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

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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 NH₄⁺, 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 NH₄⁺ concentrations higher than 3,000 mg L⁻¹ could cause obvious inhibition of methanogenesis. In another study, Hejnfelt and Angelidaki (2009) concluded that NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ 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 García-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
García-Gonzalez et al. 

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Hill, SC) was used for NH₃ 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 (Garcia-Gonzalez 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 NH₃⁺. 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 using a pH 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 NH₃⁺ (measured in the NH₃⁺ determination described above) (Hansen et al., 1998):

\[
\left[ \text{NH}_3^+ \right] / [\text{TNH}_3] = 1 + \left( \frac{10^{\text{pH} - 10^{-0.009125 + 2139927}}}{10^{-0.009125 + 2139927}} \right)^{-1}
\] (1)

Results and Discussion

NH₃⁺ concentration in digestate decreased from 4,293 ± 0 mg N L⁻¹ to 381 ± 55 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 NH₃ was recovered in the acidic solution. Similarly, NH₃⁺ 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 NH₃⁺ concentration in the recovery solution [11,200 ± 1,100 mg N L⁻¹] of almost three-fold higher than in digestate (4,293 mg N L⁻¹; Figure 1). Sixty-two percent of NH₃⁺ removed from digestate during the experimental period was recovered in the acidic solution. These findings are in agreement with those reported by Garcia-Gonzalez and Vanotti (2015) who observed a high N recovery from manure with different NH₃⁺ strengths using GPMT.

The rate of NH₃⁺ recovery was not linear and followed a 2nd-order curve (Figure 2), meaning that the NH₃ capture rate was higher during the first days, and decreased as it was being depleted from the manure.

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.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial</th>
<th>Final</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>8.01 (0)</td>
<td>8.11 (0.01)</td>
</tr>
<tr>
<td>CODt (g L⁻¹)</td>
<td>27 (1)</td>
<td>22 (0.23)</td>
</tr>
<tr>
<td>TS (g L⁻¹)</td>
<td>35 (0.32)</td>
<td>36 (0.54)</td>
</tr>
<tr>
<td>VS (g L⁻¹)</td>
<td>25 (0.33)</td>
<td>22 (0.20)</td>
</tr>
<tr>
<td>Pt (mg L⁻¹)</td>
<td>771 (3.54)</td>
<td>645 (1.06)</td>
</tr>
<tr>
<td>TKN (mg N L⁻¹)</td>
<td>4,690 (44)</td>
<td>1,244 (89)</td>
</tr>
<tr>
<td>NH₃⁺ (mg N L⁻¹)</td>
<td>4,293 (44)</td>
<td>381 (55)</td>
</tr>
<tr>
<td>NO₃⁻ + NO₂⁻ (mg L⁻¹)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO₃ L⁻¹)</td>
<td>19,038 (0)</td>
<td>8,923 (947)</td>
</tr>
</tbody>
</table>

Figure 1 – Removal of ammonia in digestate (△) by the gas membrane system and recovery and concentration in the acid tank (●). 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 mg N L$^{-1}$ 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 mg N L$^{-1}$ 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 keep 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 ± 947 mg CaCO$_3$ L$^{-1}$ (Figure 3).

In contrast with previous studies carried out with raw manure, both the maximum NH$_4^+$ recovery rate and 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 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$_2$O) emissions (Amon et al., 2006; Bacenetti et al., 2013; Nkoa, 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
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Table 2 − Mass balances of the recovery of nitrogen in digestate using gas-permeable membranes.\(^a\)

