

Effective surface area of a gas permeable membrane system in removing and retention of ammonia from dairy manure

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ABSTRACT

Excess ammonia (NH₃) emitted from animal feeding operations (AFOs) are considered a source of odor and some environmental pollution. Gas-permeable membranes (GPMs) provide a new solution for reducing NH₃ concentration in total ammoniacal nitrogen sources and recovering it in an acidic solution which results in decreasing NH₃ emissions to the environment. This study assessed the efficacy of NH₃ capture from liquid dairy manure (LM), NH₃ mass flux and its mass transfer coefficient (K_m) for diffusion into a tubular GPM. Three bench-scale test rigs were fabricated to vary surface areas of LM in closed chambers. A sulfuric acid solution was circulated through the GPM system, submerged in all LM chambers and also in the headspace of one of the chambers, above the LM. The experiment with nearly 3:1 LM to GPM surface area ratio had the greatest K_m and recovered the most concentrated ammonium sulfate in the acidic solution. For the same experiment, one cm² of GPM extracted nearly 50% of NH₃ in 18 d from 3 cm² surface area of LM.

Keywords: Ammonia mitigation; Ammonium; Ammonium sulphate; Gas-permeable membrane; Gas diffusion; Liquid manure; Mass transfer coefficient

1. Introduction

Ammonia (NH₃) emissions to the atmosphere have been increasing in the regions with concentrated animal feeding operations [1]. Excess NH₃ emitted from animal feeding operations (AFOs) are reported as one of the sources of odor and environmental pollution [2,3]. The emitted NH₃ may contribute to formation of fine particulate matter in the presence of certain acidic compounds in the atmosphere [4]. Ammonia deposition causes eutrophication of water bodies and contamination of groundwater. Ammonia also contributes to the formation of nitrous oxide, a potent greenhouse gas [4–6]. Excessive emissions of NH₃ from AFOs also result in the loss of a valuable plant nutrient [7]. Hence, reducing emission of NH₃ from animal manure and capturing it is beneficial to the environment. Additionally, the captured

NH₃ may be used as fertilizer to potentially offset the cost of commercial fertilizer on the farm.

Ammonia and ammonium (NH₄⁺) are the total ammoniacal nitrogen species (TAN) present in liquid manure and other organic waste effluents. A balance or equilibrium exists between NH₃ and NH₄⁺ depending on the pH and temperature of the liquid [3,8]. The effect of temperature on the equilibrium is negligible for laboratory experiments; however, the pH causes a great difference on NH₃/NH₄⁺ equilibrium. At pH greater than 6.8 in regular lab temperature, NH₄⁺ in solution dissociates partly and converts to NH₃ gas. The concentration of NH₄⁺ will decrease to zero if the pH exceeds 12 [9].

Several technologies and approaches have been reported in the literature for capture and/or recovery of NH₃ such as using acidic solution-sprayed scrubbers, bio-filters, chemicals such as acidified clays or sodium bisulfate (NaHSO₄) and gas-permeable membranes (GPM). Application of each method depends on the source of NH₃ emission, contami-

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nation level, environmental conditions and type of manure handling and storage systems [10–14].

Various techniques have been used based on the main concept of NH_3 capturing by the GPM system. Imai et al. [15], Blet et al. [16], Rothrock et al. [17] and Mukhtar et al. [18] used an acid-filled GPM to extract and recover NH_3 gas from either an aqueous buffer NH_3 solution or manure [19,20]. Alternatively, Semmens et al. [21] demonstrated the extraction and recovery of NH_3 gas from a TAN solution-filled membrane in an acidic solution surrounding the membrane. Although these membranes were introduced in the early 1970s [15,22], their novel application in the area of gaseous pollutants was developed recently to remove NH_3 from poultry litter and liquid manure [17,18].

Based on the literature, the mitigation process starts when NH_3 gas molecules around the acid-filled tubular GPM surface diffuse through the membrane pores (Fig. 1). The gradient of NH_3 concentration between the source and the acidic solution is the primary reason for NH_3 diffusion through the membrane pores. Then, acid flowing inside the tube traps and captures NH_3 molecules that enter it.

Eq. (1) shows the reactions that cause NH_3 to be released by its source and forms free NH_3 (FA). NH_3 dissociation and equilibrium equations presented in Fig. 1 and Eq. (1) can be used in LM as it was discussed for the pure synthetic solutions. Although different ions may affect the interactions, temperature and pH are the most effective parameters on NH_3 dissociation and volatilization even in a mixed solution. In fact, the overall effect of pH is dominant among all effective parameters and so the references applied those equations into different types of liquid manure or NH_3 mixed solution regarding the effect of pH [4,19,21,23].

The FA consists of NH_3 in the aqueous phase and NH_3 in the gaseous phase. The FA in ppm is calculated from Eq. 2 using TAN concentration [TAN], pH and temperature (T) in $^\circ\text{C}$ [11,24].



$$\text{FA} = \frac{17}{14} * \frac{[\text{TAN}] * 10^{\text{pH}}}{e^{\frac{6,344}{273+T}} + 10^{\text{pH}}} \quad (2)$$

NH_3 and NH_3 are both in an equilibrium in a solution [23] depending upon their concentrations and environmental conditions, especially the temperature (Eq. (3)).



