



Recovery of ammonia from swine manure using gas-permeable membranes: Effect of waste strength and pH



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ARTICLE INFO

Article history:

Received 17 March 2014

Accepted 17 January 2015

Available online 14 February 2015

Keywords:

Gas-permeable membranes

Ammonia recovery

Swine manure

Waste management

ABSTRACT

Nitrogen recovery from swine manure was investigated using gas-permeable membranes. The process involved a continuous recirculation of an acidic solution through a gas-permeable membrane submerged in manure. Ammonia from manure was concentrated in the acidic solution increasing its pH, while pH decreased in manure. In the first set of experiments, nitrogen recovery efficiency was evaluated with no pH adjustment of manure; whereas in the second, manure with three different ammonia (NH₃) concentrations (from 1070 to 2290 mg/L) was used adjusting their pH to 9 whenever pH decreased below 7.7. With no pH adjustment, NH₃ recovery from manure was 55%, while NH₃ recovery averaged 81% when pH of manure was adjusted. This work showed that as waste strength and available NH₃ content increased in manure, more N was captured by the membrane. These results suggested that the gas-permeable membranes are a useful technology for NH₃ recovery from manure, reducing environmental pollution whilst converting NH₃ into a valuable ammonium (NH₄⁺) salt fertilizer.

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1. Introduction

Important mitigation strategies of ammonia (NH₃) emissions for concentrated livestock operations often involve capturing or trapping the fugitive gases and subsequent treatment of the captured air with bio-filters and bio-covers to remove the NH₃ (Ndegwa et al., 2008); which means N loss for further agriculture use and therefore, an important economic loss. In this sense, fertilizers represent 28% of the total energy consumed in the USA farms (Miranowski, 2004). Fertilizer production consumes approximately 1.2% of the world's total energy on an annual basis (IFA, 2009). Since NH₃ production accounts for some 87% of the fertilizer industry's total energy consumption, the fuel and feedstock used to produce NH₃ are by far the main energy requirements (IFA, 2009).

The Haber–Bosch process is used by the chemical industry to combine nitrogen gas (from the atmosphere) with hydrogen (from natural gas) under high pressure and temperature, in the presence of a catalyst, to produce NH₃, which is a plant fertilizer. The price of N fertilizers is directly related to the price of natural gas, since anhydrous NH₃ fertilizer is synthesized from the Haber–Bosch process, as well as most of the other popular N fertilizer derived from

this compound (Funderburg, 2013). Manufacturing 1 ton of anhydrous NH₃ fertilizer requires 949 m³ of natural gas (Funderburg, 2013), while emitting 1.6 ton of carbon dioxide (IFA, 2009).

In some countries the fertilizer prices have increased more than 50% in the last decade. As an example of increasing prices, urea price has increased 57% in Spain and 66% in the USA from 2002 to 2012. In the same period, ammonium sulphate (NH₄)₂SO₄ has increased 53% and 59% in Spain and the USA, respectively. Thus, in 2012 a land farmer paid 440 €/ton of (NH₄)₂SO₄ in Spain, and 497 \$/ton of (NH₄)₂SO₄ in the USA (375 € if considering a conversion of 1EUR = 1.327USD) (MAGRAMA, 2013; USDA, 2013). According to Heffer and Prud'homme (2013), increases in demand are projected for all the three major nutrients, showing average annual growth rates of 1.5% for N, 1.8% for P and 3.0% for K in 2017; which may result in additional increases in fertilizer prices in the coming years.

New technologies for NH₃ emissions abatement in livestock operations are focussed on N recovery. The technologies for N recovery include: (1) reverse osmosis using high pressure and hydrophilic membranes (Masse et al., 2010; Thorneby et al., 1999); (2) air-stripping using stripping towers and acid absorption (Bonmati and Flotats, 2003); (3) zeolite adsorption through ion exchange (Milan et al., 1997); (4) co-precipitation with phosphate and magnesium to form struvite (Uludag-Demirer et al., 2005); and (5) a new process using gas-permeable membranes at low

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pressure (Vanotti and Szogi, 2011a). The gas-permeable membrane process includes the passage of gaseous NH_3 through a microporous hydrophobic membrane and capture and concentration in a stripping solution on the other side of the membrane (Fig. 1). The membrane manifolds are submerged in the liquid and the NH_3 is removed from the liquid before it escapes into the air (Vanotti and Szogi, 2011a); the NH_3 permeates through the membrane pores reaching the acidic solution located on the other side of the membrane. Once in the acidic solution, NH_3 combines with free protons to form non-volatile NH_4^+ ions that are converted into a valuable NH_4^+ salt fertilizer. The gas-permeable membranes can be also used to recover volatilized NH_3 from poultry litter directly from the air (Rothrock et al., 2010, 2013).

