Water Research 137 (2018) 201–210

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

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

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ARTICLE INFO

Article history:
Available online 6 March 2018

Keywords:
Ammonia recovery
Ammonia capture
Gas-permeable membranes
Livestock wastewater
Ammonia emissions control

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 (3000–6000 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.

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 1000 mg L^{-1} in industrial wastewater, such as those generated by the production of chemical fertilizers, and from about 400 to 5000 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 3751 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.,

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https://doi.org/10.1016/j.watres.2018.03.013
0043-1354/Published by Elsevier Ltd.

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 (Fig. 1). With a pH < 2, the acidic solution dissolves the NH_3 in the form of ammonium.

$$NH_4^+ + OH^- \leftrightarrow NH_{3(g)} + H_2O \tag{1}$$

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).

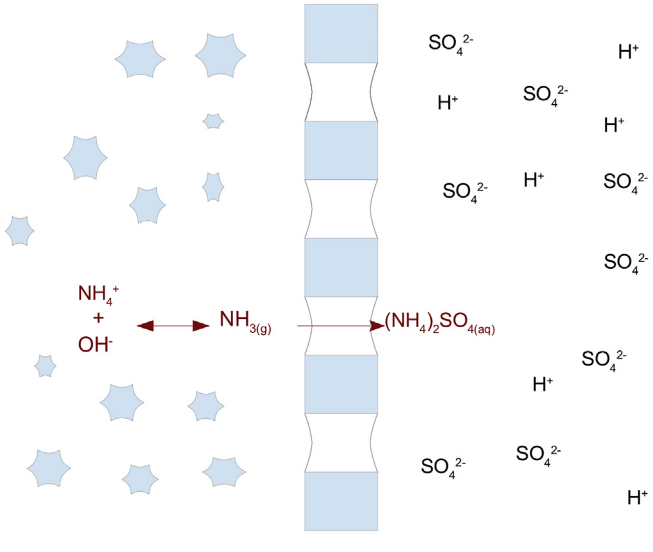

Fig. 1. Gaseous ammonia [$NH_{3(g)}$] permeation through the gas-permable membrane from the wastewater with dissolved and suspended solids into the stripping sulfuric acid solution.

$$HCO_3^- + air \rightarrow CO_2 + OH^- \tag{2}$$

However, according to Eq. (3), the recovery of $NH_{3(g)}$ through the gas-permeable membrane causes an increase of acidity in the wastewater environment being treated as the 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 (García-González and Vanotti, 2015).

$$NH_4^+ \rightarrow NH_{3(g)} + H^+ \tag{3}$$

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 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 ($0.18\ kW\,h \cdot kg^{-1} NH_3$), 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 NH_4^+ recovery. With the aeration approach applied to waste effluents from raw liquid swine manures, the 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 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 alkalinities 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 1 h (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_2SO_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:

$$\text{FA as } NH_3\ (\text{mg } L^{-1}) = (17/14) \times \{(NH_4\text{-N} \times 10^{pH})/\ [(K_b/K_w)+ 10^{pH})]\} \tag{4}$$

Where K_b and K_w are ionization constants for NH_3 and H_2O and the ratio $(K_b/K_w) = \exp\ [6344/(273 + T)]$.

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_2SO_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 (García-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-$\text{liquid}^{-1}\text{min}^{-1}$). 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).

Table 1
Main characteristics of the tubular membrane used.

Length (cm)	60
Outer diameter (mm)	10.25
Width of the wall (mm)	0.75
Average pore size (μm)	2.5
Bubble point (kPa)	210
Polymer density (g/cm^3)	0.39

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^+/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^+/HCO_3^- molar ratios were 0.5, 1.0, 1.5 and 2. The synthetic wastewaters were prepared with the addition of NH_4NO_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

