AMMONIA RECOVERY FROM DIGESTED DAIRY MANURE AS NITROGEN FERTILIZER

By

ANPING JIANG

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of ANPING JIANG find it satisfactory and recommend that it be accepted.

Shulin Chen, Ph.D., Chair

Claudio O Stöckle, Ph.D.

Richard Zollars, Ph.D.

Pius Ndegwa, Ph.D.

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Abstract

by Anping Jiang, Ph.D.
Washington State University
December 2009

Chair: Shulin Chen:

Manure management on large dairy farms has become a major issue due to air quality and water quality concerns caused by excess nitrogen and phosphorus. Prior research efforts have not been able to develop a practical solution beyond manure land application. In this study, a novel combined nutrient recovery and biogas upgrading system (combined system) was developed to mitigate the environmental concerns as well as to harvest value added by-products from the anaerobically digested manure. The combined system was proven both technically feasible and economically advantageous. Ammonia stripping is the main unit process of the combined system. Temperature and pH were identified as the most cost sensitive parameters of ammonia stripping. Economical optimization of the stripping process was studied and optimized parameters were provided for future application of the technology. The results suggest that the combined system can be a practical solution for the environmental problems associated with excess nitrogen and phosphorus on large dairy farms and can partially purify the biogas from the anaerobic digestion (AD).

The performance of the combined system is highly dependent upon the chemical equilibriums of the digested manure. Current physic-chemical process models for wastewater cannot explain slow crystallizing precipitants formed in the effluent of dairy AD with long hydraulic retention time (HRT). In addition, current chemical models need detailed chemical data as input which are difficult to obtain for dairy wastewater. In this study, a two-step, three-phase chemical equilibrium model was developed for the supernatant of dairy AD. The model input was reduced by introducing a new parameter Δions to account the difference between inert cations and anions. The model can differentiate the precipitates formed in the AD with long HRT from that in the post-AD treatment with short HRT. Model validation showed that crystallizing HAP (hydroxyapatite) formed slowly in the effluent of dairy AD with long HRT. The model was applied to the unit processes of the combined system and the results suggest that the two-step, three-phase chemical equilibrium model can be used to predict the performance of the combined system.

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Dedication

This dissertation is dedicated to my beloved wife, Qinghua Zhu.

CHAPTER ONE

INTRODUCTION

1.1 Background

The effect of animal farming on the environment has become a major social concern in the U.S. and other countries due to the growing numbers of Concentrated Animal Feeding Operations (CAFOs). In the U.S., the 6% of farms larger than 1,000 animal units (AUs) were estimated to generate 65% of excess nitrogen and 68% of excess phosphorus in 1997 (Ribaudo *et al.* 2003). Ammonia, the main form of the nitrogen compound in the manure after digestion, can potentially lead to numerous air and water quality problems. With regard to air quality, animal operations contribute a total of 81% of ammonia emissions in the U.S. (Battye *et al.* 1994). Ammonia not only can be harmful to farm workers as well as surrounding residents by itself but can also interact with other air constituents to produce particulate matter concentrations (US-EPA 2004) detrimental to human health with long time exposure, particularly those with existing lung disorders. With regard to water quality, leaching and runoff are capable of transporting ammonia and its inorganic derivatives, nitrite and nitrate, to the ground and surface water. In the U.S., about 22% of domestic wells in agricultural areas exceeded the maximum contaminant level (MCL) of nitrate (Ward *et al.* 2005). Nitrite is a known carcinogen but not a major environment concern because of the quick conversion of nitrite to nitrate by nitrifying bacteria. Ammonia and nitrate are more stable and they are also harmful to both human and aquatic animals, with ammonia being toxic to aquatic organisms and nitrate capable of causing methemoglobinemia and birth defect (WS-DOH 2005, Ward *et al.* 2005). Inorganic nitrogen can also cause water system eutrophication. In the U.S., nitrogen from non-point sources was the primary cause of coastal eutrophication (National Science and Technology Council 2003). With a total of 139 estuaries examined, 44 showed high overall levels of eutrophication and 40 exhibited moderate levels eutrophication (National Science and Technology Council 2003). Recovering ammonia nitrogen from animal manure can mitigate the air quality problems as well as reduce the threat to water pollution, especially for CAFOs where approximately 36% and 55% of all dairy CAFOs experience nitrogen and phosphorous overloads, respectively (USDA-APHIS 2004).

Anaerobic Digestion (AD), the widely recognized animal manure management technology, can produce biogas for energy production and control part of manure odor problems by degrading volatile organic compounds, but it does not reduce nitrogen, instead it converts part of the organic nitrogen to volatile ammonia. After digestion, the ammonia-N concentration of the dairy manure increased 25% in a case study (Martin 2005), which increased the ammonia emission problem. On the other hand, the increased ammonia-N concentration can be beneficial if ammonia recovery was followed the digestion. In addition, AD effluent always has higher temperature and lower amounts of solids, which are favorable for all ammonia removal and recovery technologies.

1. 2 Review of the ammonia removal/recovery technologies

Ammonia removal has been extensively studied for municipal and industrial wastewater treatment. All wastewater nitrogen removal processes that developed for municipal and industrial wastewater have been studied for animal wastewater treatment, mainly Biological Nitrogen Removal (BNR), ammonia stripping, ion exchange, and struvite crystallization.

1.2.1 Biological Nitrogen Removal (BNR)

There are three kinds of BNR techniques: 1) conventional nitrification and denitrification; 2) nitritation and denitritation; and 3) partial nitritation and anammox. All BNR processes include two or more steps of reactions (1-5).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad (2)$$

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad (3)$$

$$NO_2^- + 4H^+ + 3e^- \rightarrow 0.5N_2 + 2H_2O \qquad (4)$$

$$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O \qquad (5)$$

Conventional nitrification and denitrification, which is the most widely used wastewater BNR process, includes the entire process of oxidation of ammonia to nitrate (reactions 1-2) and reduction of nitrate to nitrogen gas (reactions 3-4). It has been studied for ammonia removal from animal wastewater at full scale without anaerobic digestion

(Vanotti 2005, Choi *et al.* 2005, Tilche *et al.* 2001). After nitrification and denitrification, the ammonia emission from an animal wastewater lagoon were reduced by 90% (Szögi *et al.* 2006). However, nitrification and denitrification cannot be used for post-treatment of AD because there are not enough electron donors (biodegradable organic carbon) for denitrification. Most biodegradable organic carbon was converted to CO_2 and CH_4 in the AD.

Nitritation and denitritation processes that only include reactions (1) and (4) have been developed for wastewater that does not have sufficient biodegradable organic carbon for conventional denitrification. SHARON (Hellinga *et al.* 1998), shortcut BNR (Ciudad *et al.* 2005), and Simultaneous Nitrification and Denitrification (SND) via nitrite (Yoo *et al.* 1999) are all processes based on this concept. Nitritation and denitritation can be applied to wastewater treatment plants for nitrogen removal from digester supernatant of municipal wastewater treatment plants (Fux *et al.* 2003). Unfortunately, the Dairy AD effluent does not contain enough biodegradable material for denitritation because of the large amount of nitrogen needs to be removed.

For wastewater that does not contain enough organic carbon for denitritation, a completely autotrophic BNR process (reactions 1 and 5) was developed. The newly developed process of partial nitritation + anammox (ANaerobic AMMonium Oxidation) does not need any biodegradable organic carbon (van Dongen *et al.* 2001). The disadvantage of this technique is that the anammox bacteria grow extremely slow, which cannot compete with other microorganisms and they will be easily washed out.

1.2.2 Ammonia stripping and absorption

Ammonia stripping, as a proven process for the treatment of high ammonia concentration wastewater, can be adopted for removing ammonia nitrogen from the digested manure for subsequent recovery as a fertilizer to be exported out the farm. Ammonia stripping is based on ammonium disassociation and ammonia equilibrium between liquid and gas (Eqs. 6-7) (Crittenden *et al.* 2005). Ammonia stripping efficiency is controlled by the content of the free ammonia in the liquid which is further determined by the pH and temperature as Eq. 8 (Metcalf & Eddy 2003). The value of *Ka* can be obtained from Eq. 9 (Emerson *et al.* 1975).

$$\mathrm{NH_4^+} \Leftrightarrow \mathrm{NH_3} + \mathrm{H^+} \qquad Ka=10^{-9.25} \text{ at } 20^{\circ}\mathrm{C} \qquad (6)$$

$$NH_{3(aq)} \Leftrightarrow NH_{3(gas)} \qquad H=0.0006 \text{ at } 20^{\circ}\mathrm{C} \qquad (7)$$

$$\mathrm{NH_3},\% = \frac{100}{1+\dfrac{[\mathrm{H^+}]}{Ka}} \qquad (8)$$

$$Ka = 10^{-(0.0897+\frac{2729}{\mathrm{T}})} \qquad (9)$$

Where *Ka* is the ammonium disassociation constant; *H* is the Henry's constant, dimensionless; $[\mathrm{H^+}]$ is the $\mathrm{H^+}$ concentration, mole/L; T is temperature in $^{\circ}$K.

Packed towers or tray towers operated with countercurrent flow of wastewater and air or steam are always applied for stripping out of contaminates including ammonia. Ammonia stripping efficiency is highly dependent on the temperature, pH, and air/liquid ratios (US-EPA 2000). Ammonia stripping is relatively simple and not affected by wastewater fluctuation and toxic compounds that could disrupt the performance of a biological system if pH and air temperature remain stable (US-EPA 2000).

Ammonia stripping studies for landfill leachate (Cheung *et al.* 1997), sludge digester supernatant of municipal wastewater treatment plant (Katehis *et al.* 1998), swine wastewater (Bonmatí & Flotats 2003, Liao *et al.* 1995, Liehr *et al.* 2006), and dairy manure digester supernatant (Zeng *et al.* 2005, Zeng *et al.* 2006) have already been reported. Ammonia stripping has already been successfully applied at full scale for large municipal wastewater treatment plants (Janus & van der Roest 1997, Thorndahl 1993, Zeng *et al.* 2005) and landfill leachate. Janus and van der Roest (1997) found that ammonia stripping with air was one of the two most cost effective processes after compared with other ammonia removal technologies at pilot scale for the supernatant of the digested wastewater treatment sludge. The other most cost effective processes that Janus and van der Roest (1997) recommended, nitritation and denitritation, cannot be applied to digested dairy wastewater because the wastewater contains insufficient biodegradable organic carbon for denitritation.

The major concern of applying ammonia stripping to animal manure is the chemical demand, including both alkali for raising pH prior to the stripping and acid for lowering pH after stripping. Exhaust gas from the electricity generator using biogas (Li *et al.* 2006) and air (Vanotti 2005) can be used to re-adjust the high pH back to acceptable level and CO_2 absorption is contributed to the pH drop. The biogas from the anaerobic digester contains 25-45% of CO_2 and 0-3% of H_2S which can also be used to re-adjust the pH of the ammonia stripping effluent back to acceptable level (Lei *et al.* 2007). Using biogas for pH readjustment can upgrade the biogas by absorbing part of CO_2 and H_2S. It can improve the biogas heat capacity and reduce its causticity. Since the anaerobic digestion effluent usually has a mesophilic temperature, about 35 ℃, it is possible to operate ammonia stripping at lower pH, so the CO_2 and H_2S in the biogas may be sufficient to reduce the pH to the levels that meet the environment requirement, normally 6-9.

1.2.3 Ion-Exchange

Ion exchange is another widely studied ammonia removal and recovery technology because of its ability for handling shock loads and wide ranges of operating temperatures. The ion exchange process follows certain exchange sequences for different ions. The conventional strong acid resin has an ion exchange sequence of $Fe^{3+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+}$ which cannot be used for ammonia removal, because NH_4^{+} need to compete with other abundant ions in the wastewater. Zeolites have been known as having high affinity to NH_4^{+} (Pansini 1996). According to experiments, the affinity sequence of common ions to clinoptilolite and chabazite is: $K^+ > NH_4^+ > Na^+ > Ca^{2+}$ (Hedström 2001). Zeolites, including other members of the zeolite group such as mesolite and especially clinoptilolite, showed good ammonia removal performance for synthesize wastewater (Ji *et al.* 2007, Wen *et al.* 2006, Njoroge & Mwamachi 2004), flocculent treated sewage(Booker *et al.* 1996), filtered anaerobic digestion sludge liquor from wastewater treatment facility (Thornton *et al.* 2007), membrane filtered digested cattle manure effluent (Guo *et al.* 2008), landfill leachate (Karadag *et al.* 2008), and dairy lagoon water (Bolan *et al.* 2004).

Jorgensen and Weatherley (2003) found that the ammonium exchange capacity of zeolite was increased with organics present. Sodium soaking followed water rinsing was usually applied for zeolite pretreatment to increase the zeolite absorption capacity (Karadag *et al.* 2008, Guo *et al.* 2008, Hedström 2001). Calcium can be also applied for clinoptilolite pretreatment and regeneration but it will lower the ammonium exchange capacity (Ji *et al.* 2007).

Potassium, which is abundant in the digested dairy wastewater, is the major competitor for the ammonium exchange of zeolite. Guo (2008) observed the K^+ uptake by the clinoptilolite is faster than NH_4^+. Karadage (2008) and Wang (2006) observed competitors, mainly K^+, Ca^{2+}, and Mg^{2+}, significantly lowered the absorption capacity of the clinoptilolite. Because of the strong combination of potassium with zeolite, the ion exchange capacity of zeolite cannot be fully regenerated (Liu & Lo 2001). It suggests the regenerated zeolite will have lower ammonium and potassium exchange capacity.

After ion exchange, the ammonium saturated zeolite can be applied to the field as nitrogen fertilizer (Bolan *et al.* 2004), used for ammonia recovery by ammonia stripping and acid absorption followed by chemical regeneration, or regenerated by converting the ammonia to nitrate using biological regeneration (reactions 10 and 11) (Dimova *et al.* 1999).

Ion exchange: $[Zeolite]NH_4^+ + Na^+ \rightarrow [Zeolite]Na^+ + NH_4^+$ (10)

Nitrification: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ (11)

Clogging is the major problem for using ion exchange with wastewater, especially animal wastewater. Most of the studies used synthesize wastewater. Membrane filtration such as UF and Reverse Osmosis (RO) (Guo *et al.* 2008), ceramic filtration (Thornton *et al.* 2007), or protecting filtration layer (Cooney *et al.* 1999) was used in order to prevent the experiment system from clogging when wastewater was used for the studies. With protecting filtration coal layer, periodical backwash was needed to avoid clogging even the suspended solid (SS) was less than 20 mg/L (Booker *et al.* 1996). Because of the clogging problem was difficult to solve, Bolan *et al.*, (2004) directly applied the ammonium saturated zeolite as nitrogen fertilizer.

1.2.4 Struvite crystallization

A newly-developing chemical technology for P removal and recovery, struvite (magnesium ammonium phosphate hexahydrate, or $MgNH_4PO_4.6H_2O$) crystallization can also be applied for partial ammonia recovery. It has already been applied for phosphorus recovery from the AD supernatant of several municipal wastewater treatment plants. It can also recover some ammonia because only magnesium was added to these systems. In dairy manure liquid, although there is abundance of phosphorus, but most phosphate was bound with calcium as fine particulate which is not available for struvite crystallization and the chemical for releasing the phosphorus is too expensive (Zhang *et al.* 2009). If ammonia recovery was the major purpose of struvite crystallization, not only magnesium, phosphorus also was added to the wastewater (Uludag-Demirer *et al.* 2005, Altinbas *et al.* 2002). Remaining phosphorus may be a more severe pollution potential for the water systems. On the other hand, phosphorus is more valuable than ammonia because phosphorus is non-renewable resource. To save the valuable phosphorus, the crystallized struvite was put in a oven to release ammonia (stripping) and the remaining magnesium and phosphorus was recycled (Turker & Celen 2007).

1.2.5 Comparison of ammonia removal or recovery technologies for dairy wastewater

Among the ammonia removal and/or recovery technologies reviewed, the struvite crystallization was only applied for municipal phosophorus recovery with little ammonia removal. It cannot remove the high concentration of ammonia in the dairy manure. The ion-exchange has no demonstration of large scale application even for other wastewater treatment. Similarly, the partial nitritation + anammox technology also lack of demonstration even for wastewaters other than manure. Other BNR technologies and ammonia stripping have plenty of demonstrations for other types of wastewater treatment, but only ammonia stripping can be applied to the AD supernatant which contains limited biodegradable organic carbon that is not enough for denitrification or denitritation. Ammonia stripping is a potential technology for ammonia removal from digested dairy manure. The effluent of ammonia stripping has high pH which is not suitable for long time storage or land application but it is possible to use the biogas generated from the AD to readjust the pH of the ammonia stripped effluent to environmental acceptable levels. In addition, ammonia stripping usually includes pre pH elevation by lime settling, which is capable of phosphorus removal.

1.3 Process strategy

Based on the previous review and comparison, a combined nutrient recovery and biogas upgrading system (combined system) was developed as shown in Figure 1-1 (Jiang *et al.* 2009). This process contains a flocculation reactor mainly for phosphorus removal, a pH adjustment reactor and settler which can also separate the phosphorus, an ammonia stripping and acid absorption system for ammonia recovery, and a biogas scrubbing reactor for the pH readjustment of the ammonia stripped effluent and biogas purification. The combined system may be a practical solution to the environmental problems of CAFOs with excess nitrogen and phosphorus. The combined system has potential of generating a wastewater stream with low nutrient content and three value added by-products: 1) phosphorus rich solid from flocculation and lime settling; 2) ammonium sulfate solution as nitrogen fertilizer from ammonia stripping and acid absorption; 3) purified biogas from biogas scrubbing.

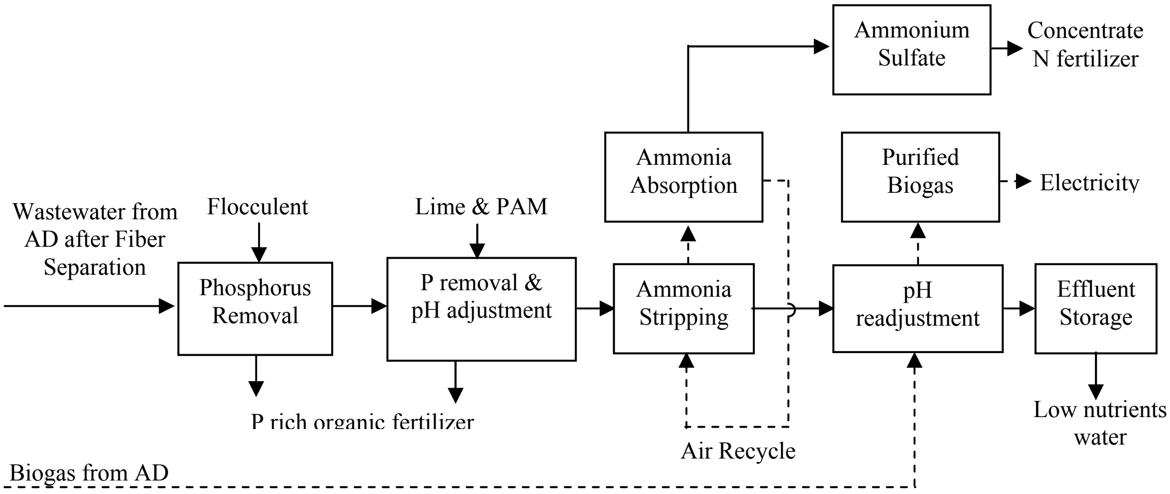

Figure 1-1: Flowchart of the combined nutrient recovery and biogas upgrading system

1.4 Chemical equilibrium model

Chemical equilibrium is the core of the unit processes of the combined system. Previous chemical equilibrium models were developed as part of biological wastewater treatment models such as Activated Sludge Model (Henze *et al.* 2000) and Anaerobic Digestion Model (Batstone *et al.* 2002). It always focused on the chemical equilibrium around neutral pH in order to enhance the biological activities or at lower pH to assist the biological hydrolysis process. Chemical-physical processes model were also developed separately for assisting the understanding of the chemical-physical procedure of wastewater treatment such as struvite crystallization (Celen *et al.* 2007, Gadekar & Pullammanappallil 2009). In these chemical equilibrium models, not only dissolved species in liquid phase, but also gas and solid phases were always included (Batstone et al. 2002, Gadekar & Pullammanappallil 2009, Musvoto *et al.* 2000). The most common gas specie included is CO_2. Activated Sludge Model No. 1 (ADM1) also included H_2 and CH_4 because they are the major products/intermediates from AD (Batstone *et al.* 2002). H_2S, an important AD inhibitor, which also affects the usage of biogas, should also be included in the chemical equilibrium model if the biogas quality or the H_2S inhibition is concerned, but it was not included in current chemical equilibrium models for wastewater. Solid species included in the chemical equilibriums were various because of the different wastewater used for the research and the different research interests, e.g. struvite was added for phosphorus recovery (Gadekar & Pullammanappallil 2009, Celen *et al.* 2007), all carbonates were neglected as synthesis wastewater did not contain carbonates (Gadekar & Pullammanappallil 2009). No chemical equilibrium model for wastewater considered the reaction time in the AD with long hydraulic retention time (HRT) where the slow crystallizing species may form. In addition, chemical equilibrium models calculate pH by electroneutrality which needs all the cations and anions known or calculated. All inert species need to be measured because they cannot be calculated based on other species which is difficult especially for digested dairy manure.

For the complicate dairy wastewater system, simulating the chemical equilibriums needs careful selection of the chemical species of all three phases. Slow forming species should also be considered for the AD effluent because of the long reaction time in the AD. The model should reduce the measurements for the model input especially for the dairy wastewater.

1.5 Research objectives

The goal of this dissertation research is to study applying the combined nutrient recovery and biogas upgrading system (Figure 1) to solve ammonia concern of storage or land application of dairy manure and develop a chemical equilibrium model suitable for the digested dairy manure wastewater which can be applied to the unit processes of the system. The research hypotheses are: 1) by taking advantage of the temperature of the anaerobic digestion effluent, the ammonia stripping can be operated without heating and with lower pH than the conventional 10.8-11.5 range (US-EPA 2000); 2) since the pH of the ammonia stripping is lower, the biogas scrubbing can be used to re-adjust the ammonia-stripped effluent back to environmentally acceptable levels; 3) after economically optimize the ammonia stripping parameters, the cost of the combined system can be reduced to make it economical feasible; 4) a three-phase chemical equilibrium model will be suitable to describe the chemistry of the unit processes of the combined system. Specific research objective included:

1) To study the feasibility of the combined nutrient recovery and biogas upgrading system;

2) To identify the economic sensitive ammonia stripping parameters and economically optimize them to provide optimum ammonia stripping parameters for the application of the combined nutrient recovery and biogas upgrading system.