In Eq. (3), Henry's Law constant (H) influences the presence of ammonia either as NH_3 or NH_3 and is the ratio of NH_3 and NH_3 [25,26]. The higher the H value results in the greater ammonia in the form of NH_3 . Elzing and Monteny [27] determined H using the relationship in Eq. (4) developed by Hashimoto and Ludington [28]. The H is non-dimensional and depends on temperature (T $^\circ\text{K}$).

$$H = 1384 * 1.053^{(293-T)} \quad (4)$$

The amount of NH_3 capture in acidic solution using a GPM system depends upon the NH_3 diffusion and permeation through the membrane. Based on the Fick's Law of diffusion, the concentration gradient between recipient media (acidic solution with no initial TAN) and TAN source (LM), across the membrane, is the driving force of NH_3 diffusion into the membrane [29]. In fact, NH_3 in the TAN source is the cause of NH_3 gas partial pressure gradient developed between the TAN source and the recipient solution inside a tubular membrane [30,31]. By measuring NH_3 concentrations in the TAN source and the recipient solution, Eq. 5 can be used to calculate NH_3 flux.

$$J = K_m (C_1 - C_2) \quad (5)$$

Where J is NH_3 mass flux ($\text{g m}^{-2} \text{d}^{-1}$), C_1 and C_2 are NH_3 concentrations (g m^{-3} or mg L^{-1}) in the TAN source and in

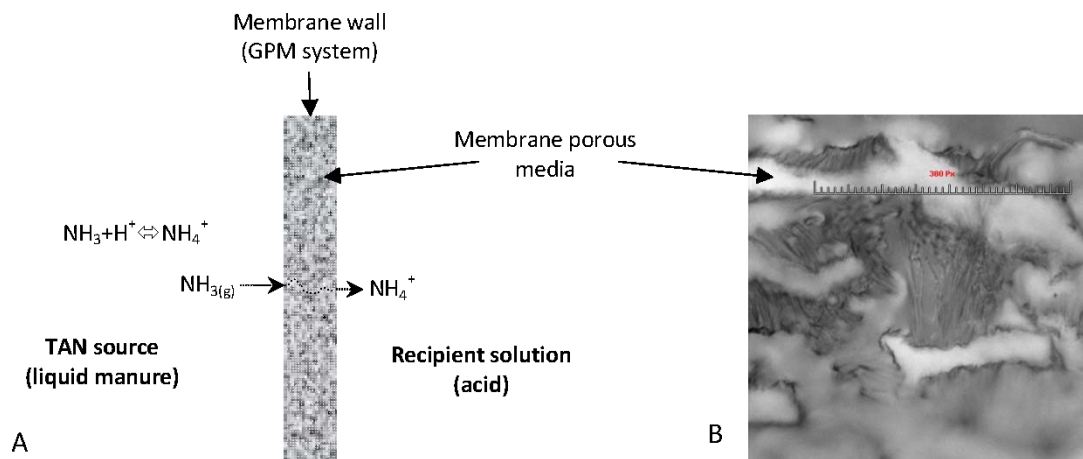


Fig. 1. (A) Schematic NH_3 diffusion through a membrane wall, (B) 1000X electronic microscopic photo of a membrane.

the recipient solution, respectively, and K_m is the mass transfer coefficient ($m\ d^{-1}$) [32,33]. When captured in an acidic solution such as sulfuric acid (H_2SO_4), NH_3 reacts with the acid and forms the ammonium ion (Eq. 6), in this case ammonium sulfate $[(NH_4)_2SO_4]$, a useful by-product and fertilizer [34,35].



While GPM techniques were used in the past to extract NH_3 from different sources including poultry litter and synthetic TAN [17,36], this study focused on LM with higher fiber content and so the potential of greater membrane sealing than swine and poultry manure [37]. It was expected that due to these concerns, micro pores of membrane walls in contact with LM could clog thereby reducing its diffusion efficiency. Additionally, this study was conducted to determine the optimum ratio of surface areas between the LM and the membrane for maximum removal and recovery of NH_3 from LM and from the headspace. The goal of this lab-scale study was to compare the results of extracting

NH_3 from LM H_2SO_4 filled GPM systems when LM surface areas in the chambers were changed. The K_m values of NH_3 diffusion were also determined from these experiments to measure NH_3 flux rates from different LM surface areas.

2. Materials and methods

The schematic diagram in Fig. 2 describes NH_3 extraction process from LM by pumping H_2SO_4 solution with a peristaltic pump into the GPM system. This method of NH_3 extraction was tested in laboratory experiments to investigate the influence of different parameters on the efficacy of the process. These parameters included pH and NH_3 concentration of acidic solution, pH and NH_3 concentration of LM, volumes of acidic solution and liquid manure, surface areas of GPM and LM in the chamber. Three chamber sizes (one size per experiment) labelled 1X, 2X and 4X (Fig. 3A) were used to vary the surface area of LM while the depth of LM was kept constant in all chambers. As shown in Table 1, the surface cross-sectional area of LM in chamber