All over the world there is a major interest from swine producers in implementing best control technologies that will abate NH_3 emissions from confined livestock operations; the gas-permeable membrane technology has the advantage of capturing and recovering N and thus avoiding NH_3 emissions. The recovered N is conserved un-volatilized in the form of a valuable fertilizer (NH_4) $_2$ SO_4 , which is desirable to export N off the farm to other regions where N is needed, and thus avoiding environmental pollution to soil, air and water. The following four advantages relative to the state of the art have been identified: (1) compared to reverse osmosis that requires high pressure, the gas-permeable membrane process requires low pressure; (2) compared to air stripping towers and zeolite adsorption techniques that require some clarification pre-treatment of the manure, the gas-permeable membrane process does not require clarification; (3) compared to the struvite precipitation method, which requires 1:1:1 ratios of Mg, NH_4 and PO_4 vs. typical ratios of 1:16:1.2 for liquid manure (Nelson et al., 2000), the gas-permeable membrane process could remove all the NH_4 without need to add Mg and PO_4 required to balance the stoichiometry of struvite precipitation; (4) another advantage is that gas-permeable membrane process can be combined with other treatment technologies to improve their performance, i.e. anaerobic digestion. The inhibition of methanogens by high NH_3 concentration in manure severely inhibits the production of biogas, thus the use of gas-permeable membranes to recover NH_3 without damaging the carbonaceous material will improve the process.

The research goal of this work was to compare wastewater strength and pH of manure on NH_3 recovery through tubular gas-permeable membranes at lab scale. In a first set of experiments, NH_3 recovery from manure was investigated when manure pH was not adjusted. In a second set of experiments, the influence of NH_3 concentration in manure on NH_3 recovery was evaluated. Moreover, the influence of manure pH on the recovery of NH_3

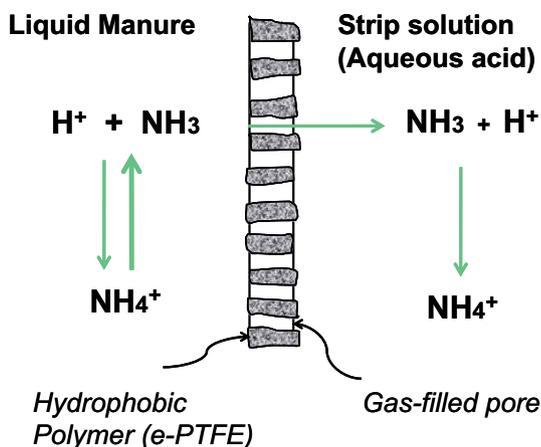


Fig. 1. Cross section of a hydrophobic gas-permeable membrane.

was also studied, adjusting manure pH with alkali when it was below 7.7.

2. Materials and methods

2.1. Experimental procedure

Fig. 2 shows a schematic diagram of the experimental device for NH_3 capture from manure that was used in all the experiments. Batch experiments were conducted in 2-L wastewater vessels consisting of polyethylene terephthalate (PET) plastic jars for an effective manure volume of 1.3 L. The acid tank consisted of 500-mL Erlenmeyer flasks containing 300 mL 1 N H_2SO_4 . A diaphragm pump (Alldos, TrueDos model, Denmark) was used to continuously circulate the acid through the tubular membranes inside the manure vessels and back into the acid tank using a constant flow rate of 5.8 L/day. Gas-permeable tubing made of expanded polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock Hill, SC) was used for NH_3 capture. The length of the gas-permeable membrane tubing used in this work was 60 cm, with outer diameter of 10.25 mm and wall thickness of 0.75 mm. The membrane manifolds were submerged in the manure liquid contained in the PET jars, which were kept closed but not hermetic. Ports were installed on top of the reactor vessels to obtain samples and monitor pH (Fig. 2). The manure was continuously agitated using magnetic stirrers.

Two sets of batch experiments were carried out. In the first one, nitrogen efficiency was evaluated with no pH adjustment of the manure. In the second set of experiments, the effect of NH_3 concentration was evaluated by using three different manure strengths with pH adjustment of the manure. Adjustment consisted in increasing the manure pH using sodium hydroxide (5 N), which was added as needed to endpoint pH 8.5–9.0 whenever the pH of the manure decreased below 7.7. Swine manure samples from the wastewater vessels and acidic solution samples from the concentrator tank were withdrawn daily in order to monitor pH, alkalinity and NH_4^+ . In addition, initial and final samples of swine manure were analysed for pH, alkalinity, total solids (TS), volatile solids (VS), total chemical oxygen demand (COD_T), NH_4^+ , total Kjeldahl nitrogen (TKN), nitrite (NO_2^-), nitrate (NO_3^-), and total phosphorous (Pt) determination. All experiments were done at constant temperature of 25 °C in duplicate and results are expressed as means.