3) To develop a chemical equilibrium model which can be applied to the post AD treatment for dairy manure. The model should include three phases suitable for the long HRT dairy AD effluent which can also reduce the measurements for the model input.

1.6. Structure of this dissertation

This dissertation includes three manuscripts followed this introductory chapter that reflect the three specific objectives and a summary. The three manuscripts are prepared for publication in peer-reviewed journals. Below is a brief, chapter by chapter, overview of the dissertation.

Chapter 1 gave introduction why this research topic was chosen and how it will be done.

Chapter 2 examined the technical feasibility of the developed combined nutrient recovery and biogas upgrading system and conducted a case study for economic analysis.

Chapter 3 studied the economical optimization of the ammonia stripping to give guideline for application it to digested dairy manure.

Chapter 4 developed a two-step, three- phase chemical equilibrium model for digested dairy manure and the model was applied to the unit processes of the combined nutrient recovery and biogas upgrading system.

Chapter 5 summarized this research and recommended future research topics.

1.7 References

Altinbas, M., I. Ozturk & A. F. Aydin (2002) Ammonia recovery from high strength agro industry effluents. *Water Science and Technology,* **45**(12)**,** 189-196.

Batstone, D. J., J. Keller, I. Angelidaki, S. V. Kalyuzhnyi, S . G. Pavlostathis, A. Rozzi, W. T. M. Sanders, H. Siegrist & V. A. Vavilin (2002) *Anaerobic digestion model no. 1 - IWA task group for mathematical modelling of anaerobic digestion processes.* IWA publishing, London, UK.

Battye, R., W. Battye, C. Overcash & S. Fudge (1994) Development and selection of ammonia emission factors. 68-D3-003, US-EPA, Washington DC, USA.

Bolan, N. S., L. Wong & D. C. Adriano (2004) Nutrient removal from farm effluents. *Bioresour. Technol.,* **94**(3)**,** 251-260.

Bonmatí, A. & X. Flotats (2003) Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management,* **23**(3)**,** 261-272.

Booker, N. A., E. L. Cooney & A. J. Priestly (1996) Ammonia removal from sewage using natural Australian zeolite. *Water Sci. Technol.,* **34**(9)**,** 17-24.

Celen, I., J. R. Buchanan, R. T. Burns, R. B. Robinson & D. R. Raman (2007) Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research,* **41**(8)**,** 1689-1696.

Cheung, K. C., L. M. Chu & M. H. Wong (1997) Ammonia stripping as a pretreatment for landfill leachate. *Water Air and Soil Pollution,* **94**(1-2)**,** 209-221.

Choi, E., D. Kim, Y. Eum, Z. Yun & K. S. Min (2005) Full-scale experience for nitrogen removal from piggery waste. *Water Environment Research,* **77**(4)**,** 381-389.

Ciudad, G., O. Rubilar, P. Munoz, G. Ruiz, R. Chamy, C. Vergara & D. Jeison (2005) Partial nitrification of high ammonia concentration wastewater as a part of a shortcut biological nitrogen removal process. *Process Biochemistry,* **40**(5)**,** 1715-1719.

Cooney, E. L., N. A. Booker, D. C. Shallcross & G. W. Stevens (1999) Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Sep. Sci. Technol.,* **34**(14)**,** 2741-2760.

Crittenden, J. C., R. R. Trussell, D. W. Hand, K. J. Howe & G. Tchobanoglous (2005) Water treatment: principles and design (second ed.). John Wiley & Sons, Inc., Hoboken, New Jersey.

Dimova, G., G. Mihailov & T. Tzankov (1999) Combined filter for ammonia removal - Part I: Minimal zeolite contact time and requirements for desorption. *Water Sci. Technol.,* **39**(8)**,** 123-129.

Emerson, K., R. C. Russo, R. E. Lund & R. V. Thurston (1975) Aquous ammonia equilibrium calculations: effect of pH and temperature. *Journal of the Fisheries Research Board of Canada,* **32**(12)**,** 2379-2383.

Fux, C., K. Lange, A. Faessler, P. Huber, B. Grueniger & H. Siegrist (2003) Nitrogen removal from digester supernatant via nitrite - SBR or SHARON? *Water Science and Technology,* **48**(8)**,** 9-18.

Gadekar, S. & P. Pullammanappallil (2009) Validation and applications of a chemical equilibrium model for struvite precipitation. *Environ Model Assess,* DOI 10.1007/s10666-10009-19193-10667.

Guo, X., L. Zeng, X. M. Li & H. S. Park (2008) Ammonium and potassium removal for anaerobically digested wastewater using natural clinoptilolite followed by membrane pretreatment. *J. Hazard. Mater.,* **151**(1)**,** 125-133.

Hedström, A. (2001) Ion exchange of ammonium in zeolites: A literature review. *Journal of Environmental Engineering-Asce,* **127**(8)**,** 673-681.

Hellinga, C., A. A. J. C. Schellen, J. W. Mulder, M. C. M. van Loosdrecht & J. J. Heijnen (1998) The SHARON process: An innovative method for nitrogen removal from ammonium-rich waste water. *Water Science and Technology,* **37**(9)**,** 135-142.

Henze, M., W. Gujer & T. Mino (2000) *Activated sludge models ASM1, ASM2, ASM2d and ASM3 - IWA task group for mathematical modelling for design and operation of biological wastewater treatment.* IWA publishing, London, UK.

Janus, H. M. & H. F. van der Roest (1997) Don't reject the idea of treating reject water. *Water Science and Technology,* **35**(10)**,** 27-34.

Ji, Z. Y., J. S. Yuan & X. G. Li (2007) Removal of ammonium from wastewater using calcium form clinoptilolite. *J. Hazard. Mater.,* **141**(3)**,** 483-488.

Jiang, A., T. Zhang, C. Frear & S. Chen (2009) Combined nutrient recovery and biogas scrubbing system integrated in series with animal manure anaerobic digester. US Patent Application No.: 20090206028.

Jorgensen, T. C. & L. R. Weatherley (2003) Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Res.,* **37**(8)**,** 1723-1728.

Karadag, D., S. Tok, E. Akgul, M. Turan, M. Ozturk & A. Demir (2008) Ammonium removal from sanitary landfill leachate using natural Gordes clinoptilolite. *J. Hazard. Mater.,* **153**(1-2)**,** 60-66.

Katehis, D., V. Diyamandoglu & J. Fillos (1998) Stripping and recovery of ammonia from centrate of anaerobically digested biosolids at elevated temperatures. *Water Environment Research,* **70**(2)**,** 231-240.

Lei, X., N. Sugiura, C. Feng & T. Maekawa (2007) Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification. *Journal of Hazardous Materials,* **145**(3)**,** 391-397.

Li, X., L. Zeng & E. A. Jenson (2006) Process for removal and recovery of nutrients from digested manure or other organic wastes. United States Patent, US7014768B2.

Liao, P. H., A. Chen & K. V. Lo (1995) Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology,* **54**(1)**,** 17-20.

Liehr, S. K., J. J. Classen, F. J. Humenik, C. Baird & M. Rice (2006) Ammonia Recovery from Swine Belt Separated Liquid. *2006 ASABE Annual International Meeting.* Portland, Oregon.

Liu, C. H. & K. V. Lo (2001) Ammonia removal from compost leachate using zeolite. III. Regeneration of zeolite columns. *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.,* **36**(10)**,** 1825-1843.

Martin, J. H. (2005) An evaluation of a mesophilic, modified plug-flow anarobic digester for dairy cattle manure. Final report for EPA Contract GS10F-0036K, U.S. Environmental Protection Agency, Washington, DC.

Metcalf & Eddy (2003) *Wastewater engineeering treatment and reuse (fourth ed.).* McGraw-Hill, NY, USA.

Musvoto, E. V., M. C. Wentzel, R. E. Loewenthal & G. A. Ekama (2000) Integrated chemical-physical processes modelling - I. Development of a kinetic-based model for mixed weak acid/base systems. *Water Research,* **34**(6)**,** 1857-1867.

National Science and Technology Council (2003) An Assessment of Coastal Hypoxia and Eutrophication in U.S. Waters. National Science and Technology Council, Committee on Environment and Natural Resources.

Njoroge, B. N. K. & S. G. Mwamachi (2004) Ammonia removal from an aqueous solution by the use of a natural zeolite. *J. Environ. Eng. Sci.,* **3**(2)**,** 147-154.

Pansini, M. (1996) Natural zeolites as cation exchangers for environmental protection. *Mineralium Deposita,* **31**(6)**,** 563-575.

Ribaudo, M., N. Gollehon, M. Aillery, J. Kaplan, R. Johansson, J. Agapoff, L. Christensen, V. Breneman & M. Peters (2003) Manure management for water quality: costs to animal feeding operations of applying manure nutrients to land. U.S. Department of Agriculture, Economic Research Service, Resource Economics Division. Agricultural Economic Report 824.

Szögi, A. A., M. B. Vanotti & A. E. Stansbery (2006) Reduction of ammonia emissions from treated anaerobic swine lagoons. *Transactions of the ASABE,* **49**(1)**,** 217-225.

Thorndahl, U. (1993) Nitrogen removal from returned liquors. *Journal of the Institution of Water and Environment Management,* **7**(5)**,** 492-496.

Thornton, A., P. Pearce & S. A. Parsons (2007) Ammonium removal from digested sludge liquors using ion exchange. *Water Res.,* **41**(2)**,** 433-439.

Tilche, A., G. Bortone, F. Malaspina, S. Picinini & L. Stante (2001) Biological nutrient removal in a full-scale SBR treating piggery wastewater: results and modelling. *Water Science and Technology,* **43**(3)**,** 363-371.

Turker, M. & I. Celen (2007) Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate. *Bioresource Technology,* **98**(8)**,** 1529-1534.

Uludag-Demirer, S., G. N. Demirer & S. Chen (2005) Ammonia removal from anaerobically digested dairy manure by struvite precipitation. *Process Biochem.,* **40**(12)**,** 3667-3674.

US-EPA (2000) Wastewater technology fact sheet: ammonia stripping. EPA Report 832-F-00-019, U.S. Environmental Protection Agency, Office of Water, Washington, DC.

US-EPA (2004) National emission inventory - ammonia emissions from animal husbandry. U.S. Environmental Protection Agency, Washington, DC.

USDA-APHIS (2004) Dairy 2002: nutrient management and the U.S. dairy industry in 2002. U.S. Department of Agriculture, Animal and Plant Health Inspection Service, Washington, DC.

van Dongen, U., M. S. M. Jetten & M. C. M. Van Loosdrecht (2001) The SHARON$^{®}$-Anammox$^{®}$ process for treatment of ammonium rich wastewater. *Water Science & Technology,* **44**(1)**,** 153-160.

Vanotti, M. (2005) Evaluation of environmentally superior technology: swine waste treatment system for elimination of lagoons, reduced environmental impact, and improved water quality. USDA Agreement 58-6657-2-202 / NCSU Subcontract #2001-0478-02 / USDA-ARS CRIS Project # 6657-13630-001-05, USDA-ARS.

Wang, Y. Q., S. J. Liu, Z. Xu , T. W. Han, S. Chuan & T. Zhu (2006) Ammonia removal from leachate solution using natural Chinese clinoptilolite. *J. Hazard. Mater.,* **136**(3)**,** 735-740.

Ward, M. H., T. M. deKok, P. Levallois, J. Brender, G. Gulis, B. T. Nolan & J. VanDerslice (2005) Workgroup report: Drinking-water nitrate and health-recent findings and research needs. *Environmental Health Perspectives,* **113**(11)**,** 1607-1614.

Wen, D. H., Y. S. Ho & X. Y. Tang (2006) Comparative sorption kinetic studies of ammonium onto zeolite. *J. Hazard. Mater.,* **133**(1-3)**,** 252-256.

WS-DOH (2005) Nitrogen reducing technologies for onsite wastewater treatment systems : report to the Puget Sound Action Team. DOH Pub 334-083, Division of Environmental Health, Washington State Department of Health, Olympia.

Yoo, K., K. H. Ahn, H. J. Lee, K. H. Lee, Y. J. Kwak & K. G. Song (1999) Nitrogen removal from synthetic wastewater by simultaneous nitrification and denitrification (SND) via nitrite in an intermittently-aerated reactor. *Water Research,* **33**(1)**,** 145-154.

Zeng, L., X. Li, J. Liu & E. Jenson (2005) Feasibility study of air stripping of ammonia from digested cattle manure. *ADSW 2005 conference proceedings*, pp. 656-663.

Zeng, L., C. Mangan & X. Li (2006) Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology*, **54**(8)**,** 137-145.

Zhang, T., K. E. Bowers, J. H. Harrison & S. Chen (2009) Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy effluent. *Water Environment Research,* **81,** (Accepted. uncorrected page proofs.).

CHAPTER TWO

A COMBINED NUTRIENT RECOVERY AND BIOGAS UPGRADING SYSTEM FOR APPLICATION WITH ANAEROBICALLY DIGESTED DAIRY MANURE

2.1 Abstract

Dairy manure contains appreciable amount of nitrogen and phosphorus which on concentrated animal feeding operations (CAFOs) often leads to air quality and water quality concerns. Prior research efforts have not been able to lead to a practical solution beyond manure land application. In this study, a novel combined nutrient recovery and biogas upgrading system (the combined system) was developed for recovering ammonia from the effluent of dairy AD. First, phosphorus containing solids was removed from the effluent and the pH of the effluent was elevated through the addition of lime. Then the ammonia in the effluent was stripped out and subsequently absorbed in acid as N-fertilizer. Finally, biogas from the AD was used to readjust the pH of the ammonia stripped effluent back to an accepted level while concurrently upgrading the biogas by absorbing H_2S and CO_2 from the biogas into the effluent. The study proved that the combined system is not only technically feasible but also economically advantageous. Majority of phosphorus (80%) can be removed using just settling caused by lime addition. At a temperature of 35^{o}C and pH 10, approximately 65% of ammonia can be stripped out of a 1.5-m packed column with near 100% absorption by keeping the pH of the acid solution to be less than 2.0. The pH of the ammonia stripped effluent can be neutralized to the same level prior to the treatment with the combined system. As high as 90% of H_2S removal can be achieved from a starting concentration of 2000 ppm with a biogas/liquid ratio of ten (v/v).

Key Words: Nutrient recovery, ammonia stripping, diary wastewater, biogas upgrading, H_2S removal

2.2 Introduction

With approximately 696 million tons of animal manure produced yearly in the U.S., and 46% of that being generated on CAFOs (Ribaudo *et al.* 2003), animal waste management is becoming an important environmental concern due to excess nitrogen and phosphorus on the farms. Although AD has been widely accepted as an alternative animal manure management practice for methane entrapment, reduction of volatile organics, solids, chemical oxygen demand, vector, and pathogen removal, it does not reduce or recover nutrients. In fact, AD can make ammonia emission even more problematic as it converts the organic nitrogen to ammonia form. Land application is the final manure utilization alternative. The excess nitrogen and phosphorus can be transported to the water bodies by runoff and infiltration after land application which can cause water pollution. Nitrogen in runoff from agricultural operations has already been identified as a major contributor to costal eutrophication (National Science and Technology Council 2003), and phosphorous in runoff from agricultural operations was identified as a major contributor to water pollution (Woli *et al.* 2004). Thus, to protect air and water quality, ammonia and phosphorous (both remaining and altered from AD operations) need to be removed or recovered to minimum levels.

Both biological and physicochemical ammonia and phosphorus removal technologies are widely applied for municipal and industrial wastewater treatment. But the high concentrations of ammonia, phosphorus, and solids in the AD effluent of animal manure make any biological treatment not practical. Although conventional nitrification and denitrification can be applied to animal wastewater for nitrogen removal without AD (Vanotti 2005, Choi *et al.* 2005, Tilche *et al.* 2001), the need for large amount of oxygen to oxidize ammonia to nitrate and biodegradable organic carbon to CO_2 is questionable. The biodegradable organic carbon can be used to produce energy while this process consumes energy to oxidize it to CO_2. The biological phosphorus removal needs readily biodegradable carbon (Metcalf & Eddy 2003), which is also deficient in the AD effluent. A recently developed process, "anammox" (ANaerobic AMMonium OXidation) carried out by *planctomycetes*, does not need biodegradable carbon for nitrogen removal (Mulder *et al.* 1995), but the extremely slow growth rate of the *planctomycetes* (Strous *et al.* 1999) makes it easily out-competed by other microorganisms.

Removal of ammonia should be considered in connection with phosphorous recovery to reduce the process complexity. Physicochemical phosphorus removal technologies mainly include solids separation technology such as flocculation, electronic coagulation, dissolved air floatation, and struvite crystallization (Garcia *et al.* 2007, Krumpelman *et al.* 2005, Timby *et al.* 2004, TX-WRI 2006, Uludag-Demirer *et al.* 2005). Unfortunately, the majority of the phosphorus in dairy AD effluent is in a micro-solid form (Güngör & Karthikeyan 2008) requiring liberation from its particulate form with chemicals such as ethylenediaminetetra-acetic acid (EDTA) for struvite crystallization, which is costly (Zhang *et al.* 2009). Flocculation of animal manure has been widely studied with or without filtration (Krumpelman et al. 2005, Powers & Flatow 2002, Ndegwa *et al.* 2001, Singh *et al.* 2006, Zhang & Lei 1998, Vanotti & Hunt 1999), but its use on the large-scale farms is problematic because of the high cost of coagulant/polymer addition. Improved micro-screening apparatus in conjunction with adapted flocculation methods aimed at reducing chemical costs, and other standby technologies such as belt presses, decanting centrifuges, and settling weirs, are all being actively researched as a means for accomplishing separation of the micro-solid as well as the phosphorus solids. Upon separation, a phosphorus-rich organic solid can be obtained for eventual transporting off the farm and reducing the environmental concern due to P overloading. The resultant liquid waste stream with reduced levels of total and suspended solids is more suitable for subsequent ammonia removal or recovery.

The major physicochemical technology for ammonia removal is ammonia stripping, which can be easily integrated with acid absorption for ammonia recovery. Ammonia stripping has already been successfully applied to the AD supernatant of municipal wastewater treatment plants (Janus & vanderRoest 1997, Meyer & Wilderer 2004, Thorndahl 1993), landfill leachate, and industrial wastewater at full scale. It was also tested at laboratory scale for swine manure wastewater (Bonmatí & Flotats 2003, Liao *et al.* 1995, Lei *et al.* 2007) and digested dairy manure supernatant (Zeng *et al.* 2005, Zeng *et al.* 2006). Ammonia stripping performance is highly dependent on temperature (US-EPA 2000); however, the mesophilic or thermophilic temperatures (35 °C or 55 °C) of AD effluent are favorable for ammonia stripping. Elevation of effluent pH to a range of 10.8–11.5 is required to shift the ammonia equilibrium in favor of free ammonia, thereby allowing for transfer of the free ammonia to the stripped out and recovered as N fertilizer. The ammonia-stripped wastewater is high in pH and unsuitable for lagoon storage and/or field application. Fortunately, the other product of AD, biogas, contains H_2S and about 25–50% of CO_2, both of which are unwanted acidic impurities that can be used, via absorption, to neutralize the ammonia stripped effluent to a more desirable storage and application-friendly pH (Lei et al. 2007). The absorption of H_2S and CO_2 by the ammonia stripped effluent can also increase the quality of biogas and thereby enhance Combined Heat and Power (CHP) operation, reduce CHP operation and maintenance costs, or facilitate the production of a compressed fuel.

Integration of the aforementioned phosphorus and ammonia removal technologies into a combined nutrient recovery and biogas upgrading system (combined system) is developed (Jiang *et al.* 2009). Ammonia stripping and absorption can take advantage of the previous solids removal for phosphorus flocculation, the elevated liquid temperature, and the increased ammonia concentration in the AD effluent. Importantly, the pH readjustment of the ammonia stripped effluent via the use of AD biogas can eliminate additional chemical costs that would otherwise be required for pH readjustment, while can also in partial purify the biogas. The specific objectives of this study were: 1) to evaluate the ammonia stripping efficiency for different anaerobically digested dairy wastewaters; 2) to examine the acid absorption efficiency of the stripped ammonia; 3) to test the possibility of using the biogas for pH readjustment of the ammonia stripped effluent and evaluate the compositional change of the biogas; and 4) to investigate the techno-economics of the combined system through a case study.

2.3 Materials and methods

2.3.1 Wastewater

Dairy wastewaters obtained in both flush (wastewater #1) and scrape manure management practice (wastewater #2) were evaluated in this study. The wastewater #1 was taken from the flush manure handling system at the Washington State University (WSU) Dairy Center in Pullman, WA. The flush wastewater was produced by hydraulically flushing alley-scraped fresh manure with lagoon-stored wastewater twice a day and then removing solids by using both a screen separator with 0.5-cm opening and a high-solids pond. Gravity overflow from the high-solids pond resulted in the production of the stored flush wastewater. Sampling of the wastewater #1 occurred at this gravity overflow point.

AD effluent resulted from a commercial digester treating scraping dairy manure in Lynden, WA was used as wastewater #2. In the commercial dairy fresh manure was scraped to an underground pit three times a day and it was then sent to a mixing pit for mixing with outside food processing wastes used in co-digestion (17% v/v food substrates). The resulting mixture was fed every 2 h into an axial-mixed plug-flow mesophilic digester (GHD Inc., Chilton, WI). Coarse fibrous solids were separated with a 0.3-cm slope screen (US Farms, Tulare, CA) while the supernatant flowed into a storage lagoon. Sampling of wastewater #2 occurred at this lagoon entry pipe. Both kinds of sampled wastewater were stored at room temperature for at most 2 weeks before experimentation. Both wastewaters were mixed just prior to experimentation to avoid solids settling. The characteristics of the two sources of wastewater are listed in Table 2-1.

Table 2-1: Characteristics of the dairy wastewaters [a]

Source	TS (mg/L)	VS (mg/L)	TAN (mg/L)	TP (mg/L)	Note
Flush	7530~8054	4723~5109	602~662	7.6~8.52	Wastewater #1
Scrape AD	28545~33400	19065~22800	2271~2729	385~425	Wastewater #2

[a] TS, total solids; VS, volatile solids; TAN, total ammoniac nitrogen; TP, total phosphorous.