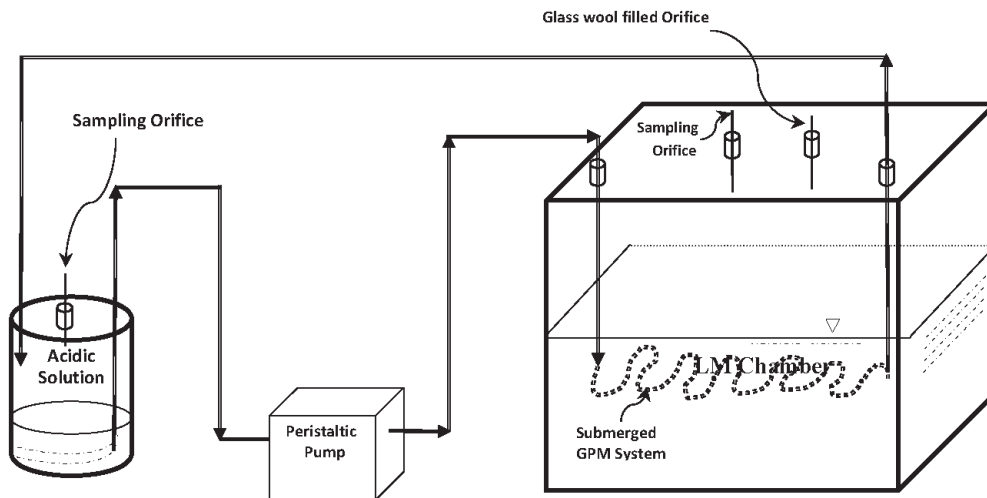


Fig. 2. Schematic diagram of NH_3 extraction process from LM using a GPM system.

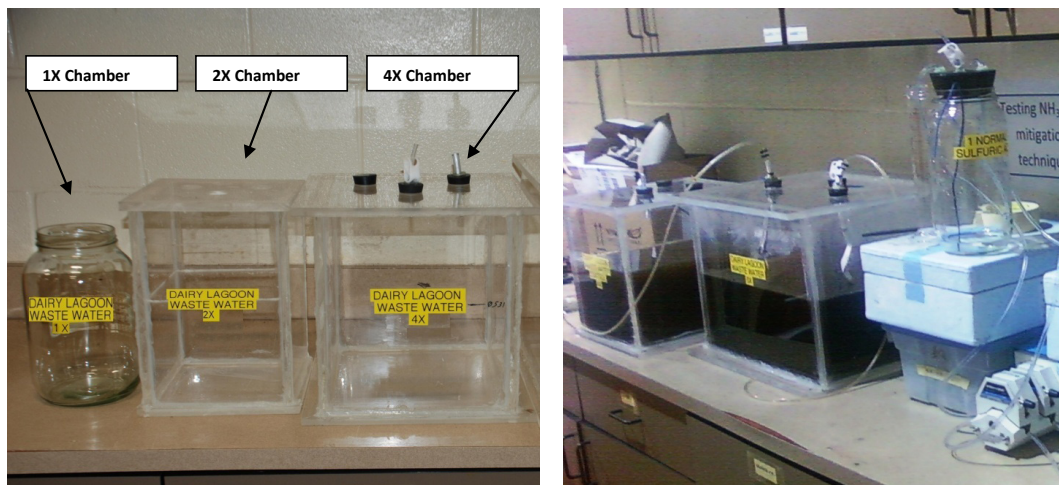


Fig. 3. (A) Chamber for four different sizes, (B) Experiment in progress.

Table 1
Properties of liquid manure chambers

Experiment (chamber label)	Chamber inside dimensions				Depth of LM in chamber (cm)	Liquid manure volume (L)	Headspace volume (L)
	Length (cm)	Width (cm)	Height (cm)	Surface area (cm ²)			
1X	–	7.7 ^a	23	186	16.2	3	1.3
2 X	19.1	19.1	29	365	16.2	5.9	4.7
4 X	29.2	25.4	29	742	16.2	12	9.5

^aThis entry is radius (cm) of the 1X cylindrical jar

1X was equal to 184 cm² and LM surface areas in chambers, 2X and 4X were two and four times greater than the surface area of LM in chamber 1X, respectively. Additionally, one 4X chamber filled with the LM from the same manure source was added as a control (not treated with the GPM system) for NH₃ extraction experiments with the 4X chamber. All chambers were fabricated using Plexiglas, except 1X Chamber, which was a glass jar.

On the top of each chamber lid, holes were drilled for H₂SO₄ inflow and outflow ports, one for a small tube filled with glass wool to equilibrate air pressure of the headspace inside the chamber with atmospheric pressure, and one for sampling LM for NH₃ during an experiment (Fig. 2).

The GPM tube used in this study was an expanded polytetrafluoroethylene (ePTFE) membrane (Phillips Scientific Inc., Rock Hill, South Carolina). This material was used because it is microporous, flexible and hydrophobic. Also, one of the main advantages of the ePTFE is its high permeability rate for gas flow with low pressure differentials between the inside and outside of the ePTFE tube. The pore size of the tube allows it to remove the gaseous molecules and volatile contaminants from the liquid [16,21]. The specifications of the ePTFE membrane used in this study are reported in Table 2.

The length of GPM tube was kept constant at 107 cm for all experiments and it was installed nearly 2 cm below the surface of LM in all chambers. The shallow placement of the GPM tube was due to the likelihood of greater NH₃ accumulation near the surface of the LM [4,23].

Raw LM was collected from the secondary cell of a treating manure lagoon, flushed from alleys in a free-stall dairy barn, located in east central Texas. The raw manure was transported to the laboratory by using covered five-gallon buckets and was used fresh for 2X and 4X experiments but stored, frozen, and then thawed for using in 1X experiments.

