

11-20-2015

Ammonium Removal from High Strength Wastewater Using a Hybrid Ion Exchange Biological Process

Veronica Ester Aponte-Morales

University of South Florida, aponte.veronic@gmail.com

Follow this and additional works at: <http://scholarcommons.usf.edu/etd>

 Part of the [Environmental Engineering Commons](#)

Scholar Commons Citation

Aponte-Morales, Veronica Ester, "Ammonium Removal from High Strength Wastewater Using a Hybrid Ion Exchange Biological Process" (2015). *Graduate Theses and Dissertations*.
<http://scholarcommons.usf.edu/etd/5901>

This Dissertation is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.

Ammonium Removal from High Strength Wastewater Using a
Hybrid Ion Exchange Biological Process

by

Verónica E. Aponte-Morales

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Engineering Science
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Major Professor: Sarina J. Ergas, Ph.D.
Norma Alcantar, Ph.D.
Kamal Alsharif, Ph.D.
Treavor Boyer, Ph.D.
Jeffrey A. Cunningham, Ph.D.

Date of Approval:
November 17, 2015

Keywords: Anaerobically digested swine centrate, bioregeneration, nitrification inhibition,
simultaneous nitrification-denitrification, zeolite pretreatment

Copyright © 2015, Verónica E. Aponte-Morales

DEDICATION

I dedicate this dissertation to my family. Thanks for all the unconditional support throughout the pursuit of the doctoral degree. Who I am and what I have accomplished is an image of your love and caring. Also, to my extended family (Villalobos family, Issa, Delza, Ramón, Trina, Lucie, Idu, Mariam, Verónica, Cristian and William R.), who always energizes and keeps me positive. Finally, to Sergio, you gave me the strength to finish this goal.

ACKNOWLEDGEMENTS

I would like to thank the members of my dissertation committee for their consistent support, encouragement, constructive criticism during the course of this dissertation. Special thanks to my advisor Sarina Ergas, she was key in the development of this research, facilitated opportunities for my professional growth and help me become an assertive researcher. Also, to Bernard Batson who was responsible for my recruitment in USF and since we meet had help me keep focus and confident in accomplishing my degree. There are other people that contributed to the completion of this dissertation work that I am grateful for their assistance, these are: Shuan Tong (operation and data collection of chabazite-SBR), Karl Payne (mathematical model of bioregeneration studies), Adib Amini (SEM-EDX testing of zeolite), Merrill P. Dilbeck (operation of pilot AD), and Donald D. Dill (performed zeo-pack studies). Also, I am grateful for Dr. Ergas' research group that provided feedback, exchange ideas and help in the laboratory, in special the support of Laura Rodriguez, Meng Wang, Alex Lin (the original SMaRTIES) and Maureen Kinyua. Finally, this research was supported by Florida Education Fund – Mcknight Doctoral Fellowship (FEF-MDF), Alfred P. Sloan Foundation – Graduate Scholarship Program (SLOAN), the United States – Israel Binational Agricultural Research and Development Fund (BARD) grant No. IS-4360-10, and National Science Foundation – Partnerships for International Research and Education (NSF-PIRE) grant No. 1243510. Any opinions, findings, conclusions, or recommendations expressed in this study are those of the authors and do not necessarily reflect the views of FEF-MDF, SLOAN, BARD or NSF-PIRE.

TABLE OF CONTENTS

LIST OF TABLES.....	iii
LIST OF FIGURES.....	iv
ABSTRACT.....	vi
CHAPTER 1: INTRODUCTION.....	1
1.1. Background.....	1
1.2. Research Objectives.....	5
1.3. Research Impact.....	6
CHAPTER 2: LITERATURE REVIEW.....	7
2.1. Biological Nitrogen Removal.....	7
2.2. Anaerobically Digested Swine Waste Centrate Treatment.....	9
2.3. Innovative Nitrogen Removal Systems for High Ammonium Strength Wastewater.....	11
2.4. Ion Exchange for Nitrogen Removal.....	12
2.5. Zeolite in a Sequencing Batch Reactor (Zeo-SBR).....	14
CHAPTER 3: CHABAZITE PRETREATMENT.....	16
3.1. Introduction.....	16
3.2. Materials and Methods.....	19
3.2.1. Chabazite Pretreatment.....	19
3.2.2. Isotherm and Kinetics Studies.....	19
3.2.3. Chabazite Characterization.....	21
3.2.4. Analytical Methods.....	21
3.2.5. Statistical Analysis.....	22
3.3. Results and Discussion.....	22
3.3.1. Chabazite and Groundwater Characterization.....	22
3.3.2. Isotherm Studies.....	25
3.3.3. Ammonium Uptake by Chabazite.....	28
3.3.4. Kinetics Studies.....	30
3.4. Conclusions.....	31
CHAPTER 4: BIOREGENERATION OF CHABAZITE DURING NITRIFICATION OF ANAEROBICALLY DIGESTED CENTRATE.....	33
4.1. Introduction.....	33
4.2. Materials and Methods.....	36
4.2.1. Anaerobically Digested Swine Waste Centrate.....	36

4.2.2. Chabazite.....	37
4.2.3. Ion Exchange Studies.....	37
4.2.4. Nitrification Inhibition Studies.....	38
4.2.5. Chabazite Amended Nitrification Studies.....	40
4.2.6. Analytical Methods.....	41
4.2.7. Statistical Analysis.....	41
4.3. Results and Discussion.....	41
4.3.1. Ion Exchange Studies.....	41
4.3.2. Nitrification Inhibition Studies.....	43
4.3.3. Chabazite Amended Nitrification Studies.....	45
4.4. Conclusions.....	49
CHAPTER 5: CHABAZITE AMENDED SEQUENCING BATCH REACTOR FOR THE TREATMENT OF ANAEROBIC DIGESTION SIDESTREAMS.....	50
5.1. Introduction.....	50
5.2. Materials and Methods.....	53
5.2.1. Anaerobically Digested Swine Waste Centrate.....	53
5.2.2. Chabazite Preparation and Dose Calculation.....	54
5.2.3. Chabazite – SBR.....	55
5.2.4. External Electron Donor Dose Studies.....	56
5.2.5. Analytical Methods.....	56
5.3. Results and Discussion.....	57
5.3.1. Overall Reactor Performance.....	57
5.3.2. Fate of Nitrogen During a Typical Operating Cycle.....	61
5.3.3. External Electron Donor Dose Studies.....	64
5.3.4. Effectiveness of Ammonium Exchange.....	65
5.4. Conclusions.....	66
CHAPTER 6: CONCLUSIONS.....	68
REFERENCES.....	72
APPENDIX A: ZEOLITE SELECTION.....	79
APPENDIX B: PHOSPHATE REMOVAL BY CHABAZITE.....	84
APPENDIX C: BIOREGENERATION OF CHABAZITE INSIDE A MEMBRANE.....	86

LIST OF TABLES

Table 3-1:	Groundwater characterization of the Upper Floridan aquifer and solution chemistry after chabazite pretreatment (PT).....	23
Table 3-2:	Composition of natural and pretreated chabazite.....	24
Table 3-3:	Langmuir and Ion Exchange Isotherm coefficients for chabazite.....	26
Table 3-4:	Pseudo first order kinetic model and film diffusion coefficients.....	30
Table 4-1:	Characterization of anaerobically digested swine waste centrate.....	37
Table 4-2:	Nitrification rate for the treatment of synthetic and anaerobically digested swine wastewaters with and without addition of chabazite.....	47
Table 5-1:	Characteristics of ADSW centrate from the pilot-scale reactor.....	54
Table A-1:	Composition of zeolite.....	83

LIST OF FIGURES

Figure 1-1: Proposed treatment for swine manure that will result in the production of methane for energy and a clean effluent to replace potable water in irrigation systems.....	4
Figure 2-1: Bioregeneration mechanism for Z-NH ₄ ⁺	15
Figure 3-1: Cation concentrations at equilibrium during NH ₄ ⁺ uptake.....	26
Figure 3-2: Isotherm models for: (A) GW pretreatment, (B) Na ⁺ pretreatment and (C) DI pretreatment.....	27
Figure 3-3: Ammonium uptake by GW pretreated chabazite; comparison with (A) Na ⁺ and DI pretreatment; and (B) 10 and 30 mg L ⁻¹ HA pretreatment.....	29
Figure 4-1: Ion exchange equilibrium: (A) IX isotherm model for NH ₄ ⁺ uptake; (B) Effect of chabazite dose on the observed removal efficiency of NH ₄ ⁺	42
Figure 4-2: (A) Effect of contact time on NH ₄ ⁺ removal onto chabazite; (B) Liquid phase concentrations of cations (meq L ⁻¹) over time during the kinetic study.....	43
Figure 4-3: Nitrification inhibition: Effect of NH ₄ ⁺ -N concentration on the rate of (A) nitrification; and (B) nitrification.....	45
Figure 4-4: Ammonium, nitrite and nitrate concentration during nitrification of 1,000 mg NH ₄ ⁺ -N L ⁻¹ ; synthetic wastewater S-2 (A) no addition of chabazite, (B) with addition of 150 g L ⁻¹ of chabazite.....	46
Figure 4-5: Ammonium, nitrite and nitrate concentration during nitrification of 1,000 mg NH ₄ ⁺ -N L ⁻¹ with addition of 150 g L ⁻¹ of chabazite; (A) synthetic waste S-1, and (B) real ADSW centrate.....	47
Figure 4-6: Nitrification of 100 mg L ⁻¹ NH ₄ ⁺ -N; (A) no Na ⁺ and (B) with 2,000 mg L ⁻¹ Na ⁺	49
Figure 5-1: Schematic of chabazite-SBR operation showing stages over a 7-day cycle.....	53
Figure 5-2: Influent and effluent concentrations of (A) TN, (B) sCOD and (C) TP during chabazite-SBR operation.	58

Figure 5-3: Influent and effluent alkalinity concentrations during chabazite-SBR operation.....	59
Figure 5-4: Concentrations of Na^+ and K^+ before and after IX for cycles towards the (A) initial and (B) final phases of chabazite-SBR operation.....	60
Figure 5-5: Nitrogen profile during a cycle operation in the chabazite-SBR.....	62
Figure 5-6: Photograph of the chabazite-SBR during the aerobic stage showing zeolite material settling despite mixing.....	63
Figure 5-7: Concentrations of (A) NO_3^- and (B) NO_2^- after nitrification and denitrification during chabazite-SBR operation.....	65
Figure 5-8: Bioregeneration efficiency during 40 cycles of chabazite-SBR operation.....	66
Figure A-1: Effect of time in NH_4^+ uptake by zeolite in contact with a solution of NH_4^+ in deionized water and with competing cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}).....	81
Figure A-2: Effect of NH_4^+ uptake at varying dose of zeolites.....	82
Figure B-1: Chabazite in contact with a PO_4^- solution, with and without NH_4^+ exchange...	85
Figure C-1: Nitrogen concentrations during nitrification of Z- NH_4^+ (A) zeo-pack and (B) free floating zeolite.....	87

ABSTRACT

Anaerobic digestion (AD) has been shown to be an effective technique for energy recovery and stabilization of livestock wastes, municipal sludges and industrial wastewaters. However, further treatment is required to remove nitrogen from AD effluents to avoid detriments to surface and ground waters. The high free ammonia (FA) concentrations present in AD effluents can inhibit nitrification processes in conventional biological nitrogen removal (BNR) systems. The overall goal of this research was to develop a process for removal of nitrogen from AD swine waste (ADSW) effluent. The proposed solution was to incorporate particulate chabazite, which has a high cation exchange capacity, into a sequencing batch reactor (SBR) to adsorb ammonium and therefore ease nitrification inhibition. The process developed is called a chabazite-SBR. Three research questions were used to guide this research.

First question (Chapter 3): How does chabazite pretreatment with groundwater (GW) affect the kinetics and cation exchange capacity during ammonium (NH_4^+) uptake? Kinetics and isotherm batch tests were performed with GW pretreated chabazite. In addition, sodium chloride (NaCl), and deionized water (DI) pretreated chabazite was included for comparison because these are typically used pretreatment methods. The Ion Exchange (IX) isotherm model was used to calculate the cation exchange capacity and the pseudo-first and film diffusion kinetics models were applied to quantify the effect of the pretreatment on the reaction rate. Results showed that the exchange capacity was slightly higher for GW pretreated chabazite compared with the other common pretreatment strategies; however, the enhancement was not significantly different. The

kinetics of NH_4^+ uptake during the first four hours of contact was significantly improved by GW pretreatment when compared with other common pretreatment strategies. This was caused by an enhancement in film diffusion mechanisms. The findings of this first part of the research were important because it was shown that NaCl pretreatment is not needed to improve the kinetics and cation exchange capacity of chabazite.

Second question (Chapter 4): How does addition of chabazite to ADSW centrate affect nitrification rates? Nitrification batch test with varying NH_4^+ concentrations were performed to identify the inhibitory NH_4^+ concentration. Additional nitrification batch tests treating real and synthetic waste with initial NH_4^+ concentration of $1,000 \text{ mg-N L}^{-1}$ with added zeolite were performed. For the mixed liquor tested in this study, NH_4^+ concentrations must be maintained below 200 mg-N L^{-1} to relieve nitrification inhibition. Treatment of ADSW centrate requires a chabazite dose of 150 g L^{-1} to ease FA inhibition of nitrification. The rate of nitrification increased, by approximately a factor of 3, when chabazite was added to a batch reactor treating high NH_4^+ strength wastewater. However, Na^+ release from the chabazite also plays a role in nitrification inhibition. The findings of this part of the research showed the potential for using chabazite for overcoming FA inhibition of nitrification during treatment of high NH_4^+ strength wastewater.

Third question (Chapter 5): How effective is the chabazite-SBR in removing total nitrogen concentrations from ADSW centrate? A chabazite-SBR was operated for 40 weeks (cycles) to study the TN removal efficiency with varying carbon source. The efficiency of IX was also monitored over time. The chabazite-SBR process achieved stable TN removal from ADSW centrate during the 40 weeks of operation. Simultaneous nitrification-denitrification reduced chemical input requirements. Addition of an external organic carbon source at a rate of

3.2 g-COD g-N⁻¹ resulted in maximum TN removal. An overall TN removal efficiency of 84% was achieved, with specific nitrification and denitrification rates of 0.43 and 1.49 mg-N g-VSS⁻¹ hr⁻¹, respectively. The IX stage of the chabazite-SBR was able to reduce FA concentrations to below the inhibitory level for nitrification inhibition over 40 chabazite-SBR cycles with no loss in IX efficiency over time and no fresh zeolite added to the reactor.

CHAPTER 1

INTRODUCTION

1.1. Background

Livestock farming has been transformed from small family owned farms to larger scale industrial farms to adequately supply food to an increasing population. The number of large farms, also called confined animal feeding operations (CAFOs), in the U.S. increased from 3,600 up to 12,000 in a period of 20 years (GAO 2008). CAFOs have improved the efficiency of animal production; however, large amounts of manure are produced that must be treated and disposed. This waste contains high concentrations of organic matter, nutrients (such as nitrogen and phosphorus), pathogens, trace metals, pharmaceuticals and salts. Livestock production also results in emissions of particulate matter and gas phase pollutants, such as ammonia and methane, into the atmosphere. If manure is not managed properly, it becomes an environmental threat to both surface and groundwater systems. Among these threats, excess organic matter and nutrients in receiving waters can result in eutrophication, low levels of dissolved oxygen and stimulation of toxic algal blooms, which can be harmful to aquatic life (Bowman et al. 2000).

In the livestock industry, the largest transformation from small to large-scale industrial farming has been observed in swine farming, which represents 40% of the world's meat demand (Choi, 2007). The common practice at these facilities is to retain the waste in an anaerobic lagoon to stabilize the organic matter and nutrients before spreading it as a solid or liquid fertilizer on nearby cropland (USEPA 2000). This process is low in cost, but is limited by the

assimilative capacity of the soil and crops receiving the waste. If the land is overloaded with nutrients, they run off into surface waters or leach into groundwater. Another manure management strategy is to transport the manure to other sites or composting facilities that can handle the nutrient loads (Key et al. 2011).

CAFOs are regulated by the U.S. Environmental Protection Agency (USEPA) under the Clean Water Act (CWA). CAFOs that discharge manure effluent to a receiving water must obtain a National Pollutant Discharge Elimination System (NPDES) permit and must also provide a nutrient management plan (Federal Register 2008). To meet current regulatory limits, technologies that treat or recover nutrients to a higher degree than anaerobic lagoons are needed. To help farmers with the high cost of implementing new technologies, the U.S. Department of Agriculture (USDA) has provided financial assistance through the Environmental Quality Incentives Program (Key et al. 2011). In addition, because both energy and chemical fertilizer prices have increased, methods that help farmers to recover energy and nutrients from animal wastes are needed (USEPA 2000).

A technique that satisfies the requirement of capturing a portion of the energy present in swine manure is anaerobic digestion (AD); (Costa et al. 2007; Feng et al. 2008; Sakar et al. 2009; Massé et al. 2011). AD is a biological process that promotes manure decomposition in an oxygen-free environment. A major advantage of AD is the production of both a fuel gas (methane) and a stabilized residue that is rich in nutrients, and can be used as a soil amendment. The implementation of AD is increasing due to governmental endorsement and market incentives for green energy production (USEPA 2012). In adopting AD technology, farmers can offset their operational costs by using the produced biofuel to generate power for their facilities (Cantrell et al. 2008). Although the effluent from AD is rich in nutrients and can be used as a

fertilizer, available cropland near large CAFOs often cannot handle all of the nutrients and further treatment of the anaerobically digested swine waste (ADSW) effluent is needed to either remove nutrients (Massé et al. 2011) or recover them as an easy to transport salable fertilizer (Amini, 2014).

Biological nitrogen removal processes, such as nitrification and denitrification, have been successfully applied to treat ADSW centrate in some swine production CAFOs (Yang & Gan 1998; Vanotti et al. 2007; Kunz et al. 2009). However, these operations have a number of challenges including:

- The need to reduce operational costs by reducing the addition of chemicals that provide needed alkalinity and organic carbon (Deng et al. 2008; Onnis-Hayden & Gu 2008).
- Inhibition of nitrification due to high concentrations of free ammonia (FA, NH_3 ; Anthonisen et al. 1976).
- High organic carbon concentrations, since nitrification activity is decreased due to competition by heterotrophic bacterial growth (Ling & Chen 2005).

The proposed treatment train for swine manure in this research is shown in Figure 1-1. This includes AD to produce methane for energy, follow by a hybrid ion exchange (IX) biological treatment process. In a real system at the farm, a slotted floor allows collection of the manure and urine. The waste can be fed to the AD by gravity or pump. During AD organic material is broken down, releasing nutrients and producing methane gas. The methane is collected to be used as an energy source; for example the farm can use it to provide heating to the AD reactor or the barns or to generate electricity. The digested effluent later goes to the hybrid treatment system for nutrient removal. The final treated effluent could replace potable

water use for irrigation systems in a farm. The results on the AD operation can be found in Kinyua (2014).

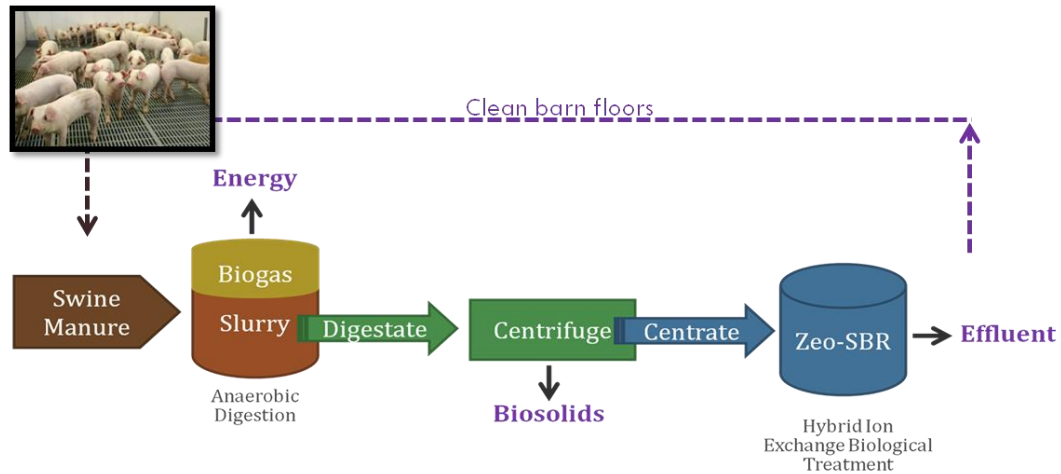


Figure 1-1. Proposed treatment for swine manure that will result in the production of methane for energy and a clean effluent to replace potable water in irrigation systems.

The overall goal of this research was to develop a novel process for removal of nitrogen from ADSW effluent. This was accomplished by using chabazite (a type of zeolite) to ease nitrification inhibition by FA in a sequencing batch reactor (chabazite-SBR). Chabazite is added to the reactor at startup. Chabazite adsorbs ammonium (NH_4^+) temporarily to reduce its concentration in the liquid phase. During nitrification the chabazite is bioregenerated by nitrifying bacteria, allowing its reuse in subsequent cycles. During bioregeneration, microbes convert the adsorbed NH_4^+ to nitrate (NO_3^-), which is subsequently removed via denitrification. Chabazite addition also brings another challenge, the possibility of sodium (Na^+) inhibition (Sanchez et al. 2004). Chabazite is loaded naturally with a variety of cations, mainly sodium

(Na⁺). During NH₄⁺ exchange, Na⁺ is released into the solution. In an attempt to reduce Na⁺ loaded into the zeolite, pretreatment with groundwater (GW) was performed.

1.2. Research Objectives

To accomplish this goal, the following research questions and specific objectives were used to guide this research:

1. *How does chabazite pretreatment with groundwater affect the kinetics and cation exchange capacity during NH₄⁺ uptake?* (Chapter 3)

- Specific Objectives:

- Investigate changes in the zeolite composition after GW pretreatment.
- Determine if there is an enhancement in the kinetics and exchange capacity with GW pretreatment when compared with other common pretreatment practices.

2. *How does chabazite addition to ADSW centrate affect nitrification rates?* (Chapter 4)

- Specific Objectives:

- Determine the chabazite dose and contact time needed to ease FA inhibition.
- Determine the effectiveness of chabazite addition in reducing nitrification inhibition during treatment of ADSW centrate.

3. *How effective is the chabazite-SBR in removing total nitrogen concentrations from ADSW centrate?* (Chapter 5)

- Specific Objectives:

- Investigate the fate of nitrogen compounds in a chabazite-SBR during treatment of ADSW centrate.
- Investigate the effect of varying external electron donor dose on reactor performance.

- Investigate IX efficiency of the zeolite material in the chabazite-SBR.

1.3. Research Impact

This research envisions that implementing the chabazite-SBR in a CAFO will reduce the footprint of the nitrification/denitrification process; since only a single tank will be needed to carry out the process and the nitrification rate will be increased. Also, the cost and energy requirements are reduced due to reduced chemicals needed in the system. For example, the need to add chemicals to regenerate the zeolite is not required, since nitrifying bacteria oxidize the bioavailable NH_4^+ , breaking the equilibrium between the solid and liquid phase allowing desorption of NH_4^+ . Another benefit is that clean effluent is produced that can be discharged into surface waters without a negative ecological impact. Further cost reduction can be achieved if potable water is substituted with the effluent for irrigation of crops or grazing land, or to clean barn floors. A further contribution is the possibility of implementing this technology for treatment of other waste streams with high concentrations of NH_4^+ , such as industrial wastewaters, municipal AD centrate, landfill leachate, or source separated urine.

