APPLICATION OF GAS-PERMEABLE MEMBRANES FOR MITIGATION OF AMMONIA GAS FROM ANIMAL MANURE

A Dissertation

by

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ABSTRACT

Excessive ammonia (NH_3) emissions from animal feeding operations are reported as a source of environmental pollution. Moreover, NH_3 emissions result in the loss of nitrogen (N) as a plant nutrient, and so its mitigation and capture is beneficial to the environment. In laboratory study, acrylic chambers were filled with liquid dairy manure (LM) at a constant depth as a source of total ammoniacal nitrogen (TAN). Four chamber sizes (one size per experiment) labeled 1X, 2X, 4X and 8X were used to vary the surface area of LM while the depth of LM was kept constant in all chambers. Identical tubular gas-permeable membrane (GPM) systems were used in each chamber and allowed NH_3 diffusion from LM into the GPM system and produced an ammonium sulfate ($(NH_4)_2SO_4$) by-product (ASB).

A concentrated H_2SO_4 (pH=0.36) was circulated through the GPM systems of the chambers. The 4X chamber resulted in the best NH_3 mitigation and recovered the most concentrated ASB, but its final pH was 0.67 and not applicable as a plant nutrient. The H_2SO_4 solution was diluted to pH 2, 3, 4, and 5 and circulated in the 4X chamber. Results showed that NH_3 was recovered by diluted acids but the pH 2 experiment produced more concentrated ASB. The NH_3 flux and its mass transfer coefficient were calculated and the values showed that NH_3 diffusion occurred during the entire period of the experiments due to NH_3 gas partial pressure gradient and the solution circulation flow rate.

For increasing the ASB concentration, the circulation flow rate of the diluted acidic solution was increased and its pH was controlled between 2 and 6. The overall flow rate was increased from 5.6 to 36 and from 40 to 280 mL min^{-1} in the lab-scale and field-scale experiments, respectively, that enhanced the overall ASB concentration up to 50%.

Finally, the recovered ASB from diluted acid experiments was used in greenhouse wheat seed cultivation tests and compared to inorganic $(NH_4)_2SO_4$. The ASB treatments increased wheat germination, biomass, dry mass, biomass per plant and dry mass per plant, especially when the soil pH was adjusted between 5.6 and 6.

DEDICATION

This dissertation is dedicated to my wife, Mrs. Katayoon Keyhanian, my daughter, Nargis, and my parents, Mrs. Zohreh Adelnia and Mr. Khodamorad Samani Majd.

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CHAPTER I

INTRODUCTION

Introduction

Ammonia (NH_3) is a colorless pungent gas generated mostly by anthropogenic activities as a result of nitrogenous substance decay and decomposition. Almost 90% of anthropogenic NH_3 emissions are from agricultural facilities and animal feeding operations (AFOs) such as densely housed flocks of birds, dairies, cattle and swine farms, manure storages, and also, from applied fertilizers in field and plant cultivation (Hiranuma *et al.*, 2010; Hristov *et al.*, 2011). Ammonia release from AFOs is one of the major air quality problems in agriculture. The emitted NH_3 may contribute to the formation of fine particulate matter in the presence of certain acidic compounds in the atmosphere (Hristov *et al.*, 2011). Also, NH_3 deposition causes eutrophication of water bodies and contamination of groundwater. Ammonia may even be an initiation of nitrous oxide, a potent greenhouse gas (Aneja *et al.*, 2008; Fenn *et al.*, 2003; Hristov *et al.*, 2011). Excessive emissions of NH_3 from AFOs also result in the loss of a valuable nutrient for plants (Sakirkin *et al.*, 2011). High concentration of NH_3 is reported as a toxic component with adverse health effect on the workers and animals in the AFOs (Donham *et al.*, 2008; Schneider *et al.*, 1994). Higher NH_3 concentrations in an animal body elevate the glutamine concentration in the cells and improve the antibody production and decrease the growth rate of animal (Schneider *et al.*, 1994). Increasing public concerns over environmental impacts of NH_3 emission made US lawmakers

establish a corresponding rule for NH_3 emissions from livestock facilities. The federal rule set in 2009 requires reporting of NH_3 emission from AFOs in quantities ≥ 45 kg within any 24 hr period. This act is known as the Emergency Planning and Community Right-to-Know Act or EPCRA (Mukhtar and Auvermann, 2011).

The physical characteristics of NH_3 are important based on its molecular polarity. The molecular geometry of NH_3 has a trigonal pyramidal shape with 101.7 pm edge dimension and 107.3 degree of vertices. Thus, NH_3 is highly soluble in water (47% at 0^oC and 31% at 25^oC) and so the ammonium hydroxide (NH_4OH) is a solution of NH_3 and H_2O (eq. 1). Furthermore, the gaseous molecule of NH_3 can be dissolved (with no chemical bond) in water as $NH_{3(aq)}$ or emitted as $NH_{3(g)}$. The total concentration of $NH_{3(aq)}$ and $NH_{3(g)}$ is recognized as free NH_3 (FA) concentration.

$$NH_3+H_2O \leftrightarrow (NH_4)\,OH \quad (1)$$

At the AFOs, animals excrete a significant amount of manure in the forms of solid (feces) and liquid (urea) manure. The microbial processes (hydrolyzing and catalyzing) of urea and uric acid of the manure produce ammonium (NH_4^+). The aqueous NH_4^+ may be converted to NH_3 based on equation 2 depending on pH and temperature of the NH_4 and NH_3 sources. Thereafter, NH_3 can be emitted from the liquid or the solid part of animal excreta (Hiranuma *et al.*, 2010; Ni *et al.*, 2011).

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad (2)$$

Ammonia and NH_4^+ are the total ammoniacal nitrogen (TAN) in gaseous and aqueous phases, respectively. In an aqueous solution, they are in equilibrium (fig. 1), depending on pH and temperature (Emerson *et al.*, 1975; Ni *et al.*, 2011). Equation 3

illustrates the equilibrium between NH_3 and NH_4^+ in a solution based on the pH and the temperature of the TAN source. Then, NH_3 production and emission will result in decreasing pH of the solution since more hydrogen ion (H^+) is being produced at the same time.

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad (3)$$

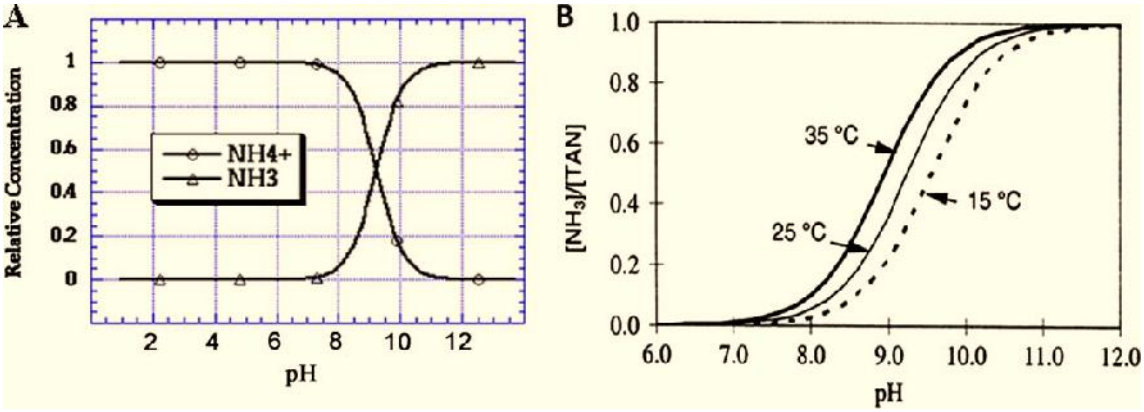


Figure 1. TAN equilibrium in aqueous solution based on pH and temperature (Reprinted from Hristov et al., 2011).

In the presence of an acidic solution such as H_2SO_4, NH_3 reacts with the acid (eq. 4) and converts it to $(NH_4)_2SO_4$, a potential useful by-product with valuable nutrients (Boswell and Friesen, 1993; Chien *et al.*, 2011a; Semmens *et al.*, 1990).

$$2NH_3 + H_2SO_4 \leftrightarrow (NH_4)_2SO_4 \quad (4)$$

Ammonia emissions from manure storage systems are important since it is not only an environmental issue but also losing a significant amount of excreted nitrogen that might be a nutrient for plants. In an anaerobic lagoon, the nitrogen loss may reach to

85% because of gaseous emission, especially NH_3 emission (EPA, 2004; MWPS, 2001; Vaddella *et al.*, 2012). Hence, prevention of NH_3 emission and capturing it is beneficial for environmental protection and using captured NH_3 as a plant nutrient may be an offset for the cost of commercial fertilizer on the farm.

The significance of NH_3 emissions to air quality led researchers to explore and develop different abatement technologies for various NH_3 emission sources (Ullman *et al.*, 2004). One of the practical options to decrease NH_3 concentration in the poultry houses is increasing ventilation rate of air exchanged between inside and outside air (Rothrock *et al.*, 2010). However, this option is limited to closed buildings and by the higher cost of ventilation. Also, it is still releasing NH_3 in the air and lacking in capturing and recovering NH_3. Next option might be air scrubbers capable to remove and capture emitted NH_3 from the confined animal feeding operations (CAFOs). Different types and styles of air scrubber such as spray, packed bed scrubbers (Melse and Ogink, 2005), cyclonic spray and venturi scrubbers (Cooper and Alley, 2011) have been developed. Yet, high operation costs and suitable specific scrubbing solution circulation system such as concentrated acidic solution are required for this technology (Manuzon *et al.*, 2007; Ocfemia *et al.*, 2005). Although filters are the most common air cleaning technologies and can capture dust with attached NH_3 molecules (Ullman *et al.*, 2004), they are not efficient in removing NH_3 from air. Biofilters may provide more effective solution for NH_3 removal under the category of filters but at very low ventilation rates (Hartung *et al.*, 2001). Chemical oxidants such as ozone, chlorine, potassium permanganate and chlorine peroxide are the other option for oxidizing NH_3 to

nitrate and decreasing its concentration before emission. Also, some other chemical amendments like aluminum sulfate and sodium biosulfate may be mixed directly into the solid manure and prevent NH_3 volatilization by slowing down the microbial process (Heber *et al.*, 2000; Rothrock *et al.*, 2010). However, the chemicals do not perfectly mitigate NH_3 emissions and may negatively impact the environment.

Gas separation using polymeric gas-permeable membranes is a recently developed technology to remove NH_3 gas from TAN sources and recover it as a recipient (EL-Bourawi *et al.*, 2007; Mukhtar *et al.*, 2011; Rothrock *et al.*, 2010). The technology is working based on gas diffusion principles and due to liquid surface tension. The size of pores on membranes in contact with the liquid molecule would create a strong molecular bond film which would not let the liquid molecule pass through. However, the dissolved gas molecule would evaporate and penetrate through the membrane. This is technology is applicable to both liquid and solid TAN sources with no environmental impact that can remove NH_3 from the source and recover that in a solution. Application of each method depends on the quantity and quality of the source of NH_3 emission, contamination level, environmental conditions and type of manure handling and storage systems (Cook *et al.*, 2008; EL-Bourawi *et al.*, 2007; Rothrock *et al.*, 2010; Semmens *et al.*, 1990; Szogi *et al.*, 2006; Ullman *et al.*, 2004).

The process of NH_3 mitigation using gas-permeable membranes is correlated to the diffusion parameters including NH_3 concentrations of the TAN source (Rothrock *et al.*, 2010; Vanotti and Szogi, 2010), membrane structure and morphology (Kong and Li, 2001; Li *et al.*, 2000; Tang *et al.*, 2007), temperature of the TAN solution, flow rates of

the solutions (Ahn *et al.*, 2011; Schneider *et al.*, 1994; Semmens *et al.*, 1990) and pH conditions of the source (Ahn *et al.*, 2011; Rothrock *et al.*, 2010).

The goal of this study was to assess the efficacy of extracting NH_3 from LM using a sulfuric acid-filled GPM system and to investigate the use of recovered NH_3 as a plant nutrient. To achieve the goal of this study, the following hypotheses were tested and results are discussed in chapters II to V.

I. Acid-filled tubular GPM system might remove and capture NH_3 from liquid dairy manure.
II. The captured and recovered NH_3 in an acidic solution ($(NH_4)_2SO_4$) would be a new plant nutrient option.
III. Optimized lab-scale parameters might be applicable for scaling up to the pilot-scale under field conditions.

Detailed Literature Review

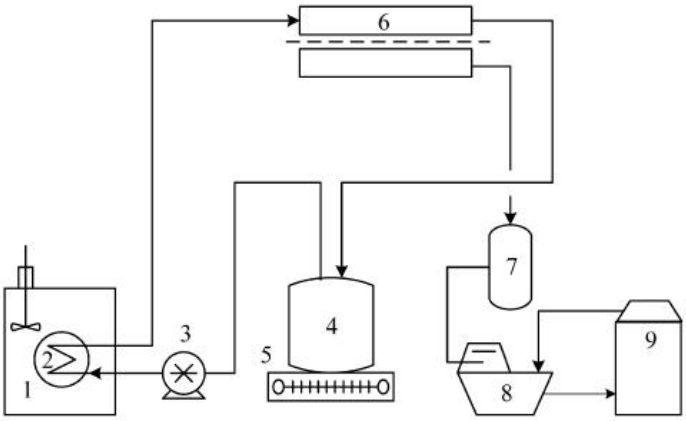
The technology of gas separation using synthetic membranes has been developed since the middle of the twentieth century in order to separate specific gases and volatile components such as nitrogen, oxygen, hydrogen, methane and NH_3 from gas mixtures or solutions. Polymeric textured GPMs are the most common membranes used for gas separation in medicine and industry such as blood oxygenators and filtrations; respectively. A variety of polymeric membranes including polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polyvinylidene fluoride (PVDF), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA), ethylene-tetrafluoroethylene (ETFE), polyetheretherketone (PEEK), polytetrafluoroethylene

(PTFE) and expanded polytetrafluoroethylene (ePTFE) have been extruded for different applications (Baker, 2012; Zeus, 2011). Regardless of the material used in the GPMs, they operate the gas separation process based upon the gas diffusion from the gas source into the membranes and capturing the gas molecule on the other side of the membrane by an apparatus or a recipient solution.

The PTFE and ePTFE membranes are the most commonly used membranes for gas diffusion NH_3 extraction from TAN sources (Moskvin and Nikitina, 2004). These synthetic membranes are hydrophobic and can be constructed in different configurations as hollow fiber, tubular, flat sheet and spiral-wound cylinders. Selection and application of these membranes depends on their flexibility, texture, resistance against fouling, as well as their costs and accessibilities. The diffusion performance of the PTFE and ePTFE membranes was discussed in the literature using various set-ups in order to investigate the effective diffusion parameters (Baker, 2012; Hwang and Kammermeyer, 1975; Moskvin and Nikitina, 2004). The PTFE material (Teflon) was invented in 1938 and then formed as a PTFE tape in 1966. In 1969, expanded polytetrafluoroethylene (ePTFE) was discovered and patented later under the trademark of Gore-Tex (Gore, 1976, 1980). The porous PTFE/ePTFE membranes have a wide variety of industrial and medical applications including air and liquid filtration and purification, substances sensation and measurement, vascular draft, cardio vascular patch and suture stitching (Kramer and G., 2002; Zeus, 2011). The earliest investigation of extracting and capturing NH_3 gas with the tubular GPM method using PTFE membrane was published in 1982 (Blet *et al.*, 1989; Imai *et al.*, 1982). More recently, the PTFE/ePTFE

membranes were used to remove NH_3 from poultry litter, liquid swine manure and synthetic TAN solution (Ahn *et al.*, 2011; Rothrock *et al.*, 2010; Vanotti and Szogi, 2010).Overall, two approaches have been proposed to extract NH_3 from TAN sources using GPM systems. The first approach of NH_3 extraction was based on a vacuum membrane distillation (VMD) system. Figure 2 illustrates two examples of this method for NH_3 gas extraction from liquid with a permeable membrane between the feeding system and vacuum system (Ding *et al.*, 2006; EL-Bourawi *et al.*, 2007).

(A)



(B)

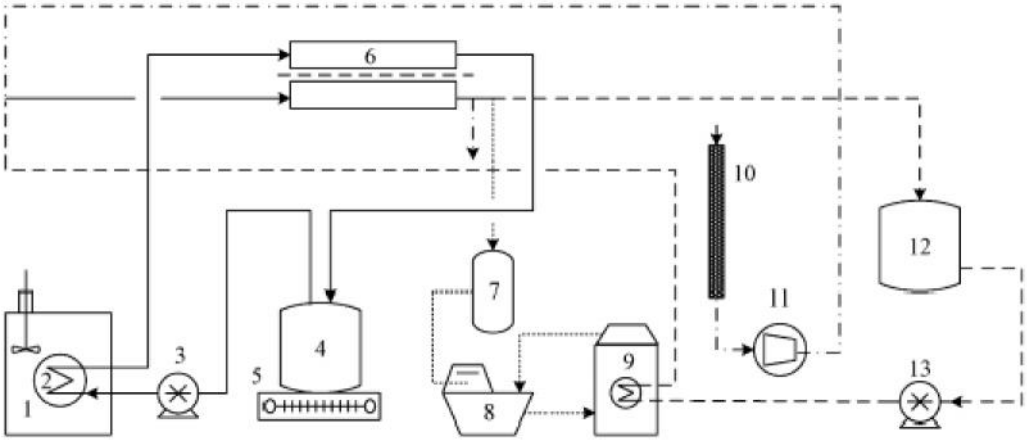


Figure 2. Schematic design of a vacuum membrane distillation (VMD) system for NH_3 removal, (A) 1-4, feeding system; 5, electric balance; 6, flat sheet membrane module; 7, buffer tank; 8, vacuum pump; 9, chiller (Reprinted from EL-Bourawi *et al.*, 2007); (B) 10, pipe for air drying; 11, air fan; 12-13, permeate tank and pump (Reprinted from Ding *et al.*, 2006).

EL-Bourawi*et al.*,(2007) used a flat PTFE membrane and showed that the vacuum pressure, high temperature and initial concentration of the feed, and pH levels enhanced the NH_3 removal efficiency; however, the research pointed out that NH_3 removal using VMD approach was difficult and inefficient especially with no pH

adjustment. Also, Ding *et al.*(2006) used PTFE membrane in the concept of VMD approach and showed that the membrane characteristics was important for increasing NH_3 removal efficiency in addition to EL-Bourawi *et al.*(2007) findings. Increasing the feed temperature up to 57°C was the key point in improving the NH_3 removal efficiency by this approach. But, the temperature increase of the TAN source was just applicable in lab research and would not be practical for the actual field implement.

The second approach of NH_3 removal utilizing GPM systems was designed by using a recipient solution circulation system through or around PTFE or ePTFE GPM systems (fig. 3).The main idea of this approach was to extract NH_3 gas by circulating a recipient solution into or outside a GPM system immersed in a TAN source. Also, the extracted NH3 can be captured in a recipient solution for further application. The driving force for gas diffusion through the membrane was the gas concentration gradient on both sides of the membrane. The NH_3 gas concentrations across the membrane were also due to gas partial pressure identified by Henry's law (Ahn *et al.*, 2011).

Ahn *et al.*(2011) used a membrane module consisted of a tubular PTFE membrane installed in an enclosed polypropylene vessel (fig. 3(A)). Synthetic NH_3 solutions were fed into the tubular membrane and concentrated H_2SO_4 solutions (10%, w/w with nearly zero pH) were supplied on the outside of the membrane flowing in the opposite direction of the feed flow. The initial $NH_3$and suspended solid concentrations were altered from 250 to 1000 mg L^{-1}, NH_3 solution flow rate (10 and 20 mL min^{-1}) and recipient solution flow rate (8 and 16 mL min^{-1}) in order to evaluate the mitigation process. Likewise in figure 3(B), Schneider *et al.*(1994) utilized a tubular PTFE

membrane in a synthetic NH_3 solution reactor and investigated the effective parameters. The initial NH_3 concentration was varied from 34 to 51 mg L^{-1} and a concentrated phosphoric acid solution (5 M with very low pH) was circulated into the membrane in a reactor. The PTFE membrane (fig. 3(C) and fig. 3(D)) was also used by Blet *et al.*(1989) and Imai *et al.*(1982) to mitigate NH_3 from synthetic TAN solution with the initial concentration of 170 mg L^{-1} and 170-1700 mg L^{-1}, respectively. Blet *et al.* (1989) used a more diluted solution with pH 5 and Imai *et al.* (1982) implemented a more concentrated H_2SO_4 solution with pH 0.69 to 1.69.

The most recent NH_3 mitigation research using an ePTFE membrane was conducted for the actual application (Rothrock *et al.*, 2010; Vanotti and Szogi, 2010) to remove NH_3 from poultry manure and liquid swine manure, respectively. Figure 3(E) and figure 3(F) show the set-ups with circulating concentrated solution (pH = 0.32). Both research verified that NH_3 can be extracted by the ePTFE membrane from the air above the poultry litter and from the liquid swine manure (as the TAN sources) and recovered in the H_2SO_4 solution. In those investigations, the pH of TAN sources was increased up to 12 to increase the NH_3 removal efficiencies.

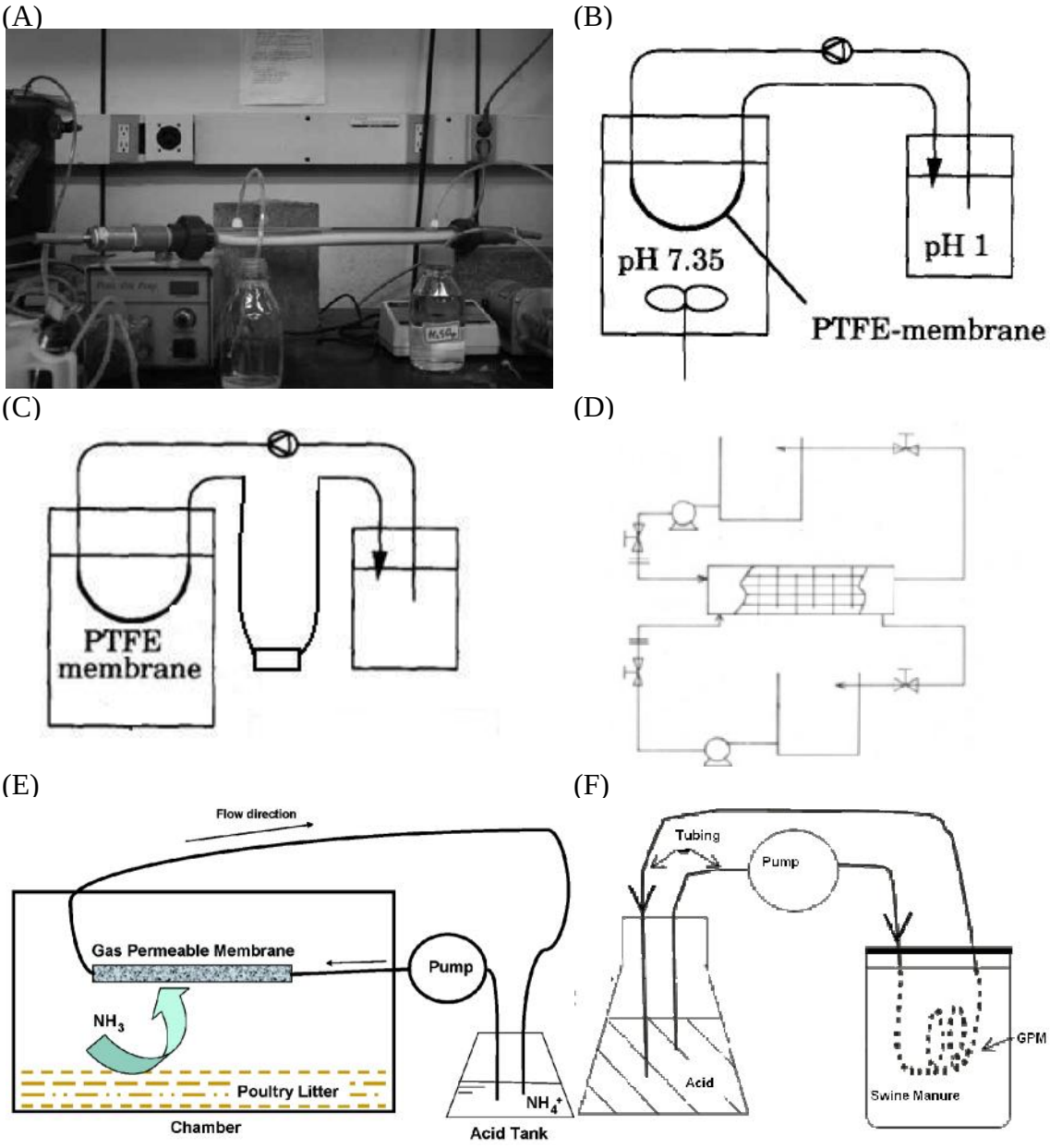


Figure 3. Experimental designs for NH_3 removal using PTFE or ePTFE membranes (A) Lab scale membrane contactor for removing NH_3 from synthetic NH_4^+ solution using PTFE membrane (Reprinted from Ahn *et al.*, 2011) (B) An NH_3 reactor using a tubu1ar PTFE membrane (Reprinted from Schneider *et al.*, 1994). (C) The capturing process from an ammonium solution using PTFE membrane (Reprinted from Blet *et al.*, 1989). (D) A tube-bundle PTFE GPM system (Reprinted from Imai *et al.*, 1982). (E) Schematic diagram of the capturing process from the poultry litter using ePTFE membrane (Reprinted from Rothrock *et al.*, 2010). (F) Schematic diagram of the capturing process from the swine liquid manure using ePTFE (Reprinted from Vanotti and Szogi, 2010).