Real time TAN concentrations in the LM and the acidic solution were measured using ion selective electrode (ISE) ammonia electrode (Hach ammonia electrode, Model 51297-00, Hach Company, Loveland, CL, USA) which measures the TAN of a sample and converts and reports it as NH₃-N concentration in mg L⁻¹ or ppm. The

electrode was capable of measuring NH₃-N between 0 to 14,000 mg L⁻¹ with ±5% accuracy. Later, the measured NH₃-N data by ammonia electrode was verified with a spectrophotometric NH₄-N measurement method [38], by analyzing the same LM or acidic solution sample that was saved for this purpose. The pH of LM and acidic solution was measured with a gel-filled pH electrode with an accuracy of ±0.05 pH units (IntelliCAL PHC101 Standard Gel Filled pH Electrode, Hach Company, Loveland, CL, USA). In addition to the initial measurements, TAN concentration and pH of LM and acidic solution were measured twice a week, during each experiment. For all measurements using the ISE electrode, the temperatures of the samples were also measured. Both NH₃ and pH electrodes were installed on a Hach HQ440d Benchtop Meter fabricated with a built-in thermometer. Samples from the LM chambers and acidic solution jars were taken in triplicates. The openings of all sampling ports were pinched shut while not in use.

2.1. Ammonia extraction process from the LM in 1X and 2X chambers

The main concept of NH₃ removal was used in 1X and 2X chamber (Table 1) by circulating concentrated H₂SO₄ in the GPM system based on the acid volume and flow rate mentioned in Table 3. The table also shows the ratio of the volumes of LM and acidic solution. The volumetric ratio of 6 was applied based on the literature (Rothrock et al., 2010; Vanotti et al., 2010). The changes of NH₃ concentrations and pH values of the acidic solution and the LM in the chambers were measured and recorded. The K_m values for both 1X and 2X chambers were calculated and the results of 1X and 2X experiments were compared based on the same flow rates applied to both experiments.

2.2. Ammonia extraction process from the LM in 4X chamber

The surface area of the LM in the 4X chamber was doubled (742 cm²), with respect to 2X experiments, in order to investigate the performance of the GPM system in broader

Table 2
Gas-permeable membrane specifications

Type of membrane	Inside diameter, ID (cm)	Outside diameter, OD (cm)	Flat width (cm)	Wall thickness (cm)	Porosity (%)	Mean pore diameter (µm)	Bubble pressure (kPa)
ePTFE	0.672	0.80	1.25	0.066	83	2.4 ± 0.14	9.4 ± 0.94

Table 3
Initial volume of LM, and volume and flow rate of sulfuric acid in the experiments

Experiment	Initial volume of LM (L)	Acidic solution		Ratio of liquid manure to GPM surface areas
		Initial volume (L)	Flow rate (L d ⁻¹)	
1 X	3	0.5	1.9	0.68
2 X	5.9	1	1.9	1.36

emission surface of NH₃. So, the ratio of LM to GPM surface area was 2.76. In addition, the flow rate of the circulating acid in 4X was increased (9.2 L⁻¹) and the volume of acidic solution was decreased to 190 mL in order to produce more concentrated by-product [(NH₄)₂SO₄] than what were generated in the 1X and 2X experiments. Thus, the ratio between the initial volumes of the LM and acidic solution were assigned 64. Likewise, the K_m and J values for 4X chambers were calculated using Eqns. (2), (4) and (5).

2.3. Calculation of NH_{3(g)} concentrations and K_m

The practical measurement of J and the NH_{3(g)} concentration using Eqns. (2) and (4) will be used to calculate K_m values using Eq. (5) for each experiment. Once the K_m value of a membrane is known, mass flux of NH_{3(g)} diffusion through this membrane can be predicted.

Eq. (2) was used to calculate free ammonia (FA) concentration of LM, in each experiment, based on average TAN concentrations, temperature and pH of LM at the same time intervals used to calculate NH₃ flux. The values of H and J were calculated using Eqns. 4 and 5. Eq. 7 was derived and used to calculate gaseous ammonia (NH_{3(g)}).

$$C_{NH_{3(g)}} = \frac{FA}{(1+H)} \quad (7)$$

One-sample Student's t -tests ($p < 0.05$) were used to determine if the average of the calculated K_m in experiments were significantly different.

3. Results and discussion

The pH and NH₃ concentrations changed in all experiments because of the GPM treatment system. Experiments with all chambers demonstrated that the GPM system successfully extracted LM NH₃ by diffusion through the permeable membrane. The system extracted nearly 50% of the TAN of the corresponding LM from 1X, 2X, and 4X chambers as compared to their initial concentration (measured on day zero) in less than 20 days.

3.1. Results of NH₃ extraction process from 1X and 2X chambers

Results of NH₃ extraction in 1X and 2X are presented in Fig. 4. All NH₃ concentration and pH data in this figure

