



Recovery of ammonia from swine manure using gas-permeable membranes: Effect of aeration



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ARTICLE INFO

Article history:

Received 4 November 2014

Received in revised form

7 January 2015

Accepted 10 January 2015

Available online 17 January 2015

Keywords:

Gas-permeable membranes

Ammonia recovery

Nutrient recovery

Swine manure

Aeration effect

ABSTRACT

The gas-permeable membrane process can recover ammonia from manure, reducing pollution whilst converting ammonia into an ammonium salt fertilizer. The process involves manure pH control to increase ammonium (NH_4^+) recovery rate that is normally carried out using an alkali. In this study a new strategy to avoid the use of alkali was tested applying low-rate aeration and nitrification inhibition. The wastewater used was raw swine manure with 2390 mg $\text{NH}_4^+\text{-N/L}$. Results showed that aeration increased pH above 8.5 allowing quick transformation of NH_4^+ into gaseous ammonia (NH_3) and efficient recovery by permeation through the submerged membrane. The overall NH_4^+ recovery obtained with aeration was 98% and ammonia emissions losses were less than 1.5%. The new approach can substitute large amounts of alkali chemicals needed to obtain high NH_4^+ recovery with important economic and environmental savings.

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1. Introduction

The agricultural sector remains the major source of NH_3 emissions. In Europe, despite total emissions of NH_3 falling by 26% between the years 1990 and 2011 in the 33 member countries of the European Environment Agency, agriculture contributed 96% of total emissions in 1990 and 94% in 2011 (EEA, 2014). These emissions are derived mostly from animal and poultry wastes. In the United States, the largest source of NH_3 emissions is also livestock agriculture; NH_3 emissions from animal husbandry operations (dairy, beef, poultry and swine) were estimated at 2.4 million tons/year in 2010 and 2.5 million tons/year in 2015 (EPA, 2014). Therefore, significant efforts are required in Europe and the U.S. to abate NH_3 emissions from livestock operations. In this context, new technologies to recover the NH_3 are needed.

Strategies for reducing or minimizing NH_3 losses from livestock production are focused on: 1) reduction of N excretion, 2) reduction of volatile N, 3) building designs and manure managements, 4) land application strategies, and 5) emissions capture and treatment (Ndegwa et al., 2008). Among emissions capture and treatment strategies, some technologies are focussed on the recovery of the N

for further re-use. These technologies include: 1) reverse osmosis using high pressure and hydrophilic membranes (Massé 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 struvites (Uludag-Demirer et al., 2005), and 5) a new process using gas-permeable membranes at low pressure (Vanotti and Szogi, 2011a, b).

The gas-permeable membrane process includes the passage of gaseous ammonia through a microporous, hydrophobic membrane, and capture and concentration in a stripping solution on the other side of the membrane. 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, b); 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, ammonia combines with free protons to form non-volatile ammonium ions that are converted into a valuable ammonium salt fertilizer. Various inorganic or organic acids can be used in the acidic solution, such as sulphuric, hydrochloric, phosphoric, lactic acid, etc. The recovered N is conserved un-volatilized in the form of valuable ammonium fertilizer sources (ammonium sulphate, ammonium chloride, ammonium phosphate, ammonium lactate, etc), which are desirable to export N off the farm to other regions

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where N is needed, and thus avoiding environmental pollution to soil, air and water in regions of high livestock density.

Compared to reverse osmosis that requires high pressure, the gas-permeable membrane process requires low pressure. 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. Compared to the struvite precipitation method, which requires 1:1:1 ratios of Mg^{2+} , NH_4^+ and PO_4^{3-} 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^{2+} and PO_4^{3-} required to balance the stoichiometry of struvite precipitation. Another advantage is that gas-permeable membrane process can be combined with other treatment technologies to improve their performance, i.e. anaerobic digestion (García and Vanotti, 2014).

Gas-permeable membranes have been successfully used to recover NH_4^+ from swine manure (Vanotti and Szogi, 2011b). According to these authors, at equal N concentration in the wastewater the rate of ammonia recovery by the gas-permeable membrane was greatly increased with increased pH of the wastewater, using alkali to adjust pH. García and Vanotti (2014) worked with different manure strengths with and without manure pH control, recovering 81% and 55% of NH_4^+ respectively, demonstrating that as manure strength and NH_3 content increased in manure, more N was recovered by the membrane system. A strategy to improve farmer's adoption of gas-permeable membrane technology to capture NH_3 emissions is to seek a more simple alternative to using alkali chemical amendments in the farm to raise the pH of the manure.

