Ammonia Removal and Recovery from Wastewater Using Natural Zeolite: An Integrated System for Regeneration by Air Stripping Followed Ion Exchange

By

Qiaosi Deng

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Civil Engineering

Waterloo, Ontario, Canada, 2014

Author’s Declaration

I hereby declare that I am the sole author of this thesis, except where noted. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Co-authorship

Chapter 3 Ammonium nitrogen removal from the AnMBR permeate by natural zeolite, Qiaosi Deng, Bipro Ranjan Dhar, Dr. Elsayed Elbeshbishy and Dr. Hyung-Sool Lee. Qiaosi Deng is the principle author of this manuscript. A version of this chapter has been submitted to Journal of Environmental Technology for peer review and publication.

Chapter 4 An integrated system for ammonia recovery: regeneration of exhausted zeolite with air stripping, Qiaosi Deng, Dr. Elsayed Elbeshbishy and Dr. Hyung-Sool Lee. Qiaosi Deng is the principle author of this manuscript.

Abstract

This study revealed that ammonium ion exchange of natural zeolite could be a feasible method of nitrogen removal and recovery from permeate from anaerobic membrane bioreactors (AnMBRs). NaCl concentrations optimized for chemical regeneration in batch experiments did not match those in continuous column tests. Instead, the mass ratio of Na^+ to Zeolite-NH_4^+-N was significant for improving regeneration efficiency in column experiments; this mass ratio was 750 g Na^+/g Zeolite-NH_4^+-N required for regeneration efficiency over 90% in 2 hours at pH 9. To decrease the NaCl dose in regeneration of exhausted zeolite, a high pH regeneration method was developed using an NaCl concentration of 10 g/L at pH 12 (the mass of Na^+ to Zeolite-NH_4^+-N of 4.2) which achieved a regeneration efficiency about 85%.

The recovery of ammonium nitrogen from the exhausted zeolite was assessed with air stripping followed by ammonia collection in an acid scrubber. The effects of shaking and air stripping were investigated in batch tests and the results showed the superiority of air stripping over shaking. Liquid circulation and air flow rates were varied for optimization of ammonia recovery in a continuous zeolite-packed column combined with a regeneration chamber and a stripping column. The liquid circulation rate had no significant effect on either the regeneration efficiency or the ammonia transfer efficiency from ammonium nitrogen to ammonia gas, while the ammonia transfer efficiency significantly increased with the air flow rate. Furthermore, the effect of pH on ammonia recovery was tested. Both the regeneration efficiency and the ammonia transfer efficiency were significantly improved with increasing pH. When the pH was increased from 9.5 to 12, the regeneration efficiency increased from 9.2% to 84% and the ammonia transfer efficiency increased from 54% to 92%. The nitrogen recovery process that combines zeolite ammonium exchange and air stripping can decrease chemical costs for regeneration of exhausted zeolite and efficiently collect ammonium nitrogen to be reused as fertilizers. Hence, the integrated nitrogen process can resolve the challenge of nitrogen removal in anaerobic membrane bioreactors treating organic wastewater in sustainable manners.

Acknowledgements

I would like to express my deepest gratitude to my supervisor Dr. Hyung-Sool Lee for the guidance and active participation during this research. His encouragement and patience were a great help to me.

I would like to thank Dr. Elsayed Elbeshbishy for his enormous help by various experimental techniques and advice for my research. I would also wish to thank Bipro Ranjan Dhar for his help with the manuscript writing.

I am also grateful to all of my colleagues in our research group in the past two and half years: Dr. Weiwei Du, Dr. Junyeong An, Yaohuan Gao, Hyoengu Yeo, Mohammed Galib, Junyeong Sim for their help. Greatly thank Yu Hou, for his patience, encouragement, and love.

I would like to thank Prof. Wayne Parker and Prof. Marianna Polak for reviewing my thesis.

I would like to appreciate staffs, technicians, and co-op students who provided invaluable help in my research.

I would like to acknowledge the financial support from the Ministry of Economic Development and Innovation OCRIF project entitled "Development of sustainable anaerobic wastewater treatment technologies: recovery of value-added products".

And last but certainly not least, I wish to express my deepest gratitude to my family members. Thank them for all the unconditional love and support to me. Their love has been and will always be a great source of inspiration in my life.

Table of Contents

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

List of Tables

List of Figures

List of Abbreviations

AS	Air stripping
ATE	Ammonia transfer efficiency
AnMBR	Anaerobic membrane bioreactor
A_0	Interfacial surface area
BAU	Breakthrough ammonium uptake (mg N/g zeolite)
BOD	Biological oxygen demand (mg/L)
BV	Bed volume (L)
CEC	Cation exchange capacity (mg or meq/g zeolite)
C_N	Ammonium concentration (mg N/L)
COD	Chemical oxygen demand (mg/L)
DO	Dissolved oxygen (mg/L)
EAU	Equilibrium ammonium uptake (mg N/g zeolite)
G	Air flow rate through the stripping tower (moles air/hr)
H_c	Henry’s law constant
IC	Ion chromatograph
IE	Ion exchange
L_q	Liquid flow through the stripping tower (moles water/hr)
$M_{exhaused}$	Ammonium mass exchanged by zeolite (mg N)
M_{NH3}	Mass of ammonia (mg N)
MAP	Magnesium ammonium phosphate (Struvite)

MCP	Mono calcium phosphates
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NH_3	Ammonia (mg N/L)
NH_4^+	Ammonium ion (mg N/L)
NH_4Cl	Ammonium chloride
$(NH_4)_2SO_4$	Ammonium sulfate
NO_2^-	Nitrite
NO_3^-	Nitrate
O&M	Operation and maintenance
Q_{air}	Air flow rate (L/hr)
Q_{liquid}	Liquid circulation rate (L/hr)
$Q_{release}$	Ammonium release rate during regeneration(mg N/g-hr)
R	Resistance to the rate of mass transfer
RE	Regeneration efficiency
rpm	Revolution per minute
TSS	Total suspended solids (mg/L)
Zeolite -NH_4^+-N	Zeolite fixed ammonium nitrogen (mg)

Chapter 1 Introduction

1.1 Background

In domestic wastewater, most nitrogen is contributed by human urine, fecal material, food residue, and personal care products. The total nitrogen in domestic wastewater ranges from 20 to 70 mg N/L [Tchobanoglous et al., 2003]. The most common forms of nitrogen can be classified as ammonia/ammonium (NH_3/NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and organic nitrogen. Domestic wastewater is usually composed of 60-70% ammonium nitrogen and 30-40% organic nitrogen. The fractions of ammonium nitrogen of the total nitrogen are increased further in anaerobic wastewater treatment effluent, including permeates of anaerobic membrane bioreactors (AnMBRs), due to the lack of nitrogen oxidation.

The accumulation of ammonium nitrogen in water results in eutrophication, algae blooms and depletion of dissolved oxygen, all of which are harmful to aquatic life [Tan et al., 2006; Sarioglu, 2005]. Such adverse effects of ammonium nitrogen have promoted the development of different technologies for its removal, such as biological nitrification-denitrification, catalytic liquid-phase oxidation, air stripping, struvite precipitation, membrane separation, and selective ion exchange. Up to now, biological nitrogen removal processes have mainly been used for wastewater treatment, due to their relatively high economic efficiency, as compared to other physical/chemical processes. AnMBRs, which can treat domestic wastewater more sustainably than the existing activated sludge process, are receiving tremendous attention these days, because energy and water security issues have become significant in our society, along with climate change. Literature commonly shows that AnMBRs can produce high-quality effluent from domestic wastewater [Saddoud et al., 2007; Lin et al., 2009; Liao et al., 2006; Ho and Sung, 2009]. This effluent has no suspended solids and chemical oxygen demand (COD) can be removed up to 95-99% [Saddoud et al., 2007; Lin et al., 2009]. In addition, operating and maintenance costs in AnMBRs can be substantially reduced due to the lack of air supply and low production of excessive sludge [Liao et al., 2006; Ho and Sung, 2009]. Methane gas can be collected from AnMBRs and reused as heat energy. These merits of AnMBRs facilitate their application to municipal wastewater treatment. However, there are several challenges to AnMBRs to be addressed, and one of them is nutrients control. Adding coagulants to AnMBRs can readily remove phosphorus [Aiyuk et al., 2004], but nitrogen control is not as simple as phosphorus removal. Biological nitrogen removal systems can be used as post-treatment to AnMBRs. However, this conventional option can significantly weaken the competitiveness of AnMBRs against existing wastewater treatment processes (e.g., activated sludge), due to substantial costs needed for such post-treatment. The success of AnMBRs in treating domestic wastewater requires more sustainable and economic nitrogen removal technologies that fit well into the characteristics of AnMBR permeates.

The first feature of AnMBR permeates is the lack of particulate matter. The second is that the majority of nitrogen species are in the form of ammonium nitrogen in the permeates. These two features are ideal for ammonium ion exchange systems. Synthetic ion exchange resins are expensive for large-scale systems, but using relatively low-cost natural resin, such as natural zeolites, could be economically viable.

Natural zeolites are micro porous, crystalline materials having three-dimensional aluminosilicate tetrahedral frameworks where aluminum (Al^{3+}) and silicon (Si^{4+}) structure atoms are bonded through covalent bonds to common oxygen atoms to form internal channels [Englert et al., 2005]. Each aluminium (Al^{3+}) atom substitution for silicon (Si^{4+}) in the zeolite framework generates a deficiency of positive charges on the framework [Nguyen and Tanner, 1998]. Then, the deficiency partially leads to negative charge within zeolite pores, which is balanced by various mono or divalent cations, such as NH_4^+, Na^+, K^+, Ca^{2+}, or Mg^{2+}. Interestingly, the cations in zeolites are exchangeable with those present in bulk liquid, depending on zeolites' affinity to given ions and concentration gradient. These ion exchange properties of natural zeolite enable us to remove ammonium nitrogen in water and wastewater, such as AnMBR permeates or any wastewater in which ammonium nitrogen is rich.

Different types of natural zeolites have been explored for ammonium removal from wastewater, but previous studies examined ammonium removal from wastewaters with a high concentration of suspended solids (over 100 mg/L); as a result, serious clogging issues occurred in zeolite-packed columns, and the column systems failed to provide consistent ammonium removal [Liao and Lin, 1981; Watten and Engilish, 1985]. However, AnMBR permeates, an ammonium-rich wastewater with no suspended solid, are very ideal for ion exchange using natural zeolite. Hence, it is valuable to revisit natural zeolite for ammonium removal from AnMBR permeates. Zeolite processes would control nitrogen in more economical, sustainable ways than biological nitrogen removal systems using substantial amounts of oxygen molecules and chemicals. The sustainability of zeolite processes will be improved more if we are able to recover ammonium nitrogen from the processes and reuse it. In this study, the performance of natural zeolites on ammonium nitrogen exchange and chemical regeneration was investigated in phase I. In phase II, ammonium nitrogen recovery using natural zeolites and air stripping was assessed in a new process integrating the zeolites with air stripping.

1.2 Objectives

This research is primarily focused on ammonium ion exchange using natural zeolite, and recovery of ammonia with an integrated system of ion exchange and air stripping. The specific objectives of this study are

- To optimize the operating conditions for ammonium exchange of natural zeolite, such as initial ammonium concentration, pH, reaction time, NaCl dose, and mixing intensity.
- To select the most efficient zeolite for ammonium nitrogen ion exchange and regeneration in batch experiments
- To evaluate the performance of a selected natural zeolite on ammonium nitrogen exchange in batch experiments using NH_4Cl solution and AnMBR permeate.
- To explore optimal operating conditions for ammonium nitrogen exchange and chemical regeneration in a continuous zeolite-packed column.
- To investigate the renewability of the exhausted zeolite in repetitive regeneration using the packed column in continuous mode.
- To develop an innovative system integrating the zeolite column with air stripping for ammonia recovery.
- To evaluate the performance of ammonia recovery with the integrated system, and to optimize the operating conditions for regeneration and ammonia stripping.

1.3 Scope

This research investigated the impacts of operating conditions on ammonium removal and recovery from wastewater in lab-scale tests and developed an integrated regeneration system with air stripping followed ion exchange. The scope of this research included:

- Operation of batch experiments to investigate the impact of various operating parameters (initial ammonium concentrations, pH, reaction time, and mixing intensities) on the equilibrium ammonium uptake (EAU) and regeneration efficiency (RE) of natural zeolite using NH_4Cl solution.
- Operation of batch experiments for evaluation of EAU and RE of four natural zeolites and one synthetic resin, and selection of a best natural zeolite that will be used in a continuous zeolite-packed column test.
- Operation of batch experiments using AnMBR permeates for the ion effects on the EAU and RE of the selected zeolite.
- Operation of batch experiments for investigation of the effects of operating parameters, such as pH, mixing intensity, initial ammonium concentration temperature, and working volume, on ammonia transfer.
- Operation of continuous zeolite-packed column for the evaluation of breakthrough curves for NH_4Cl solution and AnMBR permeates, and the high pH regeneration.
- Development of an integrated regeneration system and evaluation of the impact of pH, air flow rate and liquid circulation rate on regeneration and ammonia transfer efficiency.

- Evaluation of renewability of chemically regenerated zeolite in continuous zeolite-packed column.

1.4 Layout of dissertation

This thesis is comprised of five chapters and conforms to the integrated-article format.

Chapter 2 reviews the existing literature related to this research project.

Chapter 3 evaluates natural zeolite and synthetic resin for ammonium removal from both NH_4Cl and AnMBR permeate, and the influence of various operating parameters. This chapter also presents the performance of a continuous zeolite-packed column.

Chapter 4 introduces a novel integrated system that combines ion exchange with air stripping for ammonia recovery. Operating parameters for ammonia recovery are assessed to optimize the integrated nitrogen-recovering system.

Chapter 5 presents the summary of major findings from this research and recommendations for future research.

Chapter 2 Literature Review

2.1 Nitrogen recovery technologies

Recovery of nutrients has gained tremendous attention due to decreasing natural resources and increasing sustainability issues. Instead of simply removing nitrogen from wastewater with substantial amounts of energy and materials invested, ammonium nitrogen or nitrate salt can be recovered and reutilized before the nitrogen goes back into natural nitrogen cycle. In this chapter, the existing technologies for nitrogen recovery from organic wastewater (mainly sewage) are discussed to justify the competitiveness of ion exchange technologies over other existing ones.

2.1.1 Struvite

Struvite, magnesium ammonium phosphate hexahydrated (MAP) ($MgNH_4PO_4.6H_2O$) is a white crystalline inorganic mineral [Doyle and Parsons, 2002]. Struvite is more often associated with scaling that affects treatment processes, as it leads to operational failures associated with sludge build-up in pipes, centrifuges, heat exchangers and flow-meters [Neethling and Benisch, 2004]. However, struvite crystallisation, if controlled, represents a promising solution for phosphorus and nitrogen removal and recovery from waste or wastewater. MAP precipitates with three chemical species, magnesium, ammonium, and phosphate, in 1:1:1 molar ratio, according to the following equation:

$$Mg^{2+} + NH^{+} + H_2PO_4^{-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + 2H^{+} \qquad \text{(Eq. 2.1)}$$

The performance of nitrogen removal by struvite precipitation from different wastewater sources is summarized in Table 2.1. Nitrogen removal was higher than 85% from all these wastewater sources. As a slow-releasing fertiliser, struvite has proved to be a good source of phosphorus for crops, almost equal in efficiency to mono calcium phosphates (MCP) [Johnston and Rechards, 2003]. Struvite crystallisation also presents other major advantages in that it can help reduce the volumes of sludge generated by conventional P removal processes, from 5% up to 49% [Woods et al., 2000].

Table 2.1: Example of nitrogen removal by struvite precipitation

References	Source	Nitrogen Removal
Maekawa et al. (1995)	Swine wastewater	More than 90%
Priestley et al. (1997)	BPR anaerobic digested effluents	98%
Kim et al. (2004)	Slurry type swine wastewater	Up to 99%
Tunay et al. (1997)	Synthetic samples Industrial wastewater	Over 85%
Miles and Ellis (1998)	Anaerobically treated swine waste	93%
Uludag-Demirer et al. (2005)	Anaerobically digested dairy manure	>95%
Kabdasli et al. (2006b)	Human Urine	Up to 95%

However, the methods developed for struvite formation require exogenous doses of expensive chemicals, such as magnesium salts or phosphate salts, due to the 1:1:1 molar ratio needed for struvite generation. For instance, the molar ratio of ammonium to phosphate ranges from 1.5 to 12.5 in domestic wastewater, and thus a phosphate source should be added to the wastewater for struvite precipitation [Mackawa et al., 1995; Priestley et al., 1997; Kim et al., 2004; Tunav et al., 1997]. This requirement narrows down the application of struvite into specific wastes or wastewater streams (see Table 2.1), where phosphate is relatively rich, such as animal manure or anaerobic digestion effluent (or concentrate) [Priestley et al., 1997; Miles and Ellis, 1998; Uludag-Demirer et al., 2005]. In addition, struvite precipitation needs an alkaline pH 8.5~ 9.5 [Miles and Ellis, 1998; Uldag-Demirer et al., 2005; Kabdasli et al., 2006b; Nelson et al., 2003], which can increase operating costs further. For these reasons, struvite would not be ideal for nutrients control and recovery from domestic wastewater (including AnMBR permeates from the wastewater).