<table>
<thead>
<tr>
<th>Days in the batch(^b)</th>
<th>Initial NH(_4)^+N in digestate</th>
<th>Remained NH(_4)^+N in digestate</th>
<th>NH(_4)^+N removed from digestate(^c)</th>
<th>NH(_4)^+N recovered in the acidic solution</th>
<th>NH(_4)^+N removal efficiency(^d)</th>
<th>NH(_4)^+N recovery efficiency(^e)</th>
<th>Maximum NH(_4)^+N recovery rate(^f)</th>
<th>Average NH(_4)^+N recovery rate(^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First part (0-25 days)</td>
<td>5581 (0)</td>
<td>929 (240)</td>
<td>4689 (240)</td>
<td>3316 (308)</td>
<td>84</td>
<td>71</td>
<td>1244</td>
<td>405</td>
</tr>
<tr>
<td>Second part (25-32 days)</td>
<td>892 (240)</td>
<td>495 (71)</td>
<td>396 (169)</td>
<td>180 (85)</td>
<td>44</td>
<td>45</td>
<td>168</td>
<td>81</td>
</tr>
<tr>
<td>All (0-32 days)</td>
<td>5581 (0)</td>
<td>495 (71)</td>
<td>5086 (71)</td>
<td>3136 (308)</td>
<td>91</td>
<td>62</td>
<td>1244</td>
<td>324</td>
</tr>
</tbody>
</table>

\(^a\) 1.3 L of digestate in a 2 L vessel, using 280 ml 1 N H\(_2\)SO\(_4\) of acidic solution in the concentrator tank (recirculation rate = 5.8 L d\(^{-1}\)). \(^b\) Data 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). \(^c\) NH\(_4\)^+ removed from digestate = initial NH\(_4\)^+ in digestate − remained NH\(_4\)^+ in digestate. \(^d\) NH\(_4\)^+ removal efficiency = (NH\(_4\)^+ lost from digestate/initial NH\(_4\)^+ in digestate) × 100. \(^e\) NH\(_4\)^+ recovery efficiency = (NH\(_4\)^+ recovered in the acidic solution/ NH\(_4\)^+ lost from digestate) × 100. \(^f\) Highest NH\(_4\)^+ mass recovered in 1 day; 0.0323 m\(^2\) of membrane surface area.

Table 3 − Comparison of free ammonia (FA) and average NH\(_4\)^+ recovery rate by the gas-permeable membrane reactor in digestate and manure from previous studies.\(^a\)

<table>
<thead>
<tr>
<th>Type of wastewater</th>
<th>Initial NH(_4)^+N in manure reactor</th>
<th>NH(_4)^+N volatilized in the air(^b)</th>
<th>FA(^c)</th>
<th>NH(_4)^+N recovery efficiency</th>
<th>Maximum NH(_4)^+N recovery rate(^f)</th>
<th>Average NH(_4)^+N recovery rate(^f)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manure(^d)</td>
<td>2310</td>
<td>187</td>
<td>45</td>
<td>91</td>
<td>412</td>
<td>148</td>
<td>García-Gonzalez and Vanotti, 2015</td>
</tr>
<tr>
<td>Manure(^e)</td>
<td>3410</td>
<td>50</td>
<td>80</td>
<td>99</td>
<td>780</td>
<td>184</td>
<td>García-Gonzalez et al., 2015</td>
</tr>
<tr>
<td>Manure(^e)</td>
<td>3930</td>
<td>220</td>
<td>40</td>
<td>93</td>
<td>810</td>
<td>172</td>
<td>García-Gonzalez et al., 2015</td>
</tr>
<tr>
<td>Digestate(^f)</td>
<td>5581</td>
<td>1373</td>
<td>178</td>
<td>71</td>
<td>1244</td>
<td>405</td>
<td>This study</td>
</tr>
</tbody>
</table>

\(^a\) The reactors in all referenced studies contained a 60 cm length polytetrafluoroethylene (ePTFE) membrane tubing with a 0.0323 m\(^2\) surface area and were operated with a recirculation rate of 5.8 L d\(^{-1}\). NH\(_4\)^+ removed from digestate = initial NH\(_4\)^+ in digestate − remained NH\(_4\)^+ in digestate. NH\(_4\)^+ removal efficiency = (NH\(_4\)^+ lost from digestate/initial NH\(_4\)^+ in digestate) × 100. NH\(_4\)^+ recovery efficiency = (NH\(_4\)^+ recovered in the acidic solution/ NH\(_4\)^+ lost from digestate) × 100. \(^f\) Highest NH\(_4\)^+ mass recovered in 1 day; 0.0323 m\(^2\) of membrane surface area.

as mitigating NH\(_3\) 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 [NH\(_4\)]\_SO\(_4\), 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 NH\(_4\)^+ 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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References