An alternative method to enhance the removal of ammonia from livestock effluents using the hydrophobic gas permeable system proposed by Vanotti and Szogi (2011a) is the use of aeration. Such conditions applied to stored livestock effluents result in a pH increase of about 1 unit that enhances NH_3 release. This effect has been demonstrated in experiments of aeration of swine manure through bubbling or mixing. For instance, passing air, 0.5 or 4.9% O_2 gas mixtures, through slurry caused an increase in pH of about 1 unit in 1–2 days and about 2 units in 10 days (from 7 to between 8.5 and 9) (Stevens and Cornforth, 1974). Likewise, in an experiment of aeration of swine lagoon wastewater without nitrification due to lack of nitrifying biomass, Vanotti and Hunt (2000) obtained an increase in wastewater pH of 1.5 units, from 7.5 to 9, in the first 18 h of aeration. Others showed that a continuous aeration of manure increased pH in almost 2 units (Zhu et al., 2001). With respect to aeration by mixing, García et al. (2007) found that manure pH almost raised one unit after 24 h of stirring. For the purpose of NH_3 recovery with gas-permeable membranes, Vanotti and Szogi (2011a) indicated that the aeration of the waste needs to be accompanied by nitrification inhibition because the nitrification of NH_3 reduces the pH of the liquid and the recovery of the NH_3 . Nitrification inhibition can be achieved in various effective ways such as: reducing aeration rates, reducing nitrifying biomass, increasing temperatures, and adding a commercial nitrification inhibitor.

In this context, an alternative method to raise manure pH without addition of alkali is the application of aeration to the manure while inhibiting nitrification. Therefore, the main goal of this study was to evaluate the efficiency of NH_3 recovery from liquid manure using gas-permeable membranes applying aeration as an alternative to use alkali to raise manure pH. As a comparison, three more conditions were studied (Table 1) using the same raw swine manure: one without aeration or alkali chemical amendment, another adjusting manure pH with alkali but without aeration, and the last one applying aeration to manure without a gas-permeable membrane recovery system to study NH_3 release.

Table 1
Characteristics of each treatment studied.

	Aerated	Not aerated	With alkali chemical	Aerated control without membrane
	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Membrane recovery system	Yes	Yes	Yes	No
Aeration	Yes	No	No	Yes
Alkali chemical added to manure	No	No	Yes	No
N-inhibitor	Yes	No	No	Yes

2. Materials and methods

2.1. Experimental procedure

Batch experiments were conducted in 2-L wastewater vessels consisting of polyethylene terephthalate (PET) plastic jars for an effective manure volume of 1.5 L (Fig. 1). The acid tank used to concentrate the NH_3 consisted of 500-mL Erlenmeyer flasks containing 250 mL 1 N H_2SO_4 . A peristaltic pump (Heidolph, pump-drive 5001, Germany) 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. In the aerated treatments, air was supplied using an aquarium air pump (Hailea, Aco-2201) from the bottom of the vessel through a porous stone, and was controlled using an airflow meter (Aalborg, Orangeburg, NY, USA) that provided air at an airflow rate of $0.24 L_{air} L_{manure}^{-1} min^{-1}$. This low airflow rate was selected to effectively increase the pH of manure based on preliminary aeration tests runs but at the same time it was low enough to avoid nitrification of the NH_4^+ (that reduces pH in manure). The aeration rate selected was about 4 times lower than aeration rates of $0.9 L_{air} L_{liquid}^{-1} min^{-1}$ used by Magrí et al. (2012) that greatly inhibited nitrite production activity in experiments of partial nitrification of swine wastewater. Another strategy to avoid nitrification was the addition of a commercial nitrification inhibitor (Vanotti and Szogi, 2011a). In this study we used both low-aeration and a nitrification inhibitor (allylthiourea) to stop NH_4^+ oxidation.

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

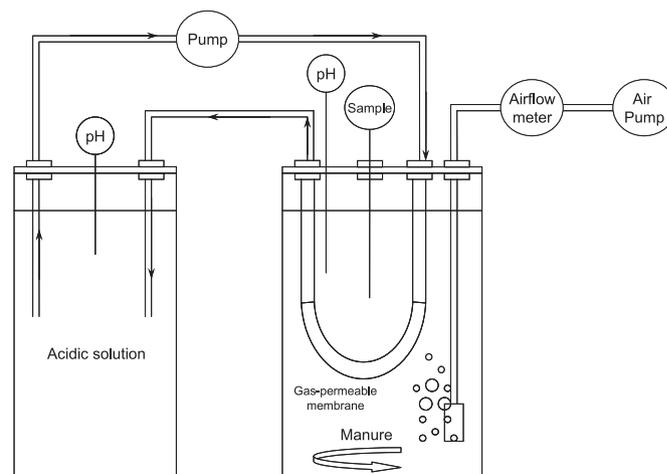


Fig. 1. Experimental device for ammonia capture from manure using gas-permeable membranes and low-level aeration to raise manure pH.

used in this work was 60 cm, with outer diameter of 10.25 mm and wall thickness of 0.75 mm. Physical characteristic of the ePTFE tubular membrane were: average pore size = 2.5 μm , and bubble point = 210 kPa. 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, to monitor pH and to supply air (Fig. 1). The manure was continuously agitated using magnetic stirrers.

Four sets of experiments were carried out, called treatment 1–4 (Table 1). In treatment 1 (aerated manure), aeration was applied to the manure in order to increase the pH and the recovery of NH_4^+ ; in treatment 2 (not aerated), manure pH was not adjusted with either aeration or chemical; in treatment 3 (with alkali chemical), manure pH was adjusted to 8.5 with 5 N sodium hydroxide whenever the pH of the manure decreased below 7.7; and in treatment 4 (aerated control without membrane), aeration was applied to the manure without a membrane recovery manifold installed. Nitrification inhibitor allylthiourea (10 mg/L) was added to the influent of the aerated treatments (1 and 4) at 10 mg/L rate (100 μM concentration) (Jantii et al., 2013). Thus, NO_2^- and NO_3^- were not detected in the final effluents.