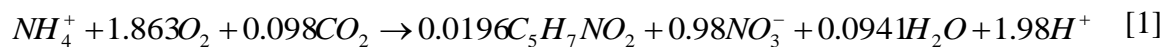
CHAPTER 2

LITERATURE REVIEW

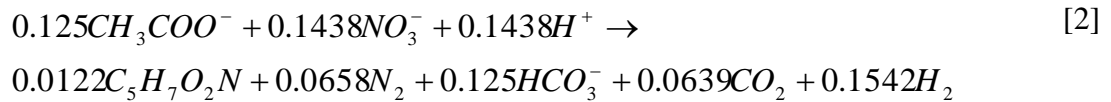
The aim of this literature review is to provide a summary of the common practices for nitrogen (N) removal of high strength wastewater and the challenges encountered during treatment. The works discussed in this review provide a platform for the research presented in this dissertation.

2.1. Biological Nitrogen Removal

The key processes for biological nitrogen removal (BNR) in wastewater treatment are nitrification and denitrification. Nitrification is the microbiological oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) by autotrophic bacteria. The process takes place in two steps. In the first step (nitritation) ammonia oxidizing bacteria (AOB), such as *Nitrosomonas*, convert NH_4^+ to nitrite (NO_2^-). In the second step (nitratation) nitrite oxidizing bacteria (NOB), such as *Nitrobacter*, convert the NO_2^- to NO_3^- . Equation 1 shows the overall reaction of NH_4^+ oxidation; for each gram of NH_4^+ -N converted to NO_3^- -N, 4.25 g of oxygen (O_2), 7.07 g of alkalinity (as CaCO_3), and 0.08 g of inorganic carbon are utilized. Additionally, a small amount of biomass, 0.16 g-VSS, is produced (Metcalf and Eddy 2003).



Denitrification is the microbiological reduction of NO_3^- to nitrogen gas (N_2) in a multi-step process. This process is usually accomplished by facultative heterotrophic bacteria, which have the ability to use O_2 , NO_2^- , or NO_3^- as terminal electron acceptors for the oxidation of organic matter. Because facultative denitrifying bacteria prefer O_2 instead of NO_3^- as an electron acceptor, it is critical to carry out denitrification in an anoxic environment (below $0.50 \text{ mg O}_2 \text{ L}^{-1}$). A readily bioavailable carbon source, such as acetate, glucose, molasses, methanol, acetic acid, or organic substrates in wastewater, is needed. Equation 2 shows the overall reaction of NO_3^- reduction using acetate as a carbon source; for each gram of NO_3^- converted to N_2 , 3.57 g-CaCO_3 of alkalinity and 0.69 g-VSS biomass are produced. The required carbon source is 3.97 g-COD for each g of NO_3^- (Rittmann and McCarty 2001).



Both nitrification and denitrification reactions are influenced by temperature, pH and dissolved oxygen (DO). However, nitrification is the limiting step in the BNR process because nitrifying bacteria have a lower growth rates compared with heterotrophic bacteria. Thus, high solids retention times (SRT) are required for an efficient nitrification process (Li & Wu, 2014). Longer SRTs require reactors with a larger volume, which can be translated into more space utilization for wastewater treatment. The immobilization of nitrifying bacteria on an appropriate carrier has been shown to be effective in wastewater treatment plants to increase removal rates and lower SRT (Strotmann and Windecker 1997).

An additional factor that affects nitrification is high concentrations of NH_4^+ , which increases the concentration of free ammonia (FA; NH_3) in solution. Anthonisen et al. (1976)

showed that FA concentrations in the range of 10-150 mg L⁻¹ cause nitrification inhibition, affecting mainly the NOBs. Ions, such as NH₄⁺, are transported by a specific carrier in the bacterial cell membrane, while uncharged compounds, such as FA, don't require a specific carrier and rapidly diffuse through the membrane (Kleiner, 1985). The increase in FA concentration promotes an imbalance in the intracellular and extracellular pH, affecting the proton motive force (Jin et al., 2012; Martinelle et al., 1996; Sharma & Ahlert, 1977). As a consequence, many energy-requiring functions of the cell are inhibited.

Another factor affecting nitrification is high concentrations of carbonaceous oxygen demand (COD) because it promotes competition between the autotrophic and heterotrophic microorganism population. Carrera et al. (2004) investigated the effect of COD/N ratio on an immobilized biomass system treating high strength NH₄⁺ wastewater, showing that an increase of COD/N ratio negatively affected the nitrification rate. However, if controlled DO is provided, high COD/N ratio can be a benefit to overall BNR processes because simultaneous nitrification-denitrification (SND) can take place (Sun et al., 2010). An advantage of SND is that the alkalinity produced through denitrification offsets alkalinity consumption by nitrification. This results in reduced chemical addition, hence a decrease in operational cost. Also SND eliminates the need for two separate tanks, reducing the system footprint.

2.2. Anaerobically Digested Swine Waste Centrate Treatment

Anaerobic digestion (AD) of swine waste has been shown to be effective at stabilizing the waste and producing biogas, a mixture of methane and carbon dioxide (Costa et al. 2007; Feng et al. 2008). However, effluents from AD contain high concentrations of COD, total nitrogen (TN), and phosphorus (Deng et al. 2006). The typical range of NH₄⁺ concentrations in

centrate from anaerobically digested swine waste (ADSW) is 800 mg L^{-1} to more than $4,000 \text{ mg L}^{-1}$, depending on the kind of farm management, system used, dilution of the waste, and evolution of NH_4^+ during storage (Boiran et al. 1996; Deng et al. 2008). Land application is the most common and economical way of disposing of the AD effluent because crops can benefit from this organic fertilizer. AD effluent N is mainly in the NH_4^+ form, which results in a slower runoff because soil is negatively charged, allowing plants to uptake the nutrient. However, soil has a limited adsorption capacity and in most cases CAFOs do not have nearby land available, requiring transport of the effluent to another site (Hatfield et al., 1998).

Direct treatment of ADSW centrate via nitrification-denitrification is a challenge, since this type of wastewater with high NH_4^+ concentrations will inhibit nitrifying bacteria. To overcome this problem, bacteria can be acclimated to high NH_4^+ concentrations in a step-wise manner. This approach promotes the adaptation and selection of bacteria tolerant to high NH_4^+ concentrations, but requires a long acclimation period (Antileo et al. 2002). Vanotti et al. (2007) operated a full-scale BNR process for the treatment of ADSW centrate, after an acclimation period the system was successful in removing pollutants (removal efficiency of 98.7% TN, 95.0% TP, and 87.4% COD). The bioreactor configuration used by Vanotti et al. (2007) and Kunz et al. (2009) consisted of a solid/liquid separation unit, anoxic treatment unit (denitrification), aerobic unit (nitrification) and settling unit. Having this type of system on a farm occupies a large space that could be use for cropland. In addition, it has been shown that these types of systems are not economically sustainable (Kunz et al. 2009).

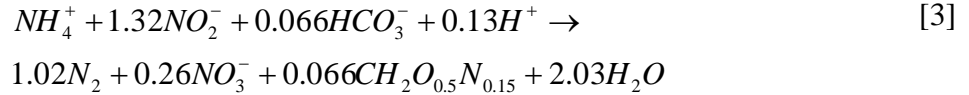
Currently BNR practice is shifting towards the use of sequencing batch reactors (SBR) because they are less complex, more cost-effective and highly efficient (Oleszkiewicz & Barnard, 2006). SBRs are activated sludge systems, in which the biological reactions and solid-

liquid separation takes place in one reactor in a defined and repeated time sequence (Irvine & Busch, 1979; Singh & Srivastava, 2011). There is a growing interest in the utilization of SBRs for nitrification and denitrification of ADSW centrate, which have demonstrated high removal efficiency (Deng et al., 2006; Dosta et al., 2008; Obaja et al., 2003). Advantages of SBRs are their small land requirements and that they can be easily adapted for continuous variations in pollutant concentrations (Mace and Mata-Alvarez 2002).

2.3. Innovative Nitrogen Removal System for High Ammonium Strength Wastewater

Since the late 1990s, novel BNR processes have been developed where NH_4^+ is transformed to N_2 with reduced oxygen and organic substrate requirements (Sun et al., 2010). One of these processes is SHARON (Single reactor for High activity Ammonia Removal Over Nitrite) where NH_4^+ oxidation is stopped at the nitrification step, and then denitrification takes place to reduce NO_2^- to N_2 . Conditions that favor AOB over NOB are: high temperatures (30-40°C), low DO concentrations and low SRT (Hellings et al. 1998). In addition, when treating high NH_4^+ strength wastewater there is an increase in FA concentrations causing greater inhibition of NOB than AOB providing an additional control to prevent NO_2^- oxidation.

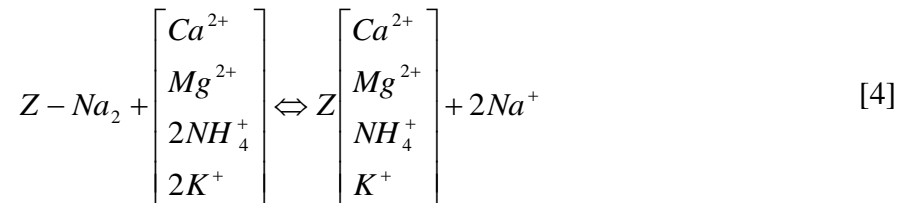
Another innovative BNR method is ANAMMOX (ANAerobic AMMonium OXidation) where anammox bacteria (AnAOB) convert NH_4^+ to N_2 under anoxic conditions with NO_2^- as the electron acceptor. This process is considered cost effective since it eliminates the need for external organic carbon addition and reduces oxygen requirements by 50% (Fux et al. 2002). Equation 3 shows the ANAMMOX overall reaction, for complete NH_4^+ oxidation $\text{NO}_2^-/\text{NH}_4^+$ ratio should be 1.3. To accomplish NH_4^+ removal, partial nitrification is performed first to oxidize 60% of NH_4^+ to NO_2^- , followed by ANAMMOX.



These two pathways are advantageous because of the decreased operational costs compared to conventional BNR. However, they require very strict control of operating parameters such as pH, DO and SRT (Sun et al., 2010). The use of real-time control methods to regulate DO and pH in the reactor is critical for successful treatment (Peng & Zhu 2006).

2.4. Ion Exchange for Nitrogen Removal

Ion exchange (IX) is a reversible chemical process, as shown in Equation 4 an ion of a given species from solution is exchanged with a similar ionic species that is attached to an immobile-insoluble solid particle (Hedström 2001). In wastewater treatment, IX is considered to be a simple and effective technique for the removal of inorganic ions, such as NH_4^+ (Wang and Peng 2010). The most commonly used material for cation exchange in wastewater treatment is natural zeolite. Natural zeolite is a hydrated aluminosilicate mineral, with a porous structure, high adsorption capacity and high affinity for NH_4^+ (Langwaldt 2008). There are more than 50 different species of zeolite, but clinoptilolite is the most abundant and most commonly used (Virta 2012). However, when compared with chabazite, it has a lower adsorption capacity (Wang and Peng 2010; Langwaldt 2008).



IX treatment is usually performed in columns operated in two modes, NH_4^+ uptake and regeneration (desorption of NH_4^+). A common practice is to perform pretreatment of zeolite with

a sodium (Na^+) solution (e.g. NaOH or NaCl) to enhance the kinetics and cation exchange capacity, which are key parameters in the design (Alshameri et al., 2014; Lin et al., 2013). Cyrus and Reddy (2011) treated ADSW centrate using a bench-scale column (volume of 245 mL) packed with 100 g of zeolite operated in adsorption and desorption mode. At a continuous flow rate of 1 mL min^{-1} , breakthrough capacity was achieved at 180 hours of operation. The use of an acid or salt solution for regeneration of the NH_4^+ saturated zeolite (Z-NH_4^+) is a common practice; however, it generates a brine with high strength NH_4^+ concentrations that requires further treatment (Hedstrom, 2001). An alternative is to perform BNR treatment using halophilic bacteria; however, after removing N, the brine effluent still presents a disposal problem (Long & Wang, 2006).

Instead of regenerating Z-NH_4^+ for reuse, a feasible alternative is to utilize Z-NH_4^+ as a N fertilizer or soil amendment (Cyrus & Reddy, 2011). This practice of nutrient recovery by utilization of zeolite is increasing and is particularly beneficial for ADSW centrate because of the presence of other cations (Mg^{2+} , Ca^{2+} , and K^+) in this wastewater (Huang et al., 2014; Lin et al., 2014). ADSW centrate has high concentrations of magnesium (Mg^{2+}) and with the right pH it can be precipitated with NH_4^+ and phosphate (PO_4^{3-}) to form struvite crystals ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$); (Lin, 2012). Despite high Mg^{2+} concentrations in ADSW, this is not higher than PO_4^{3-} and limits the precipitation (recovery). To enhance struvite precipitation, zeolite pretreated with MgCl has been used; as NH_4^+ is uptaken Mg^{2+} is desorbed avoiding limitations of the precipitation (Huang et al., 2014). This alternative of nutrient recovery is feasible if there is a market for this N rich fertilizer.

2.5. Zeolite in a Sequencing Batch Reactor (Zeo-SBR)

Hybrid systems in which cation exchange and biological process are combined for the treatment of wastewater have been used to enhance methanogenesis and nitrification rates by reducing NH_4^+ concentrations that cause inhibition of biological processes (Jung et al., 2004; Milan et al., 2003). He et al. (2007) treated municipal wastewater with TN concentration of 54 mg-N L^{-1} by BNR using a SBR amended with zeolite (Zeo-SBR). Compared with a control SBR (without zeolite), the Zeo-SBR increased the nitrification rate by a factor of 2. Also, zeolite addition has been shown to alleviate the effect of shock loads in the system (He et al., 2007; Park et al., 2002). Clinoptilolite as a powder (particle size of < 0.25 mm) was the zeolite added to the SBR in this study; no other zeolite (e.g. chabazite) has been tested. The zeolite acts as an IX medium and biofilm carrier. The formation of bio-flocculated zeolite has been observed in the system, resulting in an enhancement of retention of biomass (Park et al., 2002). The effect of biofilm formation in zeolite was studied in batch tests by Lahav and Green (2000); they observed that biofilm on the zeolite particles decreased IX kinetics. Also, that the adsorption capacity of the zeolite was not lost, but that a longer time was needed to reach full capacity. However, in continuous operation of bioreactor studies it was shown that biofilm formation on zeolite did not limit the IX efficiency or bioregeneration (Jung et al., 1999). Other works attributed the enhanced efficiency of TN removal to the biofilm, since there are anoxic zones within the zeolite flocs that provided the conditions for SND (He et al., 2007).

Regeneration of zeolite within the Zeo-SBR took place without the need of chemical addition. This process is called bioregeneration, because microorganisms utilized the ion adsorbed in the zeolite as their substrate (Semmens et al., 1977). This is beneficial since reuse of the material is possible. Figure 2-1 provides a schematic of the bioregeneration mechanism.

After IX, the NH_4^+ in solution is oxidized by nitrifying bacteria, this breaks the existing equilibrium between the solid/liquid phases, promoting NH_4^+ desorption. In addition, the cations present in the wastewater and chemicals added to supplement alkalinity losses during nitrification contribute to NH_4^+ desorption. Desorption continues until the NH_4^+ concentration in the solution decreases to negligible values. Although, zeolite is regenerated, this material is not completely reused in the Zeo-SBR. During wasting of biomass to control the SRT, a fraction of zeolite is lost. To compensate, a dose of zeolite is added after the feeding stage in every cycle (He et al., 2007; Jung et al., 2004; Jung et al., 1999; Wei et al., 2011). This practice results in additional operational costs for Zeo-SBR systems. A Zeo-SBR operated without constant dosing of zeolite had not been previously studied. In addition, studies using Zeo-SBR are limited to the treatment of municipal or synthetic wastewater (Jung et al., 1999; Park et al., 2002; Wei et al., 2011). Treatment with real wastewater, such as ADSW centrate, had not been performed.

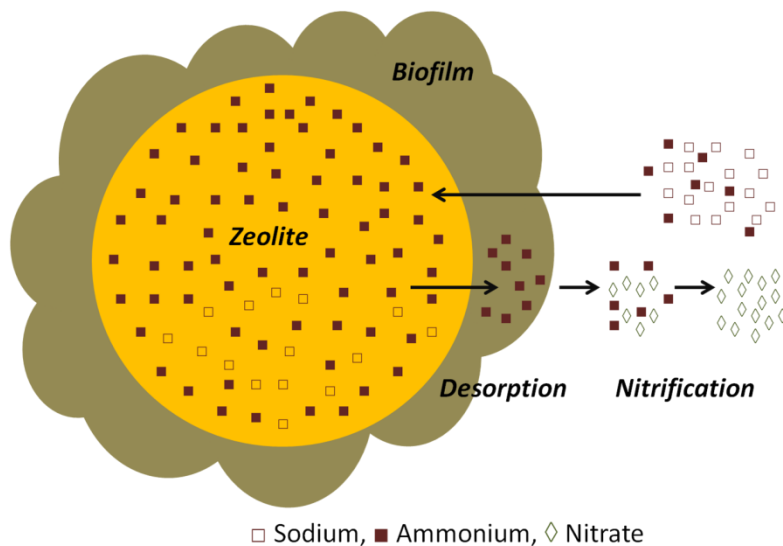


Figure 2-1. Bioregeneration mechanism for Z- NH_4^+ .

CHAPTER 3

CHABAZITE PRETREATMENT

3.1. Introduction

Natural zeolites are used in a broad range of environmental applications, including as a soil amendment for water and nutrient retention, removal and storage of radionuclides from nuclear wastes, removal and recovery of heavy metal cations from industrial wastewaters, water softening, and ammonium (NH_4^+) removal and recovery from wastewaters of various origins (Colella, 1999). Zeolites are aluminosilicate minerals with a tetrahedral ring framework and extraframework cations that exhibit both molecular-sieve and cation exchange properties. More than 50 different species of natural zeolites have been identified (Andronikashvili, 1992). Chabazite, clinoptilolite, erionite, modernite and phillipsite are the most predominant zeolites species in the United States (US). There are seven deposits of zeolites in the US, five are of clinoptilolite (Virta 2012); resulting in clinoptilolite being the least expensive and most studied and used natural zeolite. However, the cation exchange capacity for chabazite is much higher than that of clinoptilolite (Karmen et al., 2013), making it a preferred alternative in systems where the zeolite material is regenerated and reused for multiple cycles (Lahav & Green, 2000; Lahav et al., 2013).

Numerous studies have investigated NH_4^+ removal and recovery from wastewaters using clinoptilolite due to its high affinity for this cation (Hedström & Amofah, 2008; Huang et al., 2014; Jorgensen & Weatherley, 2003; Lin et al., 2014). Two parameters considered in the design

of an ion exchange (IX) treatment system are the kinetics and exchange capacity. These are needed to determine the dose and contact time required for treatment and to size the reactors. Usually clinoptilolite is pretreated (modified) to enhance and optimize these parameters. Three frequent practices for pretreatment that are used individually or in combination, are: (1) wash with deionized water; (2) soak in a solution containing salts, acid or base; or (3) heating (Alshameri et al., 2014; Jha & Hayashi, 2009; Liang & Ni, 2009; Rožić et al., 2005).

The practice of rinsing zeolite with deionized water removes surface dust that remains after the grinding process, resulting in an enhancement in kinetics (Inglezakis et al., 1999). Soaking the zeolite in an aqueous solution containing salts, acids or bases under specific conditions, such as solution volume, temperature, mixing, contact time, is also a common practice. The use of either acids or bases (e.g. HCl or NaOH) has been shown to remove impurities, such as quartz, thereby increasing the purity of the zeolite (Jha & Hayashi, 2009; Rožić et al., 2005). When pretreatment was carried out using an acid solution, dealumination of clinoptilolite took place, resulting in an amorphous material, hence reducing NH_4^+ adsorption (Rožić et al., 2005). The use of NaCl and NaOH pretreatment resulted in a homoionic form of Na^+ -clinoptilolite, which enhanced the kinetics and cation exchange capacity (Alshameri et al., 2014; Lin et al., 2013). Sodium (Na^+) is a cation that can be easily removed (exchanged) compared with other cations. Heating the zeolite to 150 °C was shown to remove water molecules and organics, causing an increase in pore volume and diameter. However, it did not provide a significant improvement in NH_4^+ removal. Significant increases in removal of NH_4^+ were observed when zeolite previously treated with NaCl was heated to 400 °C (Liang & Ni, 2009).

Compared with clinoptilolite, there is a lack of information on the effect of pretreatment on NH_4^+ exchange using chabazite. Leyva-Ramos et al. (2010) is the only prior study that investigated whether pretreatment processes performed on clinoptilolite are also effective on chabazite. Chabazite pretreatment consisted of a combination of rinsing with deionized water, heating at 110 °C and soaking in a 2 M NaCl solution for 7 days. Results showed that the exchange capacity and kinetics were enhanced by the pretreatment when compared with non-pretreated chabazite (Leyva-Ramos et al., 2010).

An application of zeolite that is gaining popularity consists of a hybrid process in which IX and biological processes are combined for the treatment of high NH_4^+ strength wastewater (Jung et al., 2004; Milan et al., 2003). High concentrations of free ammonia (FA) cause inhibition of anaerobic digestion and nitrification processes (Carrera et al., 2004; Yenigün & Demirel, 2013). FA concentration is a function of total ammonia concentration in solution, pH and temperature (Anthonisen et al., 1976). The addition of the natural zeolite to the bioreactor is used to overcome FA inhibition by reducing the NH_4^+ concentration in the solution (Montalvo et al., 2012). However, during NH_4^+ exchange, other cations are released to the solution, such as Na^+ , which can also be inhibitory to microorganisms (Sanchez et al., 2004). Milan et al. 2003 used zeolite pretreated with nickel (Ni^{2+}), cobalt (Co^{2+}) and magnesium (Mg^{2+}) to reduce the FA concentration in an anaerobic digester. Ni^{2+} , Co^{2+} and Mg^{2+} were selected for pretreatment because methanogens utilize these micronutrients for their growth. The rate of methane production was enhanced by the addition of all pretreated zeolites, with Mg^{2+} pretreated zeolite resulting in the best performance.

In a prior study in our laboratory chabazite was pretreated with local groundwater (GW) from the upper Floridian aquifer to reduce Na^+ release during biological nitrification studies

(Aponte-Morales et al. 2014). It was observed that NH_4^+ removal efficiency increased during the first five hours of contact time compared with Na^+ pretreated chabazite in these preliminary experiments. GW pretreatment of zeolite materials has not been previously described in the literature. Therefore, the goal of this research was to compare GW pretreatment of chabazite with other common pretreatment practices in terms of NH_4^+ exchange capacity and kinetics.

3.2. Materials and Methods

3.2.1. Chabazite Pretreatment

Chabazite (ZS500H) was obtained from the St. Cloud Zeolite company (Winston, New Mexico) and was sieved to obtain a particle size between 1 and 2 mm. Chabazite was washed with deionized water to remove residual powder and dried at 100 °C for 24 hr (DI pretreatment). The dried chabazite (30 g) was placed in 250 mL Erlenmeyer flasks and immersed for 3 hr in 200 mL of: (1) local GW (University of South Florida Botanical Garden; GW pretreatment), (2) 3% NaCl (Na^+ pretreatment), or (3) 10 and 30 mg L⁻¹ of humic acid (HA pretreatment) on a shaker table at 200 rpm. The solution was decanted and the chabazite was rinsed with deionized water and dried at 100°C for 24 hr. Given that Na^+ pretreatment is a common practice, it was included in this research for comparison purposes. Also, HA pretreatment was included for comparison because prior studies have shown that the presence of HA improved NH_4^+ exchange (Moussavi et al., 2011).