2.1.2 Air stripping

Air stripping is a mature technology that has been used for nitrogen control [Stumm and Morgan, 1996; Idelovitch and Michail, 1981; Culp et al., 1978]. With a pKa of 9.3 of ammonium/ammonia equilibrium, ammonium nitrogen can be easily transferred from a liquid to dissolved ammonia gas. In ammonia air stripping processes, lime or caustic soda is typically used to increase pH up to 10.8-11.5, a step that converts ammonium ions to dissolved ammonia, and transfers to ammonia gas with air supply according to the following reaction:

$$NH_4^+ + OH^- \xrightarrow{air} H_2O + NH_3\ (g)$$

The following equation (Eq.2.2) defines the relationship between ammonium and ammonia in an aqueous solution:

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+]/K_a} \qquad \text{(Eq. 2.2)}$$

where $[NH_3]$ is the free-ammonia concentration, $[NH_3+NH_4^+]$ is the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration, and Ka is the acid ionization constant for ammonia [Gustin and Marinsck-Logarb, 2011]

The air stripping process would be relatively simple, and more economical than struvite formation [Ozturk et al. 2003]. In some traditional equipment for ammonia stripping (free or forced ponds), ammonia removal efficiency is not very high. Idelovitch and Michail (1981) reported the ammonia removal in a high pH pond was 70% after 7 days in summer, and was only 55% to 60% after 7 days in winter. This literature [Idelovitch and Michail, 1981] clearly indicates that mass transfer is a key for ammonia stripping. In order to improve ammonia removal efficiency, ammonia stripping is usually operated with a packed stripping tower. Air stripping usually takes place in a packed tower to provide a large surface area for mass transfer [Dicbbar and Naraiz; 1998]. Figure 2.1 illustrates a countercurrent air stripping tower. The tower contains a large number of packing materials that enlarge the interface where the mass transfer of ammonia from the aqueous to the gaseous phase takes place. A liquid distributor at the top of the tower evenly distributes the influent water over the packing material in a fine spray. A high-capacity blower forces ambient or heated air into the bottom of the air stripping tower. Free ammonia can be stripped from falling water droplets into the air stream, and then discharged to the atmosphere. [Culp et al., 1978]

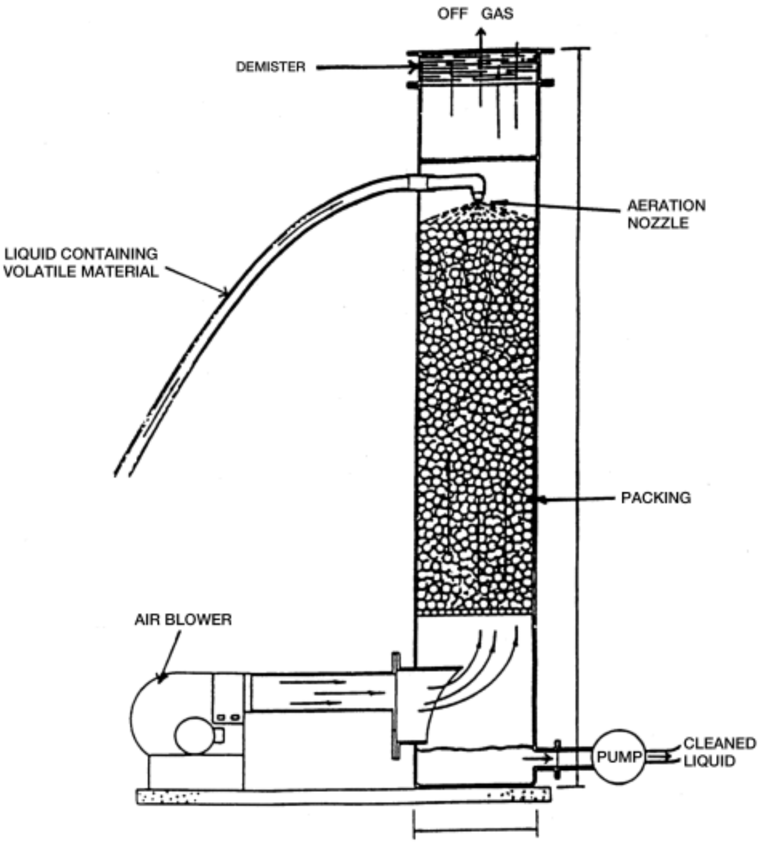


Figure 2.1. Diagram of an air stripping tower (Huang, 2009)

There are several factors that can affect the performance of ammonia air stripping, such as the ammonia concentration of the wastewater, hydraulic wastewater loading, the air flow rate, packing depth, water temperature, water distribution uniformity, and so on. However, the most important parameters are the pH and temperature [Guo et al., 2010; Liao et al., 1995; Norddahl et al., 2006; Quan et al., 2009; Bonmati and Flotats, 2003; Katchis et al., 1998].

Guo et al. reported that ammonia transfer efficiencies increased from 80% to 92% when the pH was increased from 8 to 11 and increased slightly further when the pH was increased from 11 to 13. Gustin and Marinsek-Logarb observed only 27% ammonia transfer to the gaseous phase at pH 8.5, and the transfer efficiency rapidly rose to 92% at pH 11. Liao et al. observed the highest ammonia transfer efficiency of 90.3 % at a pH of 11.5. Norddahl et al. concluded that a pH of 11.5 yielded the best result in terms of ammonia mass transfer. Quan et al. reported that a pH of 11-12 is the optimum to promote the conversion of molecular ammonia in an aqueous solution to ammonia gas.

A few studies also reported that the optimum pH could be lower than 11 at higher temperatures. Gustin and Marinsek-Logarb reported that a pH of 10.5 could be sufficient for ammonia stripping if the temperature is increased to 50°C. Bonmati and Flotats achieved an ammonia transfer efficiency of 87% at pH 9.5 when the temperature was 80°C, and they also concluded that the air stripping became independent of pH at a temperature of 80°C. Furthermore, Katehis et al. found that ammonia stripping became pH insensitive at 75°C.

Although air stripping is a mature technology with high removal efficiency and relatively low cost (over struvite), it has some limitations. First, air stripping in packed towers usually leads to scaling and fouling events because of reactions with the CO_2 in the air, and with some metal ions in wastewater [Norddahl et al., 2006]. Second, air stripping is not efficient for large systems, such as municipal wastewater treatment plants due to substantial amounts of air supply and chemicals for pH adjustment [Gustin and Marinsek-Logarb, 2011; Guo et al., 2010; Liao et al., 1995; Norddahl et al., 2006; Quan et al., 2009]. Hence, air stripping would be applicable for nitrogen recovery from domestic wastewater if pre-treatment can concentrate diluted ammonium (~30 mg N/L) in the wastewater, to reduce the amounts of air and chemicals needed in air stripping.

2.1.3 Membrane

Membrane contactors offer a superior solution for ammonia removal because they provide a large surface area that facilitates speedy separation of dissolved ammonia from wastewater, with relatively low energy input [Norddahl et al., 2006]. Ashrafizadeh and Khorasani (2010) reported 99% of the ammonia removal using a gas-permeable hollow-fibre membrane. Volatile compounds, including dissolved ammonia, will readily diffuse through the gas-permeable membrane driven by vacuum pressure, and then the ammonia gas can be collected with an acid solution [Nunes and Peimmann, 2001]. Figure 2.2 describes the principles of ammonia recovery using such membrane contactors [Hasanoglu et al., 2010].

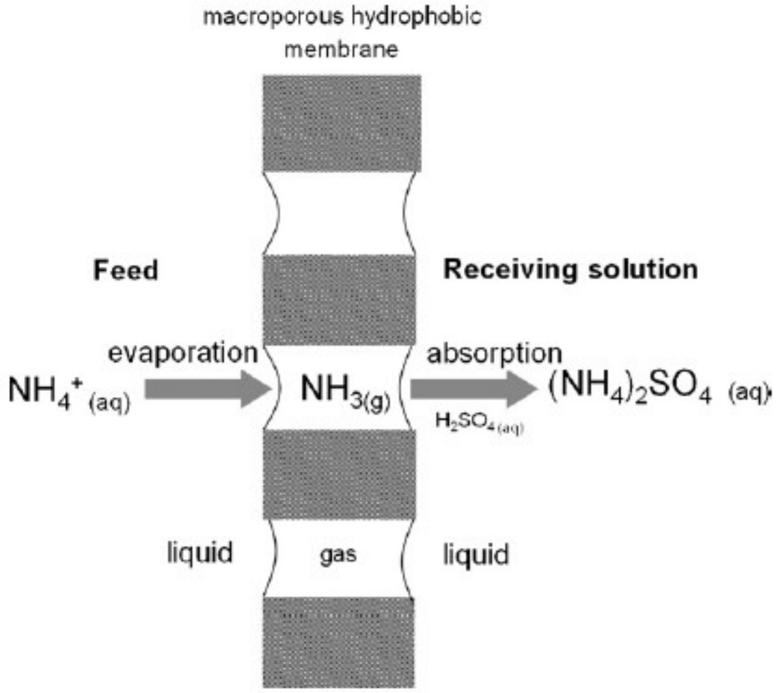


Figure 2.2. Principle of membrane extraction process (Hasanoglu et al., 2010)

Compared to conventional absorption or stripping processes, the use of hollow-fiber membrane contactors provides a number of advantages: (1) a large contact area, (2) independency of ammonia recovery from gas or liquid flow rates in reactors, (3) the lack of any secondary pollutants in ammonia concentrates. Furthermore, the concentration of ammonia does not affect ammonia removal efficiency [Ashrafizadch and Khorasani, 2010]. Therefore, membrane separation would be a good solution for removal and recovery of ammonia from wastewater, but economic efficiency of the membrane contactors seems questionable [Hasanoglu et al., 2010; Koyuncu et al., 2001]. This cost-effectiveness would become more doubtful for AnMBR permeates, the target wastewater to the proposed research, because they need significant investment and maintenance costs to liquid separation membrane. Hence, supplemental addition of membrane for gas separation that can increase those expenses should be avoided to improve competitiveness of AnMBRs.

2.1.4. Ion exchange

Ion exchange has been successfully used to purify target ions from water and wastewater [Koon and Kaufman, 1975]. Ion exchange reactions typically occur between two or more phases, usually liquid and solid in the environmental engineering field [Colella, 1996; Liao and Lin, 1981]. Ion transfer is regulated by the ion concentration in both phases and the ion selectivity of a given exchanger [Colella, 1996]. The quantity of ions exchangeable by a solid exchanger, depending on its chemical and structural features, is called the ion exchange capacity. Ion exchange is generally a reversible reaction, although it can be irreversible [Dyer, 1988].

Natural zeolites are cationic exchangers and have been widely used for removing metals or ammonium ions from water and wastewater. Natural zeolite has a greater affinity for ammonium ions than other exchange media, and is much cheaper than synthetic sorbents. In recent years, many researchers have investigated the cation exchange capacity of various types of zeolite (Table 2.2). The literature commonly reports that clinoptilolite is the best natural zeolite for ammonium exchange reactions, with the cation exchange capacity varing from 2 to 21.5 mg N/g (Table 2.2). These results indicate that clinoptilolte may be beneficial in ammonium ion exchange, and making it the most widely used natural zeolite for ammonium nitrogen removal.

Table 2.2: Summary of cation exchange capacities for various materials

Author	Material	Capacity (mg/g zeolite)
Du. et al. (2005)	Clinoptilolite	5.81 – 7.74
Farkas et al. (2005)	Clinoptilolite	6.0 – 13.65
Sprynskyy et al. (2005)	Clinoptilolite	13.56 – 21.52
Rahmani et al. (2004)	Clinoptilolite	17.31-18.98
Jung et al. (2004)	Zeolite	6.0 – 7.4
Weatherly and McVeigh (2000)	Clinoptilolite	6.58 – 13.3
Nguyen and Tanner (1998)	Clinoptilolite	3.7-6.5
Beler Baykal and Guven (1997)	Clinoptilolite	2.0 – 3.6
Booker et al. (1996)	Australian Zeolite	4.5

The cost for a typical natural zeolite ion exchange systems ranges from \$0.08 to \$0.21 per 1,000 liters treated [FRTR, 4.48]. The relatively low cost, ease of operation, and high efficiency make natural zeolite more competitive with other nitrogen recovery methods (e.g., struvite and air stripping) from domestic wastewater. However, the disadvantage of natural zeolite ion exchange is the chemical regeneration required after zeolite is saturated by ammonium ion exchange [Ashrafizadech and Khorasani, 2010]. High regeneration costs for chemicals (e.g., NaCl) will mitigate the merits of zeolite for nitrogen removal and recovery. Incomplete regenerated zeolite after chemical regeneration will need the replacement of existing zeolite with new one. The two factors can substantially increase operating and maintenance costs for zeolite processes. For these reasons, zeolite processes would be viable for nitrogen removal and recovery when the two limitations (cost-effective regeneration and reliable function of reutilized zeolite) are addressed. To fully understand the features of natural zeolite as a nitrogen recovery material, the following sections will discuss about the type of zeolite, important operating/environmental parameters, and chemical regeneration for ammonium ion exchange reactions.

2.2 Ammonium ion exchange by zeolite

Ammonium ion exchange using natural zeolite has been used successfully to remove ammonium ions from synthetic wastewater in lab- and pilot-scale experiments [Ferreiro et al., 1995; Bergero et al., 1994; Teo et al., 1989; Horsh and Holway, 1983; Klieve and Semmens, 1980]. Ion exchange by natural zeolite is more competitive than other ammonium removal methods because of its cost-effectiveness in operation and maintenance, as described above. Most studies demonstrating the ammonium removal efficiency of zeolites have been conducted using clinoptilolite, due to its high affinity for ammonium nitrogen.

As clearly shown in Table 2.2, the cation exchange capacity of natural zeolite is not constant, due to different chemical and physical characteristics of zeolite and wastewater qualities, including ammonium concentration, ionic strength, pH, and organic matter content. The zeolite type, granule sizes, and flow rate through the exchange bed also affect cation exchange capacity (or ammonium removal efficiency) [Pansini, 1996]. Several of the above-mentioned factors are subsequently discussed in relation to their significance for the ion exchange process.

2.2.1 Zeolite types

There are both natural and synthetic zeolites, and selectivity for specific cations varies according to zeolite types [Hawkins, 1983]. Table 2.3 shows some physical characteristics of important zeolites that can be employed for ammonium removal from water and wastewater [Mumpton, 1983; Chiayvareesajja and Boyd, 1993]. Zeolites can be grouped by their Si:(Al+Fe) structural cation ratios and their K^+, Na^+ and Ca^{2+} (exchangeable cation) ratios. Clinoptilolite and mordenite are silica-rich zeolites with large Si:(Al+Fe) ratios; heulandite, chabazite, phillipsite, and erionite are intermediate silica zeolites; and analcime and laumontite are silica-poor zeolites [Liao and Lin, 1981]. The exchangeable cations of analcime are predominantly Na^+; clinoptilolite's are Na^+ and K^+, and laumontite's are almost invariably Ca^{2+} [Semmens, 1983].

Table 2.3: Representative formulae and selected physical properties of zeolites

Zeolite	Representative Formula	Void Volume (%)	Thermal stability	Cation Exchange Capacity (mg NH_4^+-N/g)
Analcime	$Na_2(Al_{16}Si_{32}O_{96})16H_2O$	18	High	4.54
Chabazite	$(Na_2,Ca)_6(Al_{12}Si_{24}O_{72})40H_2O$	47	High	3.84
Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72})24H_2O$	34	High	2.16
Erionite	$(Na,Ca_{0.5}K)(Al_9Si_{27}O_{72})27H_2O$	35	High	3.12
Heulandite	$Ca_4(Al_8Si_{28}O_{72})24H_2O$	39	Low	32.91
Laumontite	$Ca_4(Al_8Si_{16}O_{48})16H_2O$	34	Low	4.25
Mordenite	$Na_8(Al_8Si_{40}O_{96})24H_2O$	28	High	2.29
Phillipsite	$(Na,K)_5(Al_5Si_{11}O_{32})20H_2O$	31	Medium	3.31

2.2.2 Particle size

The ammonium removal efficiency of natural zeolite can be affected by particle size related to individual fragments, porosity and permeability of the zeolite. These factors affect the access of fluids to zeolite's exchange sites. Some researchers have found that large granules are less efficient than smaller ones in ammonium removal, due to the reduced surface area for diffusion [Xu and Zhou, 2003]. Marking and Bills (1982) observed a lower cation exchange capacity of 5.37 mg/g for larger granules (8x18 mesh), as opposed to 8 mg/g for smaller granules. Jorgensen et al. also found that the uptake of ammonium ions by clinoptilolite increased significantly with decreasing particle size. Hlavay et al. (1982) investigated grain sizes in the intervals of 0.5–1.0, 0.3–1.6, and 1.6–4.0 mm. The smallest fraction resulted in the highest cation exchange capacity. However, the head loss in zeolite-packed columns increases with smaller grain sizes. Hlavay et al. (1982) and Odegaard (1992) recommended minimum grain sizes of 0.4–0.5 mm to maintain high cation exchange capacity of natural zeolite and low head loss in zeolite-packed columns. Thus, the size range of natural zeolite must be optimized for target wastewater (e.g., the concentration of suspended solids) and flow rate of the wastewater to zeolite-packed columns.

