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Removal and Recovery of Ammonia from Liquid Manure Using Gas-Permeable Membranes

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Abstract. *We investigated the use of gas-permeable membranes as components of a new process to capture and recover ammonia from liquid manures and other concentrated effluents. The process includes the passage of gaseous ammonia through a microporous hydrophobic membrane and capture and concentration with circulating diluted acid on the other side of the membrane. The membranes can be assembled in modules or manifolds and can be tubular or flat. The membrane manifolds are submerged in the liquid and the free ammonia is removed from the liquid matrix before it escapes into the air. The concept was successfully tested using concentrated swine manure effluents (digested and un-digested liquid manure) containing 300 to 1500 mg/L NH_4-N. After ten batches, the ammonia was recovered and concentrated in a clear solution containing 53,000 mg/L NH_4-N. Soluble compounds such as soluble COD did not pass through the membrane pores. The results obtained in this study show that the use of gas-permeable membrane technology could be an effective approach to recover ammonia from livestock wastewater. The final products are (1) reduced environmental emissions from livestock facilities, and (2) concentrated liquid nitrogen that can be re-used in agriculture as a valued fertilizer.*

Keywords. Gas-permeable membranes, ammonia recovery, manure effluents, mitigation of ammonia emissions in farms.

Introduction

One of the largest environmental concerns associated with livestock and poultry production is the loss of ammonia gas (NH_3) from the manure (Aneja et al., 2001, Paerl, 1997). The Research Triangle Institute International (RTI, 2003) estimated the monetized economic benefits to North Carolina households of changes in environmental quality resulting from the generalized adoption of alternative waste technologies (2,300 swine operations). Results indicated that adoption of technologies that provides a 50% reduction of NH_3 emissions account for an estimated benefit of $190 million/year in avoided human health impacts (RTI, 2003).

New waste management methods should protect the environment and allow manure management to switch back to a recycling view of manure handling (Martinez et al., 2009). Conservation and recovery of nitrogen (N) is important in agriculture because of the high cost of commercial NH_3 fertilizers. Thus, there is major interest from producers and the public on implementing best control technologies that would abate NH_3 emissions from confined livestock operations by capturing and recovering N.

Gas Permeable Membranes

Gas-permeable membranes have been used in biomedical engineering applications in membrane oxygenator devices to imitate the function of the lungs in cardiopulmonary bypass, to add oxygen to, and to remove carbon dioxide from the blood (Gaylor, 1988). Brose and Van Eikeren (1990) used gas-permeable membranes in a method for removal of toxic ammonia formed during the culturing of mammalian cells. We investigated the use of gas-permeable membranes as components of new processes to capture and recover ammonia from liquid manures.

Materials and Methods

The basic process includes the passage of gaseous ammonia through a microporous hydrophobic membrane and capture and concentration with circulating diluted acid on the other side of the membrane and production of a concentrated ammonium salt (Fig. 1). The membranes can be assembled in modules or manifolds. We found that both tubular and flat gas-permeable membranes are useful extracting ammonia from manures, but in this paper we only show tubular configurations. They were used to remove ammonia from liquid manures.

The enclosure consisted of a 2-L, polyethylene terephthalate (PET) plastic jar. The acid tank (Fig. 2) consisted of a 500-mL glass flask containing 300 mL 1N H_2SO_4. A peristaltic Manostat pump (Cole-Parmer,Vernon Hills, IL, USA) was used to continuously circulate the acid through the tubular membranes inside the chamber and back into the acid tank using flow rates of 70-80 mL day^{-1}. Gas-permeable tubing made of expanded polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock Hill, SC) was used in the interior of the chamber for NH_3 capture. The length of the tubing used in all experiments was 66 cm with inner diameter 5.25 mm and wall thickness 1.00 mm. The membrane manifolds were submerged in the manure liquid (1.8 L) and the free ammonia (FA or un-ionized form) was removed from the liquid matrix before it escaped into the air (Fig. 2). The concept was successfully tested in ten batches using liquid swine manure containing about 1500 mg/L NH_4-N. The same acidic solution was used in the consecutive batches. Concentrated acid was added to the acidic solution as needed when pH increased from <1 to about 2.

