

Recovery of ammonia from anaerobically digested manure using gas-permeable membranes

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ABSTRACT: Nitrogen (N) can be recovered from different types of wastewaters. Among these wastewaters, anaerobically digested swine manure (digestate) has the highest N content in ammonia form (NH₃). It is desirable to reduce N in digestate effluents to safely incorporate them in arable soil in N vulnerable zones (NVZ) and to mitigate NH₃ emissions during N land application. Additional benefit is to minimize inhibition of the anaerobic process by removing NH₃ during the anaerobic digestion process. This work aimed to apply the gas-permeable membrane technology to evaluate ammonia (NH₃) recovery from high-ammonia digested swine manure. Anaerobically digested swine manure with NH₄⁺ content of 4,293 mg N L⁻¹ was reduced by 91 % (to 381 mg N L⁻¹) during the 32-day experiment. Although the results showed a total N recovery efficiency of 71 %, it is possible to increase this recovery efficiency to > 90 % by adjusting the area of the membrane system to match the high free ammonia concentration (FA) in digested swine manure. Moreover, final digestate pH and alkalinity were kept around 8.1 and 8,923 mg-CaCO₃ L⁻¹, which are convenient for the anaerobic process or incorporation in arable soil when the process is finished.

Keywords: N removal, digestate, manure management, membrane technology

Introduction

Anaerobic digestion (AD) is a widely used technique with an increasing number of full biogas-plants under operation for organic solid waste treatment and energy recovery (Carrosio, 2014). The rise in environmental concerns associated with energy production and CO₂ mitigation policies has renewed interest in digestion technologies.

Ammonia inhibition in AD has been reported with a wide range of inhibiting NH₃, because of differences in the nature of substrates, inocula, environmental conditions and acclimation periods (Chen et al., 2008). Sung and Liu (2003) and Procházka et al. (2012) showed that NH₃ concentrations higher than 3,000 mg L⁻¹ could cause obvious inhibition of methanogenesis. In another study, Hejnfelt and Angelidaki (2009) concluded that NH₃ levels of 1,500-7,000 mg L⁻¹ caused a decrease in methane production.

The gas-permeable membrane technology (GPMT) has been successfully used to recover NH₃ from swine manure (García-Gonzalez and Vanotti, 2015; García-Gonzalez et al., 2015). This technology can be combined with other treatment technologies such as AD and phosphorus recovery to improve their performance (Vanotti and Szogi, 2015). In the case of anaerobic digestion, the process can be applied inside a digester to remove ammonia without damaging the carbonaceous material and therefore improving the anaerobic process, as reported by Garcia-Gonzalez and Vanotti (2015). Other studies reported AD performance improvement in semi-batch experiments using GPMT to treat slaughterhouse waste (Lauterbock et al., 2014). Hence, if a large quantity of NH₃ is removed from digestate, the typical inhibition caused by this compound will be minimized, improving both AD and methane production.

Nowadays, AD is an important technology and strategy to manage manure worldwide and in many countries, with high number of NVZ (Nitrate Vulnerable Zones), thus, land application of the digestate is an important strategy to recycle nutrients and organic matter. However, the application is limited by the N content of digestate (European Council, 1991). Reducing ammonia from digestate using GPMT could help reduce environmental pressure in these intensive livestock production areas. This study aimed to apply GPMT to evaluate NH₃ recovery from digested swine manure at lab scale. The pH of the digested manure was kept above 7.7 by adding sodium hydroxide when necessary to enhance ammonia capture by the membrane.

Materials and Methods

Experimental procedure

A batch experiment was conducted in 2 L wastewater vessels consisting of polyethylene terephthalate (PET) plastic jars for an effective digestate volume of 1.3 L using the experimental device and diagram described in Garcia-Gonzalez and Vanotti (2015). The acid tank consisted of 500 mL Erlenmeyer flasks containing 280 mL 1 N H₂SO₄. A diaphragm pump (Alldos, TrueDos model, Denmark) was used to continuously circulate the acid through tubular membranes inside the digestate vessels and back into the acid tank using a constant flow rate of 5.8 L d⁻¹. The pH in the acidic tank increased, as ammonia was captured by the membrane, therefore, the acid pH was adjusted to keep it below 1.5. Gas-permeable tubing (60 cm long, 10.25 mm outer diameter and 0.75 mm wall thickness) made of expanded polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock

Hill, SC) was used for NH_3 capture. The membrane manifolds were submerged in digestate contained in PET jars, which were kept closed but not airtight. Ports were installed on top of the reactor vessels to obtain samples and monitor pH. The digestate was continuously agitated using magnetic stirrers.