2.2.3 pH

The exchange of ammonium ions in zeolite is significantly affected by pH. At low pH, protons compete with NH_4^+ for exchangeable sites of zeolite. In comparison, the concentration gradient of ammonium ions between bulk liquid and zeolite decreases at high pH due to NH_4^+ loss as NH_3 gas. Koon and Kaufman's research (1975) concluded that the optimum pH conditions for ammonium ion exchange were between pH 4~8 and the highest ammonium removal efficiency was observed at pH 6. A pH over 9 resulted in a sharp decrease of cation exchange capacity which should be due to the formation of dissolved ammonia (the pK_a of NH_4^+ ion is 9.3). A few studies have reported lower exchange capacity at low pH, probably due to the competition of other cations (e.g., H^+) for active exchange sites [Xu and Zhou, 2003; Hedstrom, 2001]. Natural zeolite may be partially dissolved at low pH, subsequently change its physical properties, and cation exchange capacity can drop seriously [Hedstrom, 2001]. Therefore, a neutral pH will be optimal for the exchange process between zeolite and bulk liquid.

2.2.4 Ammonium concentration and ionic strength

Jorgensen et al.'s (1979) found that a greater ammonium concentration resulted in a larger amount of adsorbed ammonium ions. It can be interpreted that the higher the ammonium concentration in the solution is, the higher the solute concentration gradient is. This concentration gradient provides the driving force necessary for ammonium ions to take the place of cations at the exchange site of zeolite.

The ionic strength of a solution and water hardness can have an impact on the ammonium uptake by zeolites. Municipal wastewater mostly contains sodium, potassium, calcium and magnesium ions that can be exchanged by the zeolite [Semmens, 1983]. These cations will compete with ammonium ions for exchange sites, which can significantly reduce the ammonium uptake. It has been observed that the concentration of NH_4^+ ions and the concentration of competing cations such as K^+, Na^+, Ca^{2+} and Mg^{2+} influence the capacity of zeolites for ammonium

[Semmens, 1978]. Jorgensen et al. (1976) showed that zeolite had a lower ammonium uptake in tap water than that of distilled water, due to the water hardness such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). The ion selectivity for clinoptilolite is determined as:

$K^{+} > NH_4^{+} > Na^{+} > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^{+}$

This sequence is consistent with the fact that zeolites are ion selective, with a preference for ions with a high ionic radius and low hydration energy [Ames, 1965]. Thus, cation specificity may be viewed as a result of interactions between cations and water, and cations and anionic sites [McLaren and Farquhar, 1973]. In summary, the ammonium uptake by zeolite would generally decrease with increasing ionic strength of a solution.

2.2.5 Flow rate and organic matter

The influence of flow rate is important for ammonium ion exchange in packed-bed column systems that are typical for ion exchange or adsorption technologies. A high flow rate will result in a reduced fraction of mass flow in the influent, and the exchange cannot take place at short contact time; moreover, the physical fracturing may happen at an extreme flow rate [Jorgensen et al., 1976]. A very low flow rate results in poor water distribution across the exchange bed and leads to dead zones or unsaturated exchange bed. Semmens (1978) concluded that this phenomenon occurs because liquid always takes the path of least resistance through the exchange bed, which is a narrow column inside the exchanger. At a low flow rate, the exchange bed exhausts very quickly. Thus, flow rate should be optimized by considering wastewater characteristics, the size distribution of zeolite, and effectiveness of the zeolite bed.

The presence of organic matter in wastewater reduces the cation exchange capacities of zeolite by causing physical blockage of the exchange bed and coating the ion exchange substrate [Watten and Engilish, 1985]. The build-up of biofilm or other organic matters on the surface of the exchanger interferes with both ion diffusion and liquid dispersion. Johnson and Sieburth (1974) reported a 74% reduction of cation exchange capacity after treatment of wastewater containing 30 mg/L of DOC compared with a control of synthetic wastewater with the same ammonium concentration. Watten and English (1985) recorded that organic matters had a highly significant effect on exchange capacity. In Liao and Lin’s pilot study (1981), it was clearly demonstrated that solids removal prior to the wastewater entering the ion exchange column was necessary to maintain high cation exchange capacity. Therefore, zeolite exchange systems need a reliable separation step to mitigate organic content and suspended solids. A secondary clarifier in domestic wastewater treatment systems can work as the pre-separation step to zeolite systems, but ammonium nitrogen is almost oxidized to nitrite or nitrate in an aeration tank. Zeolite processes can be placed before the aeration tank, but domestic wastewater contains high-suspended solids that can easily deteriorate the cation exchange capacity of zeolites. These limitations explain why zeolite processes have been unpopular for nitrogen control in domestic wastewater treatment. In comparison, the permeates from AnMBRs contain a small concentration of chemical oxygen demand (>30 mg/L) and few suspended solids (too small to be quantified). Moreover, no oxidation of ammonium nitrogen occurs in AnMBRs. For these reasons, AnMBR permeates are ideal for zeolite systems to remove or recover ammonium nitrogen.

2.2.6 Temperature and scaling up

Koon and Kaufmann (1975) discussed the temperature effect on the ammonium exchange process and claimed that temperatures between 10℃ and 20℃ did not impact on the processes. Atkins and Scherger (1997) mentioned that one advantage of employing ammonium exchange for nitrogen treatment was the temperature independence of this method.

When scaling up an ion exchange system, the larger system will probably not achieve the same operating cation exchange capacity as one of a smaller laboratory scale. Hlavay et al. (1982) observed that, when scaling up a system 100-fold, just 60% of the ammonium breakthrough capacity could be reached compared to that of the smaller system. The explanation given was that channeling occurred in the ion exchange column in the larger system because of the larger dimensions of the column.

2.2.7 Chemical regeneration of exhausted zeolite

Chemical regeneration aims at replacing ammonium ions from zeolite with other monovalent cations (e.g., Na^+), which allows exhausted zeolite to have exchangeable sites for ammonium ion again. The chemical regeneration process is often based on the following reaction using NaCl:

$$NH_4\text{-}Z + Na^+ + Cl^- = Na\text{-}Z + NH_4^+ + Cl^-$$

Chemical regeneration theoretically requires 1 to 1 molar ratio of Na^+ to NH_4^+, but a large concentration of sodium ion is essential to accelerate the regeneration reaction rate. Fast kinetics are preferred to decrease system footprint, and thus high NaCl concentrations are employed in the field. However, a huge amount of NaCl during chemical regeneration will increase operating and maintenance costs in zeolite processes, and hence NaCl dose should be optimized to meet the requirements for footprint and operating costs.

Many studies have used sodium chloride in a range of 0.17–1 M NaCl [Hlavay et al., 1982; Semmens et al., 1978; Liberti et al., 1981; Conney et al., 1999; Demir et al., 2002] for chemical regeneration. The volume of NaCl brine needed for satisfactory regeneration of the exhausted zeolite was varied from 10-35 bed volume (BV), and depended on the NaCl concentration of the brine. Table 2.4 provides regeneration efficiency of exhausted zeolite and NaCl concentration and volume for chemical regeneration. High regeneration efficiency over 95% can be achieved in most studies using 0.2 M NaCl for chemical regeneration. However, there is no quantitative information on NaCl dose. Liberti et al. (1981) reported that 20 BV of 0.6 M regeneration brine were required at pH 7 for chemical regeneration; almost 100% ammonium nitrogen was regenerated under this condition. Semmens and Porter (1978) found that chemical regeneration needed 12 to 20 BV brine at a neutral pH using 0.3 M NaCl. In 2004, Rahmani et al. reported 20 BV brine was required when using 0.3 M NaCl for chemical regeneration at a pH of 7, and the volume of brine could be reduced to 15 BV when the NaCl concentration was increased to 1 M. The maximum regeneration efficiency in Rahmani's study was in the range of 95% to 98%. In conclusion, the optimal NaCl concentration for chemical regeneration should be in the range of 0.3-1 M, and the volume of the regeneration brine should be optimized as 10 to 20 BV for satisfactory regeneration efficiency.

Other parameters that might affect the performance of chemical regeneration, such as flow rate and pH, were investigated in previous studies. The flow rate of the NaCl brine might affect mixing conditions during the regeneration process; however, Koon and Kaufmann (1975) found that the regeneration performance was independent of the flow rate within the range 4–20 BV/hr, and chose 15 BV/hr [29]. Similar results were observed by Semmens and Porter (1979), who varied the regeneration flow rate between 12 and 20 BV/hr and continued with the regeneration flow rate of 12 BV/hr. Liberti et al. (1981) investigated the performance of a pilot plant and employed a flow rate of 24 BV/hr. Demir et al. (2002) also reported that the regeneration performance didn't change significantly when the flow rate was in a range of 16-25 BV/hr. These results clearly showed the flow rate of regeneration brine would not affect the performance of chemical regeneration in a desirable range, as 4-25 BV/hr.

pH can affect the chemical regeneration process because ammonium nitrogen will be transformed to dissolved ammonia under alkaline pH, which can improve the regeneration. Odegaard (1992) recommended a mixture of sodium chloride and sodium hydroxide as the regeneration brine for increasing the pH to improve the regeneration efficiency. Koon and Kaufmann (1975) investigated the impact of pH on the regeneration performance. At a pH of 11.5 and a 0.34 M NaCl concentration, 20 BV of regeneration brine was needed to achieve about 100% regeneration. When the pH was increased to 12 and 12.5, 20 and 10 BV of 0.21 M brine were needed for chemical regeneration, respectively [Koon and Kaufman, 1975]. Higher pH would decrease the volume of regeneration brine compared to using only sodium chloride, and significantly reduce the cost of NaCl dose in the chemical regeneration process.

However, there is no quantitative information on this aspect in literature, despite of high potential of chemical regeneration at alkaline pH.

One of the most important aspects in chemical regeneration of exhausted zeolite is its renewability. The reduction of the cation exchange capacity of exhausted zeolite can substantially increase operating costs in zeolite processes. To engineer zeolite for nitrogen removal and recovery, it is necessary to understand the renewability of the exhausted zeolite after chemical regeneration. Several studies reported that there was no significant change on the cation exchange capacity after 2 or 3 regeneration cycles [Rahmani et al., 2004; Demir et al., 2002; Milan et al., 2011]. However, it is questionable that the exhausted zeolite could maintain a constant cation exchange capacity as chemical regeneration is repeated over three cycles. Unfortunately, there are no published articles that quantitatively assess the renewability of the exhausted zeolite with increasing regeneration cycles, although detailed information on its renewability is critical for engineering zeolite processes.

Table 2.4: Summary Table of Chemical Regeneration

Parameter	Koon and Kaufmann (1975)	Liberti et al. (1981)	Semmens and Porter (1979)	Hlavay et al. (1982)	Cooney et al. (1999)	Demir et al. (2002)	Rahmani et al. (2004)
NaCl Conc.	0.21-0.34 M	0.6 M	0.3 M	0.34 M	0.6 M	0.17-0.34 M	0.3-1M
Flow rate (BV/hr)	15	30	12-20	5-7.5	1-2	16-25	10
Brine Volume	10-20	20	12-20	10-20	20	25-35	15-20
pH	11.5-12.5	7	7-8.4	12.3	10	12.3	7
Regeneration Efficiency	~100%	~100%	/	98-99%	/	/	95-98%

2.2.8 Summary

It is clear that the performance of natural zeolite in ammonium ion exchange process depends on various chemical and physical factors. Clinoptilolite is reported as the best natural zeolite for ammonium exchange, due to its high affinity for ammonium nitrogen. However, the cation exchange capacity of natural zeolite is also determined by its physical properties or operating conditions, such as particle size, pH, ammonium concentration, ionic strength, flow rate, organic matters, and so on.

Chemical regeneration with NaCl solution is essential for reusing exhausted zeolite for nitrogen removal and recovery from wastewater. High regeneration efficiency over 95% can be achieved under an optimal NaCl concentration and pH of the regeneration brine. The cost of NaCl for chemical regeneration seems substantial under neutral pH. This cost could be reduced under alkaline pH conditions, but currently there is no quantitative approach that evaluates the effect of alkaline pH regeneration on NaCl dose. The renewability of exhausted zeolite after repetitive chemical regeneration is critical for engineering zeolite processes for nitrogen removal and recovery from wastewater. However, the literature has not provided any quantitative evidence on the renewability of zeolite processes. For these reasons, alkaline chemical regeneration and the renewability of the exhausted zeolite should be further investigated to address the main limitations of zeolite processes.

Chapter 3 Ammonium nitrogen removal from AnMBR permeate by natural zeolite

3.1. Introduction

Aerobic biological treatment systems (i.e., activated sludge processes) have been widely used for municipal and industrial wastewater. Due to the significant costs of aeration and sludge disposal in aerobic systems, alternatives are necessary to simultaneously decrease the aeration/sludge disposal costs and recover value-added products. The alternative technologies include anaerobic digestion [Resch et al., 2006], anaerobic membrane bioreactors (AnMBRs) [Kiss et al., 2009], dark fermentation [Gomez et al., 2006], microbial fuel cells [Logan and Regan, 2006], or microbial electrolysis cells [Lee and Rittmann, 2010]. AnMBRs generally produce higher-quality effluent than the other technologies, with no suspended solids, and 95-99% of chemical oxygen demand (COD) removal [Saddoud et al., 2007; Lin et al., 2009]; this high-quality permeate facilitates AnMBR application to municipal wastewater treatment. AnMBRs have significant economic benefits including the absence of aeration, methane recovery, and reduced sludge production [Liao et al., 2006; Ho and Sung, 2009]. For these reasons, AnMBRs can provide significant economic benefits and improved sustainability in municipal wastewater treatment.

However, the application of AnMBRs to domestic wastewater has several challenges, such as membrane fouling [Liao et al., 2006], nutrient control [Kin and Pagilla, 2002], and dissolved methane [Kim et al., 2011]. Adding coagulants to AnMBRs can readily remove phosphorus [Tchobanoglous et al., 2003], but nitrogen removal seems challenging. Biological nitrification and denitrification processes subsequent to AnMBRs are able to control nitrogen, but the cost and energy savings in AnMBRs would be traded off by extra costs and materials required for biological nitrogen removal. For instance, in biological nitrogen removal systems, intensive air supply is essential for nitrification, and significant amounts of exogenous electron donors (e.g., ethanol) are required for denitrification. Air stripping, struvite precipitation, membrane separation, and ion exchange can be used for nitrogen removal from AnMBR permeates, but they also have drawbacks, such as costs related to chemicals, aeration, and membrane [Tchobanoglous et al., 2003, Aiyuk et al., 2004; Bott et al., 2007; Jorgensen and Weatherley, 2003; Kim et al., 2007].

Ion exchange using natural zeolites has been found to recover nitrogen with moderate operation and maintenance costs [Jorgensen and Weatherley, 2003; Kim et al., 2007; Dimirkou and Doula, 2008; Zhao et al., 2008; Li et al., 2011]. Although utilizing ion exchange alone may not be attractive, the combination of ion exchange with AnMBRs increases the merits of each process unit, due to their complementary features. First, organic nitrogen is hydrolyzed to ammonium nitrogen in AnMBR permeates, which is ideal for ion exchange with natural zeolites. Second, AnMBR permeates do not contain any particulate matter, which can attenuate clogging events in subsequent zeolite exchange columns, due to their separation by the membrane. Finally, ammonium nitrogen can be recovered and reused as fertilizer. Thus, it is valuable to revisit ammonium ion exchange with natural zeolites for removing and recovering ammonium nitrogen from AnMBR permeates.

