH$_4^+$ L$^{-1}$) just matches the concentration of bicarbonate initially added (115 mmol L$^{-1}$). Therefore, approximately 1 mmol of NH$_4^+$ was removed by the process per 1 mmol of HCO$_3^-$ initially present in the solution. The percentages of NH$_4^+$ recovery as (NH$_4$)$_2$SO$_4$ (ratio of NH$_4^+$ recovered in the acidic solution to the NH$_4^+$ removed from wastewater) were high (>84%) in all treatments. These results indicate that the bottleneck in the process was the availability of gaseous NH$_3$ and this availability was positively affected by the relative abundance of inorganic carbon. The difference between the NH$_4^+$ that was removed from wastewater and the NH$_4^+$ that was recovered in the acidic solution is an unaccounted mass fraction (Table 3). The unaccounted fraction was similar in percentage, approximately 10% of the influent, irrespective of the NH$_4^+$/HCO$_3^-$ molar ratio. It is concluded that there are two distinct and interconnected mechanisms affecting the recovery of NH$_4^+$ using gas-permeable
membranes and low-rate aeration in the presence of inorganic carbon. One mechanism is  
the release of OH\(^-\) from the natural carbonates that does not remove total alkalinity but  
increases the wastewater pH (Eq. (2)), which in turn promotes NH\(_3\) formation (Eq. (1)) and N  
recovery by the membrane system. The other mechanism is the release of acidity and  
consumption of alkalinity in the wastewater environment by the continuous passage of N  
through the gas-permeable membrane (Eq. (3)). As shown in this experiment (treatments 3  
and 4 in Figs. 3, 4 and Table 4), this acidification of the wastewater due to an imbalance in  
the NH\(_4^+\)/HCO\(_3^-\) ratio can completely halt the N recovery process by inhibiting the formation  
of unionized ammonia (NH\(_3\)). Therefore, an abundant inorganic carbon supply in balance  
with the NH\(_4^+\) is needed for a successful operation of the process without addition of alkali  
chemicals.