The experiment was carried out to evaluate N recovery from anaerobically digested swine manure. Chemical characteristics are shown in Table 1. The biogas plant was located in Salamanca (Spain). The plant was a co-digestion plant treating the manure of a farm with 6,000 fattening pigs as well as agro-food wastes. Digestate was collected directly from the mesophilic digester in plastic containers, transported in coolers to the laboratory and subsequently stored at 4 °C for further use.

The pH of the digestate was adjusted whenever it decreased below 7.7, according to (García-González and Vanotti, 2015). This adjustment consisted in increasing the digestate pH using sodium hydroxide (5 N), which was added when necessary to endpoint pH 8.5-9.0. Digestate samples from the vessels and acidic solution samples from the concentrator tank were collected daily to monitor pH, alkalinity and NH_4^+ . All experiments were carried out in duplicate and results were expressed as means. The test was run at room temperature to simulate ammonia recovery from the digested manure in a system external to the anaerobic digestion.

Analytical methods

Analyses of total solids (TS), volatile solids (VS), total chemical oxygen demand (CODt), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were performed in duplicate in accordance with APHA Standard Methods (1989). The 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 standardized sulphuric acid needed to bring the sample to a pH endpoint of 4.5 and expressed as $\text{mg CaCO}_3 \text{ L}^{-1}$. NO_3^- and NO_2^- were monitored using colorimetric strips (MQuant™, Merck). NH_4^+ concentrations were determined using a NH_3 gas-sensing electrode Orion 900/200 (Thermo Electron Cor-

Table 1 – Chemical characteristics of the digestate at the beginning and at the end of each batch experiment. The standard deviation of duplicate experiments are shown in parenthesis.

	Initial	Final
pH	8.01 (0)	8.11 (0.01)
CODt (g L^{-1})	27 (1)	22 (0.23)
TS (g L^{-1})	35 (0.32)	36 (0.54)
VS (g L^{-1})	25 (0.33)	22 (0.20)
Pt (mg L^{-1})	771 (3.54)	645 (1.06)
TKN (mgN L^{-1})	4,690 (44)	1,244 (89)
NH_4^+ (mgN L^{-1})	4,293 (0)	381 (55)
$\text{NO}_3^- + \text{NO}_2^-$ (mg L^{-1})	0	0
Alkalinity ($\text{mgCaCO}_3 \text{ L}^{-1}$)	19,038 (0)	8,923 (947)

poration, Beverly, USA) after adjusting sample to pH > 11. Free NH_3 (FA) was quantified theoretically according to Eq. (1), where NH_3 was the FA content and TNH_3 was the total NH_4^+ (measured in the NH_4^+ determination described above) (Hansen et al., 1998):

$$[\text{NH}_3]/[\text{TNH}_3] = 1 + \left(\frac{10^{-\text{pH}}}{10^{-(0.09018 + 272992/T)}} \right)^{-1} \quad (1)$$

Results and Discussion

NH_4^+ concentration in digestate decreased from $4,293 \pm 0 \text{ mg N L}^{-1}$ to $381 \pm 55 \text{ mg N L}^{-1}$ in the 32 days of experiment (Figure 1). Ammonia capture by the membrane continuously increased until day 25, after which, little or no more NH_3 was recovered in the acidic solution. Similarly, NH_4^+ in digestate decreased little at the end of the experiment, from 433 (day 27) to 381 (day 32) mg N L^{-1} at the end of the experiment (Figure 1). The acidic solution was the same during the entire experiment, thus, the recirculation of this liquid occurs in a closed loop between the treatment vessel and the acid tank, which achieved an NH_4^+ concentration in the recovery solution ($11,200 \pm 1,100 \text{ mg N L}^{-1}$) of almost three-fold higher than in digestate ($4,293 \text{ mg N L}^{-1}$; Figure 1). Sixty-two percent of NH_4^+ removed from digestate during the experimental period was recovered in the acidic solution. These findings are in agreement with those reported by García-González and Vanotti (2015) who observed a high N recovery from manure with different NH_4^+ strengths using GPMT.

