

RECOVERY OF AMMONIA FROM ANAEROBICALLY DIGESTED MANURE USING GAS-PERMEABLE MEMBRANES

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SUMMARY: The gas-permeable membrane process can recover ammonia from wastewater with high nitrogen load, 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. Different types of wastewaters can be used to recover N, among these wastewaters anaerobically digested swine manure (digestate) is one of those who contains more nitrogen. It is well known that high NH_3 content in swine manure reduce biogas production by anaerobic digestion inhibition, being one of the reasons to use different substrates to co-digest with manure. Hence, if a large quantity of NH_3 is removed during the anaerobic digestion process, inhibition caused by this compound will be minimized, improving anaerobic digestion and thus methane production. Moreover, final digestate pH is maintained around 7.7 to 8.0, which is convenient for the process or to incorporate in arable soil when the process is finished. As a result, the use of gas-permeable membranes to capture NH_3 from digestate could be used to improve anaerobic digestion process and methane production. In this work we studied the recovery of N using gas-permeable membranes from anaerobically digested swine manure with N content of $4,293\text{mgN-NH}_4^+ \text{ L}^{-1}$. Results showed a total N recovery efficiency of 62% during the 32-days experimentation, and that the recovery rate was higher during the first 25-days of experimentation, with 71% of the N recovered.

Keywords: Gas-permeable membranes, ammonia recovery, anaerobic digestion, manure management

INTRODUCTION

The anaerobic digestion process could be defined as the breaking-down of organic material in the absence of oxygen (Burton and Turner, 2003). Several reactions and microorganisms are involved in the process to carry out the different transformations. Mankind has used this process in order to obtain such benefits as energy or the cleaning of effluents from either anaerobic wastewater treatment plants or the digestion systems of solid wastes. There are many parameters affecting anaerobic digestion such as pH, temperature, volatile fatty acids and ammonia, among others. Ammonia is an important inhibitor in anaerobic digestion specially when treating manure; free NH_4^+ inhibits methanogenesis at initial concentration of $100\text{-}1100 \text{ mgNL}^{-1}$ (Angelidaki and Ahring, 1993). Thus the use of gas-permeable membranes is a good technology to recover NH_4^+ and avoid this inhibition; therefore, different strategies to reduce and recover ammonia from manure can be addressed: as recovery prior to anaerobic digestion, during the process or at the end of the process. In the present study, tubular gas-permeable membranes were used at the end of the anaerobic digestion process to evaluate NH_3 recovery from digestate at lab scale.

Gas permeable membranes

The gas-permeable membrane process includes the passage of gaseous NH_3 through a microporous hydrophobic membrane and capture and concentration in a

stripping solution on the other side of the membrane (fig. 1). The membrane manifolds are submerged in the liquid and the NH_3 is removed from the liquid before it escapes into the air (Vanotti and Szogi, 2011); the NH_3 permeates through the membrane pores reaching the acidic solution located on the other side of the membrane. Once in the acidic solution, NH_3 combines with free protons to form non-volatile NH_4^+ ions that are converted into a valuable NH_4^+ salt fertilizer.

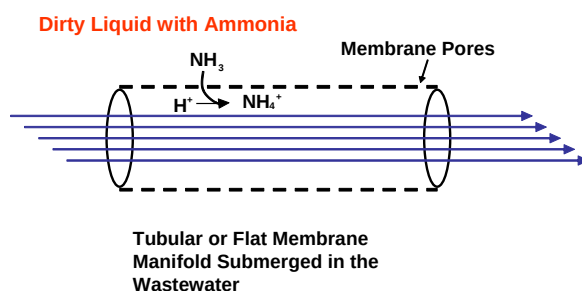


Figure 1. Longitudinal section of a hydrophobic gas-permeable membrane

MATERIAL AND METHODS

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. The acid tank consisted of 500-mL Erlenmeyer flasks containing 280 mL 1 N H_2SO_4 . A diaphragm pump (Alldos, TrueDos model, Denmark) was used to continuously circulate the acid through the tubular membranes inside the digestate vessels and back into the acid tank using constant flow rate of 5.8 L/day. Gas-permeable tubing (length 60 cm, outer diameter 10.25 mm and wall thickness 0.75 mm) made of expanded polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock Hill, SC) was used for NH_3 capture.

The experiment was carried out to evaluate nitrogen recovery from manure anaerobically digested. pH adjustment of the digestate was carried out. Adjustment consisted in increasing the digestate pH using sodium hydroxide (5 N), which was added as needed to endpoint pH 8.5-9.0 whenever the pH of the manure decreased below 7.7. Digestate samples from the vessels and acidic solution samples from the concentrator tank were withdrawn daily in order to monitor pH, alkalinity and NH_4^+ . In addition, initial and final samples of swine manure were analyzed in duplicate in accordance with APHA Standard Methods (1989) for pH, alkalinity, total solids (TS), volatile solids (VS), total chemical oxygen demand (CODt), NH_4^+ , total Kjeldahl nitrogen (TKN), nitrite (NO_2^-), nitrate (NO_3^-), and total phosphorous (Pt) determination. All experiments were carried out in duplicate and results are expressed as means.