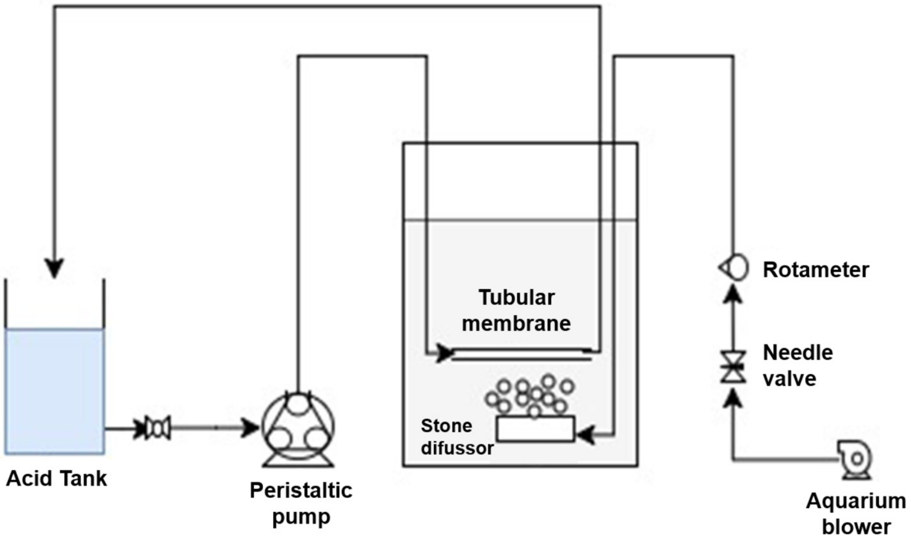

Fig. 2. Experimental device for NH_4^+ capture from manure using gas-permeable membrane and low-level aeration to increase wastewater pH and NH_3 transfer using endogenous carbonates.

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_4Cl (3820 mg L^{-1}) in all cases that provided a constant NH_4-N concentration across treatments (1000 mg L^{-1} NH_4-N or 71.4 mmol NH_4^+ L^{-1}). The pH of the freshly made control solution (NH_4Cl 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_2SO_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_4NO_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%) (García-González 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.

Table 2
Characteristics of the swine manures.

Parameters	Raw Manure (semi-solid)	1:3 dilution Manure 1	1:5 dilution Manure 2
pH	7.77	8.10	8.07
EC (mS/cm)	21.2	5.90	4.20
Total Solids (%)	14.60	3.65	2.43
Total Volatile Solids (%)	10.40	2.60	1.73
Ammonia Nitrogen (mg N/kg)	13,728	4939	2749
Density (g/L)	725	931	954

3. Results and discussion

3.1. Effect of the ratio NH_4^+/HCO_3^- on NH_4^+ removal and recovery

Fig. 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 min during the first hour of the experiment and from that moment on, every 24 h. 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 h varied among treatment: in the two samples with lower NH_4^+/HCO_3^- ratios (0.5 and 1.0), the pH increases were 0.91–1.15 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 h of 8.3–8.5. 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 (8.36–9.47) 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 ratios 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_2CO_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 $(NH_4)_2SO_4$ (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