The rate of NH_4^+ recovery was not linear and followed a 2nd-order curve (Figure 2), meaning that the NH_3 capture rate was higher during the first days, and decreased as it was being depleted from the manure.

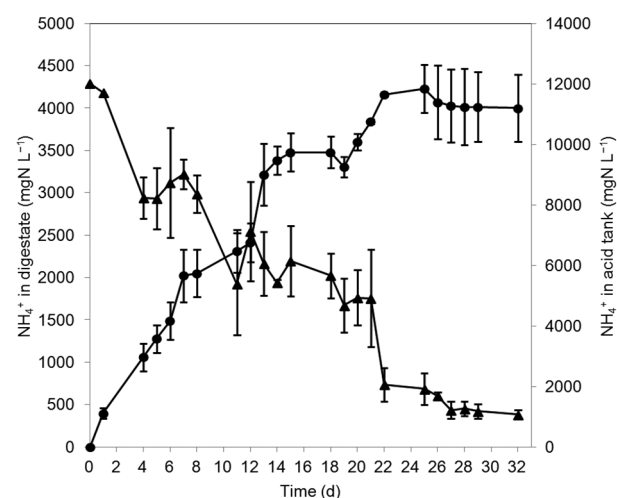


Figure 1 – Removal of ammonia in digestate (\blacktriangle) by the gas membrane system and recovery and concentration in the acid tank (\bullet). The error bars are the standard deviation of duplicate experiments.

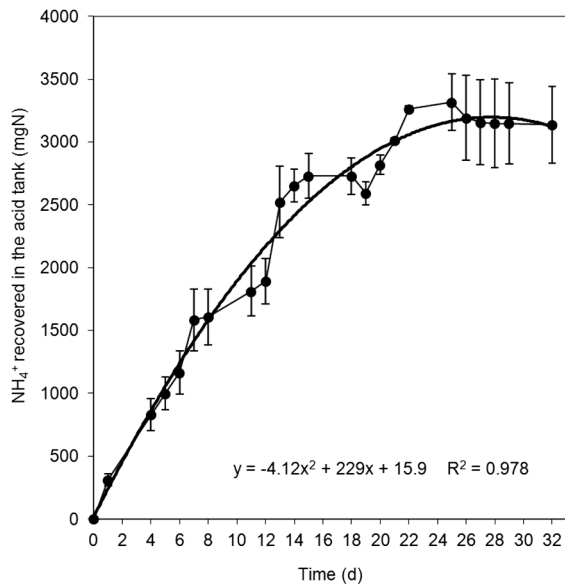


Figure 2 – Mass of ammonia recovered in the acid tank. A second-order equation and R^2 are represented. The error bars are the standard deviation of duplicate experiments.

Similar to what was observed in raw swine manure, when FA content in the manure was low, the rate of NH_3 captured by the membrane decreased (García-Gonzalez and Vanotti, 2015).

Most of the NH_3 recovery occurred during the first 25 days of the experimental period, with an average recovery rate of $405 \text{ mg N L}^{-1} \text{ d}^{-1}$ and a high NH_4^+ recovery efficiency of 71 % (Table 2). The average recovery rate during the second part of the batch (25-32 days) was $81 \text{ mg N L}^{-1} \text{ d}^{-1}$ and the corresponding NH_4^+ recovery efficiency was 45 % of the remaining NH_4^+ . The inability of the membrane to recover additional N from day 25 to the end of the experiment can be explained by the NH_3 content in digestate. The average free NH_3 in digestate until day 25 of the experiment was 178 mg N L^{-1} , however, from that day until the end of the experiment, average free NH_3 in digestate decreased to 69 mg N L^{-1} . This means that NH_3 concentration in digestate was low and permeated slowly through the membrane. Therefore, it was necessary to keep a high level of free NH_3 to continuously recover N, which was achieved by keeping the pH of digestate above 8.5 (García-Gonzalez and Vanotti, 2015). As NH_3 was removed, the pH of the digestate was kept around 8.0 for the first 19 days of the experiment by adjusting it with alkali on days 21 and 27 (Figure 3). This indicates that, although alkalinity was consumed to neutralize digestate acidification due to NH_3 removal, the buffer capacity of digestate was very high. Therefore, a 53 % decrease in the digestate alkalinity was observed with a consumption of $10,115 \pm 947 \text{ mg CaCO}_3 \text{ L}^{-1}$ (Figure 3).