As NH_4^+ was depleted from manure and transferred to the acid tank, the pH of the acid solution increased. A protocol was established: concentrated acid was added to the acid solution to an endpoint pH < 1 whenever the pH of the acid solution increased > 2. This occurred twice in treatment 1 (days 7 and 10) and once in treatment 2 (day 16).

Swine manure samples from the wastewater vessels were withdrawn daily in order to monitor pH, alkalinity and NH_4^+ . At the same time, acid solution samples from the concentrator tank were collected to monitor pH and NH_4^+ . In addition, initial and final samples of swine manure were analyzed for determination of pH, alkalinity, total solids (TS), volatile solids (VS), total chemical oxygen demand (CODt), NH_4^+ , total Kjeldahl nitrogen (TKN), nitrate (NO_3^-), nitrite (NO_2^-), and total phosphorous (Pt). All experiments were done in duplicate at a constant temperature of 25 °C. Data results were statistically analyzed by means and standard deviation (proc MEANS), analysis of variance (proc ANOVA), least significant difference at a 0.05 probability level (LSD_{0.05}), linear regression (proc REG) with SAS (SAS Institute, 2008).

2.2. Origin of the swine manure

Raw manure was collected from a farm located in Narros de Cuellar (Segovia, Spain). The manure was collected from the pit under slatted floor of a farrowing sow's house. Chemical characteristics of the manure used in the present work are shown in Table 2 (first column). Manure was collected in plastic containers, transported in coolers to the laboratory and subsequently stored at 4 °C for further use. The manure did not receive previous treatment and contained 1.4% TS. Manure strength was ranked as medium

strength (0.8–1.7% TS) according to García et al. (2009). The manure was homogenized by mechanical agitation while filling the reactor vessels.

2.3. Analytical methods

Analyses of TS, VS, CODt, TKN and TP were performed in duplicate in accordance with APHA Standard Methods (1989). Total alkalinity and pH 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 and expressed as mg CaCO_3/L . Nitrate and NO_2^- were monitored using colorimetric strips (MQuant™, Merck). Ammonia concentrations were determined using an NH_3 gas-sensing electrode Orion 900/200 (Thermo Electron Corporation, Beverly, USA) after adjusting the sample to pH > 11. Free ammonia (FA) was quantified according to Eq. (1), where NH_3 was the FA content, TNH_3 was the total ammonium (measured in the NH_4^+ determination described above), T was the manure temperature, and pH was measured in the manure (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 NH_3 by the gas membrane system: effect of aeration versus no aeration

Aeration of manure in treatment 1 (aerated with membrane) had an important effect on pH, as it increased from 7.5 to 8.5 the first day and remained in the pH range of 8.5–9 units during most of the experimental time (Fig. 2). The pH changes were also monitored during the first 6 h of aeration: 0 h = 7.48 \pm 0, 1 h = 8.03 \pm 0.11, 2 h = 8.43 \pm 0.20, 3 h = 8.44 \pm 0.12, 4 h = 8.56 \pm 0.16, 5 h = 8.54 \pm 0.06, 6 h = 8.53 \pm 0.04, 24 h = 8.54 \pm 0.09. The hourly data show that the pH increase above 8.5 was quick and occurred in the first 4 h. During aeration of the manure, there was an instant release of OH^- that raised its pH consuming carbonate alkalinity according to Eq. (2). On the contrary, when manure was not aerated (treatment 2) the pH remained lower than with aeration treatment within a range of 7.5–8 units during most of the experimental time (Fig. 2).



Increases in pH due to aeration affected both the formation of NH_3 , as defined in Eq. (3), and the effectiveness of the membrane system to recover the N in the manure. When aeration was added, NH_4^+ concentration in manure was almost depleted: it declined

Table 2

Chemical characteristics of manure at the beginning (initial) and at the end of each set of experiments. The standard deviation of duplicate experiments are shown in parenthesis.

	Initial ^a	Aerated	Not aerated	With chemical	Aerated control without membrane
pH	7.50 (0.02)	9.20 (0.01)	8.10 (0.10)	7.80 (0.10)	9.30 (0.10)
CODt (mg/L)	16,780 (1020)	5900 (1580)	6550 (300)	17,680 (960)	7230 (560)
TS (g/L)	14.4 (0.50)	13.4 (1.30)	12.9 (0.20)	14.8 (0.50)	12.5 (0.90)
VS (g/L)	7.50 (0.40)	4.80 (0.50)	5.70 (0.20)	8.20 (0.40)	5.40 (0.30)
Pt (mg/L)	140 (4.00)	140 (1.00)	140 (2.80)	90 (4.80)	140 (3.50)
TKN (mgN/L)	2700 (50)	320 (50)	1080 (50)	1880 (280)	1180 (190)
NH_4^+ (mgN/L)	2390 (160)	20 (30)	790 (100)	400 (4.00)	910 (110)
Alkalinity (mg CaCO_3/L)	13,350 (50)	3590 (410)	6830 (240)	11,820 (260)	7160 (620)

^a Manure initial composition was the average of four samples.