3.2.2. Isotherm and Kinetic Studies

Batch cation exchange capacity (CEC) experiments were carried out by placing varying masses of chabazite (0, 2.5, 0.5, 1.25, 3.75, 5, 7, and 10 g) in contact with a fixed volume (200 mL) of NH_4^+ solution (1,000 mg-N L⁻¹, pH = 7.5) in 250 mL Erlenmeyer flasks. The flasks were

covered with parafilm and maintained at 22°C for 48 hr on a shaker table at 170 rpm. Water quality analysis was performed at the beginning and end of the experiments, as described below (section 3.2.4). Data were evaluated by linear analysis using Langmuir (Eq. 1) and IX (Eq. 2) isotherm models (Alberti et al., 2012):

$$q_e = \frac{q_{\max} K_L C_{NH_4^+}}{1 + K_L C_{NH_4^+}} \quad [1]$$

$$q_e = \frac{q_{\max} K_{IX} C_{NH_4^+}}{C_{Na^+} + K_{IX} C_{NH_4^+}} \quad [2]$$

where q_e is the amount of NH_4^+ adsorbed per unit mass of chabazite ($\text{meq-N g-chabazite}^{-1}$); $C_{NH_4^+}$ is the equilibrium concentration of NH_4^+ (meq-N L^{-1}); C_{Na^+} is the equilibrium concentration of Na^+ (meq L^{-1}); q_{\max} is the maximum adsorption capacity constant ($\text{meq-N g-chabazite}^{-1}$); K_L is a constant related to the affinity of the binding site and energy of adsorption (L meq-N^{-1}); and K_{IX} is a constant related to affinity for the exchanger.

Ion exchange kinetics were determined under the same experimental conditions as the CEC studies; however, samples were collected over 24 hours using a set chabazite mass of 30 g. Water quality analysis was performed on the samples as described below (section 3.2.4). Data were evaluated using an empirical pseudo first order kinetic model (Eq. 3) and film diffusion coefficient (Eq. 4) (Alberti et al., 2012):

$$q_t = q_e \times (1 - e^{-k_1 t}) \quad [3]$$

$$D_f = \frac{k_1 C_s r_o \delta}{C_l} \quad [4]$$

where q_t is the amount of NH_4^+ adsorbed at time t ($\text{mg-N g-chabazite}^{-1}$); k_1 the pseudo first order rate constant (hr^{-1}), and t the contact time (hours); r_0 is the radius of the chabazite particles ($5.00\text{E-}04$ m); D_f is the diffusion coefficient in the solution phase ($\text{m}^2 \text{hr}^{-1}$); δ is the thickness of film around the zeolite particle (10^{-5} m for poorly stirred solution; (Lin et al., 2013; Moussavi et al., 2011)); C_l and C_s are NH_4^+ equilibrium concentrations at the liquid and solid phases, respectively (mg-N L^{-1}) and are determined experimentally. The q_e and k_1 parameters were determined by non-linear analysis of the pseudo first order kinetic model. The k_1 values were used to determine D_f coefficient.

3.2.3. Chabazite Characterization

Scanning Electron Microscopy Energy Dispersive with X-Ray Spectroscopy (SEM-EDX) was used to determine the elemental composition of the chabazite using a Hitachi S800 instrument (Naka, Japan) for SEM and EDAX Phoenix Pro (Mahwah, NJ) for EDX. Chabazite pretreated with DI, GW, Na^+ , and HA were analyzed and means reported to reflect five replicates. SEM-EDX analysis was done at the Nanotechnology Research and Education Center (NREC) at the University of South Florida (USF).

3.2.4. Analytical Methods

Concentrations of sulfate (SO_4^{2-}), ammonium (NH_4^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) were measured using a Metrohm 881 Compact IC Pro (Herisau, Switzerland) ion chromatograph (IC Application No. C-115 and No. S-236). Standard Methods (APHA et al. 2012) were followed to measure: pH (4500-H); total iron (Fe^{Total}) and ferrous iron (Fe^{2+}) by the 1-10 phenanthroline method (3500-Fe B); Ferric iron (Fe^{3+}) was

determined by subtraction of Fe^{2+} from Fe^{Total} ; and manganese (Mn^{2+}) by the persulfate method (3500-Mn B). The humic acid (HA) concentration was determined by UV spectrophotometry at 254 nm (Rodrigues et al., 2009).

3.2.5. Statistical Analysis

Student's t-tests or one way ANOVA test were used to determine whether two sets of data were significantly different from each other. The test was performed at a confidence level of 95%, rejecting the hypothesis with P-value < 0.05 . All experiments were performed in duplicate. All values in tables and figures are presented as means.

3.3. Results and Discussion

3.3.1. Chabazite and Groundwater Characterization

Chabazite was pretreated with groundwater from the Upper Floridian aquifer obtained from a well at the University of South Florida (USF) Botanical Gardens. The chemical composition of the groundwater used in this study is shown in Table 3-1; which also includes groundwater chemistry data from other studies (Sacks and Tihans 2000; Katz et al. 2007) to include information on water quality parameters not measured in this study. The main cation present was calcium (Ca^{2+}) and the main anion was bicarbonate (HCO_3^-). Groundwater chemistry will depend on the mineral composition of the aquifer material and soil. USF is located in the Hillsborough watershed system in which the lithology mainly consists of limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Sacks and Tihans 2000, Katz et al. 2007). Cation concentrations were measured in the solution after chabazite GW pretreatment (Table 3-1). All cation concentrations increased except for iron (Fe^{2+} and Fe^{3+}). The concentration of Na^+

increased from 25 to 1,500 mg L⁻¹, indicating that GW pretreatment decreased its content in the chabazite. This is expected to decrease microbial inhibition, as discussed previously.

Table 3-1. Groundwater characterization of the Upper Floridan aquifer and solution chemistry after chabazite pretreatment (PT).

Ion - Chemical Formula (mg L ⁻¹)		GW-FL ^{*1}	GW-FL ^{*2}	GW-USF	After PT
Sodium	Na ⁺	5.75 ± 0.96	11.06 ± 0.49	25 ± 0.10	1,500 ± 80.32
Potassium	K ⁺	0.68 ± 0.46	1.08 ± 0.07	1.0 ± 0.03	4.0 ± 0.14
Calcium	Ca ²⁺	65.75 ± 39	105.22 ± 4.83	230 ± 0.60	345 ± 14.31
Magnesium	Mg ²⁺	1.83 ± 0.42	9.57 ± 1.14	7.0 ± 0.09	38 ± 3.38
Manganese (II)	Mn ²⁺	-	-	0.05 ± 0.01	0.20 ± 0.07
Iron (Total)	Fe	0.99 ± 0.66	-	-	-
Iron (II)	Fe ²⁺	-	-	0.50 ± 0.02	0.18 ± 0.04
Iron (III)	Fe ³⁺	-	-	0.30 ± 0.01	0.22 ± 0.03
Bicarbonate	HCO ₃ ⁻	195 ± 114.62	185 ± 9.11	-	-
Carbonate	CO ₃ ²⁻	0.23 ± 0.05	72.36 ± 23.93		
Chloride	Cl ⁻	9.25 ± 2.75	23.12 ± 3.20		
Fluoride	F ⁻	0.15 ± 0.06	0.30 ± 0.00	-	-
Sulfate	SO ₄ ²⁻	7.00 ± 5.48	-		
Humic acid		-	-	14 ± 1.40	0 ± 0.00

*1 Sacks and Tihans 2000

*2 Katz et al. 2007

The apparent reduction in the Na⁺ content in the chabazite was confirmed by comparison of the composition of natural and GW pretreated chabazite from the SEM-EDX analysis. As shown in Table 3-2, Na⁺ was reduced by half; Ca²⁺ increased by 5 times its initial content; Fe

decreased by a factor of 1.5; K^+ and Mg^{2+} content did not change; and F initially was not present but was part of the composition after pretreatment. Even though F was not measured in the groundwater in this study, other studies have shown that it is present in FL GW (Table 3-1). The appearance F as part of the zeolite composition after GW pretreatment can be attributed to adsorption of the cation from the groundwater. Water chemistry and SEM-EDX data for Ca^{2+} are conflicting, with water chemistry data showing that Ca^{2+} is released (Table 3-1) and SEM-EDX data indicating Ca^{2+} adsorption after GW pretreatment. The reasons for this discrepancy are unknown but may be related to impurities in the zeolite minerals. In addition to the data presented in Table 3-1, the pH increased by 1 unit after zeolite was in contact with GW. Perić et al. (1999) reported that zeolite in contact with water will result in a hydrolysis reaction ($Na^+ - Z + H_2O \leftrightarrow H^+ - Z + OH^-$), causing a pH increase. Since Na^+ pretreatment is commonly used, it was included in this research for comparison. The composition of Na^+ pretreated chabazite is shown in Table 3-2. It was observed that Na^+ decreased by 14%; Fe decreased by 1.5 times; and the Ca^{2+} , K^+ and Mg^{2+} content did not change. Neither pretreatment affected the Si/Al ratio, which is an indication that no structural damage occurred (Alshameri et al., 2014).

Table 3-2. Composition of natural and pretreated chabazite.

Components (wt %)	Chabazite Pretreatment			
	Natural	GW	Na^+	30 HA
Si	31.65 ± 1.33	28.14 ± 4.06	30.23 ± 1.66	27.30 ± 2.95
Al	9.04 ± 0.35	8.63 ± 1.07	9.17 ± 0.29	8.46 ± 1.07
Fe	6.25 ± 1.80	4.06 ± 2.01	4.75 ± 1.27	6.73 ± 1.71
Na	7.19 ± 0.61	4.16 ± 0.79	6.25 ± 0.53	4.45 ± 0.44
K	1.02 ± 0.13	1.11 ± 0.08	0.87 ± 0.21	1.01 ± 0.10

Table 3-2. (Continued)

Components (wt %)	Chabazite Pretreatment			
	Natural	GW	Na ⁺	30 HA
Ca	0.83 ± 0.05	5.57 ± 4.58	1.23 ± 0.85	3.29 ± 1.48
Mg	0.54 ± 0.05	0.55 ± 0.09	0.48 ± 0.02	0.60 ± 0.14
F	-	0.58 ± 0.07	-	0.71 ± 0.25
S	2.52 ± 0.93	2.61 ± 1.18	0.60 ± 0.56	1.23 ± 1.18
Si/Al ratio	3.50 ± 0.07	3.25 ± 0.08	3.30 ± 0.12	3.22 ± 0.02

3.3.2. Isotherm Studies

The equilibrium cation concentrations in meq L⁻¹ with varying masses of GW pretreated chabazite are shown in Figure 3-1. During NH₄⁺ uptake, it was observed that Na⁺ and Ca²⁺ were mainly exchanged, confirming the IX process. The other pretreatment strategies showed similar trends. Langmuir and IX isotherm models were fit to the experimental data (Figure 3-2) and the isotherm coefficient values are summarized in Table 3-3. Both models fit the equilibrium data well for all pretreatment strategies, as shown by the correlation coefficients (R²). Although the IX isotherm is the more appropriate model, the Langmuir isotherm equation is commonly applied to describe sorption of NH₄⁺ onto chabazite; perhaps due to the need to measure the concentration of the exchanged cation (Green et al., 1996; Leyva-Ramos et al., 2010). The Langmuir model is consistent with IX processes, as it assumes the surface of the adsorbent has a specific number of sites where the solute molecules can be adsorbed, the adsorption involves the attachment of only one layer of molecules to the surface (monolayer adsorption) and no interactions occur between the sorbed molecules (Boyer, 2014).

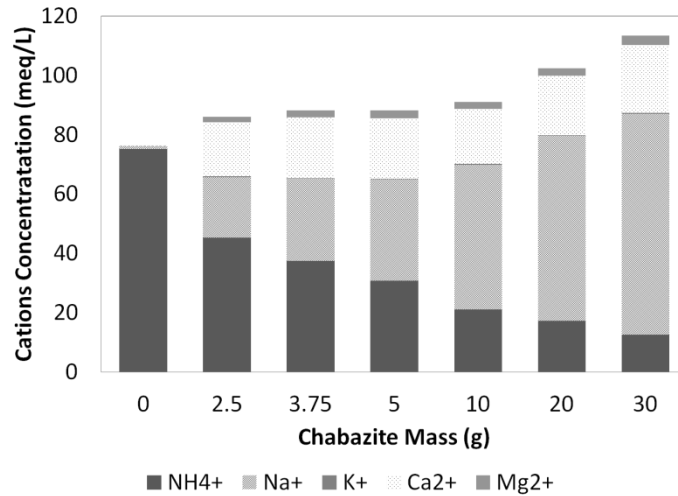


Figure 3-1. Cation concentrations at equilibrium during NH₄⁺ uptake.

Table 3-3. Langmuir and Ion Exchange Isotherm coefficients for chabazite.

Chabazite Pretreatment	Langmuir Coefficients			IX Coefficients		
	q _{max} (meq/g)	K _L (L/meq)	R ²	q _{max} (meq/g)	K _{IX}	R ²
GW	9.01	5.83E-03	0.990	2.89	0.92	0.946
Na ⁺	4.44	1.69E-02	0.979	2.55	1.67	0.961
DI	13.12	4.33E-03	0.997	2.71	1.93	0.999

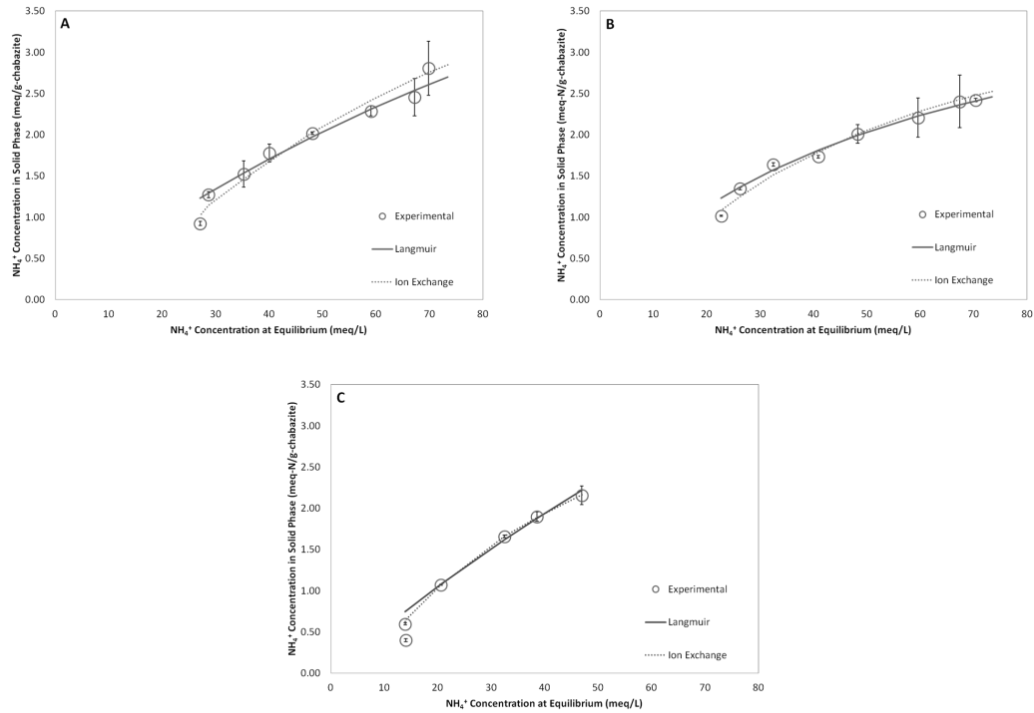


Figure 3-2. Isotherm models for: (A) GW pretreatment, (B) Na⁺ pretreatment, and (C) DI pretreatment.

Based on the Langmuir model, the isotherm constant q_{\max} , which represents the maximum adsorption capacity, was found to be $9.01 \text{ meq-N g-Chabazite}^{-1}$ for GW pretreatment and 13.12 and $4.44 \text{ meq-N g-Chabazite}^{-1}$ for DI and Na⁺ pretreatment, respectively (values are significantly different with a p-value of 0.018). The exchange capacity of chabazite reported by the supplier was $2.50 \text{ meq g-chabazite}^{-1}$; when compared with the values obtained by the Langmuir isotherm model this is an overestimation. The IX isotherm model resulted in q_{\max} values closer to what was reported by the zeolite supplier. The obtained q_{\max} values were 2.89 , 2.55 , and $2.71 \text{ meq-N g-chabazite}^{-1}$ for GW, Na⁺ and DI pretreatment, respectively. These values are not significantly different (p-value 0.13). Both models are in agreement that Na⁺ pretreatment

did not enhance the exchange capacity. Previous studies performed by Green et al. (1996) and Leyva-Ramos et al. (2010) determined a q_{\max} value of 2.64 meq-N g-Chabazite⁻¹ for NH₄⁺ uptake on Na⁺ pretreated chabazite, which is slightly higher than this study. The differences between prior studies and our observations could be due to different mineral compositions, which naturally vary between and within deposits (Hedstrom, 2001).

3.3.3. Ammonium Uptake by Chabazite

The uptake of NH₄⁺ by chabazite pretreated with GW over time was compared with two frequently used zeolite pretreatment methods; sodium chloride and deionized water (Figure 3-3A). During the first 4 hours of contact, the following order of uptake (removal) was observed: GW (83%) > DI (72%) > Na⁺ (54%); GW pretreatment was superior to Na⁺ and DI pretreatment (p-value 9.90E-05 and 1.14E-03, respectively). At 24 hours, the uptake (removal) order was: DI (92%) > GW (90%) > Na⁺ (79%); GW pretreatment was superior to Na⁺ pretreatment, but not DI pretreatment (p-value 3.44E-05 and 0.12, respectively). In the isotherm studies it was shown that there is no difference between the pretreatment strategies, however, the kinetics studies have shown that the pretreatment did have a significant effect at the first four hours of reaction. The kinetics studies was performed up to 24 hours of reaction time, if more time were given the Na⁺ pretreatment will result in a similar NH₄⁺ removal efficiency as the GW and DI pretreatment strategies.

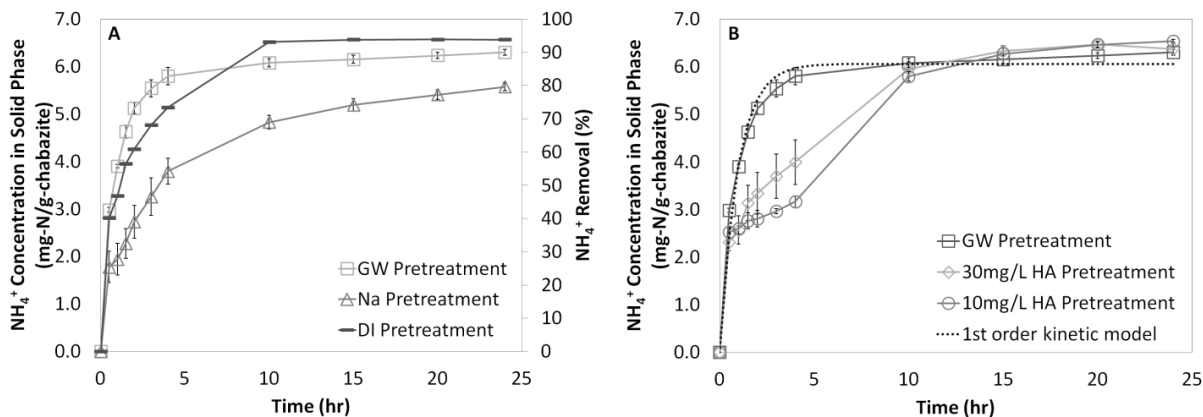


Figure 3-3. Ammonium uptake by GW pretreated chabazite; comparison with (A) Na⁺ and DI pretreatment; and (B) 10 and 30 mg L⁻¹ HA pretreatment.

Moussavi et al. (2011) showed that the presence of humic acid (10 mg L⁻¹) improved NH_4^+ uptake by reducing the mass transfer resistance from the bulk solution onto the adsorbent (Moussavi et al., 2011). HAs are also well known to play a role in sequestration of metal cations by forming complexes with -OH and -COOH groups (Pandey et al., 1999). Groundwater used in this study had a HA concentration of 14 mg L⁻¹. After pretreatment all of the HA was adsorbed (Table 3-1). Therefore, it is possible that the enhancement in the NH_4^+ removal rate was caused by the loading of HA into the chabazite. To test this theory, chabazite was treated with HA at concentrations of 10 and 30 mg L⁻¹ (Figure 3-3B). At a contact time of 4 hours the uptake (removal) order was: GW (83%) > 30HA (56%) > 10HA (45%). At a contact time of 24 hours all treatments had an uptake of approximately 90%. An increase in HA concentration enhanced the NH_4^+ uptake, but not as much as the GW pretreatment. HA pretreatment significantly affected the kinetics during the first 4 hours of contact (p-value 2.86E-03 and 4.42E-04 for 10 and 30 HA pretreatment, respectively). At 10 to 24 hours of contact, the kinetics were slightly improved when compared with GW pretreatment (p-value 0.951 and 0.401 for 10 and 30 HA

pretreatment, respectively). Based on these results, the presence of HA in GW was not responsible in enhancing the NH_4^+ uptake observed.

3.3.4. Kinetics Studies

Kinetic data were analyzed using a pseudo first-order kinetic model (Eq. 3). All experimental data fit the model well based on R^2 values, except for 30HA pretreatment strategy, as shown in Table 3-4. The model fit to the GW pretreatment data is shown in Figure 3-3B, which was similar for the other pretreatments tested in this study. The calculated coefficient of q_e was 6.06, 5.57, and 6.39 mg-N g-chabazite⁻¹ for GW, Na⁺, and DI pretreatment, respectively. The k_1 obtained was 1.05, 0.37, and 0.63 h⁻¹ for GW, Na⁺, and DI pretreatment, respectively; GW pretreatment having the highest value (p-value 0.0028). The higher the value of k_1 , the greater the adsorption. As shown previously (Sec. 3.3.3.), the NH_4^+ uptake of the pretreatment strategies followed an order of GW > DI > Na > 30HA > 10HA which is in agreement with the determined k_1 coefficient.

Table 3-4. Pseudo first order kinetic model and film diffusion coefficients.

Chabazite Pretreatment	$q_{e, \text{exp}}$ (mg-N/g)	K_1 (h⁻¹)	$q_{e, \text{cal}}$ (mg-N/g)	R^2	D_f (m²/hr)
GW	6.30	1.05	6.06	0.986	5.44E-10
Na	5.57	0.37	5.25	0.961	3.83E-10
DI	6.62	0.63	6.39	0.942	2.33E-10
10 HA	6.58	0.28	6.35	0.866	1.12E-10
30 HA	6.41	0.38	6.24	0.925	1.96E-10

Ion exchange kinetics are controlled mainly by three mechanisms: (1) diffusion across the liquid film surrounding the particle - film diffusion; (2) diffusion in the liquid contained in the pores and/or along the pore walls – intra-particle diffusion; and (3) adsorption and desorption between the adsorbate and active sites – mass action (Qiu et al., 2009). Of these steps, film and intra-particle diffusion usually offer greater resistance to mass transfer; therefore, either can act as rate limiting steps in the process (Alberti et al., 2012; Qiu et al., 2009). The mechanism of NH_4^+ uptake by the different pretreatment strategies was further analyzed by using the film diffusion coefficient (Eq. 4). Coefficients for this model are summarized in Table 3-4. Film diffusion depends on the thickness of liquid film around the zeolite (δ); in this study a value of 10^{-5} m for poorly stirred solution was utilized (Lin et al., 2013; Moussavi et al., 2011). Kinetic batch tests were mixed at 170 rpm; which is sufficient to decrease external mass transfer resistance and decrease δ (Erdoğan & Ülkü, 2011). The greater the film diffusion coefficient (D_f) indicates a decrease in the external mass transfer resistance. Comparison of D_f between pretreatment strategies indicates that GW pretreatment resulted in a greater value, hence showing that the pretreatment significantly improved the film diffusion mechanism (p-value 0.029).