3.2. Effect of inorganic carbon on NH\(_4^+\) removal and recovery

Based on the foregoing study, a synthetic wastewater with abundant inorganic  
carbon content in balance with the NH\(_4^+\) was designed and tested with the gas-permeable  
membrane process with low-rate aeration. This ideal wastewater contained about 15%  
more HCO\(_3^-\) than needed to remove all the NH\(_4^+\) by the gas-permeable membrane process.  
It was prepared with NaHCO\(_3\) and NH\(_4\)Cl and contained 4100 mg/L alkalinity and 1000 mg/L  
NH\(_4\)-N (82 mmol HCO\(_3^-\) L\(^-1\) and 71.4 mmol NH\(_4^+\) L\(^-1\) with an NH\(_4^+\)/HCO\(_3^-\) molar ratio = 0.87).  
The ideal wastewater was compared with a carbon deficient synthetic wastewater  
containing the same NH\(_4\)-N content but half the HCO\(_3^-\) (41 mmol HCO\(_3^-\) L\(^-1\) and 71.4 mmol  
NH\(_4^+\) L\(^-1\) with an NH\(_4^+\)/HCO\(_3^-\) molar ratio = 1.74). A control treatment without inorganic  
carbon was also included in the trials (0 mmol HCO\(_3^-\) L\(^-1\) and 71.4 mmol NH\(_4^+\) L\(^-1\)). Figure 5a  
shows the observed changes in wastewater N concentration in the all three treatments and
the simultaneous N concentration increase in the acid tank, while Fig. 5b shows the cumulative N mass removed from the separation tank and the N mass recovered in the acid tank. Over a period of 7 days, the treatment that used wastewater with abundant inorganic carbon content in balance with the NH$_4^+$ content (NH$_4^+$/$\text{HCO}_3^-$ ratio = 0.87) removed 97% of the NH$_4^+$ with 93% of it recovered in the acid tank (Table 4). The NH$_4^-$-N concentration in wastewater followed a negative exponential curve (NH$_4^-$-N = 939 e$^{-0.0271 \times \text{hours}}$, R$^2$ = 0.999) with daily decreases of 52%. However, when inorganic carbon was deficient (NH$_4^+$/$\text{HCO}_3^-$ ratio = 1.74), the % N removals by the membrane systems were significantly less (57%). When the carbonate was absent (control), the N removal by this system collapsed (6%). Figures 5c,d show the evolution of pH and alkalinity of the three treatments over the same period. In the treatment with NH$_4^+$/$\text{HCO}_3^-$ ratio of 0.87, the pH rose from 7.9 to 8.7 the first day and it was maintained high till the end of treatment (pH = 8.9) at day 7 when only 3% of the N remained in the separation tank. The initial FA concentration in the wastewater calculated using Eq. (4) was 39 mg N L$^{-1}$. The FA increased to 101 mg N L$^{-1}$ the first day as a result of the higher pH, even though the NH$_4^+$ in wastewater was reduced 52% the first day. Subsequently (days 4-7), FA decreased from 62 to 7 mg N L$^{-1}$ as N was being depleted. The initial alkalinity (3913 mg L$^{-1}$) was significantly consumed (87%) during the N recovery process leaving a residual alkalinity of 490 mg/L (Fig. 5d). With deficient inorganic carbon relative to ammonia (NH$_4^+$/$\text{HCO}_3^-$ ratio = 1.74), the pH of wastewater (7.9) increased 0.6 units the first day and afterwards declined steadily to pH 5.5, a net pH decrease over initial of 2.4 units. The initial alkalinity (2310 mg L$^{-1}$) was exhausted (98% reduction) by day 4 (Fig. 5d). At the same time, the wastewater pH declined to 6.9 (Fig. 5a) and the N recovery process stopped leaving 43% of the NH$_4^+$ in the effluent (Fig. b,c). The FA concentrations in the wastewater were 94 mg N L$^{-1}$ at day 1 with the higher pH, 2.0 mg N L$^{-1}$ at day 4 when the
recovery stopped, and < 0.2 afterwards. In the control without inorganic carbon, the small
initial alkalinity of 80 (due to NaOH addition) was eliminated the first day. The initial pH
(7.8) decreased to 6.1 the first day and to 5.07 at day 5; corresponding FA concentrations
were nil: 0.7 and 0.06 mg N/L. Therefore, it is concluded that the N uptake by the
membrane could be greatly affected when the inorganic carbonate level is deficient relative
to the NH$_4^+$. This was evident in treatment 2 when alkalinity was consumed and the pH
decreased below about 7 that halted the N uptake by the gas-permeable membrane system.
It is also concluded from results obtained in this experiment that abundant inorganic carbon
in relation to the NH$_4^+$ is needed to sustain high N removal efficiencies by this gas-
permeable membrane and low-rate aeration process.
Table 5 shows the alkalinity consumption in the ideal synthetic wastewater
(treatment 1) compared with results obtained with manures of various origins by other
authors (Dube et al., 2016 and Garcia-Gonzalez et al., 2015). Using the synthetic
wastewater made with inorganic carbon and NH$_4^+$, approximately 3.7 g of carbonate
alkalinity was consumed per g of NH$_4$-N removed by the process. This consumption
approaches the theoretical ratio of 3.57 when 1 mmol of HCO$_3^-$ is destroyed per mmol of
NH$_4^+$ removed. The comparison with other manures reveals that the ratio for alkalinity
consumption to NH$_4$-N removal of 3.7 obtained in the synthetic wastewater with only
inorganic carbon and NH$_4^+$ was similar than the alkalinity consumption obtained with the
three manures (average 4.1) and that this ratio varied little (3.99-4.12) among manures of
varied characteristics.
The data in table 5 also reveal that all the manures contained an ample supply of
alkalinity (approximately 33% higher than minimal needs) to sustain the N recovery process
with gas-permeable membranes and low-rate aeration so as to be able to extract all the
\[ \text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-} \] (5)

Therefore, a substantial part of the inorganic carbon in manure is produced during decomposition of organic compounds that provide a balanced effluent for the membrane N recovery process.