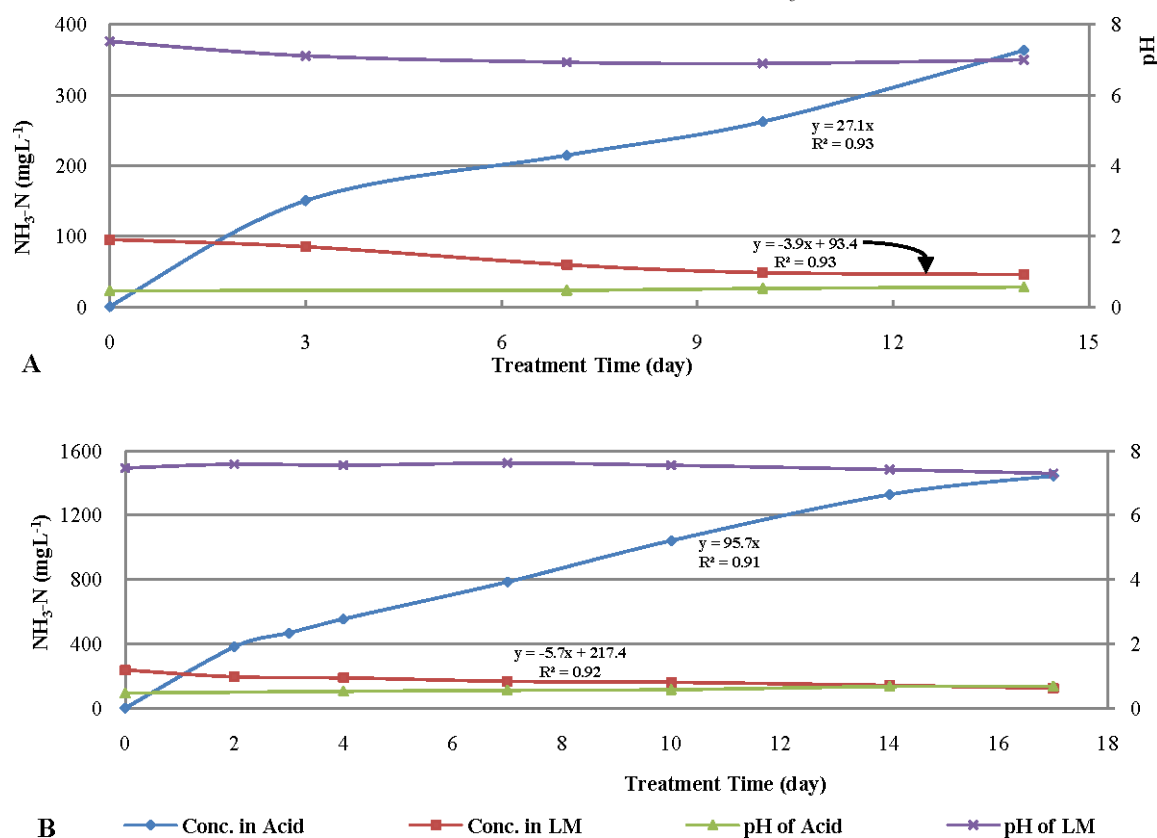


Fig. 4. Ammonia and pH in acidic solution and LM in (A) 1X, (B) 2X.

are the mean values of duplicate samples with the standard deviation values of 5 mg L^{-1} or less for NH_3 concentrations, and 0.04 or less for pH.

The pH of the treated LM decreased a little in chambers and increased slightly in the acidic solution during all experiments. The concentrated acid, with initial pH 0.36 and the large volume of LM in the chambers were the reasons for those small changes in the pH of acidic solution and LM, respectively. At the same time, the NH_3 concentration reduced in LM and increased in the acidic solution, respectively. However, these changes in the chambers were smaller than the changes in the corresponding acidic solution jars due to much larger LM volumes than acidic solution volumes. All changes in the LM chambers and acidic solution jars occurred simultaneously due to the loss and gain of NH_3 in chambers and their corresponding jars, respectively (Eqns. (1) and (2)). In spite of different initial values of the NH_3 concentration in chambers (initial concentrations ranged from 96 mg L^{-1} to 238 mg L^{-1}), the experiments trended similarly in terms of NH_3 loss and gain in chambers and jars, respectively.

As shown in Fig. 4, the concentration of NH_3 in acidic solution increased overtime. High coefficients of determination ($R^2 > 0.91$) for experiments indicated that the daily NH_3 extracted (gained) from LM using the GPM system was linearly correlated to the duration (time) of treatment. Likewise, in the treated LM chambers, R^2 value of the linear regression was 0.88 and higher, indicating a linear behav-

ior of daily NH_3 loss with time due to its extraction by the GPM system.

3.2. Results of NH_3 extraction process from 4X chamber

Over an 18-d study period, negligible changes occurred in the temperature, pH and NH_3 concentrations of the LM in the control chamber. Results of NH_3 extraction in 4X is presented in Fig. 5. All NH_3 concentration and pH data in this figure are the mean values of triplicate samples with the standard deviation values of 5 mg L^{-1} or less for NH_3 concentrations and 0.04 or less for pH. As shown in Fig. 5, the concentration of NH_3 in acidic solution increased and great coefficients of determination ($R^2 = 0.90$) a linearly correlated behavior of NH_3 extraction and recovery.

3.3. Ammonia gas ($\text{NH}_{3(g)}$) diffusion into tubular GPM system

The mass of NH_3 in acidic solution at each experiment was calculated using the data of measured TAN concentration (presented as $\text{NH}_3\text{-N}$ in Figs. 4 and 5) and volume of acidic solution in the jar. Thereafter, the NH_3 diffusion flux (J) of each experiment was computed by dividing the calculated mass with the tubular GPM surface area and the time duration of each experiment. Table 4 shows that the J values of experiments ranged from $0.26 \text{ g m}^{-2} \text{ d}^{-1}$ for the 1X experiment to $0.67 \text{ g m}^{-2} \text{ d}^{-1}$ for the 4X experiment. These flux values were