In contrast with previous studies carried out with raw manure, both the maximum NH_4^+ recovery rate and

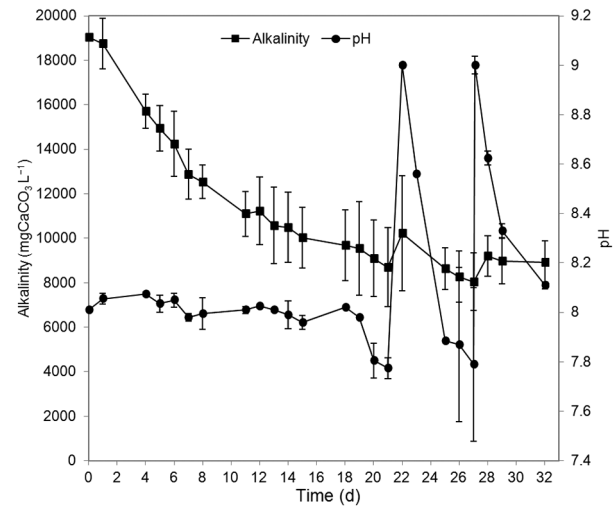


Figure 3 – Changes in pH and alkalinity of digestate along the experimental period. The pH was corrected on days 21 and 27. The error bars are the standard deviation of duplicate experiments.

the average NH_4^+ recovery rate obtained in this study were very high as well as the FA content in the digestate (Table 3). According to previous studies, mass recovery of NH_4^+ through the membrane increased as FA content increased in manure because of pH adjustment (with aeration treatment or alkali addition). However, in the present study, FA content remained high during the first 25 days of experimentation (178 mg N L^{-1}). This high FA content allowed active permeation of NH_3 through the membrane. Yet, the absorption capacity of the membrane was not enough to recover all FA in digestate and a fraction of NH_4^+ was volatilized, as the reaction vessels were not airtight. This volatilization loss was significant in the mass balance, representing $1,370 \text{ mg N}$ or 25 % of initial NH_4^+ . These volatilization losses were high compared with results from García-Gonzalez and Vanotti (2015), who treated raw manure and obtained volatilization losses of 187 mg N (8 % of initial NH_4^+), also compared with results from García-Gonzalez et al. (2015) who obtained volatilization losses also in raw manure of 50 and 220 mg N (2 to 6 % of initial NH_4^+) using similar reactor vessels and tubular membrane length (Table 3). Thus, to recover all N and to avoid significant volatilization from digestate, the reaction device should be totally hermetic for the membrane manifold work at its maximum absorption capacity.

As previously mentioned, digestate from on-farm biogas plants is commonly used as fertilizer in countries with high intensive livestock pressure. Digested slurries have been found to be significant sources of ammonia (NH_3), methane (CH_4) and nitrous oxide (N_2O) emissions (Amon et al., 2006; Bacenetti et al., 2013; Nkoo, 2014), with potential implications for local-to-regional climate (NRC, 2002; Ravishankara et al., 2009). Thus, an important challenge is to develop strategies that help to control the impact of agriculture on the environment, such

Table 2 – Mass balances of the recovery of nitrogen in digestate using gas-permeable membranes^a.

Days in the batch ^b	Initial NH ₄ ⁺ -N in digestate	Remained NH ₄ ⁺ -N in digestate	NH ₄ ⁺ -N removed from digestate ^c	NH ₄ ⁺ -N recovered in the acid solution	NH ₄ ⁺ -N removal efficiency ^d	NH ₄ ⁺ -N recovery efficiency ^e	Maximum NH ₄ ⁺ -N recovery rate ^f	Average NH ₄ ⁺ -N recovery rate
First part (0-25 days)	5581 (0)	892 (240)	4689 (240)	3316 (308)	84	71	1244	405
Second part (25-32 days)	892 (240)	495 (71)	396 (169)	180 (85)	44	45	168	81
All (0-32 days)	5581 (0)	495 (71)	5086 (71)	3136 (308)	91	62	1244	324