3.3. The effect of organic matter (humic acids) on NH$_4^+$ recovery

Figure 6A shows the evolution of the pH with time for the three concentrations of humic acids evaluated (3000, 4500, and 6000 mg L$^{-1}$) with wastewater having an NH$_4^+$/$\text{HCO}_3^-$ molar ratio of 0.5. The pH increase due to the low-rate aeration was consistent among treatments: it increased about 1 unit, most (0.8 units) in the first day, reaching a final pH of around 9.2 units. The modified wastewater environment conditions were optimal for N recovery by the gas-permeable membrane process. Figure 6B shows the corresponding evolution of NH$_4^+$ concentration in the wastewater. In all three organic matter treatments, the concentration of NH$_4^+$ in wastewater was consistently decreased, about > 80% at 1.5 days, and > 95% at the end of the run (3 days). The NH$_4^+$ recovery efficiencies were also high (> 87%) and not affected by the organic matter treatments (Table 6). Therefore, the presence of organic matter (humic acids) did not affect the ammonium removal rate and efficiency. These results indicate that, while inorganic carbon in wastewater is critical, the organic matter, in the concentrations evaluated, do not inhibit the process of N recovery with gas-permeable membranes.
3.4. **NH$_4^+$ recovery from swine manure**

Figure 7A shows the evolution of pH during the experiment that treated two liquid swine manures of very-high and high strength: swine manure 1 (TS 36,500 mg L$^{-1}$) and swine manure 2 (TS 24,300 mg/L). They were 1:3 and 1:5 dilutions of the collected semisolid manure (table 2). The experiment set-up and operating conditions were the same as experiment 1. The pH increased as expected, approximately 0.5-0.7 units in one day. The pH of manure 1 was about 0.2 units higher, probably due to the lower dilution and higher strength. The higher pH environment obtained in the manure undoubtedly benefited the N removal and recovery process. The manure NH$_4^+$ contained in the separation tanks decreased at a steady state while the NH$_4^+$ in the concentrator tanks (acid tanks) increased accordingly (Fig. 7B). The final level of NH$_4^+$ obtained in the acid tanks after 4 days of treatment was 37,400 ± 4,200 mg NH$_4$-N L$^{-1}$ in the first treatment (manure 1) and 25,000 ± 2,800 mg NH$_4$-N L$^{-1}$ in the second treatment (manure 2). Table 7 shows the corresponding NH$_4^+$ mass balances. During the short time frame of the experiment, the system removed 65% and 85% of the ammonia initially present in manure 1 and 2, respectively. The NH$_4^+$ recovery rate was improved with the higher strength manure: the recovery rate of treatment 1 was about 1720 mg N day$^{-1}$ compared with 1340 mg N day$^{-1}$ in treatment 2 (Table 7). Corresponding ammonia fluxes were 8.90 and 7.11 mg N per cm$^2$ of membrane per day. The results obtained with manures showed that the amounts of NH$_4^+$ recovered in the acidic solution were higher than the amount removed from the liquid manure, providing NH$_4^+$ recovery efficiencies of 107% and 115% (table 7). This is probably due to mineralization of organic nitrogen during the 4-d treatment contributing additional NH$_4^+$ to the recovered NH$_4^+$ pool. In any case, the results with fresh manures showed that the low-rate aeration increased pH of the manure resulting in an active NH$_4^+$ uptake by the gas-
permeable membrane that gave quantitative recoveries of the NH$_4^+$ and that the overall N recovery was thus optimized.

4. Conclusions

This research determined the role of inorganic carbon (bicarbonate alkalinity) on the effectiveness of ammonia recovery using gas-permeable membranes and low-rate aeration. There were two distinct and interconnected mechanisms in this new approach. One was the release of OH$^-$ from the natural carbonates that increased the wastewater pH and promoted gaseous ammonia formation and membrane uptake. The other was the release of acidity and consumption of alkalinity by the N recovery. This acidification of the wastewater can completely halt the N recovery process. Therefore, an abundant inorganic carbon supply in balance with the NH$_4^+$ is needed for a successful operation of the technology. Fortunately, most swine manures contain ample supply of endogenous inorganic carbon and the process can be used to more economically recover ammonia using this endogenous, natural inorganic carbon instead of expensive alkali chemicals. Finally, we found that the process was not inhibited by increasing levels of organic matter in the wastewater.

Acknowledgements

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Project 6082-13630-001-00D “Improvement of Soil Management Practices and Manure Treatment/Handling Systems of the Southern Coastal Plains” is acknowledged. Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA.