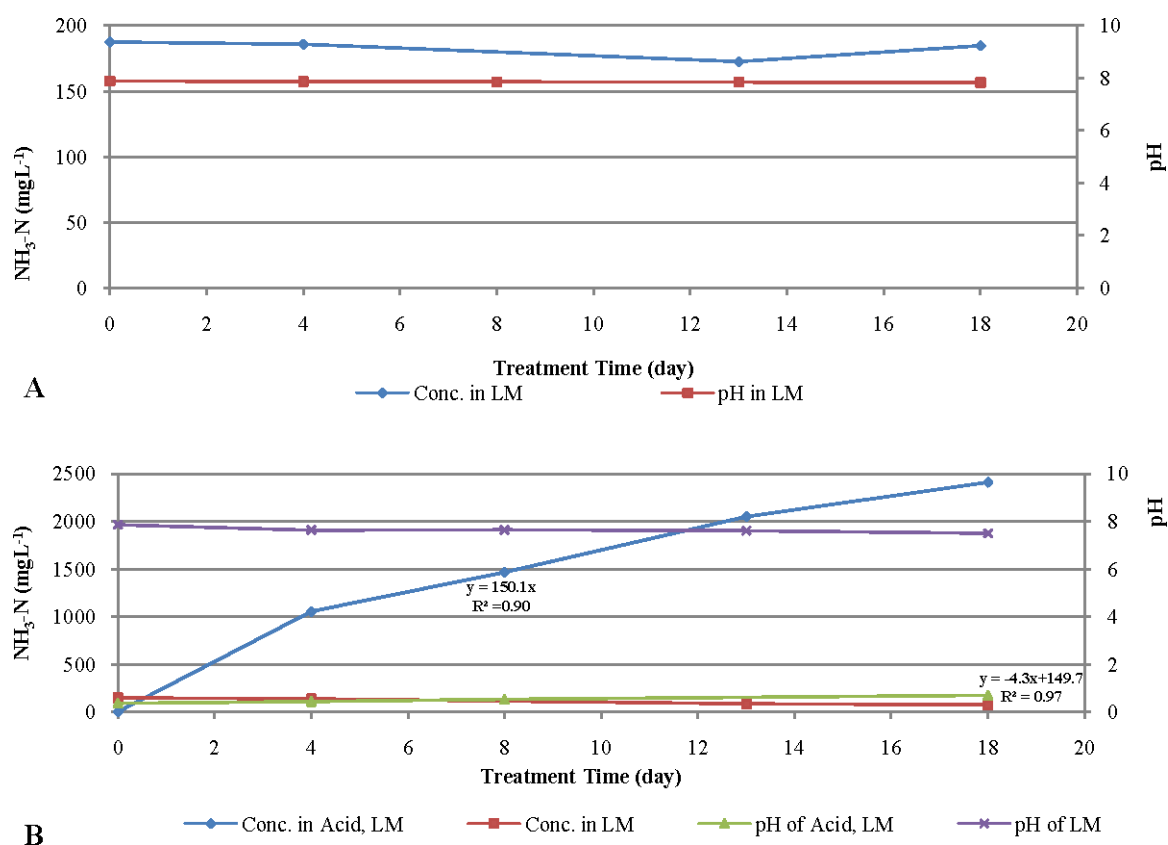


Fig. 5. Ammonia and pH in acidic solution and LM in (A) 4X control chamber and (B) 4X treatment chamber.

Table 4
Ammonia gas concentration in LM and its mass transfer coefficient and fluxes into GPM systems

Exp. #	J ($\text{g m}^{-2} \text{d}^{-1}$)	FA in LM (mg L^{-1} of $\text{NH}_3\text{-N}$)	H in LM	C_1 of $\text{NH}_{3(\text{g})}$ in LM (mg L^{-1})	C_2 of $\text{NH}_{3(\text{g})}$ in acid (mg L^{-1})	K_m (m s^{-1})
1X	0.26	0.60	1125.7	0.53	0	5.53E-6
2X	0.62	1.75	1125.7	1.56	0	4.58E-6
4X	0.67	1.53	1185.3	1.29	0	5.97E-6

directly proportional to $\text{NH}_{3(\text{g})}$ concentration gradient across the membrane and the corresponding K_m (Eq. (5)).

The FA concentrations of LM, in each experiment, were calculated (Table 4), based on the average TAN concentrations, temperatures and pH of LM at the same time intervals used to calculate NH_3 flux. Availability of FA in LM indicated greater dependence on pH and TAN concentration of LM than on its temperature. For example, a pH value of LM at 10 or higher would have increased FA concentration in LM as much as 80% of its corresponding TAN concentration. That increase in pH would also have increased the flux by nearly 80%. On the other hand, the calculated values of Henry's Law constant, H, were highly sensitive to temperature changes in LM.

The $\text{NH}_{3(\text{g})}$ concentrations were calculated using Eq. (7). In Table 4, C_1 values refers to the concentration of $\text{NH}_{3(\text{g})}$ in LM and C_2 values refer to the concentration $\text{NH}_{3(\text{g})}$ in the acidic solution. The C_2 values approached zero because all acidic solutions remained very low in pH (less than 1) through all experiments (Figs. 4 and 5).

The $\text{NH}_{3(\text{g})}$ flux and gradient concentration (C_1 – C_2) resulted in calculation of K_m for each experiment (Table 4). These values ranged from $4.58 \times 10^{-6} \text{ ms}^{-1}$ in 2X Experiment to $5.97 \times 10^{-6} \text{ ms}^{-1}$ in 4X Experiment (Table 4). The K_m values calculated for the ePTFE membrane used in this study were comparable to those measured for the PTFE membranes [21,30]. Moreover, the reported K_m coefficients by Ahn et al. [36] was $3.05 \times 10^{-6} \text{ ms}^{-1}$ for NH_3 diffusion into different types (morphology) of PTFE membranes used in ammonia diffusion from synthetic aqueous solutions.