Research Gaps

The literature showed that a tubular GPM system was feasible for extracting NH_3 gas from an aqueous synthetic NH_3 solution, poultry litter and liquid swine manure. However, NH_3 mitigation of liquid dairy manure (LM) using GPM had not been studied. The investigation on LM was important because of the complexity of ionization in liquid manure (Semmens *et al.*, 1990) and also its solid contents that might potentially clog the membrane pores (Jones *et al.*, 2006). Also, there are few other research gaps between the previous investigations as follows:

- Is the mitigation process feasible for NH_3 extraction from LM as a source of TAN?
- What are the effective parameters in the mitigation process?
- Assuming the feasibility of the mitigation process, what is the efficacy of the process for different situations? And how it can be determined?
- What is the most efficient set-up for the process in bench-scale experiments?
- What is the optimum pH value of acidic solution?
- What are the properties of the by-product of the recovery process ($(NH_4)_2SO_4$)? And, can it be used as a plant fertilizer?
- Is it possible to upscale the results from the most efficient set-up to a pilot-scale?

CHAPTER II

AN INVESTIGATION OF A GAS-PERMEABLE MEMBRANE SYSTEM FOR REMOVAL AND RETENTION OF AMMONIA FROM LIQUID DAIRY MANURE[*]

Overview

Pollution of air, soil and water caused by excessive ammonia (NH_3) emission and deposition from animal manure is as an environmental concern. Gas-permeable membranes (GPM) may provide a solution for controlling NH_3 emission to the environment by extracting it from liquid manure and potentially using the recovered NH_3 as nutrients. For this purpose, three lab-scale experiments were conducted to investigate the capture and recovery of NH_3 from liquid manure by circulating an acid solution through a tubular GPM submerged into the liquid dairy manure. During these experiments, the depth of liquid manure in chambers of different dimensions and the tubular membrane parameters including diameter, length and pore size were held constant in order to study the effect of acid-filled membrane on NH_3 extraction from different surface areas (1X, 2X, 4X and 8X) of liquid manure. Results showed that nearly 50% of the liquid manure NH_3 measured prior to the start of each experiment from all was captured in less than 20 days by acid-filled membranes. Also, NH_3 extraction by the GPM system from liquid manure and NH_3 gain in acidic solution were

[*] Reprinted with permission from "An Investigation of Ammonia Extraction from Liquid Manure Using a Gas-Permeable Membrane" by Mukhtar S., A. M. Samani Majd, M. S. Borhan and J. F. Beseda II, 2011. 2011 ASABE Annual Meeting, Louisville, KY, Copyright 2011 American Society of Agricultural and Biological Engineers.

linearly correlated. The study showed that the experiment with the 4X chamber resulted in optimum NH_3 extraction using the GPM system.

Introduction

Excessive ammonia (NH_3) emissions from animal feeding operations (AFOs) are considered a source of odor and environmental pollution (Mukhtar *et al.,* 2008; Ni *et al.,* 2011; Zhang *et al.*, 2005). Once emitted, NH_3 may contribute to formation of fine particulate matter in the presence of certain acidic compounds in the atmosphere. Deposition of NH_3 may cause eutrophication of water bodies and contamination of ground water and may even be a constituent of nitrous oxide, a potent greenhouse gas (Fenn *et al.*, 2003; Hristov *et al.*, 2011; Ni *et al.*, 2011; USEPA, 2004). Excessive emissions of NH_3 from AFOs also result in the loss of a valuable nutrient for plants. Hence, prevention of excessive emission of NH_3 and capturing it is beneficial for environmental protection and using captured NH_3 as plant nutrients may potentially offset cost of commercial fertilizer on the farm (Hristov *et al.,* 2011; Rothrock *et al.*, 2010).

In liquid manure and other organic waste effluents, a balance or equilibrium exists between NH_3 and NH_4^+ [$H^+ + (NH_3) \leftrightarrows (NH_4^+)$], depending on the pH and temperature of the liquid (Emerson *et al.*, 1975; Ni *et al.*, 2011). The effect of temperature on the equilibrium is negligible for laboratory experiments; however, the pH causes a great difference on NH_3/NH_4^+ equilibrium. At pH greater than 6.8, NH_4^+ in

solution dissociates partly and converts to NH_3 gas. The concentration of NH_4^+ will decreases to zero if the pH exceeds 12 (Blet *et al.*, 1989).

Several technologies and approaches have been reported in the literature for capture and/or recovery of NH_3 such as using acidic solution-sprayed scrubbers, bio-filters, chemicals such as acidified clays or sodium bisulfate ($NaHSO_4$) and gas-permeable membranes (GPM). Application of each method depends on the source of NH_3 emission, contamination level, environmental conditions and type of manure handling and storage systems (EL-Bourawi *et al.*, 2007; Melse and Ogink, 2005; Szogi *et al.*, 2006; Ullman *et al.*, 2004).

Various techniques have been used based on the main concept of NH_3capturing by the GPM. Imai *et al.* (1982), Blet *et al.* (1989), Rothrock *et al.* (2010) and Mukhtar *et al.* (2011) used an acid-filled GPM to extract and recover NH_3 gas from either an aqueous buffer NH_3 solution or manure. Alternatively, Semmens *et al.*(1990) demonstrated extraction and recovery of NH_3 gas from a TAN filled membrane in an acidic solution surrounding the membrane. Although these membranes were introduced in the early 1970s (Imai *et al.*, 1982; Santiagodelpin and Aviles, 1980), their novel application in the area of gaseous pollutants was developed recently to remove NH_3 from poultry litter and liquid manure (Mukhtar *et al.*, 2011; Rothrock *et al.*, 2010).

When NH_3 is captured in an acidic solution such as sulfuric acid (H_2SO_4), NH_3 reacts with the acid and forms the ammonium ion (eq. 5), in this case ammonium sulfate [$(NH_4)_2SO_4$], a useful by-product (Boswell and Friesen, 1993; Chien *et al.*, 2011a).

$$2NH_3 + H_2SO_4 \leftrightarrows (NH_4)_2SO_2 \qquad (5)$$

While GPM techniques to extract NH_3 from different sources including poultry litter and synthetically produced ammonia have been used in the past (Ahn *et al.*, 2011; Rothrock *et al.*, 2010), this study was conducted to extract and capture it from liquid dairy manure (LM) with higher fiber content and hence greater sealing potential of the membrane walls than swine and poultry manure (Jones *et al.*, 2006). It was expected that due to these concerns, micro pores of membrane walls in contact with LM could clog thereby reducing its diffusion efficiency. Additionally, this study was conducted to determine the optimum ratio of surface areas between the LM and the membrane for maximum removal and recovery of NH_3 from LM and from the headspace. To date, no information on removal of NH_3 from liquid dairy manure using the GPM system is available in the literature. The goal of this lab-scale study was to assess the efficacy of extracting NH_3 from liquid dairy manure (LM) and from the air in the headspace above the LM using sulfuric acid-filled GPM systems.

Materials and Methods

The schematic diagram in figure 4 describes NH_3 extraction process from LM. By pumping H_2SO_4 solution with a peristaltic pump into the GPM system, the acidic solution extracts free NH_3 gas, due to the reaction in equation 5. This method of NH_3 extraction was tested in laboratory experiments to investigate the influence of different parameters on the efficacy of the process. These parameters included pH and NH_3 concentration of acidic solution, pH and NH_3 concentration of LM, surface areas of GPM and LM in the chamber.

Four chamber sizes (one size per experiment) labeled 1X, 2X, 4X and 8X (fig. 5(A)) were used to vary the surface area of LM against the constant surface area of the GPM system while the LM depth was constant in all chambers. As shown in table 1, the surface area of LM in chamber 1X was equal to 184 cm^2 and LM surface areas in chambers, 2X, 4X and 8X were two, four and eight times greater than the surface area of LM in chamber 1X, respectively. Additionally, one 4X chamber filled with the LM from the same manure source was added as a control (not treated with the GPM system) for NH_3 extraction experiments with the 4X chamber. All chambers were fabricated using Plexiglas, except Chamber 1X, which was a glass jar. These experiments were set up to mimic NH_3 removal and capture from manure storage facilities.

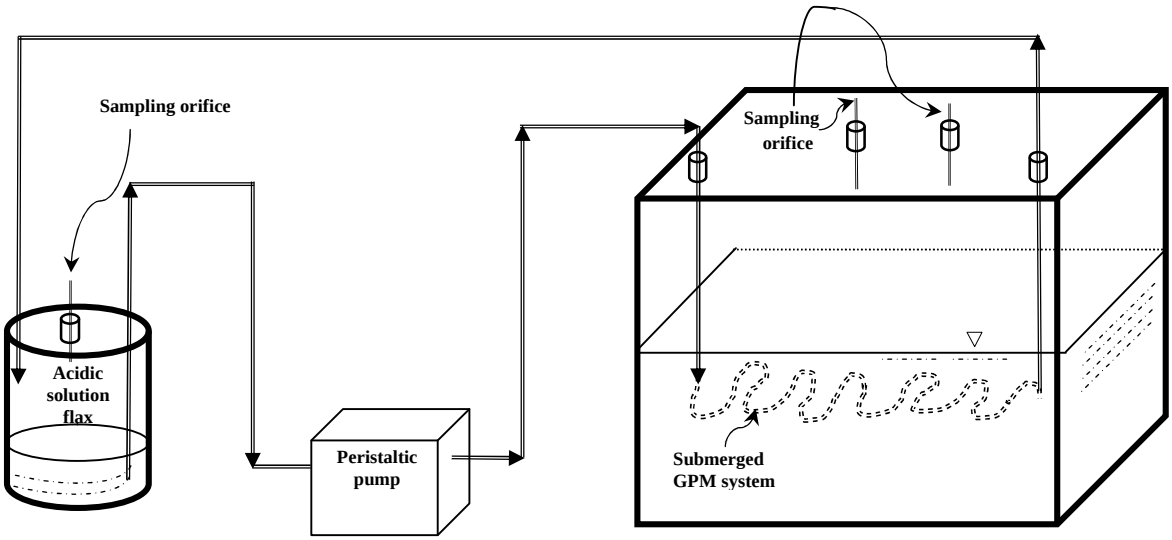


Figure 4. Schematic diagram of NH_3 extraction process from LM using a GPM system.

(A) **(B)**

Figure 5. (A) Chamber for four different sizes, (B) Experiment with a 4X chamber in progress.

On the top of each chamber lid, holes were drilled for H_2SO_4 inflow and outflow ports, one for a small tube filled with glass wool to equilibrate air pressure of the headspace inside the chamber with atmospheric pressure, and one for sampling LM for NH_3 during an experiment.

Table 1. Properties of liquid manure chambers with variable surface area.

Experiment (Chamber Label)	Chamber Inside Dimensions				LM Depth in Chamber (cm)	Liquid Manure Volume (L)	Headspace Volume (L)
	Length (cm)	Width (cm)	Height (cm)	Surface Area (cm^2)			
1X	-	7.7[a]	23	186	16.2	3	1.3
2 X	19.1	19.1	29	365	16.2	5.9	4.7
4 X	29.2	25.4	29	742	16.2	12	9.5
8X	40.6	35.6	29	1445	16.2	23.4	19

[a] This entry is radius (cm) of the 1X cylindrical jar

The GPM tube used in this study was an expanded polytetrafluoroethylene (ePTFE) membrane (Phillips Scientific Inc., Rock Hill, South Carolina). This material was used because it is microporous, flexible and hydrophobic. Also, one of the main advantages of the ePTFE is its high permeability rate for gas flow with low pressure differentials between the inside and outside of the ePTFE tube (Zeus, 2011). The pore size of the tube allows it to remove the gaseous molecules and volatile contaminants from the liquid (Blet *et al.*, 1989; Semmens *et al.*, 1990). The specifications of the ePTFE membrane to be used in this study are reported in table 2. According to Rothrock*et al.*(2010) three different tubular ePTFE, with three different specifications, performed similarly in experiments with NH_3 from poultry litter.

Table 2. Gas-permeable membrane specifications.

Type of Membrane	Inside Diameter, ID (cm)	Outside Diameter, OD (mm)	Flat Width (mm)	Surface area (cm^2)	Porosity (%)	Mean pore Diameter (μm)	Bubble Pressure (kPa)
ePTFE	6.72	8.00	12.50	269	83	2.4±0.14	9.4±0.94

The length of GPM tube was kept constant at 107 cm for all experiments and its tube top was installed nearly 2.5 cm below the surface of LM in all chambers. The shallow placement of the GPM tube was due to the likelihood of greater NH_3 accumulation near the surface of the LM (Hristov *et al.*, 2011; Ni, 1999).

The acidic solution volumes and the corresponding flow rates used in all experiments are presented in table 3. The table also shows the ratio of the volumes of

LM and acidic solution. The volumetric ratio of 6 was applied initially based on the literature (Rothrock *et al.*, 2010; Vanotti and Szogi, 2010) and then increased for 4X experiments.

Table 3. Initial volume of liquid manure, volume and flow rate of sulfuric acid.

Experiment	Initial Volume of LM (L)	Acidic Solution (pH 0.36)		Ratio of Volumes of LM to Acid	Ratio of Liquid Manure to GPM Surface Areas
		Initial Volume (L)	Flow Rate (L day^{-1})		
1 X	3	0.5	1.9	6	0.68
2 X	5.9	0.75	1.9	7.9	1.36
4 X	12	0.19	1.9	64	2.76
8X	23.4	0.37	1.9	64	5.52

Raw LM was collected from the secondary cell of a lagoon treating manure flushed from alleys in a free-stall dairy barn, located in east central Texas. The raw manure was transported to the laboratory by using covered five-gallon buckets and was used fresh for 2X and 4X experiments but stored, frozen, and then thawed for using in 1X and 8X experiments.

Real time TAN concentrations in the LM and the acidic solution were measured using Ion Selective Electrode (ISE) ammonia electrode which measures the TAN of a sample and converts and reports it as NH_3-N concentration in mg L^{-1} or ppm. The electrode was capable of measuring NH_3-N between 0 to 14000 mg L^{-1} with ± 5%

accuracy. Later, the measured NH_3–N data by Ammonia Electrode was verified with a spectrophotometric NH_4-N measurement method (Franson, 1989), by analyzing the same LM or acidic solution sample that was saved for this purpose. The pH of LM and acidic solution was measured with a gel-filled pH electrode with an accuracy of ±0.05 pH units. In addition to the initial measurements, TAN concentration and pH of LM and acidic solution were measured twice a week, during each experiment. For all measurements using the 1 electrode, the temperatures of the samples were also measured. Samples from the LM chambers and acidic solution jars were taken in duplicates for experiments. The openings of all sampling ports were pinched shut while not in use.

A separate investigation, similar to the Rothrock *et al.*(2010) demonstration was conducted during this study by installing an additional GPM system, identical to the submerged system used below the LM surface, in the headspace of the 4X chamber (fig. 5(B)) only. Recirculation of acidic solution through this GPM system was also controlled by the same peristaltic pump at the same flow rate, and pH and volume similar to the acidic solution that was circulated into the submerged GPM (table 3). So, two individual but identical GPM systems were set-up in the 4X chamber in order to evaluate the efficacy of these systems for NH_3 extraction. Changes in the volume of the acidic solution in jars due to sampling (10 ml per sample) were recorded throughout each experiment.

Results and Discussion

Feasibility of NH_3 Extraction Process from LM

Over an 18-day experiment period, negligible changes occurred in the temperature, pH and NH_3 concentrations of the LM in the control chamber. However, the pH and NH_3 concentrations changed in all experiments because of the GPM treatment system. Results of NH_3 extraction in 1X, 2X, 4X and 8X are presented in figure 6. All NH_3 concentration and pH data in this figure are the mean values of duplicate or triplicate samples with the standard deviation values of 5 mg L^{-1} or less for NH_3 concentrations, and 0.04 or less for pH.

The pH of the treated LM decreased a little in chambers and increased slightly in the acidic solution during all experiments. The strong acid, with initial pH 0.36 and the large volume of LM in the chambers were the reasons for those small changes in the pH of acidic solution and LM, respectively. At the same time, the NH_3 concentration reduced in LM and increased in the acidic solution, respectively. However, these changes in the chambers were smaller than the changes in the corresponding acidic solution jars due to much larger LM volumes than acidic solution volumes. All changes in the LM chambers and acidic solution jars occurred simultaneously due to the loss and gain of NH_3, in chambers and their corresponding jars, respectively (eq. 3 and 4). In spite of different initial values of the NH_3 concentration in chambers (initial concentrations ranged from 96 mg L^{-1} to 238 mg L^{-1}), the experiments trended similarly in terms of NH_3 loss and gain in chambers and jars, respectively. The variable initial

concentrations of NH_3 were due to different seasons of LM collection and freezing and thawing processes.

Experiments with 1X, 2X, and 4X chambers showed that the GPM system extracted nearly 50% of the NH_3 gas from LM chambers as compared to their initial concentration (measured on day zero) in less than 20 days and 8X did so in 48 days.

As shown in figure 6, for all experiments, the concentration of NH_3 in acidic solution and LM changed linearly overtime. The zero intercept was set for the trend line of the acidic solution in each experiment due to no initial presence of NH_3. High coefficients of determination (R^2 mostly>0.90) for experiments indicated that the daily NH_3 extracted (gained) from LM using the GPM system was linearly correlated to the duration (time) of treatment. Likewise, in the treated LM chambers, R^2 value of the linear regression was 0.89 and higher, indicating a linear behavior of daily NH_3 loss with time due to its extraction by the GPM system. The detailed information of the experiments in figure 6 is given in appendix A. Although all experiments were started in same situation of environmental condition in the lab and also approximate initial NH_3 level in the LM chambers, the 4X experiment resulted in better NH_3 capture and removal. Therefore, 4X experiment was recognized as the most efficient experiment among all 4 experiments. Moreover, 4X chamber removed 52% of NH_3concentration in 19 days which was greatest among all four treatment chambers.

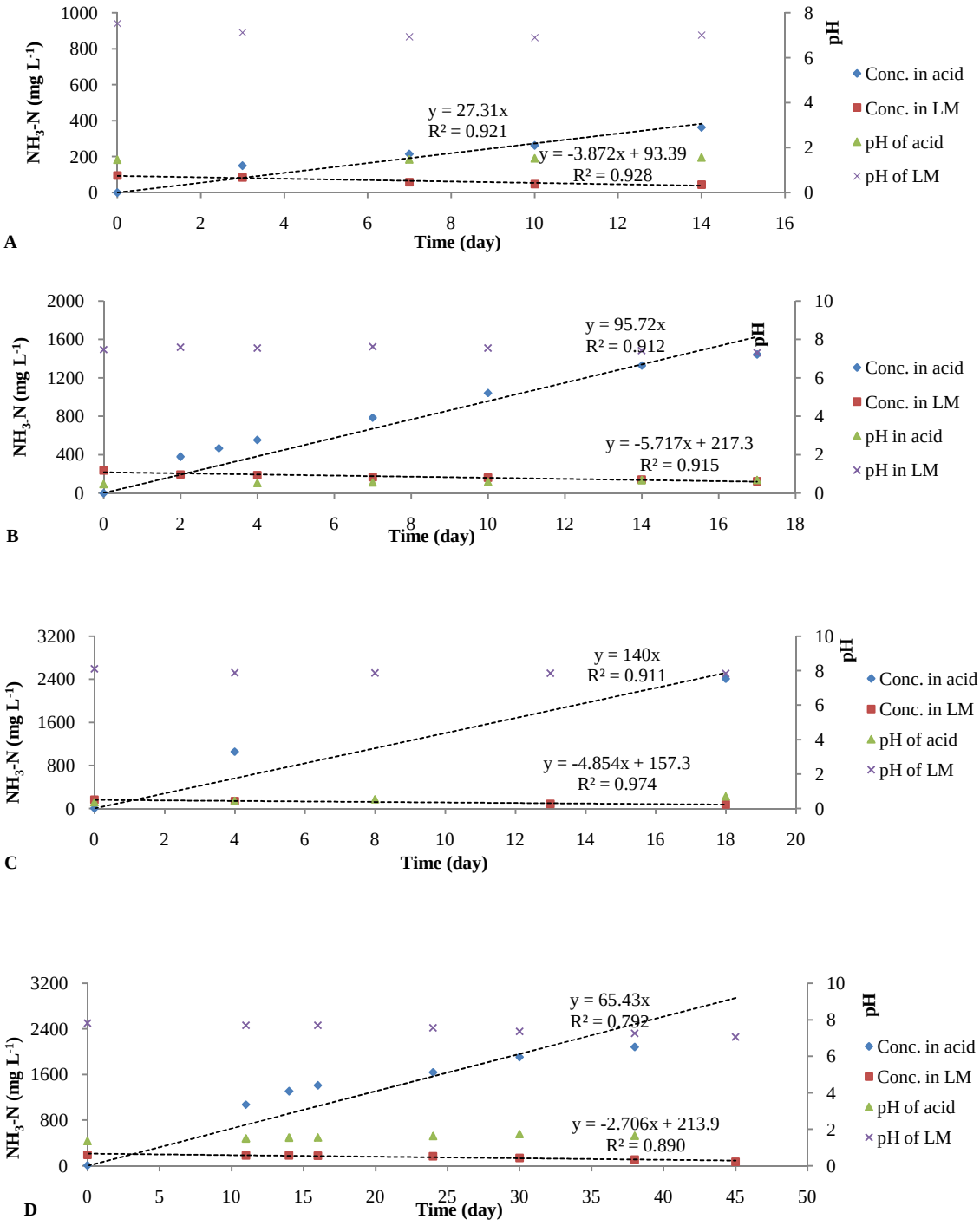


Figure 6. Ammonia and pH in acidic solution and LM in (A) 1X, (B) 2X, (C) 4X and (D) 8X experiments.

The surface area the LM in 4X chamber was 742 cm^2 , 2.75 times greater than the surface area of the GPM system (269 cm^2). That meant almost one cm^2 surface area of the GPM system or 0.4 cm of submerged length of tubing was needed to extract 50% of NH_3 in less than 20 days from three cm^2 surface area of liquid dairy manure of similar initial NH_3 concentrations.

Feasibility of NH_3 Extraction Process from Headspace

In a separate experiment, the GPM system set up in the headspace of the 4X chamber (shown in fig. 5(B)) captured 901 mg L^{-1} of NH_3 in the acidic solution, after 18 days (fig.7). This concentration was equal to 38% of NH_3 captured in the acidic solution (2410 mg L^{-1}) by the submerged GPM system in the LM of the previous 4X experiment. The suspended GPM system in the headspace lost a small amount of acidic solution due to evaporation; however, the rate of loss was less than 1.5 mL day^{-1}. Again, a strong coefficient of determination (R^2) showed NH_3 extraction from LM was linearly correlated to treatment time. Detailed results are also presented in appendix A.

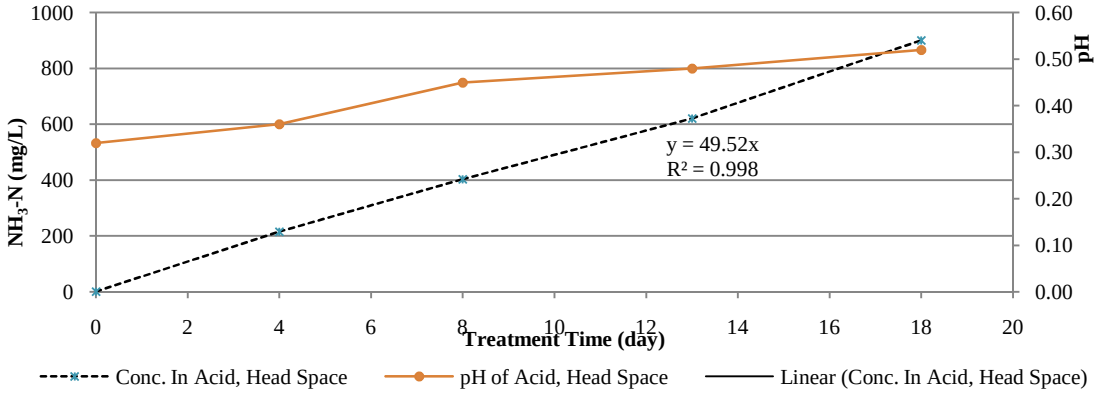


Figure 7. Ammonia concentration and pH of acidic solution from the headspace GPM system in 4X chamber

Conclusion

The main objective of this research was to assess the efficacy of extracting NH_3 from the dairy liquid manure (LM) using a GPM system. All experiments with different LM chamber sizes and surface areas showed that NH_3 gas was extracted by the tubular GPM system filled with acidic solution. However, the performance of the system highly depended upon parameters including the initial concentration of NH_3 in LM and surface areas ratios of GPM and LM. The NH_3 extraction from LM and gain in acidic solution were linearly correlated.

Based upon the relationship between number of days for NH_3 extraction and ratio of LM and GPM surface area, the 4X experiment performed the most effective extraction and removal of NH_3 from liquid dairy manure. It was estimated that one cm^2 surface area (0.4 cm of submerged length of tubing) of GPM of specifications used in

these experiments was needed to extract 50% of NH_3 in less than 20 days from three cm^2 surface area of liquid dairy manure of similar initial NH_3 concentrations.

CHAPTER III

AMMONIA DIFFUSION AND CAPTURE INTO A TUBULAR GAS-PERMEABLE MEMBRANE USING DILUTED ACIDS[*]

Overview

Tubular gas-permeable membranes (GPM) provide an alternative method for ammonia (NH_3) mitigation from liquid dairy manure (LM). A setup consisting of a closed LM chamber, two sulfuric acid (H_2SO_4) solution flasks, and two GPM systems was utilized in four experiments in order to evaluate the use of diluted acids for capturing NH_3 diffused from LM into the membrane. The H_2SO_4 solutions (recipient solutions) were circulated in the GPM systems with nominal pH values of 2, 3, 4, and 5. The initial pH values of the recipient solutions rose quickly as NH_3 was captured by them and then stabilized between 7 and the pH value of the corresponding LM treated with the GPM systems. The pH 2 solution captured the greatest concentration of NH_3 among all experiments. However, the NH_3 mass fluxes and mass transfer coefficients did not change significantly as long as the recipient solution pH values remained below 7. In all experiments, NH_3 fluxes remained positive, showing that $NH_{3(g)}$ diffused into the

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membrane not only because of the concentration gradient across the membrane but also due to gas uptake that occurred from solution circulation in the GPM tubes.