References


Figure 1. Gaseous ammonia [NH$_3$(g)] permeation through the gas-permable membrane from the wastewater with dissolved and suspended solids into the stripping sulfuric acid solution.
Figure 2. Experimental device for NH$_4^+$ capture from manure using gas-permeable membrane and low-level aeration to increase wastewater pH and NH$_3$ transfer using endogenous carbonates.
Figure 3. Effect of NH$_4^+$/HCO$_3^-$ ratio (0.5, 1.0, 1.5 and 2.0) on wastewater pH during capture of ammonia with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH$_4^+$ (56, 111, 167, and 222 mmol L$^{-1}$) and a constant level of HCO$_3^-$ (115 mmol L$^{-1}$). Corresponding N removals shown in Fig. 4 and Table 3.
Figure 4. Effect of NH$_4^+$/HCO$_3^-$ ratio of wastewater (0.5, 1.0, 1.5 and 2.0) on the removal of NH$_4^+$ with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH$_4^+$ (56, 111, 167, and 222 mmol L$^{-1}$) and a constant level of HCO$_3^-$ (115 mmol L$^{-1}$). A: NH$_4^+$ removal from wastewater in mmol L$^{-1}$. B: percent NH$_4^+$ removal. Corresponding pH data are shown in Fig. 3.
Figure 5. Removal of NH$_4^+$ with gas-permeable membranes and low-rate aeration as affected by inorganic carbon in wastewater. Treatments included three levels of inorganic carbon (82, 41 and 0 mmol HCO$_3^-$ L$^{-1}$) and the same level of ammonia (71.4 mmol NH$_4^+$ L$^{-1}$ or 1000 mg NH$_4^-$ N L$^{-1}$). A: N concentration in wastewater and recovery acid tank. B: mass N removal and recovery. C: wastewater pH. D: wastewater alkalinity. The error bars are standard deviation of duplicate reactors.
Figure 6. Evolution of pH (A) and NH$_4^+$ concentration (B) during recovery of ammonia from wastewater containing three levels of Humic Acids (3000, 4500 and 6000 mg L$^{-1}$) and a uniform NH$_4^+/\text{HCO}_3^-$ molar ratio of 0.5.
Figure 7. A: Effect of aeration on manure pH during recovery of ammonia using gas-permeable membranes. B: corresponding changes in NH$_4^+$ concentration in the manure and recovery acid tank. Manure 1 contained 36.5 g TS L$^{-1}$ (very-high strength) and manure 2 contained 24.2 g TS L$^{-1}$ (high strength). The error bars are standard deviation of duplicate reactors.
Table 1. Main characteristics of the tubular membrane used.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (cm)</td>
<td>60</td>
</tr>
<tr>
<td>Outer diameter (mm)</td>
<td>10.25</td>
</tr>
<tr>
<td>Width of the wall (mm)</td>
<td>0.75</td>
</tr>
<tr>
<td>Average pore size (µm)</td>
<td>2.5</td>
</tr>
<tr>
<td>Bubble point (kPa)</td>
<td>210</td>
</tr>
<tr>
<td>Polymer density (g/cm³)</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Table 2. Characteristics of the swine manures.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw Manure (semi-solid)</th>
<th>1:3 dilution Manure 1</th>
<th>1:5 dilution Manure 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.77</td>
<td>8.10</td>
<td>8.07</td>
</tr>
<tr>
<td>EC (mS/cm)</td>
<td>21.2</td>
<td>5.90</td>
<td>4.20</td>
</tr>
<tr>
<td>Total Solids (%)</td>
<td>14.60</td>
<td>3.65</td>
<td>2.43</td>
</tr>
<tr>
<td>Total Volatile Solids (%)</td>
<td>10.40</td>
<td>2.60</td>
<td>1.73</td>
</tr>
<tr>
<td>Ammonia Nitrogen (mg N/kg)</td>
<td>13,728</td>
<td>4939</td>
<td>2749</td>
</tr>
<tr>
<td>Density (g/L)</td>
<td>725</td>
<td>931</td>
<td>954</td>
</tr>
</tbody>
</table>
Table 3: Mass balances for the recovery of ammonia using gas-permeable membranes and low-rate aeration as affected by the $\text{NH}_4^+$/HCO$_3^-$ ratio in wastewater (experiment 1).