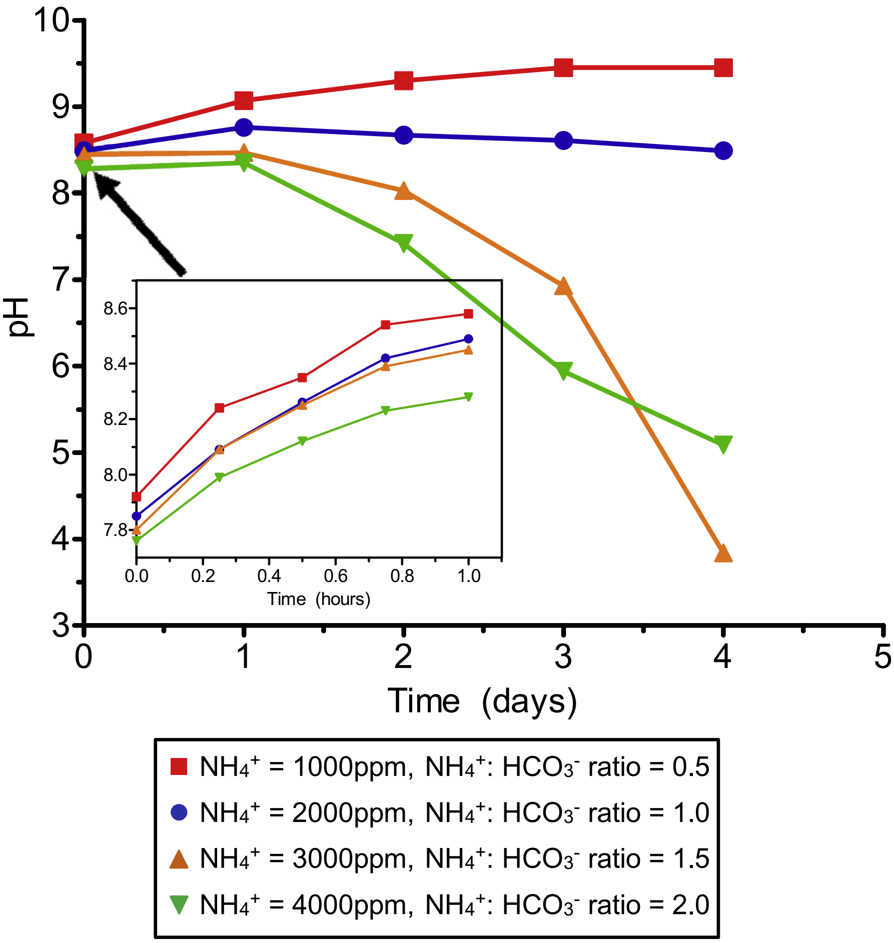

Fig. 3. Effect of NH_4^+/HCO_3^- ratio (0.5, 1.0, 1.5 and 2.0) on wastewater pH during capture of ammonia with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH_4^+ (56, 111, 167, and 222 mmol L^{-1}) and a constant level of HCO_3^- (115 mmol L^{-1}). Corresponding N removals shown in Fig. 4 and Table 3.

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 and 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_4Cl and contained 4100 mg L^{-1} alkalinity and 1000 mg L^{-1} 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}). Fig. 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^+/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 ($NH_4\text{-}N = 939\ e^{-0.0271*hours}$, $R^2 = 0.999$) with daily decreases of 52%. However, when inorganic carbon was deficient (NH_4^+/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%). Fig. 5c and d shows the evolution of pH