Currently, ammonium removal using natural zeolites has several limitations. The first is the high dose of chemicals (e.g., NaCl) required for chemical regeneration of exhausted zeolite. A high NaCl concentration (50-80 g/L) has been reported to improve regeneration efficiency [Li et al., 2011; Milan et al., 2011; Koon and Kaufman, 1975], and accounts for 50-60% of total operation and maintenance costs [Milan et al., 2011]. The second challenge is a competitive ion effect on ammonium exchange of natural zeolite. Municipal wastewaters typically contain K^+, Mg^{2+}, and Ca^{2+} in mM ranges [Hlavay et al., 1982; Laurenson et al., 2010], which can reduce the ammonium uptake by natural zeolite. Early breakthrough in zeolite-packed columns necessitates frequent regeneration, increasing chemical costs. The final challenge is the renewability of the exhausted zeolite as the regeneration of the zeolite is repeated. There is limited information on the effect of repeated regeneration on the ammonium uptake by zeolite; the literature reports earlier breakthrough as exhausted zeolite was repetitively regenerated [Milan et al., 2011; Du et al., 2005; Cooney et al., 1999]. More detailed information on the ammonium uptake by regenerated zeolite is essential for better design of zeolite-packed columns.

This study was conducted to address three major challenges of natural zeolite for nitrogen control: (1) high NaCl dose, (2) competitive ion effects on ammonium uptake, and (3) the renewability of exhausted zeolite. The impact of various operating parameters (initial ammonium concentrations, pH, reaction time, and mixing intensities) on the ammonium uptake and regeneration efficiency of a natural zeolite was investigated in batch experiments. The ammonium uptake and the regeneration efficiency of four natural zeolites (Zeobest, Zeobrite Ex, Zeobrite Lm and Zeolite-CW) and one synthetic resin (SIR-600) were then compared in batch tests to select the best natural zeolite, which was then used in a continuous zeolite-packed column test. Competitive ion effects on the ammonium uptake and the regeneration efficiency of the selected zeolite using AnMBR permeates were subsequently assessed. Finally, in the continuous zeolite-packed column, breakthrough curves for the NH_4Cl solution and AnMBR permeates were developed, and the regeneration efficiency under different conditions was evaluated. The renewability of exhausted zeolite was also evaluated in continuous column tests.

3.2. Materials and Methods

3.2.1 Batch studies

3.2.1.1 Preliminary batch study

A natural zeolite (Bear River Zeolite Corp., USA) was selected for the preliminary batch tests. The Bear River Zeolite is a clinoptilolite, which has a high cation exchange capacity and costs less than synthetic zeolite. The ammonium uptake by the Bear River natural zeolite and the regeneration efficiency of the exhausted zeolite were evaluated with batch experiments using 250 mL serum bottles. The natural zeolite was pre-treated with 20 g/L NaCl (CAS No. 7647-14-5, UPS grade, Sigma Aldrich, Canada) for one day before tests. After pretreatment, 1 g zeolite granule was placed in each bottle, and 100 mL of NH_4Cl solution was poured into the bottle to reach a desired concentration. Under each operating condition, two serum bottles were used for duplicate experiments. Average data from the duplicate tests were reported in the results section.

The initial ammonium concentrations varied from 5 mg N/L to 800 mg N/L at a fixed pH of 6.9±0.1 using a 10 mM phosphate buffer solution ($KH_2PO_4/Na_2HPO_4.12H_2O$). The serum bottles were placed in a shaker (Orbital Shaker, VWR Inc., Canada) for 6 days at a temperature of 20±2° C and a mixing intensity of 200 rpm (Appendix A1). The effect of initial pH (5.5 to 10.5) on the ammonium uptake was evaluated at a fixed NH_4^+-N concentration of 50±3.2 mg N/L. The pH was adjusted with 10 mM phosphate buffer ($KH_2PO_4/Na_2HPO_4.12H_2O$), 0.1 M HCl, or 0.1 M NaOH. Ammonium exchange tests at different pH conditions were carried out in the shaker under the aforementioned conditions.

The chemical regeneration efficiency of the exhausted zeolite was evaluated using an NaCl solution. After the ammonium exchange tests under an initial NH_4^+-N concentration of 50 mg N/L, a pH of 7 and 24 hours of reaction time, 95 mL supernatant was decanted, and 95 mL NaCl solution was added to the serum bottles, which were then shaken for 2 hours at a temperature of 20±2° C. Regeneration experiments were used to assess the impacts of three parameters: (i) NaCl concentration, (ii) initial pH, and (iii) mixing intensity. The NaCl dosage varied from 5 g/L to 30 g/L (24 hours of reaction time); the initial pH was from 7 to 9 (NaCl dose of 10 g/L and 2 hours of reaction time); and the shaking intensity was at 200 rpm and 400 rpm (pH 9, NaCl 10 g/L, 2 hours of reaction time).

3.2.1.2 Batch studies with different natural zeolites and synthetic resin

Under the optimized conditions, the ammonium uptake and the regeneration efficiency of four natural zeolites were compared, to select the best ammonium exchanger for use in the continuous column experiments. All four types of natural zeolite were clinoptilolite, which was reported as the best natural zeolite for ammonium exchange reactions in the literature [Koon and Kaufman, 1975; Hlavay et al., 1982; Semmens et al., 1981]. One cationic exchange resin (SIR-600) was used as a control to evaluate the ammonium uptake and the regeneration efficiency of the best natural zeolite. Under each operating condition, two serum bottles were used for duplicate experiments.

The ammonium uptakes by the five exchangers were compared under the following conditions: an initial pH of 6.9±0.1, an initial NH_4^+-N concentration of 50±3.2 mg N/L, a mixing intensity of 200 rpm, 4 hours reaction time, and a room temperature of 20±2°C. Table 3.1 presents the detailed characteristics of these ion exchangers. The cation exchange capacities of these five exchangers are in the range of 0.5~1.8 meq/g. The regeneration experiments for the five exchangers were carried out with a shaking intensity of 200 rpm, 2 hours reaction time, and a room temperature of 20±2°C. The initial pH was fixed at 9±0.4 (an optimum pH for regeneration determined in previous batch tests), and the NaCl dosage was changed from 20 g/L to 80 g/L.

Table 3.1: Properties of natural zeolite and cation exchange resin

	Zeobest	Zeobrite Ex	Zeobrite Lm	Zeolite-CW	Resin-SIR600
Supplier	Northern Filter Media	Zeotech Corporation	Zeotech Corporation	ZeoponiX, Inc. and Boulder Innovative Technologies, Inc	ResinTech Inc.
CAS No.	1318-02-1	12173-10-3	12173-10-3	N/A	1318-02-01
Chemical composition	Clinoptilolite, hydrated potassium, calcium, sodium, aluminosilicate or silicoaluminate	Clinoptilolite, potassium, calcium, sodium, aluminosilicate, hydrated with bonded copolymer	Clinoptilolite, potassium, calcium, sodium, aluminosilicate, hydrated	Clinoptilolite, high CEC, high in K, low in Na	Sodium/potassiumzeolite, without alumina acid sites SiO_2/Al_2O_3=1000 (90-100%) water (0-10%)
Specific gravity	1.6	2.2-2.4	2.2-2.4	N/A	1.2
Size	30 – 3/8 in	N/A	N/A	8×40 mesh	16 to 50 nominal
Physical appearance	Pale green granuals, ordoless	Off-white/green granules	Off-white/green granules	N/A	Granular, dry, tan powder, odorless
Cation exchange capacity	1.2～1.8 meq/g	0.5～0.7 meq/g	0.5~1.5 meq/g	～1.6 meq/g	1.2~1.4 meq/g

3.2.1.3 Batch studies with Zeobrite Lm using both NH_4Cl and AnMBR permeate

The ammonium uptake and the regeneration efficiency of a selected natural zeolite with the permeates of anaerobic membrane bioreactors (AnMBRs) were investigated in batch tests to assess the effect of competitive ions on the ammonium uptake at equilibrium and the regeneration efficiency. Permeates from an AnMBR pilot treating municipal wastewater (Burlington, ON, Canada) were sampled regularly. The average concentrations of chemical oxygen demand (COD) and ammonium nitrogen, and the pH were 31±8 mg/L and 31±3.5 mg N/L, and 7.2±0.3, respectively. Besides ammonium ions, other cations existing in the permeate (eg. Na^+, K^+, Mg^{2+}, Ca^{2+}) were measured in quadruplicate by an ion chromatograph before and after the ammonium ion exchange tests. Regeneration tests were carried out at two alkaline pH conditions, one of 9 and the other of 12, to demonstrate that a high pH could improve the regeneration efficiency at a lower NaCl dose, because the ammonium ions convert to dissolved ammonia or ammonia gas during regeneration.

Under each operating condition, two serum bottles were used for duplicate experiments. 100 mL of AnMBR permeate and 1 g of zeolite (Zeobrite Lm) were added to serum bottles for the ammonium exchange tests, and the experiments were conducted under the following conditions: a mixing intensity of 200 rpm, 4 hours reaction time, and a temperature of 20±2°C. The regeneration experiments were conducted with the procedure explained above. The operating conditions were 200 rpm of mixing intensity, 2 hours of reaction time, a temperature of 20±2°C, an 80 g/L NaCl dosage, and a pH of 9±0.4. After the regeneration test at pH 9, batch tests were conducted to evaluate the regeneration efficiency of zeolite at a high pH (~12), with a 10 g/L NaCl solution under the aforementioned operating condition.

All batch experiments were conducted in duplicate under the same conditions, and the ammonium nitrogen concentration was quantified in quadruplicate. The average values were reported in the results section with standard deviations.

3.2.2 Continuous column studies

A cylindrical Plexiglas column (6.35 cm in diameter, 45.7 cm in height, and a total volume 1.5 L), as shown in Figure 3.1, was manufactured, and packed with 1.3 kg of natural zeolite, resulting in a total bed volume (BV) of 0.75 L. Either an ammonium solution (30±3.1 mg N/L, pH 6.9±0.1) or AnMBR permeate (31±3.5 mg N/L, pH 7.2±0.3) was continuously fed into the zeolite-packed column with a peristaltic pump (Masterflex® L/S® economy variable-speed drive, Masterflex, Canada) at a flow rate of 4 or 8 BV/hr. Once breakthrough occurred (5% of influent ammonium nitrogen concentration in effluent), pumping of the ammonium nitrogen feed was stopped, the liquid in the column was drained, and the column was switched to regeneration mode. The breakthrough under different operating conditions was evaluated in this test. The results were shown as an averaged value from the duplicate samplings.

To assess the effect of pH on the regeneration process, the regeneration efficiency was compared under two conditions. One condition was a high dose of NaCl at pH

9±0.4 (NaCl concentration 20 g/L, 80 g/L, and 160 g/L), and the other was a low dose of NaCl at pH 12±0.5 (NaCl concentration 10 g/L, 20 g/L, and 40 g/L). After adjusting pH and NaCl concentration in the regenerant container, the NaCl regenerant was fed to the zeolite-packed column (see Figure 3.1). Duplicate experiments were conducted under each operating condition, and the ammonium nitrogen concentration was quantified in quadruplicate.

The performance of natural zeolite for repetitive regeneration, and reuse for ammonium exchange in 24 cycles was investigated. The results were shown as an averaged value from the duplicate samplings. An NH_4Cl solution (30±3.1 mg N/L, pH 6.9±0.1) was fed into the zeolite-packed column at a flow rate of 8 BV/hr. At the breakthrough point, the feed was stopped, the liquid was drained from the column, and then the column was operated in regeneration mode using a fixed NaCl concentration of 10 g/L at a flow rate of 4 BV/hr for 1 day. The results were shown as an averaged value from the duplicate samplings.

All column tests were conducted at room temperature (20±2° C), and the ammonium nitrogen concentration was quantified in quadruplicate for each sample. The average values are reported here with standard deviation.

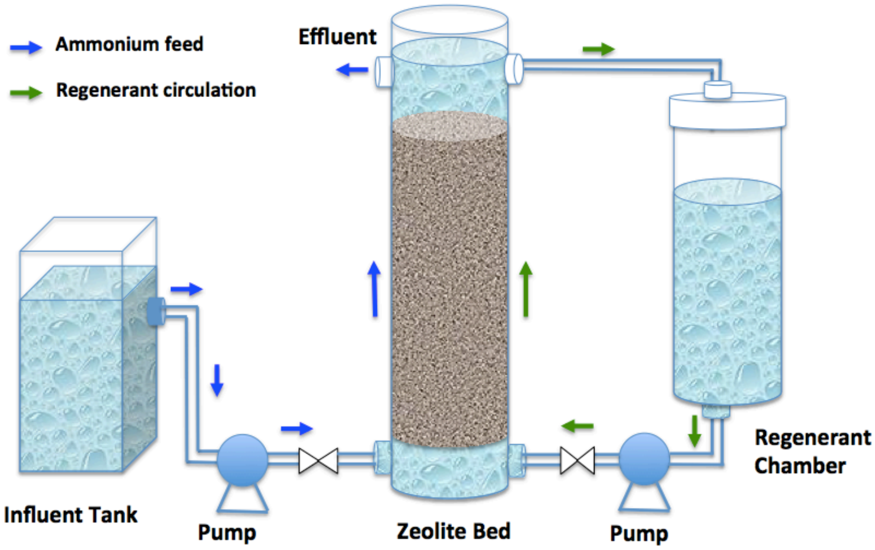


Figure 3.1. Schematic diagram of a continuous zeolite-packed column operation.

3.2.3 Analytical methods

The ammonium concentration was measured by an Auto Analyzer 3 (Bran-Luebbe, Germany) that quantifies ammonium nitrogen and dissolved ammonia (Appendix A4). A calibration curve (see Appendix B1) was developed with an NH_4Cl standard solution (0.5～30 mg N/L). pH was measured with a Benchtop pH Meter (Model 420A, Orion Research Inc., USA). Cation concentrations were measured using an ion chromatograph (Dionex DX-300, Dionex Corporation, USA) equipped with a CS16 cation column, a conductivity detector, and an automated sampler (Appendix A5). The CS16 column was used with a cation self-regenerating suppressor. The calibration curves for the cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) are shown in Appendix B2. COD concentration was measured with Hach COD analysis kits (reagent 20-1,500 mg/L COD range, Hach Company, USA), according to Hach method.

The ammonium uptake by zeolite at time t was calculated according to equation (3.1):

$$\text{Ammonium uptake}_{t} = (C_{N,ini} - C_{N,t}) \times V_N / W_{zeolite} \qquad \text{Eq (3.1)}$$

where $C_{N,ini}$ is the initial ammonium concentration (mg N/L) in the ammonium-containing solution (NH_4Cl or AnMBR permeate), $C_{N.t}$ is the ammonium concentration (mg N/L) at time t, V_N is the volume of the solution (L), and $W_{zeolite}$ is the mass of zeolite (g).

The regeneration efficiency (RE) of the exhausted zeolite was computed with equation (3.2):

$$RE = (C_N(aq) \times V_{liquid}/M_{exhausted}) \times 100 \qquad \text{Eq (3.2)}$$

Where, $C_N(aq)$ is the sum of ammonium and dissolved ammonia concentrations in NaCl regenerant (mg N/L) during regeneration, V_{liquid} is the regenerant volume (L), and $M_{exhaused}$ is the ammonium mass exchanged by zeolite (mg) determined with exchange tests.

In batch tests, the ammonium mass exchange by zeolite ($M_{exhausted}$) was computed with equation (3.3):

$$M_{exhausted} = (C_{N,ini} – C_{N.final}) \times V_N \qquad \text{Eq (3.3)}$$

Where, $C_{N,ini}$ is the initial ammonium concentration (mg N/L) in the ammonium-containing solution (NH_4Cl or AnMBR permeate), $C_{N.final}$ is the ammonium concentration (mg N/L) after ion exchange, and V_N is the volume of the solution (L).

In continuous column tests, the ammonium mass exchange by zeolite ($M_{exhaused}$) was computed with equation (3.4):

$$M_{exhausted} = \int_0^{V_{final}} (C_0 - C)dV \qquad \text{Eq (3.4)}$$

Where, C_0 is the influent ammonium concentration (mg N/L) in the ammonium-containing solution (NH_4Cl or AnMBR permeate), C is the effluent ammonium concentration (mg N/L), and V is the total volume of the ammonium feed (L).

The ammonium nitrogen release rate during regeneration ($Q_{release}$) was computed with equation (3.5):

$$Q_{release} = (C_{N,final}(aq) \times V_{liquid})/(W_{zeolite} \times t) \qquad \text{Eq (3.5)}$$

Where, $C_{N,final}$(aq) is the sum of ammonium and dissolved ammonia concentrations in NaCl regenerant (mg N/L) after regeneration, V_{liquid} is the regenerant volume (L), $W_{zeolite}$ is the mass of zeolite (g), and t is the regeneration time (hr).

The mass ratio of Na^+ to Zeolite-NH_4^+-N was computed with equation (3.6):

$$Na:N = (M_{NaCl} \times \frac{23}{58.5}) / M_{exhausted} \qquad \text{Eq (3.6)}$$

Where, M_{NaCl} is the mass of NaCl used for regeneration (g), 23 and 58.5 are the mole weight of Na and NaCl, and $M_{exhaused}$ is the ammonium mass exchanged by zeolite (g) determined with exchange tests.