Introduction

Gas-permeable membranes such as expanded polytetrafluoroethylene (ePTFE) have been used for removing ammonia (NH_3) from a total ammoniacal nitrogen (TAN) source and capturing it in an acidic solution (Mukhtar et al., 2011; Rothrock et al., 2010; Samani Majd and Mukhtar, 2013). Investigations on the applications of synthetic membranes started in 1981 with different configurations, such as hollow fiber, tubular, flat sheet, and spiral-wound cylinders (Blet et al., 1989; Imai et al., 1982; Mandowara and Bhattacharya, 2011; Tan et al., 2006). Selection of a membrane depends on its specific application, cost, and accessibility, as well as its resistance to fouling and aging.

The performance of a membrane in terms of NH_3 mass capture is directly related to the availability of NH_3 in the TAN source (Ahn et al., 2011; Rothrock et al., 2010). In any TAN source, such as animal manure and other organic waste effluents, NH_3 and ammonium (NH_4^+) are in equilibrium, as shown in equation 6:

$$NH_4^+ \leftrightarrow NH_3 + H^+ \quad (6)$$

This equilibrium depends on the pH value and temperature of the TAN source; however, the pH has a greater impact. An increase in the pH of the TAN source causes dissociation of NH_3 and forms free ammonia (FA). The FA consists of $NH_{3(aq)}$ in the

aqueous phase and $NH_{3(g)}$ in the gas phase and can be calculated using the relationship in equation 7 with the known TAN concentration [TAN], pH, and temperature (T,°C) (Anthonisen et al., 1976; Szögi et al., 2006):

$$FA = \frac{17}{14} \times \frac{[TAN] \times 10^{pH}}{e^{\left(\frac{6,344}{273+T}\right)} + 10^{pH}} \quad (7)$$

$NH_{3(aq)}$ and $NH_{3(g)}$ are in equilibrium in a solution (Ni, 1999) based on their concentrations and environmental conditions, especially the temperature (eq. 8):

$$NH_{3(g)} \overset{H}{\leftrightarrow} NH_{3(aq)} \quad (8)$$

In equation 8, Henry's law constant (H) is the ratio of $NH_{3(aq)}$ and $NH_{3(g)}$ (Hales and Drewes, 1979; Rumburg et al., 2008). Elzing and Monteny (1997) expressed H (eq. 9) in a model and determined NH_3 emission from manure in a dairy facility experimentally, based on Hashimoto and Ludington (1971). The *H* constant is non-dimensional and depends on temperature (*T*, K):

$$H = 1384 \times 1.053^{(293-T)} \quad (9)$$

The mechanism of NH_3 capture by any recipient solution using a GPM system depends on $NH_{3(g)}$ diffusion and permeation through the membrane. Based on Fick's law of diffusion, the concentration gradient across the membrane between the recipient solution and the TAN source is recognized as the driving force of $NH_{3(g)}$ diffusion into the membrane (Moskvin and Nikitina, 2004). In fact, the $NH_{3(g)}$ concentrations on both sides of the membrane wall produce a gas partial pressure gradient (Li et al., 2000; Schneider et al., 1994). The $NH_{3(g)}$ permeability into the membrane involves two

phenomena, namely Knudsen diffusion and Poiseuille flow (viscous flow), due to the gas partial pressure gradient (Kong and Li, 2001). The NH_3 flux into the membrane was calculated using a Knudsen-Poiseuille model (eq. 10) that involves the NH_3 concentration gradient and mass transfer coefficient (Kong and Li, 2001; Kreulen et al., 1993; Schneider et al., 1994):

$$J = K_m(C_1 - C_2) \tag{10}$$

where J is the NH_3 mass flux ($gm^{-2}d^{-1}$),K_m is the mass transfer coefficient ($m\ d^{-1}$), and C_1 and C_2 are the $NH_{3(g)}$ concentrations in the recipient solution and LM, respectively ($g\ m^{-3}$ or $mg\ L^{-1}$). The K_m coefficient depends on several parameters, such as the flow rate of the recipient solution through the membrane and the membrane morphology, including porosity, thickness, tortuosity, and pore size. However, it is independent of the TAN concentration (Ahn et al., 2011; Rothrock et al., 2010; Schneider et al., 1994; Semmens et al., 1990).

After diffusion, NH_3 gas can be trapped in an absorbent medium. The literature shows that an acidic solution such as sulfuric acid (H_2SO_4) can be used to capture and recover the diffused NH_3 (Ahn et al., 2011; Rothrock et al., 2010). According to equation 11, NH_3 reacts with H_2SO_4 and produces ammonium sulfate, $(NH_4)_2SO_4$.

$$2NH_3 + H_2SO_4 \leftrightarrow (NH_4)_2SO_4 \tag{11}$$

Equation 11 shows that the reaction with the acidic solution proceeds based on the availability of NH_3 and the H^+ ion concentration (recipient solution pH). An acidic solution with lower pH captures more NH_3 and produces more concentrated $(NH_4)_2SO_4$. Theoretically, the mass of NH_3 gained through the mitigation process can be estimated

using the stoichiometry of the reaction in equation 11. The captured mass of NH_3 can also be calculated using the measured concentrations of NH_3 in the acidic solution.

Although NH_3 is soluble in the solution and may produce ammonium hydroxide (NH_4OH), it first reacts with the acid and converts it to $(NH_4)_2SO_4$ as long as the recipient solution (H_2SO_4) is acidic. Since more concentrated acid with a low pH may capture more NH_3, its by-product, $(NH_4)_2SO_4$, may also have a lower pH value. This means that the by-product will be too acidic to be used as a direct fertilizer. One possible solution may be to use a diluted H_2SO_4 solution for capturing membrane-diffused NH_3 gas from a TAN source. A diluted acidic solution with a higher pH value has several advantages:

- It is safer for handling and operation.
- A diluted acidic solution is less expensive than a concentrated acid.
- The level of contamination of the TAN source with acid would be lower if the membrane ruptured inside the source.
- The pH of the diluted acidic solution can rise faster and reach closer to the pH of synthetic ammonium sulfate fertilizer (between 5.5 and 6).

The objective of this research was to evaluate the use of diluted H_2SO_4 solutions circulating in a GPM system for NH_3 recovery from raw liquid dairy manure (LM) and to investigate the NH_3 diffusion fluxes and mass transfer coefficient in different solutions.

Materials and Methods

Figure 8 shows a schematic diagram of the GPM treatment system used for NH_3

diffusion and recovery in order to investigate the objective of this research. The setup consisted of one NH_3 treatment chamber and one control chamber (fig. 9). The treatment system was comprised of a closed chamber, two H_2SO_4 flasks, and two GPM systems. The control and treatment chambers were identical and were filled with the same raw LM, but the control chamber was left untreated. Both chambers were built from Plexiglas in a cubical shape, using dimensions of the most efficient setup (table 4) from a previous study (Mukhtar et al., 2011). The most efficient setup was defined based on the greatest NH_3 concentration that was captured and recovered from the LM using identical tubular GPM and chamber dimensions. The control and treatment chambers lids were closed to the ambient air. However, a small tube filled with glass wool equilibrated the air pressure of the headspace inside the chamber with atmospheric pressure. An additional hole in each chamber lid was used for LM sampling. This sampling orifice was opened for a few seconds during LM sampling and pinched shut when not in use. Samples were collected in triplicate (25 mL) three to five times per week during each experimental period. The volume of each LM sample was considered in the volumetric calculation of NH_3 recovered in the recipient solution.

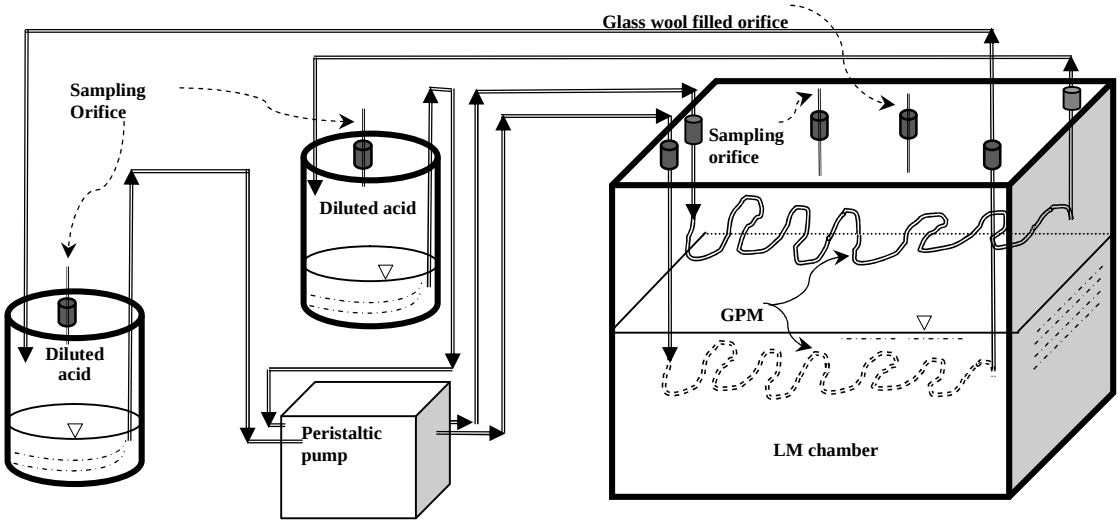

Figure 8. Schematic diagram of NH_3 treatment setup.

Table 4. Liquid manure chamber dimensions

Chamber Inside Dimensions				Depth of LM in		Headspace
Length (cm)	Width (cm)	Height (cm)	Surface Area (cm^2)	Chamber (cm)	Liquid manure Volume(L)	Volume (L)
29.2	25.4	16.2	742	16.2	12	9.5

Figure 9. An NH_3 mitigation experiment in progress.

An ePTFE membrane (Phillips Scientific, Inc., Rock Hill, S.C.) was used in this study for the GPM systems. The ePTFE membrane is hydrophobic, microporous, flexible, dielectric (does not conduct electric charge), and highly permeable for gas diffusion with low flow resistance. Table 5 shows the specifications of the tubular ePTFE membrane used in this research. The length of GPM tubing was kept constant at 107 cm for all experiments. Two tubular GPM systems were installed in the treatment chamber. One system was submerged nearly 2.5 cm below the surface of the LM in the chamber. The idea was to diffuse and capture the accumulated NH_3 in the layer just beneath the surface of the LM (Hristov et al., 2011; Ni, 1999). The second system, identical to the submerged system, was installed in the headspace of the treatment chamber and was named the suspended GPM system. Rothrock et al. (2010) demonstrated that a GPM system captured NH_3 gas from the air inside the headspace of

a chamber that was partially filled with poultry litter. Thus, it was anticipated that the suspended GPM system would enhance the overall NH_3 diffusion and recovery process.

Table 5. Specifications of the gas-permeable membrane

Inside Diameter (mm)	Outside Diameter (mm)	Flat Width (mm)	Wall Thickness (mm)	Porosity (%)	Mean Pore Diameter (μm)	Length (cm)	GPM Surface Area (cm^2)
6.72	8.00	12.50	0.66	83	2.40±0.142	107	269

A two-head peristaltic pump circulated the solutions from the flasks into the GPM systems. The volume and flow rate of the solution were kept the same for both the submerged and suspended GPM systems. The circulation flow rate was 5.6 mL min^{-1}, and the initial volume of acid in both acid flasks was 190 mL. The ratio between the volume of the LM and the acid was kept constant: between 60 and 70 parts LM and one part acid. The solution samples were collected through an orifice on the top of each flask three to five times per week, simultaneously with LM sampling during each experiment. Only 10mL of the recipient solution was sampled due to the limited volume of acid and was diluted to three 25 mL subsamples for laboratory analyses. Volumes of acid in both flasks were measured at the end of each experiment to calculate the final volume of the recipient solution in each flask.

Raw LM was collected twice from the secondary cell of a lagoon treating flushed free-stall dairy manure, located in east central Texas. The raw manure was transported in

19 L buckets that were covered during transportation from the dairy to the laboratory, frozen during storage, and thawed for experiments.

The NH_3 concentrations in the LM and recipient solutions were measured using a gas-sensing NH_3 ion-selective electrode (ISE) probe that measures the TAN concentration of a sample based on Standard Method 4500-NH_3 (APHA, 1995)and converts and reports it as NH_3-N concentration in mg L^{-1}. The electrode was capable of measuring NH_3-N between 0 to 14,000 mg L^{-1} with ±5% accuracy. The pH of the LM and recipient solutions was measured with a gel-filled pH electrode with an accuracy of ±0.05 pH units, based on Standard Method 4500-H^+ (APHA, 1995). For all experiments, temperatures of the samples were also measured using a built-in metal thermocouple associated with the pH and NH_3 probes.

Experiments

Four different recipient solutions, namely pH 2, pH 3, pH 4 and pH 5, were prepared by diluting concentrated H_2SO_4 with deionized water (table 6). Each solution was used in the setup illustrated in figures 8 and 9. All experiments were conducted once, with multiple measurements taken during the course of each experiment. Each sample was collected in triplicate in order to reduce the sampling error. For comparison, data from a low pH experiment in previous research by Mukhtar et al. (2011) are included in table 6. One-sample Student's t-tests were used to determine if the average of the calculated K_m values from experiment pH 2 to experiment pH 5 was statistically different from the K_m value obtained from the low pH experiment. Statistical power analyses using G*Power 3.1 was applied for this test (Cohen, 1969; Faul et al., 2009).

Table 6. Experimental details of recipient solutions of varying initial pH values. Data are means of triplicate samples (standard errors of means shown in parentheses).

Experiment	Experiment time(days)	Initial pH of acid	
		Submerged GPM system	Suspended GPM system
Low pH	18	0.32(±0.00)	0.36(±0.00)
pH 2	7	2.12(±0.01)	2.14(±0.00)
pH 3	7	3.08(±0.01)	3.07(±0.02)
pH4	7	4.11(±0.03)	4.14(±0.02)
pH 5	7	5.42(±0.04)	5.36(±0.03)

Calculation of NH_3 Mass and Mass Transfer Coefficient

The mass of NH_3 captured in the recipient solution was calculated using the measured concentrations of NH_3 in the recipient solutions and multiplying it by the volume of recipient solution. Alternatively, the total mass of captured NH_3can be theoretically estimated using equation 12 based on the stoichiometry of the reaction in equation 11:

$$m_{\mathrm{NH_3}} = 14{,}000 \times V_{acid}\,(10^{-\mathrm{pH_1}} - 10^{-\mathrm{pH_2}}) \qquad (12)$$

where m_{NH3} is the mass of captured NH_3 (mg), V_{acid} is the volume of the recipient solution (L), and$10^{-\mathrm{pH_1}}$ and $10^{-\mathrm{pH_2}}$ are the initial and final molar concentrations of H^+ ions, respectively.

The mass transfer coefficients (K_m values) were computed by a reverse calculation for all experiments based on J_1 fluxes and calculated $NH_{3(g)}$ concentrations. Equation 7 was used to calculate the FA concentrations of NH_3 in the LM for each

experiment, in addition to the *H* constant (eq. 9), which was calculated for estimating $NH_{3(g)}$ concentration in the corresponding LM. Since *H* is the ratio of $NH_{3(aq)}$ and $NH_{3(g)}$, and FA is the summation of $NH_{3(g)}$ and $NH_{3(aq)}$ (Rumburg et al., 2008; Szögi et al., 2006), equation 8 was solved for $NH_{3(g)}$ concentration (*C*) estimation. The C_1 and C_2 values are $NH_{3(g)}$ concentrations in the LM and the recipient solution, respectively:

$$C = \frac{\mathrm{FA}}{(1+H)} \tag{13}$$

The K_m values for NH_3 diffusion from the LM into the submerged GPM system were determined by estimating the $NH_{3(g)}$ concentration and applying it in equation 13.

Results and Discussion

Over the course of all experiments, negligible changes occurred in the temperature, pH, and NH_3 concentrations of the LM in the control chamber. The submerged GPM system was truly hydrophobic, as no increase in the volume of recipient solutions in the flasks occurred during the experiments. However, the suspended GPM system, which was exposed to the air of the chamber's headspace, lost slight amounts of its recipient solution volume due to evaporation. This rate of loss was measured as between 1 and 2 mL d^{-1} (appendix B).

The NH_3 concentrations and pH values were measured in the recipient solutions and the LM chambers for all experiments and are reported in the tables 7, 8, 9, and 10. Each data point in these tables is the mean of three samples taken per experiment. Standard errors of the measured data for pH and NH_3 concentrations are given in parentheses.

For all experiments (table 6), manure $NH_{3(g)}$ permeated through the membrane and was captured by the recipient solution circulating in the submerged and suspended GPM systems. This phenomenon resulted in an increase in pH of the initially acidic solutions in both flasks shown in figures 8 and 9. In each experiment, the pH of the recipient solution rose to a value approaching the pH value of the LM. This pH increase was due to the absorption of NH_3 from LM and the reaction between NH_3 and H_2SO_4. The time required to reach these values was 20 h, 225 min, 55 min, and 30 min for experiments pH 2, pH 3, pH 4, and pH 5, respectively. The fastest increase in pH value occurred in experiment pH 5. Figure 10 shows the increase in pH values of recipient solutions in the submerged and suspended GPM systems for the pH 5 experiment. The initial rate of pH increase was quite low during the first 10 min of NH_3 capture, but it increased greatly within the next 10 min as the NH_3 concentration in both recipient solutions increased. It then leveled off as the pH value reached closer to the pH value of the LM. Additionally, the pH value of the recipient solution in the suspended GPM system was consistently lower than the pH value of the recipient solution in the submerged system. This was due to lower rate of NH_3 diffusion from the headspace than from the LM in the chamber. The lower rate of NH_3 diffusion in the suspended GPM was due to lower NH_3 concentration in the headspace of the chambers as compared to the NH_3 concentrations in the LM. The mitigation process here included NH_3 removal from the LM and NH_3 capture or recovery in diluted acid.

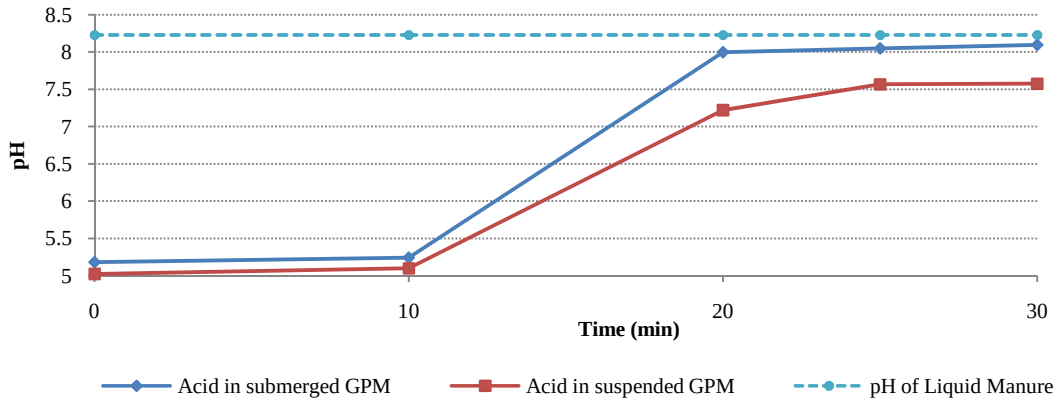

Figure 10. Accelerated increase of pH value of the recipient solutions in experiment pH5. The tubular GPMs were full after 10 min and started the complete diffusion process.

NH_3 Removal Process

Table 7 presents mean pH values and NH_3 concentrations measured in the LM for all experiments. The initial concentrations of NH_3were different since manure was used by thawing some frozen LM collected in the past. Changes in NH_3 concentration of the LM before and after NH_3 removal by the GPM system ranged from 7% to 11%, while changes in the pH values of the LM were minimal. The pH value of the LM did not decrease significantly due to availability of other alkaline substances in the LM. Among all experiments, experiment pH 2 had the greatest percentage of overall NH_3 removal (11%) in seven days. The differences in pre- and post-treated NH_3 concentrations in the LM mean that both the submerged and suspended GPM systems removed NH_3 from the treated LM chamber in all experiments.

The NH_3 removal continued throughout the seven-day treatment period for all experiments. The rates of NH_3 removal from the LM were estimated before and after the time when the recipient solutions in each experiment reached pH 7. These rates were calculated to be 2.5% to 3% per day of NH_3 removal before the pH of the recipient solution reached 7, and 1.02% to 1.32% per day of NH_3 removal after the pH of recipient solution reached 7.

Table 7. Initial and final concentrations of NH_3 and pH values in the LM chamber. Data are means of triplicate samples (standard errors of means shown in parentheses).

Exp.	Initial pH	Final pH	Initial NH_3 (mg L^{-1})	Final NH_3 (mg L^{-1})	Overall NH_3 Removal (%)
pH 2	7.94(±0.02)	7.88(±0.03)	102(±2)	91(±1)	11
pH 3	7.72(±0.03)	7.42(±0.02)	139(±3)	125(±3)	10
pH 4	7.8(±0.04)	7.78(±0.05)	170(±4)	157(±2)	8
pH 5	8.29(±0.06)	8.15(±0.04)	169(±3)	158(±4)	7

NH_3 Recovery Process

For experiments pH 2 to pH 5, the initial NH_3concentration in the acidic solution in both flasks was undetectable and assumed zero. The NH_3 concentration in the acidic solution began to increase quickly within the first hours of initiating each experiment. Thereafter, the capture of NH_3 continued but at a lower rate, as shown by figure 11. Overall, the recipient solution in the pH 2 experiment produced the most concentrated TAN, which mostly included $(NH_4)_2SO_4$, NH_4OH, and free NH_3. The masses of

recovered nitrogen (N) and sulfur (S) in the form of $(NH_4)_2SO_4$are important as plant nutrients (Boswell and Friesen, 1993; Chien et al., 2011a). In less than one day, the recipient solution with initial pH 2 recovered 146 mg L^{-1} of NH_3. On day 7, the NH_3 concentration in this recipient solution was greater than that of all other recipient solutions. This trend suggests that a GPM system with a diluted acidic solution that can be maintained at a pH value below 6 may capture a greater amount of NH_3 from LM. pH 6 is suggested since greater pH may emit $NH_3$to the atmosphere or the air above it.

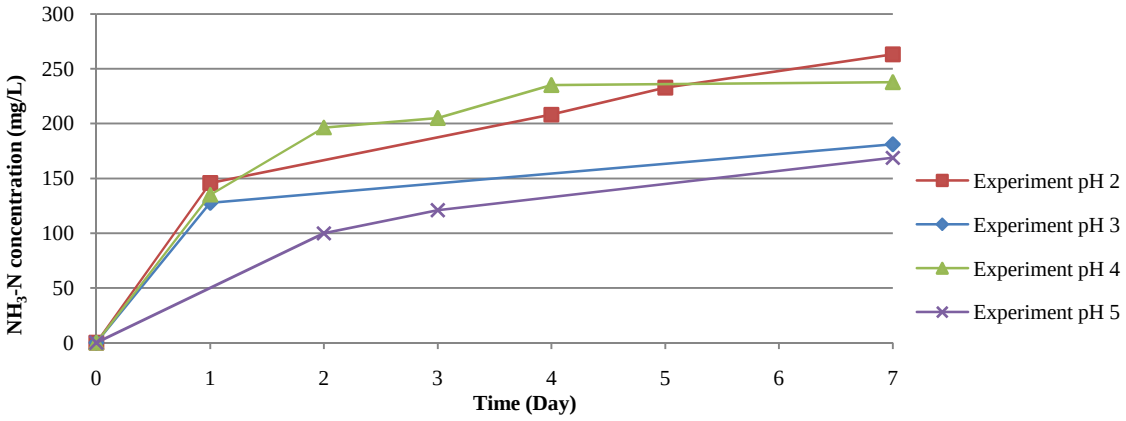

Figure 11.Timewise NH_3 concentrations in different recipient solutions of the submerged GPM system.

The actual and theoretical masses of recovered NH_3 in both recipient solution flasks are reported in table 8. The actual masses were calculated based on the final measured NH_3 concentrations and the volume of the recipient solution in both flasks. The theoretical masses of NH_3 in the corresponding experiments were calculated using

equation 7. The actual recovered masses in experiments pH 2 to pH 5 ranged from 58 to 75 mg, depending on the corresponding NH_3in the LM (ranged from 102 to 170 mg L^{-1}). The initial pH values of the acidic solutions were not correlated to the actual recovered NH_3 masses. The difference between the theoretical and actual masses of NH_3 in the low pH experiment (conducted prior to these experiments) was about 30%, but this difference increased significantly for experiments pH 2 to pH 5. In fact, compared to the measured NH_3 masses, the theoretical masses were remarkably small and nearly zero for the last two experiments. This means that as the pH value of the recipient solution rose above 7, NH_3 started to either dissolve or remained as FA in the solution rather than reacting with H_2SO_4. In this case, the measured NH_3 concentration will be mostly NH_4OH instead of $(NH_4)_2SO_4$.

Table 8. NH_3 capture and recovery by the recipient solutions.

Experiment	GPM System	Recipient Solution[a] Initial pH	Final pH	Final NH_3 (mg L^{-1})	Actual NH_3 Mass (mg)	Theoretical NH_3 Mass (mg)
Low pH	Suspended	0.36(±0.00)	0.52(±0.01)	901(±0)	523	755
	Submerged	0.32(±0.00)	0.70(±0.01)	2410(±2)		
pH 2	Suspended	2.14(±0.00)	7.82(±0.03)	243(±3)	75	36
	Submerged	2.12(±0.01)	7.64(±0.02)	263(±2)		
pH 3	Suspended	3.07(±0.02)	7.02(±0.02)	149(±1)	58	4
	Submerged	3.08(±0.01)	7.40(±0.02)	181(±1)		
pH 4	Suspended	4.14(±0.02)	8.00(±0.03)	152(±2)	69	0.41
	Submerged	4.11(±0.03)	7.81(±0.02)	238(±3)		
pH 5	Suspended	5.36(±0.03)	8.23(±0.04)	169(±2)	65	0.02
	Submerged	5.42(±0.04)	8.12(±0.04)	184(±1)		

[a] Data are means of triplicate samples (standard errors of means shown in parentheses).