<table>
<thead>
<tr>
<th>$\text{NH}_4^+$/HCO$_3^-$ molar ratio</th>
<th>Carbonate alkalinity to $\text{NH}_4^-$-N ratio</th>
<th>Influent $\text{NH}_4^+$ (mg N)</th>
<th>Effluent $\text{NH}_4^+$ (mg N)</th>
<th>Recovered $\text{NH}_4^+$ (mg N)</th>
<th>$\text{NH}_4^+$ removal efficiency $^b$ (%)</th>
<th>$\text{NH}_4^+$ recovery efficiency $^c$ (%)</th>
<th>Unaccounted $\text{NH}_4^+$ $^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>7.4</td>
<td>1523</td>
<td>33</td>
<td>1288</td>
<td>98</td>
<td>86</td>
<td>13</td>
</tr>
<tr>
<td>1.0</td>
<td>3.7</td>
<td>3091</td>
<td>123</td>
<td>2744</td>
<td>96</td>
<td>92</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>2.5</td>
<td>4569</td>
<td>1579</td>
<td>2699</td>
<td>65</td>
<td>90</td>
<td>6</td>
</tr>
<tr>
<td>2.0</td>
<td>1.8</td>
<td>6071</td>
<td>2833</td>
<td>2705</td>
<td>53</td>
<td>84</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ Treatments included four levels of $\text{NH}_4^+$: 56, 111, 167, and 222 mmol L$^{-1}$ (1000, 2000, 3000, and 4000 mg $\text{NH}_4^+$ L$^{-1}$) and a constant level of HCO$_3^-$ (115 mmol L$^{-1}$). Data are results of 4-day batches. Corresponding daily pH and N removal dynamics are shown in Figs. 3 and 4.

$^b$ $\text{NH}_4^+$ removal efficiency = ($\text{NH}_4^+$ removed from wastewater/initial $\text{NH}_4^+$) $\times$ 100;
$\text{NH}_4^+$ removed from wastewater = initial $\text{NH}_4^+$ in wastewater – remaining $\text{NH}_4^+$ in wastewater

$^c$ $\text{NH}_4^+$ recovery efficiency = ($\text{NH}_4^+$ recovered in the acidic solution/ $\text{NH}_4^+$ removed from wastewater) $\times$ 100

$^d$ Unaccounted $\text{NH}_4^+$ = (initial $\text{NH}_4^+$ in wastewater – remaining $\text{NH}_4^+$ in wastewater - $\text{NH}_4^+$ recovered in the acidic solution) $\times$ 100/ initial $\text{NH}_4^+$ in wastewater
Table 4: Mass balances for the recovery of ammonia using gas-permeable membranes and low-rate aeration as affected by inorganic carbon in wastewater (experiment 2).

<table>
<thead>
<tr>
<th>NH$_4^+$/HCO$_3^-$ molar ratio $^a$</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Influent NH$_4^+$ (mg N)</th>
<th>Effluent NH$_4^+$ (mg N)</th>
<th>Recovered NH$_4^+$ (mg N)</th>
<th>NH$_4^+$ removal efficiency $^b$ (%)</th>
<th>NH$_4^+$ recovery efficiency $^c$ (%)</th>
<th>Unaccounted NH$_4^+$ $^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.87</td>
<td>7.9</td>
<td>8.9</td>
<td>1413</td>
<td>39</td>
<td>1284</td>
<td>97</td>
<td>93</td>
<td>6</td>
</tr>
<tr>
<td>1.74</td>
<td>7.8</td>
<td>5.5</td>
<td>1526</td>
<td>663</td>
<td>766</td>
<td>57</td>
<td>89</td>
<td>6</td>
</tr>
<tr>
<td>control</td>
<td>7.8</td>
<td>5.1</td>
<td>1584</td>
<td>1494</td>
<td>35</td>
<td>6</td>
<td>39</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$ Treatments included three levels of inorganic carbon (82, 41 and 0 mmol HCO$_3^-$ L$^{-1}$), all with the same level of ammonia (71.4 mmol NH$_4^+$ L$^{-1}$ or 1000 mg NH$_4^-$N L$^{-1}$). Treatment time was 7 days. Daily pH, alkalinity and N removal dynamics are shown in Fig. 5.