2.3.2 Experimental setup and operation

The lab-scale experimental system consisted of three parts: 1) a lime reaction and settling system (Figure 2-1); 2) an ammonia stripping and acid absorption system (Figure 2-2); and 3) a biogas injection for pH readjustment system (Figure 2-3).

2.3.2.1 Lime reaction and settling

The lime reaction and settling system had a variable-speed mixer and three liquid discharge openings. The total working volume was 20 L; however, opening of the valves from top to bottom resulted in 12, 15, and 17.5 L supernatant, respectively. Lime powder was directly added into the lime reaction and settling tank. The amount of lime added was determined by titration with 1 N NaOH for wastewater #1 and titration with 5 N NaOH for wastewater #2. The stirrer was kept on for 2 h for reaction for both kinds of wastewater, and turned off prior to the settling period which was 2 h for wastewater #1 and 24 h for wastewater #2. The volume of the supernatant obtained was about 90% volume for wastewater #1 and 60% for wastewater #2.

2.3.2.2 Ammonia concentration, temperature, and pH adjustment

The TAN concentration of the lime settling supernatant for wastewater #1 was adjusted to 1500–2000 mg/L through addition of 10% ammonium hydroxide to simulate other dairy wastewaters. No ammonium hydroxide was added to wastewater #2. Temperature and pH were adjusted for both wastewaters prior to stripping experimentation. Final pH adjustment was accomplished by using 3 N KOH and 10% H_2SO_4 (w/w). Temperature adjustment was accomplished with a Heat-O-Matic Immersion Heater (Cole Parmer, Chicago, IL). Four levels of TAN concentrations for wastewater #1 with three replicates were applied to the ammonia stripping experiments to study the effect of ammonia concentration on the ammonia removal efficiency.

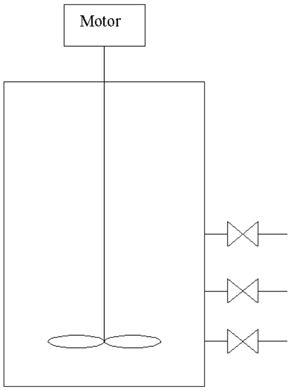

Figure 2-1: The lime reaction and settling system

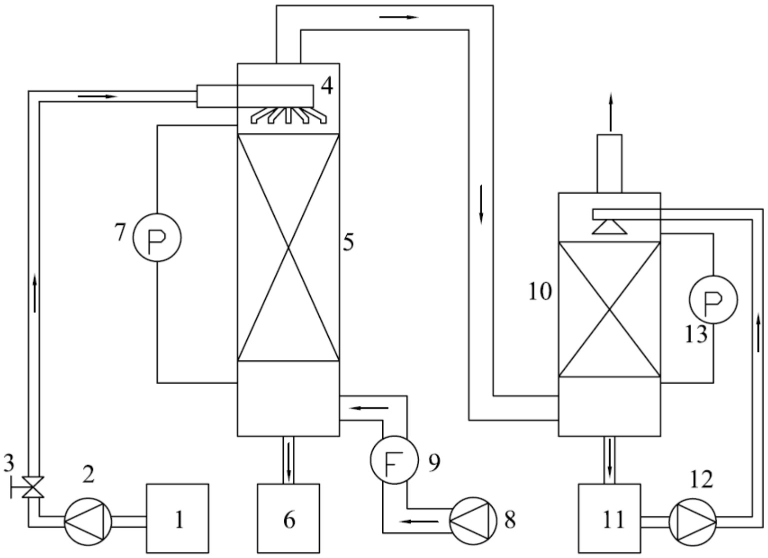

Figure 2-2: Schematic flow chart of the ammonia stripping and acid absorption system

(1. Supernatant feeding tank; 2. Centrifugal pump; 3. Flow rate control valve; 4. Nine-tube liquid distributor; 5. Ammonia stripping column; 6. Stripping effluent storage tank; 7. Pressure difference meter; 8. Blower; 9. Rotameter; 10. Ammonia absorption column; 11. Acid tank; 12. Pump; and 13. Pressure difference meter)

2.3.2.3 Ammonia stripping and acid absorption

The ammonia stripping tower was of a packing column design with an internal diameter (ID) of 0.1 m and a packing height of 1.5 m. The acid absorption tower was also of a packing tower design, utilizing the same internal diameter but a packing height of 0.8 m. The ammonia stripping tower was equipped with equally distributed nine-tube distributors with ID of 3 mm and the acid absorption tower was equipped with a sprayer with pore size of 0.8mm. Both stripping and absorption towers were packed with 25.4-mm plastic Pall rings with a surface area of 210 m^2/m^3 (Jaeger Products, Houston TX). U-tubes were installed for both towers to measure the air pressure drop. Wastewater was pumped to the ammonia stripping tower by a centrifuge pump, and acid solution was pumped to the absorption tower with a peristaltic pump. A blower was used to supply the air and the air flow rate was measured by a PX-90SCFM-8-V-F rotameter from Universal Flow Monitors (Hazel Park, MI). The wastewater flow rate was measured by the effluent volume and the operation time. During the experiment period, the air flow rate was fixed at 0.85 m^3/min. Wastewater flow rates were at various levels from 0.13 to 0.35 L/min. For wastewater #1, ammonia stripping was studied at five pH treatment levels of 9.0, 9.5, 10.0, 10.5, and 11.0; and three temperature levels of 35°C, 39°C, and 49°C. Sulfuric acid was used for ammonia absorption. The acid solution was kept in a 4-L bottle and circulated for weeks of ammonia stripping before the ammonia concentration and the final volume were measured in order to calculate the amount of ammonia absorbed. The volume and TAN concentration of ammonia stripped effluent were measured to calculate the amount of ammonia stripped out in each run. Ammonia absorption efficiency was obtained by comparing the ammonia stripped out with the ammonia absorbed. Concentrated sulfuric acid was added to lower the pH of the acid solution to less than 1.0 whenever the pH rose above 2.0.

2.3.2.4 Biogas purification and pH readjustment

Synthesized biogas was used for pH readjustment. The synthesized biogas was composed of 62.1% methane, 37.7% CO_2, and 0.20% H_2S by volume. The system (Figure 2-3) utilized a digital peristaltic pump for biogas dosing and a rotameter for flow rate measurement. The biogas flow rate was calibrated with the water displacement method with acidic water (pH = 0.8) in order to minimize the error caused by CO_2 absorption in the water. The biogas flowed into the wastewater column using a tube with an inner diameter (ID) of 3 mm. The wastewater column had an ID of 50 mm and height of 400 mm with a working volume of 700 mL. Ten 16-mm plastic Pall Rings (Jaeger Products, Houston TX) were placed in the column for biogas bubble splitting in order to enhance the mass transfer.

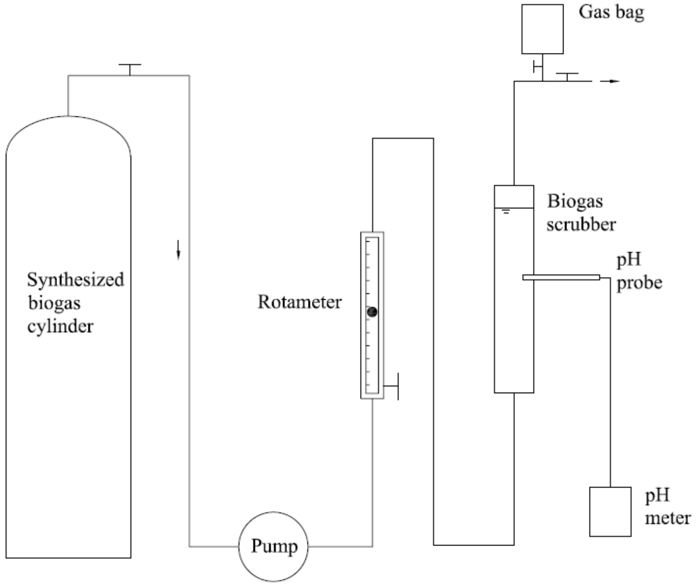

Figure 2-3: Flow chart of biogas purification and pH readjustment

2.3.3 Analytical methods

All analyses were conducted in the Water Quality Laboratory at Washington State University according to standard methods APHA (2005). The biogas content was measured using gas chromatography (GC) (Varian GC CP-3800; Palo Alto, CA) using a method as detailed in Wen *et al.* (2007). The pH was measured with a Denver Ultrabasic pH meter (Denver Instrument Co., Arvada, CO). Total ammoniac nitrogen (TAN) was measured with a Tecator 2300 Kjeltec Analyzer (FOSS North America, Eden Prairie, MN). Total solids (TS) and volatile solids (VS) were measured by drying the samples in a oven at 105 °C and then burning them in a 550 °C furnace. Total phosphorus (TP) was measured using a Flow Injection Analyzer FS 3000 (OI Analytical, College Station, TX).

2.3.4 Statistical method

Statistical Analysis System version 9.1.3 was used for statistical analysis (SAS Institute Inc., Cary, NC). A general linear model (GLM) was applied to analyze the effect of ammonia concentrations on the ammonia stripping efficiency.

2.3.5 Economic analysis

Economic analysis included major chemical and power costs only. Lime, sulfuric acid, and ammonium sulfate prices were obtained from the 28 August 2006 issue of *Chemical Market Reporter* listed on the ICIS (2009) static price webpage. The prices of the lime, sulfuric acid, and ammonium sulfate were \$70, \$87, and \$165/ton, respectively. The electricity price was assumed to be 6.39¢/kWh as the U.S. national average industrial electricity price (EIA 2009). Major power consumption resulted from the use of blowers and pumps. The power consumption from the blower was calculated using Eq. (1) (Metcalf & Eddy 2003) and the pump power consumption was calculated using Eq. (2) (Crittenden *et al.* 2005).

$$P_{blower} = \left(\frac{G_{me} R T_{air}}{n_a Eff_b}\right)\left[\left(\frac{P_{out}}{P_{in}}\right)^{n_a} - 1\right] \qquad (1)$$

Where P_{blower} = blower break power, W ; Eff_b = blower net efficiency, which accounts for both fan and motor on blower; G_{me} = mass flow rate of air, kg/s; n_a = constant used in determining blower brake power, 0.283 for air; P_{out} = outlet air pressure of the blower, any pressure unit; P_{in} = inlet air pressure in of the blower, same unit as P_{out}; R = universal gas constant, 286.7 J/kg air ·K; T_{air} = air temperature, ^oK, typically equal to liquid temperature because of the heat exchange.

$$P_{pump} = \frac{\rho_l QHg}{Eff_p} \qquad (2)$$

Where P_{pump} = pump working power, W; ρ_1 = liquid density, kg/m^3; Q = liquid flow rate, m^3/s; H = vertical distance of the liquid to be pumped plus the pressure loss, m; g = acceleration due to gravity, 9.81 m/s^2; and Eff_p= pump efficiency.

2.4 Results and discussions

2.4.1 Lime reaction and settling

Wastewater #1 had a low concentration of TS and phosphorus because of its long settling time in the lagoon; thus, the major purpose of lime addition was for pH adjustment rather than solids reduction or P-removal. After lime reaction and settling, the TS and TP of the supernatant dropped to 7.2±0.9 g/L and 4.0±0.9 mg/L (triplicates, 7.7% and 50.0% reductions), respectively. Wastewater #2 had high concentration of TS and TP; thus, lime settling was useful for solids and P-reduction as well as pH control. The TS and TP of the supernatant dropped to 16.4 g/L and 76.8 mg/L (42.9% and 80.1% reductions), respectively. Although the phosphorus was 80% removed even without other flocculent combinations, the long settling time (24 h) and the small amount of liquid obtained (60%) suggest that other P-removal pretreatments or even dewatering is necessary. Additionally, the long settling time may lower the liquid temperature, which will affect subsequent ammonia stripping.

2.4.2 Ammonia stripping

The results of ammonia stripping at different TAN concentrations are given in Table 2-2. Statistical analysis using Proc GLM of SAS version 9.1.3 showed that there was no significant difference among all of the TAN concentration levels at alpha = 0.05 ($p = 0.3593$). The initial TAN concentration only affected the later concentration both in the liquid and in the gas phase, but did not affect their gas and liquid distribution ratio if all TAN were free ammonia. The ratio acts like the Henry's constant and the difference is that it was at steady-state phase equilibrium but not a saturate equilibrium. At 35 ^{o}C and pH 10, about 92% of the TAN were free ammonia. The result suggested that the ratio was a constant at same ammonia stripping conditions at different initial TAN concentrations. Accordingly, ammonia stripping efficiencies were analyzed without consideration for changes in initial TAN concentration.

Ammonia stripping of wastewater #1 at different pH and temperatures showed that the ammonia removal efficiency increased considerably when pH increased from 9.0 to 9.5, but not that much when pH increased from 9.5 to 11.0 (Figure 2-4). At 35 °C, the free ammonia levels were 53%, 78%, 92%, 97%, and 99% of the TAN at pH 9.0, 9.5, 10.0, 10.5, and 11 (Figure 2-5), respectively. These results suggest that ammonia removal efficiency does not appreciably increase when pH is higher than a critical pH, and the critical pH is dependent on the temperature. Katehis *et al.* (1998) obtained similar results. This can also be confirmed by the Onda correlation (Onda *et al.* 1968), the two-film theory-based gas desorption and absorption model which has been widely applied for ammonia stripping. This correlation does not include pH as a parameter, since pH only affects the apparent free ammonia concentration, which does not change after the pH is high enough to convert almost all TAN to free ammonia. If the critical pH was set when 90% of TAN as apparent free ammonia, it would be about 10.0 at 35°C.

Table 2-2. Ammonia stripping efficiency at different initial TAN concentrations

Replicate	pH	Temperature (°C)	TAN (mgN/L)	Ammonia Removal
1	9.99	34.8	488	47.5%
2	9.99	34.6	480	46.7%
3	10.01	34.5	464	44.8%
1	10.02	33.8	1163	48.2%
2	10.02	34.5	1079	46.2%
3	10.03	34.2	1147	47.3%
1	10.02	34.3	1505	47.5%
2	10.02	34.5	1491	48.4%
3	10.01	34.1	1470	47.9%
1	10.01	34.2	817	46.8%
2	10.01	34.2	836	50.6%
3	10.01	33.9	811	48.3%

Increasing temperature can dramatically change the ammonia distribution in the gas and liquid (Saracco & Genon 1994), while Figure 2-5 shows a marked disparity in the effect of temperature on ammonia removal efficiency from the experimental result at constant pH. Experimental results show only a 12% increase in ammonia removal efficiency (constant pH = 10) when the temperature was increased from 35 °C to 49 °C; however, the theory using Henry's constant predicted an increase by 61%, suggesting that 23% more ammonia should be shift to the gas phase. The reason of this difference may the rapid temperature decrease of the wastewater because of heat transferred from wastewater to the air, especially through evaporation. Regardless of influent temperature (35°C to 49 °C), the measured temperature of the ammonia stripped effluent remained relatively constant, from 27°C to 29°C throughout the experiment.

Based on the above results, ammonia stripping performance of wastewater #1 and wastewater #2 at pH 10 and temperature 35°C were compared (Table 2-3). The stripping efficiency for the scrape AD wastewater was higher than the flush wastewater in the lagoon. This result is different from the literature which showed that stripping removal efficiency was not dependent upon the complexities of the dairy manure (Zeng et al. 2005). The discrepancy could be resolved in noting that wastewater #2 had a lower liquid flow rate which led to a higher air/liquid ratio. The lower flow rate was a result of wastewater #2 containing more solids which partially clogged the flow rate control valve.

2.4.3 Acid absorption

Results of the acid absorption study are shown in Table 2-4 (individual ammonia stripping data not shown). The ammonia absorption efficiency was obtained from the ammonia stripped out (Eq. 3) and ammonia absorbed (Eq. 4). At lower acid flow rates, not all of the ammonia stripped out was absorbed, although ammonia can quickly react with sulfuric acid. This was possibly because the sprayer was less efficient at lower flow rates and the packing height was relatively low (0.8 m). Thus, a portion of the ammonia-enriched air did not have a chance to gain contact with the acid before it left the absorption column. When the acid flow rate reached 487 mL/min, the calculated ammonia absorption efficiency was consistently higher than 100%, with the error most likely caused by errors in measuring the volume of the wastewater. The wastewater volume was measured from the effluent of the ammonia stripping column, which was less than the volume of the wastewater flowing in because of evaporation and wastewater retention in the tubes and ammonia stripping column. The ammonia stripping column did not have a de-mister, which made the evaporation more obvious. Although there was error in measuring the volume of wastewater being stripped, the results still showed that almost all of the stripped-out ammonia was recovered in the acid absorption tower at acid flow rates higher than 487 mL/min. This is consistent with another study in which Janus & van der Roest (1997) reported that the ammonia could be fully absorbed at pH lower than 3.5.

Table 2-3. Comparison of ammonia stripping results with dairy lagoon and commercial AD effluent

	Wastewater #1*	Wastewater #2*
pH	10.01±0.01	10.04±0.02
Temperature, °C	34.3±0.3	35.0±0.01
Liquid flow, L/min	0.33±0.004	0.21±0.002
Ammonia removal efficiency, %	46±2	50±2

*Average of three replicates

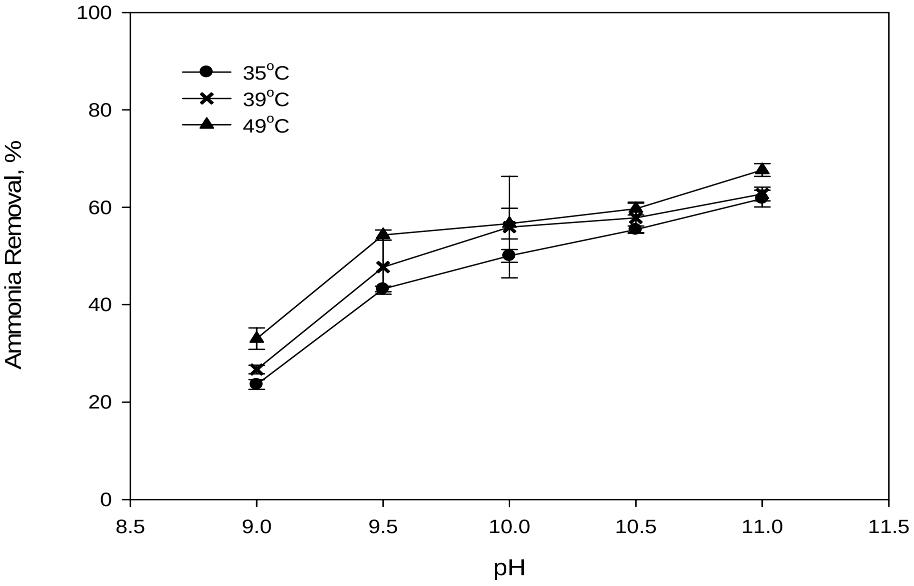

Figure 2-4: Ammonia removal efficiency versus pH at different temperatures (three replicates)

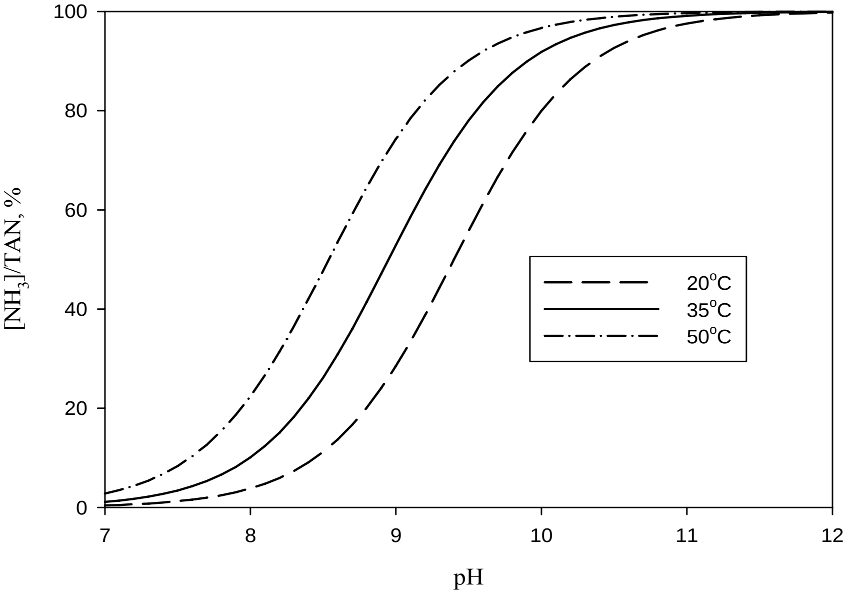

Figure 2-5: Free ammonia ratio at different pH and temperatures

$$NH_{3,stripping} = \sum_{i=1}^{n} V_i (TAN_{in,i} - TAN_{out,i}) \quad (3)$$

$$NH_{3,absorption} = V_a TAN_a \quad (4)$$

Where $NH_{3,stripping}$ = the ammonia stripped out, mg; n = times of ammonia stripping runs before measuring the absorption solution; V_i = the wastewater volume of the ith ammonia stripping run, L; $TAN_{in,i}$ and $TAN_{out,i}$ = the TAN concentration of the influent and effluent of the i^{th} ammonia stripping run, mg-N/L; $NH_{3,absorption}$ = the ammonia absorbed by acid absorption, mg; V_a = the final acid volume, L; and TAN_a = the final TAN concentration in the acid solution, mg-N/L.