Fluxes of NH_3 diffusion into the GPM (submerged system only) were also calculated based on the measured gain of $NH_{3(g)}$ in the solution of each experiment, including the previously conducted low pH experiment (Mukhtar et al., 2011), and are reported in table 9. The low pH experiment resulted in a flux rate similar to that reported for tubular GPM systems (Rothrock et al., 2010). Throughout the low pH experiment (pH = 0.36), the pH value of the acidic solution changed slightly from 0.36 to 0.7, indicating that enough H^+ ions were available to react continuously with NH_3. In addition, the large volume of LM in the chamber, in comparison to the volume of the acidic solution, supplied adequate NH_3 for this reaction. Therefore, the initial and overall NH_3 fluxes remained unchanged for the low pH experiment. However, the NH_3 fluxes

for the diluted acid experiments decreased significantly due to the low H^+ concentration as a result of an increase in the acidic solution's pH value to above 7.

The overall flux of NH_3 (J in table 9, column 2) can be divided into two segments, initial flux (J_1) and secondary flux (J_2), based on the pH of the recipient solution. The J_1 values for all experiments were calculated based on the concentration of NH_3 captured in the recipient solution until its pH value reached 7. These J_1values ranged from 0.63 to 0.78 g m^{-2} d^{-1}, similar to values reported in the literature (Rothrock et al., 2010; Schofield et al., 1987). The J_2 values were calculated when the recipient solution's pH rose from 7 to a final pH value in each experiment (table 9). The J_2 values ranged from 0.09 to 0.14 g m^{-2} d^{-1} for experiments pH 2 to pH 5. This drastic reduction in J_2 resulted as the pH values of the recipient solution increased above 7 and approached the pH value of the LM. Based on the positive values of J_2, it can be inferred that small quantities of NH_3 may still be removed from the LM, even in a solution with a pH value of nearly 7 and approaching the pH value of the LM.

Estimation of the $NH_{3(g)}$ concentration and applying it in equation 10 resulted in K_m values (table 9) for NH_3 diffusion from the LM in the submerged GPM system. The calculated K_m values were comparable to the reported K_m values for membranes other than ePTFE (Ahn et al., 2011; Li et al., 2000; Schneider et al., 1994; Semmens et al., 1990). The results of one-sample t-tests indicated no significant differences between the K_m values in experiments pH 2 to pH 5 and the K_m value of the concentrated acidic solution in the low pH experiment with $\alpha = 0.025$. It should be pointed out that the pH

of the recipient solution used for J_1 calculation was less than 7, so its corresponding FA and $NH_{3(g)}$ concentrations were nearly zero.

In table 9, the H constants range from 1179 to 1411 for the LM based on the corresponding temperatures ranging from 19.6°C to 23.1°C, respectively. These data illustrate that the $NH_{3(g)}$ available for diffusing through the GPM systems was less than 1/1000 of the FA available in the LM. In fact, this low level of $NH_{3(g)}$ is the main reason for the slow recovery process in these experiments. Since H only depends on the NH_3 source temperature (Ni, 1999), a temperature increase in the LM source or a temperature decrease in the solution may accelerate the recovery process.

Table 9. NH_3 fluxes in the submerged GPM system.

Experiment	Overall Flux J ($gm^{-2}\,d^{-1}$)	Initial Flux J_1 ($gm^{-2}\,d^{-1}$)	Secondary Flux J_2 ($gm^{-2}\,d^{-1}$)	FA Concentration of LM ($mg\,L^{-1}$)	H Constant of LM	$NH_{3(g)}$ Concentration ($mg\,L^{-1}$)	Mass Transfer K_m ($m\,s^{-1}$) [a]
Low pH	0.67	0.67	-	1.08	1281	0.846	9.17×10^{-6}
pH 2	0.27	0.69	0.09	3.10	1268	2.440	3.29×10^{-6}
pH 3	0.21	0.63	0.10	1.53	1257	1.214	5.99×10^{-6}
pH 4	0.25	0.69	0.14	3.69	1411	2.610	3.06×10^{-6}
pH 5	0.23	0.78	0.11	10.62	1179	9.002	1.01×10^{-6}

[a] K_m was calculated based on the initial flux.

Ammonia Gas Diffusion Due to Flow of Circulating Recipient Solution

Table 7 shows the $NH_{3(g)}$ concentration in the LM and recipient solutions of the submerged GPM system, calculated by equation 8, at the end of all experiments. The $NH_{3(g)}$ concentration in the LM (C_1) was lower than the $NH_{3(g)}$ concentration in the recipient solutions (C_2) at the end of each experiment. Due to this effect, a positive concentration gradient resulted across the membrane. However, Fick's law requires a negative concentration gradient as a driving force for $NH_{3(g)}$ diffusion into the membrane (Moskvin and Nikitina, 2004; Ni, 1999). Therefore, it was concluded that NH_3 gas uptake caused by the flow of circulating recipient solution was also contributing to $NH_{3(g)}$ diffusion from the LM into the GPM system. The micron-sized pores of the tubular GPM might have facilitated the gas uptake and suction phenomenon, similar to the Venturi effect.

Table 10. Final $NH_{3(g)}$ concentrations in recipient solutions and LM for submerged GPM system.

Experiment	Submerged GPM System			LM		
	Final pH[a]	TAN (mg L^{-1})[a]	$NH_{3(g)}$, C_2 (mg L^{-1})	Final pH[a]	TAN (mg L^{-1})[a]	$NH_{3(g)}$, C_1 (mg L^{-1})
Low pH	0.7 (±0.01)	2410 (±2)	0.000	7.50 (±0.03)	76 (±0)	0.846
pH 2	7.64 (±0.02)	263 (±2)	4.205	7.88 (±0.03)	91 (±1)	2.440
pH 3	7.40 (±0.02)	181 (±1)	1.793	7.42 (±0.02)	125 (±3)	1.214
pH 4	7.81 (±0.02)	238 (±3)	4.323	7.78 (±0.05)	157 (±2)	2.619
pH 5	8.12 (±0.04)	184 (±1)	11.270	8.15 (±0.04)	158 (±4)	9.002

[a] Data are means of triplicate samples (standard errors of means shown in parentheses).

Conclusion

Results from all experiments showed that NH_3 can be recovered by circulating different diluted acids in a GPM system. The pH 2 experiment produced more concentrated $(NH_4)_2SO_4$ (as a by-product of the mitigation process) and removed more NH_3 from the LM, as compared to the other diluted acid experiments. The masses of recovered NH_3 in different recipient solutions with higher pH were significantly different from their corresponding calculated values, illustrating that NH_3 diffusion continued even after the recipient solutions reached a pH value of 7 or more. The calculated flux and K_m values of the submerged GPM system were not correlated to the initial pH of the solutions at pH values of less than 7. The flux values decreased when the pH of recipient solutions reached 7 or more, but J did not reach zero, indicating continuous diffusion into the membrane during the entire course of each experiment. Moreover, in all experiments, NH_3 fluxes remained positive, indicating that $NH_{3(g)}$ diffused into the membrane not only because of the concentration gradient across the membrane but also due to gas uptake that occurred from solution circulation in the GPM tubes.

CHAPTER IV

AMMONIA RECOVERY ENHANCEMENT USING A TUBULAR GAS-PERMEABLE MEMBRANE SYSTEM IN LABORATORY AND FIELD-SCALE STUDIES[*]

Overview

Ammonia (NH_3) gas from liquid manure (LM) can be diffused into a tubular gas-permeable membrane (GPM) and recovered by capturing it in an acidic recipient solution circulating in the GPM system. The objective of this study was to assess the impact of increased rate of recipient solution circulation (flow rate) on NH_3 diffusion and recovery using a GPM system under laboratory and field conditions. A laboratory setup consisting of LM chambers, a recipient solution of diluted sulfuric acid (H_2SO_4), and two GPM systems was used to separately recover NH_3 from LM (submerged GPM system) and the headspace (suspended GPM system) of the chambers. The pH value of the recipient solution was controlled between 2 and 6 by using an acid dosing and pH controlling device. In the field, a setup similar to the laboratory study was used but with only one GPM system, with a larger surface area of the membrane, submerged in LM at a dairy lagoon. In the laboratory experiments, the results showed that increasing the flow

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rate of recipient solution in the GPM from 5.6 to 36 mL min^{-1} (more than 6 fold) increased NH_3 diffusion into the membrane and enhanced overall NH_3 recovery in the recipient solution by more than 30%. The results of the field experiments showed that increasing the flow rate of recipient solution in the GPM from 40 to 280 mL min^{-1} (7 fold) enhanced the NH_3 concentration of the recipient solution by 16.5%. Additionally, the rate of NH_3 recovery (concentration per unit time) in the field, with higher recipient solution flow rates than in the laboratory experiments, was greater than in the laboratory experiments.

Introduction

Applications of gas-permeable membranes (GPM) have been developed (Moskvin and Nikitina, 2004) for extracting gases such as ammonia (NH_3) from total ammoniacal nitrogen (TAN) sources in animal manure or from synthetic NH_3 aqueous solutions (El-Bourawi et al., 2007; Mandowara and Bhattacharya, 2011; Mukhtar et al., 2011). A GPM system of expanded polytetrafluoroethylene (ePTFE) membrane was successfully utilized in laboratory experiments for diffusing NH_3 from liquid dairy and swine manure and poultry litter (Rothrock et al., 2010; Vanotti and Szögi, 2010; Mukhtar et al., 2011).

The phenomenon of NH_3 diffusion into a GPM system is a physicochemical process depending on chemical equilibrium in the TAN source between NH_3 and ammonium (NH_4^+), absorption of ammonia gas ($NH_{3(g)}$) in the recipient solution, and the physical mechanism of gas diffusion. The NH_3 mitigation concept using a GPM system (fig. 12) is defined based on NH_3 removal from liquid manure (LM) and recovering it in

a recipient solution. The process of NH_3 gas diffusion from LM into a tubular GPM system is a consequence of the NH_3 gas concentration gradient across the membrane (Imai et al., 1982; Blet et al., 1989; Tan et al., 2006; Mandowara and Bhattacharya, 2011). Equation 14 shows how NH_3 mass flux (J, $gm^{-2}\ d^{-1}$) depends on the NH_3 mass transfer coefficient (K_m, m d^{-1}) and $NH_{3(g)}$ concentrations (C_1 and C_2, mgL^{-1}) across the membrane (Kreulen et al., 1993; Schneider et al., 1994; Li et al., 2000). Resistances against NH_3 gas diffusion by the membrane structure and its pores is defined by the K_m value based on the Knudsen-Poiseuille model (Schofield et al., 1990a, 1990b):

$$J=K_m\,(C_1-C_2) \qquad (14)$$

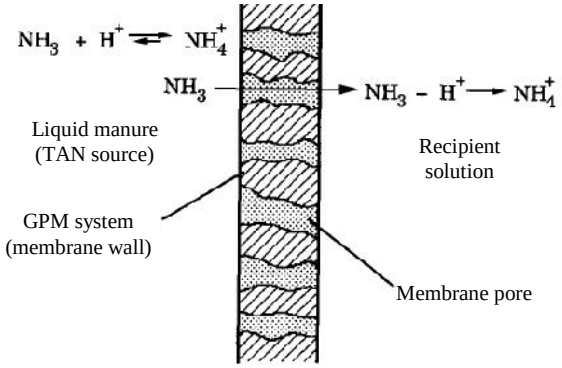

Figure 12. NH_3 diffusion into a GPM system (Reprinted from Schneider et al., 1994).

The final mass and concentration of captured NH_3 in the recipient solution depend on the NH_3 concentration of the TAN source (Rothrock et al., 2010; Vanotti and Szögi, 2010), the membrane structure and morphology (Li et al., 2000; Kong and Li,

2001; Tang et al., 2007), the flow rate of the recipient solution (Semmens et al., 1990; Schneider et al., 1994; Ahn et al., 2011), and the pH of the source (Arogo et al., 2002; Rothrock et al., 2010; Ahn et al., 2011). Increasing the recipient solution flow rate enhanced the NH_3 mitigation process in laboratory configurations when a recipient solution (mostly concentrated acidic solution) was circulated either into or around a tubular PTFE membrane that contacted TAN sources (Imai et al., 1982; Blet et al., 1989; Semmens et al., 1990; Schneider et al., 1994; Ahn et al., 2011). Imai et al. (1982) used a synthetic TAN solution with NH_3 concentrations ranging from 170 to 1700 mg L^{-1} and diluted H_2SO_4 as the recipient solution. By circulating the recipient solution at different flow rates in a tubular PTFE membrane, they concluded that if the solution flow rate was doubled, the K_m value would increase by more than 50%. Experiments by Schneider et al. (1994) showed that the K_m value of NH_3 diffusion into a PTFE membrane doubled when the flow rate of the recipient solution (a mixture of $(NH_4)_2SO_4$ and concentrated phosphoric acid) increased from 100 to 855 mL min^{-1}. Likewise, Ahn et al. (2011) showed that when the flow rate of concentrated H_2SO_4 solution flowing in a PTFE membrane doubled, the K_m value increased by 30% to 50% with initial NH_3 concentration of the source between 250 and 1000 mgL^{-1}.

In addition to the recipient solution flow rates, pH and temperature increase in TAN sources increased the availability of NH_3 gas emissions from those sources (Anthonisen et al., 1976; Szögi et al., 2006; Ahn et al., 2011) and increased the possibility of NH_3 diffusion into the GPM system. Research showed that increasing the pH of the TAN source from 7 to 12 or greater markedly increased the flux of $NH_{3(g)}$

diffusion in PTFE membranes (Blet et al., 1989) and ePTFE membranes (Rothrock et al., 2010; Vanotti and Szögi, 2010). Most of these laboratory experiments were conducted at bench-scale with synthetic ammonia solutions. Their results may differ from experiments conducted under field conditions due to the complexity of ionization in liquid manure (Semmens et al., 1990), variable environmental parameters such as temperature, and a much larger volume of natural NH_3 emission sources, such as animal manure mixed with waste feed and other fibrous material, potentially clogging the membrane pores (Jones et al., 2006).

Recently conducted research (Samani Majd et al., 2012) proved that diluted acidic recipient solution mitigated NH_3 from LM. It was also concluded that the performance of the mitigation process could be improved when the pH of the recipient solution was maintained at 6 or less. To that end, a pH controlling device (Ylén and Jutila, 1997) could be used to maintain pH of the recipient solution at a desired value. The objective of this research was to evaluate the influence of increasing flow rate and pH control of the recipient solution in enhancing the diffusion, capture, and recovery of NH_3 concentrations and masses in laboratory and field experiments.

Materials and Methods

In the lab, a GPM system was used to diffuse and capture NH_3 from LM and from the headspace above it in a closed chamber and then recover it in a recipient solution. The recipient solution was a diluted H_2SO_4 solution to trap NH_3 in the primary form of $(NH_4)_2SO_4$. The NH_3 concentrations in the LM and recipient solutions were measured as TAN concentrations (Hach Co., Loveland, Colo.) using a gas-sensing NH_3

ion-selective electrode (ISE) probe based on Standard Method 4500-NH_3 (APHA, 2005) and reported as NH_3-N concentration in mg L^{-1}. The electrode was capable of measuring NH_3-N between 0 to 14,000 mg L^{-1} with ±5% accuracy. The pH of the LM and recipient solutions was measured with a gel-filled pH electrode (Hach Co., Loveland, Colo.) with an accuracy of ±0.05 pH units, based on Standard Method 4500-H(APHA, 2005). For all experiments, temperatures of the samples were measured using built-in metal thermocouples associated with the pH and NH_3 probes. Raw LM, as a TAN source, was collected from the primary cell of a lagoon treating flushed free stall dairy manure, located in east central Texas.Both NH_3 and pH probes were calibrated based on their manufacturer's instructions before each experiment.

For the GPM system, a tubular ePTFE membrane (Phillips Scientific, Inc., Rock Hill, S.C.) was used to circulate the recipient solution for capturing diffused NH_3. The ePTFE membrane was hydrophobic, microporous, flexible, and highly permeable for gas diffusion. Table 11 lists the specifications of the tubular ePTFE membrane.

Table 11. Specifications of the gas-permeable membrane.

Diameter (mm)		Flat Width	Wall Thickness	Porosity	Mean Pore	Bubble Pressure
Inside (i.d.)	Outside (o.d.)	(mm)	(mm)	(%)	Diameter (μm)	(k.Pa)
6.72	8.00	12.50	0.66	83	2.40±0.14	9.4±0.94

Lab-Scale NH_3 Recovery Enhancement Using pH Controlling System

Results of previous research (Samani Majd et al., 2012) showed that a GPM system circulating a diluted acidic solution with pH maintained below 6 would increase the efficiency of NH_3 mitigation from LM. A pH controlling system including a pH controller, a dosing pump (Black Stone, Hanna Instruments, Inc., Temecula, Cal.), and a BNC pH probe (HEB Co., Antibes, France) was used to maintain the pH value of the recipient solution between 2 and 6 (fig. 13). The pH controller measured the pH of the solution in a range from 0.00 to 14.00 with an accuracy of ± 0.02 units. The dosing pump infused an appropriate acid medium into the solution using positive displacement solenoid pumping. This mechanism injected a specific amount of acid into the solution with each piston displacement (3 mL in this experiment). The dosing pump was self-priming and adjustable at flow rates up to 25 L min^{-1}. It was also chemical resistant and could tolerate wide temperature and humidity ranges due to its rugged design.

In order to evaluate the effectiveness of the pH controlling system, a lab-scale experiment was conducted by circulating diluted acidic solutions in an NH_3 mitigation setup (fig. 14) equipped with a pH controlling system (fig. 13). The setup consisted of one closed chamber partially filled with LM, two diluted H_2SO_4 flasks, and two GPM systems in addition to a control LM chamber identical to the treatment chamber. Both chambers were built from Plexiglas in a cubical shape with dimensions shown in table 12.

The control and treatment chamber lids were closed to ambient air. However, a small tube filled with glass wool equilibrated the air pressure of the headspace with

ambient atmospheric pressure. An additional hole in each chamber lid was used for LM sampling. LM samples (25 mL) were collected in triplicate at the beginning and end of each experiment and at different times during the experiment from the area close to the GPM. Changes in the recipient solution volume due to sampling and dosing of additional acid were noted and considered during the NH_3 mass and concentration calculations of the recipient solutions. The tubular membranes used in the submerged (2.5 cm below LM surface) and suspended (headspace) GPM systems were each 107 cm long with a surface area of 269 cm^2. The two GPM systems were identical in specifications (table 11) and were used to compare the performances of GPM systems below and above the LM surface.

The recipient solutions were prepared by diluting concentrated H_2SO_4 using deionized water and then circulating it in the GPM systems with a peristaltic pump. The initial volume and pH value of the diluted recipient solution in each flask were 200 mL and approximately 2 (molarity of 0.02), respectively. The flow rate of the circulated solutions in both GPM systems was 5.6 mL min^{-1} and kept constant for the entire period (15 days) of this experiment. The pH monitor measured the pH in the flasks waiting for increasing pH to 6 and so started injecting concentrated H_2SO_4 (pH = 0.9) into the recipient solution in each flask and reduced the pH to pH 2. The recipient solution was stirred in each flask throughout the experiments to increase the accuracy of the pH controlling system.

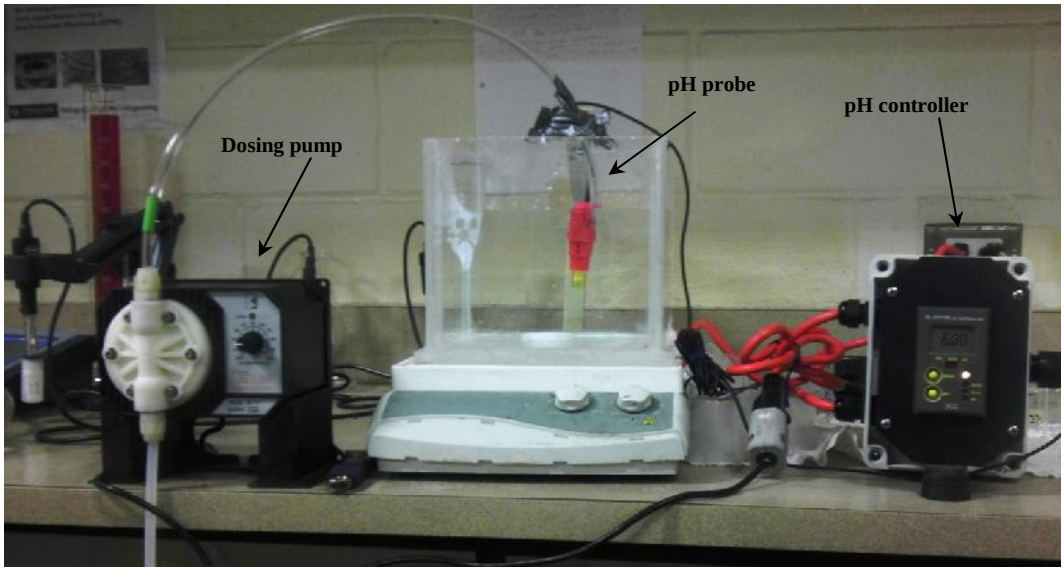

Figure 13. The pH controlling system, including a pH controller, dosing pump, and pH probe.

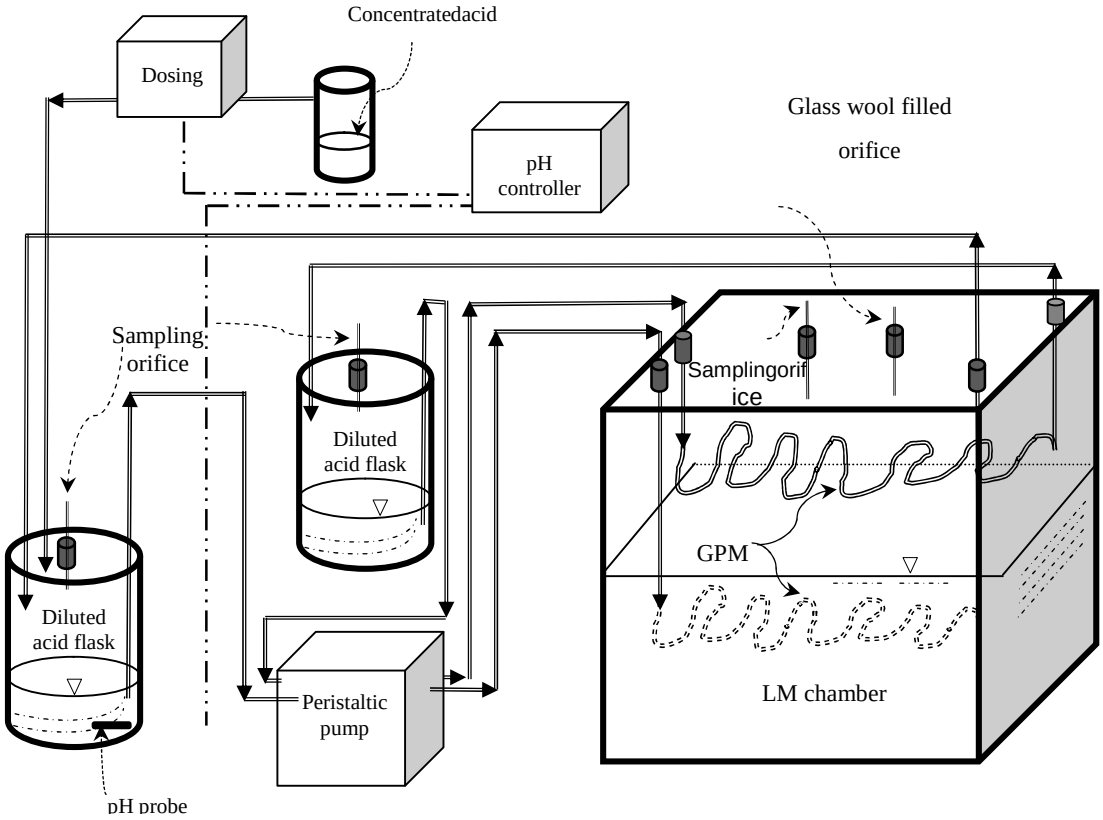

Figure 14. Schematic diagram of NH_3 treatment setup using pH controlling system.

Table 12. Liquid manure (LM) chamber dimensions.

Chamber Inner Dimensions				Depth of LM in		
Length (cm)	Width (cm)	Height (cm)	Surface Area (cm^2)	Chamber (cm)	Liquid Manure Volume (L)	Headspace Volume (L)
29.2	25.4	29	742	16.2	12	9.5

Lab-Scale Experiments with Variable Flow Rates

A second experimental setup (fig. 15) consisted of one LM chamber, two GPM systems, and an acidic solution flask. The pH controlling system was used in a set of three sub-experiments to circulate the recipient solution at three different flow rates (11, 23, and 36 mL min^{-1}). For these experiments, only one flask was used to circulate recipient solution in the submerged and suspended GPM systems in order to produce a more concentrated $(NH_4)_2SO_4$ solution. The maximum flow rate of 36 mL min^{-1} was based on the maximum capacity of the peristaltic pump. Each sub-experiment was conducted for 24 h, and no control LM chamber was used in this setup, since negligible NH_3 concentration and pH changes were expected in the control LM chamber based on the results of previous research. The same GPM systems (table 11) were used for recirculating the recipient solution with a two-head peristaltic pump.