The K_m values of the experiments were not correlated to the FA, H and C_1 of $\text{NH}_{3(\text{g})}$ which verified that K_m was independent of $\text{NH}_{3(\text{g})}$ concentration in the NH_3 source [21]. Also, the one-sample *t*-test statistical analysis showed that there was no significant difference among the K_m values of all experiments. Therefore, reusing the same GPM tube for several experiments and raw manure at different condition did not have significant affect on the K_m values. However, the 4X experiment resulted in the highest K_m coefficient while the FA value of 2X experiment was lower than the corresponding values in the 4X experiment. The greater LM surface area is providing more $\text{NH}_{3(\text{g})}$ to be captured by the GPM tube. However, the surface area cannot be extended unlimitedly since the molecules of $\text{NH}_{3(\text{g})}$ may exit the range of the GPM tube and so not get in contact with the GPM tube. This is suggesting a higher $\text{NH}_{3(\text{g})}$ flux than all other experiments if other initial parameters such as TAN concentration in the LM were the same.

4. Conclusions

The main objective of this research was to evaluate the efficacy of NH_3 extraction from dairy liquid manure (LM) and from the air in the headspace above the LM, using a gas-permeable (GPM) system. All experiments with different LM chamber surface areas showed that NH_3 gas was extracted from the LM by submerged as well as the suspended (headspace) tubular GPM system and captured it in acidic solution circulated into the system. The 4X experiment resulted in the most concentrated ammonium sulfate by-product in the acidic solution. There was no significant difference among calculated K_m coefficients of submerged GPM systems and they were not correlated to the TAN concentrations and FA concentrations.

It was estimated that one cm^2 surface area (0.4 cm of submerged length of tubing) of GPM used in the 4X experiment was needed to extract 50% of NH_3 in less than 20 days from 3 cm^2 surface area of liquid dairy manure with initial NH_3 concentrations similar to those used in these experiments.

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References

- [1] K.S. Bajwa, S.P. Arya, V.P. Aneja, Modeling studies of ammonia dispersion and dry deposition at some hog farms in North Carolina, *J. Air Waste Manage.*, 58 (2008) 1198–1207.
- [2] S. Mukhtar, A. Mutlu, S.C. Capareda, C.B. Parnell, Seasonal and spatial variations of ammonia emissions from an open-lot dairy operation, *J. Air Waste Manage.*, 58 (2008) 8.
- [3] J.Q. Ni, E.L. Cortus, A.J. Heber, Improving ammonia emission modeling and inventories by data mining and intelligent interpretation of the national air emission monitoring study database, *Atmosphere*, 2 (2011) 19.
- [4] A.H. Hristov, A. N., M. Hanigan, A. Cole, R. Todd, T.A. McAllister, P.M. Ndegwa, A. Rotz, Review: Ammonia emissions from dairy farms and beef feedlots, *Can. J. Anim. Sci.*, 91 (2011) 1–35.
- [5] M.E. Fenn, R. Haeuber, G.S. Tonnesen, J.S. Baron, S. Grossman-Clarke, D. Hope, D.A. Jaffe, S. Copeland, L. Geiser, H.M. Rueth, J.O. Sickman, Nitrogen emissions, deposition, and monitoring in the western United States, *BioScience*, 53 (2003) 391–403.