^a1.3 L of digestate in a 2 L vessel, using 280 mL 1 N H₂SO₄ of acidic solution in the concentrator tank (recirculation rate = 5.8 L d⁻¹). ^bData are average and standard deviation of duplicate reactors during 32-day experiment. First row of data shows mass balances for the first 25 days of the batch when recovery was active. Second row shows mass balances for the following period (25-32 days). ^cNH₄⁺ removed from digestate = initial NH₄⁺ in digestate – remained NH₄⁺ in digestate. ^dNH₄⁺ removal efficiency = (NH₄⁺ lost from digestate/initial NH₄⁺ in digestate) × 100. ^eNH₄⁺ recovery efficiency = (NH₄⁺ recovered in the acidic solution/ NH₄⁺ lost from digestate) × 100. ^fHighest NH₄⁺ mass recovered in 1 day; 0.0323 m² of membrane surface area.

Table 3 – Comparison of free ammonia (FA) and average NH₄⁺ recovery rate by the gas-permeable membrane reactor in digestate and manure from previous studies^a.

Type of wastewater	Initial NH ₄ ⁺ -N in manure reactor	NH ₄ ⁺ -N volatilized in the air ^b	FA ^c	NH ₄ ⁺ -N recovery efficiency	Maximum NH ₄ ⁺ -N recovery rate	Average NH ₄ ⁺ -N recovery rate	Reference
Manure ^d	2310	187	45	91	412	148	García-Gonzalez and Vanotti, 2015
Manure ^e	3410	50	80	99	780	184	García-Gonzalez et al., 2015
Manure ^f	3930	220	40	93	810	172	García-Gonzalez et al., 2015
Digestate ^g	5581	1373	178	71	1244	405	This study

^aThe reactors in all referenced studies contained a 60 cm length polytetrafluoroethylene (ePTFE) membrane tubing with a 0.0323 m² surface area and were operated with a recirculation rate of 5.8 L d⁻¹. ^bNH₄⁺-N volatilized in the air was equal to initial NH₄⁺-N in manure minus the remained NH₄⁺-N in manure minus the NH₄⁺-N recovered in the acidic solution. ^cFA is the average of data collected during the experimentation time. ^dAlkali was added to manure to raise pH. Data are average of duplicate reactors during 30 days of experiment. Data expressed as NH₄⁺ in this publication was converted to NH₄⁺-N. ^eManure was aerated to raise pH. Data are average of duplicate reactors during 18 days of experiment. ^fAlkali was added to manure to raise pH. Data are average of duplicate reactors during 18 days of experiment. ^gAlkali was added to manure to raise pH. Data are average of duplicate reactors during 25 days of experiment (Table 2).

as mitigating NH₃ emissions when applying digestate to crops. In this sense, when GMPT is applied to digested manure, an important reduction of ammonia in the digestate is observed, recovering N for further use as fertilizer (NH₄)₂SO₄, while reducing the ammonia emission potential of digested manure.

Moreover, the final digestate pH was kept around 7.7-8.0 (Figure 3), which is convenient to incorporate the digestate into arable soils at the end of the anaerobic process. Another advantage of using the gas-permeable membranes was that soluble carbonaceous compounds did not pass through the membrane (Vanotti and Szogi, 2015). According to Table 1, while the NH₄⁺ was significantly reduced, TS, VS and CODt remained almost stable from the beginning to the end of the experiment.

The non-significant VS reduction was probably due to the anaerobic digestion process still occurring in the jars. This technology represents a good example of mitigation of environmental impacts caused by agriculture and nutrient recycling due to recovery of an end product (ammonium salt fertilizer) for agriculture application.

In summary, ammonia was successfully recovered from digestate using gas-permeable membranes. Removal and recovery efficiencies were 91 and 62 % respectively, being possible to increase this recovery efficiency

if the area of the membrane system is adjusted to maximize N recovery efficiency and to shorten N recovery time. Therefore, N recovery from digestate is a good strategy to reduce N contents in digestate effluents to be safely incorporated into arable soil in nitrogen vulnerable zones (NVZ).

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