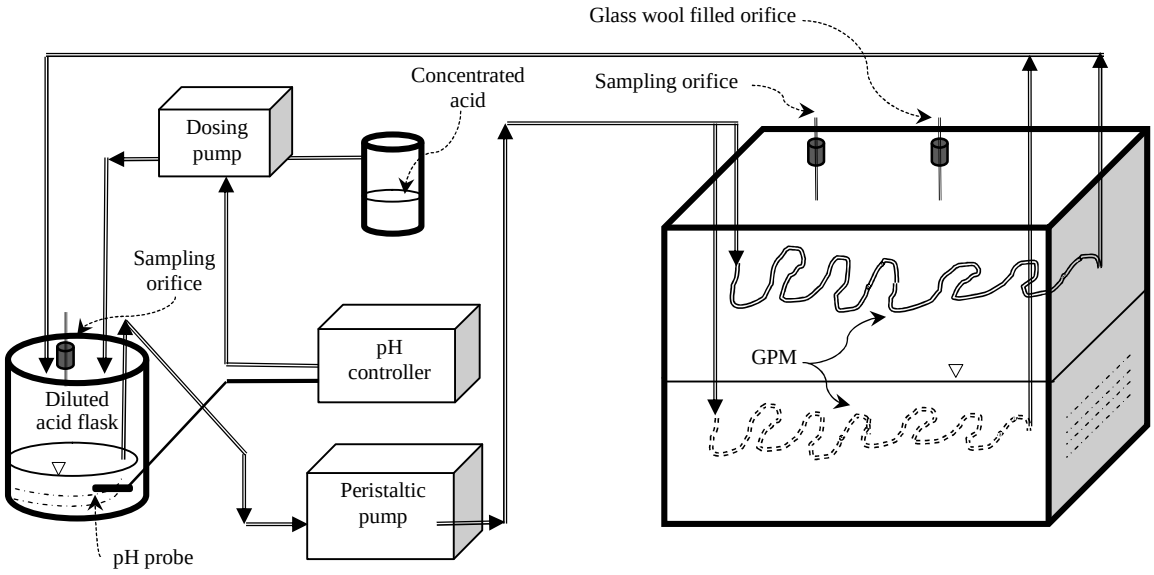

Figure 15. Schematic diagram of NH_3 treatment setup with variable flow rates and pH controlling system.

Pilot-Scale Experiments with Variable Flow Rates

Pilot-scale experiments (fig. 16) were designed for NH_3 mitigation and recovery under field condition using four different flow rates (40, 85, 190, and 280 mL min^{-1}) of recipient solution circulating in a submerged GPM system. Four experiments, each of 24 h duration and with a different recipient solution flow rate, were conducted at a dairy lagoon treating flushed manure. Real-time NH_3 concentrations as well as pH values of the lagoon manure and recipient solution were measured during each field experiment. The lagoon supernatant (liquid manure from surface to 10 cm depth) NH_3 concentration averaged 190 mg L^{-1} at a pH of 7.8 in November 2012. A 34 m long GPM tube with the listed in table 11 was attached to a wooden frame (1.3 m × 1.3 m grid) and submerged in

the lagoon so its top was nearly 5 cm below the lagoon's liquid level (fig. 16). With this arrangement, the total surface area of the submerged tubular GPM was 1 m^2.

A diluted H_2SO_4 recipient solution (pH = 2) was prepared and circulated in the GPM tube using a polymeric submersible pump (3TNJ2, Grainger, Inc., Lake Forest, Ill.) at variable flow rates. The pressure and flow rate of the solution were adjusted and measured using valves, a flowmeter, a pressure controller, and a pressure gauge (fig. 16b). The same pH controlling system used in the previous lab-scale experimental setups was used to adjust the recipient solution pH value between 2 and 6. A 12 VDC battery, charged by photovoltaic cells (EcoDirect, Carlsbad, Cal.), supplied power to the pH controlling system (fig. 16c) and the submersible pump. The pH controlling system injected concentrated H_2SO_4 at pH 0.15 into the recipient solution (fig. 16d) when the solution's pH value increased to 6.

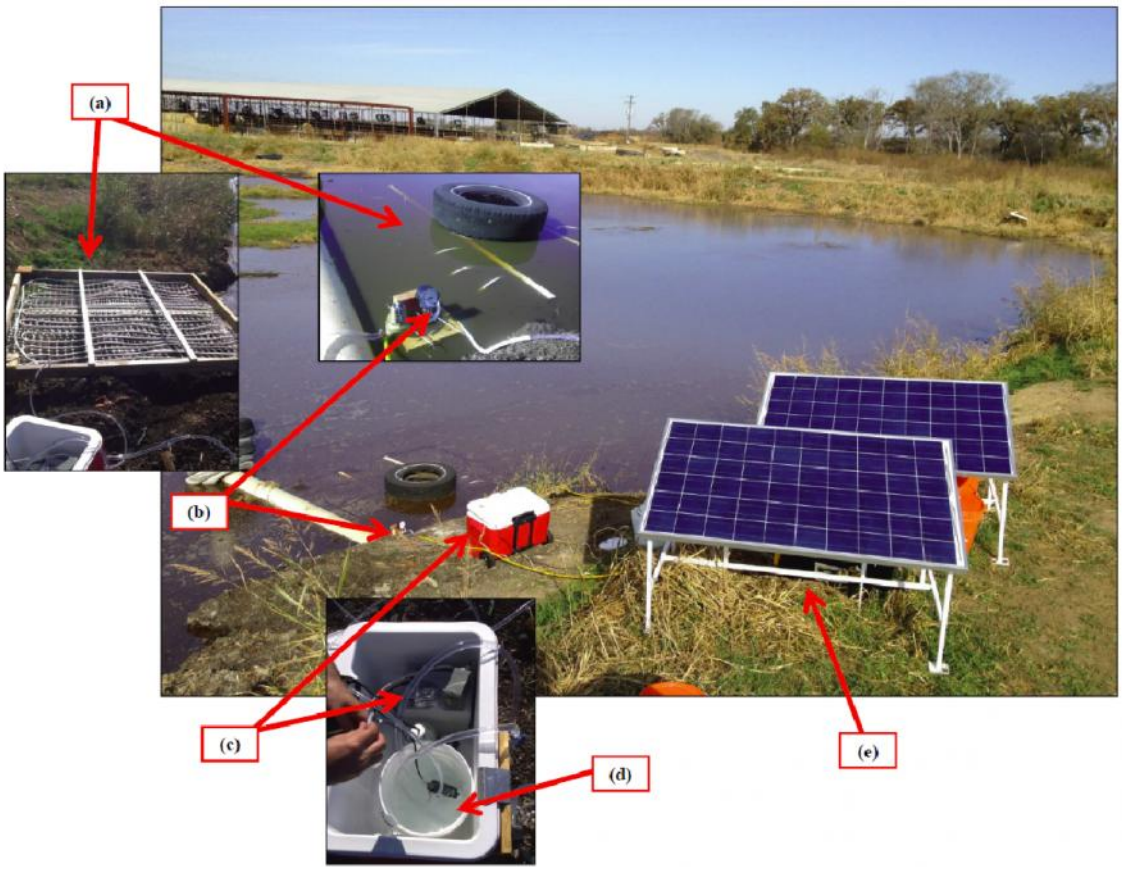

Figure 16. Pilot-scale experiment: (a) submerged GPM system fabricated on wooden frame and submerged in the lagoon, (b) pressure gauge and pressure controller to supply required head for the system, (c) pH controller and dosing system, (d) acidic solution circulating through the GPM system, and (e) solar panels for power supply to the pump and the pH controlling system.

Results and Discussion

During all lab-scale experiments, the GPM tubes remained hydrophobic, and only a negligible volumetric change occurred in the recipient solution in each flask. Previous study showed 1 to 2 mL d^{-1} loss of recipient solution due to evaporation from the suspended GPM tube (Samani Majd et al., 2012). As a result, the pH value rose due

to the absorption of NH_3 from the LM and $(NH_4)_2SO_4$ production[$(2NH_3+H_2SO_4\leftrightarrow(NH_4)_2SO_4)$]. For all experiments, mean values of all triplicate samples of NH_3 concentrations and pH are presented in tables 13 through 15. The standard errors of the measured data for pH and NH_3 concentrations were less than 0.1 and 6 ppm, respectively, for each sampling event (appendix C).

Enhancement of NH_3 Recovery Process Using pH Controlling System

Figure 17 shows the trend of NH_3 removal and recovery with submerged and suspended GPM systems using diluted recipient solutions under controlled pH conditions. The concentrations of NH_3 recovered in both diluted acid flasks increased considerably due to the recipient solution pH being managed by the pH controlling system. After 15 days of continuous operation, the NH_3 concentrations of these recipient solutions were 1905 and 734 $mgL^{-1}$with submerged and suspended GPM systems, respectively. The higher recovery of NH_3 from the submerged GPM system was due to greater NH_3 concentration in LM as compared to that in the headspace. On day 15, the NH_3 concentration of LM in the chamber decreased from 117 to 61 mg L^{-1} (about 48%), and negligible changes occurred to the NH_3 concentration and pH of LM in the control chamber.

In figure 17, the recovered NH_3 concentration data are also compared with data from two previous studies in which identical experiments were conducted using the same GPM systems. One study (Mukhtar et al., 2011) used a concentrated recipient solution (initial pH = 0.36) without a pH controlling system, and the other study (Samani Majd et al., 2012) used a diluted recipient solution (initial pH = 2) without a pH

controlling system. The initial and final values of NH_3 concentrations and pH are presented in table 13. All three experiments described in table 13 used a solution circulation flow rate of 5.6 mL min^{-1}. As shown in figure 17, NH_3 recovered by the submerged and suspended GPM systems with diluted solution using pH control and with concentrated solution without pH control were significantly greater than that recovered by the diluted solution without pH control. This was also true for the daily NH_3 recovery rate for these two experiments as compared to the diluted solution experiment without pH control. The daily recovered NH_3 concentrations in concentrated and diluted solutions with pH control were 134 and 127 mg $L^{-1}d^{-1}$, respectively, for submerged GPM systems. Likewise, the daily recovered NH_3 concentrations in concentrated and diluted solutions with pH control were 50 and 49 mg $L^{-1}d^{-1}$, respectively, for suspended GPM systems. In the experiment with diluted solution without pH control (table 13), the daily NH_3 concentrations were 38 and 35 mg $L^{-1}d^{-1}$for submerged and suspended GPM systems, respectively.

The NH_3 diffusion fluxes (J) for diluted solution experiments with and without pH control were also calculated using equation 14 and are presented in table 13. The diluted solution experiment with pH control increased the J values from 0.27 g $m^{-2}d^{-1}$ (without pH control) to 0.66 g $m^{-2}d^{-1}$ (with pH control) in submerged GPM systems, comparable to what was reported by Rothrock *et al.* (2010). Likewise, J increased from 0.15 g $m^{-2}d^{-1}$ (without pH control) to 0.24 g $m^{-2}d^{-1}$ (with pH control) in suspended GPM systems. In addition, the NH_3 removal percentages from LM were similar for the experiment with concentrated solution without pH control and the experiment with

diluted solution and pH control. Therefore, the mitigation process including NH_3 removal or capture from LM and recovery in the solution was similar for both of these experiments. However, greater advantages were associated with using diluted solution and the pH controlling system, including safer handling of diluted acid, lower cost of acid, and achieving a by-product ($(NH_4)_2SO_4$) more similar to synthetic ammonium sulfate fertilizer with pH values between 5.5 and 6.

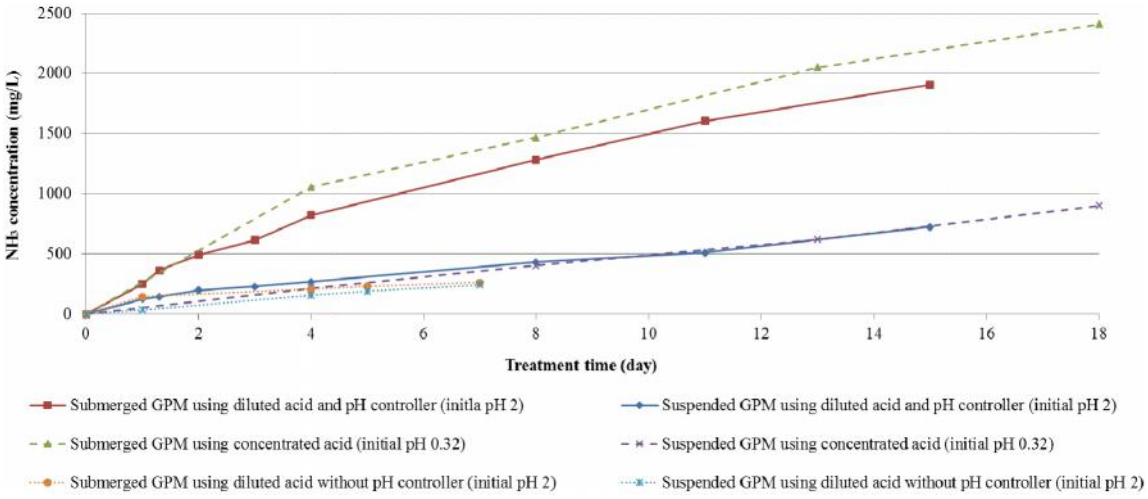

Figure 17.Concentrations of NH_3 recovered in recipient solutions of submerged and suspended GPM systems with pH control, compared with previous research using concentrated acid (Reprinted from Mukhtar et al., 2011) and diluted acid (Reprinted from Samani Majd et al., 2012) without pH control.

Flow Rate Impact on NH_3 Recovery in Lab-Scale Experiments

Results of the experiments with diluted recipient solution in submerged GPM systems using the setup shown in figure 15 with pH control at different flow rates are presented in table 14. Results of the experiments with diluted recipient solution in submerged GPM systems using the setup shown in figure 14 with pH control and a flow rate of 5.6 mL min^{-1} (table 13) are also included in table 14. The final NH_3 concentrations in the solutions varied because of different initial NH_3 concentrations in the LM chambers. To compare the data obtained by the different experiments in table 14, the available NH_3 masses in the LM chambers (m_{LM}) as well as those gained by the solutions (m_S) were calculated. The comparison between these NH_3 mass ratios showed that increasing the recipient solution flow rate from 5.6 to 36 mL min^{-1} increased the mass ratios by 4.9% to 13.2%. The overall increase in NH_3 mass was about 30.3%, indicating that increased flow rate of the recipient solution enhanced the relative NH_3 concentration recovery in the solution. Fluxes of NH_3 calculated for submerged GPM systems ranged from 0.60 to 0.77 g $m^{-2}d^{-1}$ (Rothrock et al., 2010). These fluxes were not directly proportional to the increasing flow rates of the solution because the initial NH_3 concentration in the corresponding LM was decreasing.

Flow Rate Impact on NH_3 Recovery in Pilot-Scale Experiments

The NH_3 from the lagoon LM was recovered in diluted recipient solution circulating at different flow rates based on the concept of NH_3 mitigating from LM and diffusing into the GPM system. In the field, the NH_3 concentrations in the lagoon LM varied slightly (192, 188, 187, and 191 mg L^{-1}) for corresponding recipient solution flow

rates of 40, 85, 190, and 280 mL min^{-1}, respectively. Table 5 presents the final concentrations of recovered NH_3 in recipient solutions at the end of each experiment, showing the increase of NH_3 concentration in the solutions with increasing flow rate. The hourly changes in NH_3 concentration were not linear during the 24 h of each experiment. However, the hourly concentration of NH_3 in the solution continued to increase for each experiment.

The final 24 h NH_3 concentrations of the last two experiments (flow rates of 190 and 280 mL min^{-1}) were estimated from measurements made prior to the end of these experiments due to damage to the GPM tubing by wildlife at the lagoon. The overall increase in NH_3 recovery in the recipient solution due to increasing the flow rate from 40 to 280 mL min^{-1} was 16.5%. Although the lab-scale and pilot-scale experiments were conducted under different conditions, it can be inferred that NH_3 recovery in the recipient solution was improved by increasing the solution flow rate from 5.6 to 280 mL min^{-1}. Additionally, the data in tables 4 and 5 show that the flux of NH_3 diffusion into the GPM tubing was increased by more than 12 times when the flow rate of the solution increased from 5.6 to 280 mL min^{-1} and the pH controlling system was used. Although increasing the flow rate improved the NH_3 recovery efficiencies in this field study, the rates of change for NH_3 concentration were not linear with respect to the changes in solution flow rate. Figure 18 shows that the NH_3 concentration increased from 426 to 496.5 mg L^{-1} in the recipient solution, but the corresponding NH_3 concentration per unit of flow rate decreased from 0.163% to 0.038%. This may be due to an increase in solution pressure in the GPM tube as the flow rate increased, creating resistance for

diffusion of NH_3 gas into the membrane by repelling NH_3 molecules. This result shows that flow rate increase would not linearly enhance NH_3 recovery. More investigations are needed to obtain an optimum flow rate for solution circulation for NH_3 mitigation using GPM systems.

Conclusion

Results of the experiments conducted with controlled pH of the diluted recipient solution showed that the pH controlling system improved the NH_3 mitigation process from LM and increased the NH_3 concentration in the recipient solution. This increase was similar to that achieved by using a concentrated recipient solution without a pH controlling system. However, use of a diluted solution with the pH controlled within a certain range (2 to 6 in these experiments) in a tubular GPM system to mitigate NH_3 has advantages, including safer solution handling, lower cost, and a useful by-product at a desired pH value. Lab-scale experiments showed that increasing the flow rate of the recipient solution from 5.6 to 36 mL min^{-1} in the GPM increased the NH_3 concentration in the solution by about 30.3%. Pilot-scale field experiments at a dairy lagoon showed that increased flow rates of recipient solution in the GPM using pH control increased the NH_3 concentration and flux in the recipient solution. The overall NH_3 recovery was increased by about 16.5% due to increasing the recipient solution flow rate from 40 to 280 mL min^{-1} in the field-scale experiments. Future field studies for evaluating recipient solution flow rates for optimum NH_3 mitigation and recovery from LM using different diameters of tubular GPM and a pH controlling system should be conducted.

Table 13. Ammonia mitigation experiments using diluted and concentrated recipient solutions with and without pH controlling system

Experiment	Flow Rate (mL min^{-1})	Time (d)	NH_3Concentration in LM (mg L^{-1})		NH_3 Removal (%)	Submerged GPM System: pH and NH_3 Concentration (mg L^{-1})[a] of Recovered Solution					Suspended GPM System: pH and NH_3 Concentration (mg L^{-1})[a] of Recovered Solution				
			Initial	Final		Initial pH	Final pH	Final NH_3[b]	Daily Rec.	NH_3 Flux	Initial pH	Final pH	Final NH_3[b]	Daily Rec.	NH_3 Flux
Diluted solution with pH control	5.6	15	117	61	48	2.01	6.00	1905	127	0.66	1.99	6.00	734	49	0.24
Concentrated solution[c]	5.6	18	148	76	49	0.36	0.70	2410	134	0.67	0.32	0.52	901	50	0.25
Diluted solution without pH control[d]	5.6	7	102	91	11	2.12	7.64	263	38	0.27	2.14	7.82	243	35	0.15

[a] Daily recovery (Daily Rec.) is in units of mg L^{-1} d^{-1}, and NH_3 flux is in units of g $m^{-2}d^{-1}$.
[b] The initial NH_3 concentrations in the recipient solutions were nearly zero.
[c] Mukhtar et al. (2011).
[d] Samani Majd et al. (2012).

Table 14. Ammonia recovery with variable flow rates, controlled pH and diluted recipient solution in lab-scale experiments.

Flow Rate (mL min^{-1})	Time (h)	Initial pH	Initial NH_3 Concentration in LM (C_{LM}, mg L^{-1})	Final NH_3 Concentration in Solution (C_S, mg L^{-1})	Total NH_3 Mass in LM (m_{LM}, mg)	Gained NH_3 Mass in Solution (m_S, mg)	NH_3 Mass Ratio (m_S/m_{LM})	Change in NH_3 Mass Ratio[a] (%)	OverallNH_3Mass Change[b] (%)	NH_3 Flux of submerged GPM (g $m^{-2}d^{-1}$)
5.6	24	2.01	117	176	1225	29.9	0.0244	-	30.3	0.66
11	24	2.10	94	223	1129	31.2	0.0277	13.5		0.77
23	24	2.04	79	195	961	27.9	0.0290	4.7		0.68
36	24	2.01	63	172	757	24.1	0.0318	9.7		0.60

[a] Changes in NH_3 mass ratio (m_S/m_{LM}) from a previous flow rate to the next flow rate.
[b] Overall change in NH_3 mass ratio (m_S/m_{LM}) due to flow rate increase from 5.6 to 36 mL min^{-1} $[(0.0318 - 0.0244)/0.0244) \times 100]$.

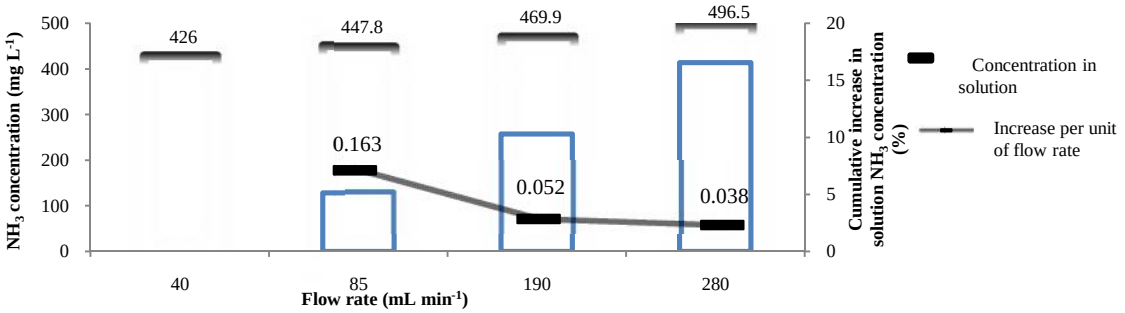

Figure 18. Concentrations of recovered NH_3 in the recipient solution at the flow rates of 40, 85, 190, and 280 mL min^{-1}. The increase in NH_3 concentrations in each flow rate respective to the previous level was accumulated as cumulative increase and showed in vertical blue bars; and NH_3 concentration increase rate per unit of flow rate as compared to the initial flow rate of 40 mL min^{-1} in the field experiments were 0.163, 0.052 and 0.038 mg L^{-1} per each mL $min^{-1}$for 85, 190 and 280 flow rates respectively.

Table 15. Ammonia recovery with variable flow rates and controlled pH diluted acid in pilot-scale field experiments

Averaged Flow Rate (mL min^{-1})	Time (h)	Initial pH	Average NH_3 Concentration in LM (C_{LM},, mg L^{-1})	Final NH_3 Concentration in solution (C_S, mg L^{-1})	Change in Final NH_3 Concentration [a] (%)	Overall change in Final NH_3 Concentration[b] (%)	NH_3 flux (g $m^{-2}d^{-1}$)
40	24	2.01	192	426	-	16.5	2.90
85	24	2.10	188	447.8	5.1		3.05
190	24	2.04	187	469.9	4.9		3.20
280	24	2.01	191	496.5	5.7		3.38

[a] Changes in final NH_3 concentration (C_s) from a previous flow rate to the next flow rate.

[b] Overall change in final NH_3 concentration ration due to flow rate increase from 40 to 280 mL min^{-1} $[(496.5 - 426)/426) \times 100]$.

CHAPTER V

EFFICACY OF AMMONIUM SULFATE PRODUCED FROM LIQUID MANURE USING AN AMMONIA RECOVERY GAS-PERMEABLE SYSTEM

Overview

Available ammonia in liquid manure can be captured and recovered using an acid-filled tubular gas-permeable membrane to produce ammonium sulfate by-product (ASB). The objective of this research was to evaluate the quality and effectiveness of ASB and compare it to synthetic ammonium sulfate (AS) fertilizer available in the market. One treatment of ASB, one treatment of AS and a Control were compared with one another in greenhouse experiments. Each treatment had four replications, and the entire set-up was called First Round Experiments (FRE). The FRE was conducted in 12 pots, each filled with 500 g of soil and initially fertilized by required phosphorus (P) and nitrogen (N) that N was supplied from ASB and AS in the treatments. Another round of experiments, similar to FRE, was conducted by adding limestone ($CaCO_3$) to FRE and called Second Round Experiments (SRE) in order investigate the impact of adjusted soil pH on experiments. Therefore, twelve pots consisting of three treatments in four replications were used in each round of experiments. The results of both rounds of experiments showed that the AS and ASB increased wheat germination, biomass, dry mass, biomass per plant and dry mass per plant. In addition, these plant parameters in the ASB treatments of both rounds were significantly greater than the AS treatments. Greater availability of N and S in liquid ASB was the cause of improved plant growth

parameters. Also, ASB left more macronutrient in the plant mass due to containing other nutrients than just N and S. In addition, applied $CaCO_3$ in SRE increased soil pH from approximately 5 to 6 and increased seed germination and other plant parameters but did not change the soil chemical parameters significantly regarding AS treatment.

Introduction

Nitrogen (N) is a required element of living cells, proteins, enzymes and metabolic processes. Likewise, S is essential for plant root growth, chlorophyll production, protein production, enzyme and vitamin development. Nitrogen and S are classified as primary and secondary macronutrients, respectively, and are constitutes of fertilizers such as ammonium sulfate [$(NH_4)_2SO_4$] available in the market. The ammonium sulfate 21-0-0-24(S) fertilizer (AS) consists of 21% N in the form of ammoniacal nitrogen and 24% sulfur in the form of sulfate. In addition to N, phosphorus (P) and potassium (K) are primary macronutrients and calcium (Ca) and magnesium (Mg) are the secondary macronutrients which are required for plant growth (Boswell and Friesen, 1993). Different amounts of macronutrients are combined to produce different types of fertilizers such as nitrate and sulfate fertilizers, N-containing diammonium phosphate (18/21-46/54-0) and monoammonium phosphate (11/12-54/62-0). These plant-beneficial fertilizers should be applied using proper nutrient management practices to avoid environmental problems (Chien *et al.*, 2011b). These benefits include:

- Increasing the potential of P and other micronutrients uptake by the plants in calcareous soils;
- Increasing the soil acidification and so decreasing the potential of NH_3 volatilization;

- Under reducing conditions, the NH_4 of AS will not denitrify as the NO_3 of NH_4NO_3;

Laboratory studies have shown that a gas-permeable membrane (GPM) technology can produce $(NH_4)_2SO_4$ solution by circulating a diluted sulfuric acid solution (H_2SO_4)through the GPM that is submerged in an ammonia (NH_3) source such as animal manure (Mukhtar *et al.*, 2011; Samani Majd and Mukhtar, 2013b; Samani Majd *et al.*, 2012). The GPM captured NH_3 gas from liquid manure (LM) and other similar total ammoniacal nitrogen sources (TAN) such as poultry litter and its headspace (Rothrock *et al.*, 2010), and synthetic lab-made TAN solution (Ahn *et al.*, 2011; Mandowara and Bhattacharya, 2011). In general, NH_3 and ammonium (NH_4^+) are in equilibrium as shown in equation 15, depending on the TAN source pH and temperature (Ni *et al.*, 2011). At pH values greater than 6.8 and room temperature, NH_4^+ dissociates partly and converts to NH_3 through volatilization (Metcalf and Eddy, 2003).

$$H^+ + NH_3 \leftrightarrows NH_4^+ \quad (15)$$

Figure 19 shows a GPM system used to recover NH_3 from raw liquid dairy manure. The system removed NH_3 from manure and the headspace and captured it in a diluted H_2SO_4 solution to produce $(NH_4)_2SO_4$ by-product (ASB) based on the availability of H^+ ions in the solution due to the relationship shown in equation 16. The concentration of the ASB produced from the GPM systems by different researchers varied from a few mg L^{-1} to54,000 mg L^{-1} (5.4%) due to different levels of pH and TAN concentration of the NH_3 source, pH of the solution and characteristics of GPM system.