3.3 Results and discussions

3.3.1 Batch studies

3.3.1.1 Effects of ammonium concentration and pH on ammonium uptake

The ammonium uptake by natural zeolite increased when the initial ammonium concentration was increased, and reached a plateau (see Figure 3.2a). The ammonium uptake was 3.6±0.24 mg N/g zeolite at an initial ammonium concentration of 47±4.8 mg N/L (close to the maximum ammonium concentration in AnMBR permeates), and increased to 12±0.29 mg N/g zeolite at 767±23 mg NH_4^+-N/L. Figure 3.2b shows that the equilibrium for the uptake of ammonium by natural zeolite was successfully applied to the Freundlich model for the purpose of providing a simple relationship between the equilibrium ammonium concentrations in the solution and solid phases. The data may be adequately represented by the expression:

$$q=k*C^n \qquad \text{Eq (3.7)}$$

where q is the equilibrium ammonium uptake by zeolite (mg N/g zeolite), C is the equilibrium ammonium concentration in the solution phase (mg N/L). The empirical constants k and n were 0.083 and 0.752, respectively (Figure 3.2b). The determination coefficient value of Freundlich isotherm was found satisfying R^2 = 0.939.

The equilibrium between ammonium concentrations in the solution and solid phases can also be presented by Langmuir isotherm as the following equation:

$$\frac{1}{q} = \frac{1}{Kb}*\frac{1}{C} + \frac{1}{b} \qquad \text{Eq (3.8)}$$

where q is the equilibrium ammonium uptake by zeolite (mg N/g zeolite), C is the equilibrium ammonium concentration in the solution phase (mg N/L). As shown in Figure 3.2c, the maximum uptake of ammonium b was 23.26 mg N/g zeolite (b=1/0.043), and the Langmuir constant K was 0.014 (K=1/(3.179*b)). The determination coefficient value (R^2) of Langmuir isotherm was found to be 0.994.

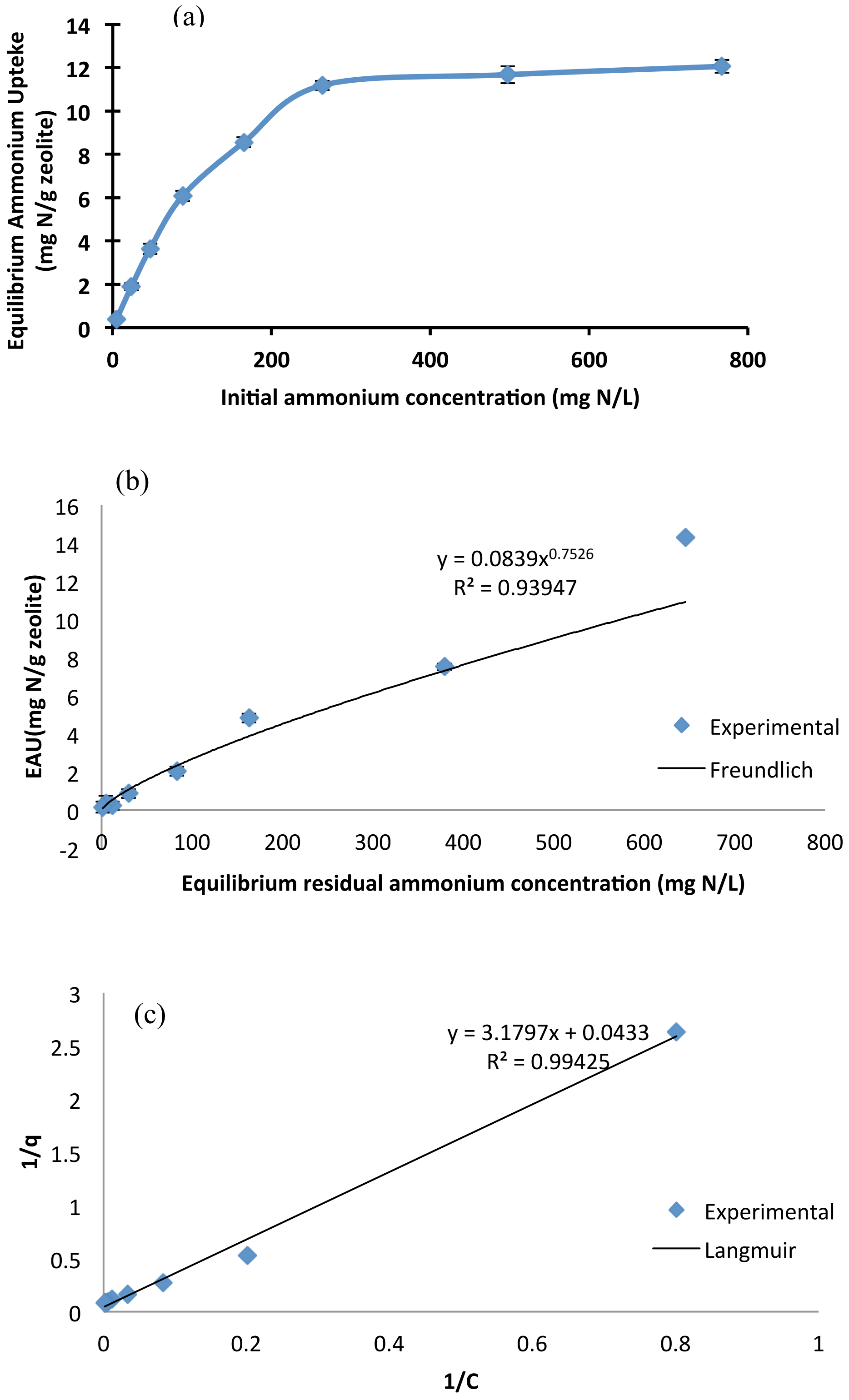


Figure 3.2. (a) Equilibrium ammonium uptake (EAU) by natural zeolite (Bear River Inc., USA) at different initial ammonium concentrations, (b)Freundlich isotherm of ammonium uptake, and (c) Langmuir isotherm of ammonium uptake

The initial pH ranging from 5.5 to 8.5 did not influence the ammonium uptake by the zeolite at equilibrium, which was constant from 3.6±0.19 to 3.9±0.09 mg N/g zeolite (Figure 3.3a). The ammonium exchange tests above pH 9 (pH 9.5 and 10.5) indicated substantial decrease of equilibrium ammonium uptake down to 1-2 mg N/g zeolite probably because of the transformation of ammonium ions into dissolved un-ionized ammonia that is inaccessible for ion exchange reactions with sodium ions, or the nitrogen loss as ammonia gas during batch tests. The following equation (Eq.3.9) defines the relationship between ammonium and ammonia in an aqueous solution:

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [H^+]/K_a} \qquad \text{(Eq. 3.9)}$$

where $[NH_3]$ is the free-ammonia concentration, $[NH_3+NH_4^+]$ is the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration, and Ka is the acid ionization constant for ammonia, which is 9.3 for NH_3 at 25° C. As Figure 3.4 shows, at a pH of 7 or below, only ammonium ions are present. As the pH increases above 7, the chemical equilibrium is gradually shifted to the left in favor of the ammonia gas formation, and only the dissolved gas is present at pH 11.5-12.

Figure 3.3b shows the relationship between solid and liquid phase ammonia at equilibrium. The ratio of solid to liquid phase ammonia was constant at a pH range 5.5 to 8.5, and it substantially decreased when the pH was raised to 9.5. It supported the transformation of ammonium ions into dissolved ammonia gas at a pH over 9, and the rate of ammonium uptake was significantly reduced.

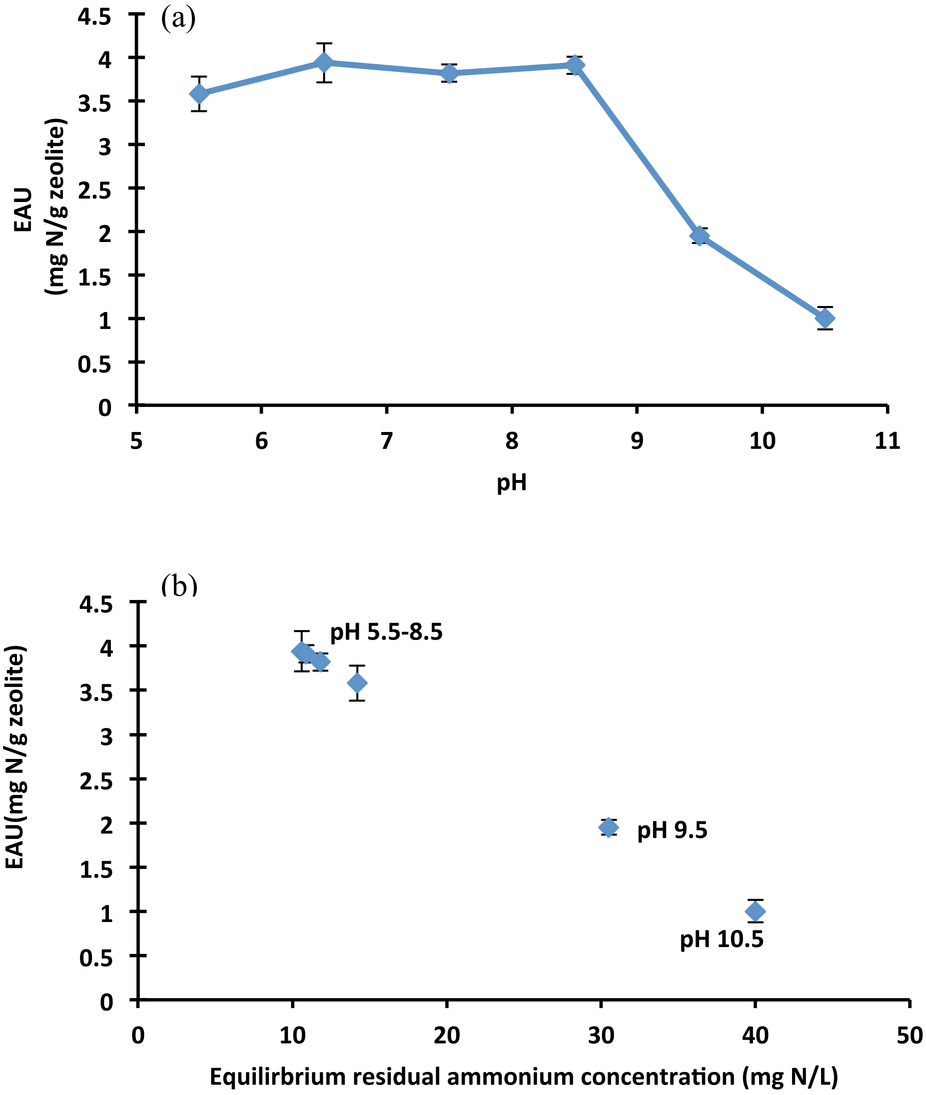


Figure 3.3. (a) Equilibrium ammonium uptake (EAU) of natural zeolite at different pH, and (b) relationship between EAU and equilibrium residual NH_4^+-N at different pH,

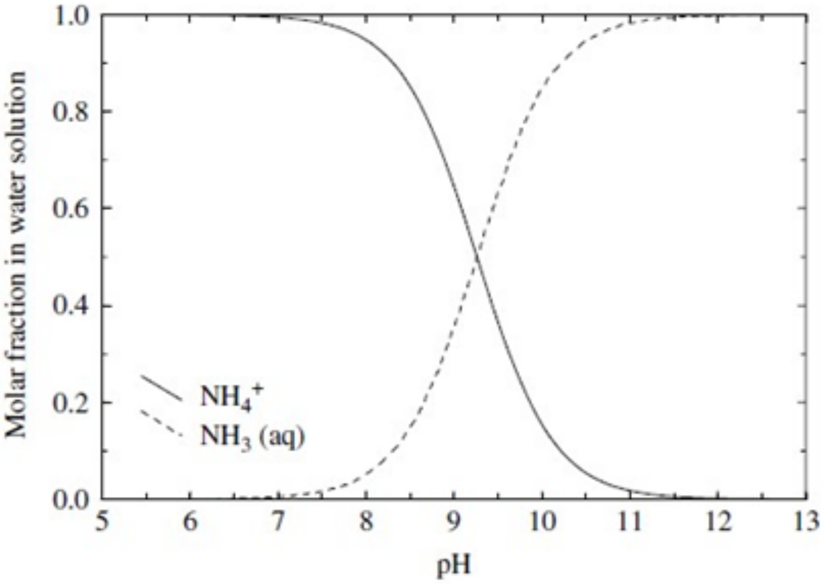


Figure 3.4. Speciation diagram of ammonia in water solution at T=25 ◦C.

3.3.1.2 Effects of NaCl dosage, pH and mixing intensity on regeneration efficiency

The regeneration efficiency of exhausted zeolite linearly increased with the NaCl dose (Figure 3.5a), and it was 64±3.1 % at an NaCl dose of 30 g/L. The regeneration efficiency was independent of pH in the range of 7 to 9 (Figure 3.5b); the maximum regeneration efficiency of 50±2.4% was obtained at a pH of 9±0.4, and thus pH 9 was used for further regeneration tests. The regeneration efficiency remained constant at different mixing intensities from 200 rpm to 400 rpm, as shown in Figure 3.5c.

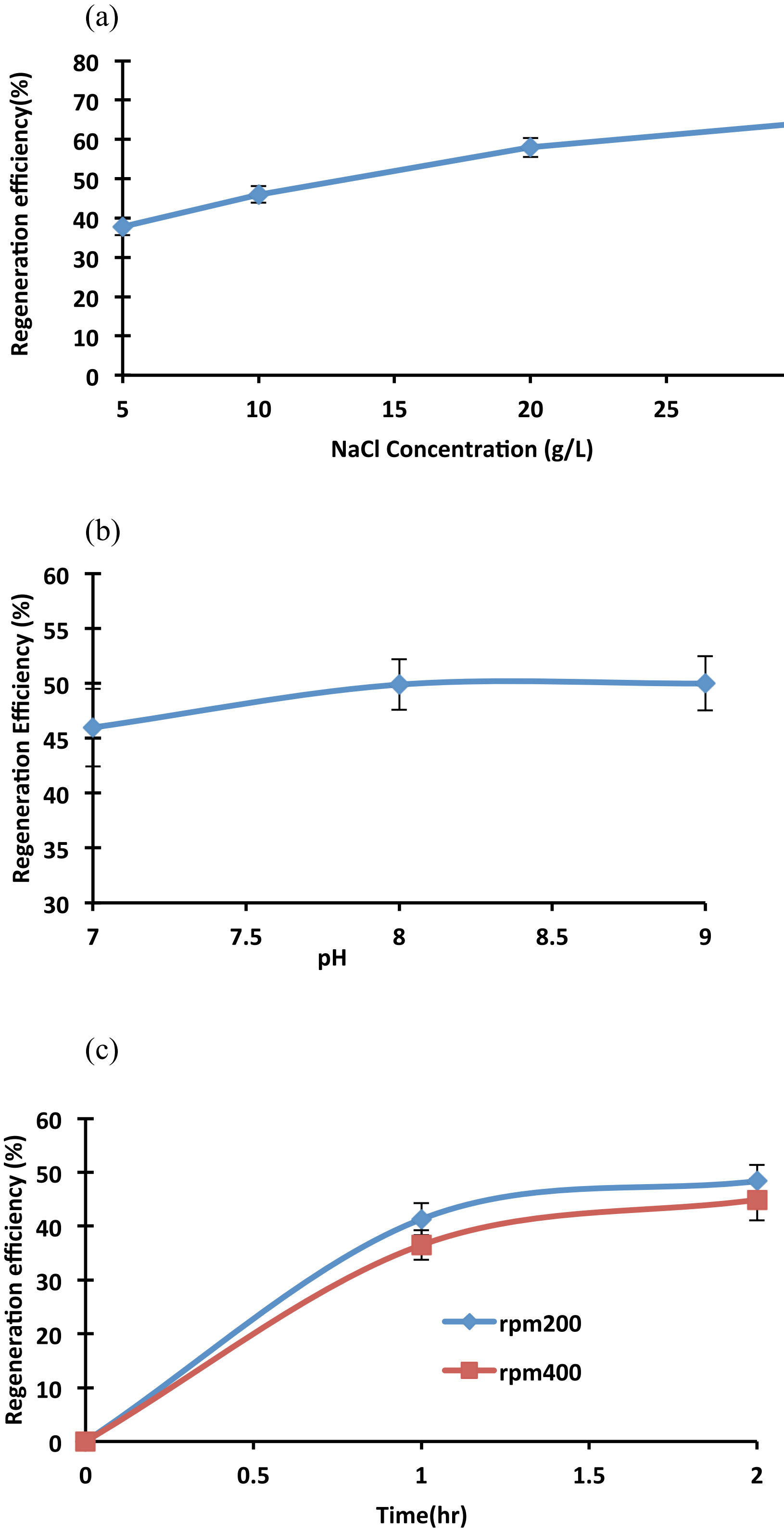


Figure 3.5. Regeneration efficiency of exhausted zeolite. (a) NaCl dose, (b) pH, and (c) mixing intensities.