3.4. Conclusions

The aim of this study was to perform GW pretreatment of chabazite to reduce Na^+ desorption and microbial inhibition. The effect of GW pretreatment with respect to kinetics and cation exchange capacity for NH_4^+ removal was evaluated and compared with other common pretreatment practices. Results showed that GW pretreatment:

- Successfully decreased the Na^+ loaded into chabazite without significantly decreasing the NH_4^+ exchange capacity.

- Improved the kinetics of NH_4^+ removal during the first four hours of contact as a result of enhanced film diffusion mechanism.

GW pretreatment was shown to be superior to the other pretreatment practices in enhancing the kinetics of NH_4^+ , while the exchange capacity was not significantly enhanced. This is an important finding since the utilization of chemicals is not necessary to improve the key parameters in IX with chabazite; resulting in a more economical pretreatment process. The results of this research can decrease reactor volume requirements in applications where IX and biological treatment processes are combined.

CHAPTER 4

BIOREGENERATION OF CHABAZITE DURING NITRIFICATION OF ANAEROBICALLY DIGESTED CENTRATE

4.1. Introduction

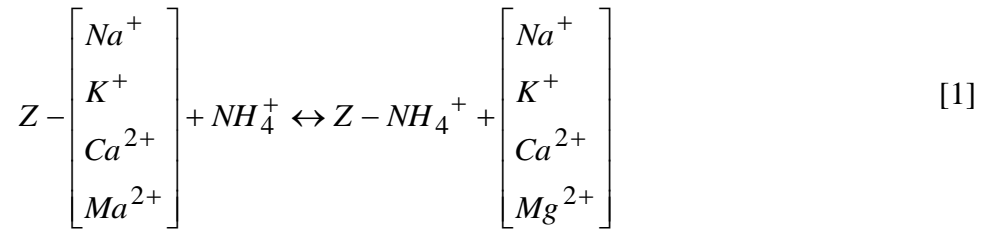
Livestock wastes can contain high concentrations of nutrients, organic matter, pathogens, trace metals, salts, pharmaceuticals, and other compounds of concern (Guan & Holley, 2003; Hatfield et al., 1998; Varel et al., 2012). If manure is not managed properly, it becomes a threat to surface and groundwater systems, resulting in eutrophication, depletion of dissolved oxygen (DO), and fish kills. To address these risks, anaerobic digestion (AD) of livestock manure from concentrated animal feeding operations (CAFOs) can stabilize organic matter while simultaneously producing methane, which can be used as a biofuel (Cantrell et al., 2008). Although the effluent from AD is rich in nutrients and can be used as a fertilizer, available cropland near large CAFOs often cannot assimilate all of the nutrients present, and further treatment of AD effluent may be needed (Massé et al., 2011). For example, biological nitrification and denitrification have been successfully applied to treat centrate (the liquid waste produced from AD effluent) in some swine-production CAFOs (Kunz et al., 2009; Vanotti et al., 2007; Yang & Gan, 1998).

A challenge in the treatment of anaerobically digested swine waste (ADSW) centrate is inhibition of the nitrification process due to the presence of high free ammonia (FA)

concentrations. Concentrations of FA in aqueous solution depend on the concentration of total ammonia nitrogen (TAN), pH, and temperature of the waste stream (Weiner, 2012).

Concentrations of FA range from 10 to 550 mg L⁻¹ (as N) in ADSWs at 20 °C with a pH range of 7.5–8.5 (Boiran et al., 1996); such concentrations have been shown to be inhibitory to nitrifying bacteria (Anthonisen et al., 1976; Kim et al., 2008).

A possible strategy for overcoming inhibition of nitrification during treatment of high-TAN wastewaters is combining ion exchange (IX) with nitrification to suppress the concentration of ammonium (NH₄⁺) in solution and, hence, FA (Green et al., 1996; Jung et al., 2004). The most commonly used materials for cation exchange in wastewater treatment are natural zeolites, which are porous aluminum silicate minerals with high cation exchange capacities and high selectivity for NH₄⁺ (Hedstrom, 2001). The equilibrium exchange reaction between cations attached to the zeolite (Z) and NH₄⁺ in solution is shown in Equation 1.



Of more than fifty species of zeolites, clinoptilolite is the most commonly used due to its low cost; however, chabazite has a higher NH₄⁺ exchange capacity than clinoptilolite (Langwaldt, 2008; Wang & Peng, 2010), which may be advantageous in applications where the zeolite can be regenerated and reused. Regeneration is most often accomplished by exposing the saturated zeolite (Z-NH₄⁺) to a concentrated salt solution, such as sodium chloride (NaCl) or sodium bicarbonate (NaHCO₃) (Guo et al., 2013; Koon & Kaufman, 1975). However, the waste brine produced from this process, which contains both high Na⁺ and NH₄⁺ concentrations,

presents a disposal problem (Farag & Harper, 2014; Maas, 1993; Sanchez et al., 2004). An attractive alternative to disposing of the waste brine is to treat it using salt-tolerant nitrifying bacteria (Green et al., 1996; Semmens & Porter, 1979). This allows the treated brine to be reused for several zeolite-regeneration cycles prior to disposal. However, this procedure still has some drawbacks, including the need to add salt for zeolite regeneration, the need for separate reactors, one for zeolite adsorption and regeneration and one for brine treatment, and the need to use halophilic nitrifying bacteria. Furthermore, a portion of the spent zeolite may need to be wasted (He et al., 2007; Wei et al., 2011).

To overcome these drawbacks, we here propose and demonstrate a novel method for IX-assisted nitrification with simultaneous direct bioregeneration of NH_4^+ -saturated chabazite. In the process described here, a small fraction of NH_4^+ is desorbed from the zeolite by cations present in the wastewater or chemicals added to supplement alkalinity losses during nitrification. Nitrifying bacteria oxidize NH_4^+ in solution, and desorption continues until the NH_4^+ concentration in solution decreases to negligible values. A major advantage of this approach is that the chabazite dose can be set so that the concentration of FA in solution remains below the inhibitory concentration for nitrification. In addition, there is no waste brine produced, the use of halophilic nitrifying bacteria is not necessary, and the process can be carried out in a single reactor.

The goal of this paper is to demonstrate the novel process described above for treatment of high-ammonia wastewaters, with particular application to ADSW. The two guiding hypotheses are that chabazite addition can increase the nitrification rate by easing inhibition from FA, and that nitrifying bacteria can directly bioregenerate chabazite- NH_4^+ , allowing reuse of the chabazite for additional cycles. The specific objectives were to (1) determine the effectiveness

of chabazite addition for reducing the inhibition of nitrification of high-TAN strength wastewaters (such as ADSW); and (2) assess the feasibility of directly bioregenerating chabazite via biological nitrification.

4.2. Materials and Methods

4.2.1. Anaerobically Digested Swine Waste Centrate

A pilot-scale anaerobic digester managed in our laboratory as a semi-continuous batch reactor with a working volume of 26 L supplied the ADSW centrate for this study. The reactor was operated at a 21 day solids retention time (SRT) by feeding 2.6 L of swine manure collected from a local farm three times per week. Additional details on pilot reactor operation can be found elsewhere (Amini, 2014). ADSW centrate was obtained by centrifuging the effluent from the reactor at 4000 rpm for 15 min in a Thermoscientific Sorvall Legend RT Plus (Waltham, MA) to remove biosolids. A characterization of the ADSW centrate is provided in Table 4-1. In addition, two synthetic wastewaters were used in the experiments. Synthetic wastewater S-1 (Table 1) was formulated to contain NH_4^+ and cations at similar concentrations to real centrate (g L^{-1}): NH_4Cl (3.8), NaHCO_3 (2.0), K_2HPO_4 (0.4), NaCl (1.9), KCl (0.9), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (2.0) and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ (2.4) in deionized water. Synthetic wastewater S-2 was used in the nitrification inhibition studies and consisted of deionized water with $2.0 \text{ g L}^{-1} \text{ NaHCO}_3$, $0.4 \text{ g L}^{-1} \text{ K}_2\text{HPO}_4$, and varying concentrations of NH_4^+ ($0.06\text{--}3.8 \text{ g L}^{-1}$).

Table 4-1. Characterization of anaerobically digested swine waste centrate.

Parameter	Units	ADSW centrate	S-1
NH ₄ ⁺	mg-N L ⁻¹	861 ± 99	1,000
Na ⁺	mg L ⁻¹	275 ± 85	700
K ⁺	mg L ⁻¹	693 ± 211	450
Ca ²⁺	mg L ⁻¹	373 ± 62	660
Mg ²⁺	mg L ⁻¹	136 ± 27	240
PO ₄ ³⁻	mg-P L ⁻¹	58 ± 9	70
Ph		7.28 ± 0.20	7.5
Alkalinity	CaCO ₃ mg L ⁻¹	3,100 ± 114	2,000
sCOD	mg L ⁻¹	1,900 ± 220	---

4.2.2. Chabazite

Chabazite (ZS500H) was obtained from St. Cloud™ Zeolite (Winston, New Mexico). St. Cloud™ Zeolite data sheet provided a characterization of chabazite indicating that sodium (Na⁺) is the main cation loaded. Chabazite was sieved to obtain a particle size range of 1 to 2 mm, and pretreated as described in Chapter 3.

4.2.3. Ion Exchange Studies

Batch ion exchange (IX) tests were performed using USEPA protocols to determine the required chabazite dose and contact time to reduce the NH₄⁺ concentration below the inhibitory level for nitrification (USEPA 1992; USEPA 2008). Varying masses of chabazite (0, 2.5, 3.75, 5, 10, 20, and 30 g) were placed in contact with a fixed volume (200 mL) of ADSW centrate (806 ±

145 mg-N L⁻¹) in 250 mL Erlenmeyer flasks. The flasks were covered with parafilm and maintained at 22°C for 48 hr on a shaker table at 170 rpm. It was assumed that the systems were sufficiently close to equilibrium after 48 hr. After 48 hr, the aqueous concentrations of NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺ were measured by ion chromatography. The concentration of NH₄⁺ adsorbed to the chabazite (meq NH₄⁺ per g chabazite) was calculated based on the difference between the initial and final concentrations of aqueous NH₄⁺, assuming that no other loss mechanisms were relevant. Experiments were performed in duplicate. The experimental data were fit to the following IX isotherm:

$$q_{NH_4^+} = \frac{QKC_{NH_4^+}}{C_{Na^+} + KC_{NH_4^+}} \quad [2]^1$$

where $q_{NH_4^+}$ is the amount of NH₄⁺ sorbed per mass of the solid, Q and K are constants in the IX isotherm related to maximum adsorption capacity and affinity for the exchanger, respectively.

Ion exchange kinetics were determined in similar systems using ADSW centrate and a chabazite dose of 150 g L⁻¹. The initial aqueous concentration of NH₄⁺ was 914 ± 7 mg L⁻¹ and the initial aqueous concentration of Na⁺ was 330 ± 2 mg L⁻¹. At specified times (0.5 hr, 1 hr, 1.5 hr, 2 hr, 3 hr, 4 hr, 10 hr, 15 hr, 20 hr, and 24 hr), samples were analyzed for aqueous concentrations of NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺. Experiments were performed in duplicate.

4.2.4. Nitrification Inhibition Studies

Batch nitrification studies were carried out to identify the NH₄⁺ concentration that will result in FA inhibition. Six 1-L beakers containing 600 mL of synthetic wastewater (S-2) with

¹ The IX isotherm and Andrews' model was applied to the experimental data in order to develop a mathematical model that describes bioregeneration. The mathematical model was developed by Karl Payne and is included in the article "Bioregeneration of chabazite during nitrification of anaerobically digested centrate: Experimental and modeling studies."

varying concentrations of NH_4^+ (50, 100, 200, 350, 500, and 1000 mg-N L^{-1}) at a pH of 7.5 were incubated at room temperature. Seed sludge was added to achieve a volatile suspended solids (VSS) concentration between 5.4 – 5.5 g L^{-1} . Seed sludge was obtained from a municipal wastewater treatment plant (Northwest Regional Water Reclamation Facility, Tampa, FL) that uses a 5-stage Bardenpho Process for biological nutrient removal. Mixing was provided at 100 rpm using a Phipps & Bird PB-700™ Jartester (Richmond, VA). Aeration was supplied with Whisper Tetra air pumps (St. Blacksburg, VA) and diffuser stones to maintain the DO concentrations above 6 mg L^{-1} to assure that DO did not limit the nitrification rate. An additional nitrification test was performed at NH_4^+ concentrations of 50 and 100 mg-N L^{-1} with 2,000 mg L^{-1} of sodium (Na^+) added to S-2. This was done to determine the impact of high concentrations of Na^+ on the rate of nitrification. Samples were collected at specific times (0 hr, 2 hr, 4 hr, 6 hr, 8 hr, 10 hr, 12 hr, 14 hr, and 16 hr) and concentrations of NH_4^+ , NO_3^- , NO_2^- and Na^+ were measured by ion chromatography as described below.

Nitrification is a two-step process in which ammonia-oxidizing bacteria (AOB) transform NH_4^+ to NO_2^- , and then nitrite oxidizing bacteria (NOB) transform NO_2^- to NO_3^- . A plot of NH_4^+ -N concentration versus time provides a slope that represents nitrification rate in units of $\text{mg-N L}^{-1} \text{hr}^{-1}$. A plot of NO_3^- -N concentration versus time provides a slope that represents the nitrification rate in units of $\text{mg-N L}^{-1} \text{hr}^{-1}$. To obtain the slope values, linear regression was performed on data from times 2 to 10 hours which corresponded with the linear portion of the reaction. Specific rates were calculated by dividing nitrification and nitrification rates by VSS concentration. The experimental data were analyzed for microbial kinetics when microbes are exposed to inhibitory substrates using the Andrew's equation:

$$r_s = - \frac{\mu_{\max} C_{\text{Substrate}} X}{Y \left(\frac{C_{\text{NH}_4^+}^2}{K_I} + K + C_{\text{Substrate}} \right)} \quad [3]^1$$

where $C_{\text{Substrate}}$ is the concentration of the substrate for either AOB or AOB (NH_4^+ or NO_3^- ; mg-N L^{-1}), $C_{\text{NH}_4^+}$ is the inhibitory substance which in this study is NH_4^+ (mg-N L^{-1}), μ_{\max} is the maximum specific growth rate (hr^{-1}), X is the biomass concentration (mg-VSS L^{-1}), Y is the yield coefficient (mg-VSS mg^{-1}), K (mg L^{-1}) is the half saturation constant, and K_I (mg L^{-1}) is the inhibition coefficient.

4.2.5. Chabazite Amended Nitrification Studies

Three batch nitrification studies were carried out to determine the effectiveness of chabazite in improving the nitrification rate during the treatment of high strength wastewater. The wastewaters utilized were real ADSW centrate and synthetic wastewaters (S-1 and S-2). The VSS concentration in this study was 2.5 g L^{-1} . The dose of chabazite added (150 g L^{-1}) to all batch tests was based on results from the IX studies presented below. During 9 days of reaction, concentrations of NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NO_3^- and NO_2^- were measured by ion chromatography at specific times (0 hr, 4hr, 24 hr, 48 hr, 72 hr, 96 hr, 120 hr, 144 hr, 168 hr, and 192 hr). Nitrification rates in units of $\text{mg-N L}^{-1} \text{ hr}^{-1}$ were calculated from the slopes obtained from the plot of NO_3^- -N concentration versus time. Specific nitrification rate was calculated by dividing nitrification rate by VSS concentration. To determine the percent of chabazite regenerated during nitrification, initial soluble TN concentration was divided by final soluble TN concentration.

4.2.6. Analytical Methods

Concentrations of anions (NO_2^- , NO_3^-) and cations (NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+) were measured using a Metrohm 881 Compact IC Pro (Herisau, Switzerland) ion chromatograph (IC Application No. C-115 and No. S-236). Detection limits are 0.20, 0.01, 0.07, 0.27, 0.20, 18.50, and 0.09 mg L^{-1} for NO_2^- , NO_3^- , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , respectively. Standard Methods (APHA et al. 2012) were used to measure: DO (4500-O), VSS (2540), pH (4500-H), alkalinity (2320), conductivity (2510), and soluble chemical oxygen demand (sCOD; 5220).

4.2.7. Statistical Analysis

All experiments were performed in duplicate. Values in tables and figures are presented as means with max/min values. Student's t-tests were used to determine if two sets of data were significantly different from each other. The test was performed at a confidence level of 95%, rejecting the null hypothesis (no difference between data sets) with p-value < 0.05.

4.3. Results and Discussion

4.3.1. Ion Exchange Studies

Results of the equilibrium IX studies are shown in Figure 4-1. The IX isotherm model (Eq. 2) was fit to the experimental data and is shown in Figure 4-1A. The isotherm constants, Q and K , were determined by linearizing the non-linear isotherm and finding the best fit values using linear regression. The correlation coefficient (R^2) obtained was 0.987. The value of Q , which represents the exchange capacity, was estimated to be 1.81 meq g^{-1} , which is about 32% lower than the value of 2.67 meq g^{-1} reported by Green et al. (1996) and Leyva-Ramos et al. (2010) (Leyva-Ramos et al., 2010). We suspect that this moderate difference is due to the

natural variability of mineral composition within different chabazite deposits (Hedstrom, 2001). The value of K obtained was found to be 2.92. The K parameter is a selectivity coefficient, indicative of the preference of one ion (NH_4^+) relative to another (Na^+) for exchange onto IX sites in chabazite (Crittenden et al., 2012). There are no prior published studies that have used the IX isotherm model with chabazite to compare with our results. The efficiency of NH_4^+ removal as a function of chabazite dose is shown in Figure 4-1B. A dose of 150 g-chabazite L^{-1} resulted in a removal efficiency of 88%, which was sufficient to reduce the NH_4^+ concentration below the inhibitory level, which will be discussed later.

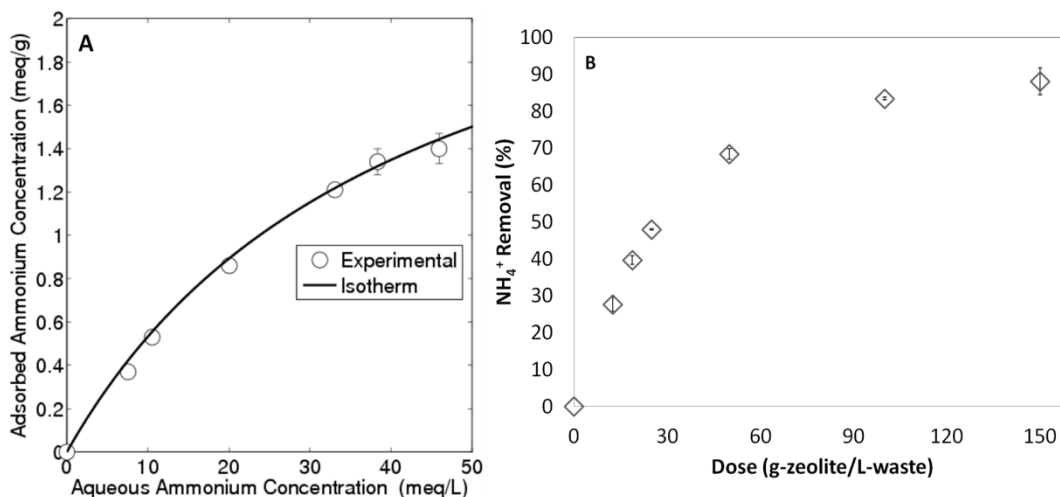


Figure 4-1. Ion exchange equilibrium: (A) IX isotherm model for NH_4^+ uptake; (B) Effect of chabazite dose on the observed removal efficiency of NH_4^+ .

The results of the kinetic study performed at a chabazite dose of 150 g-chabazite L^{-1} over 24 hours are shown in Figure 4-2A. Most of the NH_4^+ adsorption occurred within the first four hours of contact, most likely due to the greater initial availability of adsorption sites. Removal

efficiencies at times 10 and 24 hours were not significantly different (p-value 0.06), indicating that the system reached equilibrium within 10 hours. Cation concentrations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) over the 24 hour kinetic study are shown in Figure 4-2B. During ion exchange, NH_4^+ and K^+ were adsorbed and Na^+ was the main cation desorbed. The final Na^+ concentration in the solution was $2,100 \text{ mg L}^{-1}$ (91.3 meq L^{-1}). The impact of Na^+ desorption on bioregeneration will be discussed later.

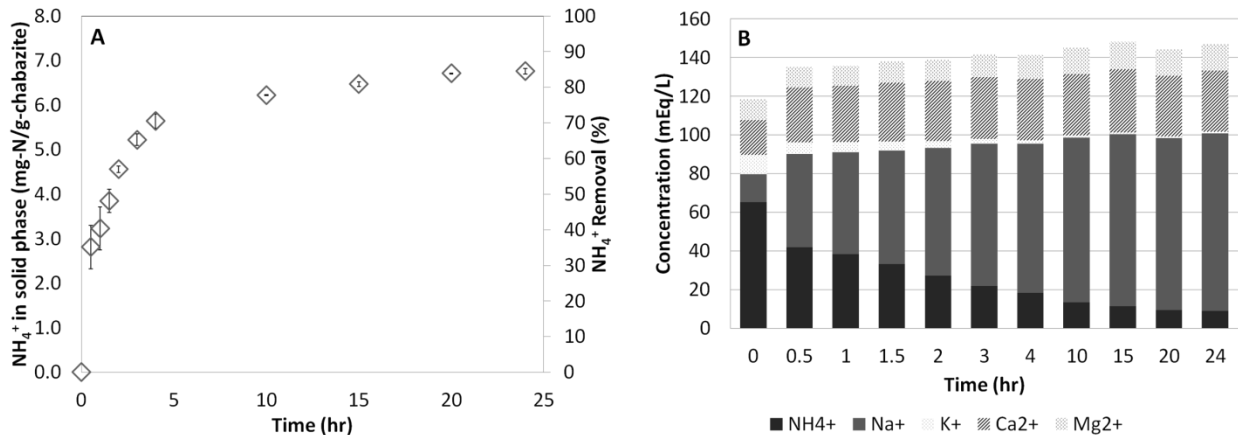


Figure 4-2. (A) Effect of contact time on NH_4^+ removal onto chabazite; (B) Liquid phase concentrations of cations (meq L^{-1}) over time during the kinetic study.

4.3.2. Nitrification Inhibition Studies

The effect of varying NH_4^+ concentrations on the rate of NH_4^+ and NO_2^- oxidation with a nitrifying wastewater seed is shown in Figure 4-3. For NH_4^+ oxidation (Figure 4-3A), as the NH_4^+ concentration increased, the rate increased up to a maximum of $0.87 (\pm 0.21) \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$ at a TAN concentrations of 100 mg-N L^{-1} ($\text{FA} = 1.47 \text{ mg-N L}^{-1}$). At TAN concentration of 50 mg-N L^{-1} and 200 mg-N L^{-1} the rates were similar. For NO_2^- oxidation

(Figure 4-3B), the rate increased up to a maximum of $0.66 (\pm 0.06) \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$ at a TAN concentration of 50 mg-N L^{-1} ($\text{FA} = 0.74 \text{ mg-N L}^{-1}$). When comparing with the rate at a TAN concentration of 200 mg-N L^{-1} the rate decreased by a factor of 2. Hence, maintaining the TAN concentration below 200 mg-N L^{-1} is recommended to operate the system below inhibitory conditions. Combining these results with results from the IX studies, a chabazite dose of $150 \text{ g-chabazite L}^{-1}$ and a contact time of 4 hours is expected to reduce the FA concentration in ADSW concentrate by approximately 90%, resulting in a NH_4^+ concentration that should not be inhibitory.