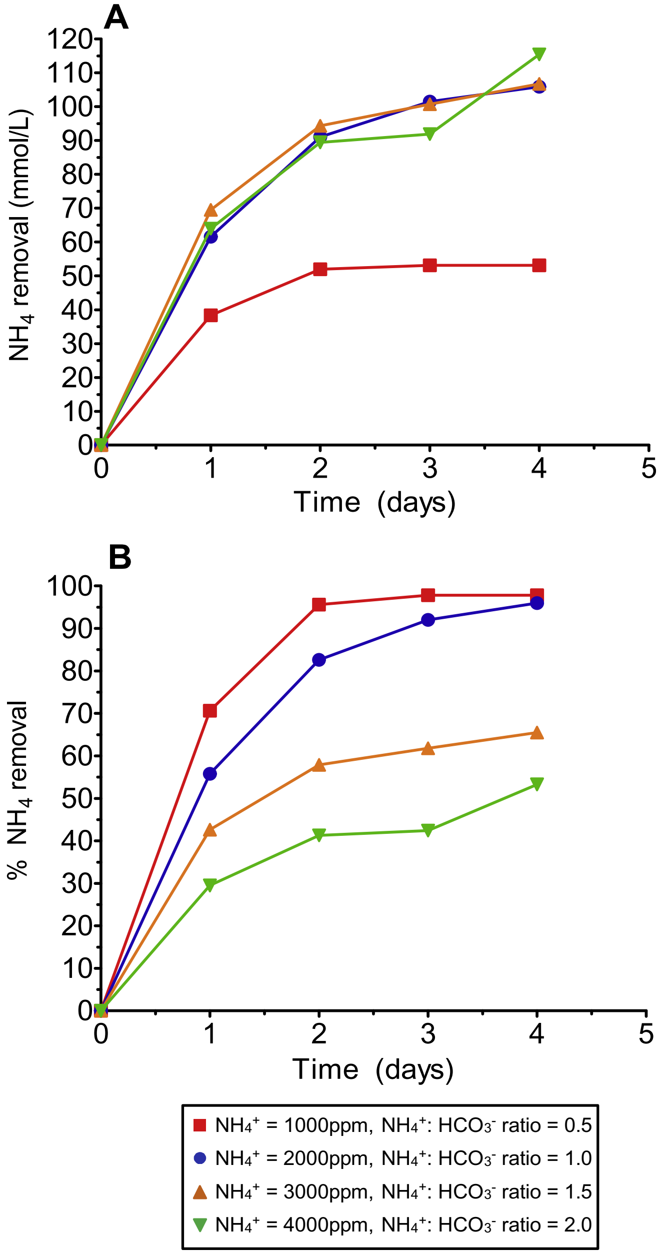

Fig. 4. Effect of NH_4^+/HCO_3^- ratio of wastewater (0.5, 1.0, 1.5 and 2.0) on the removal of NH_4^+ with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH_4^+ (56, 111, 167, and 222 mmol L^{-1}) and a constant level of HCO_3^- (115 mmol L^{-1}). A: NH_4^+ removal from wastewater in mmol L^{-1}. B: percent NH_4^+ removal. Corresponding pH data are shown in Fig. 3.

and alkalinity of the three treatments over the same period. In the treatment with NH_4^+/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^{-1} (Fig. 5d). With deficient inorganic carbon relative to ammonia (NH_4^+/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. 5b,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 García-González 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 NH_4^+ without the need of supplemental alkali chemicals. Liquid manure is a mixture of urine, water, and feces. Livestock urine contains >55% of the excreted N, of which more than 70% is in the form of urea (Sommer and Husted, 1995). Urea in combination with water and urease enzyme produces NH_4^+ and carbonate, as described in Eq. (5):

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \tag{5}$$

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*

Fig. 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^+/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. Fig. 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

Table 3
Mass balances for the recovery of ammonia using gas-permeable membranes and low-rate aeration as affected by the NH_4^+/HCO_3^- ratio in wastewater (experiment 1).

NH_4^+/HCO_3^- molar ratio [a]	Carbonate alkalinity to NH_4-N ratio	Influent NH_4^+ (mg N)	Effluent NH_4^+ (mg N)	Recovered NH_4^+ (mg N)	NH_4^+ removal efficiency [b] (%)	NH_4^+ recovery efficiency [c] (%)	Unaccounted NH_4^+ [d] (%)
0.5	7.4	1523	33	1288	98	86	13
1.0	3.7	3091	123	2744	96	92	7
1.5	2.5	4569	1579	2699	65	90	6
2.0	1.8	6071	2833	2705	53	84	9

[a] Treatments included four levels of NH_4^+: 56, 111, 167, and 222 mmol L^{-1} (1000, 2000, 3000, and 4000 mg 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] 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) ×100/initial 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).

NH_4^+/HCO_3^- molar ratio [a]	Initial pH	Final pH	Influent NH_4^+ (mg N)	Effluent NH_4^+ (mg N)	Recovered NH_4^+ (mg N)	NH_4^+ removal efficiency [b] (%)	NH_4^+ recovery efficiency [c] (%)	Unaccounted NH_4^+ [d] (%)
0.87	7.9	8.9	1413	39	1284	97	93	6
1.74	7.8	5.5	1526	663	766	57	89	6
control	7.8	5.1	1584	1494	35	6	39	3

[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) ×100/initial NH_4^+ in wastewater.