3.3.1.3 Comparison of various natural zeolites

Figure 3.6a shows the ammonium uptake by four natural zeolites (Zeobest, Zeobrite Ex, Zeobrite Lm, Zeolite-CW) and a cation exchange resin (SIR-600), using an initial NH_4^+-N concentration of 50±3.2 mg N/L and a pH of 6.9±0.1. The ammonium uptake increased sharply with reaction time and reached a plateau after one hour for all zeolites, except for Zeolite Ex that took 2 hours to reach a plateau. The EAU of the three natural zeolites (Zeolite-CW, Zeobest, and Zeobrite Lm) and the synthetic resin were comparable and the EAU ranged from 4.2±0.01 to 4.7±0.02 mg N/g zeolite (with a removal efficiency of 83% to 94%). Zeobrite Ex showed the lowest EAU of 3±0.02 mg N/g zeolite. The EAU and regeneration efficiency of the natural zeolites were similar to that of the synthetic resin (SIR-600), except for Zeobrite Ex.

Figure 3.6b shows the relationship of equilibrium residual ammonium concentration and EAU for the four natural zeolites and the cation exchange resin in exchange tests. The ratio of liquid to solid phase ammonia was constant for four natural zeolites, except for Zeobrite Ex, which showed the lowest rate of ammonium uptake.

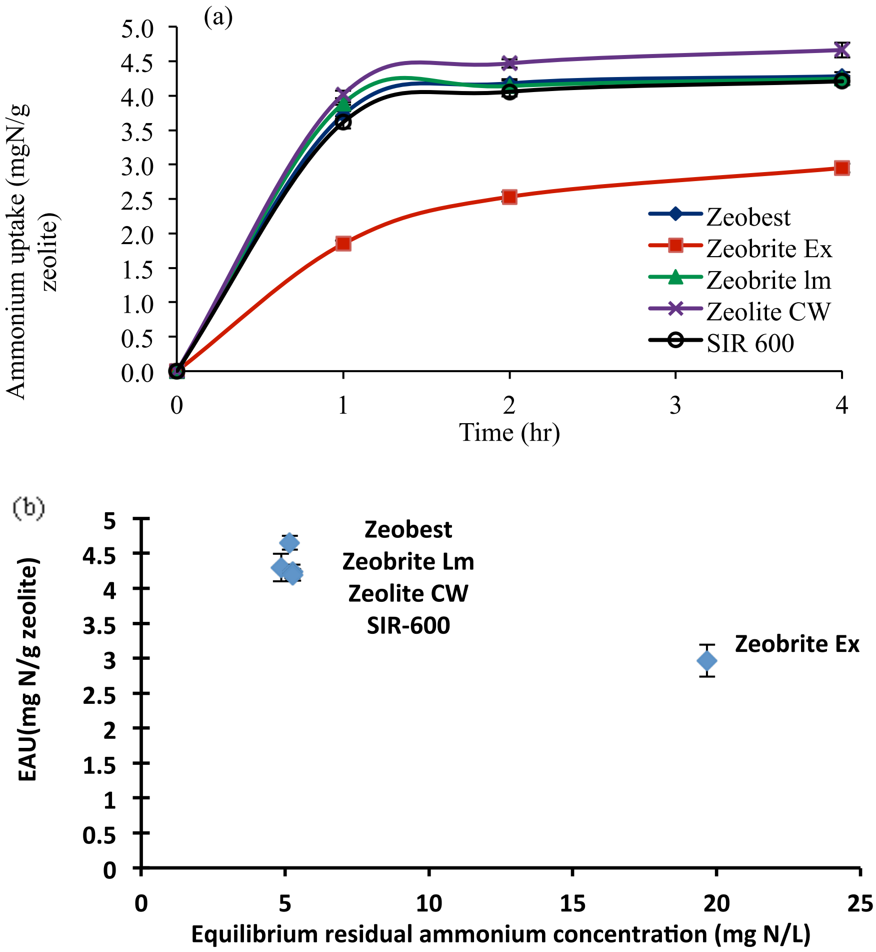


Figure 3.6. (a) Ammonium uptake by the four natural zeolites and cation exchange resin (SIR-600), (b) relationship between EAU and equilibrium ammonium concentration for the four natural zeolites and cation exchange resin (SIR-600)

Figure 3.7a shows the regeneration efficiencies for the four natural zeolites, using 20 g/L NaCl at pH 9±0.4. The regeneration efficiencies reached a plateau after 1 hour of reaction time for all the natural zeolites. Zeobrite Lm and Zeobrite Ex showed relatively higher regeneration efficiencies (61±2.4~65±3.3%) than those for Zeolite-CW and Zeobest (53±1.2%), and hence, Zeobrite Lm was selected for further experiments. Zeobrite Lm presented higher equilibrium ammonium uptake and regeneration efficiency, which mean that this zeolite would have large exchangeable site areas and high ion exchange affinity between NH_4^+ and Na^+, as compared to other zeolites [26,27].

Batch experiments were conducted in duplicate to optimize the regeneration efficiency of Zeobrite Lm at different NaCl dosages (20-80 g/L), at a fixed pH of 9±0.4, for 2 hours of reaction time. The regeneration efficiency linearly increased with increasing NaCl dosages, and reached 94±1.8% at a dosage of 80 g/L NaCl (Figure 3.7b). At equilibrium, 1 mol Na^+ in bulk can be replaced by 1 mol of ammonium nitrogen in zeolite (1.65 g Na^+/g Zeolite-NH_4^+-N), while it takes over one day to reach equilibrium due to sluggish kinetics [20,28,29]. The regeneration time was limited to 2 hours in our experiments. In this case, the high NaCl dose accelerated regeneration reactions, as reflected by rates of 2.9±0.04 mg N release/g zeolite-h in a dosage of 20 g/L NaCl vs. 4.1±0.03 mg N release/g zeolite-h in a dosage of 80 g/L NaCl. The mass ratios of sodium to exchanged ammonium nitrogen were 187 and 749 g Na^+/g Zeolite-NH_4^+-N for the NaCl concentration of 20 g/L and 80 g/L, respectively. The regeneration efficiency of Zeobrite Lm was compared with the cation exchange resin (SIR-600) under identical conditions (NaCl 80 g/L at pH 9±0.4). At the same regeneration conditions, the regeneration efficiency of Zeobrite Lm was very close to SIR-600 (slightly higher ~7% than SIR-600), as shown in Figure 3.7c. The high EAU and regeneration efficiency confirms that Zeobrite Lm is the best ammonium exchanger; moreover, it is much cheaper than the cation exchange resin.

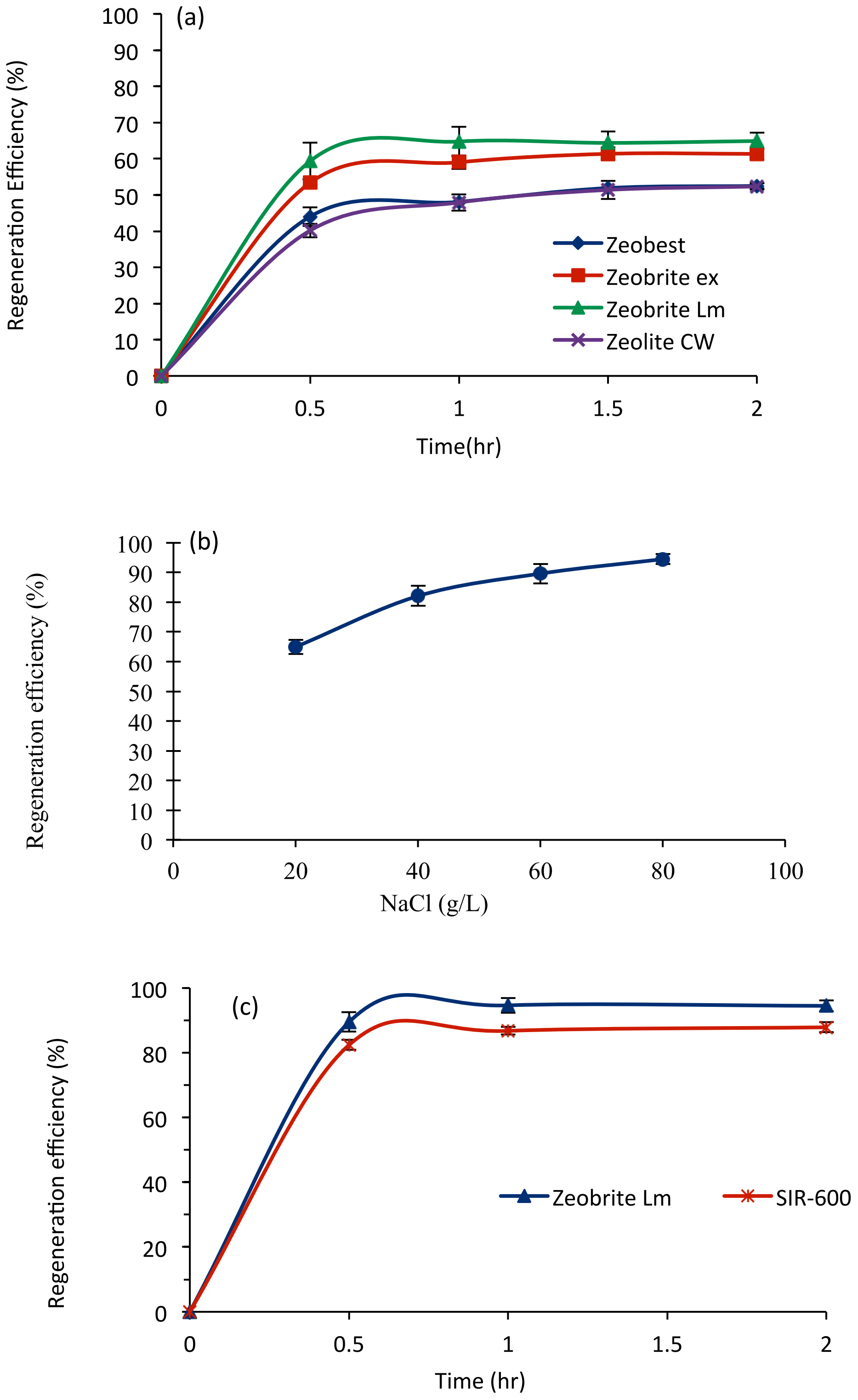


Figure 3.7. (a) Regeneration efficiency of the four natural zeolites (NaCl 20 g/L, at pH 9), (b) Regeneration efficiency using Zeobrite Lm at various NaCl dosages, (c) Comparison of regeneration efficiency between Zeobrite Lm and cation exchange resin (SIR-600) (NaCl 80 g/L at pH 9).

3.3.1.4 Competitive ion effects and high pH regeneration of natural zeolite with AnMBR permeates

Figure 3.8 shows the ammonium uptake by the natural zeolite (Zeobrite Lm) and the residual ammonium concentration in liquid phase when the AnMBR permeate and NH_4Cl solution were employed in duplicate experiments. The NH_4^+-N concentrations were 50±3.2 mg N/L and 31±3.5 mg N/L, for NH_4Cl solution and AnMBR permeate, respectively. After 4 hours, the ammonium uptake from the NH_4Cl solution and the AnMBR permeate reached equilibria, which were 4.2±0.02 mg N/g zeolite and 2.5±0.02 mg N/g zeolite, respectively.

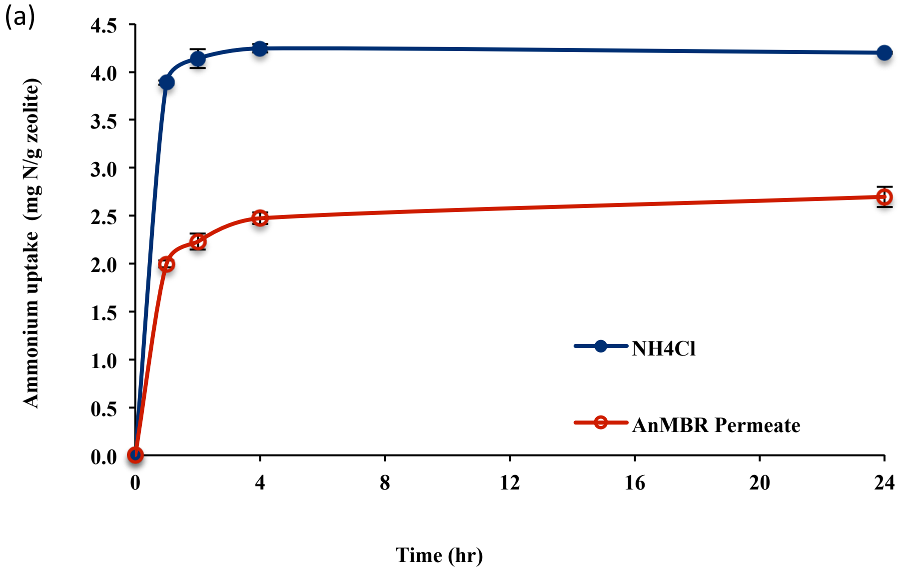


Figure 3.8. Ammonium uptake by Zeolite Lm for AnMBR permeates and NH_4Cl solution.

The EAU reduction in the AnMBR permeates indicates the presence of other competitive ions i.e., K^+, Mg^{2+}, Ca^{2+}, which would exchange with sodium ions in the zeolite, instead of ammonium ions. To assess this ion competition effect on the ammonium uptake, the exchange tests were conducted with the AnMBR permeate. Table 3.2 shows the concentrations of the five major cations of Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+ in the permeate before and after exchange experiments. At the end of the exchange tests, ammonium concentration decreased from 2.4 mM to 0.5 mM, and the concentrations of K^+, $Mg^{2+}$and Ca^{2+} also decreased. In comparison, the Na^+ concentration increased from 6.9±0.12 mM to 11.4±0.35 mM, reflecting a charge balance of 98% ($+4.5\times10^{-3}$ M against -4.6×10^{-3} M). This result supports the hypothesis of cationic competition with ammonium nitrogen during zeolite exchange reactions in the AnMBR permeate. In the NH_4Cl solution with 10 mM phosphate buffer, the estimated initial Na^+ concentration was 2.6 mM and the initial K^+ concentration was 4.8 mM; in the AnMBR permeate, they were 6.9±0.1 mM and 1.1±0.05 mM, respectively. The sum of positive charges of these two ions in the NH_4Cl solution was $+7.4\times10^{-3}$ M, which was similar to that in the AnMBR permeate ($+8.0\times10^{-3}$ M). Thus, the main competing cation to NH_4^+ was Ca^{2+}, while Mg^{2+} and K^+ ions were less competitive. This trend agrees well with the literature [Koon and Kaufman, 1975; Huang et al., 2010; Weatherley and Miladinovic, 2004]. The EAU decrease with the AnMBR permeate indicates early breakthrough in continuous column tests, as compared to NH_4Cl solution, and would necessitate more frequent regeneration of the zeolite column.

Table 3.2: Cations balance during ammonium exchange tests from AnMBR permeates.

Cations	Concentrations (mM)		$Z*\Delta C$ (mM)
	Initial	Final (after exchange experiment)	
Na^+	6.9±0.12	11.4±0.35	+4.5
K^+	1.1±0.05	0.6±0.02	-0.5
Mg^{2+}	0.5±0.01	0.4±0.01	-0.2
Ca^{2+}	1.2±0.07	0.2±0.03	-2.0
NH_4^+-N	2.4±0.04	0.5±0.01	-1.9

Note. Z and ΔC represent charge and concentration change (mM) .

The regeneration efficiency of zeolite that was exhausted with AnMBR permeates was evaluated at two conditions: a high NaCl dose (80 g/L, 749 g Na^+/g Zeolite-NH_4^+-N) at pH 9±0.4, and a low NaCl dose (10 g/L, 94 g Na^+/g Zeolite-NH_4^+-N) at pH 12±0.5. As shown in Figure 3.9, an average regeneration efficiency of 94±1.8% was achieved after 2 hours using the high NaCl dose. Interestingly, an average regeneration efficiency of 96±1.3% was obtained at the low NaCl dose at pH 12±0.5 in 2 hours.