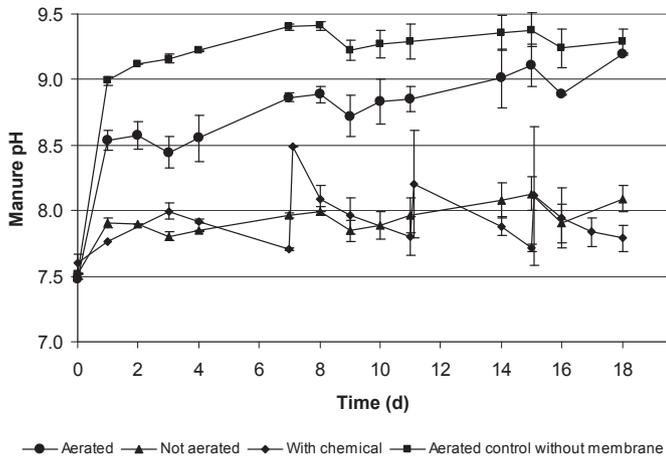


Fig. 2. Changes in pH along the experimental time of manure with NH_3 recovery manifold (aerated, not aerated, and with alkali chemical additions), and of manure in an aerated control vessel without membrane manifold. The error bars are the standard deviation of duplicate experiments.

from 2270 ± 0 to 20 ± 30 mg N/L (Fig. 3A). Without aeration, NH_4^+ concentration in manure decreased with the membrane manifold from 2330 ± 0 to 790 ± 100 mg N/L in the 18 days of the experiment (Fig. 3B).



Data in Table 3 show the N mass balances consisting of the

quantities removed from the manure vessel and recovered in the acid tank. The total mass of NH_4^+ recovered in the acid solution was significantly increased (46%) by aeration. This increase is accounted for 3320 ± 3 mg N in treatment 1 (aerated) versus 2280 ± 186 mg N in treatment 2 (not aerated). Average recovery rates in treatment 1 and 2 were also significantly different (184 and 127 mg N/L/day, respectively) (Table 3). The NH_4^+ removal efficiencies were significantly different for aerated (99%) and non-aerated (66%) treatment. However, most of the N being removed from the manure in both treatments was accounted for in the acidic solution as indicated by the lack of significant differences between recovery efficiencies (99%) of the aerated and non-aerated treatments. This indicates that even though the aeration treatment significantly increased the release of NH_3 into the liquid manure, the submerged gas-permeable membrane system was efficient to capture the increased release of NH_3 .

Another effect of aeration was the increase of FA content in manure, as it depends on the pH (Eq. (1)) (Fig. 4). While pH was below 8.0 in non-aerated manure (treatment 2), the FA concentration was maintained below 100 mg N/L during the experimentation time (average 47 ± 10 mg N/L); whereas in aerated manure (treatment 1), the FA concentration reached 250 mg N/L (average 80 ± 17 mg N/L) due to the increase in manure pH (Fig. 4). These data were in agreement with results from García and Vanotti (2014) that pointed out that FA content below 20 mg N/L in manure inhibited NH_3 capture by the gas-permeable membrane system, but FA content above 40 mg N/L allowed active permeation of NH_3 through the membranes. Thus, mass recovery of NH_4^+ through the membrane increased as FA content increased in manure as a result of aeration treatment.