$^b$ NH$_4^+$ removal efficiency = (NH$_4^+$ removed from wastewater/initial NH$_4^+$) x 100;
NH$_4^+$ removed from wastewater = initial NH$_4^+$ in wastewater – remaining NH$_4^+$ in wastewater

$^c$ NH$_4^+$ recovery efficiency = (NH$_4^+$ recovered in the acidic solution/ NH$_4^+$ removed from wastewater) x 100

$^d$ Unaccounted NH$_4^+$ = (initial NH$_4^+$ in wastewater – remaining NH$_4^+$ in wastewater - NH$_4^+$ recovered in the acidic solution) x100/ initial NH$_4^+$ in wastewater
Table 5. Relationship between wastewater alkalinity and ammonia removal using gas-permeable membranes and low-rate aeration during N recovery step.

<table>
<thead>
<tr>
<th></th>
<th>Anaerobically Digested Swine Wastewater Farm 1 (Dube et al., 2016)</th>
<th>Anaerobically Digested Swine Wastewater Farm 2 (Dube et al., 2016)</th>
<th>Raw Swine Manure (Garcia-Gonzalez et al., 2015)</th>
<th>Synthetic wastewater made with NH₄⁺ and CO₃⁻ (this study, Fig. 5, ratio = 0.87)³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Alkalinity (mg CaCO₃ L⁻¹)</td>
<td>11365</td>
<td>8121</td>
<td>13350</td>
<td>3913</td>
</tr>
<tr>
<td>Final Alkalinity (mg CaCO₃ L⁻¹)</td>
<td>3034</td>
<td>2018</td>
<td>3590</td>
<td>493</td>
</tr>
<tr>
<td>Initial NH₄⁺ (mg N L⁻¹)</td>
<td>2089</td>
<td>1554</td>
<td>2390</td>
<td>942</td>
</tr>
<tr>
<td>Final NH₄⁺ (mg N L⁻¹)</td>
<td>64</td>
<td>23</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>Final pH</td>
<td>9.26</td>
<td>9.17</td>
<td>9.20</td>
<td>8.90</td>
</tr>
<tr>
<td>Initial Alkalinity:Initial NH₄⁺ Ratio</td>
<td>5.44</td>
<td>5.23</td>
<td>5.59</td>
<td>4.15</td>
</tr>
<tr>
<td>Alkalinity Consumed (mg CaCO₃ L⁻¹)</td>
<td>8331</td>
<td>6103</td>
<td>9760</td>
<td>3420</td>
</tr>
<tr>
<td>NH₄⁺ Removed (mg N L⁻¹)</td>
<td>2025</td>
<td>1531</td>
<td>2370</td>
<td>916</td>
</tr>
<tr>
<td>NH₄⁺ recovery efficiency (%)</td>
<td>98</td>
<td>96</td>
<td>99</td>
<td>93</td>
</tr>
<tr>
<td>Alkalinity Consumed:NH₄⁺ Removed Ratio</td>
<td>4.11</td>
<td>3.99</td>
<td>4.12</td>
<td>3.73</td>
</tr>
</tbody>
</table>

³ Synthetic solution: treatment 1 in experiment 2 with NH₄⁺/HCO₃⁻ ratio = 0.87 (a mixture of 82 mmol L⁻¹ HCO₃⁻ and 71.4 mmol NH₄⁺ L⁻¹).
³ Alkalinity consumed = Initial alkalinity – final alkalinity
³ NH₄⁺ Removed from wastewater = Initial NH₄⁺ - final NH₄⁺
³ NH₄⁺ recovery efficiency = (NH₄⁺ recovered in the acid tank/ NH₄⁺ removed from wastewater) x 100
Table 6: Mass balances for the removal and recovery of ammonia from wastewater using gas-permeable membranes and low-rate aeration as affected by the presence of organic matter (experiment 3).