RESULTS AND DISCUSSION

In the experiment using digestate to recover N, NH_4^+ concentration in digestate decreased from $4293 \pm 0 \text{ mgN/L}$ to $381 \pm 55 \text{ mgN/L}$ in the 32 days of the experiment (Fig. 2). Ammonia capture by the membrane continuously increased until day 25, from which point little or no more NH_3 was recovered in the acidic solution, although NH_4^+ in digestate continued diminishing at a steady rate until the end of the experiment (Fig. 2). It is important to emphasize that the acidic solution was the same during the entire experiment, thus the recirculation of this liquid in a closed loop between the treatment vessel and the acid tank achieved an NH_4^+ concentration in the recovery solution ($11200 \pm 1100 \text{ mgNL}^{-1}$) of almost three times higher than in the digestate (4293 mgN/L ; Fig. 2). The 62% of the NH_4^+ lost from the digestate during the experimental period was

recovered in the acidic solution. This findings are in agreement with the reported by García and Vanotti (2014) who observed a high N recovery from manure with different NH_4^+ strengths using the gas-permeable membrane technology.

The NH_4^+ recovery was not linear; it followed a 2nd-order curve (Fig. 3), meaning that the NH_3 capture rate was higher during the first days and decreased as it was being depleted from the manure (Fig. 3). As it occurred with swine manure, it was observed that when FA content in the manure was low NH_3 captured by the membrane diminished (García and Vanotti, 2014).

Most of the NH_3 recovery occurred during the first 25 days of the experimental period, with an average recovery rate of 405mgN/L/day and a high NH_4^+ recovery efficiency of 71%. The average recovery rate during the second part of the batch (25-32 days) was 81mgN/L/day and the corresponding NH_4^+ recovery efficiency was 45% of the remaining NH_4^+ . The inability of the membrane to recover N from day 25 to the end of the experiment can be explained by the NH_3 content in manure. The average free NH_3 in manure until the 25-day of evaluation was 178mgN/L, however from that day until the end of the experiment average free NH_3 in manure decreased to 69mgN/L. This means that NH_3 concentration in manure was low and it permeated slowly through the membrane. Therefore, it is necessary to maintain a high free NH_3 level to continuously recover N.

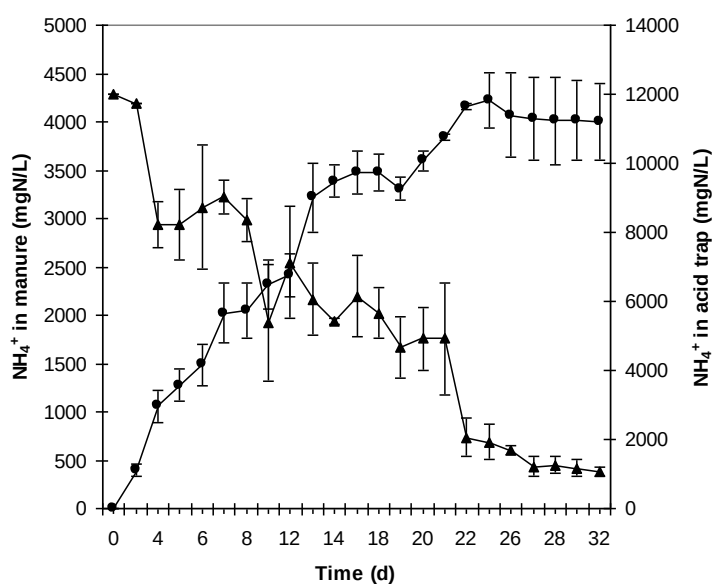


Figure 2. Removal of ammonia in digestate (▲) by the gas membrane system and recovery and concentration in the acid tank (●). The error bars are the standard deviation of duplicate experiments.

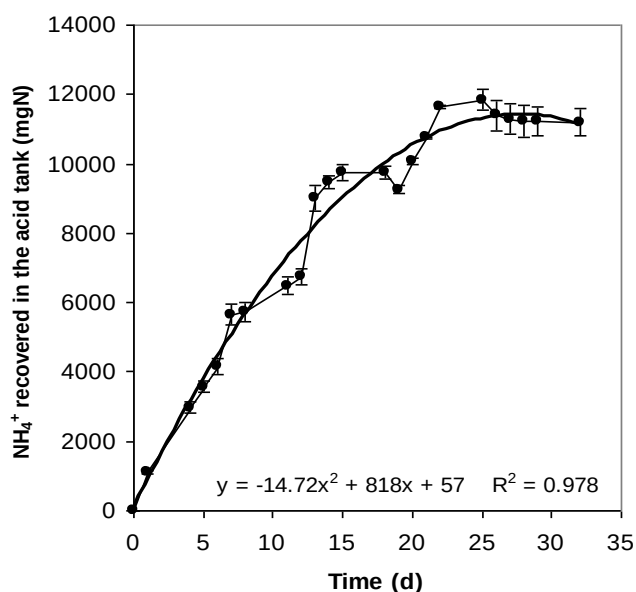


Figure 3. Mass of ammonia recovered in the acid tank. A 2nd order equation and R^2 are represented. The error bars are the standard deviation of duplicate experiments.

CONCLUSIONS

Ammonia was successfully recovered from digestate using gas-permeable membranes. Removal and recovery efficiencies were 91 and 62% respectively. Therefore, recovery of N from the digestate is a good strategy to reduce NH_4^+ in an anaerobic digester, avoiding inhibitions and reducing N in digestate that can be used to incorporate in arable soil.

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