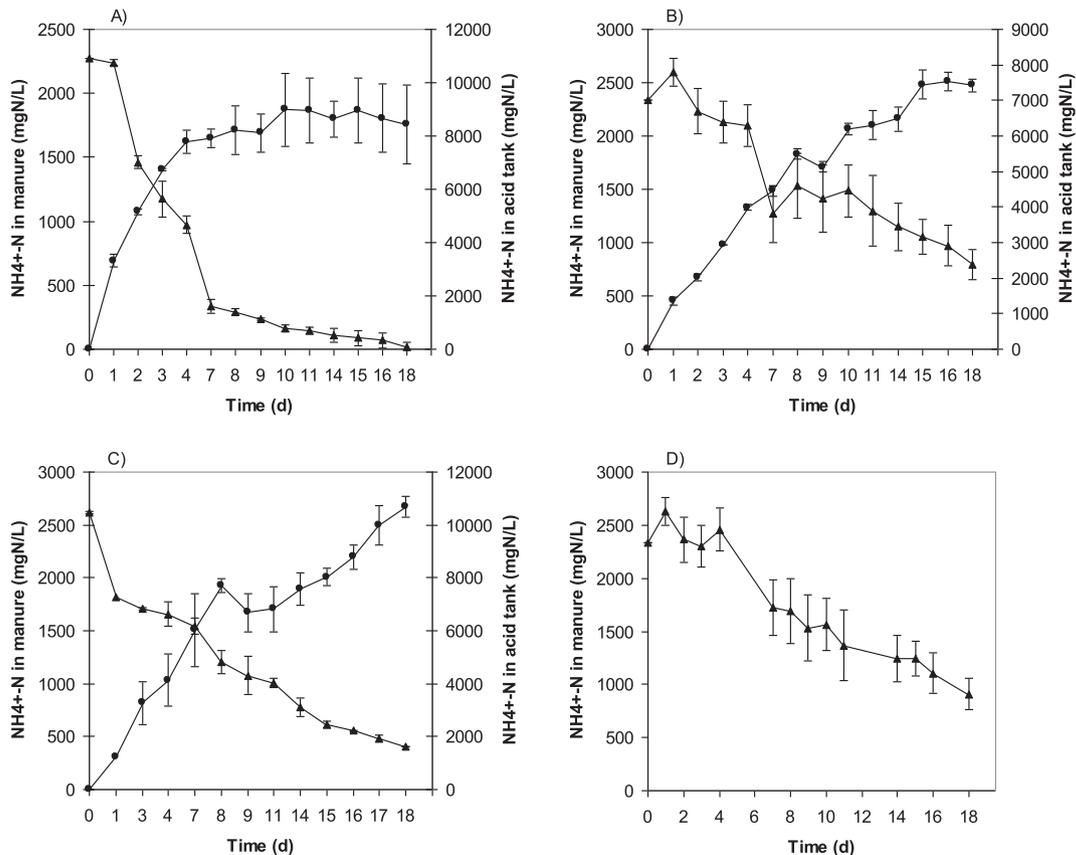


Fig. 3. Removal of ammonia in swine manure (\blacktriangle) by the gas membrane system and recovery and concentration in the acid tank (\bullet). A) aerated manure, B) not aerated manure, C) manure with chemical, D) aerated control without membrane. The error bars are the standard deviation of duplicate experiments.

Table 3Mass balances of the recovery of nitrogen using gas-permeable membranes for each treatment studied^{a,b}.

Treatments ^c	Initial NH ₄ ⁺ in manure	Remained NH ₄ ⁺ in manure	NH ₄ ⁺ -N removed from manure ^d	NH ₄ ⁺ -N volatilized in the air ^e	NH ₄ ⁺ -N recovered in the acidic solution	NH ₄ ⁺ -N removal efficiency ^f	NH ₄ ⁺ -N recovery efficiency ^g	Maximum NH ₄ ⁺ recovery rate ^h	
								(mgN)	(%)
Treatment 1	3410	33 c	3370 a	50 b	3320 a	99 a	99	780	184 a
Treatment 2	3500	1190 a	2310 b	30 b	2280 b	66 b	99	830	127 b
Treatment 3	3930	610 b	3320 a	220 b	3100 a	85 a	93	810	172 a
Treatment 4	3500	1370 a	2140 b	2140a	—	61 b	—	—	—
LSD 0.05	NS	475	473	267	398	14	NS	NS	23

^a 1.5 L of manure in a 2-L vessel, using 250 mL 1 N H₂SO₄ of acidic solution in the concentrator tank (recirculation rate was 5.8 L d⁻¹).^b Values in a column followed by the same letter are not significantly different.^c Treatment 1 was aerated manure, treatment 2 was not aerated, treatment 3 was alkali added to manure, treatment 4 was manure aerated without membrane. Data are average and std. dev. of duplicate reactors during 18-day experiment.^d NH₄⁺ removed from manure was equal to the initial NH₄⁺ in manure minus the remained NH₄⁺ in manure.^e NH₄⁺-N volatilized in the air was equal to initial NH₄⁺ in manure minus the remained NH₄⁺ in manure minus the NH₄⁺ recovered in the acidic solution.^f NH₄⁺ removal efficiency was equal to (NH₄⁺ removed from manure divided by the initial NH₄⁺ in manure) multiplied by 100.^g NH₄⁺ recovery efficiency was equal to (NH₄⁺ recovered in the acidic solution divided by the NH₄⁺ removed from manure) multiplied by 100.^h Highest NH₄⁺ mass recovered in 1 day; 0.0323 m² of membrane surface area.

The low removal efficiency obtained in treatment 2 was consistent with removals of 50 and 57% of NH₄⁺ previously obtained by Vanotti and Szogi (2011b) and by García and Vanotti (2014), respectively, using gas-permeable membranes and manure that was not aerated or received alkali chemicals to increase its pH. Our results obtained herein using low-rate aeration to increase NH₃ availability showed that this is an effective method to increase the capture of NH₄⁺ by gas-permeable membrane systems. This conclusion is supported by the very high removal and recovery efficiencies obtained (Table 3), resulting in an overall recovery of

98% of the initial NH₄⁺ in the manure.