Data from these experiments were fit using the Andrew's model (Eq. 3), which resulted in a good fit to the experimental data for both nitrification steps, as shown in Figure 4-3. The K value for the nitritation and nitrification steps were set to 5.0 and 0.9 mg-N L^{-1} , respectively, based on prior literature (Ritmann and Mccarty, 2002). The μ_{max} and Y values were combined; this parameter along with K_I were the only two adjustable parameters. The calculated K_I for AOB and NOB was $1,123 \text{ mg-N L}^{-1}$ and $122.2 \text{ mg-N L}^{-1}$, respectively. The calculated K_I confirmed that NOB activity is more significantly inhibited than AOB activity; which is consistent with previous studies (Anthonisen et al., 1976; Gee et al., 1990).

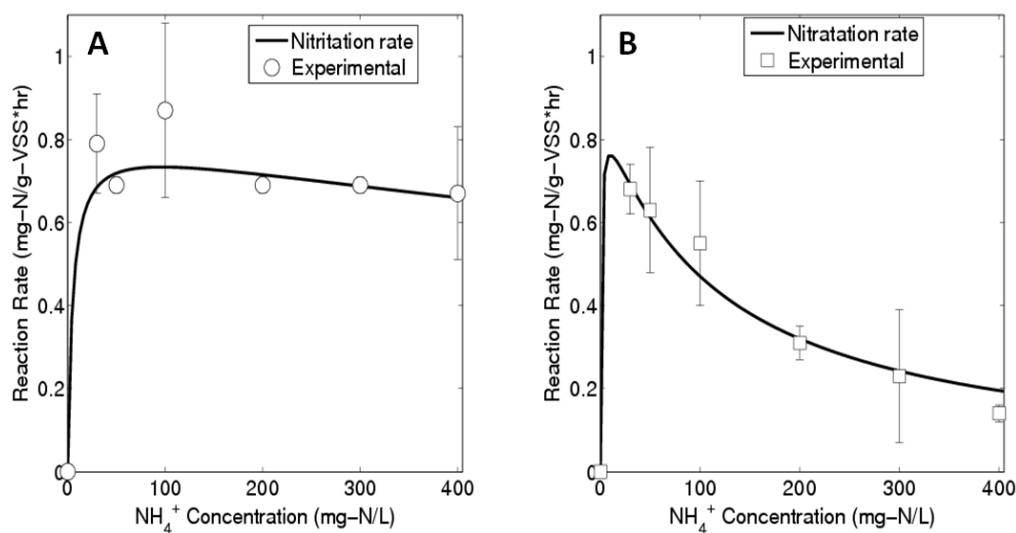


Figure 4-3. Nitrification inhibition: Effect of NH_4^+ -N concentration on the rate of (A) nitrification; and (B) nitration.

4.3.3. Chabazite Amended Nitrification Studies

The fate of NH_4^+ , NO_2^- and NO_3^- over a 9 day nitrification study with synthetic wastewater (S-2; 1,000 mg-N L $^{-1}$ of NH_4^+), without and with chabazite addition, is shown in Figures 4-4A and 4-4B. Summary data for all of the nitrification tests are shown in Table 4-2. In the reactor without the addition of chabazite, the NH_4^+ decreased by only 7% over the entire study period. This result is consistent with the nitrification inhibition studies, which showed that high NH_4^+ concentrations inhibit the nitrification process. It was observed during these experiments that NO_3^- concentrations were higher than NO_2^- concentrations, which is not in agreement with the inhibition studies. Currently experiments are being performed to explain this discrepancy. In the chabazite amended reactors, NH_4^+ concentrations decreased by 97% over the first 4 hours and remained below the inhibitory level for nitrification for the rest of the experiment. The concentration of Na^+ increased from 0 up to 1,000 mg L $^{-1}$. The rate of nitrification was 0.38 mg-N g-VSS \cdot hr $^{-1}$ and 0.16 mg-N g-VSS \cdot hr $^{-1}$ with and without chabazite,

respectively. The results show that chabazite addition improved the nitrification rate. At day nine of nitrification, 19% of chabazite bioregeneration was achieved based on the NO_3^- production.

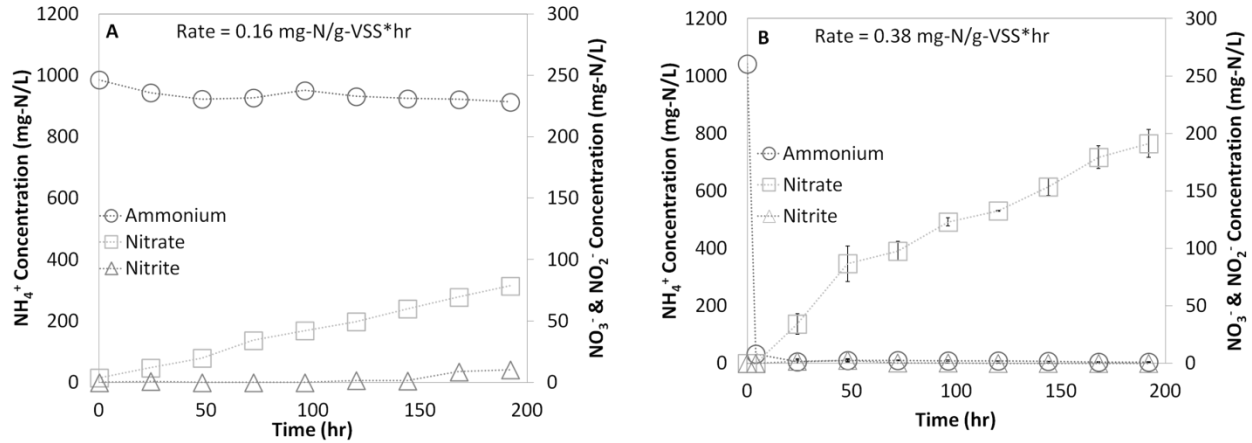


Figure 4-4. Ammonium, nitrite and nitrate concentration during nitrification of 1,000 mg NH_4^+ -N L^{-1} ; synthetic wastewater S-2 (A) no addition of chabazite, (B) with addition of 150 g L^{-1} of chabazite.

When synthetic ADSW centrate containing competing cations (S-1) was treated in the chabazite amended reactor, the nitrification rate was $0.21 \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$ (Figure 4-5A) and 16% of bioregeneration was achieved. In the synthetic ADSW, both K^+ and NH_4^+ were exchanged with Na^+ , resulting in a higher Na^+ concentration in the solution ($2,180 \text{ mg L}^{-1}$) than when S-1 was treated. The high Na^+ concentration results in inhibition of the nitrifying bacteria, which will be discussed later. When real ADSW centrate was treated (Figure 4-5B) the nitrification rate was $0.46 \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$, with a bioregeneration of 27%. The initial Na^+ concentration in the ADSW centrate was of 200 mg L^{-1} and increased up to $1,500 \text{ mg L}^{-1}$. When compared with the other bioregeneration tests, Na^+ fell at an intermediate concentration; however, the nitrification rate was superior. The increase in nitrification rate was likely due to

the high concentration of humic acid (HA) in the ADSW centrate (Cao et al., 2013). Bazin et al. (1991) showed that a HA concentrations of 100 g L^{-1} enhanced the nitrification rate by a factor of 1.5 (Bazin et al., 1991). HA provided an increase in the buffering capacity, therefore providing better control of pH, resulting in further control of FA concentrations in the system.

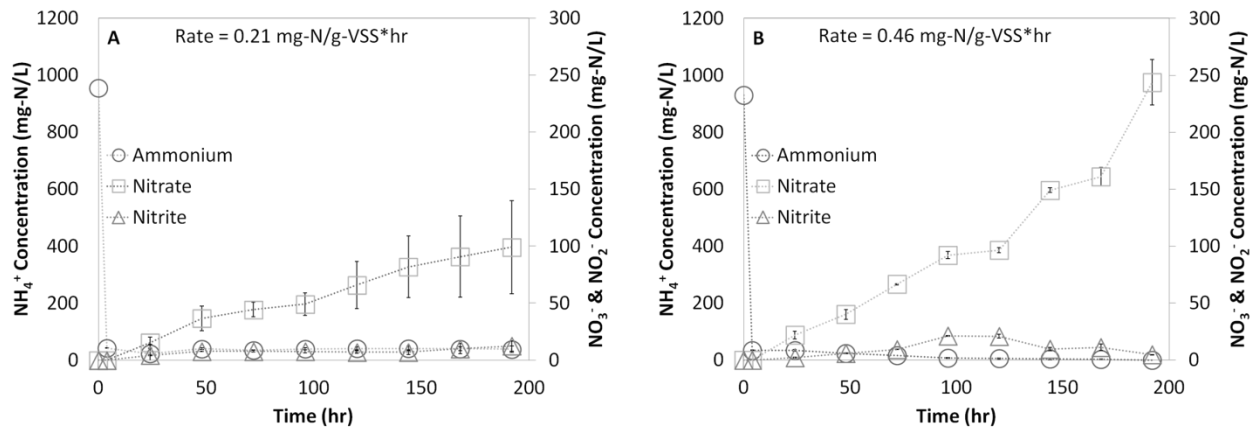


Figure 4-5. Ammonium, nitrite and nitrate concentration during nitrification of $1,000 \text{ mg NH}_4^+\text{-N L}^{-1}$ with addition of 150 g L^{-1} of chabazite; (A) synthetic waste S-1, and (B) real ADSW centrate.

Table 4-2. Nitrification rate for the treatment of synthetic and anaerobically digested swine wastewaters with and without addition of chabazite.

Wastewater	$\text{NH}_4^+\text{-N}$ (mg L^{-1})	Na^+ (mg L^{-1})	Zeolite	R_{ut} ($\text{mg-N g-VSS}^*\text{h}^{-1}$)	Regeneration (%)
S-2	1,000	$1,000 \pm 7^{**}$	Yes	0.38	19
S-2	1,000	244	No	0.16	N/A
S-1*	900	$2,180 \pm 211^{**}$	Yes	0.21	16
ADSW centrate	900	$1,500 \pm 76^{**}$	Yes	0.46	27
S-2	100	$203 \pm 3^{**}$	No	1.19	N/A
S-2	100	2,000	No	0.45	N/A

*Note S-1 contains competing cations similar to ADSW centrate.

** Final Na^+ concentrations.

To quantify the level of nitrification inhibition due to the release of Na^+ , batch studies were conducted with synthetic wastewater (S-2) with $100 \text{ mg L}^{-1} \text{ NH}_4^+\text{-N}$, with and without $2,000 \text{ mg L}^{-1}$ of added Na^+ (Figure 4-6). No chabazite was added to these reactors; however, the concentrations of NH_4^+ and Na^+ selected were based on the typical concentrations observed after $1,000 \text{ mg-N L}^{-1} \text{ NH}_4^+$ exchange (Figure 4-2B). The results confirmed the negative effect of Na^+ on nitrification in the presence of $2,000 \text{ mg L}^{-1} \text{ Na}^+$; the rate of nitrification decreased from $1.19 \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$ to $0.45 \text{ mg-N g-VSS}\cdot\text{hr}^{-1}$. Prior studies have shown that the presence of Na^+ at concentrations $\geq 2,000 \text{ mg L}^{-1}$ decreases the rate of nitrification (Sanchez et al., 2004). During IX the presence of competing cations promoted further increase in Na^+ in the system, explaining the variations in rates and regeneration values in the tested wastewaters. During continuous operation of a zeolite amended sequencing batch reactor (Zeo-SBR) washout of Na^+ will occur over time and the nitrification rate is expected to increase. Note that the nitrification rate with Na^+ addition was greater than during the bioregeneration studies, indicating that Na^+ inhibition didn't completely explain the lower nitrification rate. Bioregeneration is a two step process that depends on the NH_4^+ desorption and nitrification. In Figure 4-4B shows NH_4^+ concentration in the aqueous phase remains below the detection limits, which is an indication that the nitrification rate is faster than the desorption rate. This low rate of desorption (rate limiting) will have an effect in the overall bioregeneration rate.

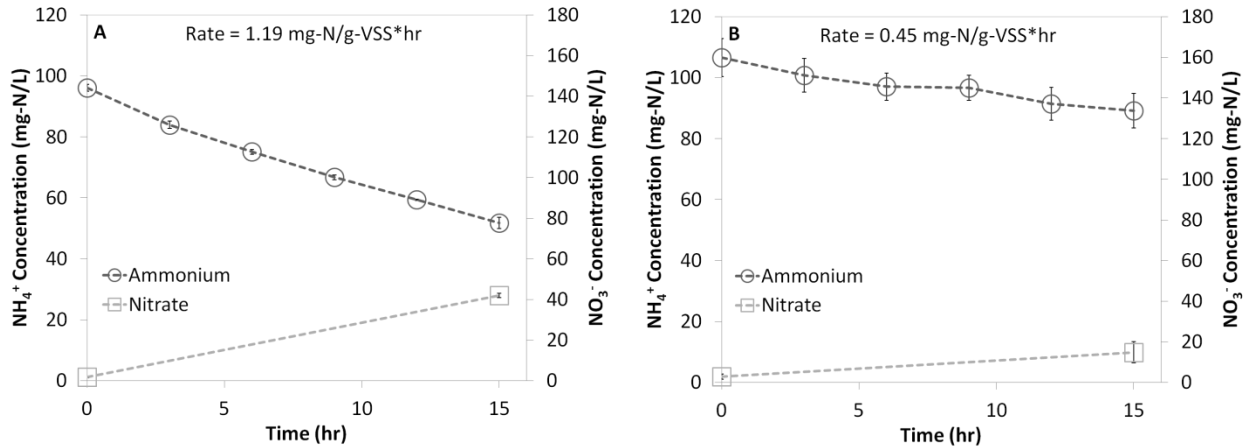


Figure 4-6. Nitrification of 100 mg L⁻¹ NH₄⁺-N; (A) no Na⁺ and (B) with 2,000 mg L⁻¹ Na⁺.

4.4. Conclusions

The treatment of high NH₄⁺ strength wastewater using a hybrid process that combines cation exchange of NH₄⁺ onto chabazite with bioregeneration by nitrification is a potential alternative to overcome nitrification inhibition when treating AD centrate. The addition of chabazite to a nitrification batch reactor treating high NH₄⁺ wastewater improved the nitrification rate. The rate of nitrification was negatively affected by Na⁺ that is released during the exchange with NH₄⁺; however, this is not expected to be a problem over many cycles of operation where the initial high Na⁺ present on the zeolite is washed out of the reactor over time. The results of this study can be used to design a zeolite amended sequencing batch reactor (Zeo-SBR) that includes a denitrification stage.

CHAPTER 5

CHABAZITE AMENDED SEQUENCING BATCH REACTOR FOR THE TREATMENT OF ANAEROBIC DIGESTION SIDESTREAMS

5.1. Introduction

Anaerobic digestion (AD) has been shown to be an effective technique for energy recovery and treatment of livestock wastes, municipal sludges and industrial wastewaters (Carrera et al., 2003; Karakashev et al., 2008; Kinyua et al., 2014). A major advantage of AD is that biogas (a mixture of methane and carbon dioxide) is produced that can be used as an energy source, potentially offsetting the cost of treatment (Cantrell et al., 2008). During AD, organic matter is mineralized, resulting in the release of nutrients (N and P) to the effluents (Massé et al., 2011). If the liquid centrate from dewatering AD effluent is not treated further, nutrients can enter surface and groundwater systems, resulting in eutrophication (Galloway et al., 2003). Removal of nitrogen from AD centrate is typically carried out using suspended growth biological nitrogen removal (BNR) processes (Oleszkiewicz & Barnard, 2006). However, a challenge associated with using conventional BNR for treatment of AD centrate is that the high free ammonia (FA) concentrations present can inhibit nitrification (Anthonisen et al., 1976; Kim et al., 2008). This is a particular problem in treatment of centrate from anaerobically digested swine waste (ADSW) centrate, which can contain total ammonia nitrogen (TAN) concentrations of 800 to more than 4,000 mg-N L⁻¹ (Boiran et al., 1996; Deng et al., 2008).

Zeolites are mineral aluminosilicates with a tetrahedral ring framework and extraframework cations with cation exchange properties (Hedstrom, 2001). Natural zeolites materials have been used for removal of ammonium (NH_4^+) in a number of wastewater applications (Huang et al., 2014; Lin et al., 2014). Given that ion exchange (IX) with zeolite is a reversible reaction, NH_4^+ saturated zeolites (Z-NH_4^+) are typically regenerated using concentrated salt solutions. However, waste brine produced from zeolite regeneration presents a disposal problem due to its very high salt and TAN concentrations. Semmens et al. (1977) showed that Z-NH_4^+ can be regenerated by biological nitrification without NaCl addition in a process called bioregeneration (Semmens et al., 1977). Nitrifying bacteria oxidize the NH_4^+ in solution that is in equilibrium with Z-NH_4^+ to nitrate (NO_3^-), promoting NH_4^+ desorption. Cations present in the wastewater or chemicals added to supplement alkalinity losses in the system help to desorb NH_4^+ , therefore supplemental salt addition is not necessary. The process continues until the concentration of NH_4^+ adsorbed to the zeolite is very low. Prior studies have used this strategy to reduce TAN concentrations in wastewater to below inhibitory levels for biological treatment (Milan et al., 2003). He et al. (2007) showed that addition of zeolite powder to a sequencing batch reactor (SBR) treating municipal wastewater improved performance by controlling shock loads of TAN. Jung et al. (2004) achieved a total nitrogen (TN) removal efficiency of 82% by coupling NH_4^+ adsorption and bioregeneration with biological denitrification in a SBR. However, in both of these studies addition of fresh zeolite was required to compensate for zeolite losses during sludge wasting, which added to the overall cost of the process.

In a prior study in our laboratory (Chapter 4) the rate of NH_4^+ oxidation was increased by a factor of ~3 during nitrification of ADSW centrate by addition of the zeolite mineral, chabazite,

to a batch reactor. Although other zeolite minerals, such as clinoptilolite, have been used in prior bioregeneration studies, chabazite was used in this research due to its higher NH_4^+ exchange capacity (Langwaldt, 2008). In this paper, a process is presented for efficiently removing TN from ADSW centrate using a particulate chabazite amended SBR (chabazite-SBR) that includes aerobic and anoxic stages, as shown in Figure 5-1. In this process, chabazite is added only at the startup of the reactor at a dose capable of reducing the FA concentrations to below levels that inhibit nitrification. Once complete nitrification is achieved, an external electron donor is added and anoxic conditions are applied to promote denitrification. Decanting and biomass wasting rates are set in a way that controls the hydraulic and solids retention times (HRT and SRT). Particulate chabazite was used in this study so that it would not be lost from the system during decanting and biomass wasting stages, allowing its reuse over many cycles. The objectives of this study were to investigate the fate of nitrogen compounds during long-term treatment of ADSW centrate in a bench-scale chabazite-SBR, to investigate the effect of varying external electron donor dose on reactor performance and to investigate the effect of the process on IX efficiency of the zeolite material.

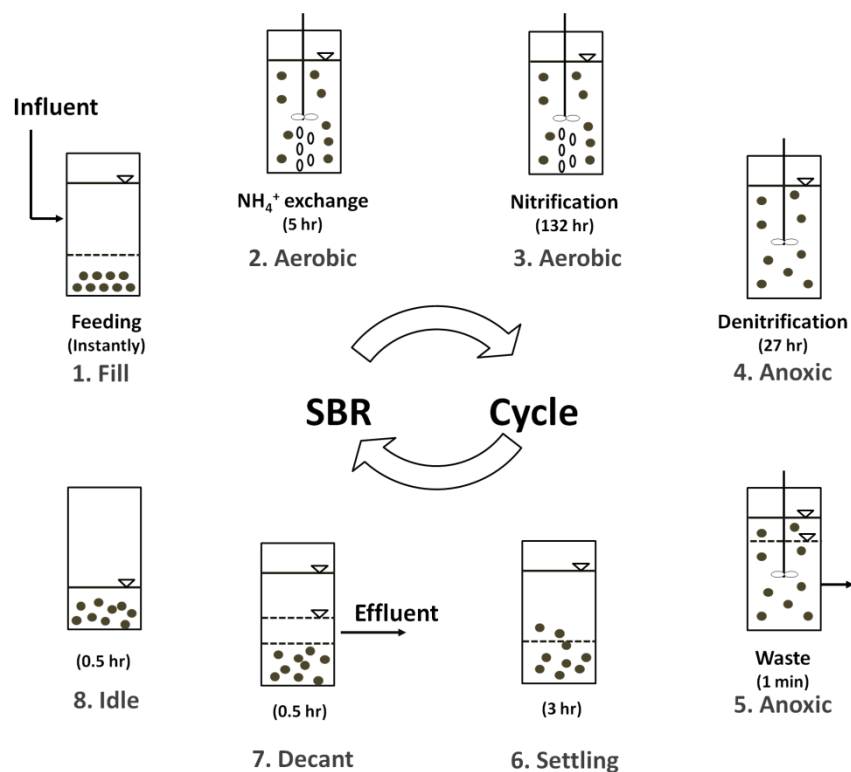


Figure 5-1. Schematic of chabazite-SBR operation showing stages over a 7-day cycle.

5.2. Materials and Methods

5.2.1. Anaerobically Digested Swine Waste Centrate

A pilot-scale (26 L) anaerobic digester supplied ADSW centrate for this study. The pilot digester was managed in our laboratory as a mesophilic (35 °C) semi-continuous batch reactor with a 21-day SRT. Swine manure was collected from a local pig farm and fed to the digester at a 5% total solids (TS) content three times per week. Additional details on pilot reactor operation can be found elsewhere (Amini, 2014). Effluent was collected from the digester and centrifuged at 3500 g for 15 minutes using a ThermoScientific Sorvall Legend RT Plus (Waltham, MA) centrifuge. Average characteristics of the ADSW centrate are provided in Table 5-1.

Table 5-1. Characteristics of ADSW centrate from the pilot-scale reactor.

Parameter	Unit	ADSW Centrate
NH ₄ ⁺	mg-N L ⁻¹	822 ± 123
Na ⁺	mg L ⁻¹	394 ± 100
K ⁺	mg L ⁻¹	684 ± 114
Ca ²⁺	mg L ⁻¹	477 ± 190
Mg ²⁺	mg L ⁻¹	258 ± 54
PO ₄ ³⁻	mg-P L ⁻¹	58 ± 9
TP	mg L ⁻¹	74 ± 11
TN	mg L ⁻¹	820 ± 91
pH		7.28 ± 0.2
Alkalinity	CaCO ₃ mg L ⁻¹	2,281 ± 449
sCOD	mg L ⁻¹	2,010 ± 500

5.2.2. Chabazite Preparation and Dose Calculation

Chabazite was obtained from St. Cloud Zeolite Company (Winston, New Mexico) and was sieved to obtain a particle size range of 1 - 2 mm. This particle size was selected based on a study by Mery et al. (2012), who observed that 1 mm zeolite particles provided a good surface for biofilm adhesion when used as biofilm carriers for nitrification (Mery et al., 2012). Chabazite was pretreated with local groundwater as described in Chapter 3. A single 200 g dose of the prepared chabazite was added to the reactor at start up. This dose was based on prior research (as described in Chapter 4), which showed that the chabazite used in this study had an NH₄⁺ adsorption capacity of 2.93 meq-N g⁻¹ (41 mg-N g-chabazite⁻¹) and that a dose of 150 g-

chabazite L^{-1} could reduce the concentration of FA in ADSW centrate below the inhibitory levels for nitrifying bacteria.