Table 2-4: Acid absorption efficiency at different acid flow rates

Acid Flow Rate (mL/min)	Final Acid Solution Volume (L)	Ammonia absorption efficiency, Calculated
327	2.0	73.8%
368	2.0	77.6%
414	2.0	89.1%
444	1.9	93.2%
487	1.9	102.2%
487	1.8	105.8%
487	1.8	109.1%

2.4.4 pH readjustment and biogas upgrading

After ammonia stripped at pH 10 and 35 °C, the pH of wastewater #2 slightly dropped to 9.7. Such a pH value was still too high for long-term storage and land application. As a means for evaluating the use of acidic compounds in biogas for pH readjustment, synthesized biogas was injected into the effluent as shown in Figure 2-3. The resultant adjustments in pH were shown in Figure 2-6. The pH can be reduced to 8.2, the pH of the AD effluent prior to lime dosing, at biogas/liquid (v/v) ratio of 20 and 24 for biogas injection rate of 47mL/min and 178 mL/min, respectively. The pH only reached 8.2 for the biogas injection rate at 280 mL/min when the biogas/liquid (v/v) ratio reached 35. Slower biogas injection rates and the resultant improvements in liquid/gas contact enhanced the CO_2/H_2S absorption, leading to greater pH drops; however, the slower rate would require longer HRT. Regardless of flow rate, high biogas/liquid (v/v) ratios present within digesters and in particular co-digestion digesters [the studied commercial digester had a liquid flow rate of 122 m^3/day and a biogas production rate of 4,650 m^3/day for a biogas/liquid (v/v) ratio of 38.1] can supply enough acidic compounds to easily readjust the pH of the effluent from pH of 10 (or even higher) to below 8.2 to allow for storage and land application.

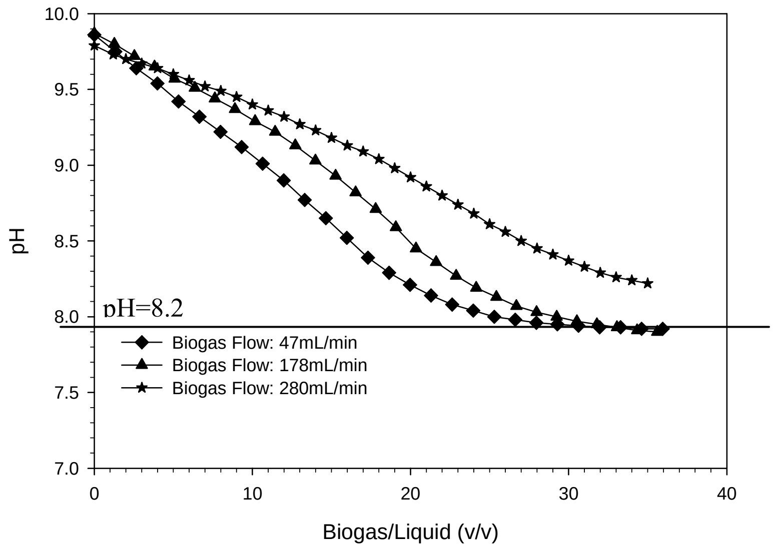

Figure 2-6: Variation of pH of the ammonia stripped effluent after biogas injection

Figure 2-7 shows the changes in CH_4 and CO_2 concentrations during the biogas injection. The CH_4 concentration increased only slightly (from 62.1% to 63.8-68.1%) during the experiment because of the vast amount of CO_2 present in the biogas. The CO_2 concentration only dropped from 37.7% to 31.9 -36.0% (Figure 2-7). On the contrary to CO_2 absorption, Figure 2-8 showed that the H_2S concentration can be reduced considerably at lower biogas/liquid ratio possible because of the much smaller amount of H_2S in the biogas than CO_2. More than 90% of H_2S ($C_0 = 2000$ ppm H_2S) was absorbed for all of the biogas injection flow rates at biogas/wastewater ratios less than 10. Ratios above 10, which as noted are typical of commercial digesters, especially those practicing co-digestion, resulted in considerably less reduction potential due to the larger volume of biogas producing a considerably higher mass of H_2S assuming the same H_2S concentration. Therefore, reducing the H_2S by other technologies such as relatively inexpensive in-vessel oxygen dosing might help this technology by reducing the initial H_2S concentration of the biogas injected to this system. Thus, high H_2S removal is possible even at high gas/liquid ratios.

2.4.5 Economic assessment – A case study

Table 2-5 summarized four scenarios for estimating the costs for ammonia stripping and recovery at the commercial dairy which supplied wastewater #2. At an AD effluent flow rate of 122 m^3/day, 732 kg of lime/day would be needed to raise the pH to 10 prior to ammonia stripping. Required additions of sulfuric acid and the amount of ammonium sulfate recovered are dependent upon the volume of supernatant

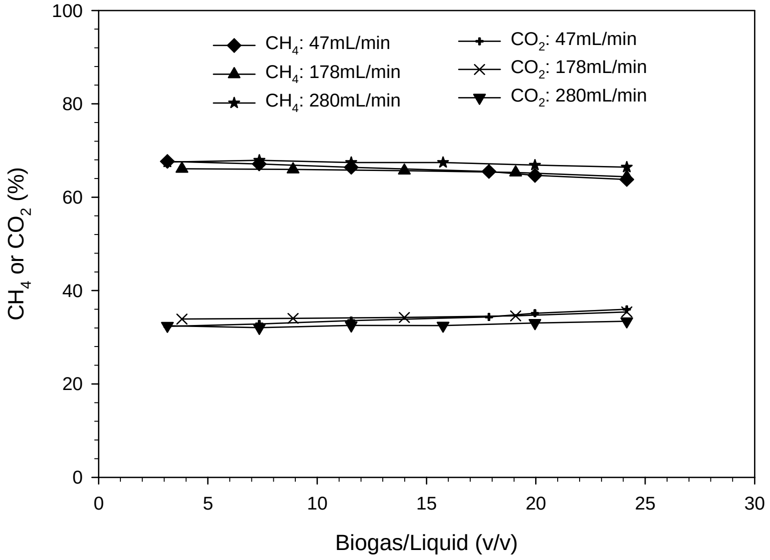

Figure 2-7: Variation of CH_4 and CO_2 concentrations of the ammonia stripped effluent after biogas injection

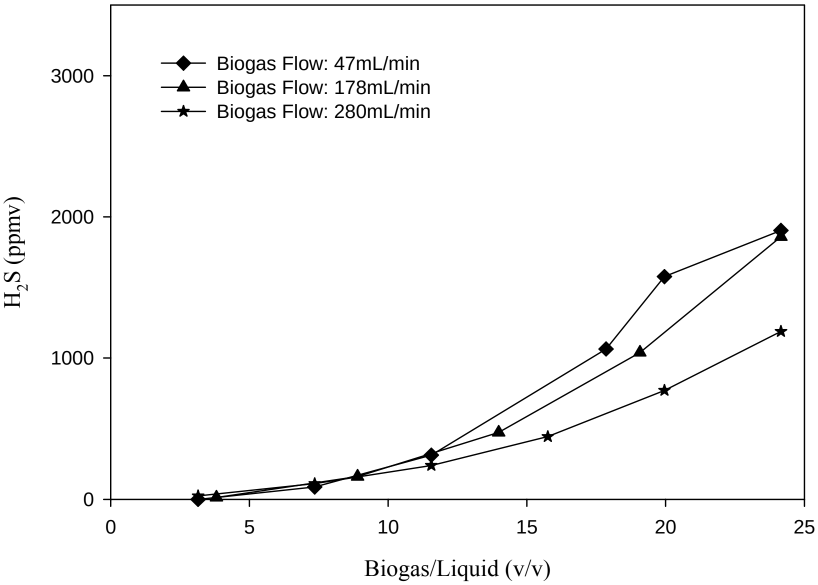

Figure 2-8: Variation of H_2S concentrations of the ammonia stripped effluent after biogas injection

Table 2-5: Economic assessment of the system for a commercial farm[1]

Item	Supernatant/AD feed (v/v)			
	60%	70%	80%	85%
Lime, kg/d	–732	–732	–732	–732
Sulfuric acid[2], kg/d	–584	–682	–780	–828
Ammonium sulfate[3], kg/d	733	856	978	1039
Electricity[4], kWh/d	–95	–111	–127	–135
Benefit, $/d	9	20	32	38

[1]. Positive value means production or benefit; negative value means consumption or loss.
[2] Based on 98% sulfuric acid with 95% of it reacted with all the ammonia stripped.
[3] Dry base. The absorption can only get <40% of ammonium sulfate solution (Siegrist 1996).
[4] The efficiency of pumps and blowers are all set to 60%. The air/liquid ratio is assumed to be 4000.

recovered after solids removal, and the ammonia stripping efficiency. The power consumption is also dependent on the volume of the supernatant. Based on the transfer unit concept (Crittenden et al. 2005) calculation, the ammonia stripping efficiency (pH = 10; T = 35 °C) will be about 85% if the packing height is increased to 6 m. The air pressure drop is considered negligible, based on laboratory results. The blower pressure was assumed to be twice the suggested pressure drop of US-EPA (2000). The highest supernatant ratio was assumed to be 85% based on all of the solids being removed and dewatered (25% solids). Based on the simulations with these scenarios, the value of ammonium sulfate can compensate for the chemical cost and a majority of the electrical cost if it is warranted by market demand [e.g., crops requiring acidic soil and high levels of N and S, such as blueberries (Austin & Bondari 1992)]; and if the price received for the produced ammonia sulfate slurry (<40% by weight, pH = 2) is equal to the market price for commercial-grade dry ammonia sulfate.

2.5 Conclusions

In this study, a new combined nutrient recovery and biogas upgrading system for anaerobically digested dairy manure was developed to address the environmental concerns caused by excess nitrogen and phosphorus on the CAFOs. The study proved that the combined system is both technically feasible and economically advantageous. Within the range tested, the initial ammonia concentration did not affect the efficiency of the ammonia stripping. Differences in the complexes of the flushing and scraping dairy wastewater had little or no effect on ammonia stripping. All ammonia stripped out could be absorbed by sulfuric acid with pH < 2.0. The biogas produced from the AD was more than enough to readjust the pH of the ammonia stripping back to the level without lime dosing, and more than 90% of the H_2S could be absorbed at a biogas/liquid ratio of 10. Even without considering the value of the upgraded quality of biogas, the process showed economic feasibility. The value of the recovered ammonium sulfate (at assumed market values equal to solid commercial ammonium sulfate) could compensate for the costs of chemical and the majority of the electricity consumption. Efficient solids removal is directly correlated to improved economics because solids removal increases the ammonia that can be recovered. Accordingly, the combined system can be a practical solution for the environmental problems associated with excess nitrogen and phosphorus on the CAFOs.

2.6 Acknowledgment

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2.7 References

APHA (2005) *Standard Methods for the Examination of Water and Wastewater, 21st ed.* American Public Health Association, American Water Works Association(AWWA), Water Environment Federation (WEF).

Austin, M. E. & K. Bondari (1992) Soil-pH effects on yield and fruit size of 2 rabbiteye blueberry cultivars. *Journal of Horticultural Science,* **67**(6)**,** 779-785.

Bonmatí, A. & X. Flotats (2003) Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management,* **23**(3)**,** 261-272.

Choi, E., D. Kim, Y. Eum, Z. Yun & K. S. Min (2005) Full-scale experience for nitrogen removal from piggery waste. *Water Environment Research,* **77**(4)**,** 381-389.

Crittenden, J. C., R. R. Trussell, D. W. Hand, K. J. Howe & G. Tchobanoglous (2005) Water treatment: principles and design (second ed.). John Wiley & Sons, Inc., Hoboken, New Jersey.

EIA (2009) Factors Affecting Electricity Prices. Energy Information Administration, U.S. Department of Energy. Retrieved from http://tonto.eia.doe.gov/energyexplained/index.cfm?page=electricity_factors_affecting_prices on October 26, 2009.

Garcia, M. C., M. B. Vanotti & A. A. Szogi (2007) Simultaneous separation of phosphorus sludge and manure solids with polymers. *Transactions of the ASABE,* **50**(6)**,** 2205-2215.

Güngör, K. & K. G. Karthikeyan (2008) Phosphorus forms and extractability in dairy manure: A case study for Wisconsin on-farm anaerobic digesters. *Bioresource Technology,* **99**(2)**,** 425-436.

ICIS (2009) Indicative chemical prices. ICIS.com. Retrived from http://www.icis.com/StaticPages/a-e.htm on May 27, 2009.

Janus, H. M. & H. F. van der Roest (1997) Don't reject the idea of treating reject water. *Water Science and Technology,* **35**(10)**,** 27-34.

Janus, H. M. & H. F. vanderRoest (1997) Don't reject the idea of treating reject water. *Water Science and Technology,* **35**(10)**,** 27-34.

Jiang, A., T. Zhang, C. Frear & S. Chen (2009) Combined nutrient recovery and biogas scrubbing system integrated in series with animal manure anaerobic digester. US Patent Application No.: 20090206028.

Katehis, D., V. Diyamandoglu & J. Fillos (1998) Stripping and recovery of ammonia from centrate of anaerobically digested biosolids at elevated temperatures. *Water Environment Research,* **70**(2)**,** 231-240.

Krumpelman, B. W., T. C. Daniel, F. G. Edwards, R. W. McNew & D. M. Miller (2005) Optimum coagulant and flocculant concentrations for solids and phosphorus removal from pre-screened flushed dairy manure. *Applied Engineering in Agriculture,* **21**(1)**,** 127-135.

Lei, X. H., N. Sugiura, C. P. Feng & T. Maekawa (2007) Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification. *Journal of Hazardous Materials,* **145**(3)**,** 391-397.

Liao, P. H., A. Chen & K. V. Lo (1995) Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology,* **54**(1)**,** 17-20.

Metcalf & Eddy (2003) *Wastewater engineeering treatment and reuse (fourth ed.).* McGraw-Hill, NY, USA.

Meyer, S. S. & P. A. Wilderer (2004) Treating of process water in large wastewater treatment plants in Germany - A case study. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering,* **39**(7)**,** 1645-1654.

Mulder, A., A. A. Vandegraaf, L. A. Robertson & J. G. Kuenen (1995) Anaerobic ammonium oxidation discovered in a denitrifying fluidized-bed reactor. *FEMS Microbiology Ecology,* **16**(3)**,** 177-183.

National Science and Technology Council (2003) An Assessment of Coastal Hypoxia and Eutrophication in U.S. Waters. National Science and Technology Council, Committee on Environment and Natural Resources.

Ndegwa, P. M., J. Zhu & A. Luo (2001) Effects of solid levels and chemical additives on removal of solids and phosphorus in swine manure. *Journal of Environmental Engineering,* **127**(12)**,** 1111-1115.

Onda, K., H. Takeuchi & Y. Okumoto (1968) Mass transfer coefficients between gas and liquid phases in packed columns. *Journal of Chemical Engineering of Japan,* **1**(1)**,** 56-62.

Powers, W. J. & L. A. Flatow (2002) Flocculation of swine manure: Influence of flocculant, rate of addition, and diet. *Applied Engineering in Agriculture,* **18**(5)**,** 609-614.

Ribaudo, M., N. Gollehon, M. Aillery, J. Kaplan, R. Johansson, J. Agapoff, L. Christensen, V. Breneman & M. Peters (2003) Manure management for water quality: costs to animal feeding operations of applying manure nutrients to land. U.S. Department of Agriculture, Economic Research Service, Resource Economics Division. Agricultural Economic Report 824.

Saracco, G. & G. Genon (1994) High temperature ammonia stripping and recovery from process liquid wastes. *Journal of Hazardous Materials,* **37**(1)**,** 191-206.

Siegrist, H. (1996) Nitrogen removal from digester supernatant - comparison of chemical and biological methods. *Water Science and Technology,* **34**(1-2)**,** 399-406.

Singh, P., M. Gamal El-Din, D. Bromley & K. Ikehata (2006) Alum settling and filtration treatment of liquid swine manure. *Transactions of the ASABE,* **49**(5)**,** 1487-1494.

Strous, M., J. A. Fuerst, E. H. M. Kramer, S. Logemann, G. Muyzer, K. T. van de Pas-Schoonen, R. Webb, J. G. Kuenen & M. S. M. Jetten (1999) Missing lithotroph identified as new planctomycete. *Nature,* **400**(6743)**,** 446-449.

Thorndahl, U. (1993) Nitrogen removal from returned liquors. *Journal of the Institution of Water and Environment Management,* **7**(5)**,** 492-496.

Tilche, A., G. Bortone, F. Malaspina, S. Picinini & L. Stante (2001) Biological nutrient removal in a full-scale SBR treating piggery wastewater: results and modelling. *Water Science and Technology,* **43**(3)**,** 363-371.

Timby, G. G., T. C. Danieli, R. W. McNew & P. A. Moore Jr (2004) Polymer type and aluminum chloride affect screened solids and phosphorus removal from liquid dairy manure. *Applied Engineering in Agriculture,* **20**(1)**,** 57-64.

TX-WRI (2006) Field Demonstration of the Performance of an Electrocoagulation System to Reduce Phosphorus and Other Substances from Dairy Lagoon Effluent (Final Report). Texas Cooperative Extension, Texas Water Resources Institute, Ecoloclean Industries, Inc.

Uludag-Demirer, S., G. N. Demirer & S. Chen (2005) Ammonia removal from anaerobically digested dairy manure by struvite precipitation. *Process Biochemistry,* **40**(12)**,** 3667-3674.

US-EPA (2000) Wastewater technology fact sheet: ammonia stripping. EPA Report 832-F-00-019, U.S. Environmental Protection Agency, Office of Water, Washington, DC.

Vanotti, M. (2005) Evaluation of environmentally superior technology: swine waste treatment system for elimination of lagoons, reduced environmental impact, and improved water quality. USDA Agreement 58-6657-2-202 / NCSU Subcontract #2001-0478-02 / USDA-ARS CRIS Project # 6657-13630-001-05, USDA-ARS.

Vanotti, M. B. & P. G. Hunt (1999) Solids and nutrient removal from flushed swine manure using polyacrylamides. *Transactions of the ASAE,* **42**(6)**,** 1833-1840.

Wen, Z., C. Frear & S. Chen (2007) Anaerobic digestion of liquid dairy manure using a sequential continuous-stirred tank reactor system. *Journal of Chemical Technology and Biotechnology,* **82**(8)**,** 758-766.

Woli, K. P., T. Nagumo, K. Kuramochi & R. Hatano (2004) Evaluating river water quality through land use analysis and N budget approaches in livestock farming areas. *Science of The Total Environment,* **329**(1-3)**,** 61-74.

Zeng, L., X. Li, J. Liu & E. Jenson (2005) Feasibility study of air stripping of ammonia from digested cattle manure. *ADSW 2005 Conference Proceedings*. *In* B. K. Ahring & H. Hartmann (eds.), *4th International Symposium on Anaerobic Digestion of Solid Waste*, pp. 656-663. Copenhagen.

Zeng, L., C. Mangan & X. Li (2006) Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology,* **54**(8)**,** 137-145.

Zhang, R. H. & F. Lei (1998) Chemical treatment of animal manure for solid-liquid separation. *Transactions of the ASAE,* **41**(4)**,** 1103-1108.

Zhang, T., K. E. Bowers, J. H. Harrison & S. Chen (2009) Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy effluent. *Water Environment Research,* **81,** (Accepted. uncorrected page proofs.).

CHAPTER THREE

ECONOMIC OPTIMIZATION OF AMMONIA STRIPPING FROM ANAEROBICALLY DIGESTED DAIRY WASTEWATER

3.1 Abstract

Dairy manure contains appreciable amount of nitrogen which on concentrated animal feeding operations (CAFOs) often leads to potential air and water quality problems. Prior research efforts have not been able to develop a practical solution beyond manure land application. In this study, the feasibility of ammonia removal through air stripping from digested dairy manure was optimized. Temperature and pH were identified as cost sensitive parameters for the process. Ammonia stripping was tested at different pH and temperature levels, allowing for development a correlation for economic optimization. When the temperature of the digester effluent was maintained at mesophilic (35°C) during the stripping process, the optimized ammonia stripping parameters were: a pH 10.28, and a corresponding lime dosage of 3.3 g/L wastewater, for 90% ammonia removal. The optimized lime dosage and preheating natural gas needed were 3.9 g lime/L and 1.3m^3 natural gas/m^3 wastewater respectively if the temperature of the digester effluent drops to 25°C prior to the ammonia stripping. The results suggest that stripping can be a practical solution for the problem associated with excess nitrogen on CAFOs.

Keywords: Ammonia removal, Air stripping, Parameter optimization, Dairy wastewater

3.2 Introduction

The excess nitrogen from CAFOs potentially leads to major air and water quality concerns. Regarding air quality, Animal operations contribute 81% of ammonia emissions in the U.S. (Battye *et al.* 1994). Ammonia odors can not only be potentially harmful to farm workers as well as surrounding residents but also interact with other air constituents to produce particulate matter concentrations detrimental to human health with long time exposure, particularly those with existing lung disorders (US-EPA 2004). In fact, monitoring results indicated that several CAFO dairy regions in the US presently exceed the 15 $\mu g/m^3$ annual and/or 35 $\mu g/m^3$ twenty-four hour PM 2.5 Standard (US-EPA 2004). Regarding water quality, leaching and runoff allow transporting nitrogen to the ground and surface water. Ammonia and its inorganic derivatives, nitrite and nitrate, have adverse effects on both human and aquatic animal health, with ammonia being toxic to fish, nitrite being a known carcinogen, and nitrate capable of causing methemoglobinemia and birth defect (WS-DOH 2005, Ward *et al.* 2005). Inorganic nitrogen can also cause eutrophication of the water system especially in semi arid areas and coastal areas. Recovering ammonia nitrogen from animal manure can mitigate air quality problems as well as reduce the threat to water pollution, especially for CAFOs where approximately 36% and 55% of all dairy CAFOs experience nitrogen and phosphorous overloads, respectively (USDA-APHIS 2004). In addition, recovery would allow the CAFOs to better meet their nutrient management plans and perhaps require less land for disposal of their nutrient-rich manure.

Anaerobic Digestion (AD), the widely accepted animal manure management technology, can be used to harvest biogas for energy production and partly control manure odor by degrading volatile organic compounds, but it does not reduce or recover nitrogen, instead it converts part of the organic nitrogen to volatile ammonia (25% increase in concentration from a dairy AD case study) (Martin 2005). Notably, the AD process also produces an effluent with higher temperature, containing lower amounts of solids, both of which, along with the higher ammonia concentration, could potentially be utilized in development of a nitrogen recovery system.

Treating animal manure AD effluent for nitrogen recovery poses a few problems. A number of ammonia removal and recovery technologies exist for wastewater. However, these are not commonly applied to animal waste because of the characteristics of manure wastewater, namely, the large amount of total solids which often exceed 50 g/L. Additionally farm economics typically preclude the use of expensive and complex removal and recovery systems. Thus, any technology developed must attend to these concerns as well as to the recovery of saleable nutrients. Because of these challenges, no ammonia removal technologies have been currently applied to dairy CAFOs at a commercial scale, with or without AD within the US.