3.2. Aeration of manure without the gas-permeable membrane NH₄⁺ recovery system

In treatment 4 (aerated without membrane recovery system), which can simulate the behaviour of an aerated manure storage tank, the applied aeration also increased the pH of the manure. It was maintained at a higher level, between 9.0 and 9.5, during all the experimentation (Fig. 2). As pH was maintained high, the NH₄⁺ in manure decreased from 2330 ± 0 to 910 ± 145 mg N/L with a removal efficiency of 61% (Fig. 3D). However, all the NH₄⁺ content in manure was volatilized in the air as no membrane recovery manifold was used in this treatment. Without a membrane recovery manifold, the FA accumulated in manure reached a maximum value of 940 ± 16 mg N/L that promoted volatilization loss (Fig. 4). This volatilization loss was significant in the mass balance (Table 3), it represented 2140 mg N or 61% of initial NH₄⁺. In comparison, NH₃ volatilization in treatments 1 and 2 were significantly lower (<1.5% of initial). Therefore, the use of gas-permeable membrane technology could significantly contribute to avoid NH₄⁺ release to the atmosphere, preventing NH₃ emissions from livestock operations.

3.3. Removal of NH₃ by the gas membrane system: effect of aeration versus chemical addition

As mentioned before, aeration of the manure in the gas-permeable membrane reactor kept the manure pH above 8.5 during the experimental time. In treatment 3, alkali chemical was used to correct pH. After each correction, the manure pH rapidly decreased below 8.0 as a result of the active NH₃ capture (Fig. 2). During the 18-day experiment the NH₄⁺ concentration in treatment 3 decreased from 2620 ± 10 to 400 ± 4 mg N/L, which represented an NH₄⁺ concentration in the recovery acidic solution 4 times higher than in manure (Fig. 3C). The amount of chemical added was 2.14 g NaOH/L_{manure}. The total mass of the NH₄⁺ recovered in the acidic solution accounted for 3100 mg N, which represented an NH₄⁺ removal efficiency of 85%, and a recovery efficiency of 93% (Table 3). Compared to treatment 2, the addition of alkali to the manure significantly increased N recovery by the membrane reactor. However, in the case of treatment 1, NH₄⁺ recovered in the acidic solution was 3320 mg N, which was not statistically different from treatment 3 (Table 3) meaning that both aeration and chemical treatments were highly effective for NH₄⁺ recovery from manure

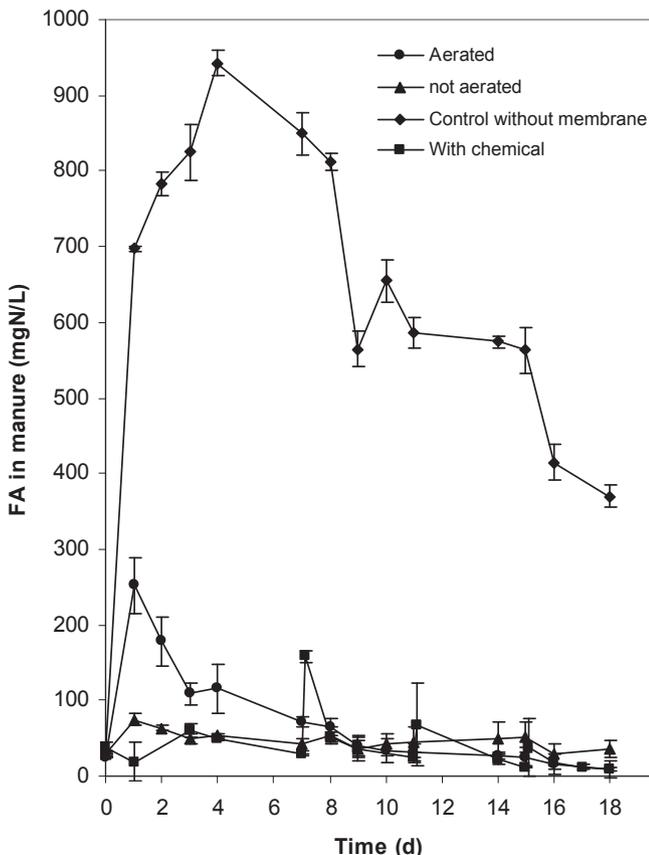


Fig. 4. Free ammonia content in manure. The error bars are the standard deviation of duplicate experiments.

using gas-permeable membrane technology.

The NH_4^+ recovery by the membrane was not linear in any of the studied assays; it followed a 2nd order curve (Fig. 5) meaning that the NH_4^+ capture rate was higher during the first days, especially in the aeration treatment. In aerated manure, FA was maintained high during the 1–4 day period with a range from about 100 to 250 mg N/L (Fig. 4) and rapidly permeated through the membrane. After day 4 and until the end of the study, FA content decreased (average 35 ± 3 mg N/L; Fig. 4) and the membrane capturing process slowed down. In the case of manure with chemical, when manure pH was between 7.5 and 8.0 FA content was low, increasing with each pH adjustment to 8.5, reaching a maximum value of 160 mg N/L on day 7 and an average of 40 ± 15 mg N/L for the 18-day period (Fig. 4).

Another effect of the recovery of NH_4^+ by the gas-permeable membranes was the alkalinity consumption in the manure, as Eq. (3) describes; thus, a decrease in the alkalinity of manure was observed in treatments 1, 2 and 4 with consumptions of 9719 ± 406 , 6552 ± 243 and 6219 ± 57 mg CaCO_3/L respectively (Fig. 6). In treatment 3, alkalinity consumption was not calculated due to NaOH additions to raise the pH above 7.7; as a result, the alkalinity remained about constant.