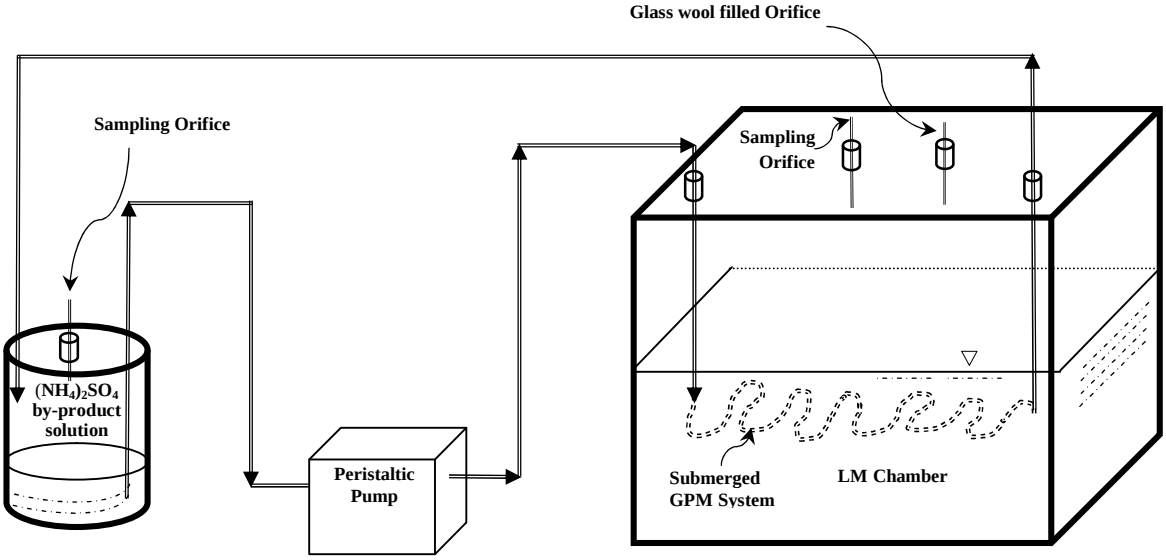

Figure 19. Schematic diagram of NH_3 recovery from LM using a GPM system and producing produce $(NH_4)_2SO_4$ by-product.

$$2NH_{3\,(g)} + H_2SO_4 \leftrightarrow (NH_4)_2SO_4 \qquad (16)$$

Although ASB had N and S nutrients, their concentrations were much lower than the N and S concentrations of the synthetic AS available in the market. Therefore, the objective of this study was to evaluate and assess the potential use of ASB for plant growth and supplying N, and Sand compare them to AS.

Materials and Methods

In this study, ASB recovered from dairy manure as a composite of all previous research (Samani Majd and Mukhtar, 2013a; Samani Majd and Mukhtar, 2013c) was used to supply N and S to plants. The average TAN concentration in ASB was 420 mg L^{-1}. The TAN concentration was measured using a gas-sensing NH_3 ion selective electrode (ISE) probe which measures TAN concentration of a sample based on the

standard method 4500-NH_3 (APHA, 2005)and reported as NH_3-N concentration in mg L^{-1}. The electrode was capable of measuring NH_3-N between 0 to 14,000 mg L^{-1} with ± 5% accuracy. The pH of ASB was about 6.2. It was measured with a gel-filled pH electrode with an accuracy of ±0.05 pH units, based on the standard method 4500-H^+ (APHA, 2005). Both NH_3 and pH probes were calibrated based on their manufacturer's instructions before each experiment.

Soil Treatment and Plant Growth Set-up

The soil for plant growth and fertilization experiments was collected from an intact soil pile which was never irrigated, cultivated or fertilized. The routine soil analysis was conducted at the Texas A&M AgriLife Extension Soil, Water and Forage Testing Laboratory using laboratory Standard operating procedures (SOPs) (http://soiltesting.tamu.edu/webpages/swftlmethods1209.html). The initial level of soil N, P and pH were 1 mg kg^{-1}, 11 mg kg^{-1} and 5 showing the soil was in need of N and P nutrients and was also acidic. Therefore, two rounds of greenhouse experiments were conducted in order to investigate wheat seed (*Triticum aestivum*) germination and growth under ASB and AS treatments in two different soil pH situations called FRE (First Round Experiments) and SRE (Second Round Experiments).

In each round of experiments, five hundred grams of soil was placed in each plastic pot (fig. 20).Therefore, twelve pots consisting of three treatments in four replications were used in each round of experiments. The treatments in each round were ASB and AS in addition to a Control. The greenhouse experiments were conducted at

room temperature (21 and 25 °C), humidity (48% to 59%) and regular sunlight behind transparent glass windows.

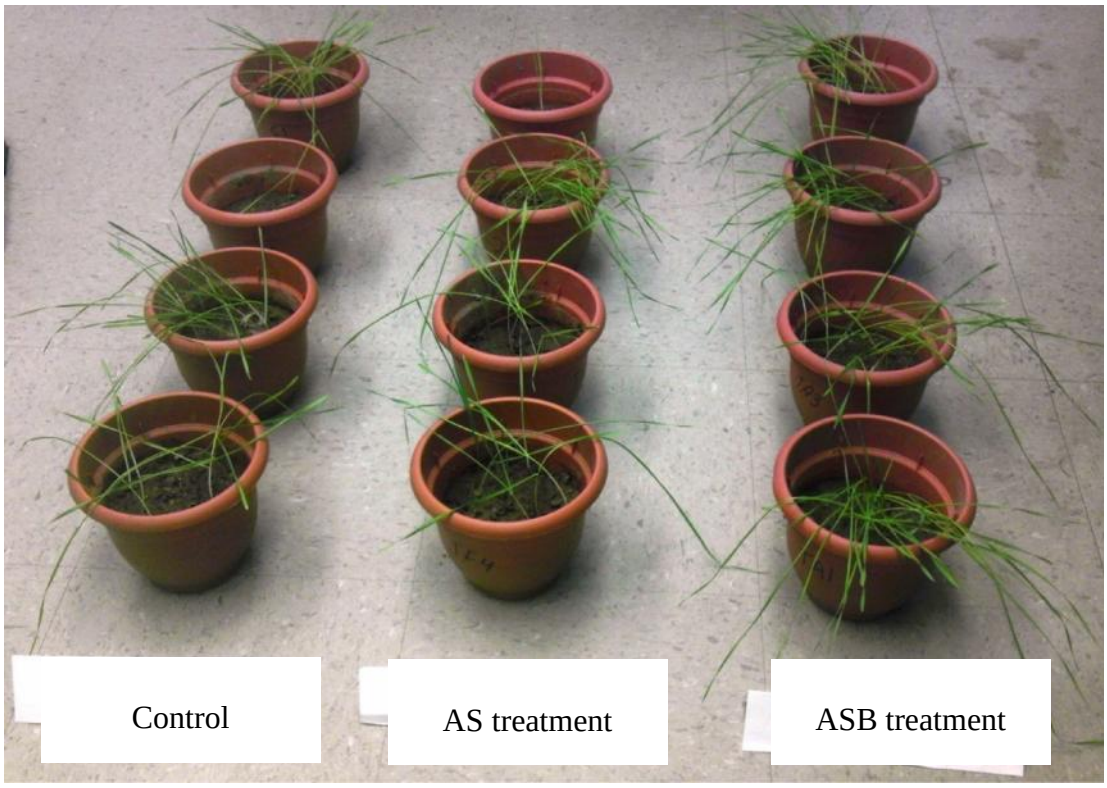

Figure 20. An example of treatments and replication in progress.

Initially, fifteen wheat seeds were planted in each pot and irrigated for 28 days since the plant growth period was set at 4 weeks in all treatments. In each pot, some of the seeds were germinated after two weeks and then the plant grew for the followingtwo weeks. Thus, the grown plants were harvested after 4 weeks. For harvesting, plants were cut at the soil level in each pot so, no under-soil level plant parts including roots were

collected for plant biomass and dry mass determinations. The plant biomass was measured when the plants were harvested fresh. Then, the plants were put in an oven for 24 hr at 100 $^{\circ}$C and the dry masses were recorded.

Reverse osmosis (RO) water was used for soil irrigation in all experiments in order to minimize the input of chemicals during the experiments (Table 16). The water was applied at a rate of 50 mL per pot every four days before and two days after seed germination. The ASB was analyzed for pH and nutrients in triplicate and average values are reported in table 16. Although some other parameters such as Fe, Zn, Cu and Mn were also detected in the ASB, they were at concentrations lower than 1 mg L^{-1} and so not included in the calculations. The nutrients in the plant tissues were also measured in the Texas A&M AgriLife Extension Soil, Water and Forage Testing Laboratory using methods of soil analysis for NO_3-N and plant tissue analysis for other minerals including P, K, S, Ca and Mg (http://soiltesting.tamu.edu/webpages/swftlmethods1209.html).

Table 16. Lab measurement parameters of RO water and by-product.

Parameter	pH	Total N (mg L^{-1})	P (mg L^{-1})	K (mg L^{-1})	Ca (mg L^{-1})	Mg (mg L^{-1})	S (mg L^{-1})
RO water	6.5	0.01[a]	0.01	1	1	1	0.33
ASB	6.2	420[b]	44.5	29.2	28.6	0.31	480

[a] Total N in the form of NO_3-N in RO water.
[b] Total N in the form of TAN measured in the by-product solution.

First Round Experiments (FRE)

The laboratory soil test N recommendation for wheat was 39.27 kg ha^{-1} (35 lbs $acre^{-1}$) as a regular N requirement (FAO, 2010) for wheat. This was calculated for each 500-g pot to be 69.4 mg per pot. The soil did not need other macronutrients except P, which was calculated to be 35 mg per pot.

In order to prepare by-product for the ASB treatment, 330 mL of the ASB comprising 69.4 mg of N was used for each pot. The specified amount of the ASB solution also contained 159 mg of S which was more than the plant requirement in addition to the preexisting S content of the soil in each pot. Furthermore, 29.5 mg of P in the form of aluminum phosphate was dissolved in the solution since the initial soil P content was 11 mg L^{-1} of P (5.5 mg per pot) and considered in addition to the P added to the solution.

Likewise, the AS treatment was prepared by dissolving 69.4 mg N in the form of crystallized AS and 29.5 mg P in the form of aluminum phosphate and added to 330 mL of RO water which was used to irrigate each pot. No nutrients were added to the Control in both rounds except the same amount of the P nutrient.

Second Round Experiments (SRE)

The ASB, AS and Control treatments were prepared with the same rate of the nutrients used in FRE. The initial soil pH was 5 referring to a strongly acidic soil (Redmon *et al.*, 2001) and so the lab recommended adding limestone ($CaCO_3$) to the soil. Thus, 5.3 g of $CaCO_3$ was added to each pot in SRE.

Data Analysis

All data presented in the tables were averages of four replications among the corresponding experiments and so the variance and standard deviation of data were calculated. One-way ANOVA tests were performed to analyze variances and significant differences of a variable among the treatments and Control of each round of experiments ($P<0.05$). All data in Figures 21, 22 and 23 as well as Table 17, including germination percentage, biomass and dry mass, N, K, P, Ca, Mg and S in plant tissue and pH, N, K, P, Ca, Mg and S in soil were compared using ANOVA. Moreover, a t-test at the 0.05 level for two independent samples was applied in order to determine the significant difference ($P<0.05$) of two corresponding variables (Bruin, 2006). The SPSS software was used to conduct the ANOVA procedure and t-test at the 0.05 level,unless another significant level was stated for a specific experiment.

Results and Discussion

Plant Data Analysis

The seed germination percentage was calculated in the FRE experiments and reported 55.0 (±18.4), 56.7 (±30.1) and 95.0 (±6.4) for Control, AS and ASB treatments, respectively. The ANOVA test indicated that the seed germination percentages were significantly different in the treatments showing the positive effect of AS and ASB over the Control. Likewise, the seed germination was calculated in SRE and was 54.9 (±13.0), 64.2 (±18.1) and 70.0 (±15.2), respectively. The result showed significant

differences between germination percentages and verified the positive effect of nutrient application on seed germination percentage, especially ASB, in both rounds.

Figure 21 indicates average values of the biomass, dry mass, biomass per plant and dry mass per plant in each treatment for both rounds after four weeks of growth. The biomass and dry mass per plant were calculated by dividing the corresponding biomass and dry mass by the number of germinated seeds in order to compare the growth of each plant if they could grow uniformly. The average values of each parameter in each round of experiment were connected to each other using a slim dotted line in order to show a trend between Control, AS and ASB values. Eight ANOVA tests were conducted among the treatments for all parameters in figure 21 and showed significant differences between treatments and Control. Therefore, the investigated trend demonstrated that the ASB was a better choice for the wheat plant and increased its germination and its biomass and dry mass, especially when soil pH was increased from approximately 5 to 6 by $CaCO_3$(appendix D).

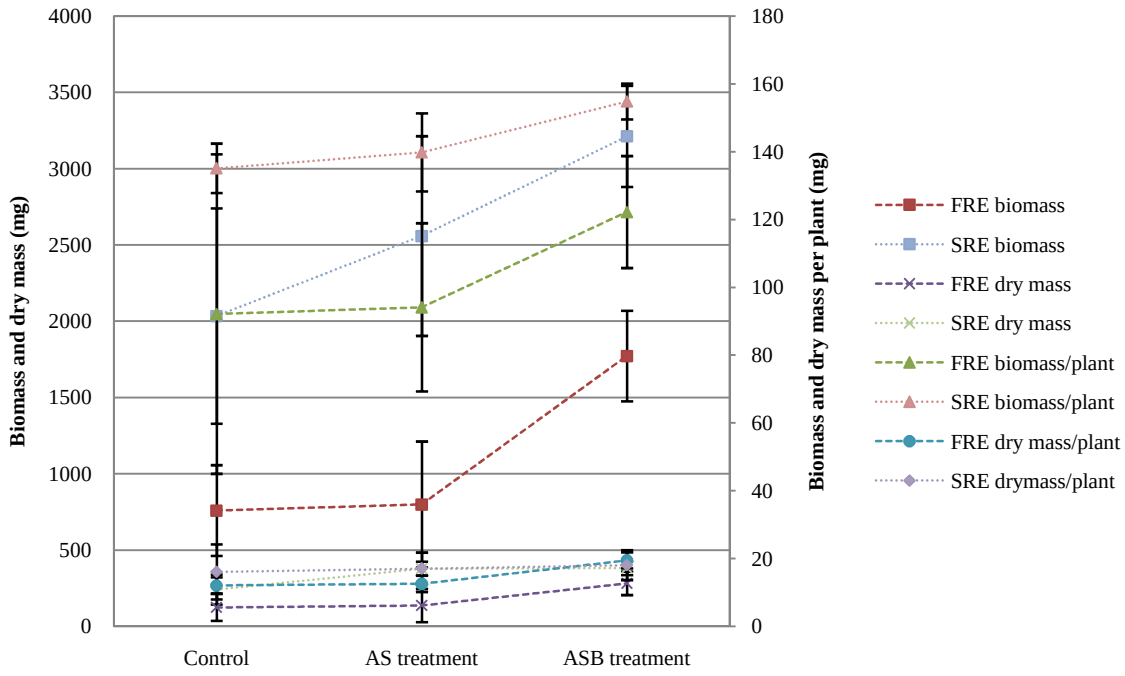

Figure 21. Biomass, dry mass, biomass and dry mass per plant in the treatments of FRE and SRE (standard deviations are presented as error bars).

Nutrients are most available to plants and are more efficiently taken up by plants between pH values 6 to 7. Thus, part of the increase in plant masses was due to more efficient uptake of nutrients due to the increased pH. Another reason was due to more available N and S nutrients in addition to other macro and micro nutrients in the ASB source which could be released fast. Also, ASB could supply some other nutrients including K, Ca, Mg, and Mn, thus, positively helping the plant growth and mass production. As it was expected, the t-test between paired plant physical parameters of FRE and SRE showed that adding $CaCO_3$ improved the plant growth. In fact, the $CaCO_3$ increased the biomass and dry mass production by 81 and 34 percent, respectively.

The results of plant tissue analysis for six macronutrients are reported in figure 22 and figure 23. Despite plant physical parameters, two distinguishing trends in FRE and SRE were observed between the values of plant tissue analysis parameters among the treatments and Control. Twelve ANOVA tests were conducted among the treatments for all twelve parameters in both rounds and showed the parameters of the treatments and Control in FRE were significantly different. The plant tissue elements of ASB treatments in this round were greater than AS and Control showing ASB could effectively increase the level of macronutrients in the plant biomass. But, the parameters in SRE behaved inconsistent with no significant difference (N- SRE and K-SRE) or slightly different (P- SRE, Mg- SRE, Ca- SRE and S- SRE) among the treatments and Control. Overall, it was concluded that ASB left the maximum macronutrient in plant tissues of FRE while the maximum residual nutrient in the SRE tests happened using AS. Conducting a paired t-test between a parameter of both rounds showed that the difference of corresponding values of the same treatment in both rounds was significant and so the data achieved in SRE which applied $CaCO_3$ had a greater value(appendix D).

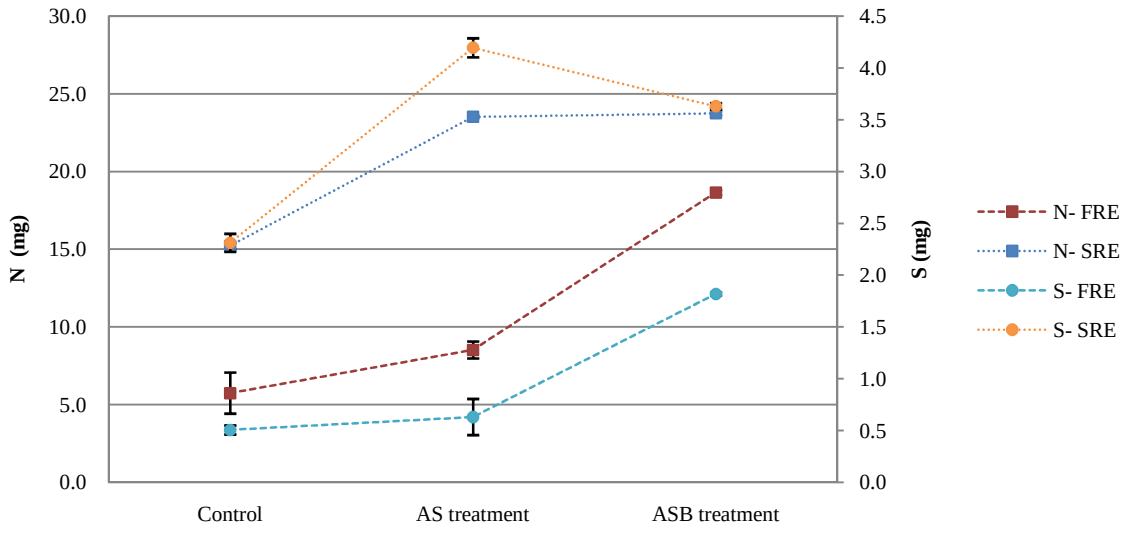

Figure 22. Nitrogen and Sulfur macronutrients collected in plant tissues of Control, AS and ASB treatment of FRE and SRE (standard deviations are presented as error bars).

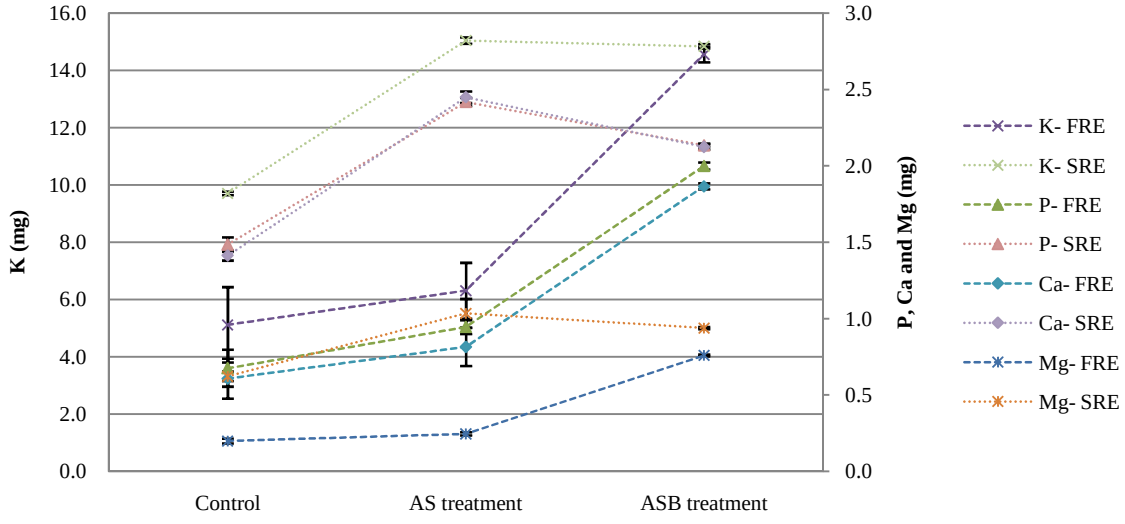

Figure 23. Potassium, calcium, phosphorous and magnesium macronutrients collected in plant tissues of Control, AS and ASB treatment of FRE and SRE (standard deviations are presented as error bars).

Regarding figure 21, 22 and 23, application of ASB can be recommended to increase wheat physical parameters and macronutrients in its biomass. Increasing weight of plant biomass and dry mass were important because of a direct association of total biomass with grain yield has been reported (Deswal *et al.*, 1996).

Soil Data Analysis

The possible changes and macronutrient addition induced by RO water were neglected since the corresponding concentrations in RO water were nearly zero (table 16). Table 17 indicates the impact of AS and ASB application on the soil pH and macronutrients in different treatments. Data are the averages and standard deviations of the measured macronutrients from the four replications at the end of the experiments (Control, AS and ASB). Also, the pH values in table 17 are the averages and standard deviations of collected samples from the replications as well.

Table 17. Soil parameters measured at the end of experiments.

Experiments		pH	NO_3-N (mg kg^{-1})	P (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	S (mg kg^{-1})
FRE	Control	4.9 (±0.1)	120 (±12.2)	31 (±4.4)	211 (±18.7)	3056 (±316.2)	453 (±31.3)	1256 (±228.3)
	AS	4.7 (±0.0)	119 (±1.8)	34 (±3.5)	228 (±7.5)	2959 (±370.3)	462 (±59.3)	1348 (±347.2)
	ASB	4.6 (±0.1)	137 (±9.4)	41(±1.8)	218 (±8.5)	3053 (±224)	422 (±18.3)	1333 (±163.4)
	p-value	0.002	0.033	0.007	0.215	0.918	0.373	0.04
SRE	Control	5.6 (±0.2)	17 (±10.8)	25 (±1.9)	201 (±9.9)	3297 (±208.2)	442 (±18.2)	1376 (±158.6)
	AS	5.8 (±0.1)	45 (±26.4)	31 (±2.9)	202 (±14.8)	4290 (±608.5)	464 (±17.8)	1803 (±327.9)
	ASB	5.6 (±0.2)	9 (±6.1)	30 (±0.3)	188 (±0.9)	3777 (±468.9)	428 (±19.2)	1727 (±355.2)
	p-value	0.224	0.032	0.005	0.162	0.097	0.061	0.028

In this research, the soil pH decreased due to $(NH_4)_2SO_4$ application. The total change was about 0.3 units in FRE showing how the added sources of nutrients in the AS and ASB treatments decreased soils pH due to the amount of H associated with the chemical. However, the pH change did not adversly affect the plant germination and growth in the range of the experiments (fig. 21). The initial soil pH in SRE was at the same level as FRE (5.0 ±0.1 and 4.9 ± 0.3, respectively) but increased up to 1.2 units in SRE by applying $CaCO_3$. Adjusting soil pH to 6.2±0.3, increased biomasses and dry masses by about two times over treatments without $CaCO_3$ (fig. 21). Increasing efficiency of nitrogen uptake because of $CaCO_3$ application and stabilizing soil pH

(Dancer *et al.*, 1973) was the most likely reason for promoting plant physical parameters.

In all experiments, added N nutrients were limited to those applied with AS or ASB (69.4 mg for each pot), and irrigation did not add any N to the pots since the N concentration of RO water was too low (0.01 mg L^{-1}). So, the final concentration of NO_3-N in the experiment should have been directly affected by sources of N and indirectly by soil pH changes caused by $CaCO_3$. Previous research reported a possible trade-off between nutrient exploitation and herbivory tolerance in some other grass species which might have been repeated in this research (Busso *et al.*, 2001). In fact, N behavior in SRE was completely different than what was accomplished in FRE, implying the great effect of $CaCO_3$ application which raised the potential of N uptake by the plant. So, it was obvious that the greater seed germination percentage, biomass, dry mass and residual N in plant tissue analysis in SRE was obtained by increasing soil pH to approximately 6 thus increasing available N and efficiency of plant uptake. The NO_3-N comparison in FRE and SRE could lead to this hypothesis that adding $CaCO_3$ was a cause of significant increase of N loss through N uptake. In fact, the difference in FRE to SRE is efficiency of uptake due to a better pH for plant growth.