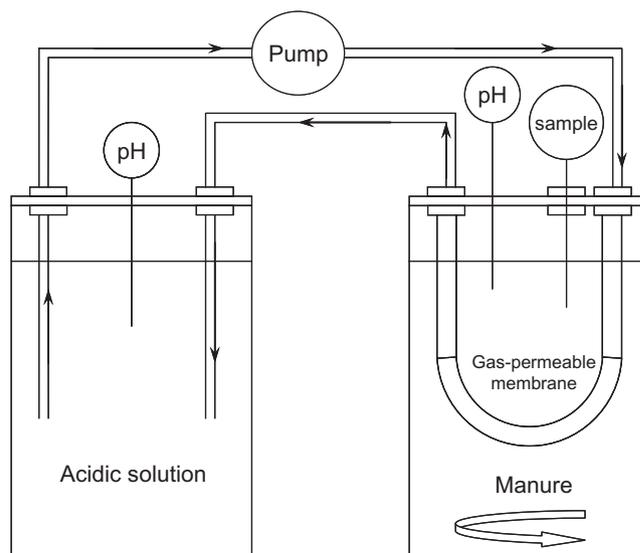


Fig. 2. Experimental device for ammonia capture from manure using gas-permeable membranes.

Table 1
Chemical characteristics of manure at the beginning and at the end of each batch experiment.

	Experiment 1		Experiment 2					
	No pH adjustment		Low strength		Medium strength		High strength	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
pH	7.50 (0)	8.20 (0.30)	8.60 (0)	8.10 (0.15)	7.60 (0)	8.00 (0.01)	7.50 (0)	7.70 (0.10)
CODt (mg/L)	6880 (260)	2630 (420)	4520 (70)	1290 (720)	24,580 (710)	19,870 (3150)	34,080 (1400)	30,480 (1130)
TS (g/L)	8.60 (0.01)	5.80 (0.20)	4.90 (0.10)	1.05 (0.50)	17.4 (0.50)	19.0 (0.40)	24.9 (5.60)	28.0 (1.30)
VS (g/L)	5.10 (0.01)	2.20 (0.40)	2.60 (0.30)	0.80 (0.40)	10.3 (0.20)	9.30 (0.40)	20.1 (1.30)	22.1 (3.30)
Pt (mg/L)	210 (4)	140 (10)	170 (6)	76.0 (20)	500 (30)	350 (20)	1290 (30)	870 (20)
TKN (mg/L)	1890 (140)	180 (10)	1340 (70)	400 (170)	2740 (120)	1010 (230)	3700 (140)	1430 (340)
NH ₄ ⁺ (mg/L)	1280 (0)	0 (0)	1070 (20)	60 (90)	1680 (30)	170 (60)	2290 (90)	270 (40)
NO ₃ ⁻ + NO ₂ ⁻ (mg/L)	0	1.60 (0.10)	0	2.10 (0.20)	0	1.50 (0.40)	0	3.50 (0.60)
Alkalinity (mgCaCO ₃ /L)	5740 (0)	1470 (150)	4580 (0)	2410 (110)	7080 (0)	5460 (270)	8540 (0)	7420 (590)

The standard deviation of duplicate experiments are shown in parenthesis.

2.2. Origin of the swine manure

In the present work four different manure samples were used to carry out two sets of experiments (Table 1). For the first set of experiments, manure was collected from the storage tank of a pig farm located in Cuellar (Segovia, Spain). In the second set of experiments, three different swine manure strengths were used according to their TS concentration (Garcia et al., 2009): low (0.4–0.8%), medium (0.8–1.7%) and high (1.7–3.2%). All of them were from the same farm located in Narros de Cuellar (Segovia, Spain). The low-strength manure was collected under the pit of a piglet house; the medium-strength manure was collected under the pit of a fattening pig house, and the high-strength manure was collected under the pit of a farrowing sow's house. Chemical characteristics of each type of manure used in the present work are shown in Table 1. Ammonia concentrations were: 1070 ± 20 mg/L for the low strength manure, 1680 ± 30 mg/L for medium and 2290 ± 90 mg/L for high. Each type of manure was collected in plastic containers, transported in coolers to the laboratory and subsequently stored at 4 °C for further use. Prior experimentation, each type of swine manure was individually homogenized by mechanical agitation.