There have been various approaches studied for nitrogen removal among which biological nitrogen removal (BNR) has been a major topic related to manure management. Researchers (Choi *et al.* 2005, Tilche *et al.* 2001) have studied full-scale nitrogen removal with sequencing batch reactor (SBR) nitrification and denitrification from piggery manure wastewater. Vanotti (2005) studied full-scale swine wastewater ammonia removal with an anoxic/oxic (A/O) nitrification and denitrification system. These processes are technically effective, as Szögi *et al.* (2006) reported that the annual ammonia emissions were reduced 90% in a swine wastewater lagoon. However, they often require a large reactor [the longest hydraulic retention time (HRT) of the SBR reactor that Choi *et al* (2005) used for nitrogen removal was 54 days], considerable oxygen inputs, and a great amount of electricity for the ammonia oxidation step. In addition, AD effluent does not contain enough biodegradable organic carbon required for denitrification. In order to achieve efficient denitrification of AD effluent, organic carbon such as methanol must be supplied (Siegrist 1996). Although the newly developed BNR process ANaerobic AMMonium OXidation [ANAMMOX; Mulder *et al.* (1995)] can remove nitrogen without biodegradable organic carbon, the extremely slow growth rate of the *planctomycetes* that contribute to the ANAMMOX process (Strous *et al.* 1999) makes it easy for other microorganisms within the manure to proliferate and outcompete *planctomycetes* within the reactor.

Other researchers (Bolan *et al.* 2004, Guo *et al.* 2008, Bonmatí & Flotats 2003, Liao *et al.* 1995, Vanotti 2005) have opted for physiochemical processes for ammonia removal, including ion exchange and ammonia stripping. Ion exchange can be precluded here because it requires extremely low solids concentration. However, ammonia stripping, as evidenced in studies on landfill leachate (Cheung *et al.* 1997), digester supernatant of a municipal wastewater treatment plant (Katehis *et al.* 1998), and digester supernatant from slaughterhouse waste (Siegrist *et al.* 2005), shows potential since it tolerates some degree of solids, requires relatively low energy, and is relatively inexpensive. Ammonia stripping has already been successfully applied to AD supernatant from municipal wastewater treatment plants, landfill leachate and industrial wastewater at commercial scale (Janus & vanderRoest 1997, Meyer & Wilderer 2004, Thorndahl 1993). It was also successfully tested in lab for swine manure wastewater (Bonmatí & Flotats 2003, Liao et al. 1995) and digested dairy manure supernatant (Zeng *et al.* 2005, Zeng *et al.* 2006) and reached more than 90% ammonia removal. In addition, ammonia stripping can be easily integrated with acid absorption to recover ammonia as a nitrogen fertilizer. Although ammonia stripping has proven to be technically feasible for ammonia removal from digested animal manure, its economic feasibility has not been studied.

In order to evaluate its economic feasibility, the operation parameters of ammonia stripping that affect the ammonia stripping efficiency as well as the cost should be optimized. Ammonia stripping efficiency is highly dependent on temperature, pH, and air/liquid ratio (US-EPA 2000). Increasing either the temperature or the pH can drive the equilibrium (Eq. 1) from NH_4^+ to $NH_{3(gaseous)}$, which can enhance the ammonia stripping efficiency. Temperature affects not only the ammonia disassociation in the liquid (Eq. 2) (Emerson *et al.* 1975), but also the equilibrium ammonia-N distribution between the liquid and gas phase (Eqs. 3 and 4) (National Research Council 1979) while pH can only affect the free ammonia ratio in the liquid (Eq. 5) (Metcalf & Eddy 2003).

$$NH_4^+ \xleftrightarrow{Ka} NH_{3(aq)} + H^+ \xleftrightarrow{H} NH_{3(gaseous)} \tag{1}$$

$$pKa = -\log_{10}(Ka) = 0.9018 + 2729.92 / T \tag{2}$$

$$H = \frac{[NH_3]_{aq}}{[NH_3]_{gaceous}} \tag{3}$$

$$\log_{10} H = \frac{1477.7}{T} - 1.6937 \tag{4}$$

$$NH_3,\% = \frac{100}{1 + 10^{pKa-pH}} \tag{5}$$

Where: Ka is NH_4^+ disassociate constant, $Ka = [NH_3][H^+]/[NH_4^+]$, H is dimensionless Henry's constant; T is temperature in ^{o}K.

Studies have also proven that higher temperature and pH can help ammonia stripping (Katehis et al. 1998, Liao et al. 1995, Zeng et al. 2005) whereas the pH beyond a critical point has little effect on stripping efficiency (Katehis et al. 1998). Steam stripping can take the advantage of high temperatures and may not even need alkali doses for pre-pH increase (Zeng et al. 2006) if cheap steam is available. Increasing the temperature of liquid is energy-intensive. Similarly, raising the pH is chemical-intensive because the AD effluent is always saturated with bicarbonate, which have high base buffer capacity.

In the air stripping process, electricity consumption without preheating of the wastewater is mainly due to the air blower and liquid pumps. Although the electricity consumption varies with different air/liquid ratios, the low air pressure required in the stripping process often makes the cost only a slight difference. The US-EPA (2000) recommends that for commercial strippers the optimum pressure drop be 1.25~1.58 mm H_2O/m, which translates to a 7.6 m stripping tower only having about 12 mm water pressure drop, requiring only 0.05-0.16 kWh for treating 1 m^3 of liquid without considering the blower/fan efficiency at the air/liquid ratio of also suggested by the US-EPA (2000).

According to the previous description, temperature and pH are identified as the most economical sensitive factors for ammonia stripping. The objective of this study is to optimize the stripping temperature and pH to make the ammonia stripping economically feasible so it can be a practical solution to the environmental problems associated with excess nitrogen for the CAFOs.

3.3 Materials and methods

The experiment was designed to evaluate the effect of two factors (temperature and pH) on the performance of ammonia stripping from dairy wastewater. Both factors were tested at four levels (25˚C, 30˚C, 35˚C, 40˚C, and pH of 9.5, 10.0, 10.5, 11.0 respectively) with repeated measurements at 10, 15 and 20 minutes. Data obtained allowed for a correlation of ammonia stripping efficiency at different pH and temperature. Together with the regression of alkali titration results, economically optimized parameters of pH and temperature were obtained.

3.3.1 Dairy manure wastewater

Flushed dairy wastewater was sampled from the Washington State University (WSU) Dairy Center (Pullman, WA) and used directly for the experiment. The wastewater was sent through a 0.50 cm mechanical screen for fibrous solids removal and then gravity fed to a solids removal and storage system with two lagoons connected in series. Characteristics of the dairy wastewater are shown in Table 3-1.

Table 3-1: Characteristics of the dairy wastewater used in ammonia stripping

Source	TS[a] (mg/L)	VS[a] (mg/L)	TAN[a] (mg N/L)	TP[b] (mg P/L)	pH[a]
Dairy Wastewater	8636 ± 1106	5015 ± 293	492 ± 23	8.06 ± 0.65	7.72 ± 0.11

[a] Data are expressed as the mean ± SD of six replicate samples

[b] Three replicates

3.3.2 Experimental set-up and operation

The lab-scale experimental system was operated within a temperature controlled room (35°C). The system consisted of a lime reaction and settling component (Figure 3-1) and an ammonia stripping and acid absorption component (Figure 3-2). The lime reaction and settling system with a total working volume of 20L had a mixer and three liquid discharge openings placed at increasing heights (12, 15, and 17.5L of supernatant respectively). The stripping and absorption towers were both packing columns, each with an Internal Diameter (ID) of 0.1m and packing heights of 1.5 and 0.8m, respectively. Both towers were packed with 25.4 mm plastic Pall rings with a surface area of 210 m^2/m^3 (Jaeger Products, Houston TX). The ammonia stripping column was equipped with nine tube-distributors with ID of 3 mm for distribution of liquid to the packing material. The absorption column was equipped with a sprayer for liquid distribution. The supernatant feeding tank was continually mixed during the experiment in order to keep the feeding homogeneous. Temperature was measured at the stripping column inlet with a thermocouple. The air flow rate was fixed at 0.85 m^3/min and the supernatant flow rate was kept at 0.40L/min throughout the entire ammonia stripping experiment.

Lime powder (CaO: JT Baker Chemical Co., Phillipsburg, NJ) was directly added into the lime reaction and settling tank. The quantity of lime added was determined by titration with 1N NaOH. The settling tank was covered to minimize ammonia loss during pretreatment and pH adjustment. The stirrer was kept on for two hours for lime reaction at which point it was turned off and settling was allowed to occur for four hours. The supernatant (85-93% volume during the experiment) was applied to the ammonia stripping tower after fine pH adjustment by 3N NaOH and 10% H_2SO_4 (w/w). Temperature was adjusted with a Heat-O-Matic Immersion Heater (Cole Parmer, Chicago, IL).

3.3.3 Analysis method

All analyses (TS, VS, TAN, and TP) were conducted in the Washington State University Water Quality Laboratory according to standard methods APHA (2005). The pH was measured with a Denver Ultrabasic pH meter (Denver Instrument, Arvada, Colorado). Total Ammoniac Nitrogen (TAN) was measured with a Tecator 2300 Kjeltec

Analyzer (FOSS North America, Eden Prairie, MN). Total Phosphorus (TP) was measured using a Flow Injection Analyzer FS 3000 (OI Analytical, College Station, TX).

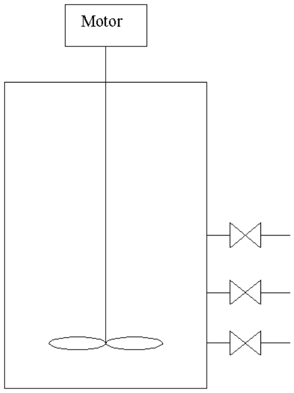

Figure 3-1: The Lime reaction and settling system

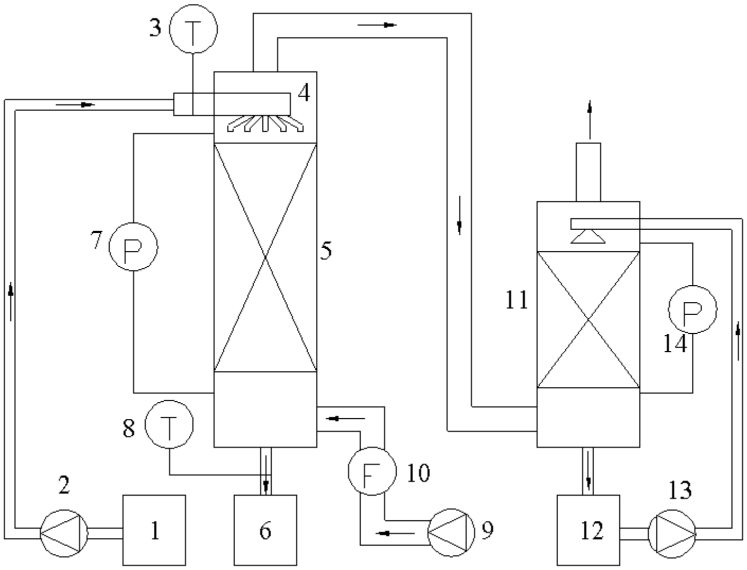

Figure 3-2: Schematic flow chart of the ammonia stripping and acid absorption system

(1. Supernatant feeding tank with mixer; 2. Digital peristaltic pump; 3. Thermometer; 4. Nine-tube liquid distributor; 5. Ammonia stripping column; 6. Stripping effluent storage tank; 7. Pressure difference meter; 8. Thermometer; 9. Blower; 10. Rotameter; 11. Ammonia absorption column; 12. Acid tank; 13. Peristaltic pump; and 14. Pressure difference meter)

3.3.4 Statistical method

Statistical Analysis System program 9.1.3 (SAS Institute Inc. NC) was used for statistical analysis. Paired T-test was used to analyze the ammonia stripping effluent at different times. Procedure GLM (General Linear Model) was applied to analyze the effect of pH and temperature. Procedure NLIN (NonLINear Regression) was used for the two parameter regression. An alpha of 0.05 was used for all statistical tests.

3.3.5 Parameter optimization

Factors affecting ammonia stripping efficiency are: 1) the specific design of the stripping system; 2) temperature; 3) pH; and 4) the air/liquid ratio. For a given system with fixed air/liquid ratio, the ammonia stripping efficiency is therefore a function of temperature and pH (Eq. 6). By separating variables, the ammonia stripping efficiency can be expressed as Eq. (7) and rewritten as Eq. (8) when applying the Taylor Series to $g(T)$ and $h(pH)$.

$$RE = f(T, pH) \tag{6}$$

$$RE = g(T)h(pH) \tag{7}$$

$$RE = (a_0 + a_1 T + a_2 T^2 + \cdots)(b_0 + b_1 pH + b_2 pH^2 + \cdots) \tag{8}$$

Where: *RE* is ammonia removal efficiency; *T* is temperature in ^{o}C; and *a* and *b* series are constants.

The packing height of an air stripping column based on two film theory follows the transfer unit approach and is described by Eq. (9) (Treybal 1980).

$$Z = NTU \times HTU \tag{9}$$

Where: Z is the height of the packing, m; NTU is the number of transfer unit; and HTU is the height of transfer unit, m. NTU and HTU are defined according to Eqs (10), (11) and (12) (Crittenden *et al.* 2005):

$$NTU = \frac{S}{S-1}\ln\left(\left(\frac{NH_{3,in}}{NH_{3,out}}(S-1)+1\right)/S\right) \quad if\ S \neq 1 \tag{10}$$

$$NTU = \frac{NH_{3,in}}{NH_{3,out}} - 1 \quad if\ S = 1 \tag{11}$$

$$\mathrm{HTU} = \frac{\mathrm{L}}{\mathrm{AK_{La}}} \tag{12}$$

Where: S is the stripping factor, dimensionless, $S = \frac{1}{H}\left(\frac{G}{L}\right)$; $NH_{3,in}$ is the free ammonia concentration in the stripping influent, mg/L; $NH_{3,out}$ is the free ammonia concentration in the stripping effluent, mg/L*;* G is the air flow rate, m^3/s; L is the liquid flow rate, m^3/s; A is the cross section of the packing column, m^2; and K_{La} is the overall liquid phase mass transfer rate constant, s^{-1}.

Lime dosing used for raising the pH of the wastewater was quantified by titration with NaOH. Three kinds of regression were selected to fit the titration result. Log regression (Eq 13) were selected because the theoretic pH correlation (Eq. 14) without buffer consideration. No constant accounts for the initial OH^- concentration $[OH^-]_0$ in the regression (Eq 13) because $[OH^-]_0$ was usually very low, 10^{-8}~10^{-5} mole/L for pH range of 6~9. Polynomial regression (Eq 15) and combined log and polynomial regression (Eq. 16) were also investigated. The best fitted correlation was applied for economical optimization. Due to the fact that lime is a weak base with low solubility, a safety factor of 1.1 was used to calculate the lime needed.

$$pH = c_0 + Log_{10}(c_1[NaOH]) \tag{13}$$

$$pH = 14 + Log_{10}([NaOH] + [OH^-]_0) \tag{14}$$

$$[NaOH] = c_0 + c_1 pH + c_2 pH^2 + Log_{10}(c_3 pH) \tag{15}$$

$$[NaOH] = c_0 + c_1 pH + c_2 pH^2 + \cdots \tag{16}$$

Where c series are constant; $[NaOH]$ is NaOH dosage in mole/L.

Parameters from Eqs. (8 and 13) obtained from the ammonia stripping and titration experiments were used to develop an optimization process shown in Figure 3-3.

3.4 Results and discussions

3.4.1 Alkali titration

The titration result with 1N of NaOH is shown in Figure 3-4. The fitted correlations shown in Figure 3-4 were obtained from Microsoft solver. The alkali needed to raise pH to 11 [suggested ammonia stripping pH (US-EPA 2000)], needed 63% more NaOH than what was needed to raise the pH to 10. This is because of the abundance of HCO_3^- present in the dairy manure, which has a pKa of 10.25 at 25°C. After overcame the buffer effect of HCO_3^-, the pH increased more rapidly with NaOH dosing (Figure 3-

4). Thus analysis of the data showed that a decrease in pH for ammonia stripping can significantly reduce the amount and cost of alkali needed. Although a corresponding decrease in ammonia stripping efficiency was concurrent with the reduced operating pH, economic analysis and optimization discussed later showed that little reduction in performance occurred especially as compared to the cost savings incurred.

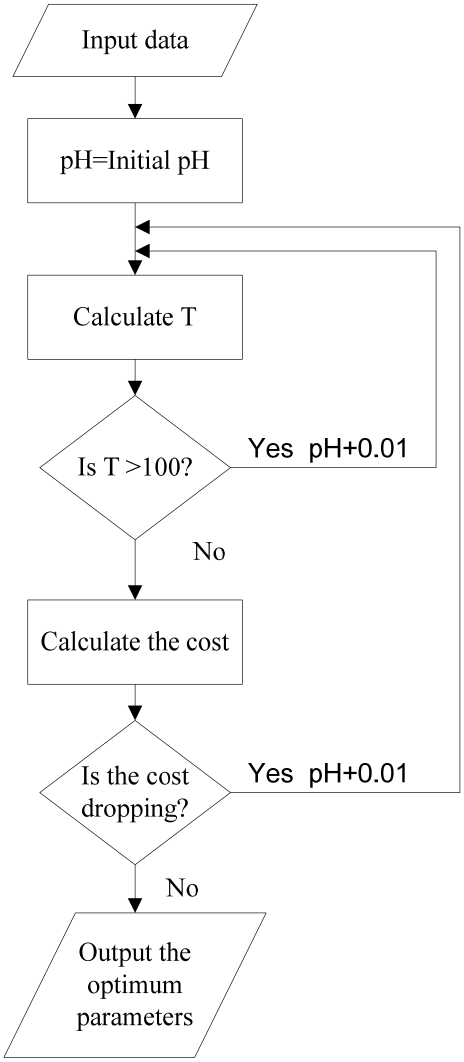

Figure 3-3: Flow chart of the parameter optimization

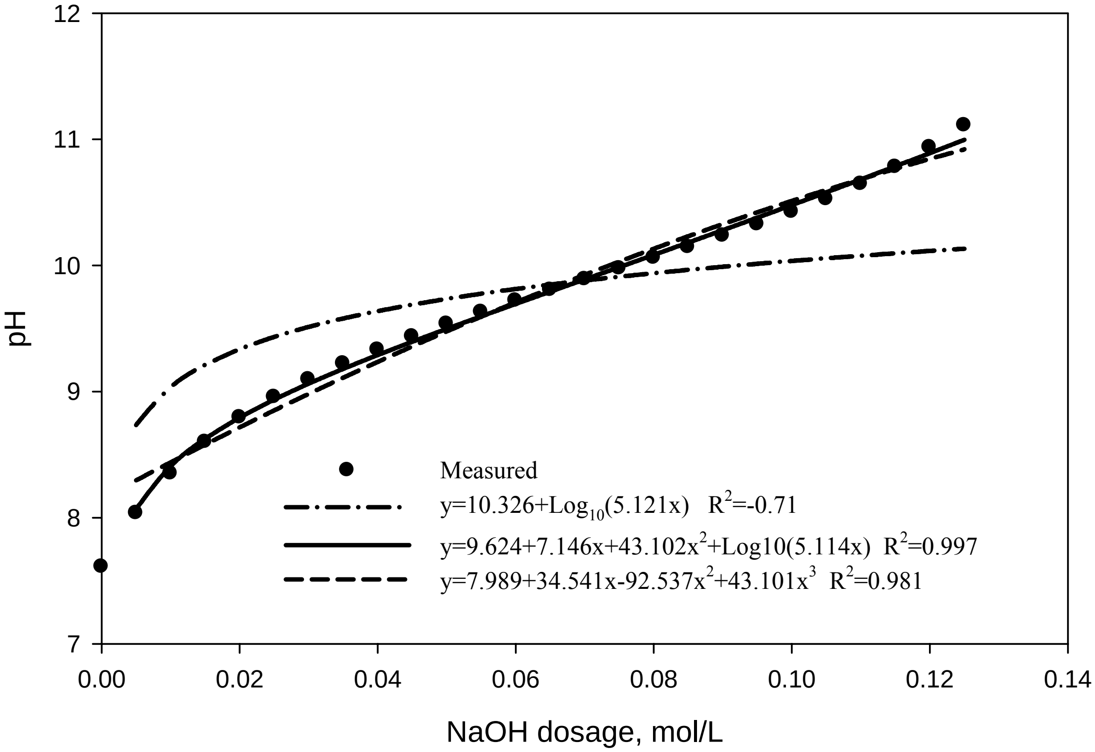

Figure 3-4: NaOH dosing and the change of pH

The log correlation (Figure 3-4) does not fit the titration data because of the strong buffer effect. The cubic polynomial regression showed good fit except both ends of the data. The combined log and polynomial regression fits the titration data best, even at the low NaOH dosage (Figure 3-4). The combined regression fits better most likely because the log part can account for the nature of the pH and the polynomial part can account for the buffer effect.

3.4.2 Statistical analysis

The ammonia removal results for the two factorial experiment is shown in Table 3-3. Since paired T-test analysis showed that there were no significant differences among the TAN concentrations at different times (data not shown), the measurements at different times were considered as replicates for the non-linear regression. Proc NLIN using Eq. (8) resulted a correlation of Eq. (14) with a R^2 of 0.83. Comparison of the measured ammonia removal with calculated results demonstrates that the measured results fall within the ± 20% of that calculated (Figure 3-5). The Onda correlation (Onda *et al.* 1968), the most widely applied gas desorption correlation for air stripping also had a ± 20% error. When it was applied to pilot or full scale air strippers, even the Onda correlation overestimated the performance at an average of 37% for 75% of the time (Thom & Byers 1993). This suggested accuracy of the correlation generated in this study can be used for further economic parameter optimization.

$$RE = (249.6 + 6.8003T + 0.066T^2)(-0.0214 + 4.12\times10^{-3} pH - 1.908\times10^{-4} pH^2) \quad (14)$$

3.4.3 Optimization

For the experiment, the lime dosing was calculated from Eq. (15). The heating was assumed using natural gas with 76% heat utilization efficiency according to the natural gas boiler efficiency suggested by EIA (2009a), which does not include the heat transfer efficiency and heat loss. The price of natural gas was assumed to be \$8.40/1000ft^3 as the average price from 2001 to July 2009 (EIA 2009b) while the price for lime was assumed to be 70\$/ton (ICIS Chemical Market Reporter, 28 August 2006).

$$LIME = \left(\frac{[NaOH] \times K}{Purity} \right) * 28000 \qquad (15)$$

Where: *LIME* is the lime (CaO) dosage, mg/L; *[NaOH]* is the NaOH dosage, mole/L; *K* is the safety factor, K=1.1 for this modeling; and *Purity* is the purity of lime, 0.90 for quicklime.