3.4. Impact of aeration on pH control

In basic aqueous solutions like swine manure, NH_3 formation and removal consume OH^- in a pH and temperature dependent process, lowering the pH of the manure (Eq. (3)). With the gas-permeable membrane system in place, as NH_3 permeated through the membrane the OH^- uptake produced acidification of manure. In the case of treatment 2 where no aeration was applied, pH decreased in some points although it maintained above 7.5 during the whole experimental time due to the high buffering capacity of manure, that contained 13.4 g CaCO_3/L of alkalinity (Fig. 6). A similar situation occurs in the nitrification process where NH_4^+ is oxidized to NO_3^- to remove N from manure. In this process there is a release of H^+ , at a rate of 2 mol for each mol of NH_4^+ oxidized, that

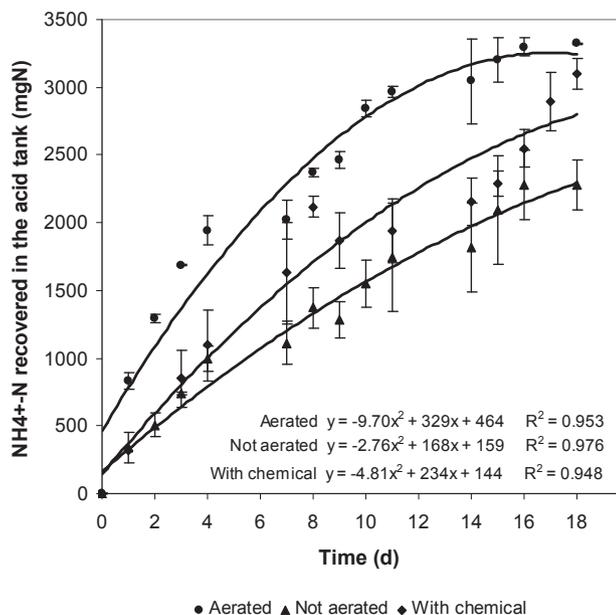


Fig. 5. Mass of ammonia recovered in the acid concentrator tank for aerated, not aerated, and chemically amended manure treatments. A 2nd order equation and R^2 are represented. The error bars are the standard deviation of duplicate experiments.

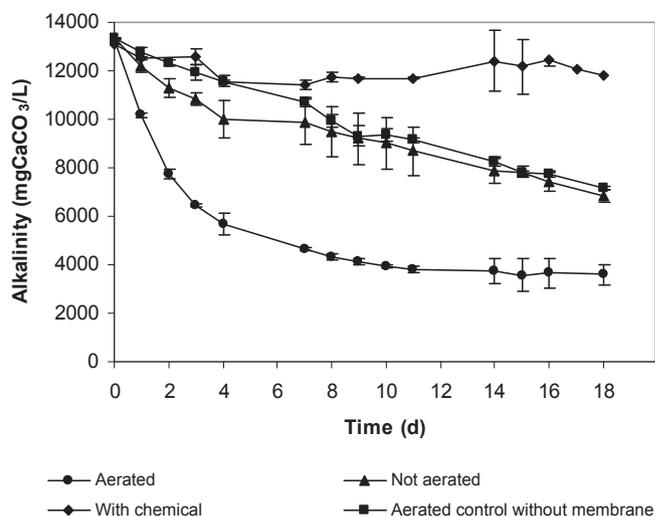


Fig. 6. Changes in alkalinity of swine manure with NH_3 recovery manifold (aerated, not aerated, with chemical treatments) and aerated control treatment without membrane manifold. The error bars are the standard deviation of duplicate experiments.

decreases the pH to an extent related to the buffering capacity of the system (Vanotti and Hunt, 2000) while air is supplied to the process. However, manure aeration without nitrification causes a pH increase due to OH^- release after bicarbonate alkalinity destruction as show in Eq. (2). Continuous air supply maintained a high pH level in manure, leading to a continuous NH_3 release that permeated through the membrane and was recovered by the acid solution. As a consequence, alkalinity was also consumed to buffer the system (Fig. 6).

Fig. 7 is a schematic diagram summarizing the recovery of NH_3 by the gas-permeable manifold system in the experiments. In treatment 1, air supply produced pH increase following Eq. (2), with enhanced NH_3 formation (Eq. (3)) that permeated through the membrane manifold also consuming alkalinity. Thus the more NH_3 was formed, the more permeated through the membrane while consuming alkalinity until NH_4^+ was completely depleted from manure. In treatment 2, as manure pH was below 8.0, less NH_3 was available to permeate through the membrane and NH_4^+ was not completely removed from manure. In treatment 4 (aeration without membrane manifold), the pH reached 9.5 which also shifted Eq. (3) balance towards NH_3 formation, however, without recovery, the FA accumulated in the manure and the balance of Eq. (3) to the right was not as extreme as in treatment 1.