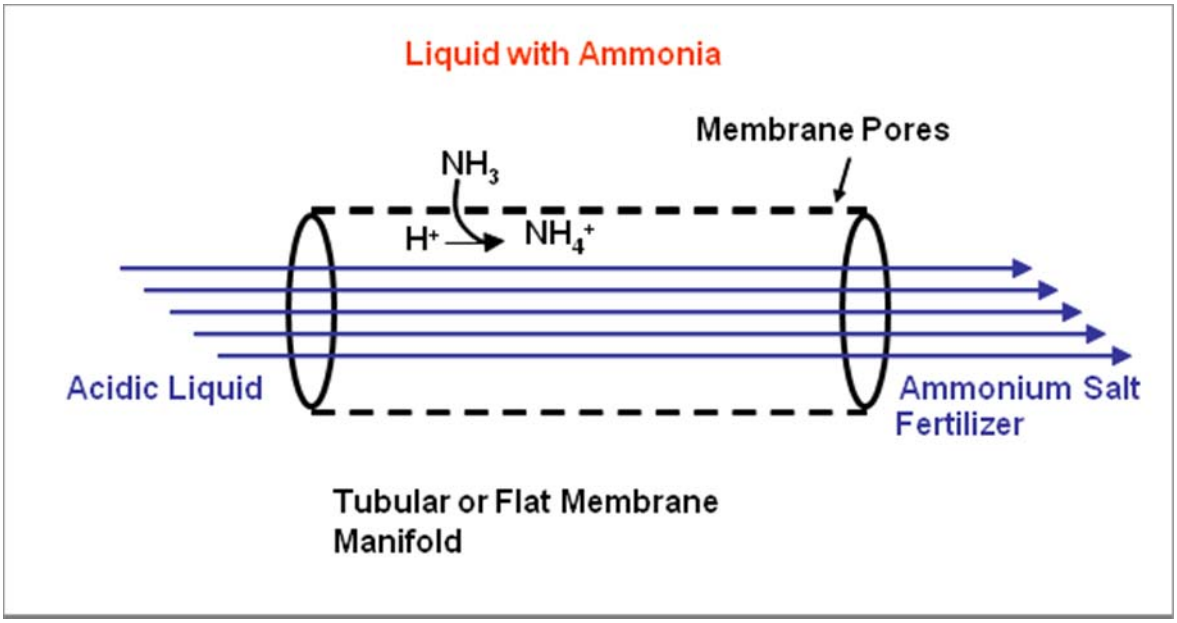

Figure 1. Cross-sectional diagram of ammonia capture using hydrophobic gas-permeable membrane. Ammonia gas (NH_3) in the liquid manure permeates through hydrophobic membrane walls with micron-sized pores, where it combines with the free protons (H^+) in the acid solution to form non-volatile ammonium ions (NH_4^+). Characteristics of flowing liquid can be modified to remove other volatile compounds (sulfide,VFA, etc).

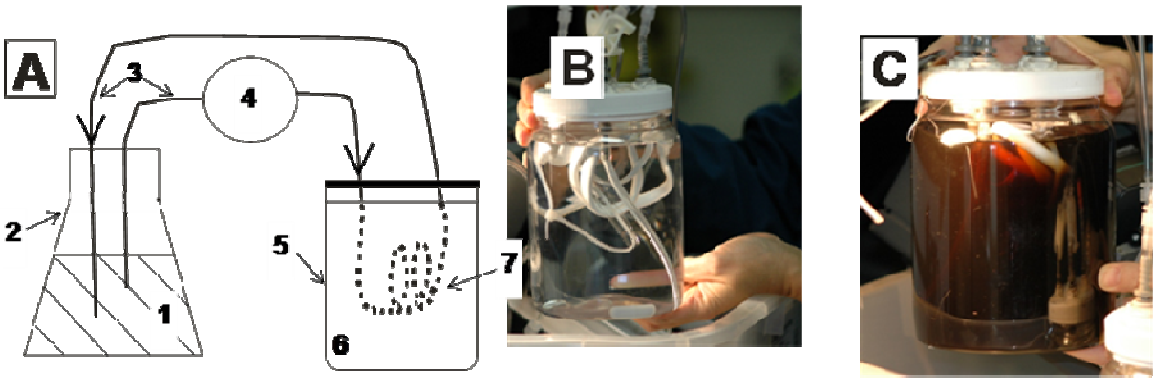

Figure 2. Ammonia capture and concentration from liquid. A. Schematic of ammonia (NH_3) capture from liquid manure using hydrophobic gas-permeable tubular membrane: 1. Acid solution (NH_3 Sink); 2. Container for acid solution; 3. Connecting tubing; 4. Fluid pump; 5. Tank with wastewater; 6. Liquid manure (NH_3 Emitting Source); 7. Hydrophobic, gas-permeable tubular membrane. B and C. Pictures of bench reactor with submerged membrane tubing, one submerged in water for illustration, and the other submerged in liquid swine manure used in the experiments.

Results and Discussion

The use of gas-permeable membranes to remove ammonia from liquid manure was effective. With the membrane manifold installed, in 9 days the NH_4-N concentration in the manure decreased about 50%, from 1,290 mg/L to 663 mg/L (Fig. 3). On the other hand, the NH_4-N concentration in the stripping solution was concentrated from 0 mg/L to 1950 mg/L during the same period. Data in Fig. 4 show that as ammonia was being removed from the liquid manure, the pH of the manure decreased, from 8.11 to 7.00. In the same 9-day treatment period, the free ammonia (FA) decreased 95%, from 1142 to 5.4 mg/L. Thus, a 50% decrease in the total ammonia concentration with the membrane module eliminated most of the free ammonia (FA). Therefore, the technology is useful to remove from liquid manure the free ammonia that is a portion of the total ammonia hat has been linked to ammonia emissions in swine farms (Szogi et al., 2006).