2.3. Analytical methods

Analyses of TS, VS, CODt, TKN and TP were performed in duplicate in accordance with APHA Standard Methods (1989). pH and total alkalinity were monitored using a pH meter Crison Basic 20 (Crison Instruments S.A., Barcelona, Spain); total alkalinity was obtained by measuring the amount of sulphuric acid needed to bring the sample to a pH of 4.5. NO₃⁻ and NO₂⁻ were analysed by ion-exchange chromatography (Agilent Technologies). NH₄⁺ concentrations were determined using a NH₃ gas-sensing electrode Orion 900/200 (Thermo Electron Corporation, Beverly, USA) after adjusting sample to pH > 11. Free NH₃ (FA) was quantified theoretically according to Eq. (1), where NH₃ was the FA content and TNH₃ was the total NH₄⁺ (measured in the NH₄⁺ determination described above) (Hansen et al., 1998):

$$[\text{NH}_3]/[\text{TNH}_3] = 1 + \left(\frac{10^{-\text{pH}}}{10^{-(0.09018+2729.92/T)}} \right)^{-1} \quad (1)$$

3. Results and discussion

3.1. Removal of NH₃ by the gas-permeable membrane system with no pH adjustment

In the first set of experiments, using the membrane manifold with no manure pH adjustment, the NH₄⁺ concentration in manure

decreased from 1280 ± 0 mg/L to zero in the 44 days of the experiment (Fig. 3A). However, only 55% of the NH₄⁺ lost from the manure during that period was recovered in the acidic solution (Table 2). Ammonia capture by the membrane continuously increasing until day 20, from which point little or no more NH₃ was recovered in the acidic solution, although the NH₄⁺ in manure continued diminishing at a steady rate until the end of the experiment (Fig. 3A). It is important to emphasize that the acidic solution was the same during the entire experiment, thus the recirculation of this liquid in a closed loop between the treatment vessel and the acid tank achieved an NH₄⁺ concentration in the recovery solution (3020 ± 250 mg/L) of almost three times higher than in the manure (1280 mg/L; Fig. 3A).

As shown in Table 2, two distinct results were found during the experiment 1 using the membrane system without pH correction. Most of the NH₃ recovery occurred during the first 20 days of the experimental period, with an average recovery rate of 64 mg/L/day and a high NH₄⁺ recovery efficiency of 92% (Table 2). Up to this point, the membrane system without pH correction removed 57% of the initial NH₄⁺. This is consistent with removals of about 50% NH₄⁺ previously obtained by Vanotti and Szogi (2011b) using gas-permeable membrane system without pH adjustment of the manure.

However, additional treatment time in our study did not improve process performance. Mass balances for the following period (20–44 days) show that the recovery was inhibited and that most of the NH₄⁺ removed was lost, probably through volatilization. Nitrification was not occurring as indicated by the low concentration of nitrate (<2 mg/L) in the final effluent (Table 1). The average recovery rate during the second part of the batch was 37 mg/L/day and the corresponding NH₄⁺ recovery efficiency was 14%. The inability of membrane to recover N from day 20 to the end of the experiment can be explained by the NH₃ content in manure. Using the Eq. (1), the average free NH₃ in manure until the 21-day of evaluation was 40 mg/L, however from that day until the end of the experiment average FA in manure decreased to 12 mg/L. This means that the NH₃ concentration in manure was very low and it was unable to permeate through the membrane. Based on these results, it is recommended that the treatment time of the membrane system should be adjusted to maximize N recovery efficiency, especially in the absence of pH control of the manure because FA concentration may drop to critically low levels.

3.2. Removal of NH₃ by the gas membrane system with pH adjustment: effect of manure strength

In the second set of experiments, three different manure strengths were used: low, medium and high. The pH of the manure was adjusted to 8.5–9 whenever the pH of the manure decreased below 7.7 using sodium hydroxide, the Eq. (2) defines the reaction:

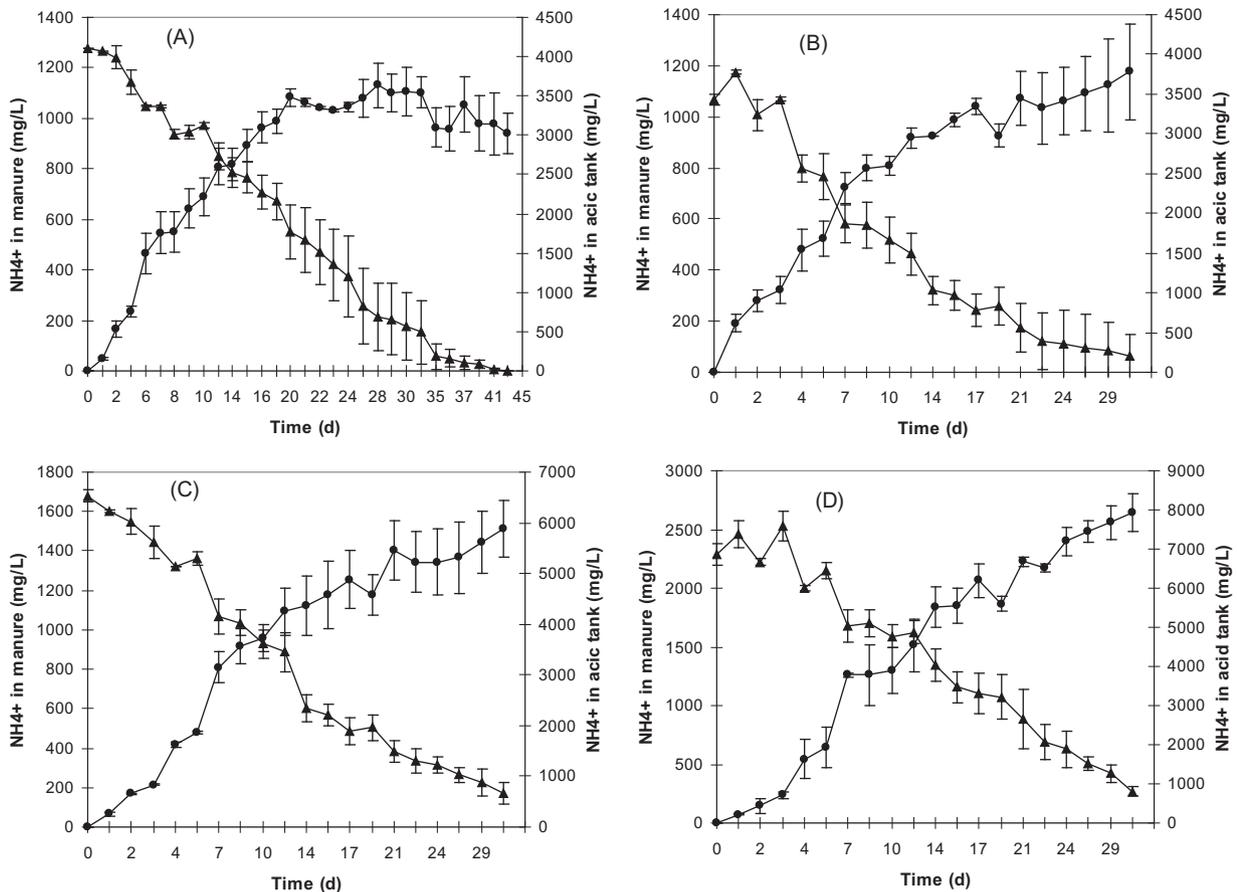


Fig. 3. Removal of ammonia in swine manure (\blacktriangle) by the gas membrane system and recovery and concentration in the acid tank (\bullet). (A) Non adjusted pH manure, (B) low-strength manure with pH adjusted, (C) medium-strength manure with pH adjusted and (D) high-strength manure with pH adjusted. The error bars are the standard deviation of duplicate experiments.



During the 30-day experiment, the NH_4^+ concentration in manure decreased from 1070, 1680 and 2290 mg/L to 60 ± 90 , 170 ± 60 and 270 ± 40 mg/L when using low, medium and high-strength manure, respectively (Table 1); achieving in all cases an NH_4^+ concentration in the recovery acidic solution 3.5 times higher than in manure (Fig. 3B–D). The total mass of NH_4^+ recovered in the acidic solution accounted for 1140 ± 180 , 1760 ± 170 and 2380 ± 150 mg in the low, medium and high-strength manure treatments, respectively (Table 3). Corresponding volatilization N losses were generally low: 13%, 10%, and 9%. More than 88% of NH_4^+ was removed from manure for the three manure strengths, and >87% of the NH_4^+ removed was recovered by the membrane manifold. Combined, the system recovered >80% of the NH_4^+ initially present in the manure.

With pH adjustment, the membrane system was not inhibited and recovered NH_3 from manure during the whole experimental period (30 days; Fig. 3). The NH_4^+ recovery was not linear; it followed a 2nd-order curve (Fig. 4), meaning that the NH_3 capture rate was higher during the first days and decreased as NH_4^+ was being depleted from the manure (Fig. 4). It was observed that when FA content in the manure was below 20 mg/L (Eq. (1)), NH_3 captured by the membrane diminished. This occurred after 15th-day of evaluation in the case of low-strength manure, and after 23rd-day of evaluation for high and medium-strength manure. In those cases, total NH_4^+ concentration in manure were below 500 mg/L.

Manure strength in terms of NH_4^+ considerably affected the recovery rate (Fig. 4 and Table 3). An increase in the NH_4^+ recovery was observed when increasing manure strength and NH_4^+ content in manure. Average NH_4^+ recovery rate was 74, 92 and 190 mg/L/day when using low, medium and high-strength manure, respectively (Table 3). It is worth mentioning that when manure pH was adjusted to 9 (Fig. 5), more NH_3 was available in manure and more N was recovered in the acidic solution the same day of the pH increase, as it was evidenced by the increase of the removal rate that reached a maximum of 270, 300 and 530 mg/L/day for low, medium and high-strength manure (Table 3). Maximum recovery rates obtained were about 2.7–3.7 times higher than the average rates. In the experiment, we used a pH band criteria of 1.3 (i.e. alkali was applied to reach pH 9 when process pH decreased below 7.7). Thus, by decreasing the pH adjustment band to about <0.5 (pH 8.5–9) and making more frequent pH corrections, it may be possible to shorten treatment time and optimize further the recovery rate of the membrane system.