Table 3-3: TAN in the influent and effluent of ammonia stripping system

Temperature, °C	Time, min	TAN (mg-N/L)							
		pH=9.50		pH=10.00		pH=10.50		pH=11.00	
		in	out	in	out	in	out	in	out
25.0	10	471.7	334.2	435.9	301.8	435.4	293.6	434.3	252.9
25.0	15	468.4	331.5	434.3	304.0	447.5	291.4	431.5	246.8
25.0	20	464.5	335.5	445.3	316.7	437.0	288.1	426.6	254.5
30.0	10	439.2	317.2	412.3	260.6	409.0	233.1	461.2	268.3
30.0	15	432.6	322.9	416.2	262.2	448.6	234.7	449.1	267.2
30.0	20	438.7	320.5	427.7	254.5	414.0	225.9	448.0	261.7
35.0	10	476.1	361.2	409.6	238.0	482.7	261.1	404.1	215.5
35.0	15	471.7	361.7	401.3	235.8	477.2	251.8	409.6	212.8
35.0	20	473.3	334.2	422.2	241.9	450.2	246.3	405.2	213.3
40.0	10	454.6	323.8	429.4	222.1	449.7	242.4	421.7	188.0
40.0	15	459.6	312.3	406.3	191.3	455.2	232.0	409.6	194.1
40.0	20	445.3	302.4	418.9	194.1	446.4	237.5	411.2	200.1

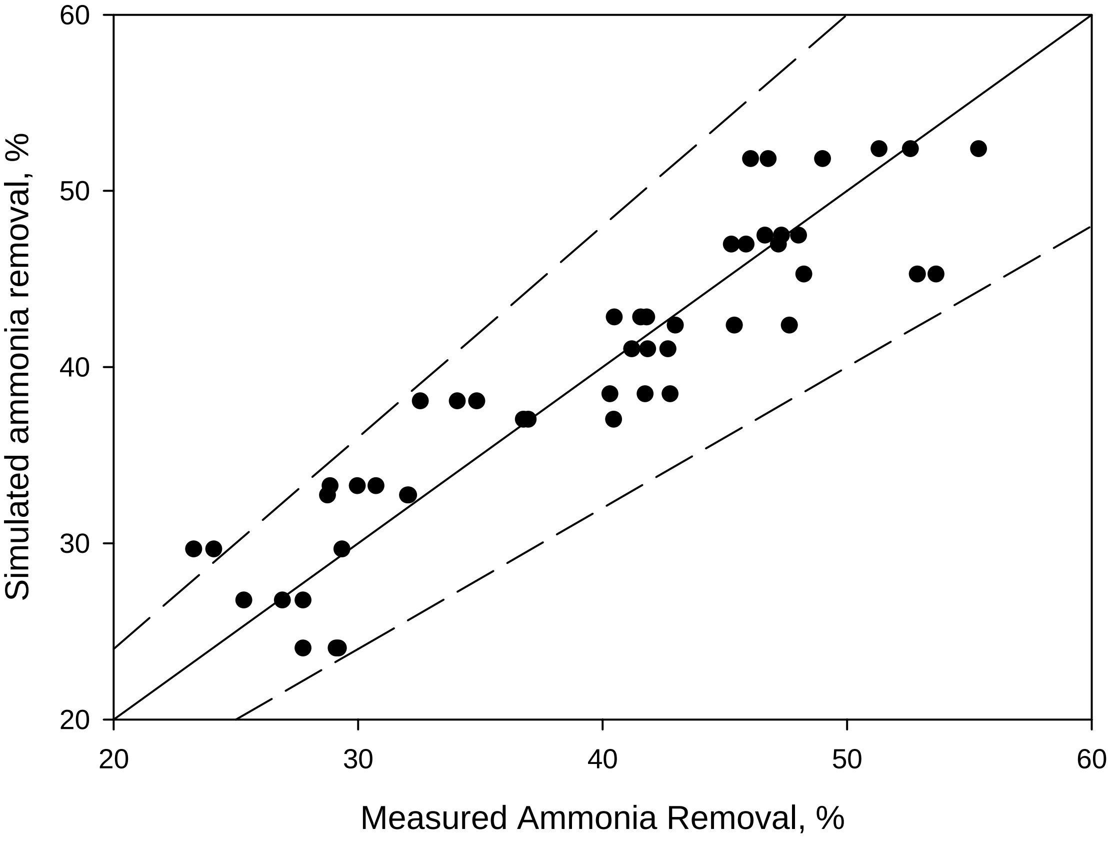

Figure 3-5: Comparison simulated and measured ammonia removal efficiency

(Upper dash line is +20% the measured and the lower dash line is -20% the measured.)

The AD effluent of dairy manure has a relatively consistent pH, but the temperature can drop considerably due to environmental temperature and the retention time prior to ammonia stripping. The optimum pH, temperature, and cost are dependent on both the ammonia removal efficiency and the initial liquid temperature before ammonia stripping. Figure 3-6 showed the simulated optimum results for three different temperatures of 25°C, 30°C, and 35°C. For a required ammonia removal efficiency and a given initial temperature, the optimized pH, temperature, and cost were shown in Figure

3-6(c), (b), and (a), respectively. The optimum cost (Figure 3-6) was only for the specific dairy manure used in this study. The approximate optimum cost for different manure with different chemical and heating energy price can be calculated by referring to the optimum pH and temperature shown in Figure 3-6: lime dosage can be obtained by a simple alkali titration and energy consumption can be calculated from the optimum temperature. With the required ammonia removal efficiency increasing, the optimum temperature kept unchanged at beginning before the optimum pH reached about 10.6 -10.7 for all three cases (Figure 3-6). Accordingly, the free ammonia reached about 96-99% of the TAN. Further increasing the ammonia removal efficiency needs to increase the temperature (Figure 3-6).

In Figure 3-6, only the optimum temperature for 95% of ammonia removal (41.7^{o}C) was slightly outside the experimental range (25-40^{o}C) which suggests the result is reliable. If the temperature of the digested effluent can be kept at the mesophilic (35°C), heating is not required even for up to 90% of ammonia removal. The corresponding optimum pH is 10.28, resulting in a lime cost of 0.23\$/m^3 (3.3 g lime/L). For the worst-case scenario, if the AD effluent temperature drops to 25^{o}C prior ammonia stripping, heating is required if more than 85% ammonia removal was required. The optimum pH, temperature and lime cost for 90% ammonia removal were 10.65, 32.2^{o}C, and \$0.52\$/m^3 (3.9 g lime/L and 1.3m^3 natural gas/m^3), respectively.

The optimized parameters of ammonia stripping lead to a lower cost than the processes reported by other researchers. Back calculation from the reported data can give an approximate estimate although the actual cost was not given in the other study. Zeng et al., (2006) used steam instead of air for ammonia stripping from animal wastewater to take advantage of the increased temperature. The stripping column temperature was 98-99°C and the steam/liquid ratio was 56-72 g/L. Although it can reach ammonia removal efficiency higher than 90%, the energy cost is far more than the optimized cost calculated in this study. Lei (2007) operated the ammonia stripping by adding 27.5g/L of calcium hydroxide, which cost about 1.94$/m^3 of liquid for just the lime which was also far more expensive than the worst-case scenario of this study. Although the difference in wastewater characteristics may affect the optimization result, Zeng et al. (2005) reported that the complex matrix of the digested dairy manure does not affect ammonia stripping. The main factor affecting the simulation result is the alkali dosing for pH control for different kinds of wastewater, which can be easily obtained from simple NaOH titration experiment and chemical cost adjustment. Ammonia stripping performance is highly dependent on air/liquid ratios (US-EPA 2000), the ammonia removal efficiency increased with higher air/liquid ratio (Zeng et al. 2005). The air/liquid ratio of this study was fixed at 2250. If the air/liquid ratio were higher, the curve of Figure 3-6(a) and 6(c) will shift downward because it can enhance ammonia stripping.

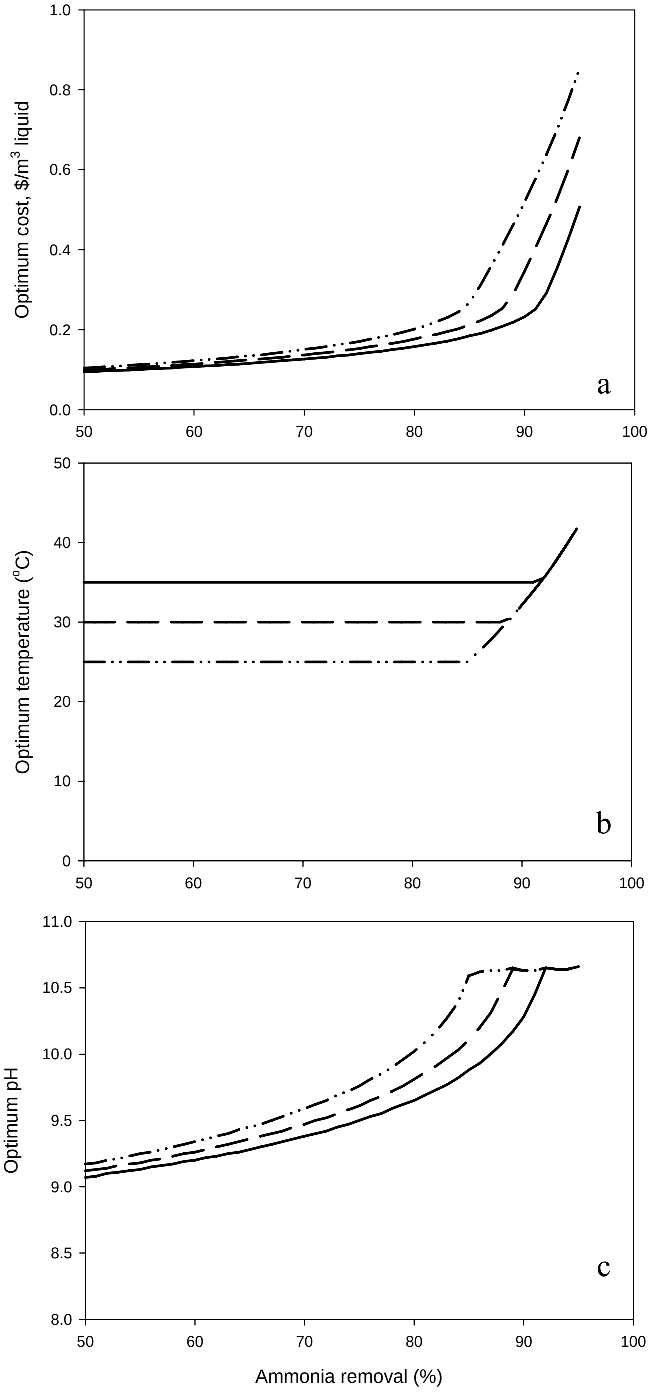

Figure 3-6: Simulated optimum pH, temperature, and costs

(Packing tower height of 7 m. Solid line: initial temperature of 35°C; long dash: initial temperature of 30°C; dash dot dot: initial temperature of 25°C.)

3.5 Conclusions

Temperature and pH are identified as the most cost sensitive ammonia stripping parameters. Raising the pH of the dairy wastewater to 11 requires 63% of more alkali than to 10 because of the abundance of bicarbonates. A combined log and polynomial correlation is suitable to fit the alkali titration. The combined correlation can describe both the nature of pH and the strong buffer effect of the dairy wastewater. A correlation of ammonia stripping efficiency was developed via a two factor experiment with four levels of pH and temperature. The ammonia stripping temperature and pH were economically optimized by combining the ammonia stripping efficiency with the titration correlation. After optimization, the cost of ammonia stripping was substantially lower than that estimated from other reports for the similar process. The results of this study make it feasible to apply ammonia stripping to the digested dairy manure for ammonia removal and subsequent recovery.

3.6 Acknowledgment

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3.7 References

APHA (2005) *Standard Methods for the Examination of Water and Wastewater, 21st ed.* American Public Health Association, American Water Works Association(AWWA), Water Environment Federation (WEF).

Battye, R., W. Battye, C. Overcash & S. Fudge (1994) Development and selection of ammonia emission factors. 68-D3-003, US-EPA, Washington DC, USA.

Bolan, N. S., L. Wong & D. C. Adriano (2004) Nutrient removal from farm effluents. *Bioresource Technology,* **94**(3)**,** 251-260.

Bonmatí, A. & X. Flotats (2003) Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management,* **23**(3)**,** 261-272.

Cheung, K. C., L. M. Chu & M. H. Wong (1997) Ammonia stripping as a pretreatment for landfill leachate. *Water Air and Soil Pollution,* **94**(1-2)**,** 209-221.

Choi, E., D. Kim, Y. Eum, Z. Yun & K. S. Min (2005) Full-scale experience for nitrogen removal from piggery waste. *Water Environment Research,* **77**(4)**,** 381-389.

Crittenden, J. C., R. R. Trussell, D. W. Hand, K. J. Howe & G. Tchobanoglous (2005) Water treatment: principles and design (second ed.). John Wiley & Sons, Inc., Hoboken, New Jersey.

EIA (2009a) Heating fuel comparison calculator. Energy Information Administration, U.S. Department of Energy. Retrieved from http: //www.eia.doe.gov/neic/experts/heatcalc. xls on October 10, 2009.

EIA (2009b) United states natural gas industrial price. Energy Information Administration, U.S. Department of Energy. Retrieved from http://tonto.eia.doe.gov/dnav/ng/hist/n3035u s3m.htm on October 10, 2009.

Emerson, K., R. C. Russo, R. E. Lund & R. V. Thurston (1975) Aquous ammonia equilibrium calculations: effect of pH and temperature. *Journal of the Fisheries Research Board of Canada,* **32**(12)**,** 2379-2383.

Guo, X., L. Zeng, X. M. Li & H. S. Park (2008) Ammonium and potassium removal for anaerobically digested wastewater using natural clinoptilolite followed by membrane pretreatment. *Journal of Hazardous Materials,* **151**(1)**,** 125-133.

Janus, H. M. & H. F. vanderRoest (1997) Don't reject the idea of treating reject water. *Water Science and Technology,* **35**(10)**,** 27-34.

Katehis, D., V. Diyamandoglu & J. Fillos (1998) Stripping and recovery of ammonia from centrate of anaerobically digested biosolids at elevated temperatures. *Water Environment Research,* **70**(2)**,** 231-240.

Lei, X. H., N. Sugiura, C. P. Feng & T. Maekawa (2007) Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification. *Journal of Hazardous Materials,* **145**(3)**,** 391-397.

Liao, P. H., A. Chen & K. V. Lo (1995) Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology,* **54**(1)**,** 17-20.

Martin, J. H. (2005) An evaluation of a mesophilic, modified plug-flow anarobic digester for dairy cattle manure. Final report for EPA Contract GS10F-0036K, U.S. Environmental Protection Agency, Washington, DC.

Metcalf & Eddy (2003) *Wastewater engineeering treatment and reuse (fourth ed.).* McGraw-Hill, NY, USA.

Meyer, S. S. & P. A. Wilderer (2004) Treating of process water in large wastewater treatment plants in Germany - A case study. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering,* **39**(7)**,** 1645-1654.

Mulder, A., A. A. Vandegraaf, L. A. Robertson & J. G. Kuenen (1995) Anaerobic ammonium oxidation discovered in a denitrifying fluidized-bed reactor. *FEMS Microbiology Ecology,* **16**(3)**,** 177-183.

National Research Council (1979) Ammonia. National Research Council, Subcommittee on Ammonia. Baltimore: University Park Press.

Onda, K., H. Takeuchi & Y. Okumoto (1968) Mass transfer coefficients between gas and liquid phases in packed columns. *Journal of Chemical Engineering of Japan,* **1**(1)**,** 56-62.

Siegrist, H. (1996) Nitrogen removal from digester supernatant - Comparison of chemical and biological methods. *Water Science and Technology,* **34**(1-2)**,** 399-406.

Siegrist, H., W. Hunziker & H. Hofer (2005) Anaerobic digestion of slaughterhouse waste with UF-membrane separation and recycling of permeate CD after free ammonia stripping. *Water Science and Technology,* **52**(1-2)**,** 531-536.

Strous, M., J. A. Fuerst, E. H. M. Kramer, S. Logemann, G. Muyzer, K. T. van de Pas-Schoonen, R. Webb, J. G. Kuenen & M. S. M. Jetten (1999) Missing lithotroph identified as new planctomycete. *Nature,* **400**(6743)**,** 446-449.

Szögi, A. A., M. B. Vanotti & A. E. Stansbery (2006) Reduction of ammonia emissions from treated anaerobic swine lagoons. *Transactions of the ASABE,* **49**(1)**,** 217-225.

Thom, J. E. & W. D. Byers (1993) Limitations and practical use of a mass-transfer model for predicting air stripper performance. *Environmental Progress,* **12**(1)**,** 61-66.

Thorndahl, U. (1993) Nitrogen removal from returned liquors. *Journal of the Institution of Water and Environment Management,* **7**(5)**,** 492-496.

Tilche, A., G. Bortone, F. Malaspina, S. Picinini & L. Stante (2001) Biological nutrient removal in a full-scale SBR treating piggery wastewater: results and modelling. *Water Science and Technology,* **43**(3)**,** 363-371.

Treybal, R. E. (1980) Mass transfer operations. McGraw-Hill, New York.

US-EPA (2000) Wastewater technology fact sheet: ammonia stripping. EPA Report 832-F-00-019, U.S. Environmental Protection Agency, Office of Water, Washington, DC.

US-EPA (2004) National emission inventory - ammonia emissions from animal husbandry. U.S. Environmental Protection Agency, Washington, DC.

USDA-APHIS (2004) Dairy 2002: nutrient management and the U.S. dairy industry in 2002. U.S. Department of Agriculture, Animal and Plant Health Inspection Service, Washington, DC.

Vanotti, M. (2005) Evaluation of environmentally superior technology: swine waste treatment system for elimination of lagoons, reduced environmental impact, and improved water quality. USDA Agreement 58-6657-2-202 / NCSU Subcontract

#2001-0478-02 / USDA-ARS CRIS Project # 6657-13630-001-05, U.S. Department of Agriculture, Agricultural Research Service, Washington, DC.

Ward, M. H., T. M. deKok, P. Levallois, J. Brender, G. Gulis, B. T. Nolan & J. VanDerslice (2005) Workgroup report: Drinking-water nitrate and health-recent findings and research needs. *Environmental Health Perspectives,* **113**(11)**,** 1607-1614.

WS-DOH (2005) Nitrogen reducing technologies for onsite wastewater treatment systems : report to the Puget Sound Action Team. DOH Pub 334-083, Division of Environmental Health, Washington State Department of Health, Olympia.

Zeng, L., X. Li, J. Liu & E. Jenson (2005) Feasibility study of air stripping of ammonia from digested cattle manure. *ADSW 2005 Conference Proceedings*. *In* B. K. Ahring & H. Hartmann (eds.), *4th International Symposium on Anaerobic Digestion of Solid Waste*, pp. 656-663. Copenhagen.

Zeng, L., C. Mangan & X. Li (2006) Ammonia recovery from anaerobically digested cattle manure by steam stripping. *Water Science and Technology,* **54**(8)**,** 137-145.

CHAPTER FOUR

A TWO-STEP, THREE-PHASE EQUILIBRIUM MODEL FOR APPLICAION WITH ANAEROBICALLY DIGESTED WASTEWATER

4.1 Abstract

Existing chemical equilibrium models cannot explain the crystallizing precipitates slowly formed in the anaerobic digestion (AD) reactor with long hydraulic retention time (HRT). In addition, these models need complete chemical species data as input which are difficult to obtain, especially from animal wastewater. A two-step, three-phase chemical equilibrium model was developed in this study for the supernatant of the digested dairy manure. This model can describe the crystallizing precipitates formed slowly in the effluent of AD with long HRT as well as reduce model input. The first step of the model included hydroxyapatite (HAP) that crystallizes slowly in order to obtain the initial chemical equilibrium. The second step of the model didn't include HAP because of the short reaction time of the post AD treatment which does not favor for the slow crystallizing HAP to form. The HAP formed in the AD was considered as inert in the second step of the model when no acid was added to dissolve the HAP. A new parameter that accounts for the difference between the inert cations and anions (Δions) was introduced in the model to reduce the required model inputs. The Δions was used in the model for electroneutrality instead of individual inert cations and anions. The Δions can be obtained by simulated KOH titration or HCl titration. Model validation proved that the slow crystallizing HAP was formed in the effluent of AD with long HRT. Model application to the unit processes of a combined nutrient recovery and biogas upgrading system for the digested dairy manure showed that: 1) the simulated NaOH titration fitted the measurement data with an R^2 of 0.95; 2) the model accurately predicted the lime dose required for raising pH pre-ammonia stripping; 3) the model predicted that the ammonia stripped effluent only absorb a small portion of CO_2 in the biogas to re-adjust the pH back to the initial level prior to post-AD treatment. The results suggest that the two-step, three-phase chemical equilibrium model can be used to predict the performance of the combined nutrient recovery and biogas upgrading system.

Keywords: Chemical equilibrium model, dairy wastewater, hydroxyapatite, ammonia stripping, biogas purification

4.2 Introduction

Mathematical models have been widely used in the design, operation, and research of wastewater treatment systems. Models such as the Activated Sludge Model (Henze *et al.* 2000) and the Anaerobic Digestion Model (Batstone *et al.* 2002) focused on biological processes because the biological process is the main part of the treatment. Chemical models embedded in these models are always focused on the chemical equilibrium around neutral pH in order to enhance the biological activities, or at a lower pH in order to assist the biological hydrolysis process. Chemical-physical process models have also been developed separately to enhance understanding of the chemical-physical processes of wastewater treatment, such as struvite crystallization (Celen *et al.* 2007, Gadekar & Pullammanappallil 2009).