5.2.3. Chabazite-SBR

The bench-scale chabazite-SBR was constructed from acrylic tubing with an inner diameter of 15.24 cm, a height of 22.86 cm, an overall volume of 3 L and a working volume of 1.9 L. The reactor was operated in a controlled temperature room at 22°C with a 29-day SRT and 13.3-day HRT. The set SRT for this experiment is within the suggested range for BNR in a SBR system (Metcalf & Eddy 2003). Seed sludge was obtained from the Northwest Regional Water Reclamation Facility in Tampa, FL, which uses a 5-stage Bardenpho BNR Process. Seed sludge was added to achieve an initial mixed liquor volatile suspended solids (MLVSS) concentration of 4 g L^{-1} . Each 7-day cycle consisted of the following Stages (Figure 5-1): (1) fill, (2) NH_4^+ exchange - 5 hr, (3) aerobic react - 132 hr, (4) electron donor addition and anoxic react - 27 hr, (5) biomass wasting from the mixed liquor, (6) settle - 3 hr, (7) decant - 0.5 hr and (8) idle - 0.5 hr. During the fill stage, the system was fed manually by quickly pouring 1 L of the ADSW centrate described above into the reactor. During the NH_4^+ exchange and aerobic stages, aeration was supplied with a Whisper Tetra air pump (Blacksburg, VA) and stainless steel diffuser. Mixing was provided during the aerobic react, anoxic react and biomass wasting stages using a Standard-Mount Variable Speed Electric Mixer (McMaster-CARR[®], Robbinsville, NJ) with a T-blade attachment. Glucose was added as an electron donor manually at the beginning of the anoxic react stage according to the dosing rate describe below. The pH was controlled manually within a range of 7.0 and 8.0 by dropwise addition of 1 M $NaHCO_3$ or HCl, over the first 15 cycles. Biomass wasting was performed using a Cole-Parmer Masterflex L/S peristaltic pump (Vernon Hills, IL) connected to a port in the middle of the reactor. Treated effluent was decanted

by gravity after the settling stage by opening an ASCO RedHat-8210 solenoid valve (Marlton, NJ). A programmable controller (ChronTrol[®], San Diego, CA) was used to automatically control the aerator, mixer and solenoid valve during operation.

5.2.4. External Electron Donor Dose Studies

An initial dose of 3.38 g-COD L⁻¹ per cycle was calculated based on the stoichiometric requirements for removal of residual DO present after the aerobic stage and complete denitrification, assuming the ADSW centrate (Table 5-1) was fully nitrified. Glucose addition was subsequently adjusted to investigate the effect of external carbon source addition (as g-COD L⁻¹) on reactor performance according to the following (cycle #): 3.38 (1-17), 2.82 (18), 1.13 (19), 0.56 (20-25), 1.13 (26), 2.25 (27-28), 1.69 (29-34), 2.25 (35-36), and 2.82 (37-40). The effectiveness in TN removal for at least four consecutive cycles of 3.38, 2.82, 1.69, 0.56 g-COD L⁻¹ addition was evaluated.

5.2.5. Analytical Methods

Concentrations of nitrite (NO₂⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻), ammonium (NH₄⁺), calcium (Ca₂⁺), magnesium (Mg₂⁺), sodium (Na⁺) and potassium (K⁺) were measured using a Metrohm 881 Compact IC Pro (Herisau, Switzerland) ion chromatograph (IC Application No. C-115 and No. S-236). Method detection limits (MDLs) were 0.20, 0.01, 0.02, 0.07, 0.27, 0.20, 18.50, and 0.09 mg L⁻¹ for NO₂⁻, NO₃⁻, PO₄³⁻, NH₄⁺, Ca₂⁺, Mg₂⁺, Na⁺, and K⁺, respectively. Standard Methods (APHA et al. 2012) were used to measure: DO (4500-O), VSS (2540), pH (4500-H), alkalinity (2320), conductivity (2510), TN (4500-C), total phosphorous (4500-E) and soluble chemical oxygen demand (sCOD; 5220).

5.3. Results and Discussion

5.3.1. Overall Bioreactor Performance

The first nine cycles of the chabazite-SBR were considered a startup phase (data not shown); during this phase, reaction times for Stages 3 and 4 were adjusted until effluent NH_4^+ and NO_3^- concentrations $< 0.50 \text{ mg-N L}^{-1}$ were observed for three consecutive cycles. Influent, reactor (at time zero after dilution) and effluent TN concentrations beginning with cycle 10 are shown in Figure 5-2A. Influent and effluent sCOD and TP concentrations are shown in Figures 5-2B and 5-2C, respectively. Note that the influent COD values shown do not include glucose addition, which was done at the beginning of the anoxic stage. Effluent from the pilot-scale AD was somewhat variable due to variations in local weather conditions, resulting variable influent concentrations to the chabazite-SBR. Despite these variations, average TN, sCOD and TP removal efficiencies of 84%, 43% and 54% were achieved, respectively. TN and COD results were similar to those of Jung et al. (2004), who used a zeolite amended SBR process that required periodic addition of zeolite powder. TN, COD and TP removal efficiencies achieved in this study were higher than results from Deng et al. (2008), who treated ADSW centrate in a conventional BNR system without supplementary organic carbon addition. The low TN (50%) and sCOD (10%) removals achieved by Deng et al. (2008) were likely due to low rbCOD concentrations in the AD effluent. In a prior study in our laboratory, Kinyua et al. (2014) showed that even though sCOD concentrations in ADSW are high, the rbCOD fraction was not sufficient to support complete denitrification. In applications where a chabazite-SBR is used to treat wastewater that is high in both TAN and rbCOD, the reactor could be operated with an initial anoxic stage to utilize the influent COD and reduce supplemental organic carbon addition. The TP removal observed may have been due to precipitation of phosphate minerals or enhanced

biomass P uptake (Huang et al., 2014; Son et al., 2000). In a prior study in our laboratory, (Lin, 2012) reported significant precipitation of amorphous calcium phosphate and struvite from ADSW centrate during storage under aerobic conditions. However, further testing is needed to identify TP mechanisms in the chabazite-SBR system.

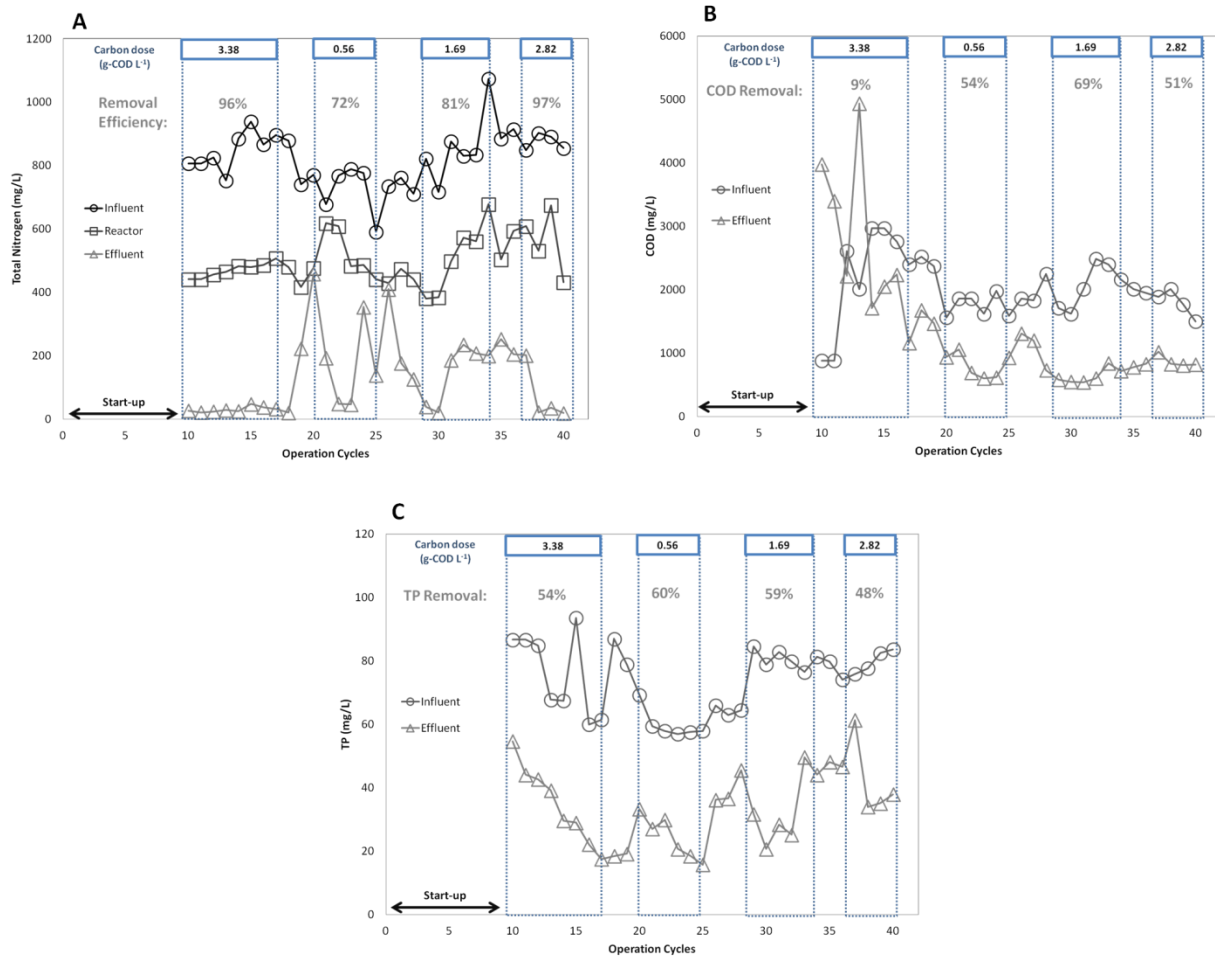


Figure 5-2. Influent and effluent concentrations of (A) TN, (B) sCOD and (C) TP during chabazite-SBR operation. Note that reactor TN (after dilution) is also shown in 5A.

Average influent and effluent alkalinity concentrations were 2,220 (± 200) and 480 (± 214) $\text{mg-CaCO}_3 \text{L}^{-1}$, respectively (Figure 5-3). An alkalinity deficit of approximately 10% was

initially predicted based on the influent characteristics and the stoichiometric requirements for nitrification. During the startup phase, NaHCO_3 was added to maintain the pH range between 7.0 and 8.0. However, after cycle 10, NaHCO_3 addition was significantly reduced and was eliminated after cycle 15. This was most likely due to simultaneous nitrification-denitrification (SND) occurring in the biofilm surrounding the chabazite particles (discussed in more detail below), since alkalinity generated by denitrification compensates for alkalinity losses due to nitrification in this process (Sun et al., 2010).

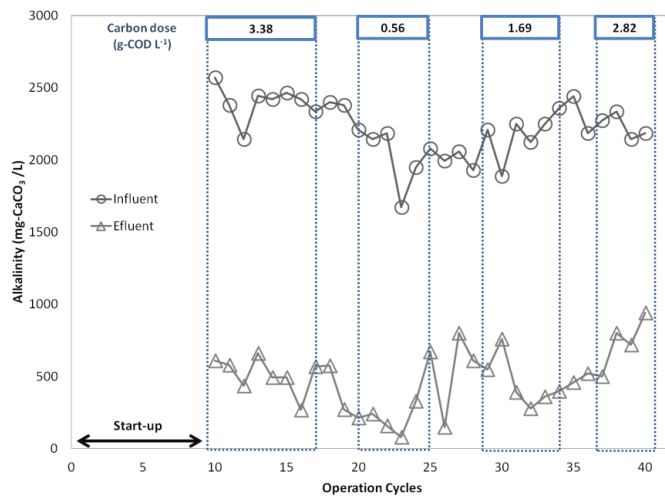


Figure 5-3. Influent and effluent alkalinity concentrations during chabazite-SBR operation.

Chabazite is naturally loaded with Na^+ and during NH_4^+ exchange, Na^+ is released into solution. This is a concern because an increase in Na^+ concentrations can also cause nitrification inhibition (Rosa, 1997; Sanchez et al., 2004). In addition to NH_4^+ , other cations are exchanged, with the order of affinity (preference) reported as: $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ (Hedstrom,

2001). Average concentrations of Na⁺ and K⁺ before and after IX are shown in Figure 5-4. The data were divided to show the adsorption and desorption trends during the initial (5-4A shows cycles 11-16) and final (5-4B shows cycles 36-40) cycles of operation. As expected, Na⁺ was desorbed during the initial cycles of reactor operation, resulting in an average effluent Na⁺ concentration of 828 (± 251) mg L⁻¹ (37 ± 2 meq L⁻¹). However, after the reactor had been operated for a number of cycles, the Na⁺ initially present in the zeolite was flushed out of the reactor. During cycles 36-40, the average effluent Na⁺ concentration was 432 ± 40 mg L⁻¹ (16 ± 0.8 meq L⁻¹). In the case of K⁺, the cation was removed during initial cycles, while during the final cycles of operation, K⁺ increased after the IX stage and then decreased after bioregeneration. The dynamics of Na⁺ and K⁺ during the operating cycle are consistent with NH₄⁺ exchange followed by bioregeneration. Na⁺ and K⁺ are initially released to the solution when NH₄⁺ is adsorbed and then re-adsorbed when NH₄⁺ is desorbed and oxidized to NO₃⁻.

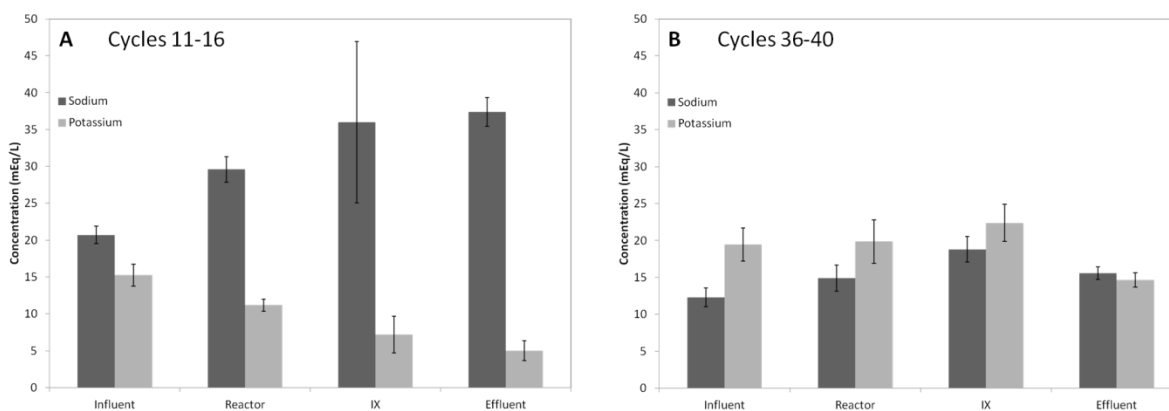


Figure 5-4. Concentrations of Na⁺ and K⁺ before and after IX for cycles towards the (A) initial and (B) final phases of chabazite-SBR operation.

5.3.2. Fate of Nitrogen During a Typical Operating Cycle

Changes in N species (NH_4^+ , NO_3^- , and NO_2^-) concentrations during treatment of ADSW centrate throughout one cycle of the chabazite-SBR are shown in Figure 5-5. Data presented in this figure represent the average concentrations for the last three cycles of chabazite-SBR operation. During these experiments, the external organic carbon dose supplied at the beginning of the anoxic cycle was $2.82 \text{ g-COD L}^{-1}$. The initial NH_4^+ concentration decreased by approximately 82% during the first 5 hours of operation due to dilution of the feed with MLSS remaining in the reactor from the previous cycle (~50%) and IX. After 24 hr, the NH_4^+ concentration decreased to 3.73 mg-N L^{-1} and was below detection limits for the rest of the operation. Despite the low aqueous NH_4^+ concentrations, NO_3^- was produced over the 5.7-day aerobic stage due to desorption of NH_4^+ and nitrification (i.e. bioregeneration). NO_3^- production was approximately linear at a rate of $0.43 (\pm 0.04) \text{ mg-N g-VSS}^{-1} \text{ hr}^{-1}$, which was similar to prior studies treating high TAN wastewaters (Carrera et al., 2003). After aeration was ended and the external carbon source was supplied, NO_3^- concentrations decreased at a rate of $1.49 (\pm 0.26) \text{ mg-N g-VSS}^{-1} \text{ hr}^{-1}$, which was 2.3 times higher than the rate reported by Carrera et al. (2003). The final NO_3^- and NO_2^- concentrations were 0.14 and 5.48 mg-N L^{-1} , respectively. An overall TN removal efficiency of 97% was obtained during these three operational cycles.

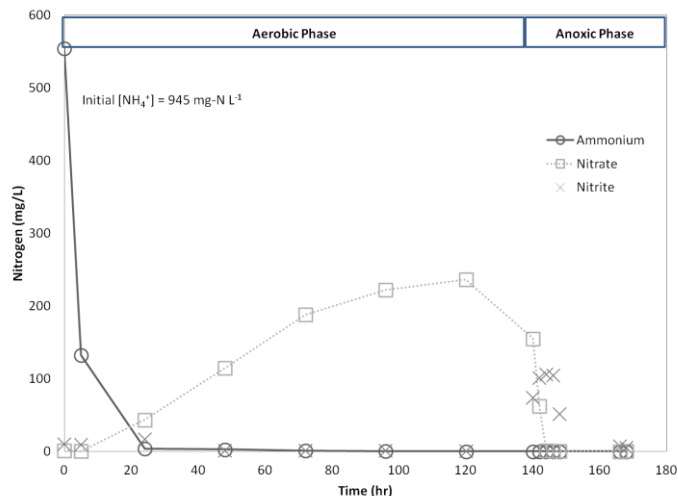


Figure 5-5. Nitrogen profile during a cycle operation in the chabazite-SBR.

A mass balance on N production over a cycle showed that NO_3^- -N produced during the aerobic stages was only 29% of the initial N added to the reactor (i.e. 71% TN removal during Stages 1 and 2). Significant N losses due to FA volatilization were unlikely due to the near neutral pH (7.0 – 8.0) and low liquid phase TAN concentrations in the reactor. Low FA volatilization has been observed by other researchers using zeolites for treatment of high TAN strength wastewaters (Espécie Bueno et al., 2015). Another explanation for the low observed NO_3^- production is the occurrence of simultaneous nitrification-denitrification (SND), which is favored by the presence of readily biodegradable COD (rbCOD) and anoxic zones in the reactor (Daigger & Littleton, 2014). During operation of chabazite-SBR, biofilm coated zeolite particles were observed at the bottom of the SBR, as shown in the photograph in Figure 5-6. Although aerobic conditions existed in the outer layers of the biofilm during Stages 1 and 2 (bulk DO concentrations were 5.5 – 6.0 mg L⁻¹) it is likely that anoxic conditions developed within the biofilm, favoring SND (Rahimi et al., 2011). rbCOD present in the ADSW or carry-over of

external organic substrate from the previous cycle most likely provided the electron donor for this process. He et al. (2007) reported that addition of zeolite powder to an SBR favored the formation of large granular sludge with anoxic zones, resulting in 38% TN removal during the nitrification stage. The higher TN removals observed during the aerobic stage in our study may have been due to the larger zeolite particles or the higher rbCOD/TN ratio during the aerobic stage.

A number of BNR processes have been developed over the last decade where NH_4^+ is transformed to N_2 with reduced oxygen and organic substrate requirements, such as shortcut nitrogen removal (Peng & Zhu, 2006) and the nitrification-anammox process (Fux et al., 2002). Those pathways are advantageous because of the decreased operational costs compared with conventional BNR. However, they require strict control of operating parameters such as pH, DO and SRT (Sun et al., 2010). In contrast, the chabazite-SBR presented in this research provided efficient TN removal without strict operational controls, which may be advantageous in on-farm operations.

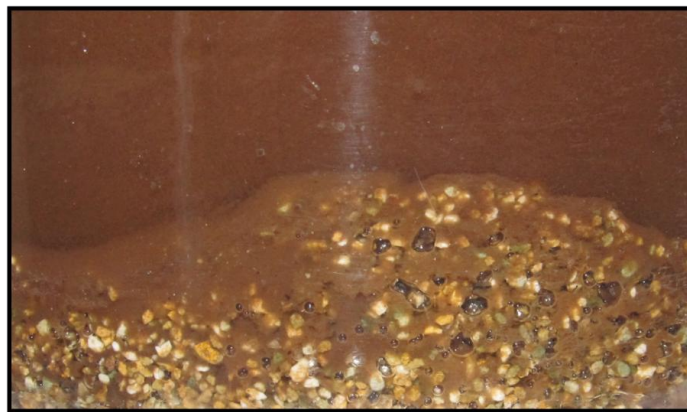


Figure 5-6. Photograph of the chabazite-SBR during the aerobic stage showing zeolite material settling despite mixing.

5.3.3. External Electron Donor Dose Studies

To investigate the effect of external carbon source addition on nitrification and denitrification in the chabazite-SBR, the glucose dose was decreased from 3.38 to 0.56 g-COD L⁻¹ in stages, and then increased to 1.69 and finally 2.82 g-COD L⁻¹. Average NO₃⁻ and NO₂⁻ concentrations after the nitrification (Stage 3) and denitrification stages (Stage 7) for each carbon dose (based on at least 4 consecutive cycles) are summarized in Figure 5-7. TN removal efficiencies of 96, 97, 81, and 72% were achieved at external carbon doses of 3.38, 2.82, 1.69, and 0.56, g-COD L⁻¹, respectively (Figure 5-2A). Average COD/N ratios of 4.0 (± 0.29), 3.2 (± 0.10), 2.0 (± 0.25), and 0.8 (± 0.09) g-COD g-N⁻¹ were calculated for the different external carbon source additions. Maximum TN removals were observed at an average COD/N ratio of 3.2 g-COD g-N⁻¹ (corresponding to external carbon addition of 2.82 g-COD L⁻¹), which is close to the theoretical required COD/N ratio of 2.86. As the external carbon dose was decreased, there were increases in NO₃⁻ concentration in the effluent due to incomplete denitrification. However, effluent NO₂⁻ concentrations increased with increasing carbon dose, except at the dose of 3.38 g-COD L⁻¹. This shows that the reduction of NO₃⁻ to NO₂⁻, which corresponds to the first reaction step of denitrification, is occurring at a faster rate. For the carbon dose of 3.38 g-COD L⁻¹, due to the excess in carbon, it promotes a complete denitrification with faster rate in both reaction steps. COD removals of 9, 51, 69, and 54% were observed at carbon doses of 3.82, 2.82, 1.69, and 0.56 g-COD L⁻¹, respectively (Figure 5-2B). Lower COD removals were observed at higher external organic carbon doses, indicating that carry-over of COD likely interfered with degradation of slowly biodegradable COD (sbCOD) present in the ADSW during the aerobic stages. The results show that organic carbon dosing needs to be carefully controlled in this process if stringent effluent TN and BOD₅ requirements need to be met.

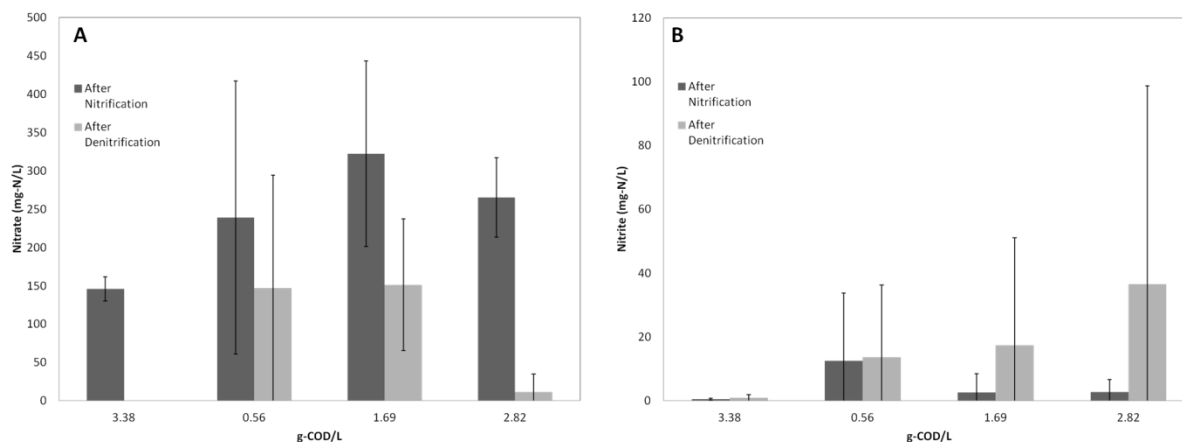


Figure 5-7. Concentrations of (A) NO_3^- and (B) NO_2^- after nitrification and denitrification during chabazite-SBR operation.