Based on nutrient calculation, 69.1 mg of the P nutrient was required for each pot but its final concentration increased in the treatments compared to the Control for both rounds (table 17). Similar to plant tissue analysis (fig. 22 and 23), a trend was observed in changes of P in both FRE and SRE experiments. Although acidic soil would decrease P uptake (Chien *et al.*, 2011a), the amount of P in plant of SRE were greater than the

corresponding treatments in FRE, showing a positive effect of using $CaCO_3$ in SRE as the pH approaches 6.

No K and Mg elements were added to soil during these experiments and no significant changes were observed. The final K values were between 201 and 228 in FRE and 188 to 202 in SRE indicating AS and ASB application did not have a significant effect on soil K. Likewise, the final Mg concentration were between 422 and 462 in FRE and 428 to 464 in SRE showed no significant differences in the soil Mg values after the experiments.

The Ca concentration did not changed significantly in the FRE experiments but it increased in SRE because of the added $CaCO_3$. Clearly, the total remaining Ca in both soil and plant of each treatment in SRE was significantly greater than the corresponding treatments in FRE.

The primary lab routine soil analysis before the experiments indicated soils were not in need of S nutrient. However, adding AS and ASB to the treatments increased the S content of the soils in the corresponding treatments. Theoretically, 74.2 mg kg^{-1} of S was supplied to the soil along with N in each experiment, except for the Control. The final level of S in the AS treatment and Control at FRE was not changed significantly but the differences were significant among other treatments showing different behavior of S in AS and ASB. Chien *et al.*(2011a) reported that the sulfate-S was more effective than elemental S since it was soluble in the water and also it was in the form ofsulfur that is taken up by plants. That reason also can be extended to the AS and ASB since it is firstly water soluble or liquid and may provide more available nutrient to the soil; and

secondly, in the form of sulfate which is immediately available for plant uptake (Boswell and Friesen, 1993; Dijksterhuis and Oenema, 1990). The result of plant germination and physical parameters showed S over application did not have an adverse effect on the growth.

Conclusion

Application of the by-product of the GPM system (ASB) offered several advantages for sources of nutrients and for wheat seeds germination and growth. Trends of the changes in plant physical parameters showed that ASB increased wheat seed germination and plant biomass, dry mass, biomass per plant and dry mass per plant; especially, by adding$CaCO_3$ to increase soil pH to approximately 6. ASB could supply some other macronutrients including K, Ca, Mg, S and micronutrients such as Mn which positively helped the plant growth and mass production. Thus, ASB not only increased wheat physical parameters but also left more macronutrients in the plant biomass. In the FRE experiments, soil pH drop did not decrease plant germination and growth in the range of the experiments because the N and S nutrient in AS and ASB made up for pH drop indicating that sufficient nutrient was more dominant. In SRE, applying $CaCO_3$ helped to promote plant germination percentage, biomass, and dry mass by approximately two times greater than treatments without $CaCO_3$ probably due to an increase in pH from approximately 5 to 6, making the nutrient uptake more efficient.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Ammonia (NH_3) is a pungent gas and its excessive emissions to the atmosphere are reported as a source of odor and environmental pollution. Different technologies and methods may be recommended to mitigate NH_3 depending on the source of NH_3, environmental conditions and type of manure handling and storage systems. However, gas-permeable membrane (GPM) systems are taking few distinguished advantages which may highlight their application. The GPM systems are able to remove NH_3 from the liquid NH_3 sources as well as the air, polluted by NH_3 gas. Moreover, they can capture the removed NH_3 in an acidic solution that can be further used as a soil fertilizer. If a sulfuric acid (H_2SO_4) solution is used to capture NH_3, an ammonium sulfate ($(NH_4)_2SO_4$) solution will be produced as the by-product of the mitigation process which is potentially a useful plant nutrient. The goal of this study was to assess the efficacy of extracting NH_3 from LM using a sulfuric acid-filled GPM system and to investigate the use of recovered NH_3 as nutrients. To achieve the goal of this study, the following steps and experiments were conducted:

Four LM chambers with different surface areas, namely 1X, 2X, 4X and 8X with a constant liquid depth were used in lab-scale experiments to assess the efficacy of extracting NH_3 from LM. The surface area of LM in chamber 1X was 183.8 cm^2 and LM surface areas in chambers, 2X, 4Xand 8X were two, four and eight times the surface area of LM in chamber 1X, respectively. A concentrated H_2SO_4 with primary pH of 0.36 was

circulated through GPM systems comprise of expanded polytetrafluoroethylene (ePTFE) tubing. During these experiments, the depth of liquid manure in chambers of different dimensions and the tubular membrane parameters including diameter, length and pore size were held constant. All experiments with different LM chamber sizes and surface areas showed that NH_3 gas was extracted by the tubular GPM system filled with acidic solution. However, the performance of the system highly depended upon parameters including the initial concentration of NH_3 in LM and surface areas ratios of GPM and LM. Results of this task showed that nearly 50% of the liquid manure NH_3 measured prior to the start of each experiment was captured in less than 20 days by acid-filled membranes. The study showed that the experiment with the 4X chamber resulted in optimum NH_3 extraction. It was estimated that one cm^2 surface area of GPM (0.4 cm of submerged length of tubing) used in these experiments was needed to extract 50% of NH_3 in less than 20 days from three cm^2 surface area of liquid dairy manure of similar initial NH_3 concentrations.

The initial experiments used concentrated H_2SO_4as recommended in the literature. However, the resulting by-product was also highly acidic and useless as a direct soil fertilizer. A setup consisting of a closed 4X LM chamber, two diluted H_2SO_4 flasks and two GPM systems was utilized in four experiments to evaluate the behavior of diluted acids. The H_2SO_4solutions (recipient solutions) were circulated in the GPM systems with pH values of 2, 3, 4, and 5. The initial pH values of the recipient solutions rose quickly as NH_3 was captured by them and then stabilized between 7 and the pH value of the corresponding LM being treated with the GPM systems. Results from all

experiments showed that NH_3 can be recovered by circulating different acids in a GPM system. The pH 2 experiment produced more concentrated $(NH_4)_2SO_4$ and removed more NH_3 from the LM, as compared to the other diluted acid experiments. The mass of recovered NH_3 in different recipient solutions with higher pH were significantly different from their corresponding calculated values, illustrating that NH_3 diffusion continued even after the recipient solutions reached a pH value of 7 or more. The calculated flux and K_m values of the submerged GPM system were not correlated to the initial pH of the solutions at pH values of less than 7. The flux values decreased when the pH of recipient solutions reached 7 or more, but *J* did not reach zero, indicating continuous diffusion into the membrane during the entire course of each experiment. Moreover, in all experiments, NH_3 fluxes remained positive, indicating that $NH_{3(g)}$ diffused into the membrane not only because of the concentration gradient across the membrane but also due to gas uptake that occurred from solution circulation in the GPM tubes.

Ammonia recovery enhancement in laboratory and field-scale studies was conducted to assess the impact of increased rate of recipient solution circulation (flow rate) on NH_3 diffusion and recovery using a GPM system. A laboratory setup consisting of a closed 4X chamber, a recipient solution of diluted H_2SO_4 and two GPM systems was used to separately recover NH_3 from LM (submerged GPM system) and the headspace (suspended GPM system). The pH value of the recipient solution was controlled between 2 and 6 sing an acid dosing and pH controlling device. In the laboratory experiments, the results showed that increasing the flow rate of recipient solution in the GPM from 5.6 to 36 mL min^{-1} (more than 6 fold) increased NH_3 diffusion

into the membrane and enhanced overall NH_3 recovery in the recipient solution by more than 30%. In the field-scale, a setup similar to the laboratory study was used but with only one GPM system, with a larger surface area of the membrane, submerged in LM at a dairy lagoon. The results of the field experiments showed that increasing the flow rate of recipient solution in the GPM from 40 to 280 mL min^{-1} (7 fold) enhanced the NH_3 concentration of the recipient solution by 16.5%. Additionally, the rate of NH_3 recovery (concentration per unit time) in the field, with higher recipient solution flow rates than in the laboratory experiments, was greater than in the laboratory experiments.

Available NH_3 in liquid manure can be captured and recovered using an acid-filled tubular gas-permeable membrane. An additional objective of this research was to evaluate the quality and effectiveness of ammonium sulfate by-product (ASB) and compare it to synthetic ammonium sulfate (AS) fertilizer available in the market. One treatment of ASB, one treatment of AS and a Control were compared with one another in greenhouse experiments. Each treatment had four replications, and the entire set-up was called First Round Experiments (FRE). The FRE was conducted in 12 pots, each filled with 500 g of soil and initially fertilized by required nitrogen (N) that was supplied from ASB and AS in the treatments and phosphorus (P) that was supplied by adding aluminum phosphate. A second round of experiments (SRE), similar to FRE, was conducted by adding limestone ($CaCO_3$) to investigate the impact of adjusted soil pH on experiments. Therefore, twelve pots consisting of three treatments in four replications were used in each round of experiments. The results of both rounds of experiments showed that the AS and ASB increased wheat germination, biomass, dry mass, biomass

per plant and dry mass per plant. In addition, these plant parameters in the ASB treatments of both rounds were significantly greater than the AS treatments. Greater availability of N and S in liquid ASB was the cause of improved plant growth parameters. Also, ASB left more macronutrient in the plant mass, which might be important as animal feed. In addition, applied $CaCO_3$ in SRE neutralized soil pH and increased seed germination and other plant parameters but did not change the soil chemical parameters significantly regarding AS treatment.

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Results of 1X experiment

Date	Slope DOP	Slope NH4+	Slope pH	Sample	Acid pH	Acid Ave.	Acid Edited Ph	Acid Conc. (mg/L)	Acid 10*Ave.	Acid Volume	Acid Mass (mg)	Acid Mass Changes (mg)	Waste Water pH	Waste Water Ave.	Waste Water Conc. (mg/L)	Waste Water 10*Ave.	Waste Water Volume	Waste Water Mass(mg)	Waste Water Mass Changes (mg)	Calculated Mass Changes (mg)		Mass Balance (mg)
10/1/2010	0.0	-58.7	-57.6	1	1.46	1.46	0.46	0.0524	0.5	0.500	0.3		7.39	7.53	9.48	95.6	2.50	239.0			239.3	
				2	1.46			0.0524				67.55	7.67		9.64				30.02			-37.5
10/4/2010	3.0	-58.7	-56.3	1	1.52			15	150.7	0.450	67.8		7.08	7.12	8.51	85.3	2.45	209.0			276.8	
				2	1.54			15.14				26.79	7.16		8.55				63.20	74.16		36.4
10/8/2010	7.0	-58.7	-57.8	1	1.48	1.48	0.48		215.0	0.440	94.6		6.96	6.94	5.83	59.8	2.44	145.8			240.4	
				2	1.47			21.5				18.28	6.91		6.12				27.45	224.39		9.2
10/11/2010	10.0	-58.7	-57.8	1	1.54	1.53	0.53	27.4	262.5	0.430	112.9		6.95	6.90	4.91	48.7	2.43	118.3			231.2	
				2	1.51			25.1				39.80	6.85		4.83				7.14	158.13		-32.7
10/15/2010	14.0	-58.7	-57.8	1	1.58	1.57	0.57	36.6	363.5	0.420	152.7		6.92	7.01	4.51	46.0	2.42	111.2			263.9	
				2	1.55			36.1				152.41	7.09		4.68				127.80	458.71		-24.6

Results of 2X experiment

Date	Slope DOP	Slope NH4+	Slope pH	Sample	Acid pH	Acid Ave.	Acid Corrected pH	Acid Conc. (mg/L)	Acid Ave.	Acid Volume	Acid Mass (mg)	Acid Mass Changes (mg)	Waste Water pH	Waste Water Ave.	Waste Water Conc. (mg/L)	Waste Water Ave.	Waste Water Volume	Waste Water Mass(mg)	Waste Water Mass Changes (mg)	Calculated Mass Changes (mg)		Mass Balance (mg)
8/2/2010	0	-58.7	-57.4	1	1.52	1.47	0.47	0	0.0	0.750	0.0		6.95	7.47	23.1	237.5	5.88	1396.5				
				2	1.42			0				273.6	7.47		24.4				256.0			-17.6
8/4/2010	2	-58	-57.8	1	1.43			36.7	380.0	0.720	273.6		7.01	7.59	19.54	195.0	5.85	1140.5				
				2	1.4			39.3				58.0	7.59		19.45				43.8			-14.1
8/5/2010	3	-58.7	-57.6	1	1.5			46.6	467.0	0.710	331.6		7.04		19.41		5.84	0.0				
				2	1.62			46.8				56.2	7.49									-56.2
8/6/2010	4	-58.7	-58	1	1.53	1.53	0.53	53.8	554.0	0.700	387.8		7.54	7.56	17.99	188.1	5.83	1096.6				
				2	1.52			57				154.2	7.57		19.63				128.5	400.6		-25.7
8/9/2010	7	-58.7	-57.5	1	1.56	1.56	0.56	76.7	785.5	0.690	542.0		7.55	7.63	16.75	166.4	5.82	968.2				
				2	1.55			80.4				166.9	7.7		16.52				34.5	195.3		-132.4
8/12/2010	10	-58.7	-57.6	1	1.61	1.58	0.58	104	1042.5	0.680	708.9		7.42	7.56	16.07	160.7	5.81	933.7				
				2	1.54			104.5				181.5	7.69		16.07				111.5	121.1		-70.0
8/16/2010	14	-58.7	-58.5	1	1.69	1.68	0.68	132.1	1329.0	0.670	890.4			7.42	14	141.8	5.80	822.2				
				2	1.66			133.7				62.9	7.42		14.35				106.5	521.0		43.6
8/19/2010	17	-58.7	-57.3	1	1.75	1.69	0.69	140.6	1444.5	0.660	953.4		6.76	7.30	12.33	123.6	5.79	715.6				
				2	1.62			148.3				953.4	7.56		12.39				680.9	1296.6		-272.51

Results of 4X experiment

Date	Slope DOP	Slope NH4+	Slope pH	Sample	Liquid Manure Acid (LMA) pH	pH Ave.	Temp. C	Temp. C Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Mass (mg)	Mass Changes (mg)	Temp. C	Temp. C Ave.	Treatment Liquid Manure (TLM) pH	pH Ave.	Temp. C	Temp. C Ave.	Conc. (mg/L)	10*Ave.	Volume	Mass(mg)	Mass Changes (mg)	Temp. C	Temp. C Ave.	Control Liquid Manure (CLM) pH	pH Ave.	Temp. C	Temp. C Ave.	Conc. (mg/L)	10*Ave.	SCS Lab	Volume	Mass(mg)	Mass Changes (mg)	Temp. C	Temp. C Ave.	Total mass	Mass Balance (mg)
1/7/2011	0	-59.1	-57.9	1												7.93		13.6		18.79							18													
				2												7.94	7.93	16.1	15.23	17.86	184.4						18	18.07												
				3												7.93		16		18.66							18.2													
1/7/2011	0	-58.1	-56.9	1												7.97		18.6		14.89							22.9													
				2												7.94	7.95	18.9	18.73	14.86	147.8	148.7	12.015	1775.82			22.8	22.80												
				3												7.95		18.7		14.59							22.7													
1/13/2011	0	-58.8	-57.8	1					0.13					23						15.45							22.8				18.16						22.8			
				2	0.36		23.90		0.12	1.4	0.188	0.26		23.9	23.23		7.86		21.90	16.29	160.2	137.8	12.015	1925.20			22.8	22.80		8.10		21.40	18.92	187.6	140.19	12.015	2253.61		22.7	22.73	1925.68	
				3					0.17				187.59	22.8						16.33				-278.86			22.8				19.19					-20.83	22.7			-53.13
1/17/2011	4	-59.3	-58	1					102.8					22.4						13.24							23.4				18.46						23.4			
				2	0.44		22.40		105.4	1055.3	0.178	187.85		22.4	22.40		7.63		23.00	13.84	137.4		11.985	1646.34			23.4	23.40		7.87		22.80	18.54	185.8		12.015	2232.79		23.4	23.40	1872.55	
				3					108.4				-187.85	22.4						14.13				-1646.34			23.4				18.75					-2232.79	23.4			-1872.55
1/21/2011	8	-57.1	-57.8	1					139					23.5						13.49							21.7				16.37									
				2	0.53		24.20		145		0.168	0.00		23.5	23.50		7.65		22.20	13.28			11.975	0.00			21.7	21.73		7.86		22.10	16.9			12.015	0.00			#DIV/0!	0.00	
				3					156					23.5						13.27				1023.01			21.8				16.71					2074.59				1023.01
1/26/2011	13	-57.1	-57.8	1																8.73							21.7				17.02						22.9			
				2													7.61		22.70	8.81	85.5	81.0	11.965	1023.01			21.7	21.73		7.85		22.70	17.52	172.7	160.47	12.015	2074.59		23	22.97	1023.01	
				3									380.78							8.11				-109.25			21.8				17.26					145.78	23			413.89
1/31/2011	18	-56.9	-57.8	1					240					21.5						7.51							21.4				18.16						21.4			
				2	0.70		21.00		242	2410.0	0.158	380.78		21.5	21.50		7.50		21.50	7.64	76.4		11.955	913.76			21.4	21.40		7.83		21.50	18.71	184.8		12.015	2220.37		21.4	21.40	1436.90	
				3					241					21.5						7.78							21.4				18.57						21.4			

Results of 8X experiment

Date	Slope DOP	Slope NH4+	Slope pH	Sample	Acid pH	pH Ave.	Temp. C	Temp. C Ave.	Conc. (mg/L)	10*Ave.	Preimary Volume	Mass (mg)	Mass Changes (mg)	Temp. C	Temp. C Ave.	Waste Water pH	pH Ave.	Temp. C	Temp. C Ave.	Conc. (mg/L)	10*Ave.	Volume	Mass(mg)	Mass Changes (mg)	Temp. C	Temp. C Ave.	Total mass	Mass Balance (mg)
11/22/2010	0	---	-57.9	1	1.36	1.36	23	23.00	0.877	8.8	0.365	3.2		23.5	23.50	7.72	7.82	22.9	22.90	61.9	192.6	23.40	4506.4		23.5	23.50	4509.6	
				2	1.36		23		0.877				378.2	23.5		7.92		22.9		65.2				215.5	23.5			-162.8
12/3/2010	11	-58.7	---	1	1.5	1.50	21.5	21.45	109.9	1074.5	0.355	381.4		20.1	20.10	7.68	7.71	21.4	21.30	18.32	183.5	23.39	4290.9		20.1	20.10	4672.3	
				2	1.5		21.4		105				70.3	20.1		7.73		21.2		18.37				57.5	20.1			-12.8
12/6/2010	14	-57.6	---	1	1.54	1.55	19.2	19.20	134	1309.5	0.345	451.8		20.1	20.10	7.12		19.3	19.35	18.03	183.9	23.02	4233.4		20.1	20.10	4685.2	
				2	1.55		19.2		127.9				21.2	20.1		7.13		19.4		18.75				107.7	20.1			86.4
12/8/2010	16	-57.9	---	1	1.53	1.55	20.9	20.40	145.9	1412.0	0.335	473.0		20.1	20.10	7.72	7.71	19.7	19.55	17.58	179.3	23.01	4125.7		20.1	20.10	4598.7	
				2	1.57		19.9		136.5				59.8	20.1		7.69		19.4		18.28				273.2	20.1			213.4
12/16/2010	24	-58.5	---	1	1.61	1.63	21	21.00	147.2	1639.5	0.325	532.8		21.8	21.85	7.57	7.56	21	21.00	16.6	167.5	23.00	3852.5		21.9	21.85	4385.3	
				2	1.65		21		180.7				68.0	21.9		7.54		21		16.9				688.8	21.8			620.8
12/22/2010	30	-57.3	---	1	1.75	1.74	22.8	22.75	193.6	1907.5	0.315	600.9		23.1	23.15	7.34	7.36	22.8	22.75	14.09	139.8	22.63	3163.7		23.1	23.10	3764.5	
				2	1.72		22.7		187.9				35.1	23.2		7.38		22.7		13.87				633.6	23.1			598.6
12/30/2010	38	-57.8	---	1	1.67	1.64	23.9	23.90	209	2085.0	0.305	635.9		24.2	24.20	7.19	7.26	24.2	24.15	11.35	111.9	22.62	2530.0		24.2	24.20	3166.0	
				2	1.61		23.9		208					24.2		7.32		24.1		11.02				906.6	24.2			906.6
1/7/2011	45	-59.1	---	1													7.06		22.60		71.8	22.61	1623.4			23.60			
				2																				#REF!				#REF!

Headspace results of 4X experimrnt

Date	DOP	Slope NH4+	Slope pH	Sample	Head Space Acid (HSA) pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Mass (mg)	Mass Changes (mg)	Temp. C	Ave.	anure A pH	Treatment Liquid Manure (TLM) pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	10*Ave.		Volume	Mass(mg)	Mass Changes (mg)	Temp. C	Ave.
				1													7.93		13.6		18.79						18	
1/7/2011	0	-59.1	-57.9	2													7.94	7.93	16.1	15.23	17.86	184.4					18	18.07
				3													7.93		16		18.66						18.2	
				1													7.97		18.6		14.89						22.9	
1/7/2011	0	-58.1	-56.9	2													7.94	7.95	18.9	18.73	14.86	147.8	148.7	12.015	1775.82		22.8	22.80
				3													7.95		18.7		14.59						22.7	
				1					0.11					22.8							15.45						22.8	
1/13/2011	0	-58.8	-57.8	2		0.32		22.90	0.11	1.1	0.188	0.21		22.7	22.73			7.86		21.90	16.29	160.2	137.8	12.015	1925.20		22.8	22.80
				3					0.12				38.15	22.7							16.33					-278.86	22.8	
				1					15.45					22.8							13.24						23.4	
1/17/2011	4	-59.3	-58	2		0.36		23.00	23.8	215.5	0.178	38.36		22.7	22.73			7.63		23.00	13.84	137.4		11.985	1646.34		23.4	23.40
				3					25.4				-38.36	22.7							14.13					-1646.34	23.4	
				1					40.1					23.8							13.49						21.7	
1/21/2011	8	-57.1	-57.8	2		0.45		23.90	41.3		0.168	0.00		23.8	23.70			7.65		22.20	13.28			11.975	0.00		21.7	21.73
				3					39.8					23.5							13.27					1023.01	21.8	
				1																	8.73						21.7	
1/26/2011	13	-57.1	-57.8	2														7.61		22.70	8.81	85.5	81.0	11.965	1023.01		21.7	21.73
				3									142.36								8.11					-109.25	21.8	
				1					90.6					21.3							7.51						21.4	
1/31/2011	18	-56.9	-57.8	2		0.52		20.30	91	901.0	0.158	142.36		21.4	21.37			7.50		21.50	7.64	76.4		11.955	913.76		21.4	21.40
				3					88.7					21.4							7.78						21.4	

APPENDIX B

Results of pH 2 experiment

Date	DOP	Head Space Acid (HSA)									Liquid Manure Acid (LMA)							
		pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.
4/12/2012	0		2.14			0 0 0	0.0	0.200				2.12			0 0 0	0.0	0.200		
4/13/2012	1	2.32 2.30 2.30	2.31	21.3 21.4 22	21.57	3.68 3.62 3.65	36.5	0.188	21.3 21.4 21.5	21.40	6.77 6.75 6.74	6.75	22 22.1 22	22.03	14.5 14.6 14.6	145.7	0.188	21.5 21.4 21.3	21.40
4/16/2012	4	7.56 7.61 7.63	7.60	21.8 21.6 21.9	21.77	15.40 15.80 15.70	156.3	0.176	21 21.2 21.1	21.10	7.59 7.58 7.58	7.58	21.6 21.7 21.7	21.67	20.80 21.40 20.30	208.3	0.176	21.1 21.2 21.1	21.13
4/17/2012	5	7.69 7.79 7.79	7.76	21.5 21.5 21.5	21.50	18.7 18.8 19.2	189.0	0.164	20.8 20.8 20.9	20.83	7.58 7.61 7.6	7.60	21.6 21.7 21.7	21.67	26 22.4 21.4	232.7	0.164	20.9 21 20.9	20.93
4/20/2012	7	7.82 7.82 7.83	7.82	21.8 21.8 21.8	21.80	23.9 24.6 24.4	243.0	0.152	21.4 21.4 21.4	21.40	7.61 7.66 7.66	7.64	22 21.8 21.8	21.87	22.6 24.9 24.3	263.0	0.152	21.4 21.5 21.5	21.47

Results of pH 2 experiment

Date	DOP	Treatment Liquid Manure (TLM)										Control Liquid Manure (CLM)							
		pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Removal	Volume (l)	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Temp. C	Ave.	Total mass
4/12/2012	0	7.87 8 7.96	7.94	18.5 19.4 19.7	19.20	79.4 89.6 92.9	102	0	12.02	20 20.9 20.2	20.37	7.87 7.89 7.93	7.90	18.5 18.6 18.8	18.63	79 85 83.2	102.0	19.5 20.1 19.3	19.63	
4/13/2012	1	7.82 7.81 7.83	7.82	21.6 21.6 21.3	21.50	95.4 98 99.6	98	4	11.94	21.4 21.3 21.4	21.37	7.86 7.91 7.92	7.90	21.5 21.4 21.6	21.50	97.3 98.2 102	101.0	21.3 21.4 21.4	21.37	
4/16/2012	4	7.85 7.9 7.91	7.89	21.3 21.3 21.3	21.30	89.6 90.5 89.9	92	10	11.86	21 21 21.1	21.03	7.98 7.98 8.01	7.99	21.1 21.2 21.2	84.77	96.6 101 96.5	101.5	21.1 21.2 21.1	21.13	
4/17/2012	5	7.91 7.91 7.93	7.92	21.6 21.3 21.3	21.40	90 90.4 89.5	90	12	11.78	21.2 21.1 21.1	21.13	8.01 8.03 8.03	8.02	21.3 21.3 21.3		102 98.4 98.9	99.8	21.2 21.1 21	21.10	
4/20/2012	7	7.96 7.97 8	7.88	21.9 21.8 21.5	21.73	90.8 90.8 90.7	91	11	11.70	21.5 21.3 21.5	21.43	8.01 8.04 8.03	8.03	21.3 21.7 21.6		98.1 104 104	101.0	21.7 21.4 21.5	21.53	