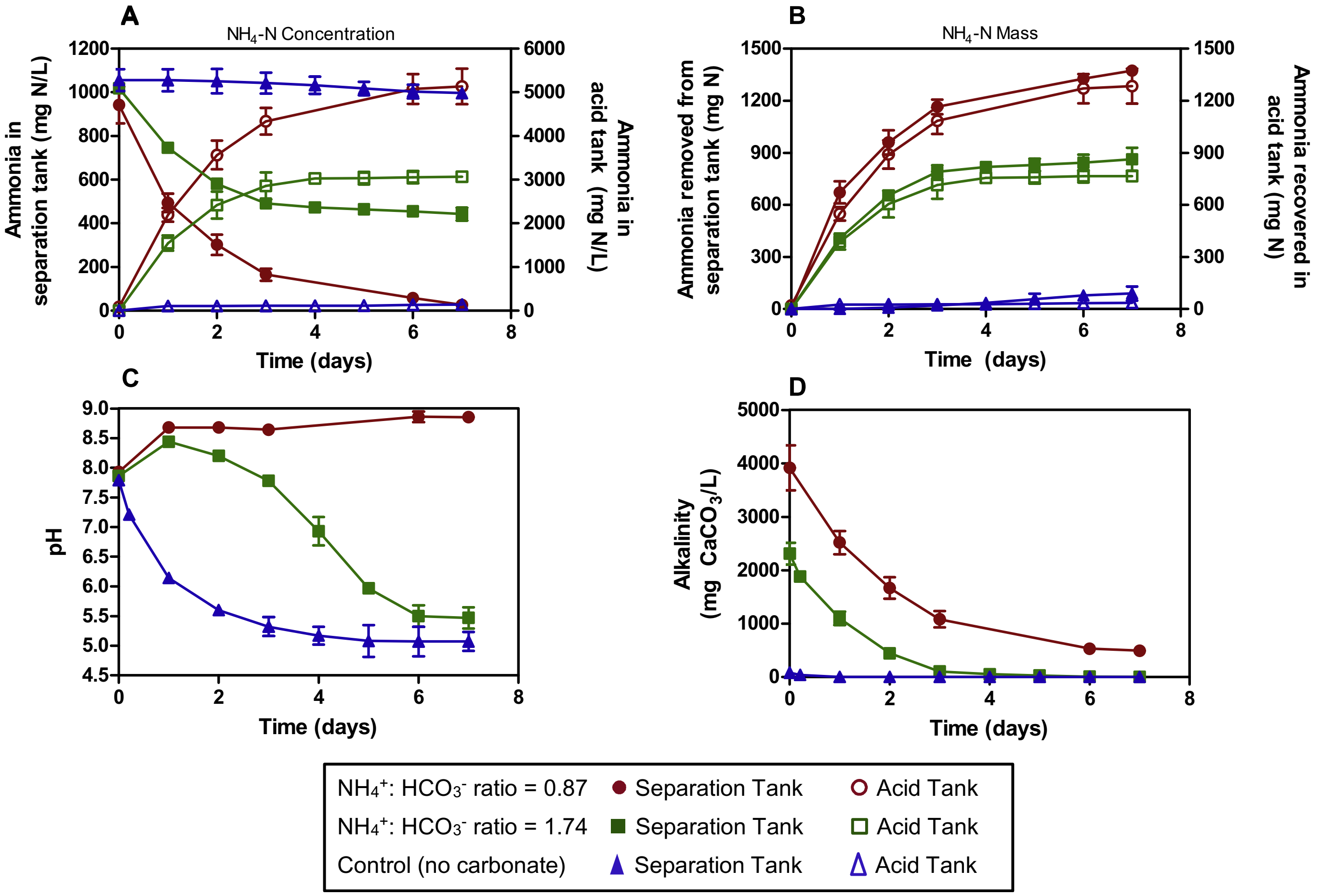

Fig. 5. Removal of NH_4^+ with gas-permeable membranes and low-rate aeration as affected by inorganic carbon in wastewater. Treatments included three levels of inorganic carbon (82, 41 and 0 mmol HCO_3^- L^{-1}) and the same level of ammonia (71.4 mmol NH_4^+ L^{-1} or 1000 mg NH_4-N L^{-1}). A: N concentration 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.

Table 5
Relationship between wastewater alkalinity and ammonia removal using gas-permeable membranes and low-rate aeration during N recovery step.