The rapid transformation rate of ammonium ions into dissolved ammonia (less than a few seconds) in bulk liquid [Rahmani et al., 2009; Stumm and Morgan, 1996; Culp et al., 1978] causes a high ammonium concentration gradient between the zeolite and liquid bulk during chemical regeneration, which can significantly accelerate the regeneration efficiency at a low mass ratio of Na^+ to Zeolite-NH_4^+-N. Under typical batch regeneration conditions, the ammonium ions liberated from the zeolite accumulate in the bulk liquid with time, hampering the regeneration, due to the low ammonium concentration gradient between the zeolite and the bulk liquid. To accelerate this replacement rate, the mass ratio of Na^+ to Zeolite-NH_4^+-N must be much higher than the thermodynamic equilibrium ratio of 1.65 g Na^+/g NH_4^+-N. A mass ratio of 749 g Na^+/g Zeolite-NH_4^+-N (80 g/L NaCl) achieved a 94±1.8% regeneration efficiency, at pH 9±0.4 after 1 hours, while at pH 12±0.5, a 96±1.3% regeneration efficiency was observed in 2 hours at a mass ratio of only 94 g Na^+/g Zeolite-NH_4^+-N (10 g/L NaCl).

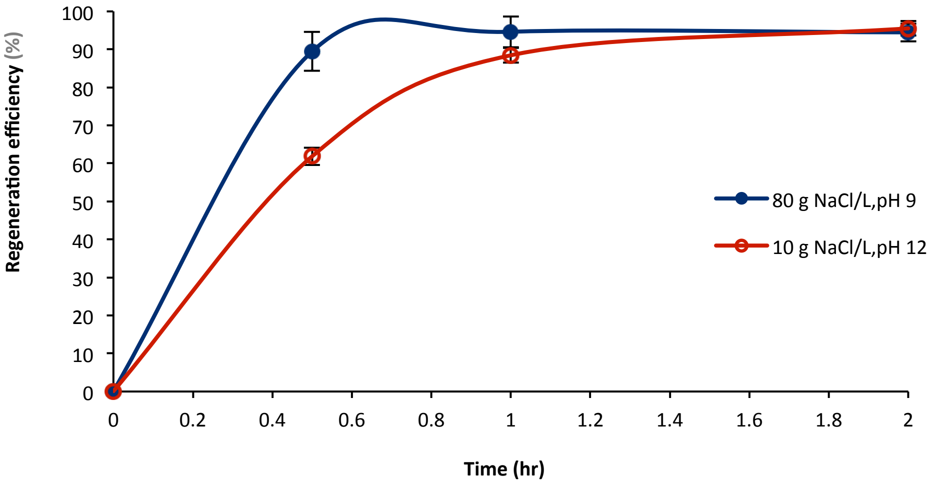


Figure 3.9. Regeneration efficiency for exhausted zeolite (80 g NaCl/L at pH 9 and 10 g NaCl/L at pH 12)

3.3.2 Continuous column tests

3.3.2.1 Breakthrough of AnMBR permeate and NH_4Cl solution

Figure 3.10a compares the breakthrough curves for NH_4Cl and AnMBR permeates at flow rates of 4 BV/hr and 8 BV/hr (BV=0.75 L). Breakthrough was defined as the point when the effluent ammonium concentration reached 5% of the influent concentration (1.5 mg N/L). For the NH_4Cl feed, the breakthrough occurred after 48 hours at 4 BV/hr, and decreased to 24 hours at 8 BV/hr. For the AnMBR permeate, the breakthrough occurred at 42 hours and 22 hours, at 4 BV/hr and 8 BV/hr, respectively. The early saturation of the zeolite column receiving AnMBR permeate was consistent with the reduced EAU observed in batch studies, because of the cation competition effect.

Figure 3.10b shows the ammonium uptake at breakthrough (BAU) for both the NH_4Cl solution and AnMBR permeates at different flow rates. The BAU decreased from 3.5±0.21 to 3.2±0.11 mg N/g zeolite when the flow rate increased from 4 BV/hr to 8 BV/hr for NH_4Cl feed. The BAU of AnMBR permeates was about 3.1±0.16 mg N/g zeolite at 4 BV/hr, and decreased to 2.9±0.18 mg N/g zeolite at 8 BV/hr. These slightly reductions of ammonium uptake for both the NH_4Cl solution and AnMBR permeates imply that dead zones in the zeolite column would be created at a high flow rate [Schoeman, 1986; Sirkecioglu and Senatlar, 1995; Kessler, 2010].

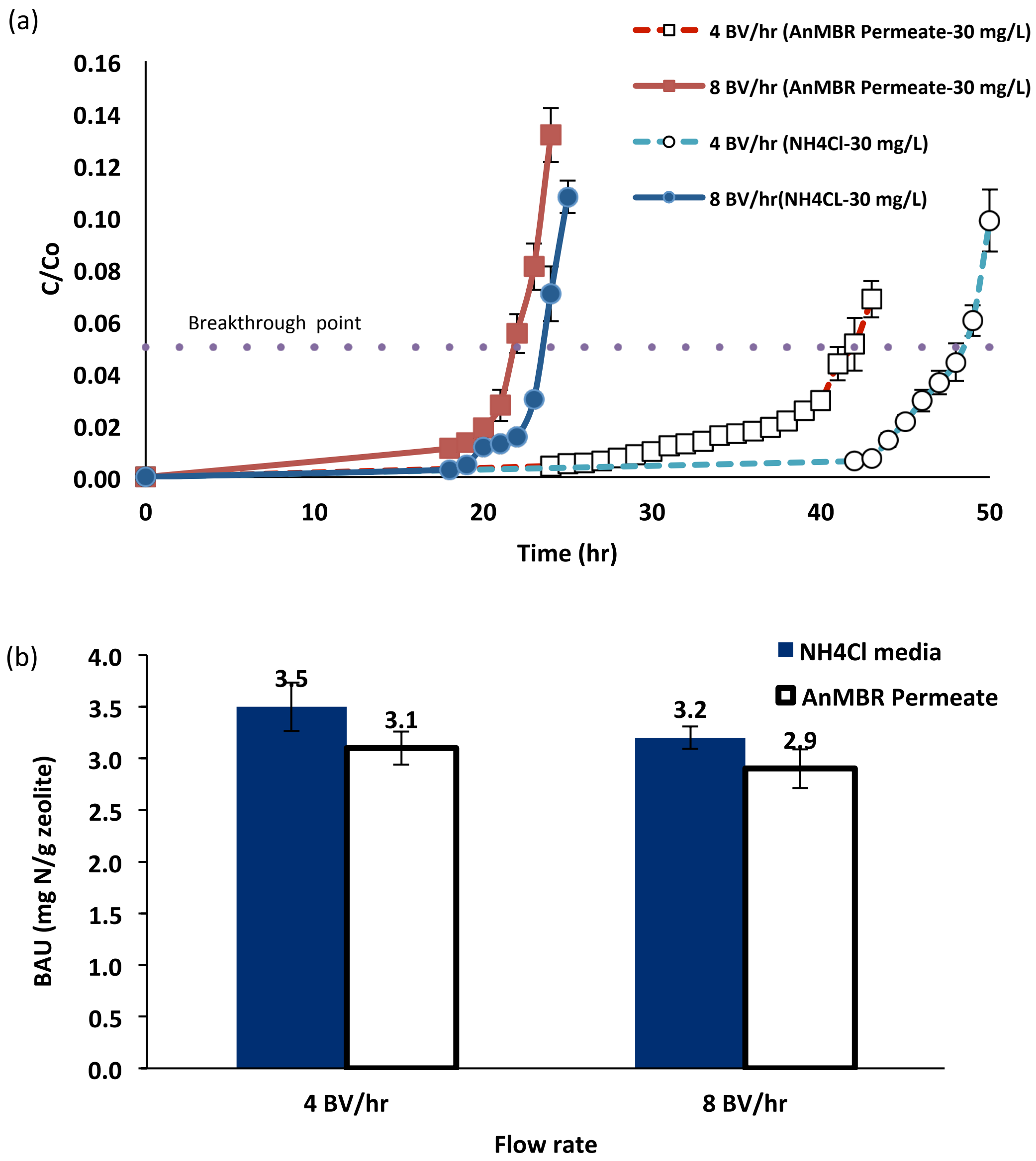


Figure 3.10. Continuous experiments using a zeolite-packed column. (a) Breakthrough curves at different flow rates using NH_4Cl solution and AnMBR permeate, and (b) BAU of zeolite in the column fed by NH_4Cl solution and AnMBR permeate at different flow rates.

3.3.2.2 Impact of NaCl dosage and pH on regeneration efficiency

Figure 3.11a shows the regeneration efficiency of the exhausted natural zeolite using different NaCl concentrations at pH 9±0.4. At pH 9±0.4, the regeneration efficiency increased with increasing NaCl dose (20 g/L, 80g/L, and 160 g/L), as observed in the batch experiments. At this pH, the maximum regeneration efficiency was 76±1.8%

at an NaCl concentration of 160 g/L, while the regeneration efficiencies were only 13±1.2% and 38±2.3%, respectively, at NaCl concentrations of 20 g/L and 80 g/L, in continuous column tests. High regeneration efficiencies of 65±3.3% and 94±1.8% at NaCl concentrations of 20 g/L and 80 g/L, respectively, were observed in batch studies at pH 9. The low regeneration efficiency in the continuous column was likely due to the small mass ratio of Na^+ to Zeolite-NH_4^+-N maintained in the column during regeneration; the mass ratios were 9.4 and 37.6 g Na^+/g Zeolite-NH_4^+-N, respectively, for the NaCl concentrations of 20 g/L and 80 g/L. However, the mass ratios were 187 and 749 g Na^+/g Zeolite-NH_4^+-N in batch tests for the same NaCl dosages. This result clearly shows that NaCl concentration should be optimized for continuous zeolite columns, not simply with batch experiments.

A high regeneration efficiency of over 85% was achieved within 2 hours of regeneration time at pH 12 using NaCl dosages from 10 to 40 g NaCl/L, as shown in Figure 3.11b. As shown in Eq 3.9 and Figure 3.4, ammonium ion will covert to dissolved ammonia when pH is higher than 7; when pH is over 11.5, 100% ammonia will exist as $NH_3(aq)$. This high regeneration efficiency at pH 12 confirms that the NH_4^+ exchanged with Na^+ would be rapidly transformed to dissolved ammonia (NH_3). The rapid deprotonation of ammonium would allow a high ammonium concentration gradient between zeolite and bulk liquid; thus, regeneration efficiency can be improved with small NaCl dose. Therefore, chemical regeneration at pH 12 would be a technically feasible approach for reducing dose of NaCl.

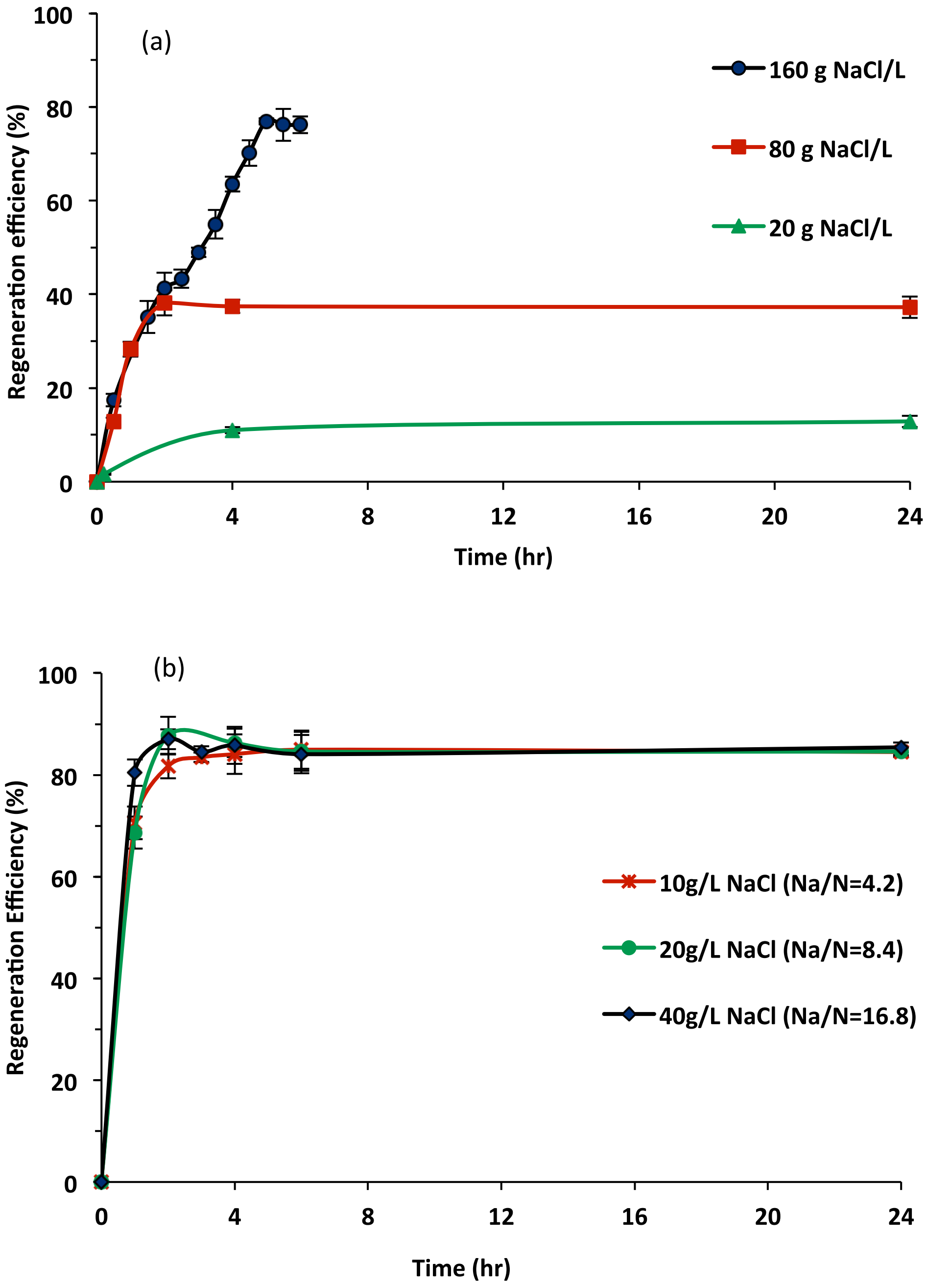


Figure 3.11. Regeneration efficiencies using different NaCl doses at (a) pH 9, (b) pH 12.

3.3.2.3 Renewability of exhausted zeolite in repetitive chemical regeneration

The performance of the zeolite-packed column was assessed as chemical regeneration was repeated (24 cycles). Chemical regeneration was conducted at a pH of 12±0.5

using an NaCl concentration of 10 g/L. The column was operated with an NH_4Cl solution in a flow rate of 8 BV/hr in service mode. Figure 3.12a shows the BAU of each cycle. The BAU of the 1st and 2nd cycles was 2.8±0.07 mg N/g zeolite; after cycle 3, the BAU decreased gradually in each cycle. The BAU at the breakthrough dropped from 2.8±0.07 mg N/g zeolite in cycle 1 to 0.6±0.1 mg N/g zeolite in cycle 24 (~80% decrease of BAU in 24 chemical regenerations). Milan et al. (2011) [20] also reported a progressive loss of cation exchange capacity of zeolite after 8 repetitive reuses, based on earlier breakthrough with repeated use of exhausted zeolite. The breakthrough decreased from 21 hours in cycle 1 to 5 hours in cycle 24, Figure 3.12b. The breakthrough ammonium uptake decreased 50% after 10 times reuse, 70% after 20 times reuse, and 80% after 24 times reuse of the exhausted zeolite. These results clearly show that exhausted zeolite should be replaced regularly to maintain a constant breakthrough (or service time for ammonium removal) in continuous zeolite columns, which would be one of the most important cost factors in zeolite columns.