3.5. Economic approach

The operational costs of using alkali vs. aeration to increase manure pH and optimize N recovery using gas-permeable membranes were calculated on the basis of treating the manure effluent from a 4000-head finishing swine operation in Segovia, Spain, and the results of this study. At 2.15 m^3 manure/head/year (RD 324/2000), the quantity of manure effluent produced yearly is 8600 m^3 (23.56 m^3/d). The quantity of NaOH required to adjust pH to 8.5 is 50.4 kg/d (2.14 g NaOH/L, treatment 3). At 0.35€/kg NaOH (\$0.46/kg) (Cortez et al., 2011), the resulting chemical cost is 6440€ per year (\$8500 per year). Operational costs for the aeration approach are: 1) the electrical power needs of the blower, and 2) the nitrification inhibitor. For electrical power, the following conditions were used (Vanotti et al., 2003): oxygen transfer efficiency of 24.2% at 4 m diffuser submergence, oxygen requirements 0.45 kg

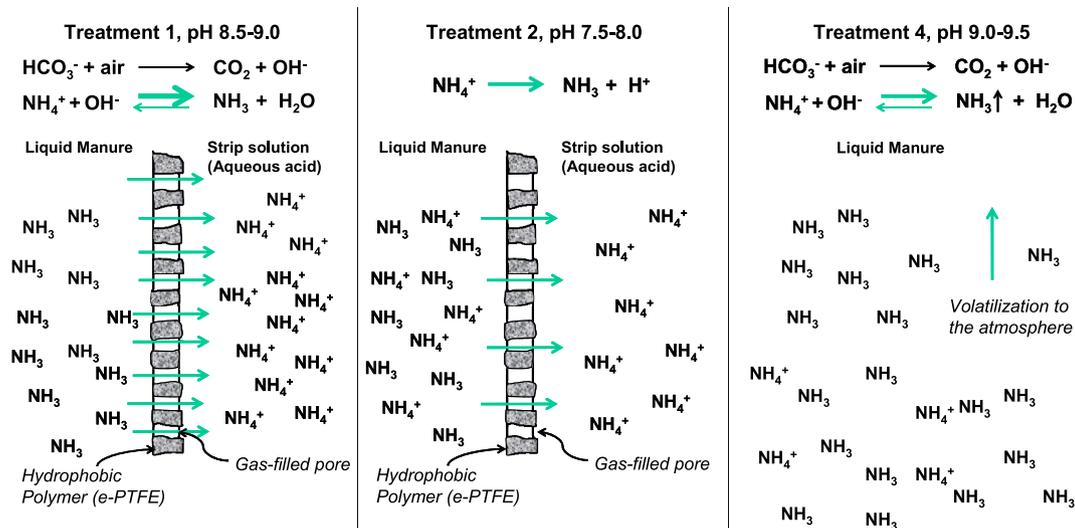


Fig. 7. Schematic diagram of treatment 1, 2 and 4 showing the recovery of NH_3 by the gas-permeable membrane manifold as it was governed by the balance in Eq. (3) that depended on manure pH.

O_2/kg BOD removed, density of air 1.202 kg/m^3 , and oxygen content in air 23.2%. BOD removal in the vessel was 3626 mg/L considering a COD/BOD ratio of 3 (treatment 1). Based on these conditions, an aeration capacity of $570 \text{ m}^3/\text{d}$ ($14 \text{ ft}^3/\text{min}$) at 4 m water depth (5.7 psi) would be required to remove 85 kg BOD/d , which can be met with a positive displacement blower with 1.6 bhp (brake horse power) rating that delivers $21 \text{ ft}^3/\text{min}$ and operated 2/3 of time. The power consumption for 16 h d^{-1} blower operation and 90% motor efficiency is 21.3 kWh/d , resulting in an annual electric cost of 505 € ($\$ 667$ per year) (unit cost = $0.065 \text{ €}/\text{kWh}$). For nitrification inhibition, using nitrapyrin (commonly used for farming) at 150 μM concentration (Jantii et al., 2013), the dosage is 35 g/m^3 of manure and the quantity required is 0.825 kg/d . The resulting cost of nitrification inhibitor is 2254 € per year ($\$2975$ per year) (unit cost = $7.58 \text{ €}/\text{kg}$ or $\$10/\text{kg}$). Therefore, the operational cost using the aeration approach (power and inhibitor) is 2759 € per year ($\$3641$ per year). Relative to alkali addition, the aeration approach reduced the operational costs of ammonia recovery by 57%.

4. Conclusions

Ammonia was successfully separated and recovered from raw liquid swine manure using a gas-permeable membrane system operated with aeration and nitrification inhibition. The aeration reacted with the natural alkalinity, which released OH^- and increased the manure pH above 8.5. This pH increase promoted gaseous NH_3 release from the manure and rapid permeation through the submerged membrane. The overall NH_4^+ recovery obtained with the aeration approach was 98%. The new approach substituted for large amounts of alkali chemical that were needed to obtain the same effect and reduced the operational costs of NH_4^+ recovery by 57%.

Acknowledgements

This work, has been funded by the INIA/FEDER Project CC09-072 “Transferencia de tecnología para la gestión de residuos ganaderos y de la industria agro-alimentaria de Castilla y León”. Cooperation with USDA-ARS Project 6657-13630-001-00D “Innovative Animal Manure Treatment Technologies for Enhanced Environmental Quality” is gratefully 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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