5.3.4. Effectiveness of Ammonium Exchange

NH_4^+ concentrations at the beginning and end of Stage 2 (IX) are shown in Figure 5-8. NH_4^+ removal efficiencies during IX were calculated from these data and are also shown in Figure 5-8. The average NH_4^+ -N concentration after the IX stage was $139 (\pm 40) \text{ mg-N L}^{-1}$. Calculated FA concentrations after Stage 2 were maintained below 7.69 mg-N L^{-1} throughout the experiment. These results show that the proposed chabazite-SBR process could maintain FA concentrations below the level shown to inhibit nitrification (Chapter 4). Over 40 cycles of operation, an average NH_4^+ removal efficiency during the IX stage of 82% was achieved, with no decreasing trend in regeneration efficiency over time. In the system, the nitrification rate was $2.40 \text{ mg-N L}^{-1} \text{ hr}^{-1}$, therefore only 1.3% of NH_4^+ removal could be attributed to biological nitrification during the first five hours. These results show that in contrast to prior studies (He et al., 2007; Jung et al., 2004; Wei et al., 2011), additional zeolite was not required to maintain the IX efficiency in the chabazite-SBR over forty weeks of operation.

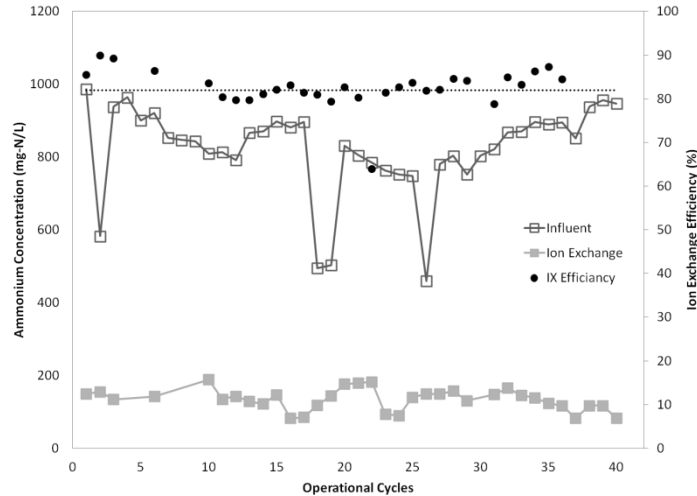


Figure 5-8. Bioregeneration efficiency during 40 cycles of chabazite-SBR operation.

5.4. Conclusions

The goal of this research was to develop a process that could efficiently remove TN from ADSW centrate using a particulate chabazite amended SBR that included aerobic and anoxic stages. Long-term experiments were conducted with a bench-scale chabazite-SBR. An overall TN removal efficiency of 84% was achieved, with specific nitrification and denitrification rates of 0.43 and 1.49 mg-N g-VSS⁻¹ hr⁻¹, respectively. A TP removal efficiency of 54% was achieved, most likely due to precipitation of P minerals and biomass uptake. Based on an N species mass balance, SND appeared to be occurring in the biofilm surrounding the chabazite particles, resulting in improved TN removal and alkalinity control. The effectiveness in TN and COD removal was dependent on the external organic carbon dose added at the beginning of the denitrification stage, with a COD/N ratio of 3.2 g-COD g-N⁻¹ resulting in both high TN (97%) and COD (51%) removal efficiencies. The IX stage was able to reduce FA concentrations to below the inhibitory level for nitrification inhibition over 40 chabazite-SBR cycles with no loss

in IX efficiency over time and no fresh zeolite added to the reactor. The results indicate that bioregeneration efficiency did not decrease over time and that chabazite was not lost during biomass wasting or decanting stages. The chabazite-SBR was shown to work well for treatment of high NH_4^+ strength wastewaters without requiring strict control of operational parameters.

CHAPTER 6

CONCLUSIONS

Anaerobic digestion (AD) has been shown to be an effective technique for energy recovery and treatment of livestock wastes, municipal sludges and industrial wastewaters. However, further treatment is required to remove nitrogen from AD effluents to avoid detriments to surface and ground waters. The high free ammonia (FA) concentrations present in AD effluents can inhibit nitrification processes in conventional biological nitrogen removal (BNR) systems. The overall goal of this research was to develop a process for removal of nitrogen from AD swine waste (ADSW) effluent. The proposed solution was to incorporate particulate chabazite, which has a high cation exchange capacity, into a sequencing batch reactor (SBR) to adsorb ammonium and therefore ease nitrification inhibition. The process developed is called a chabazite-SBR. The research was divided in three parts; their corresponding research questions, objectives and major findings were:

1. How does chabazite pretreatment with groundwater (GW) affects the kinetics and cation exchange capacity during NH_4^+ uptake? (Chapter 3)

- *Objective 1: Investigate changes in zeolite composition after GW pretreatment.*

GW pretreatment did not affect chabazite structure; however, Na^+ was the main cation in the chabazite composition that was decreased.

- *Objective 2: Determine if there is an enhancement in the kinetics and exchange capacity with GW pretreatment when compared with other common pretreatment practices.*

The exchange capacity was slightly higher for GW pretreated chabazite compared with the other common pretreatment strategies; however, this enhancement was not significant. The kinetics of NH_4^+ uptake during the first four hours of contact significantly improved when pretreatment of GW was performed compared with other common pretreatment strategies. This was caused by an enhancement in film diffusion mechanisms

The findings of this first part of the research were important because it was shown that NaCl pretreatment is not needed to improve the kinetics and cation exchange capacity of chabazite. A benefit of using GW for pretreatment is that less Na^+ is exchanged, lessening the negative effect of Na^+ inhibition on nitrification when used in a biological process.

2. How does addition of chabazite to ADSW centrate affect nitrification rates? (Chapter 4)

- *Objective 1: Determine the chabazite dose and contact time needed to ease FA inhibition.*

For the mixed liquor tested in this study, NH_4^+ concentrations must be maintained below 200 mg-N L^{-1} to relieve nitrification inhibition. Treatment of ADSW centrate with an initial NH_4^+ concentration of $1,000 \text{ mg-N L}^{-1}$ requires a chabazite dose of 150 g L^{-1} to ease FA inhibition of nitrification.

- *Objective 2: Determine the effectiveness of chabazite addition in reducing nitrification inhibition during treatment of ADSW centrate.*

The rate of nitrification increased by approximately a factor of 3 when chabazite was added to a batch reactor treating high NH_4^+ strength wastewater. However, Na^+ release from the chabazite also plays a role in nitrification inhibition.

The findings of this part of the research showed the potential for using chabazite for overcoming FA inhibition of nitrification during treatment of high NH_4^+ strength wastewater. Results were used in the design the chabazite-SBR.

3. How effective is the chabazite-SBR in removing total nitrogen concentrations from ADSW centrate? (Chapter 5)

- *Objective 1: Investigate the fate of nitrogen compounds in a chabazite-SBR during treatment of ADSW centrate.*

The chabazite-SBR process achieved stable TN removal from ADSW centrate during the 40 weeks of operation. Simultaneous nitrification-denitrification reduced alkalinity requirements.

- *Objective 2: Investigate the effect of varying external electron donor dose on reactor performance.*

Addition of an external organic carbon source at a rate of $3.2 \text{ g-COD g-N}^{-1}$ resulted in maximum TN removal. An overall TN removal efficiency of 84% was achieved, with specific nitrification and denitrification rates of 0.43 and $1.49 \text{ mg-N g-VSS}^{-1} \text{ hr}^{-1}$, respectively.

- *Objective 3: Investigate IX efficiency of the zeolite material in the chabazite-SBR.*

The IX stage of the chabazite-SBR was able to reduce FA concentrations to below the inhibitory level for nitrification inhibition over 40 chabazite-SBR cycles with no loss in IX efficiency over time and no fresh zeolite added to the reactor. In addition, bioregeneration efficiency did not decrease over time and chabazite was not lost during biomass wasting or decanting stages.

The chabazite-SBR developed in this research was efficient in removing TN and other pollutants (TP and COD) from ADSW centrate. Chemical addition requirements for pH control,

alkalinity and carbon source were reduced compared with conventional BNR making the process more-cost effective. This system was shown to work well for treatment of high strength NH_4^+ wastewaters without requiring strict control of operational parameters, which is required in other side-stream treatment processes, such as SHARON-Anammox. The chabazite-SBR operated at a high SRT that results in prolonged aeration, increasing energy consumption; further research is needed to reduce the SRT. Also, further research should be performed in increasing the loading rate for this process.

REFERENCES

- Alberti, G., Amendola, V., Pesavento, M., Biesuz, R. 2012. Beyond the synthesis of novel solid phases: Review on modelling of sorption phenomena. *Coordination Chemistry Reviews*, **256**(1–2), 28-45.
- Alshameri, A., Ibrahim, A., Assabri, A.M., Lei, X., Wang, H., Yan, C. 2014. The investigation into the ammonium removal performance of Yemeni natural zeolite: Modification, ion exchange mechanism, and thermodynamics. *Powder Technology*, **258**(0), 20-31.
- Amini, A. 2014. Sustainable Energy and Nutrient Recovery from Swine Waste, University of South Florida.
- Andronikashvili, T.G.F.L.D.K.G.N.T.G.V. 1992. *Natural zeolites*. Ellis Horwood Limited, Chichester.
- Anthonisen, A.C., Loehr, R.C., Prakasam, T.B.S., Srinath, E.G. 1976. Inhibition of Nitrification by Ammonia and Nitrous Acid. *Journal (Water Pollution Control Federation)*, **48**(5), 835-852.
- Antileo, C., Aspé, E., Urrutia, H., Zaror, C., Roeckel, M. 2002. Nitrifying Biomass Acclimation to High Ammonia Concentration. *Journal of Environmental Engineering*, **128**(4), 367-375.
- APHA, AWWA, and WEF. (2012). Standard Methods for the Examination of Water and Wastewater, 22nd ed. American Public Health Association, Washington, DC.
- Aponte-Morales, V., Payne, K., Cunningham, J., Ergas, S.J. 2014. Use of Chabazite to Overcome Ammonia Inhibition During Nitrification of High Strength Wastewater. *Proceedings of the Water Environment Federation*, **2014**(9), 1431-1442.
- Bazin, M.J., Rutili, A., Gaines, A., Lynch, J.M. 1991. Humic acid relieves pH-inhibition of nitrification in continuous-flow columns. *FEMS Microbiology Letters*, **85**(1), 9-14.
- Boiran, B., Couton, Y., Germon, J.C. 1996. Nitrification and denitrification of liquid lagoon piggery waste in a biofilm infiltration-percolation aerated system (BIPAS) reactor. *Bioresource Technology*, **55**(1), 63-77.
- Boyer, T.H. 2014. 3.10 - Physical–Chemical Processes for Nitrogen Removal. in: *Comprehensive Water Quality and Purification*, (Ed.) S. Ahuja, Elsevier. Waltham, pp. 163-195.
- Bowman, A., Mueller, K., and Smith, M. (2000). Increased animal waste production from concentrated animal feeding operation: Potential implications for public and environmental health. Rep. No. 2-2000. Nebraska Center for Rural Health Research, Omaha, N.E.
- Brown, A.M. 2001. A step-by-step guide to non-linear regression analysis of experimental data using a Microsoft Excel spreadsheet. *Computer Methods and Programs in Biomedicine*, **65**(3), 191-200.
- Cantrell, K.B., Ducey, T., Ro, K.S., Hunt, P.G. 2008. Livestock waste-to-bioenergy generation opportunities. *Bioresource Technology*, **99**(17), 7941-7953.

- Carrera, J., Jubany, I., Carvallo, L., Chamy, R., Lafuente, J. 2004. Kinetic models for nitrification inhibition by ammonium and nitrite in a suspended and an immobilised biomass systems. *Process Biochemistry*, **39**(9), 1159-1165.
- Choi, E. 2007. *Piggery waste management: Towards a sustainable future*. IWA Publishing.
- Colella, C. 1999. Environmental Applications of Natural Zeolitic Materials Based on Their Ion Exchange Properties. in: *Natural Microporous Materials in Environmental Technology*, (Eds.) P. Misaelides, F. Macásek, T.J. Pinnavaia, C. Colella, Vol. 362, Springer Netherlands, pp. 207-224.
- Costa, R.D., Tavares, C.R.G., Cossich, E.S. 2007. Stabilization of Swine Wastes by Anaerobic Digestion. *Environmental Technology*, **28**(10), 1145-1151.
- Cyrus, J.S., Reddy, G.B. 2011. Sorption and desorption of ammonium by zeolite: Batch and column studies. *Journal of Environmental Science and Health, Part A*, **46**(4), 408-414.
- Daigger, G.T., Littleton, H.X. 2014. Simultaneous Biological Nutrient Removal: A State-of-the-Art Review. *Water Environment Research*, **86**(3), 245-257.
- Deng, L.-W., Zheng, P., Chen, Z.-A. 2006. Anaerobic digestion and post-treatment of swine wastewater using IC-SBR process with bypass of raw wastewater. *Process Biochemistry*, **41**(4), 965-969.
- Deng, L., Zheng, P., Chen, Z., Mahmood, Q. 2008. Improvement in post-treatment of digested swine wastewater. *Bioresource Technology*, **99**(8), 3136-3145.
- Dosta, J., Rovira, J., Galí, A., Macé, S., Mata-Álvarez, J. 2008. Integration of a Coagulation/Flocculation step in a biological sequencing batch reactor for COD and nitrogen removal of supernatant of anaerobically digested piggery wastewater. *Bioresource Technology*, **99**(13), 5722-5730.
- Erdoğan, B.C., Ülkü, S. 2011. Ammonium sorption by Gördes clinoptilolite rich mineral specimen. *Applied Clay Science*, **54**(3-4), 217-225.
- Espécie Bueno, S.C., Filho, M.B., de Almeida Jr, P.S.G., Polidoro, J.C., Olivares, F.L., Stel, M.S., Vargas, H., Mota, L., da Silva, M.G. 2015. Cuban zeolite as ammonium carrier in urea-based fertilizer pellets: Photoacoustic-based sensor for monitoring N-ammonia losses by volatilization in aqueous solutions. *Sensors and Actuators B: Chemical*, **212**, 35-40.
- Farag, A.M., Harper, D.D. 2014. A review of environmental impacts of salts from produced waters on aquatic resources. *International Journal of Coal Geology*, **126**(0), 157-161.
- Federal Register. (2008). 73(No. 225: November 20), 70418.
- Feng, C., Shimada, S., Zhang, Z., Maekawa, T. 2008. A pilot plant two-phase anaerobic digestion system for bioenergy recovery from swine wastes and garbage. *Waste Management*, **28**(10), 1827-1834.
- Foo, K.Y., Hameed, B.H. 2010. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, **156**(1), 2-10.
- Fux, C., Boehler, M., Huber, P., Brunner, I., Siegrist, H. 2002. Biological treatment of ammonium-rich wastewater by partial nitrification and subsequent anaerobic ammonium oxidation (anammox) in a pilot plant. *Journal of Biotechnology*, **99**(3), 295-306.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J. 2003. The Nitrogen Cascade. *BioScience*, **53**(4), 341-356.
- Green, M., Mels, A., Lahav, O. 1996. Biological-ion exchange process for ammonium removal from secondary effluent. *Water science and technology*, **34**(1-2), 449-458.

- Guan, T.Y., Holley, R.A. 2003. Pathogen Survival in Swine Manure Environments and Transmission of Human Enteric Illness—A Review Sponsoring organizations: Manitoba Livestock Manure Management Initiative and Manitoba Rural Adaptation Council. *J. Environ. Qual.*, **32**(2), 383-392.
- Guo, X., Zeng, L., Jin, X. 2013. Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite. *Journal of Environmental Sciences*, **25**(5), 954-961.
- Hatfield, J., Brumm, M., Melvin, S. 1998. Swine manure management. *Agricultural uses of municipal, animal, and industrial byproducts*, **44**, 78-90.
- He, S.-b., Xue, G., Kong, H.-n., Li, X. 2007. Improving the performance of sequencing batch reactor (SBR) by the addition of zeolite powder. *Journal of Hazardous Materials*, **142**(1-2), 493-499.
- Hedstrom, A. 2001. Ion Exchange of Ammonium in Zeolites: A Literature Review. *Journal of Environmental Engineering*, **127**(8), 673-681.
- Hedström, A., Amofah, L.R. 2008. Adsorption and desorption of ammonium by clinoptilolite adsorbent in municipal wastewater treatment systems. *Journal of Environmental Engineering & Science*, **7**(1), 53-61.
- Hellinga, C., Schellen, A.A.J.C., Mulder, J.W., van Loosdrecht, M.C.M., Heijnen, J.J. 1998. The sharon process: An innovative method for nitrogen removal from ammonium-rich waste water. *Water Science and Technology*, **37**(9), 135-142.
- Huang, H., Xiao, D., Pang, R., Han, C., Ding, L. 2014. Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization. *Chemical Engineering Journal*, **256**(0), 431-438.
- Inglezakis, V.J., Diamandis, N.A., Loizidou, M.D., Grigoropoulou, H.P. 1999. Effect of Pore Clogging on Kinetics of Lead Uptake by Clinoptilolite. *Journal of Colloid and Interface Science*, **215**(1), 54-57.
- Irvine, R.L., Busch, A.W. 1979. Sequencing Batch Biological Reactors: An Overview. *Journal (Water Pollution Control Federation)*, **51**(2), 235-243.
- Jha, V.K., Hayashi, S. 2009. Modification on natural clinoptilolite zeolite for its NH₄⁺ retention capacity. *Journal of Hazardous Materials*, **169**(1-3), 29-35.
- Jin, R.-C., Yang, G.-F., Yu, J.-J., Zheng, P. 2012. The inhibition of the Anammox process: A review. *Chemical Engineering Journal*, **197**(0), 67-79.
- Jorgensen, T.C., Weatherley, L.R. 2003. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Research*, **37**(8), 1723-1728.
- Jung, J.-Y., Chung, Y.-C., Shin, H.-S., Son, D.-H. 2004. Enhanced ammonia nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research*, **38**(2), 347-354.
- Jung, J.-Y., Pak, D., Shin, H.-S., Chung, Y.-C., Lee, S.-M. 1999. Ammonium exchange and bioregeneration of bio-flocculated zeolite in a sequencing batch reactor. *Biotechnology Letters*, **21**(4), 289-292.
- Katz B., Crandall C. A., Metz P. A., McBride W. S., and Berndt M. P. (2007). Chemical characteristics, water sources and pathways, and age distribution of ground water in the contributing recharge area of a Public-Supply Well near Tampa, Florida, 2002-05. USGS Scientific Investigative report 2007-5139, Reston, VA.

- Karakashev, D., Schmidt, J.E., Angelidaki, I. 2008. Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure. *Water Research*, **42**(15), 4083-4090.
- Karmen, M., Nataša Zabukovec, L., Mario, Š., Anamarija, F. 2013. Natural Zeolites in Water Treatment – How Effective is Their Use.
- Key, N., McBride, W., Ribaud, M., and Sneeringer, S. (2011). Trends and developments in hog manure management: 1998-2009. Rep. No. EIB-81. U.S. Department of Agriculture, Economic Research Service, Washington, D.C.
- Kim, Y.M., Park, D., Lee, D.S., Park, J.M. 2008. Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment. *Journal of Hazardous Materials*, **152**(3), 915-921.
- Kinyua, M.N., Cunningham, J., Ergas, S.J. 2014. Effect of solids retention time on the bioavailability of organic carbon in anaerobically digested swine waste. *Bioresource Technology*, **162**(0), 14-20.
- Kleiner, D. 1985. Bacterial ammonium transport. *FEMS Microbiology Letters*, **32**(2), 87-100.
- Koon, J.H., Kaufman, W.J. 1975. Ammonia Removal from Municipal Wastewaters by Ion Exchange. *Journal (Water Pollution Control Federation)*, **47**(3), 448-465.
- Kunz, A., Miele, M., Steinmetz, R.L.R. 2009. Advanced swine manure treatment and utilization in Brazil. *Bioresource Technology*, **100**(22), 5485-5489.
- Lahav, O., Green, M. 2000. Bioregenerated ion-exchange process: The effect of the biofilm on ion-exchange capacity and kinetics. *Water S.A.*, **26**(1), 51-57.
- Lahav, O., Schwartz, Y., Nativ, P., Gendel, Y. 2013. Sustainable removal of ammonia from anaerobic-lagoon swine waste effluents using an electrochemically-regenerated ion exchange process. *Chemical Engineering Journal*, **218**, 214-222.
- Langwaldt, J. 2008. Ammonium removal from water by eight natural zeolites: A comparative study. *Separation science and technology*, **43**(8), 2166-2182.
- Leyva-Ramos, R., Monsivais-Rocha, J.E., Aragon-Piña, A., Berber-Mendoza, M.S., Guerrero-Coronado, R.M., Alonso-Davila, P., Mendoza-Barron, J. 2010. Removal of ammonium from aqueous solution by ion exchange on natural and modified chabazite. *Journal of Environmental Management*, **91**(12), 2662-2668.
- Li, B., Wu, G. 2014. Effects of Sludge Retention Times on Nutrient Removal and Nitrous Oxide Emission in Biological Nutrient Removal Processes. *International Journal of Environmental Research and Public Health*, **11**(4), 3553.
- Liang, Z., Ni, J. 2009. Improving the ammonium ion uptake onto natural zeolite by using an integrated modification process. *Journal of Hazardous Materials*, **166**(1), 52-60.
- Lin, A.Y. 2012. Precipitation of Phosphate Minerals from Effluent of Anaerobically Digested Swine Manure.
- Lin, L., Lei, Z., Wang, L., Liu, X., Zhang, Y., Wan, C., Lee, D.-J., Tay, J.H. 2013. Adsorption mechanisms of high-levels of ammonium onto natural and NaCl-modified zeolites. *Separation and Purification Technology*, **103**(0), 15-20.
- Lin, L., Wan, C., Lee, D.-J., Lei, Z., Liu, X. 2014. Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite. *Separation and Purification Technology*, **133**(0), 351-356.
- Ling, J., Chen, S. 2005. Impact of organic carbon on nitrification performance of different biofilters. *Aquacultural Engineering*, **33**(2), 150-162.