Collectively, our results showed that the limiting factor for high N recovery efficiency was the NH_3 concentration in manure and that both the manure strength and pH adjustment with alkali improved the availability of the NH_3 in manure and its capture by the membrane system. This fact was supported by the results obtained from adjusting manure pH to 9, which demonstrate that membrane manifold captured more NH_3 after pH adjustment. These findings were in agreement with those observed by Vanotti and Szogi (2011b). These authors studied the nitrogen recovery from synthetic wastewater, adjusting the pH at two

Table 2Mass balances of the recovery of nitrogen using gas-permeable membranes without pH adjustment^a.

Days in the batch ^b	Initial NH ₄ ⁺ in manure	Remained NH ₄ ⁺ in manure (mg)	NH ₄ ⁺ lost from manure ^c	NH ₄ ⁺ recovered in the acidic solution	NH ₄ ⁺ removal efficiency ^d (%)	NH ₄ ⁺ recovery efficiency ^e	Maximum NH ₄ ⁺ recovery rate ^f (mg/L/day)	Average NH ₄ ⁺ recovery rate
First part (0–20 days)	1660 (0)	720 (140)	940	870 (30)	57	92	120	63
Second part (20–44 days)	720 (140)	0 (0)	720	100 (70)	100	14	120	37
All (0–44 days)	1660 (0)	0 (0)	1660	910 (70)	100	55	120	49

^a 1.3 L of manure in a 2-L vessel, using 300 mL 1 N H₂SO₄ of acidic solution in the concentrator tank (recirculation rate = 5.8 L d⁻¹). The manure strength used was medium-low (Table 1, experiment 1).

^b Data are average and std. dev. of duplicate reactors during 44-day experiment. First row of data shows mass balances for the first 20 days of the batch when recovery was active. Second row shows mass balances for the following period (20–44 days) when the membrane recovery was inhibited and ammonia was lost in the air (Fig. 3A).

^c NH₄⁺ lost from manure = initial NH₄⁺ in manure – remained NH₄⁺ in manure.

^d NH₄⁺ removed = (NH₄⁺ lost from manure/initial NH₄⁺ in manure) × 100.

^e NH₄⁺ recovery = (NH₄⁺ recovered in the acidic solution/NH₄⁺ lost from manure) × 100.

^f Highest NH₄⁺ mass recovered in 1 day; 0.0323 m² of membrane surface area.

Table 3Mass balances of the recovery of nitrogen using gas-permeable membranes under various manure strengths and with pH adjustment^{a,b}.

Manure strength	Initial NH ₄ ⁺ in manure	Remained NH ₄ ⁺ in manure (mg)	NH ₄ ⁺ lost from manure ^c	NH ₄ ⁺ recovered in the acidic solution	NH ₄ ⁺ removal efficiency ^d (%)	NH ₄ ⁺ recovery efficiency ^e	Maximum NH ₄ ⁺ recovery rate ^f (mg/L/day)	Average NH ₄ ⁺ recovery rate
Low	1390 (28)	80 (110)	1300	1140 (180)	94	87	270	74
Medium	2180 (37)	220 (74)	1960	1760 (170)	90	90	300	92
High	2970 (120)	350 (50)	2620	2380 (150)	88	91	530	190

^a 1.3 L of manure in a 2-L vessel, using 300 mL 1 N H₂SO₄ of acidic solution in the concentrator tank (recirculation rate = 5.8 L d⁻¹). Manure pH adjustments with alkali shown in Fig. 5.

^b Data are average and std. dev. of duplicate reactors during 30-day experiment.

^c NH₄⁺ lost from manure = initial NH₄⁺ in manure – remained NH₄⁺ in manure.

^d NH₄⁺ removed = (NH₄⁺ lost from manure/initial NH₄⁺ in manure) × 100.

^e NH₄⁺ recovery = (NH₄⁺ recovered in the acidic solution/NH₄⁺ lost from manure) × 100.