- [6] V.P. Aneja, J. Blunden, K. James, W.H. Schlesinger, R. Knighton, W. Gilliam, G. Jennings, D. Niyogi, S. Cole, Ammonia assessment from agriculture: US status and needs, *J. Environ. Qual.*, 37 (2008) 515–520.
- [7] S.L.P. Sakirkin, N.A. Cole, R.W. Todd, B.W. Auvermann, Ammonia emissions from cattle-feeding operations. Part 1 of 2: Issues and emissions., *Air Quality in Animal Agriculture*. Available at: <http://www.extension.org/sites/default/files/ammonia%20from%20cattle%20part%201%20FINAL.pdf>, 2011.
- [8] K. Emerson, R.C. Russo, R.E. Lund, R.V. Thurston, Aqueous ammonia equilibrium calculations: effect of pH and temperature, *J. Fish. Res. Board Can.*, 32 (1975) 4.
- [9] I. Metcalf & Eddy, *Wastewater engineering treatment and reuse*, McGraw- Hill, New York, 2003.
- [10] M.S. EL-Bourawi, R. Ma, M. Khayet, Z. Ding, Z. Li, X. Zhang, Application of vacuum membrane distillation for ammonia removal, *J. Membrane Sci.*, 301 (2007) 200–209.
- [11] A.A. Szogi, M.B. Vanotti, A.E. Stansbery, Reduction of ammonia emissions from treated anaerobic swine lagoons, *T. Asabe*, 49 (2006) 217–225.
- [12] J.L. Ullman, S. Mukhtar, R.E. Lacey, J.B. Carey, A review of literature concerning odors, ammonia, and dust from broiler production facilities: 4. remedial management practices, *J. Appl. Poult. Res.*, 17 (2004) 8.
- [13] R.W. Melse, N.W.M. Ogink, Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands, *T. Asae*, 48 (2005) 2303–2313.
- [14] A.M. Samani Majd, A. Kalbasi, G.L. Riskowski, S. Muhhtar, L.Y. Zhao, W. Fang, Electrolyzed water spray scrubber for removing ammonia from air, *T. Asabe*, Under review (2014).
- [15] M. Imai, S. Furusaki, T. Miyauchi, Separation of volatile materials by gas membranes, *Ind. Eng. Chem. Proc. Dd* 21, (1982) 421–426.
- [16] V. Blet, M.N. Pons, J.L. Greffe, Separation of ammonia with a gas-permeable tubular membrane, *Analytica Chimica Acta*, 219 (1989) 3.
- [17] M.J. Rothrock, A.A. Szogi, M.B. Vanotti, Recovery of ammonia from poultry litter using gas-permeable membranes, *T. Asabe*, 53 (2010) 1267–1275.
- [18] S. Mukhtar, A.M. Samani Majd, M.S. Borhan, J.F. Beseda II, An investigation of ammonia extraction from liquid manure using a gas-permeable membrane, *ASABE International Meeting*, Paper Number: 1111178 (2011).
- [19] A.M. Samani Majd, and S. Mukhtar, Ammonia diffusion and capture into a tubular gas-permeable membrane using diluted acids, *T. Asabe*, 56 (2013) 8.
- [20] A.M. Samani Majd, S. Mukhtar, Ammonia recovery enhancement using a tubular gas-permeable membrane system in laboratory and field-scale studies, *T. Asabe*, 56 (2013) 8.
- [21] M.J. Semmens, D.M. Foster, C.E. L., Ammonia removal from water using microporous hollow fibers, *J. Membrane Sci.*, 51 (1990) 14.
- [22] E.A. Santiagodelpin, T. Aviles, Experimental and Clinical Use of Polytetrafluoroethylene Vascular Grafts, *Am. J. Surg.*, 140 (1980) 315–319.
- [23] J.Q. Ni, Mechanistic models of ammonia release from liquid manure: a review, *J. Agr. Eng. Res.*, 72 (1999) 1–17.
- [24] A.C. Anthonisen, R.C. Loehr, T.B.S. Prakasam, E.G. Srinath, Inhibition of nitrification by ammonia and nitrous-acid, *J. Water Pollut. Con. F.*, 48 (1976) 835–852.
- [25] J.M. Hales, D.R. Drewes, Solubility of ammonia in water at low concentrations, *Atmos. Environ.*, 13 (1979) 1133–1147.
- [26] B. Rumburg, G.H. Mount, D. Yonge, B. Lamb, H. Westberg, M. Neger, J. Filipy, R. Kincaid, K. Johnson, Measurements and modeling of atmospheric flux of ammonia from an anaerobic dairy waste lagoon, *Atmos. Environ.*, 42 (2008) 3380–3393.
- [27] A. Elzing, G.J. Monteny, Modeling and experimental determination of ammonia emissions rates from a scale model dairy-cow house, *T. Asabe*, 40 (1997) 721–726.
- [28] A.G. Hashimoto, and D. Ludington, Ammonia desorption from concentrated chicken manure slurries, *International Symposium on Livestock Wastes* Ohio State University, 1971, pp. 117–121.
- [29] L.N. Moskvina, and T.G. Nikitina, Membrane methods of substance separation in analytical chemistry, *J. Anal. Chem.*, 59 (2004) 2–16.
- [30] M. Schneider, I.W. Marison, U. Vonstockar, Principles of an efficient new method for the removal of ammonia from animal-cell cultures using hydrophobic membranes, *Enzyme Microb. Tech.*, 16 (1994) 957–963.
- [31] K. Li, J.F. Kong, X.Y. Tan, Design of hollow fibre membrane modules for soluble gas removal, *Chem. Eng. Sci.*, 55 (2000) 5579–5588.
- [32] J.F. Kong, K. Li, An improved gas permeation method for characterising and predicting the performance of microporous asymmetric hollow fibre membranes used in gas absorption, *J. Membr. Sci.*, 182 (2001) 271–281.
- [33] H. Kreulen, C.A. Smolders, G.F. Versteeg, W.P.M. Vanswaaij, Microporous hollow-fiber membrane modules as gas-liquid contactors. 1. Physical mass-transfer processes, a specific application, mass-transfer in highly viscous-liquids, *J. Membr. Sci.*, 78 (1993) 197–216.
- [34] C.C. Boswell, D.K. Friesen, Elemental sulfur fertilizers and their use on crops and pastures, *Fertilizer Research* 35 (1993) 22.
- [35] S.H. Chien, M.M. Gearhart, V. S., Comparison of ammonium sulfate with other nitrogen and sulfur fertilizer in increasing crop production and minimizing environmental impact: A review, *Soil Sci.*, 176 (2011) 10.
- [36] Y.T. Ahn, Y.H. Hwang, H.S. Shin, Application of PTFE membrane for ammonia removal in a membrane contactor, *Water Sci. Technol.*, 63 (2011) 2944–2948.
- [37] D. Jones, R.K. Koelsch, S. Mukhtar, R. Sheffield, J.W. Worley, Closure of earthen manure structures (including basins, holding ponds and lagoons), *Biological Systems Engineering, DigitalCommons@University of Nebraska - Lincoln*. Available at: <http://digitalcommons.unl.edu/biosysengpres/4/>, Nebraska - Lincoln, 2006.
- [38] M.A.H. Franson, *Automated Phenate Method. Standard Methods for the Examination of Water and Wastewater*, 4500-NH₃H, American Public Health Association, Washington, D.C, 1989.