Results of pH 3

Date	DOP	Head Space Acid (HSA)									Liquid Manure Acid (LMA)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.
3/6/2012	0		3.08		20.80	0 0 0	0.0	0.200		20.80		3.07			0 0 0	0.0	0.200		
3/7/2012	1		7.05		21.20	3.51 3.54 3.58	35.4	0.188	20.8 20.8 20.8	20.80		7.39		21.20	12.6 12.9 12.8	127.7	0.188	20.1 20.7 20.7	20.50
3/13/2012	7		7.02		22.30	4.93 5.01 4.88	149.0	0.176	21.5 21.5 21.5	21.57		7.40		22.40	14.80 14.20 14.90	181.0	0.176	21.6 21.5 21.6	21.57
3/14/2012	8	7.3 7.33 7.32	7.32	22 22.1 22	22.03	5 4.83 4.88			21.2 21.2 21.2	21.20	7.07 7.06 7.07	7.07	21.9 21.9 21.9	21.90	16.1 15.5 15.6			21.2 21.2 21.2	21.20

Results of pH 3

Date	DOP	Treatment Liquid Manure (TLM)									Control Liquid Manure (CLM)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Volume	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Volume	Temp. C	Ave.
3/6/2012	0	7.68 7.72 7.75	7.72	21.3 20.6 20	20.63	164 163 163	139.0	12.020	20.8 20.3 20.3	20.47	7.68 7.61 7.61	7.63	20 21 20.9	20.63	166 165 165	141.0	12.020	20.8 20.3 20.8	20.63
3/7/2012	1	7.68 7.74 7.71	7.71	20.9 20.6 20.8	20.77	121 118 122	127.0	11.645	20.4 20.4 20.5	20.43	7.63 7.66 7.68	7.66	20.9 20.7 20.8	20.80	147 137 132	138.7	11.945	20.5 20.5 20.5	20.50
3/13/2012	7	7.39 7.41 7.47	7.42	22 22 21.6	21.87	65.5 96 93	125.0	11.870	21.8 21.6 21.6	21.67	7.48 7.53 7.47	7.49	21.4 21.6 21.7	21.57	137 141 146	141.3	11.870	21.8 21.4 21.5	21.57
3/14/2012	8	7.35 7.39 7.4	7.38	21.6 21.5 21.5	21.53	43.7 47 39.1			21.2 21.2 21.2	21.20	7.35 7.39 7.4	7.38	21.5 21.5 21.5	21.53	112 114 112			21.1 21.2 21.1	

Results of pH 4 experiment

Date	DOP	Head Space Acid (HSA)									Liquid Manure Acid (LMA)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.
		4.14		20		0					4.10		20		0				
1/31/2012	0	4.14	4.14	20	20.03	0	0.0	0.220			4.11	4.11	20	20.03	0	0.0	0.220		
		4.15		20.1		0					4.12		20.1		0				
		7.46		21.8		6.09			21.1		7.35		21.7		15.4			20.9	
2/1/2012	1	7.45	7.45	21.7	21.70	6.05	61.0	0.208	21.2	21.17	7.36	7.36	21.8	21.80	15.5	155.0	0.208	20.9	20.93
		7.44		21.6		6.16			21.2		7.37		21.9		15.6			21	
		7.78		21.6		10.20			21		7.7		21.5		19.20			21.2	
2/2/2012	2	7.77	7.78	21.7	21.67	10.30	103.0	0.196	20.9	20.97	7.71	7.71	21.7	21.67	19.70	196.3	0.196	21.1	21.13
		7.78		21.7		10.40			21		7.73		21.8		20.00			21.1	
		7.86		21.4		14.1			21.3		7.75		21.4		22.6			21.1	
2/3/2012	3	7.9	7.89	21.4	21.37	14.3	143.0	0.184	21.4	21.33	7.74	7.76	21.3	21.33	24	236.3	0.184	21	21.03
		7.92		21.3		14.5			21.3		7.79		21.3		24.3			21	
		7.9		20.9		15.4			20.3		7.78		22.3		21.4			20.7	
2/4/2012	4	7.92	7.92	21.5	21.43	14.9	151.3	0.172	20.6	20.50	7.78	7.78	21.6	22.03	22.4	235.0	0.172	20.8	20.70
		7.94		21.9		15.1			20.6		7.77		22.2		22			20.6	
		7.98		19.8		19.4			19.4		7.78		19.8		23.4			19.6	
2/6/2012	7	8.01	8.00	19.8	19.70	19.7	152.0	0.160	19.4	19.37	7.81	7.81	19.8	19.80	23.7	237.7	0.160	19.6	19.53
		8.02		19.5		20.1			19.3		7.83		19.8		24.2			19.4	

Results of pH 4 experiment

Date	DOP	Treatment Liquid Manure (TLM)									Control Liquid Manure (CLM)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	Ave.	Volume	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	Ave.	Volume	Temp. C	Ave.
		7.5		21.5		179			20.1		7.73		21.5		188			20.7	
1/31/2012	0	7.65	7.80	18.6	19.53	180	170.1	12.02	20.2	20.27	7.64	7.80	18.6	19.53	186	170.0	12.02	20.4	20.37
		7.59		18.3		183			20.5		7.73		18.3		200			20	
		7.77		21.6		249			20.9		7.71		22.1		278			20.4	
2/1/2012	1	7.77	7.79	21.6	21.60	236	159.0	11.95	20.9	20.73	7.73	7.72	22.1	22.03	272		11.95	20.7	20.67
		7.83		21.6		257			20.4		7.73		21.9		267			20.9	
		7.75		21.9		158			20.8		7.73		23.5		173			21.1	
2/2/2012	2	7.8	7.78	21.9	21.93	161	156.7	11.87	20.7	20.73	7.75	7.76	23.3	23.57	174	170.3	11.87	21.2	21.13
		7.8		22		153			20.7		7.75		23.9		164			21.1	
		7.78		25.1		150			21.1		7.84		30.3		170			20	
2/3/2012	3	7.82	7.79	29.1	27.57	154	155.0	11.80	21	21.03	7.83	7.84	28.8	29.07	169	170.0	11.80	21.1	20.37
		7.78		28.5		161			21		7.85		28.1		171			20	
		7.81		30.8		158			20.2		7.8		31.1		171			20.1	
2/4/2012	4	7.79	7.80	26.8	27.80	160	158.1	11.72	19.9	19.97	7.8	7.80	28.8	30.73	174	171.3	11.72	19.9	19.90
		7.8		26		163			19.8		7.81		22.3		173			18.7	
		7.81		19.6		158			19.6		7.81		19.9		169			18.9	
2/6/2012	7	7.82	7.78	19.7	19.63	155	157.0	11.65	18.8	19.07	7.82	7.79	20	19.93	172	170.0	11.65	19.1	19.03
		7.78		19.6		161			18.8		7.73		19.9		169			19.1	

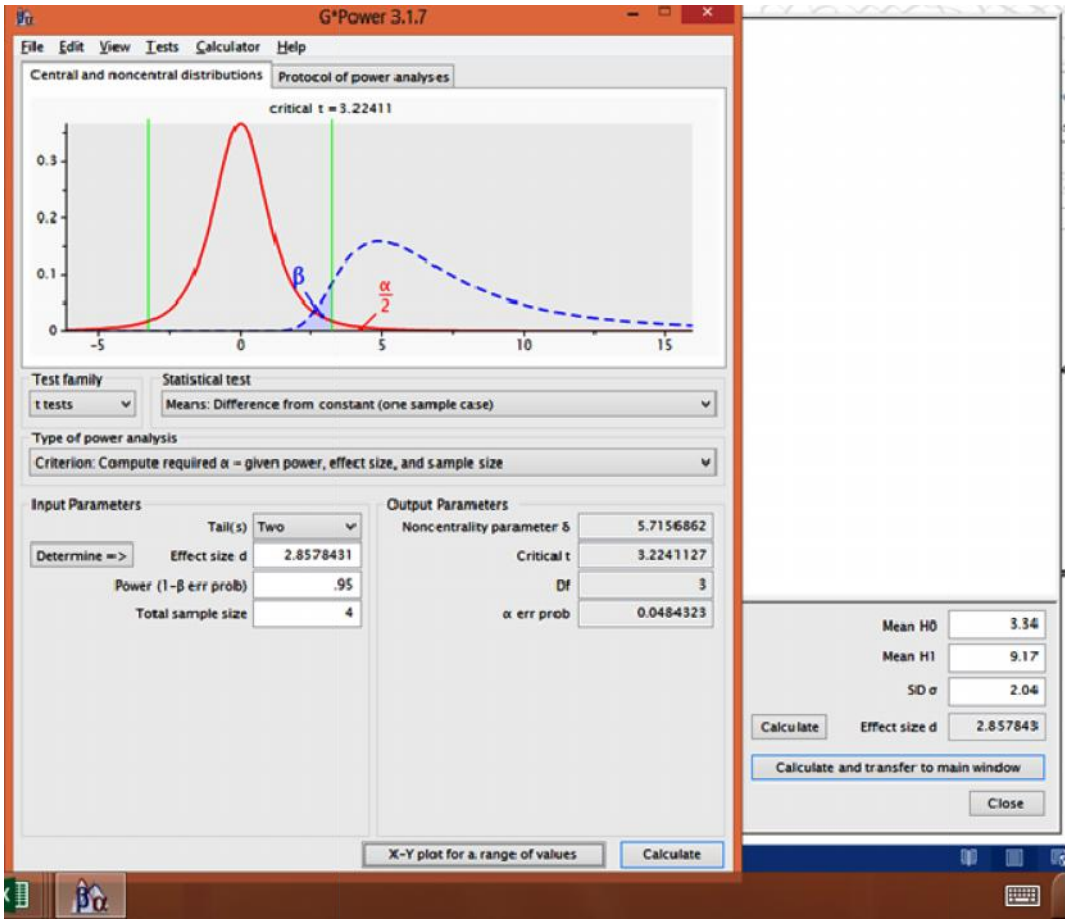
Results of pH 5 experiment

Date	DOE	Head Space Acid (HSA)									Liquid Manure Acid (LMA)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10*Ave.	Volume (l)	Temp. C	Ave.
						0.856			20.1				20.1		0.119			20.1	
10/18/11	0		5.36		20.10	0.856	0.0	0.220	20.1	20.10		5.42	20.1	20.10		1.2	0.220		20.10
		8.24		20.2		12.3			20		8.16		20.3		18.03			20.3	
10/20/11	2	8.23	8.23	20.3	20.27	12.25	100.8	0.208	20	19.97	8.17	8.17	20.3	20.30	17.7	170.0	0.238	19.9	20.03
		8.23		20.3		12.25			19.9		8.17		20.3		17.46			19.9	
		8.23		21.1		12.02			20.9		8.11		21.1		17.22			20.9	
10/21/11	3	8.24	8.24	20.9	20.97	12.33	120.8	0.196	20.9	20.90	8.13	8.13	21.1	21.10	17.3	177.4	0.196	20.9	20.90
		8.24		20.9		11.39			20.9		8.14		21.1		18.71			20.9	
		8.22		24.4		15.53			23.8		8.12		24.2		18.58			23.6	
10/25/11	7	8.22	8.23	24.4	24.40	17.5	168.9	0.184	23.7	23.67	8.11	8.12	24.2	24.20	17.99	184.3	0.184	23.7	23.60
		8.24		24.4		17.54			23.5		8.13		24.2		18.71			23.5	

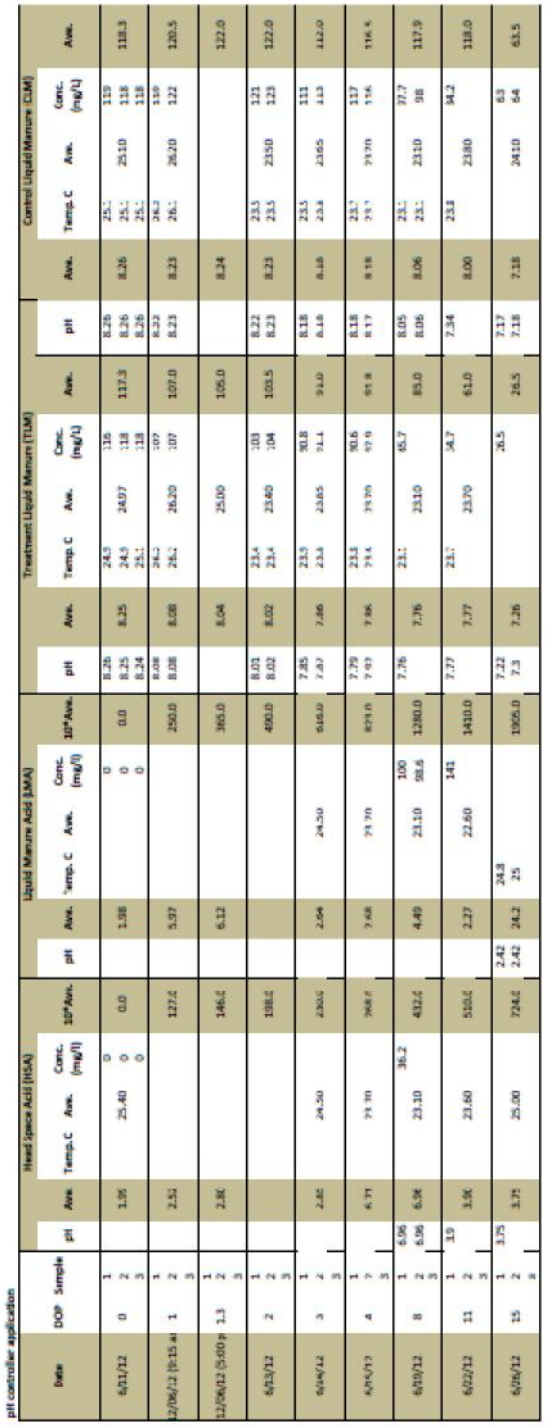
Results of pH 5 experiment

Date	DOE	Liquid Manure-Treatment (LMT)									Liquid Manure-Control (LMC)								
		pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Volume	Temp. C	Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/L)	Ave.	Volume	Temp. C	Ave.
		8.3		19.8		169			20.1		8.3		20.2		170.6			20.1	
10/18/11	0	8.29	8.29	20.2	20.07	168.3	169.0	12.020	20.1	20.10	8.3	8.30	20.4	20.27	164.4	163.9	12.020	20.1	20.10
		8.29		20.2					20.1		8.3		20.2		156.7			20.1	
		8.29		19.6		158.5			19.7		8.27		19.6		166			19.8	
10/20/11	2	8.29	8.29	19.3	19.40	154.5	157.0	11.945	19.8	19.77	8.3	8.29	19.5	19.50	164.1	165.4	11.945	19.8	19.77
		8.29		19.3		158.1			19.8		8.3		19.4		166			19.7	
		8.27		21.1		160					8.26		20.4		161.4			21.2	
10/21/11	3	8.28	8.28	20.9	20.97		160.0	11.870			8.26	8.26	20.3	20.37	166.2	164.5	11.870	21.2	21.20
		8.28		20.9							8.26		20.4		166			21.2	
		8.22		23.1		158.5			23.3		8.15		23.1		171			23.5	
10/25/11	7	8.22	8.15	23.1	23.07	162.6	157.0	11.795	23.3	23.27	8.15	8.15	23.1	23.10	163.3	167.8	11.795	23.4	23.43
		8.24		23		161.4			23.2		8.15		23.1		167.9			23.4	

A one-sample Student's t test was performed for this comparison and presented in M&M section. To conduct this test, G*Power 3.1 was used and an example of the software is shown below:



APPENDIX C



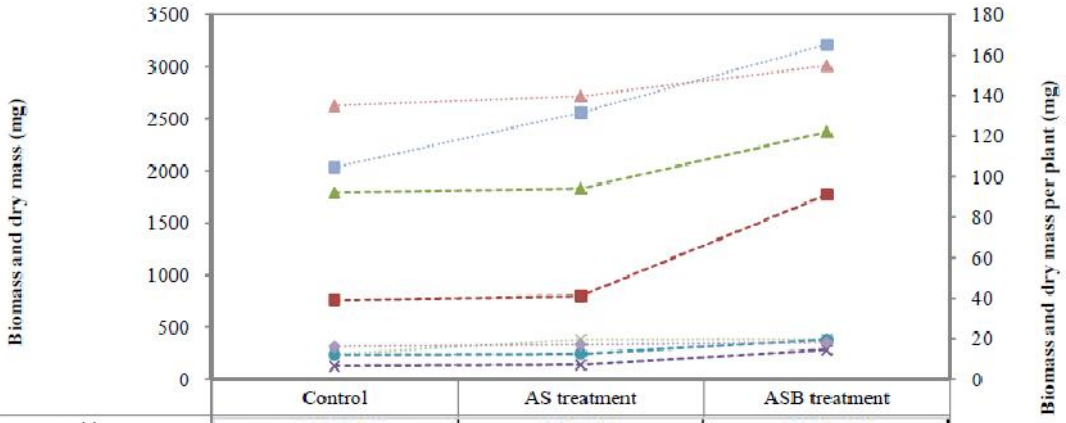
pH controller application				Head Space Acid (HSA)				Liquid Manure Acid (LMA)					Treatment Liquid Manure (TLM)					Control Liquid Manure (CLM)				
Date	DOP	Sample	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10^Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	10^Ave.	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	pH	Ave.	Temp. C	Ave.	Conc. (mg/l)	Ave.
6/11/12	0	1		1.95		25.40	0	0.0		1.98		24.50	0	0.0	8.26	8.25	24.5	24.07	116	8.26	8.26	25.1	25.10	119	118.3
		2					0						0		8.25		24.3		118	8.26		25.1		118	
		3					0						0		8.24		25.1		118	8.26		25.1		118	
12/06/12 (0:15 a	1	1		2.51				127.6		5.37				250.0	8.08	8.08	24.2	26.20	107	8.23	8.23	24.3	26.20	119	120.5
		2													8.08		26.2		107	8.23		26.1		122	
		3																							
12/06/12 (5:00 p	1.3	1		2.80				146.6		6.12				365.0		8.04		25.00		8.24					122.0
		2																							
		3																							
6/13/12	2	1						198.6						490.0	8.01	8.02	23.4	23.40	103	8.22	8.23	23.5	23.50	121	122.0
		2													8.02		23.4		104	8.23		23.5		123	
		3																							
6/14/12	3	1		2.85		24.50		230.6		2.04		24.50		615.0	7.85	7.86	23.3	23.65	90.8	8.18	8.18	23.5	23.65	111	112.0
		2													7.87		23.9		91.1	8.18		23.8		113	
		3																							
6/15/12	4	1		6.93		24.90		968.6		3.68		24.90		824.0	7.79	7.93	23.8	23.90	90.6	8.18	8.18	23.7	23.90	117	116.5
		2													7.93		23.9		91.0	8.17		23.7		116	
		3																							
6/19/12	8	1	6.96	6.04	23.1	23.10	36.2	432.6		4.49		23.10	100	1280.0	7.76	7.76	23.1	23.10	65.7	8.05	8.06	23.1	23.10	97.7	117.9
		2	6.96										98.6							8.06		23.1		98	
		3																							
6/22/12	11	1	3.9	3.96	23.7	23.60		510.6		2.27		22.60	141	1410.0	7.77	7.77	23.7	23.70	54.7	7.34	8.00	23.8	23.80	84.2	118.0
		2																							
		3																							
6/26/12	15	1	3.75	3.75	25.1	25.00		724.6	2.42	2.42	24.8	25		1905.0	7.22	7.3			26.5	7.17	7.18		24.10	63	63.5
		2																						64	
		3																							

Field-scale experiment

11/20-11/21						11/21-11/22						11/22-11/23						11/23-11/24					
Flow rate: 40						Flow rate: 85						Flow rate: 190						Flow rate: 280					
	Acid		LM				Acid		LM				Acid		LM				Acid		LM		
Time	pH	TAN	pH	TAN	Temp	Time	pH	TAN	pH	TAN	Temp	Time	pH	TAN	pH	TAN	Temp	Time	pH	TAN	pH	TAN	Temp
1	2.15	0	7.79	185	23.9	1	2.15	0				1	2.24	0			23.8	1	2.24	0			23.3
2	2.3	11.8	7.79	206	23.2																		
3	2.4	16.5	7.77	191	23.8																		
4	2.47	24.1	7.81	183	24.1																		
5	2.53	30.5	7.86	197	24.3																		
6	2.58	40	8.05	202	23.9																		
22	2.2	101	7.79	189	22.9																		
23	2.55	111	7.69	199	23.1	23	2	120	7.76	205	21.8												
24	2.54	121	7.71	181	23.3	24	1.08	201			22.7	24	0.98	134		190	19.6	24	0.98	134		190	19.5
Lab	1.91	222				Lab	1.17	220					1.12	216					4.49	4.49	105		
Average				193	23.61					205	22.25					190	21.7					190	21.7
Ideal NH3 Conc.		419						439						467						537.05			
NH3 mass (mg)		2328						3073						3269						3759.4			
NH3 mass (Mol)		0.202						0.220						0.234						0.269			
H Calculated mass(g)		0.205						0.216						0.227						0.239			
Calculated NH3-N(g)		2.874						3.023						3.172						3.340			
Final Dosing (mL)		426						447.8						469.9						494.8			
Acid final pH		4.49						5.5						2.1					1.95				
Concentrated acid for dosing:																							
Vol of injected acid=		290	ml					305	ml					320	ml					337	ml		
pH=		0.15						0.15						0.15						0.15			

APPENDIX D

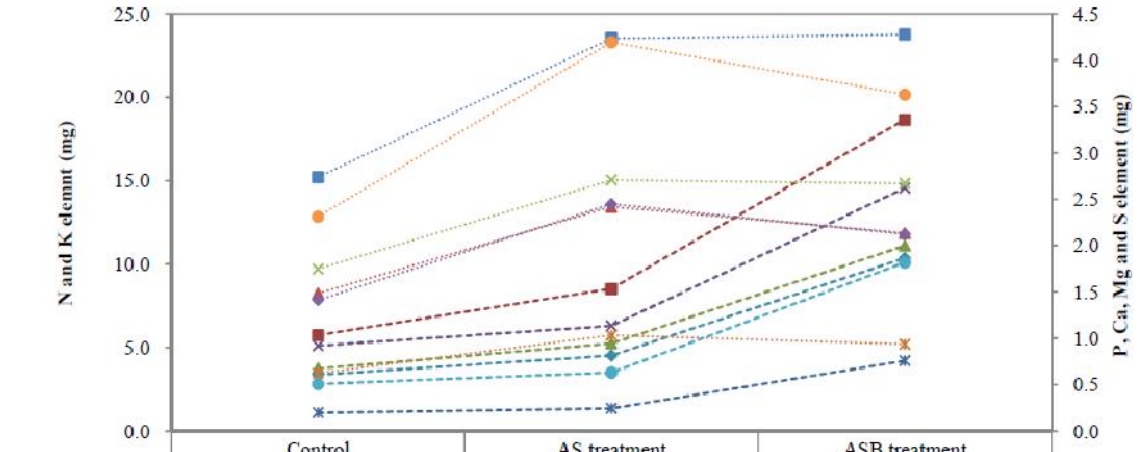
The biomass, dry mass, biomass per plant and dry mass per plant in each treatment of both rounds after four weeks of cultivations. The average values of each parameter in the treatments were presented in the graph and the corresponding variances are presented in the table below the graph.



	Control	AS treatment	ASB treatment
FRE biomass	(±297.1)	(±412.5)	(±296.1)
SRE biomass	(±706.0)	(±654.1)	(±331.2)
FRE dry mass	(±88.3)	(±109)	(±76.8)
SRE dry mass	(±98)	(±45.0)	(±46.5)
FRE biomass/plant	(±26.4)	(±48.5)	(±20.4)
SRE biomass/plant	(±47.1)	(±24.8)	(±16.5)
FRE dry mass/plant	(±7.3)	(±11.5)	(±5.3)
SRE drymass/plant	(±8.1)	(±4.7)	(±4.4)

re 3. Biomass, Dry mass, biomass and dry mass per plant in the treatments of FRE and SRE. Standard deviation of the four replications in each treatment is reported in the table below the graph.

The results of plant tissue analysis for six macronutrients are reported in the following graph. The average values of each parameter in the treatments were presented in the graph and the corresponding variances are presented in the table below the graph.



	Control	AS treatment	ASB treatment
N- FRE	(±1.3)	(±0.5)	(±0.2)
N- SRE	(±0.2)	(±0.1)	(±0.1)
K- FRE	(±1.3)	(±1.0)	(±0.3)
K- SRE	(±0.1)	(±0.1)	(±0.1)
P- FRE	(±0.1)	(±0.0)	(±0.0)
P- SRE	(±0.0)	(±0.0)	(±0.0)
Ca- FRE	(±0.1)	(±0.1)	(±0.0)
Ca- SRE	(±0.0)	(±0.0)	(±0.0)
Mg- FRE	(±0.0)	(±0.1)	(±0.0)
Mg- SRE	(±0.0)	(±0.0)	(±0.0)
S- FRE	(±0.0)	(±0.2)	(±0.0)
S- SRE	(±0.1)	(±0.1)	(±0.0)

e 4. Macronutrients collected in plant tissues of Control, AS and ASB treatment of FRE and SRE. Standard deviation of the four replications in each treatment is reported in the table below the graph.