The chemical equilibrium model consists often a group of chemical balance equations. If all the components and reactions are known, the theoretic chemical equilibrium equations can be built according to either the charge balance method or the tableau method (Batstone et al. 2002, Morel & Hering 1993) and can be solved by either theoretical or the numeric method. The main problems that affect the applicability of chemical equilibrium model are associated with the interactions among different equilibriums, the reaction rates, and the complexity of the wastewater. For example, Mg^{2+}, organics, and solids may affect the nucleation and the rate of precipitation of $CaCO_3$ and hydroxyapatite [HAP, $Ca_5(PO_4)_3(OH)$] (Celen et al. 2007, Salimi *et al.* 1985).

The complexity of the liquid can also affect the equilibrium constants such as the disassociation constant of ammonium (NH_4^+) (Hafner *et al.* 2006).

For modeling chemical equilibriumof water and wastewater, the dissolved species in liquid phase as well as the gas and solid phases have always been included in the calculation (Batstone et al. 2002, Gadekar & Pullammanappallil 2009, Musvoto *et al.* 2000b). The most common gas included is CO_2. Anaerobic Digestion Model No. 1 (ADM1) also includes H_2 and CH_4 because they are the major products/intermediates of AD (Batstone *et al.* 2002). H_2S is another important product of AD because it affects the usage of biogas and it is also an important inhibitor of AD. H_2S should also be included in the chemical equilibrium model if the biogas quality or H_2S inhibition is a concern. $CaCO_3$ has been the most common solid included in water/wastewater chemical equilibrium models and has been extensively studied for its precipitation because $CaCO_3$ scaling is a major problem for wastewater treatment (van Langerak & Hamelers 1997). Other solids have also been added to the chemical equilibrium models because of individual research interests, e.g., struvite for phosphorus recovery (Gadekar & Pullammanappallil 2009, Celen et al. 2007).

Solids are the most complicated components in a wastewater system. Solids such as carbonate and phosphates, which have strong effects on the acid buffer of a wastewater system, have always been considered in the chemical models. Because of the complexity of solids that may be formed in the wastewater, researchers discarded solid species in their modeling systems in various ways: Celen *et al.* (2007) excluded $CaCO_3$ whereas Musvoto *et al.* (2000a) included it; Gadekar and Pullammanappallil (2009) excluded all the carbonate species because their synthesized chemical system did not contain carbonates; slow-crystallizing solids such as HAP and dolomite [$CaMg(CO_3)_2$] were not included in all chemical models for wastewater systems.

The major buffer systems of AD effluent are carbonates, ammonium/ammonia, and phosphates. The major metal ions that affect the chemical equilibrium are calcium and magnesium. In this type of systems, HAP and dolomite are the most thermodynamically favorable crystallization species but they have very slow precipitation rates. Although both of them are discarded in all chemical models for wastewater systems, Güngör *et al.* (2007) measured HAP from dairy AD effluent. The formation of HAP includes four steps with three kinds of intermediate. Octacalcium phosphate [OCP, $Ca_8H_2(PO_4)_6{\cdot}5H_2O$, also written as $Ca_4H(PO_4)_3{\cdot}3H_2O$] is the first intermediate in forming HAP, which is unstable and will very quickly transform into the second intermediate, amorphous calcium phosphate [ACP, $Ca_3(PO_4)_2{\cdot}x\mathrm{H2O}$] (Liu *et al.* 2001). ACP will gradually transform into the third intermediate calcium-deficient hydroxyapatite [DCP, $Ca_{10\sim z}(HPO_4)_z(PO_4)_{6\text{-}z}(OH)_{2\text{-}z)}{\cdot}nH_2O$] and will finally become stable HAP (Liu *et al.* 2001). Although the formation of HAP occurs very slowly, it was reported that pure HAP can be formed within 24 h at 25°C (Liu *et al.* 2001) or within 4 h at 70°C (Mo *et al.* 2006). Dairy AD always has an HRT more than 20 days with a mesophilic temperature around 35°C which is favorable for HAP forming. Although Amjad *et al.* (1984), Salimi *et al.* (1985), and Abbona & Franchiniangela (1990) reported that magnesium can lower the speed of HAP formation, it is possible that HAP may be formed in the AD with the long HRT. Therefore, HAP should be included in the chemical equilibrium model.

The mechanism of dolomite precipitation is not well understood; even its formation equilibrium constant (K value) is not precisely known (Warren 2000). Sulfate may be an important inhibitor (Baker & Kastner 1981) and sulfate-reducing bacteria can help dolomite formation (Vasconcelos *et al.* 1995, Warthmann *et al.* 2000, Wright 1999). The formation of dolomite is very slow (Mamais *et al.* 1994). Vasconcelos *et al.* (1995) reported that it can be formed after more than one year of incubation with the assistance of sulfate-reducing bacteria at 4°C, and Baker & Kastner (1981) measured dolomite formation in 2 weeks at 200°C incubation. Mesophilic AD, which contains sulfate-reducing bacteria, might have a little chance for dolomite formation. HAP and dolomite crystallization can compete with struvite for phosphate and magnesium. Although struvite is less thermodynamically favorable than HAP and dolomite, neglecting HAP and dolomite in the chemical model may result in struvite thermodynamically favorable.

Chemical models calculate the pH based on electroneutrality (Eq. 1) (Batstone et al. 2002, Schecher & McAvoy 2003). In ADM1, inert cations and anions are considered separately as Eq. 2 (Batstone *et al.* 2002). Although the inert cations and anions are only useful for the electroneutrality calculation, they are still needed to be known as inputs, either from literatures or measurements, in order to calculate the pH. In wastewater systems, especially animal manure wastewater, the detailed components are complicated and difficult to obtain. It is not worth to measure the complete inert cations and anions for only the pH calculation.

$$\sum_m ch_m \times cat^+{}_m - \sum_n ch_n \times an^-{}_n = 0 \qquad (1)$$

$$\sum_i ch_i \times cat^-{}_i - \sum_j ch_j \times an^-{}_j + \sum_k ch_k \times cat^+{}_k - \sum_l ch_l \times an^-{}_l = 0 \qquad (2)$$

Where *ch* are the charges of cations cat^+ or anions an^-; *m, n* series are all the cations and anions in the wastewater system; *i, j* series are major cations and anions included in the chemical model for equilibrium calculation; *k, l* series are inert cations and anions such as [Na^+], [K^+], and [Cl^-].

The objective of this research is to develop a chemical equilibrium model which can be used for post-AD treatment. The model needs to be able to explain the slowly crystallizing precipitates that can be formed in the AD with long HRT. In addition, the model needs to reduce input in order to minimize the measurements. The model will be used to the unit processes of the combined nutrient recovery and biogas upgrading system (Jiang *et al.* 2009) for the supernatant of digested dairy manure as a case study. The combined nutrient recovery and biogas upgrading system includes (1) pre-ammonia-stripping pH adjustment; (2) ammonia stripping; and (3) biogas purification with ammonia stripped effluent. Briefly, this involves ammonia stripping with rising pH levels and biogas injection into the ammonia stripped effluent for pH readjustment, as well as biogas upgrading (purification) by using high-pH ammonia stripping effluent to absorb CO_2 and H_2S from the biogas produced from the AD.

4.3 Materials and methods

A three-phase chemical equilibrium model was developed which included all the dissolved and precipitated chemical species discussed in the literature (Celen et al. 2007, Gadekar & Pullammanappallil 2009, Musvoto et al. 2000a, Schecher & McAvoy 2003). A new parameter ($\Delta ions$) which accounts for the difference between the inert cations and anions was introduced to the model in order to reduce the needed for model input. $\Delta ions$ was obtained by simulated NaOH or HCl titration. Solids formed in the model were compared with measurements in order to properly remove the solids species from the model. Then a two-step, three-phase model was developed and was then validated by titration and applied to the unit processes of the combined nutrient recovery and biogas purification system described above.

4.3.1 Model development

All the related species from the MINEQL+ 4.6 database or as reported in other literatures (Celen et al. 2007, Gadekar & Pullammanappallil 2009, Musvoto et al. 2000a, Schecher & McAvoy 2003) are considered in this model. These chemical species and their chemical equilibrium constants are shown in Table 4-1 as tableau format. Subsequent elimination of solid species was determined according to the comparison of four models: (1) Model 1: including all the solids species; (2) Model 2: excluding HAP;

(3) Model 3: excluding dolomite; and (4) Model 4: excluding both HAP and dolomite. The model equilibrium equations include chemical equilibriums, phase equilibriums, mass balance, and electroneutrality.

4.3.1.1 Chemical equilibriums

The equilibriums of the chemical species listed in Table 4-1 can be written as following:

$$\text{For dissolved species } [B_i]\text{: } K_i = \frac{\prod_j [A_j]^{C_{ij}}}{[B_i]} \qquad (3)$$

$$\text{For solid species } [B_i]\text{: } K_i \geq \prod_j [A_j]^{C_{ij}} \text{ when } [B_i] = 0 \qquad (4a)$$

$$K_i = \prod_j [A_j]^{C_{ij}} \text{ when } [B_i] > 0 \qquad (4b)$$

Where K_i series are the equilibrium coefficients which can be calculated from the last column (logK_i) of Table 4-1; $[A_j]$ series are the chemical species of the 1st row of Table 4-1 except water; $[B_i]$ series are chemical species in the 1st column of Table 4-1; and c_{ij} series are the coefficients of the matrix in Table 4-1.

4.3.1.2 Phase equilibriums

Gas-liquid equilibrium in the chemical models can be calculated according to Henry's law (Batstone et al. 2002, Schecher & McAvoy 2003). There are different forms of Henry's constants according to different gas and liquid concentration units. The

Henry's constant used in this study is defined by Eq. 5. H_2S and CO_2 are included in this chemical equilibrium model (Eqs. 6-7).

$$H = \frac{[A_{gas}]}{[A_{aq}]} \tag{5}$$

$$H_2S_{gaseous} = H_{H_2S} \times [H_2S_{(aq)}] \tag{6}$$

$$CO_{2\,gaseous} = H_{CO_2} \times [H_2CO_{3(aq)}] \tag{7}$$

Where H is the Henry's constant, dimensionless; $[A_{gas}]$ is the concentration of gas in air, mole/l air; $[A_{aq}]$ is the concentration of gas in water, mole/l water; $H_2S_{gaseous}$ and $CO_{2\,gaseous}$ are the saturated partial pressures of H_2S and CO_2, respectively; H_2S; H_{H_2S} and H_{CO_2} are the Henry's constants of H_2S and CO_2, respectively; $[H_2CO_{3(aq)}] = [CO_{2(aq)}] + [H_2CO_3]$.

According to the equilibrium of the reaction $\mathrm{CO_{2(aq)}} + \mathrm{H_2O} \Leftrightarrow \mathrm{H_2CO_3}$, $[H_2CO_3]$ concentration is much lower than $[CO_{2(aq)}]$. Therefore $[H_2CO_{3(aq)}] \approx [CO_{2(aq)}]$, and $[H_2CO_{3(aq)}]$ is utilized in most chemical equilibrium calculations (Crittenden *et al.* 2005).

4.3.1.3 Mass balance

$$[(Total - A)_j] = \sum_i [A_j] + c_{ij}[B_i] \tag{8}$$

Where $[(Total - A)_j]$ series are total concentrations of chemical species A_j and its derivatives in mole/L excluding $[H^+]$.

4.3.1.4 Electroneutrality

A new parameter, Δ*ions* was introduced in this model to balance the difference between inert cations and anions (Eq. 9). Substituting Eq. 9 into Eq 2. results in Eq. 10. Δ*ions* was determined by the simulated NaOH or HCl titration to fit the initial pH.

$$\Delta ions = \sum_k ch_k \times cat^+{}_k - \sum_l ch_l \times an^-{}_l \tag{9}$$

$$\sum_i ch_i \times cat^+{}_i - \sum_j ch_j \times an^-{}_j + \Delta ions = 0 \tag{10}$$

4.3.1.5 Model calculation

Modeling system such as Aquasim (Musvoto et al. 2000b), Minteq (Celen et al. 2007), MINEQL+ (Schecher & McAvoy 2003), and mathematic software such as Maple (Gadekar & Pullammanappallil 2009) can be used to solve the model equations. Using mathematic software to solve the model equations needs complete coding while using modeling system only needs to input the equilibrium matrix (such as MINEQL+) or the equations (such as Aquasim). In this study, the model equations except the phase equilibriums were solved by MINEQL+ version 4.6. The phase equilibriums were calculated separately according to Eqs 6-7.

Table 4-1. Chemical matrix of the chemical equilibrium model

Chemical Species	H_2O	H^+	Ca^{2+}	Cl^-	CO_3^{2-}	Mg^{2+}	Na+	NH_4^+	PO_4^{3-}	HS^-	LogK	Source
1. dissolved species												
OH^-	1	–1									–14.0	a
HCO_3^-		1			1						10.25	c
$H_2PO_4^-$		2									19.5	d
HPO_4^{2-}		1									12.3	d
S^{2-}		–1									16.04	c
$H_2CO_3(aq)$		2			2						16.62	c
H_3PO_4		3									21.6	d
$H_2S(aq)$		1									7.04	c
$CaCO_3(aq)$			1		1						3.2	b
$MgCO_3(aq)$					1	1					3.4	b
$CaHPO_4(aq)$		1	1								15.03	b
$MgHPO_4(aq)$			1			1					14.8	b
$NH_3(aq)$		–1						1			–9.25	a
$CaOH^+$	1	–1	1								–12.6	b
$MgOH^+$	1	–1				1					–11.8	b
$CaHCO_3^+$		1	1		1						11.51	b
$MgHCO_3^+$		1			1	1					11.41	b
$Ca(NH_3)_2^{2+}$		–2	1					2			–18.8	a
$Ca(NH_3)^{2+}$		–1	1					1			–9.14	a
$CaH_2PO_4^+$		2	1								20.91	b

Table 4-1. Chemical matrix of the chemical equilibrium model (continued)

Chemical Species	H_2O	H^+	Ca^{2+}	Cl^-	CO_3^{2-}	Mg^{2+}	Na+	NH_4^+	PO_4^{3-}	HS^-	LogK	Source
$MgH_2PO_4^+$		2				1			1		21.25	a
$CaPO_4^-$			1						1		6.46	b
$MgPO_4^-$						1			1		3.13	b
2. Solid species												
CaO (Lime)	1	–2	1								–33.1	a
$CaCO_3$ (aragonite)			1		1						8.3	a
$CaCO_3$ (Calcite)			1		1						8.48	a
$MgCO_3$ (Magnesite)					1	1					7.46	a
$Ca(OH)_2$ (Portlandite)	2	–2	1								–22.9	a
MgO (Periclase)	1	–2				1					–21.6	a
$Mg(OH)_2$ (Brucite)	2	–2				1					–16.8	a
$Mg(OH)_2$ Active)	2	–2				1					–18.8	a
$Mg(OH)_2 \cdot 6H_2O$	8	–2				1					–17.3	f
$Ca_3(PO_4)_2(\beta)$			3						2		28.92	a
$Mg_3(PO_4)_2$						3			2		23.28	a
$Mg_3(PO_4)_2 \cdot 8H_2O$	8					3			2		23.98	f
$Mg_3(PO_4)_2 \cdot 22H_2O$	22					3			2		22.89	f
CaS		–1	1							1	–6.86	f
$CaHPO_4 \cdot 2H_2O$	2	1	1						1		18.99	a
$CaHPO_4$		1	1						1		19.27	a
$MgHPO_4 \cdot 3H_2O$	3	1				1			1		18.17	a

Table 4-1. Chemical matrix of the chemical equilibrium model (continued)

Chemical Species	H_2O	H^+	Ca^{2+}	Cl^-	CO_3^{2-}	Mg^{2+}	Na+	NH_4^+	PO_4^{3-}	HS^-	LogK	source
$Ca_4H(PO_4)_3 \cdot 3H_2O$	3	1	4						3		47.08	a
$(NH_4)MgPO_4 \cdot 6H_2O$ (Struvite)	6					1		1	1		12.6	e
$Ca_5(PO_4)_3(OH)$ (HAP)	1	–1	5						3		44.33	a
$Mg_2CO_3(OH)_2 \cdot 3H_2O$ (Artinite)	5	–2			1	2					–9.6	a
$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Hydromagnesite)	6	–2			4	5					8.766	a
$Mg(HCO_3)(OH) \cdot 2H_2O$ (Nesquehonite)	3	–1	1		1	1					4.67	a
$CaMg_3(CO_3)_4$ (Huntite)			1		4	3					29.97	a
$CaMg(CO_3)_2$ (Dolomite ordered)			1		2	1					17.09	a
$CaMg(CO_3)_2$ (Dolomite disordered)			1		2	1					16.54	a

Sources: a. MINEQL+ 4.6 thermodynamics database; b. Ferguson & McCarty (1971); c, Crittenden *et al.*(2005); d. Metcalf & Eddy (2005); e. Jaffer *et al.* (2003); f. Gadekar & Pullammanappallil (2002).

4.3.2 Digested dairy manure

Digested dairy manure was taken from AD effluent produced by a commercial digester treating scraped dairy manure in Lynden, WA and stored at 4°C before use. The commercial dairy scraped fresh manure into an underground pit three times a day. The manure was then sent to a pit for mixing with outside food processing wastes used for co-digestion (17% v/v food substrates). The resulting mixture was fed every 2 h into an axial-mixed plug-flow mesophilic digester (GHD Inc., Chilton, WI). Coarse fibrous solids were separated with a 0.3-cm slope screen (US Farms, Tulare, CA) while the supernatant flowed into a storage lagoon. Sampling occurred at the lagoon's entry pipe. The design size of the AD was 1,500 cows but the farm has only about 700 cows, so various food wastes were also fed to the digester. The actual HRT of the digester was about 32 days. The characteristics of the dairy manure are listed in Table 4-2.

4.3.3 Analytical methods

All analyses were conducted in the Water Quality Laboratory at Washington State University according to standard methods APHA (2005). The pH was measured with a Denver Ultrabasic pH meter (Denver Instruments, Arvada, CO). The total ammoniac nitrogen (TAN) was measured with a Tecator 2300 Kjeltec Analyzer Unit Analyzer (FOSS North America, Eden Prairie, MN). Total solids (TS) and volatile solids (VS) were measured by drying a sample in a 105ºC oven and then burning it in a 550ºC furnace. The calcium and magnesium were measured using an atomic absorption spectrometer SpectrAA 220 (Varian, Palo Alto, CA). Lanthanum (10,000 µg/mL) was used to eliminate the interferences. The SpectrAA 220 was run under the conditions suggested by the manufacturer. The TIP (total inorganic phosphorus) and OP (ortho-phosphorus) were measured by the ascorbic acid method with a Spectronic 20 Genesys spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA).

Soluble components were measured from the liquid part obtained after centrifuge at 4,500 rpm for 30 min for three times repeatedly, followed by filtration in series with pore sizes 11μm, 8 μm, 5 μm, 2.5 μm, 1.5 μm, 0.8 μm, 0.45 μm, and 0.2 μm. Total calcium (Total Ca), total magnesium (Total Mg), and TIP were measured from the liquid obtained after being acidified with 6N HCl to pH < 2.0, followed by centrifuge at 4,500 rpm for 30 min and filtration in series with pore sizes 0.45 μm and 0.2 μm.

Total inorganic carbonate (TIC) was measured by the alkalinity titration method after subtracting the ammonia and phosphate alkalinity from the total alkalinity (Eqs. 11-12). Soluble carbonic alkalinity was calculated according to APHA (2005). The concentrations of the soluble species were calculated according to the disassociation of ammonium and phosphates.

$$\mathrm{Alk_C(aq) = Alk_T(aq) - [NH_3] - 3[PO_4^{3-}] - 2[HPO_4^{2-}] - [H_2PO_4^{-}]} \quad (11)$$

$$\mathrm{Alk_C(s) = Alk_T - Alk_T(aq) - 3(TIP - OP)} \quad (12)$$

Where $\mathrm{Alk_C(s)}$ is the solid carbonic alkalinity; $\mathrm{Alk_T}$ is the total alkalinity; $\mathrm{Alk_C(aq)}$ is the soluble carbonic alkalinity; $\mathrm{Alk_T(aq)}$ is the total alkalinity of the liquid after solids removal; the unit of alkalinity is in Eq/L; all other units are in mol/L.

Table 4-2. Characteristics of the digested dairy manure

Item	**Unit**	**Value**
Total Ca	mmole/L	16.8
Soluble Ca	mmole/L	0.66
Total Mg	mmole/L	6.69
Soluble Mg	mmole/L	0.619
TIP	mmole-P/L	6.95
OP	mmole-P/L	0.643
Total Sulfide	mmole-S/L	1.56
TIC	mole-C/L	0.183
TAN	mole-N/L	0.146
TKN	mole-N/L	0.219
TS	g/L	27
TSS	g/L	11
VS	g/L	17
VSS	g/L	4.79

4.4 Results and discussions

4.4.1 Model selection and validation

The comparison between the outputs of the four models (Model 1-4)) and measurements is shown in Table 4-3. All four models showed that almost all the calcium and magnesium were in solid form. The measurements also showed similar results. The main difference was the phosphate content in the solids. Model 2, which was designed without HAP, can be eliminated first because the simulated result showed that all phosphates were soluble as dolomite and $CaCO_3$ consumed the Ca and Mg which might form precipitates with phosphorus. The measurements on the other hand, showed that most inorganic P was bound with solids. Güngör & Karthikeyan (2008) and Zhang *et al.* (2009) also reported that inorganic P was mostly associated with particulate solids in dairy manure. In this study, only 9% of inorganic phosphorus was measured as soluble OP. This suggests that the true soluble inorganic P content was less than 9% because not all solid P could be separated, even with 0.2-μm filtration. If HAP was formed, the crystal was always very small, with length less than 100 nm (Liu *et al.* 2001). The 0.2-μm filtration could not fully intercept it. Other solids may have encountered a similar situation, so the actual Ca, Mg, and inorganic P in the solids might be greater than the measured values listed in Table 4-3. The only model result that fits this was model 3, which included HAP but excluded dolomite. Güngör *et al.* (2007) measured HAP from AD effluent and proved that HAP can form in a long-HRT mesophilic anaerobic digester. Güngör *et al.* (2007) also found struvite in the digester effluent using x-ray diffraction (XRD), which differs from the model prediction from this study. We failed to detect struvite in the effluent of dairy AD using XRD because the noise of the solids complex seemed to match $CaCO_3{\cdot}H_2O$ (data not shown). The lack of agreement might be due to two reasons: First, we tried to measure stuvite from the total solid while Güngör *et al.* (2007) measured struvite after sieving and only measured solids sizes between 25 μm and 53 μm, which is only a small fraction of the solids; this might magnify the percentage of some species of solids at that specific size. Second, HAP is more thermodynamically stable but forms slowly; thus the HAP will replace the struvite if the HRT is long enough to reach equilibrium. The HRT of the digester that Güngör *et al.* (2007) used was 20 days, whereas the HRT of the digester used in this study was 32 days. This may have led to the equilibrium going to the HAP side (Eq. 13).

$$\mathrm{(NH_4)MgPO_4 \cdot 6H_2O \Leftrightarrow NH_4^+ + Mg^{2+} + PO_4^{3-} + H_2O \cdots + Ca^{2+} + OH^- \Leftrightarrow Ca_5(PO_4)_3(OH)} \tag{13}$$

Table 4-3. Model predicted and measured Ca, Mg, and P concentrations of the solids

Item	Model 1 (mM)	Model 2 (mM)	Model 3 (mM)	Model 4 (mM)	Measured (mM)
HAP	2.03		2.25		
Dolomite	6.63	6.66			
Struvite				3.62	
$CaCO_3$		10.1	5.53	16.8	
$MgCO_3$			6.39	2.76	
Δions[1]	36.3	38.1	36	37.8	
Ca	16.78	16.76	16.78	16.8	16.1
Mg	6.63	6.66	6.39	6.38	6.07
P	6.09	0	6.75	3.62	6.30±0.02[2]

[1] Considered as K^+; if positive; considered as Cl^-if negative.