^f Highest NH₄⁺ mass recovered in 1 day; 0.0323 m² of membrane surface area.

different values (8.3 and 10), and found that at equal N concentration in the wastewater the rate of N recovery increased 10 times at pH of 10. Moreover, Rothrock et al. (2013) found higher NH₃ concentrations with higher lime application rates to poultry waste

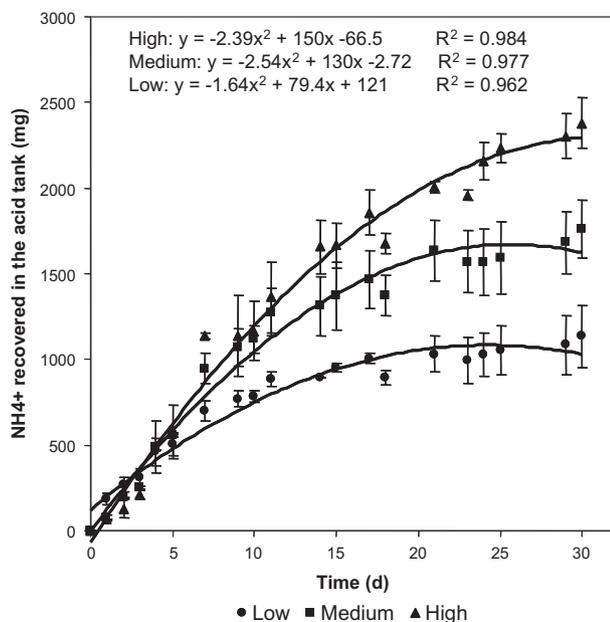


Fig. 4. Mass of ammonia recovered in the acid tank for low, medium and high manure strengths. A 2nd order equation and R^2 are represented. The error bars are the standard deviation of duplicate experiments.

when investigating enhanced NH₃ recovery from poultry litter using gas-permeable membranes.

The mechanism that explains these results is related to the acid-base reaction of NH₄⁺/NH₃. In basic aqueous solution like swine manure, NH₄⁺ ions are dissociated to form free NH₃ and H⁺ in a process dependent on pH and temperature. With the gas-permeable membrane system in place, as NH₃ permeates through the membrane the remaining H⁺ produces acidification of manure (Fig. 1). The more NH₃ permeates through the submerged membrane the more acidification of the manure occurs, until pH decreases and NH₃ formation stops. As a consequence, NH₃ removal from manure

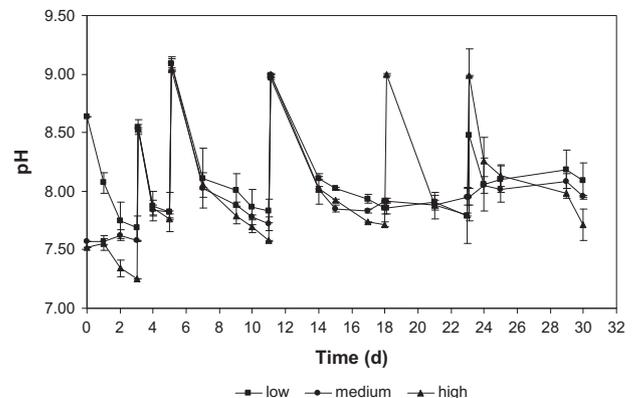


Fig. 5. Changes in pH of low, medium and high strength manures along the experimental period. The error bars are the standard deviation of duplicate experiments.