	Anaerobically Digested Swine Wastewater Farm 1 (Dube et al., 2016)	Anaerobically Digested Swine Wastewater Farm 2 (Dube et al., 2016)	Raw Swine Manure (García-González et al., 2015)	Synthetic wastewater made with NH_4^+ and CO_3^- (this study, Fig. 5, ratio = 0.87)[a]
Initial Alkalinity (mg $CaCO_3$ L^{-1})	11365	8121	13350	3913
Final Alkalinity (mg $CaCO_3$ L^{-1})	3034	2018	3590	493
Initial NH_4^+ (mg N L^{-1})	2089	1554	2390	942
Final NH_4^+ (mg N L^{-1})	64	23	20	26
Final pH	9.26	9.17	9.20	8.90
Initial Alkalinity:Initial NH_4^+ Ratio	5.44	5.23	5.59	4.15
Alkalinity Consumed [b] (mg $CaCO_3$ L^{-1})	8331	6103	9760	3420
NH_4^+ Removed [c] (mg N L^{-1})	2025	1531	2370	916
NH_4^+ recovery efficiency [d] (%)	98	96	99	93
Alkalinity Consumed:NH_4^+ Removed Ratio	4.11	3.99	4.12	3.73

[a] Synthetic solution: treatment 1 in experiment 2 with NH_4^+/HCO_3^- ratio = 0.87 (a mixture of 82 mmol L^{-1} HCO_3^- and 71.4 mmol NH_4^+ L^{-1}).
[b] Alkalinity consumed = Initial alkalinity − final alkalinity.
[c] NH_4^+ Removed from wastewater = Initial NH_4^+ - final NH_4^+.
[d] NH_4^+ recovery efficiency = (NH_4^+ recovered in the acid tank/NH_4^+ removed from wastewater) x 100.

>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.

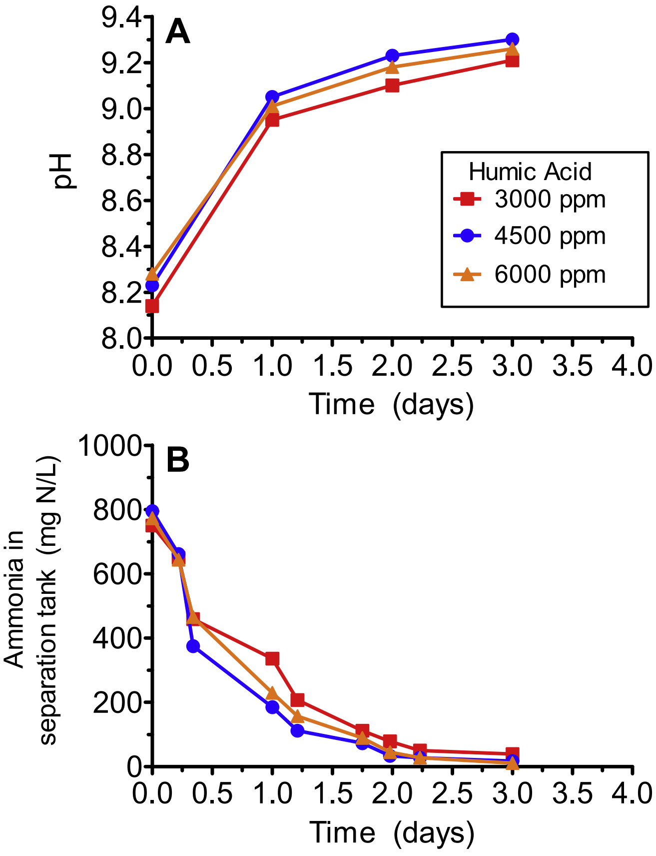

Fig. 6. Evolution of pH (A) and NH_4^+ concentration (B) during recovery of ammonia from wastewater containing three levels of Humic Acids (3000, 4500 and 6000 mg L^{-1}) and a uniform NH_4^+/HCO_3^- molar ratio of 0.5.

3.4. NH_4^+ recovery from swine manure

Fig. 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^{-1}). 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 ± 4200 mg NH_4-N L^{-1} in the first treatment (manure 1) and 25,000 ± 2800 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

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).

Humic acid concentration (mg L^{-1})	NH_4^+ Removal Efficiency [a] (%)	NH_4^+ Recovery Efficiency [b] (%)	Unaccounted NH_4^+ [c] (%)
3000	95	109	0
4500	98	87	11
6000	99	96	3

[a] 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.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) x 100.
[c] Unaccounted NH_4^+ = (initial NH_4^+ in wastewater − remaining NH_4^+ in wastewater - NH_4^+ recovered in the acidic solution) ×100/initial NH_4^+ in wastewater.