- Long, T.R., Wang, X.D. 2006. Review of biological treatment of hypersaline wastewater. *Journal of Central South University of Technology*, **13**, 195-197.
- Maas, E. 1993. Testing crops for salinity tolerance. *Proc. Workshop on Adaptation of Plants to Soil Stresses*. p. pp. 247.
- Mace, S., Mata Alvarez, J. 2002. Utilization of SBR technology for wastewater treatment: An overview. *Industrial & engineering chemistry research*, **41**(23), 5539-5553.
- Martinelle, K., Westlund, A., Häggström, L. 1996. Ammonium ion transport—a cause of cell death. *Cytotechnology*, **22**(1-3), 251-254.
- Massé, D.I., Talbot, G., Gilbert, Y. 2011. On farm biogas production: A method to reduce GHG emissions and develop more sustainable livestock operations. *Animal Feed Science and Technology*, **166–167**(0), 436-445.
- Mery, C., Guerrero, L., Alonso Gutierrez, J., Figueroa, M., Lema, J.M. 2012. Evaluation of natural zeolite as microorganism support medium in nitrifying batch reactors: Influence of zeolite particle size. *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering*, **47**(3), 420-427.
- Metcalf & Eddy. (2003). *Wastewater engineering: Treatment and reuse*, 4th ed. McGraw-Hill, Boston.
- Milan, Z., Villa, P., Sanchez, E., Montalvo, S., Borja, R., Ilangovan, K., Briones, R. 2003. Effect of natural and modified zeolite addition on anaerobic digestion of piggery waste. *Water Science and Technology*, **48**(6), 263-269.
- Montalvo, S., Guerrero, L., Borja, R., Sanchez, E., Milan, Z., Cortes, I., de la la Rubia, M.A. 2012. Application of natural zeolites in anaerobic digestion processes: A review. *Applied Clay Science*, **58**, 125-133.
- Moussavi, G., Talebi, S., Farrokhi, M., Sabouti, R.M. 2011. The investigation of mechanism, kinetic and isotherm of ammonia and humic acid co-adsorption onto natural zeolite. *Chemical Engineering Journal*, **171**(3), 1159-1169.
- Obaja, D., Mace, S., Costa, J., Sans, C., Mata Alvarez, J. 2003. Nitrification, denitrification and biological phosphorus removal in piggery wastewater using a sequencing batch reactor. *Bioresource Technology*, **87**(1), 103-111.
- Oleszkiewicz, J.A., Barnard, J.L. 2006. Nutrient Removal Technology in North America and the European Union: A Review. *Water Quality Research Journal of Canada*, **41**(4), 449-462.
- Onnis-Hayden, A., Gu, A.Z. 2008. Comparisons of organic sources for denitrification: biodegradability, denitrification rates, kinetic constants and practical implication for their application in WWTPs. *Proceedings of the Water Environment Federation*, **2008**(17), 253-273.
- Park, S.J., Sool Lee, H., Il Yoon, T. 2002. The evaluation of enhanced nitrification by immobilized biofilm on a clinoptilolite carrier. *Bioresource Technology*, **82**(2), 183-189.
- Pandey, A.K., Pandey, S.D., Misra, V., Viswanathan, P.N. 1999. Formation of Soluble Complexes of Metals with Humic Acid and Its Environmental Significance. *Chemistry and Ecology*, **16**(4), 269-282.
- Peng, Y., Zhu, G. 2006. Biological nitrogen removal with nitrification and denitrification via nitrite pathway. *Applied Microbiology and Biotechnology*, **73**(1), 15-26.
- Perić, J., Trgo, M., Čurković, L. 1999. Monitoring of hydrolysis in natural zeolite-H₂O systems by means of pH and electrical conductivity measurements. in: *Studies in Surface Science and Catalysis*, (Eds.) G.P.-B.J.B.N. I. Kiricsi, H.G. Karge, Vol. Volume 125, Elsevier, pp. 761-767.

- Qiu, H., Lv, L., Pan, B.-c., Zhang, Q.-j., Zhang, W.-m., Zhang, Q.-x. 2009. Critical review in adsorption kinetic models. *Journal of Zhejiang University SCIENCE A*, **10**(5), 716-724.
- Rahimi, Y., Torabian, A., Mehrdadi, N., Shahmoradi, B. 2011. Simultaneous nitrification–denitrification and phosphorus removal in a fixed bed sequencing batch reactor (FBSBR). *Journal of Hazardous Materials*, **185**(2–3), 852-857.
- Rittman, B. E., McCarty, P. L. (2001). *Environmental biotechnology: Principles and applications*. McGraw-Hill, Boston.
- Rodrigues, A., Brito, A., Janknecht, P., Proenca, M.F., Nogueira, R. 2009. Quantification of humic acids in surface water: effects of divalent cations, pH, and filtration. *Journal of Environmental Monitoring*, **11**(2), 377-382.
- Rosa, M. 1997. Nitrification of saline effluents. *Brazilian Journal of Chemical Engineering*, **14**.
- Rožić, M., Cerjan-Stefanović, Š., Kurajica, S., Mačefat, M.R., Margeta, K., Farkaš, A. 2005. Decationization and dealumination of clinoptilolite tuff and ammonium exchange on acid-modified tuff. *Journal of Colloid and Interface Science*, **284**(1), 48-56.
- Sacks, L. A., Tihanskey, A. B. 200. Hillsborough River Watershed Management Plan. Southwest Florida Water Management District (SFWMD), Brooksville, FL.
- Sakar, S., Yetilmezsoy, K., Kocak, E. 2009. Anaerobic digestion technology in poultry and livestock waste treatment - a literature review. *Waste management & research*, **27**(1), 3-18.
- Sanchez, O., Aspe, E., Marti, M.C., Roeckel, M. 2004. The effect of sodium chloride on the two-step kinetics of the nitrifying process. *Water environment research*, **76**(1), 73-80.
- Semmens, M., Porter, P. 1979. Ammonium removal by ion exchange: using biologically restored regenerant. *Journal (Water Pollution Control Federation)*, 2928-2940.
- Semmens, M.J., Wang, J.T., Booth, A.C. 1977. Nitrogen Removal by Ion Exchange: Biological Regeneration of Clinoptilolite. *Journal (Water Pollution Control Federation)*, **49**(12), 2431-2444.
- Sharma, B., Ahlert, R.C. 1977. Nitrification and nitrogen removal. *Water Research*, **11**(10), 897-925.
- Shen, L., Lu, Y., Liu, Y. 2012. Mathematical modeling of biofilm-covered granular activated carbon: a review. *Journal of Chemical Technology & Biotechnology*, **87**(11), 1513-1520.
- Singh, M., Srivastava, R.K. 2011. Sequencing batch reactor technology for biological wastewater treatment: a review. *Asia-Pacific Journal of Chemical Engineering*, **6**(1), 3-13.
- Son, D., Kim, D., Chung, Y.-C. 2000. Biological nitrogen removal using a modified oxic/anoxic reactor with zeolite circulation. *Biotechnology Letters*, **22**(1), 35-38.
- Strotmann, U.J., Windecker, G. 1997. Kinetics of ammonium removal with suspended and immobilized nitrifying bacteria in different reactor systems. *Chemosphere*, **35**(12), 2939-2952.
- Sun, S.P., Nacher, C.P.I., Merkey, B., Zhou, Q., Xia, S.Q., Yang, D.H., Sun, J.H., Smets, B.F. 2010. Effective Biological Nitrogen Removal Treatment Processes for Domestic Wastewaters with Low C/N Ratios: A Review. *Environmental Engineering Science*, **27**(2), 111-126.
- U.S. Environmental Protection Agency (USEPA). (2000). Profile of the agricultural livestock production industry. Rep. No. EPA 310-R-00-002. Enforcement and Compliance Assurance, Washington, D.C.

- U.S. Environmental Protection Agency. (2012). Renewable energy production incentives: Federal and State incentives for generating energy from waste. EPA Website: <<http://www.epa.gov/osw/hazard/wastemin/minimize/energyrec/rpsinc.htm>>.
- U.S. Government Accountability Office (GAO). (2008). "Concentrated animal feeding operations." Rep. No. GAO-08-944. Washington, D.C.
- Vanotti, M.B., Szogi, A.A., Hunt, P.G., Millner, P.D., Humenik, F.J. 2007. Development of environmentally superior treatment system to replace anaerobic swine lagoons in the USA. *Bioresource Technology*, **98**(17), 3184-3194.
- Varel, V.H., Wells, J.E., Shelver, W.L., Rice, C.P., Armstrong, D.L., Parker, D.B. 2012. Effect of anaerobic digestion temperature on odour, coliforms and chlortetracycline in swine manure or monensin in cattle manure*. *Journal of Applied Microbiology*, **112**(4), 705-715.
- Virta, R. L. (2012). USGS 2012 Minerals Yearbook. Zeolites, US Geological Survey, Reston, Virginia.
- Wang, S., Peng, Y. 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, **156**(1), 11-24.
- Wei, Y., Ye, Z., Wang, Y., Ma, M., Li, Y. 2011. Enhanced ammonia nitrogen removal using consistent ammonium exchange of modified zeolite and biological regeneration in a sequencing batch reactor process. *Environmental Technology*, **32**(12), 1337-1343.
- Weiner, E.R. 2012. *Applications of Environmental Aquatic Chemistry: A Practical Guide, Third Edition*. Taylor & Francis.
- Yang, P.Y., Gan, C. 1998. An on-farm swine waste management system in Hawaii. *Bioresource Technology*, **65**(1-2), 21-27.
- Yenigün, O., Demirel, B. 2013. Ammonia inhibition in anaerobic digestion: A review. *Process Biochemistry*, **48**(5-6), 901-911.

APPENDIX A:
ZEOLITE SELECTION

During the development of this dissertation work, there were additional experiments performed that are not presented in the main chapters of this document. These experiments are preliminary results that support the work performed in this dissertation; also, could be further developed into more complex research questions.

Of the more than 50 types of zeolites, clinoptilolite is the most abundant; therefore is readily available making it the most studied and utilized zeolite. However, chabazite has higher cation exchange capacity and based on this fact, it was selected for the amended SBR studies. The cost of chabazite is estimated to be \$3,500 per ton, while clinoptilolite was estimated to be \$250 per ton (Amini, 2014). When implementing a technology, cost is fundamental in decision making. If there were a need in reducing cost of the chabazite-SBR system presented in this dissertation, an alternative could be to replace chabazite with clinoptilolite.

The goal of this experiment was to compare the performance of NH_4^+ uptake by chabazite with that of clinoptilolite from different tuft. The information obtained from this study could be used to perform an in depth cost analysis. Also, the information could aid with decisions in modifications of the chabazite-SBR system. Specific objectives were to: (1) determine dose and contact time for NH_4^+ removal using four types of zeolites; and (2) determine the efficiency of NH_4^+ removal when there are competing cations present in the wastewater.

Chabazite was purchased from St. Cloud Mining Company (Winston, New Mexico); in addition the company provided samples of clinoptilolite from two different tufts. The clinoptilolite identification numbers given by the company are ZS403H and ZK408H; in this study we referred to the products as clinoptilolite-A and clinoptilolite-G, respectively. A third clinoptilolite sample was supplied from Zeo Inc called ZeoSand[®] that we referred to as clinoptilolite-V. The four zeolites were pretreated with groundwater following the protocol described in Chapter 3. The particle size of the tested zeolite was 0.60 mm. Testing of zeolite included kinetics and isotherm batch studies and SEM-EDX which are described in Chapter 3.

The NH_4^+ uptake efficiency during 24 hours of contact using the four tested zeolites is shown in Figure A-1. Two solutions were tested which contained an initial NH_4^+ concentration of $1,000 \text{ mg-N L}^{-1}$ in deionized water and in a solution containing competing cations ($390 \text{ mg L}^{-1} \text{ Na}^+$, $490 \text{ mg L}^{-1} \text{ K}^+$, $460 \text{ mg L}^{-1} \text{ Mg}^{2+}$, $270 \text{ mg L}^{-1} \text{ Ca}^{2+}$). At a contact time of 4 hours, when testing the NH_4^+ in deionized water, the NH_4^+ uptake efficiency was 92%, 82%, 70% and 40% for chabazite, clinoptilolite-Y, clinoptilolite-V and clinoptilolite-G, respectively. At a contact time of 24 hours the NH_4^+ uptake efficiency was 93%, 91%, 89%, and 64% for chabazite, clinoptilolite-Y, clinoptilolite-V and clinoptilolite-G, respectively. Chabazite resulted in superior uptake efficiency as expected, because it has a higher exchange capacity. However, the maximum adsorption occurs at 4 hours of contact, while the tested clinoptilolite requires > 24 hours of contact for maximum uptake. The NH_4^+ uptake efficiency, when competing cations were present, resulted in a decrease in NH_4^+ adsorption for all the tested zeolites; however, chabazite was the least affected.

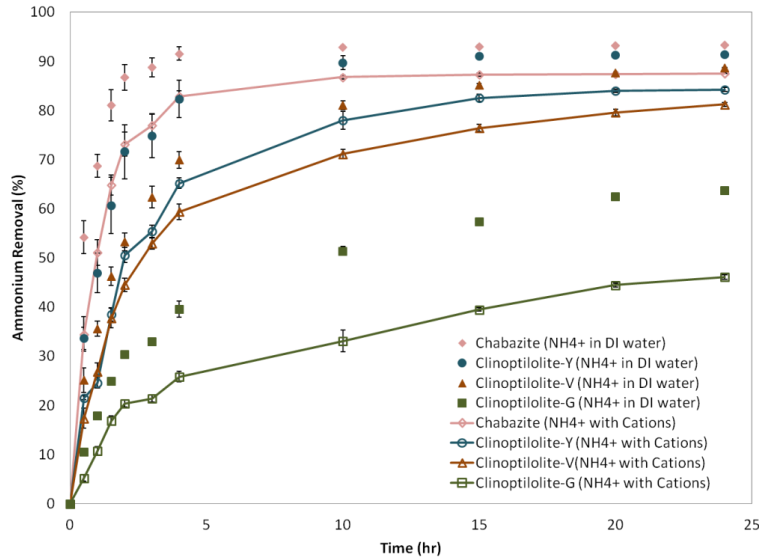


Figure A-1. Effect of time in NH_4^+ uptake by zeolite in contact with a solution of NH_4^+ in deionized water and with competing cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}).

The effect of zeolite dose in the NH_4^+ uptake efficiency is shown in Figure A-2. At a dose of $150 \text{ g-zeolite L}^{-1}$ the uptake efficiency observed was 90%, 86%, 89% and 57% for chabazite, clinoptilolite-Y, clinoptilolite-V and clinoptilolite-G, respectively. However, clinoptilolite-G will require a dose of $300 \text{ g-zeolite L}^{-1}$ to result in higher uptake efficiency.

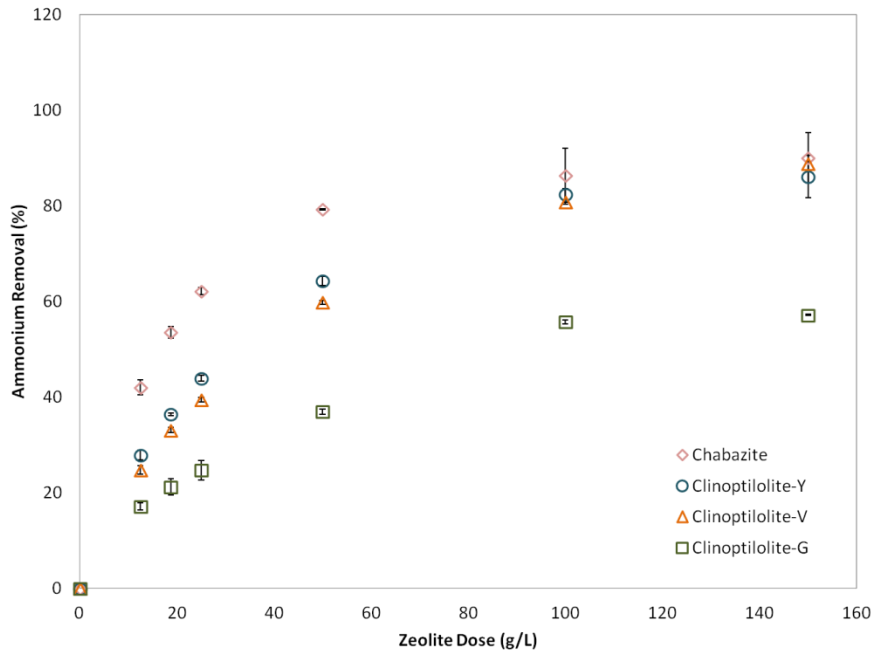


Figure A-2. Effect of NH_4^+ uptake at varying dose of zeolites.

Knowing which cations are loaded in the zeolite could be beneficial, since during the exchange this will be released into solution. The zeolite could be selected for the desired application based in the cation loaded either to benefit microbes providing macronutrients or promote a mineral precipitation such as struvite. The composition of the tested zeolites is provided in Table A-1. The main cation loaded in chabazite is Na^+ , for clinoptilolite G and V is iron (Fe), and for clinoptilolite-Y is K^+ . For the application of hybrid IX biological process tested in this dissertation, clinoptilolite looks favorable because it has less Na^+ , hence it could lessen nitrification inhibition caused by the Na^+ .

The replacement of chabazite with clinoptilolite to lower cost in the hybrid IX biological process tested in this dissertation (chabazite-SBR) is feasible if clinoptilolite Y or V are used. However, when competing cations are present, chabazite is the best option due to its lower impact during NH_4^+ uptake.

Table A-1. Composition of zeolite.

Components wt (%)	Chabazite	Clinoptilolite – G	Clinoptilolite – Y	Clinoptilolite - V
Si	31.65 ± 1.33	37.57 ± 1.23	36.78 ± 2.99	36.19 ± 2.20
Al	9.04 ± 0.35	7.40 ± 0.23	6.15 ± 0.65	6.82 ± 1.04
Fe	6.25 ± 1.80	4.09 ± 1.30	2.20 ± 0.84	7.85 ± 4.08
Na	7.19 ± 0.61	0.26 ± 0.05	2.09 ± 0.16	0.53 ± 0.12
K	1.02 ± 0.13	3.63 ± 0.77	4.18 ± 0.90	5.71 ± 0.72
Ca	0.83 ± 0.05	3.44 ± 0.35	4.05 ± 3.77	2.16 ± 0.31
Mg	0.54 ± 0.05	0.84 ± 0.07	0.73 ± 0.48	0.32 ± 0.06
Si/Al ratio	3.50 ± 0.06	5.09 ± 0.27	6.02 ± 0.65	5.42 ± 0.86

APPENDIX B:

PHOSPHATE REMOVAL BY CHABAZITE

During the operation of chabazite-SBR it was observed an overall TP removal of 54 percent. Phosphate (P) minerals are precipitated in the presence of cations and given the appropriate pH. For example, struvite is a phosphate crystal with molecular formula of $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, that at a pH of 8.5-9.0 (Huang et al., 2014) precipitates; our system operated at a pH lower than 8.5. Zeolites are described to also be capable of sieve molecules; due to this capability TP removal could have gone thru this mechanism. To test this idea, a batch test was performed to answer the following research question: Is chabazite capable of removing P by molecular adsorption?

The batch test consisted in placing chabazite (9 g) in contact with 200 mL phosphate (PO_4^-) solution (100 mg-N L^{-1}) with mixing for 24 hrs. An additional batch test containing chabazite (9 g) in contact with 200 mL of NH_4^+ (400 mg-N L^{-1}) and PO_4^- (100 mg-P L^{-1}) solution was included. As shown in Figure A-3, there is no P removal when both tested solutions were in contact with chabazite. It can be concluded that PO_4^- is not removed by molecular sieve.

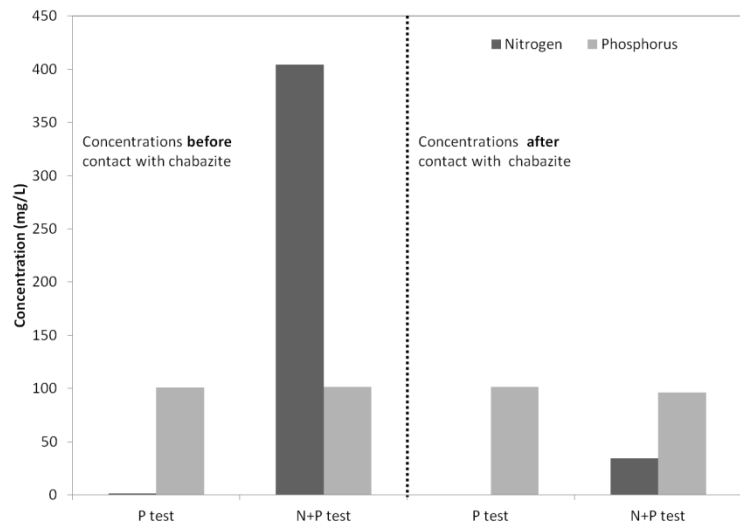


Figure B-1. Chabazite in contact with a PO_4^- solution, with and without NH_4^+ exchange.

APPENDIX C:

BIOREGENERATION OF CHABAZITE INSIDE A MEMBRANE

During batch testing it was observed that mixing of solutions containing free zeolite particles has led to the breakdown of particles. This created the concern of a possible zeolite loss during chabazite-SBR operation at the biomass wasting or decanting the treated effluent. Losing zeolite will result in the need of dosing additional chabazite. An alternative that may avoid loss of zeolite is to place the material inside a fine meshed pouch (zeo-pack). However, having the material in a pouch could affect nitrification rate, hence bioregeneration. The research question answered in this experiment was: Is nitrification rate of $Z\text{-NH}_4^+$ affected by enclosing the material in a pouch?

Two nitrification batch tests with free floating and inside a pouch chabazite (90 g) were carried out to treat 600 mL of synthetic wastewater ($1,000 \text{ mg L}^{-1} \text{ NH}_4^+\text{-N}$). The pouch was made of 30 microns mesh size nylon fabric (SEFAR NITEX[®], Heiden, Switzerland) that seals by heating. Sampling at time 0, 4, 24, 48, 72, 96, 120, 144, and 168 hours was performed to measure NH_4^+ and NO_3^- concentrations. The batch test had 4.2 g L^{-1} of VSS concentration and pH was maintained to 7.5.

NH_4^+ and NO_3^- concentrations over 168 hours of nitrification of $Z\text{-NH}_4^+$ are shown in C-1. Specific nitrification rates of 0.19 and $0.08 \text{ mg-N g-VSS}^{-1} \text{ hr}^{-1}$ were obtained for zeo-pack and free floating zeolite, respectively. Nitrification rate was not affected by placing the zeolite in the

pouch, on the contrary the rate was improved by a factor of 2.4. A possible reason for the increased nitrification rates may be due to an increase in biofilm carrier surfaces.

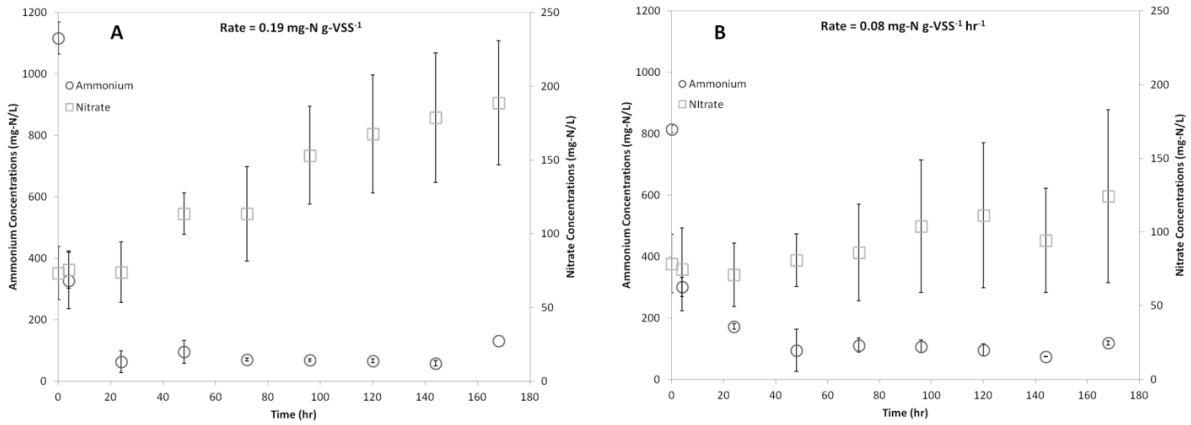


Figure C-1. Nitrogen concentrations during nitrification of Z-NH₄⁺ (A) zeo-pack and (B) free floating zeolite.