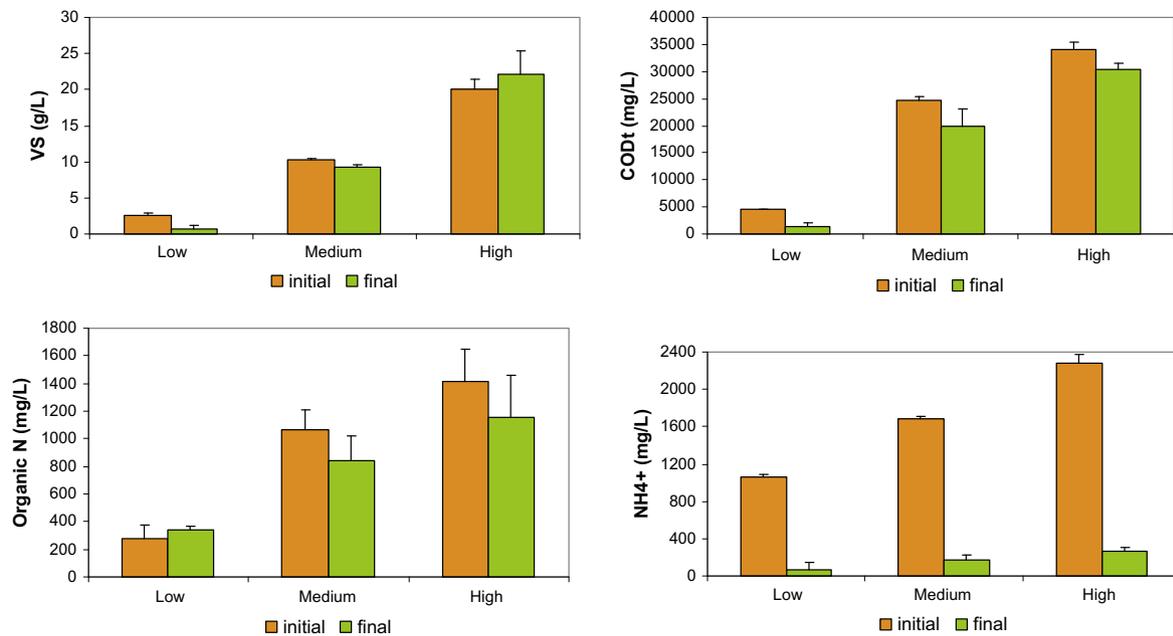


Fig. 6. Volatile solids (VS), chemical oxygen demand (COD_t), organic N and NH₄⁺ concentrations in initial (day 0) and final (day 30) samples of low, medium and high strength manures. The error bars are the standard deviation of duplicate experiments.

also stops. Data in Fig. 5 show that as NH₃ was removed from manure the pH of the manure decreased; moreover, the pH of the manure was continuously decreasing after the pH was adjusted to 9 indicating active N capture. The active capture process was extended by frequent pH adjustments (Figs. 3 and 5). For that reason, N recovery in manure with pH adjustment was higher compared with results of the first experiment without pH control.

Ammonia removal from manure through the membrane also consumed alkalinity to neutralize manure acidification. This could be clearly quantified in the experiment 1 with the non adjusted manure treatment (Table 1): alkalinity consumption was 4270 mg/L (75%), which means a ratio of alkalinity/NH₃ removed of 3.35. This value is close to the theoretical calculations that relate alkalinity consumption and NH₃ removed from manure, which implies that to remove 1 mg of NH₃ from manure 3.58 g of HCO₃⁻ are consumed.

Another important aspect to be studied is the behaviour of P when manure pH decrease, as organically bound P and insoluble inorganic phosphate complexes can release soluble-P when pH drops below 4.5 (Szogi and Vanotti, 2009), although in our study manure pH did not drop below 7.70.

3.3. Implications of the technology for energy generation through anaerobic digestion

An important characteristic of the recovery of NH₄⁺ using gas-permeable membranes is that soluble carbonaceous compounds such as glucose (BOD standard) or potassium hydrogen phthalate (COD standard) do not pass through the gas membrane (Vanotti and Szogi, 2011a,b). According to Fig. 6, VS, COD_t and organic N remained almost stable from the beginning to the end of the experiments in the manure vessel even though the soluble NH₃ was being removed effectively, which support the concept that soluble carbon does not pass through the membrane manifold.

Capturing of NH₃ without removing the energy-rich carbonaceous compounds from manure could be an advantage considering further treatment to extract energy from manure. In this sense, the gas-permeable technology can be used combined with anaerobic digestion. It is well known that high NH₃ content in pig manure

reduce biogas production by anaerobic digestion inhibition (Angelidaki and Ahring, 1993; Hansen et al., 1998), being one of the reasons to use different substrates to co-digest with manure (Molinuevo-Salces et al., 2012; Riaño et al., 2011). Hence, if a large quantity of NH₃ is removed from manure, inhibition caused by this compound will be minimized, improving anaerobic digestion and thus methane production. Moreover, final manure pH is maintained around 7.7–8.0 (Table 1), which is convenient for anaerobic digestion or to incorporate in arable soil. As a result, the use of gas-permeable membranes to capture NH₃ from manure could be used to improve anaerobic digestion process and methane production.

Results of this laboratory study show that the gas-permeable membrane system was effective to recover NH₃ from a variety of real, concentrated liquid manures that received no pre-treatment such as clarification or solid–liquid separation. Further on-farm pilot studies in real life field conditions would be necessary to test the applicability of the technology during cold and warm weather conditions, its response to manure variability during growing cycles, and the ability of farmers to manage it.

4. Conclusions

Ammonia was successfully recovered from liquid swine manure using gas-permeable membranes. With no pH adjustment, NH₄⁺ was captured by the membranes reaching 57% removal with 92% recovery. When pH of manure was adjusted to 9, NH₄⁺ removal efficiencies considerably increased to 88–94%. Results showed that NH₄⁺ recovery rates raised as manure strength increased, and also as pH increased, thus the limiting factor for high N recovery was FA concentration in manure. Volatile solids did not pass through the membrane and remained stable; as a consequence, the treated manure with the NH₄⁺ removed could be used with other treatment technologies to obtain energy.

Acknowledgments

This work has been funded by the INIA/FEDER under the project CC09-072. Cooperation with USDA-ARS Project 6657-13630-001-00D “Innovative Animal Manure Treatment Technologies for

Enhanced Environmental Quality” is grateful 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 U.S. Department of Agriculture.

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