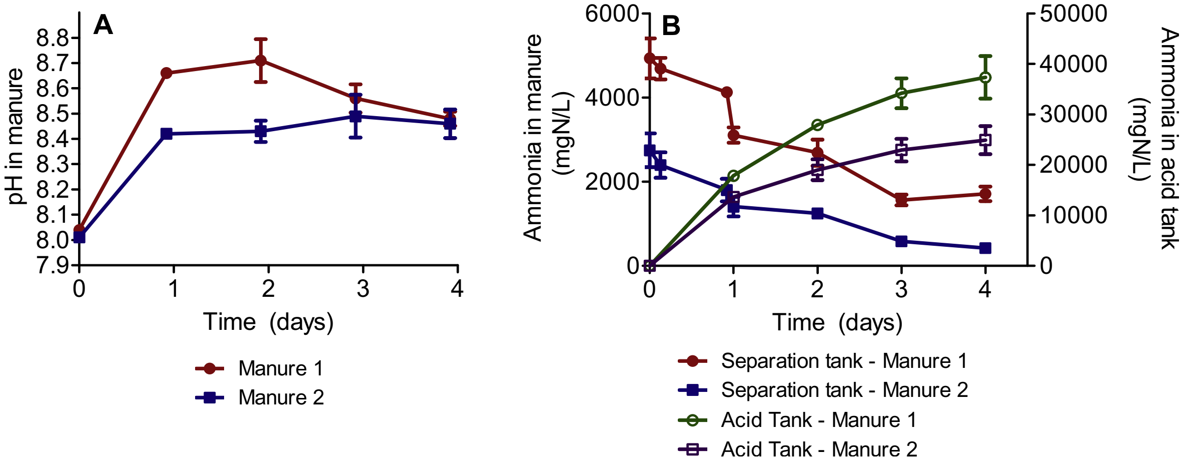

Fig. 7. A: Effect of aeration on manure pH during recovery of ammonia using gas-permeable membranes. B: corresponding changes in NH_4^+ concentration in the manure and recovery acid tank. Manure 1 contained 36.5 g TS L^{-1} (very-high strength) and manure 2 contained 24.2 g TS L^{-1} (high strength). The error bars are standard deviation of duplicate reactors.

Table 7
Mass balances of the recovery of ammonia from swine manure using gas-permeable membrane module with low-rate aeration (experiment 4)[a].

Treatments	Time	Initial NH_4^+ in Manure	Remaining NH_4^+ in Manure	NH_4^+ removed from manure [b]	NH_4^+ recovered in acidic solution	NH_4-N removal efficiency [c]	NH_4-N recovery efficiency [d]	Average NH_4^+ recovery rate [e]	Average NH_4^+ Flux [f]
	(days)		(mg N)			(%)		mg N/day	mg N/cm^2/day
Swine manure 1	4	9880	3430	6450	8841	65	107	1719	8.90
Swine manure 2	4	5500	840	4660	6908	85	115	1343	7.11

[a] Data are average of duplicate reactors. Characteristics of the manures are provided in Table 2.
[b] NH_4^+ removed from manure = initial NH_4^+ in manure - remaining NH_4^+ in manure.
[c] NH_4^+ removal efficiency= (NH_4^+ removed from manure/initial NH_4^+ in manure) x 100.
[d] NH_4^+ recovery efficiency = (NH_4^+ recovered in the acidic solution/NH_4^+ removed from manure) x 100.
[e] Average NH_4^+ recovery rate = mass NH_4-N recovered in the acidic solution/treatment time.
[f] Average NH_4^+ flux = average NH_4^+ recovery rate/membrane surface. Membrane surface = 193 cm^2.

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

This research was part of Silvana Daguerre-Martini work for Master in Management, Treatment and Valorization of Organic Residues at Orihuela Polytechnic Superior School, University Miguel Hernandez (UMH). It was co-financed by the Ministry of Economy & Competitiveness of Spain and the European Regional Development Fund (ERDF, “Una manera de hacer Europa”) (Project

AGL2013-41612-R). Cooperation with USDA-ARS 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.

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