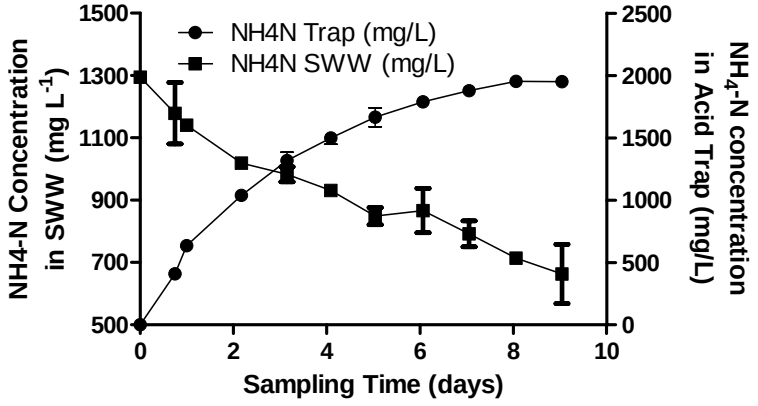

Figure 3. Removal of NH_4-N from swine wastewater (SWW) and recovery in the stripping solution (trap) using a gas-permeable membrane module.

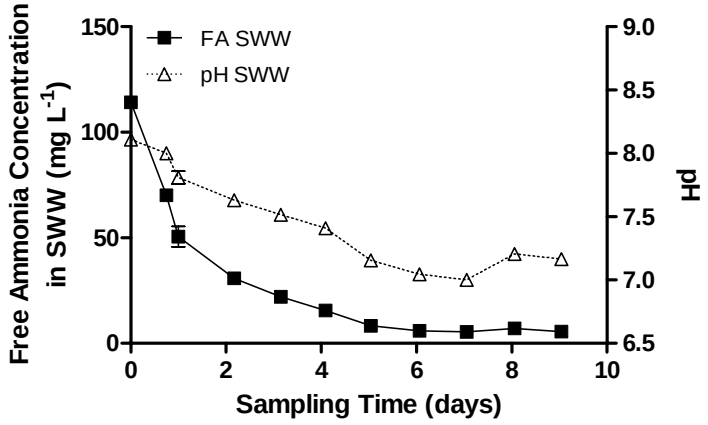

Figure 4. Removal of free ammonia (FA) from swine wastewater (SWW) using gas permeable membranes and changes in the pH of SWW.

We also evaluated application of alkali to the manure to increase pH and accelerate ammonia removal by the membranes. The alkali was applied at the end of batches 1-3 and at the beginning of batches 4-10 (Fig. 5). We used various process pH in the range of 9 to 12. With higher pH due to alkali addition, the ammonia in the liquid manure decreased faster and its recovery by the membrane system was quicker. After ten batches, the ammonia was recovered and concentrated in a clear solution containing 53,000 mg/L NH_4-N (Fig. 5). Soluble compounds such as soluble COD did not pass through the gas membrane, thus the concept represents an advantage for N removal from manure over biological systems.

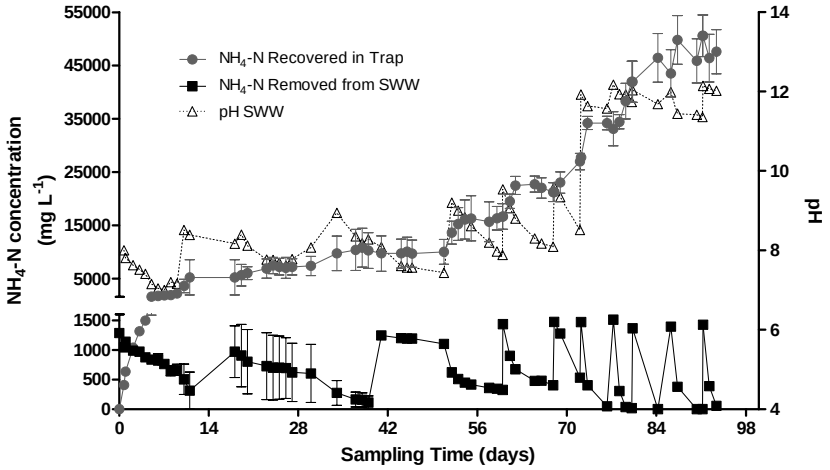

Figure 5. Removal of NH4-N from swine wastewater (SWW) in ten consecutive batches using gas permeable membranes and corresponding N concentration increase in the acidic solution (trap).

Conclusion

The results obtained in this study show that the use of gas-permeable membrane technology could be an effective approach to recover ammonia from swine wastewater and and other livestock operations. The final products are (1) reduced environmental emissions from livestock facilities, (2) cleaner air inside swine houses with benefits to animal health, and (3) concentrated liquid nitrogen that can be re-used in agriculture as a valued fertilizer.

Acknowledgements

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