<table>
<thead>
<tr>
<th>Humic acid concentration (mg L(^{-1}))</th>
<th>NH(_4^+) Removal Efficiency (^a) (%)</th>
<th>NH(_4^+) Recovery Efficiency (^b) (%)</th>
<th>Unaccounted NH(_4^+) (^c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>95</td>
<td>109</td>
<td>0</td>
</tr>
<tr>
<td>4500</td>
<td>98</td>
<td>87</td>
<td>11</td>
</tr>
<tr>
<td>6000</td>
<td>99</td>
<td>96</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) NH\(_4^+\) removal efficiency = (NH\(_4^+\) removed from wastewater/initial NH\(_4^+\)) \times 100 ;

NH\(_4^+\) removed from wastewater = initial NH\(_4^+\) in wastewater – remaining NH\(_4^+\) in wastewater.

Wastewater contained a uniform NH\(_4^+\)/HCO\(_3^-\) molar ratio of 0.5. pH and N removal dynamics are shown in Fig. 6.

\(^b\) NH\(_4^+\) recovery efficiency = (NH\(_4^+\) recovered in the acidic solution/ NH\(_4^+\) removed from wastewater) \times 100

\(^c\) Unaccounted NH\(_4^+\) = (initial NH\(_4^+\) in wastewater – remaining NH\(_4^+\) in wastewater - NH\(_4^+\) recovered in the acidic solution) \times 100/ initial NH\(_4^+\) in wastewater
Table 7. Mass balances of the recovery of ammonia from swine manure using gas-permeable membrane module with low-rate aeration (experiment 4)\(^a\).

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Time (days)</th>
<th>Initial $\text{NH}_4^+$ in Manure (mg N)</th>
<th>Remaining $\text{NH}_4^+$ in Manure (mg N)</th>
<th>$\text{NH}_4^+$ removed from manure (mg N)</th>
<th>$\text{NH}_4^+$ recovered in acidic solution (mg N)</th>
<th>$\text{NH}_4$-N removal efficiency (%)</th>
<th>$\text{NH}_4$-N recovery efficiency (%)</th>
<th>Average $\text{NH}_4^+$ recovery rate (mg N/day)</th>
<th>Average $\text{NH}_4^+$ Flux (mg N/cm(^2)/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swine manure 1</td>
<td>4</td>
<td>9880</td>
<td>3430</td>
<td>6450</td>
<td>8841</td>
<td>65</td>
<td>107</td>
<td>1719</td>
<td>8.90</td>
</tr>
<tr>
<td>Swine manure 2</td>
<td>4</td>
<td>5500</td>
<td>840</td>
<td>4660</td>
<td>6908</td>
<td>85</td>
<td>115</td>
<td>1343</td>
<td>7.11</td>
</tr>
</tbody>
</table>

a. Data are average of duplicate reactors. Characteristics of the manures are provided in table 2.
b. $\text{NH}_4^+$ removed from manure = initial $\text{NH}_4^+$ in manure - remaining $\text{NH}_4^+$ in manure
c. $\text{NH}_4^+$ removal efficiency = ($\text{NH}_4^+$ removed from manure/initial $\text{NH}_4^+$ in manure) \times 100
d. $\text{NH}_4^+$ recovery efficiency = ($\text{NH}_4^+$ recovered in the acidic solution/$\text{NH}_4^+$ removed from manure) \times 100
e. Average $\text{NH}_4^+$ recovery rate = mass $\text{NH}_4$-N recovered in the acidic solution /treatment time
f. Average $\text{NH}_4^+$ flux = average $\text{NH}_4^+$ recovery rate /membrane surface. Membrane surface = 193 cm\(^2\)
Low-rate aeration enhanced ammonia recovery of the gas-permeable membrane process

Aeration reacted with the inorganic carbon and increased pH

Approximately 4.1 kg alkalinity was consumed per kg of N removed

NH$_4^+$ removal efficiencies > 96% were obtained with NH$_4^+$ to HCO$_3^-$ molar ratios ≤ 1

In 4 days, the recovered NH$_4^+$ from swine manure contained 48,000 mg L$^{-1}$
Manure Effluent

\[
\text{CO}_2 \quad \text{NH}_4^+ \rightarrow \text{NH}_3 \rightarrow \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+
\]

- Higher pH environment
- Alkalinity destruction

Low rate aeration

Hydrophobic polymer

Gas-permeable membrane

Gas-filled pore

Strip Solution (H⁺)

\[
\text{HCO}_3^- \rightarrow \text{OH}^- \rightarrow \text{H}^+ \rightarrow \text{NH}_4^+
\]

Recovered ammonium