[2] Average of three replicates

Since the HAP crystallization rate is very slow and it is present in the digester effluent, a two-step three-phase model was necessary for modeling the digester effluent. Step one was to simulate the initial condition of the digester effluent, which included HAP but excluded dolomite. Step two excluded both HAP and dolomite which was used for the treatment of the AD effluent when chemicals were added due to the short reaction time. The HAP formed was considered as inert when no acid was added to dissolve the HAP. If acid was added to the manure, the HAP would dissolve, thus only step two of the model should be used alone to describe the chemical equilibriums.

4.4.2 Model validation: sodium hydroxide titration

Digested dairy wastewater (Table 4-2) was used for the model validation. The two-step, three-phase model was applied because NaOH was used as the titrant which cannot dissolve the HAP formed. The model simulated NaOH titration also showed good fit with the experiment titration data with an R^2 of 0.95 (Figure 4-1), even for digested dairy wastewater which had 27 g/L of TS. Titration fitting of the chemical equilibrium model can work better with less complex wastewater, so it can even be used to measure some weak acid contents (Van Vooren *et al.* 2001, Van Hulle *et al.* 2006).

4.4.3 Model application to the unit processes of a post-AD combined nutrient recovery and biogas upgrading system- a case study

4.4.3.1 Pre-ammonia stripping pH adjustment

Lime was used to increase pH prior to ammonia stripping because of its low price.

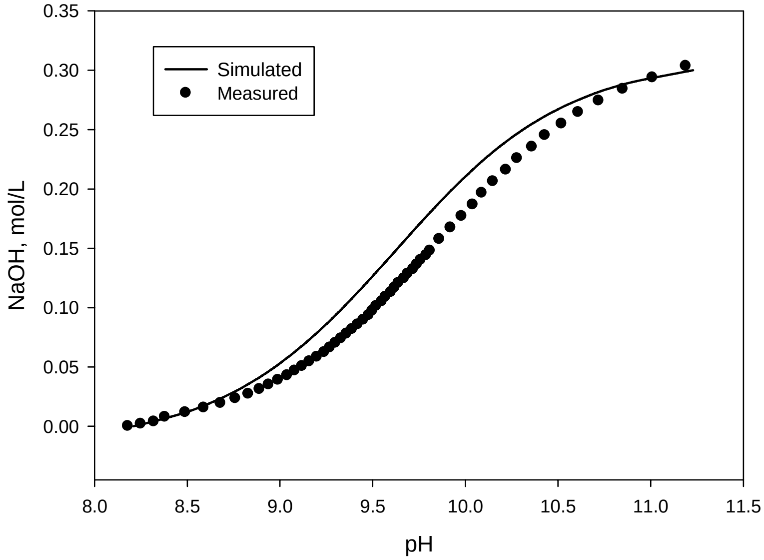

Figure 4-1. Simulated and measured NaOH dosage and pH change

Based on the simulation with the two-step, three-phase chemical equilibrium model, 6.98 g/L of lime would be needed to increase the pH of the digested dairy wastewater to 9.9. In our previous ammonia stripping experiment, when 7.84 g/L of quicklime was added to the digested dairy manure obtained from the same farm at different time, the pH was 9.9. Considering the purity (90%) of the quicklime, the actual lime used was 7.06g/L, which was only 1% difference from the simulation result. According to the simulation, 7.3g/L of lime dosing is needed to increase the pH to 10, with precipitates of 2.25 mmole/L of HAP, 0.136 mole/L of calcite and 6.58 mmole/L of magnesite formed in the wastewater.

4.4.3.2 Ammonia stripping

The model was also applied to predict the pH change during ammonia stripping and the potential of the ammonia stripped effluent for CO_2 and H_2S absorption or desorption. Assuming the ammonia stripping only stripped out the ammonia and there was no CO_2 and H_2S exchange with the air, the simulated pH change and the theoretical equilibrium partial pressure of CO_2 and H_2S vs. the ammonia removal were shown in Figure 4-2. When the ammonia removal efficiency increased from 0 to 85%, the pH of the wastewater dropped from 10 to 9.3; the theoretical equilibrium partial pressure of CO_2 changed from 110 ppm to 940 ppm, and that of H_2S changed from 14 ppm to 66 ppm. With the closed air loop ammonia stripping and acid absorption system of the combined nutrient recovery and biogas upgrading process described by Jiang *et al.* (2009), there would be no exchange of CO_2 and H_2S with the biogas. Thus the predicted pH change can thus be applied to measure the performance of the ammonia stripping. The simulated equilibrium partial pressure of H_2S gives lowest possible H_2S concentration that can be obtained if the ammonia stripped effluent was used to absorb the H_2S from the biogas. The simulated equilibrium partial pressure of H_2S will be lower if the sulfide in the AD effluent was reduced by other in-vessel sulfide removal technology applied.

4.4.3.3 Post-ammonia stripping biogas purification capacity

The pH of the ammonia stripped effluent was readjusted using biogas in the combined nutrient recovery and biogas purification system (Jiang *et al.* 2009). The biogas contained much more CO_2 than H_2S, and CO_2 absorption was the main reason for the pH

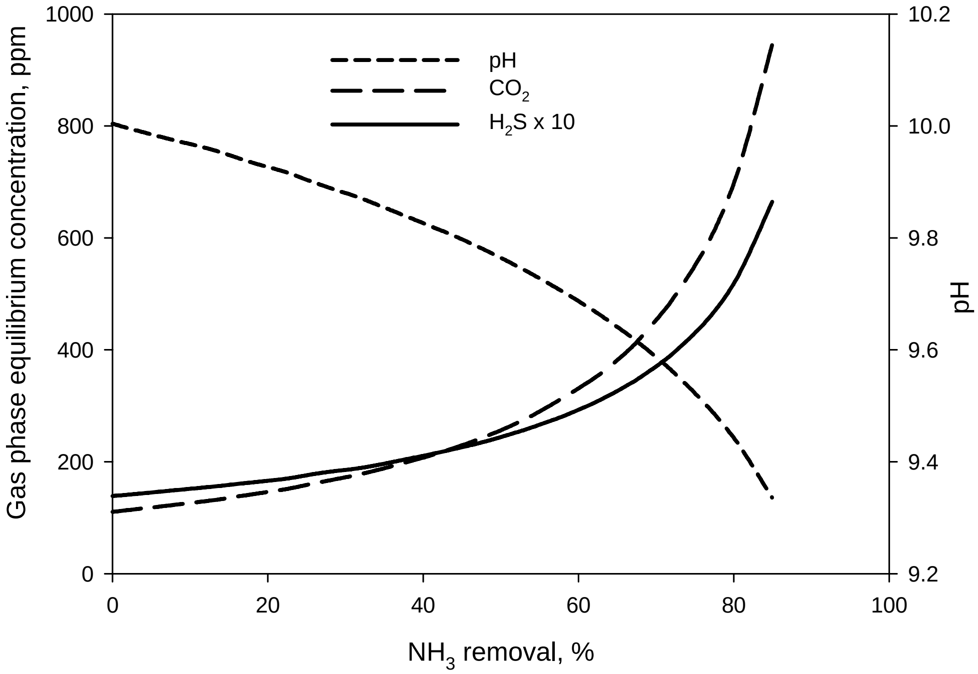

Figure 4-2. The pH and theoretical equilibrium partial pressures of CO_2 and H_2S at different ammonia removal efficiencies

drop during biogas injection. When lime was added, the majority of the solid formed was calcite. The calcite may help absorbing the CO_2 according to reaction (Eq. 14). While for ammonia stripping, the packed column method needs to have almost all solids removed, whereas aeration or some type of tray columns does not require solids removal. Table 4-4 shows the simulated pH change according to varying CO_2 absorption at different solids removal levels. The simulated results showed almost no difference at different solids removal levels because of the small pH drop. This suggests that only a small amount of the calcite was dissolved during the CO_2 absorption even the pH dropped to about 7. The pH did not drop low enough to dissolve all the calcite. The simulation also showed that the biogas is more than sufficient to readjust the pH of the ammonia stripped effluent back to the level before post-AD treatment (pH=8.2). Only 0.016 M of CO_2 was absorbed to drop the pH to below 8.2, which is approximately equal to the CO_2 in 1 m^3 of biogas for every m^3 of ammonia stripping effluent. The biogas purification capacity of the ammonia stripping effluent is able to focus only on H_2S because of the small quantity of CO_2 required.

$$\mathrm{CaCO_3 + CO_2 + H_2O = CaHCO_3} \qquad (14)$$

Table 4-4. pH of different solids removal scenarios*

	pH					
CO_2 Absorption (M)	0% Solids Removal	20% Solids Removal	40% Solids Removal	60% Solids Removal	80% Solids Removal	100% Solids Removal
0.005	9.059	9.094	9.058	9.057	9.061	9.061
0.010	8.77	8.815	8.768	8.759	8.772	8.771
0.015	8.325	8.402	8.321	8.307	8.328	8.315
0.020	7.697	7.771	7.694	7.682	7.699	7.597
0.025	7.335	7.371	7.334	7.328	7.295	7.195
0.030	7.133	7.155	7.132	7.104	7.052	6.977
0.035	6.997	7.013	6.991	6.935	6.895	6.829

* Ammonia stripping at pH 10 and assuming 85% ammonia removal.

4.5 Conclusions

A two-step, three-phase chemical equilibrium model was developed and validated for digested dairy manure wastewater. The first step of the model included HAP, which was formed in the AD with long-HRT. The second step of the model did not include HAP because the short HRT of the post AD treatment did not favor the slow formation of crystallizing HAP. The HAP formed at the first step model was considered as inert if no acid was added to make it dissolved. A new parameter that accounts for the difference between the inert cations and anions (Δions) was introduced in the model which can reduce the model input. The model validation proved that there was HAP formed in the AD effluent. The model was applied to a combined nutrient recovery and biogas purification system as a case study. The model predicted with good accuracy the alkali dose needed for raising pH as required. The model can also enhance understanding of the related biogas purification process. The results suggest that the two-step, three-phase chemical equilibrium model is suitable for the digested dairy wastewater. Thus, it can be used to predict the performance of the unit processes of the combined nutrient recovery and biogas upgrading system.

4.6 Acknowledgment

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4.7 References

Abbona, F. & M. Franchiniangela (1990) Crystallization of calcium and magnesium phosphates from solutions of low concentration. *J. Cryst. Growth,* **104**(3)**,** 661-671.

Amjad, Z., P. G. Koutsoukos & G. H. Nancollas (1984) The crystallization of hydroxyapatite and fluorapatite in the presence of magnesium-ions. *Journal of Colloid and Interface Science,* **101**(1)**,** 250-256.

APHA/AWWA/WEF (2005) *Standard methods for the examination of water and wastewater.* 21st ed. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF).

Baker, P. A. & M. Kastner (1981) Constraints on the formation of sedimentary dolomite. *Science,* **213**(4504)**,** 214-216.

Batstone, D. J., J. Keller, I. Angelidaki, S. V. Kalyuzhnyi, S. G. Pavlostathis, A. Rozzi, W. T. M. Sanders, H. Siegrist & V. A. Vavilin (2002) *Anaerobic digestion model no. 1 - IWA task group for mathematical modelling of anaerobic digestion processes.* IWA publishing, London, UK.

Celen, I., J. R. Buchanan, R. T. Burns, R. B. Robinson & D. R. Raman (2007) Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research,* **41**(8)**,** 1689-1696.

Crittenden, J. C., R. R. Trussell, D. W. Hand, K. J. Howe & G. Tchobanoglous (2005) Water treatment: principles and design (second ed.). John Wiley & Sons, Inc., Hoboken, New Jersey.

Ferguson, J. F. & P. L. McCarty (1971) Effects of carbonate and magnesium on calcium phosphate precipitation. *Environmental Science & Technology,* **5**(6)**,** 534-540.

Gadekar, S. & P. Pullammanappallil (2009) Validation and applications of a chemical equilibrium model for struvite precipitation. *Environ Model Assess***,** DOI 10.1007/s10666-10009-19193-10667.

Güngör, K., A. Jurgensen & K. G. Karthikeyan (2007) Determination of phosphorus speciation in dairy manure using XRD and XANES Spectroscopy. *Journal of Environmental Quality,* **36**(6)**,** 1856-1863.

Güngör, K. & K. G. Karthikeyan (2008) Phosphorus forms and extractability in dairy manure: A case study for Wisconsin on-farm anaerobic digesters. *Bioresource Technology,* **99**(2)**,** 425-436.

Hafner, S. D., J. J. Bisogni & W. J. Jewell (2006) Measurement of un-ionized ammonia in complex mixtures. *Environmental Science & Technology,* **40**(5)**,** 1597-1602.

Henze, M., W. Gujer & T. Mino (2000) *Activated sludge models ASM1, ASM2, ASM2d and ASM3 - IWA task group for mathematical modelling for design and operation of biological wastewater treatment.* IWA publishing, London, UK.

Jaffer, Y., T. A. Clark, P. Pearce & S. A. Parsons (2002) Potential phosphorus recovery by struvite formation. *Water Research,* **36**(7)**,** 1834-1842.

Jiang, A., T. Zhang, C. Frear & S. Chen (2009) Combined nutrient recovery and biogas scrubbing system integrated in series with animal manure anaerobic digester. US Patent Application No.: 20090206028.

Liu, C., Y. Huang, W. Shen & J. Cui (2001) Kinetics of hydroxyapatite precipitation at pH 10 to 11. *Biomaterials,* **22**(4)**,** 301-306.

Mamais, D., P. A. Pitt, Y. W. Cheng, J. Loiacono & D. Jenkins (1994) Determination of ferric-chloride dose to control struvite precipitation in anaerobic sludge digesters. *Water Environment Research,* **66**(7)**,** 912-918.

Metcalf & Eddy (2003) *Wastewater engineeering treatment and reuse (fourth ed.).* McGraw-Hill, NY, USA.

Mo, L. R., Y. B. Li, G. Y. Lv, J. D. Li & L. Zhang (2006) Comparison of hydroxyapatite synthesized under different conditions. *Materials Science Forum,* **510-511,** 814-817.

Morel, F. & J. G. Hering (1993) *Principles and applications of aquatic chemistry.* Wiley, New York.

Musvoto, E. V., M. C. Wentzel & G. A. Ekama (2000a) Integrated chemical-physical processes modelling - II. Simulating aeration treatment of anaerobic digester supernatants. *Water Research,* **34**(6)**,** 1868-1880.

Musvoto, E. V., M. C. Wentzel, R. E. Loewenthal & G. A. Ekama (2000b) Integrated chemical-physical processes modelling - I. Development of a kinetic-based model for mixed weak acid/base systems. *Water Research,* **34**(6)**,** 1857-1867.

Salimi, M. H., J. C. Heughebaert & G. H. Nancollas (1985) Crystal-growth of calcium phosphates in the presence of magnesium-ions. *Langmuir,* **1**(1)**,** 119-122.

Schecher, W. D. & D. C. McAvoy (2003) *Mineql+ a chemical equilibrium modeling system version 4.5 for Windows User's manual.* Environmental Research Software, Hallowell, ME.

Van Hulle, S. W. H., U. Zaher, G. Schelstraete & P. A. Vanrolleghem (2006) Titrimetric monitoring of a completely autotrophic nitrogen removal process. *Water Science & Technology,* **53**(4-5)**,** 533-540.

van Langerak, E. P. A. & H. V. M. Hamelers (1997) Influent calcium removal by crystallization reusing anaerobic effluent alkalinity. *Water Science and Technology,* **36**(6-7)**,** 341-348.

Van Vooren, L., M. Van de Steene, J. P. Ottoy & P. A. Vanrolleghem (2001) Automatic buffer capacity model building for the purpose of water quality monitoring. *Water Science and Technology,* **43**(7)**,** 105-113.

Vasconcelos, C., J. A. McKenzie, S. Bernasconi, D. Grujic & A. J. Tien (1995) Microbial mediation as a possible mechanism for natural dolomite formation at low-temperatures. *Nature,* **377**(6546)**,** 220-222.

Warren, J. (2000) Dolomite: occurrence, evolution and economically important associations. *Earth-Science Reviews,* **52**(1-3)**,** 1-81.

Warthmann, R., Y. van Lith, C. Vasconcelos, J. A. McKenzie & A. M. Karpoff (2000) Bacterially induced dolomite precipitation in anoxic culture experiments. *Geology,* **28**(12)**,** 1091-1094.

Wright, D. T. (1999) The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. *Sedimentary Geology,* **126,** 147-157.

Zhang, T., K. E. Bowers, J. H. Harrison & S. Chen (2009) Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy effluent. *Water Environment Research,* **81,** (Accepted. uncorrected page proofs.).

CHAPTER FIVE

SUMMARY

In this study, a novel combined nutrient recovery and biogas upgrading system (combined system) was developed to mitigate environmental concerns associated with the storage and land disposal of waste stream from dairy operations. The system includes recovering ammonia with air stripping followed by acid absorption and using the biogas produced by anaerobic digestion (AD) to readjust the pH of the ammonia stripped effluent to accepted levels while concurrently upgrading the biogas. In addition, optimization of the ammonia stripping was also studied and optimized parameters were provided for future application of the combined system. Furthermore, a two-step, three-phase chemical equilibrium model was developed to describe the chemistry of the unit processes of the combined system. The main conclusions obtained from this research and recommendations for future work are summarized below:

1. Combined nutrient recovery and biogas upgrading system

The combined system developed in this study for digested dairy manure can be a practical solution for the environmental concerns caused by excess nitrogen and phosphorus on large dairy farms. A wastewater stream with lower nutrient content and three value added by-products can be produced from the combined system: 1) phosphorus rich solid; 2) ammonium sulfate solution as nitrogen fertilizer; 3) biogas with majority of

H_2S removed. The combined system was proven both technically feasible and economically advantageous. All ammonia removed by air stripping can be absorbed with sulfuric acid to produce an ammonium sulfate solution with $pH < 2.0$. More than 90% of the H_2S in the biogas could be absorbed by the ammonia stripping effluent at a biogas/liquid ratio of ten with initial H_2S concentration of 2000 ppm. The biogas produced from the AD is enough to re-adjust the pH of the ammonia stripped effluent back to the initial pH before entering the combined system. A case study showed that the value of the recovered ammonium sulfate can compensate the costs of chemical and the majority of the electricity consumed by the combined system.

2. Economic optimization of ammonia stripping for the anaerobically digested dairy wastewater

Ammonia stripping is the major component of the developed combined system. Temperature and pH were identified as the most cost sensitive parameters for ammonia stripping. A correlation of ammonia stripping efficiency versus temperature and pH was developed based on a two factor experiment with four levels of pH and four levels of temperature. A correlation of pH versus NaOH dosage was also developed using a combined log and polynomial correlation. The ammonia stripping temperature and pH were economically optimized by combining the ammonia stripping efficiency correlation with the pH correlation. After optimization, the cost of ammonia stripping was substantially lower than that estimated from other reports for the similar process. The optimized parameters can be used as a guideline for future application of this technology.

3. Two-step, three-phase chemical equilibrium model

The two-step, three-phase chemical equilibrium model developed in this study was suitable for the supernatant of the digested dairy manure because it can explain both the slow crystallizing precipitates formed in the digester with long hydraulic retention time (HRT) and other precipitates formed in the post AD treatment with short HRT. The first step of the model included the slow crystallizing HAP [hydroxyapatite, $Ca_5(PO_4)_3(OH)$] which was formed in the AD with long HRT. The second step of the model didn't include HAP because the short HRT of the post AD treatment doesn't favor HAP formation. The HAP formed in the AD which was calculated from the first step model was considered as inert in the second step model when no acid was added to dissolve the HAP. A new parameter, Δions, which accounts for the difference between the inert cations and anions was introduced to the model to reduce the measurements for the model input. The Δions can be obtained by either simulated KOH titration or the simulated HCl titration. The model validation proved that there was HAP formed slowly in the effluent from dairy AD with long HRT. Simulated NaOH titration fitted well with the measurements (R^2 of 0.95). The model was also applied to the unit processes of the integrated system with good fit. The results suggest that the two-step, three-phase chemical equilibrium model can be used to predict the unit performances of the combined system.

4. Future research recommendations

According to the result of this study, the following areas were recommended for future research:

1) Further H_2S removal with biogas/liquid ratio higher than 10 (v/v) needs to be investigated. CO_2 removal by other technology also needs to be investigated in order to produce higher value methane gas. In this study, the H_2S removal efficiency can reach 90% when the biogas/liquid ratio was 10 (v/v) and there was only little CO_2 was removed.

2) Ammonia stripping with different types of tower needs to be investigated. Pilot test of the combined nutrient recovery system needs to be conducted. This study only tested packing tower for the ammonia stripping.

3) Future research needs to investigate the highest nitrogen concentration and the pH of the fertilizer can be recovered. In addition, the application of the fertilizer also needs to be evaluated. The concentration of the recovered nitrogen fertilizer in the lab was low and also with a low $pH < 2.0$.