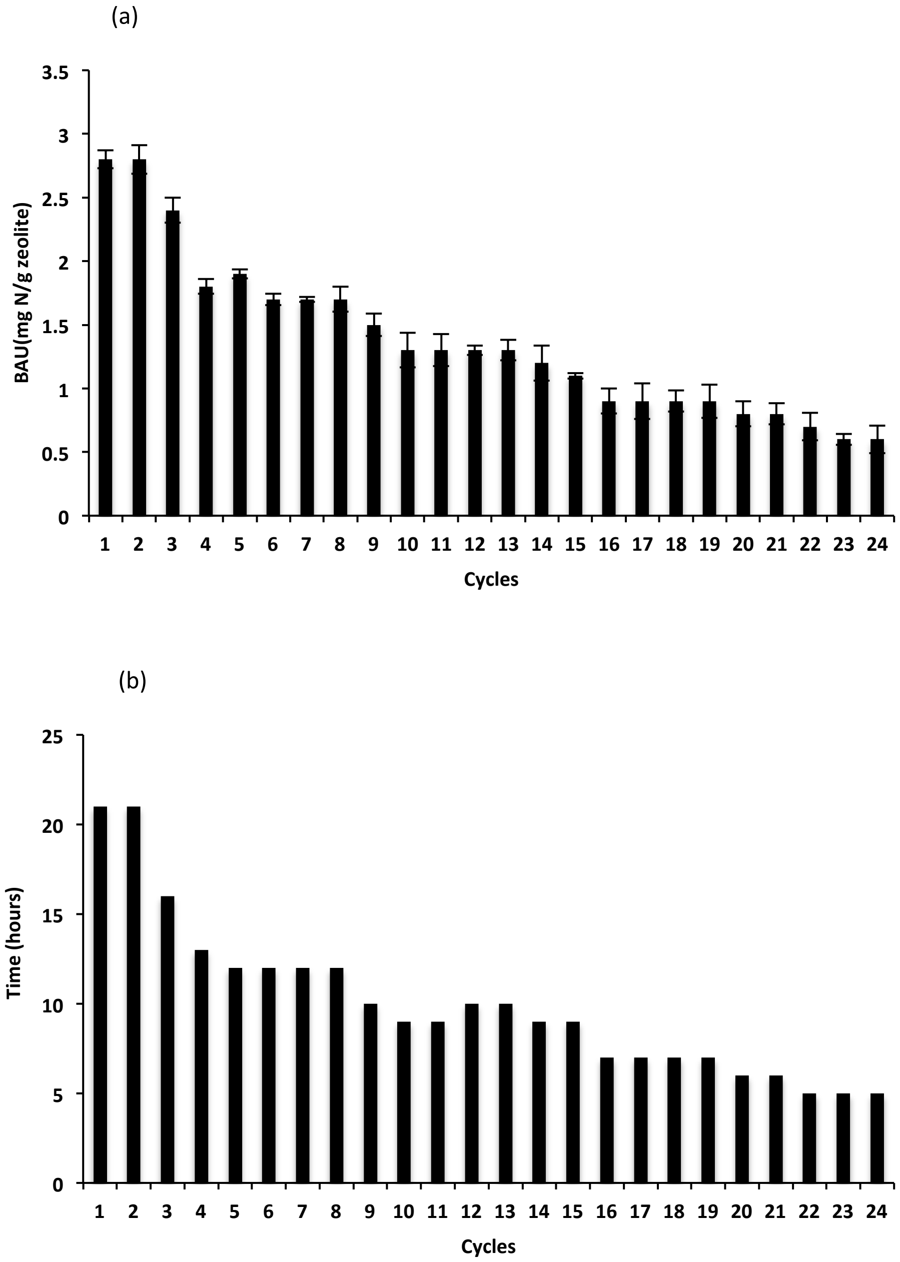


Figure 3.12. a) Breakthrough ammonium uptake (BAU) during different 24 regeneration and reuse cycles, b) Breakthrough time during different 24 regeneration and reuse cycles

3.4 Conclusion

Zeobrite Lm showed EAU (4.2 mg N/g zeolite) and RE (65%) superior to other natural zeolites; however, the presence of cation (mainly Ca^{2+}) in AnMBR permeates decreased the EAU of natural zeolite from 4.2 to 2.5 mg N/g zeolite. The mass ratio of Na^+ to Zeolite-NH_4^+-N is significant for improving the regeneration efficiency, and substantial NaCl amounts are needed to achieve high regeneration efficiency. To decrease the NaCl dose, a high pH regeneration method using NaCl 10 g/L at pH 12 (mass ratio of 4.2), which could achieve a regeneration efficiency of 85%, has been developed. The chemical dose for high pH regeneration is lower than that of the conventional regeneration methods, because the lower mass ratio required for chemical regeneration. Hence, the proposed technology can improve the zeolite ion exchange processes. However, the ammonium exchange performance of the regenerated zeolites was significantly reduced as chemical regeneration was repeated: The breakthrough ammonium uptake decreased 50% after 10 times reuse, 70% after 20 times reuse, and 80% after 24 times reuse of the exhausted zeolite. Further studies are essential to improve chemical regeneration efficiency of exhausted zeolite.

Chapter 4 Ammonia recovery from exhausted zeolite: investigation of regeneration by air stripping

4.1 Introduction

Ammonium nitrogen control plays a key role in wastewater treatment. Nitrogen removal technologies include biological nitrification-denitrification, ion exchange, and air stripping. Biological treatment is a traditional method of ammonium nitrogen removal; numerous studies devoted to the various aspects of the nitrification/denitrification processes. Despite the high efficiency of biological systems, the costs of biological treatment are relatively high due to intensive aeration for nitrification and exogenous electron donor for denitrification. Air stripping is also a mature technology for nitrogen removal, with high removal efficiency and stable operations; however, there are still some drawbacks, including (1) high operating costs due to the need of continuously addition of alkaline chemicals during the treatment process and reduction of pH by acid dosing before discharge takes place; (2) fouling (calcification) of the packed stripping tower and pipework due to the formation of calcium carbonate scale; and (3) air stripping being suitable only for removing of low concentrations ammonia nitrogen [Shen et al., 2005; Wang, 2001]. Finally, the application of zeolite as an ion exchanger for ammonium removal is one effective technology that has received considerable attention in recent years.

It would be more sustainable than the other two methods if ammonium nitrogen is reutilized for our society, such as fertilizers. Many researchers have investigated ammonium nitrogen removal by ion exchange using zeolite since the 1970s [Du et al., 2005; Haralambous et al., 1992; Celik et al., 2001; Demir et al., 2002; Rahmani, 2004]. The main limitation of the ion exchange method is the need for chemical regeneration of used zeolite and disposal of the concentrated ammonium-sodium brine produced [Celik et al., 2001]. Hence, to reduce the operation costs, it is very important to improve the regeneration efficiency of used zeolite. In this chapter, a system is developed to remove NH_4^+ ions from synthetic wastewater by ion exchange, followed by the regeneration of exhausted natural zeolite by air stripping to collect concentrated ammonium nitrogen.

Air stripping is considered to be feasible for ammonia recovery after ion exchange, because of the relatively low ammonium concentration and absence of solid particles in the secondary effluent of municipal wastewater. In the improved regeneration process, the ionized ammonia (NH_4^+) can be removed from the exhausted zeolite by converting NH_4^+ ions to dissolved NH_3 at alkaline conditions. After that, dissolved ammonia can be released as NH_3 gas by passing the alkaline effluent through a stripping tower downward, and drawing air flow upward from the bottom openings [Corbitt, 1999; Roberts and Alley, 2000]. Furthermore, the NH_3 gas can be recovered with sulfuric acid to form $(NH_4)_2SO_4$, which is a valuable fertilizer for local farmers.

This study evaluated the efficiencies of the regeneration of used zeolite and ammonia transfer from dissolved ammonia to ammonia gas under various operating conditions. Zeobrite Lm, a natural zeolite that showed the best performance in previous tests, was selected for both batch and continuous experiments. In batch tests, the pH and mixing intensity, reported as the most significant factors in ammonia stripping in the literature, were initially investigated. Secondly, other operating parameters, such as initial ammonium concentration, temperature, and working volume, which might be rate-limiting factors for ammonia transfer, were also evaluated in batch tests. Finally, the impact of the pH, air flow rate and liquid circulation rate on regeneration and ammonia transfer efficiency were investigated in continuous column tests, with the integrated system for regeneration by air stripping following ion exchange. The operating conditions were also optimized in continuous tests.

4.2 Materials and methods

4.2.1 Evaluation of ammonia air stripping in batch studies

Batch experiments were conducted to study the regeneration of exhausted zeolite by shaking or air stripping. Under each operating condition, two serum bottles were used for the duplicate experiments. The Zeobrite Lm sample was pre-treated with 20 g/L NaCl (CAS No. 7647-14-5, UPS grade, Sigma Aldrich, Canada) for one day before tests. To prepare the exhausted zeolite, 1 g pre-treated zeolite (Zeobrite Lm), and 100 mL NH_4Cl solution of 30±3.1 mg N/L and pH 6.9±0.1 were added to serum bottles. Then the bottles were put in an incubator (Orbital Shaker, VWR Inc., Canada) at a mixing intensity of 200 rpm and room temperature of 22±3℃ for 4 hours.

Regeneration experiments with shaking were conducted by putting 1g exhausted zeolite into a serum bottle containing 100 mL 10g/L NaCL solution. Four different pH conditions (9.5, 10, 11, and 12) were applied in this test to optimize the pH in the proposed regeneration. The pH in each bottle was adjusted with 10 mM phosphate buffer ($KH_2PO_4/Na_2HPO_4.12H_2O/Na_3PO_4$) and 0.5 M NaOH solution. For each pH condition, a control bottle containing only 100 mL NH_4Cl solution at a concentration of 30 mg N/L was also applied. All 12 bottles were put in a incubator with a mixing intensity of 200 rpm and a room temperature of 22±3℃ for 6 days.

For air stripping batch tests, 1g exhausted zeolite and 100 mL 10 g/L NaCl solution were inserted into a sealed bottle equipped with a ceramic air stone (0.6''×1.2'') (Appendix A2). An aquarium air pump (Tetra, USA) pumped air into the sealed serum bottle, at a flow rate of 30 L/hr. Four different pH conditions (9.5, 10, 11, and 12) were also applied in this test. For each pH, there was also a control bottle containing only 100 mL NH_4Cl solution at a concentration of 30 mg N/L. Each bottle was sealed with a rubber stopper, and connected to a 100 mL bottle filled with a 1N H_2SO_4 solution. The dissolved ammonia left in the regenerant and gaseous ammonia absorbed in the acid were measured after 1 day.

After testing under different pH conditions, the results showed pH 12 was the optimal pH for air stripping tests. To extend the research, different operating conditions, including ammonia concentration (50 mg N/L and 500 mg N/L), working volume (250 mL and 500 mL), and temperature (22°C and 50°C), were applied for air stripping tests at a high pH (pH 12) condition. The fraction of dissolved ammonia left in the regenerant was measured after 1 day. All the operating conditions are summarized in Table 4.1.

Table 4.1 Operating conditions for ammonia air stripping batch tests

Parameters	Test 1	Test 2	Test 3	Test 4
Volume (mL)	250	250	500	500
NH_3 Conc. (mg N/L)	50	500	500	500
Temp.	22±3°C	22±3°C	22±3°C	50±5°C

All batch experiments were conducted in duplicate under the same conditions, and the ammonium nitrogen concentration was quantified in quadruplicate. The average values were reported along with standard deviation.

4.2.2 Evaluation of ammonia air stripping in column studies

The regeneration and ammonia transfer efficiencies were evaluated with a column system: a zeolite-packed column and an air stripping column. The column was packed with 1.3 kg of Zeobrite Lm, and the total bed volume (BV) was 0.75 L. The ammonium solution (30±3.1 mg N/L, pH 6.9±0.1) was fed into the zeolite-packed column with a peristaltic pump (Masterflex® L/S® economy variable-speed drive, Masterflex, Canada) at a flow rate that varied from 50 to 100 mL/min. Once breakthrough occurred, i.e., when the ammonium nitrogen concentration in the effluent reached 5% of the influent, the ammonium feed was stopped, the liquid was drained from the column, then the column was switched to regeneration mode. Figure 4.1 provides a schematic diagram of the continuous-flow zeolite-packed column with the regeneration system. The regenerant chamber was packed with glass swirl packing materials (Kemtech America) to increase the surface area for ammonia transfer. In the regeneration process, regenerant was pumped from the regenerant chamber into the bottom of the zeolite-packed column, and circulated clockwise. To enlarge the contact area, the regenerant was sprayed with a sprinkler installed at the top of the regenerant chamber; meanwhile, the air flow was supplied from the bottom of the regenerant chamber and distributed with ceramic air stones (1.2’’×3’’), at a flow rate from 0 to 360 L/hr. For the ammonia recovery, the regenerant chamber was connected with a sulfuric acid scrubber, to absorb the ammonia gas emitted from the regenerant chamber (Appendix A3).

The regeneration efficiency and ammonia transfer efficiency were compared at five different liquid circulation rates (1.6-32.4 L/hr) and eight different air flow rates (0-360 L/hr), for the optimization of air stripping. The effect of pH on regeneration efficiency and ammonia transfer efficiency was also evaluated at four different pH conditions, from 9.5 to 12. The dissolved ammonia left in the regenerant and the gaseous ammonia absorbed in acid were measured after 1 day.

All column tests were conducted at room temperature (22±3°C). Duplicate experiments were conducted under each operating condition, and the ammonium nitrogen concentration was quantified in quadruplicate. The average values were reported along with standard deviation.

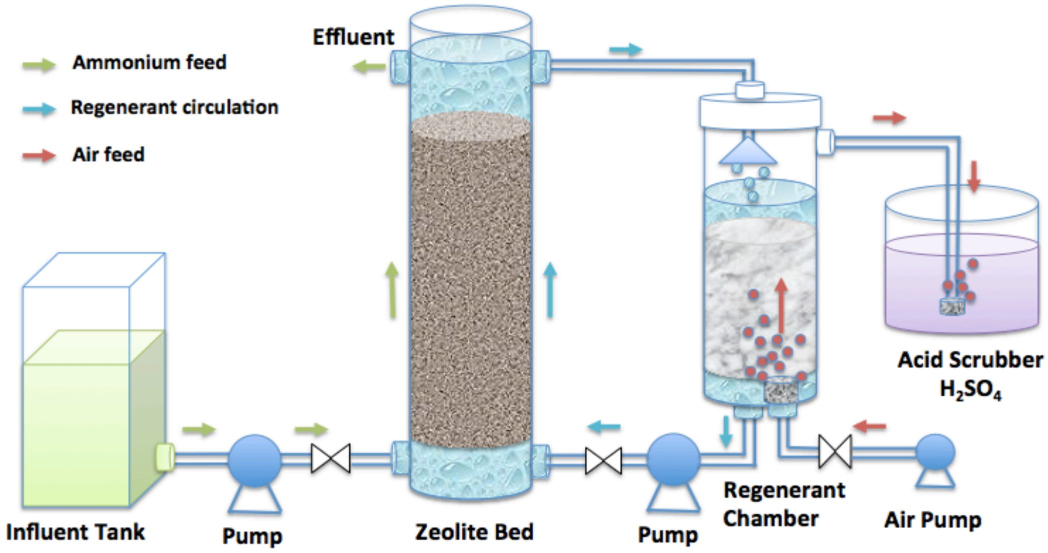


Figure 4.1. Schematic diagram of the continuous-flow zeolite-packed column and stripping system

4.2.3 Analytical methods

The ammonium concentration was measured by an Auto Analyzer 3 (Bran-Luebbe, Germany) that quantifies ammonium nitrogen and dissolved ammonia. A calibration curve (see Appendix B1) was built with an NH_4Cl standard solution (0.5～30 mg N/L). The pH was measured with a Benchtop pH Meter (Model 420A, Orion Research Inc., USA) after calibrating it with standard buffers of 4.01, 7.00 and 10.01 at every measurement.

The masses of dissolved ammonia in the regenerant and the gaseous ammonia absorbed by the acid were calculated using equations (4.1) and (4.2), respectively:

$$M_{NH3(aq)} = C_N(aq) \times V_{regenerant} \qquad \text{Eq (4.1)}$$

$$M_{NH3(g)} = C_N(gas) \times V_{acid} \qquad \text{Eq (4.2)}$$

where, $C_N(aq)$ is the measured ammonia concentration in the regenerant bulk liquid (mg N/L), $V_{regenerant}$ is the regenerant volume (L), $C_N(gas)$ is the measured ammonium nitrogen concentration in the sulfuric acid bottle (mg N/L), and V_{acid} is the volume of sulfuric acid (L).

The regenerant and the sulfuric acid were regularly sampled from each container, to determine how $C_N(aq)$ and $C_N(gas)$ changed over time during the alkaline regeneration at pH 12. Two sulfuric acid bottles were used for sequential ammonia gas adsorption, and no ammonium ions were detected in the second bottle. It suggested that ammonia gas reacted with sulfuric acid immediately in the first bottle.

The regeneration efficiency (RE) of the exhausted zeolite and the ammonia transfer efficiency (ATE) were computed with equations (4.3) and (4.4):

$$RE = (M_{NH3(aq)} + M_{NH3(g)}/M_{exhausted}) \times 100 \qquad \text{Eq (4.3)}$$

$$ATE = (M_{NH3(g)}/M_{NH3(aq)} + M_{NH3(g)}) \times 100 \qquad \text{Eq (4.4)}$$

where $M_{NH3(aq)}$ is the mass of ammonia in the regenerant bulk liquid (mg), $M_{NH3(g)}$ is the mass of ammonium nitrogen in the sulfuric acid bottle (mg), and $M_{exhausted}$ is the ammonium mass exchanged by the zeolite (mg).

In batch tests, the ammonium mass exchange by zeolite ($M_{exhausted}$) was computed with equation (4.5):

$$M_{exhausted} = (C_{N,ini} - C_{N.final}) \times V_N \qquad \text{Eq (4.5)}$$

Where, $C_{N,ini}$ is the initial ammonium concentration (mg N/L) in the NH_4Cl solution, $C_{N.final}$ is the final ammonium concentration (mg N/L) after ion exchange, and V_N is the volume of the solution (L).

In continuous column tests, the ammonium mass exchange by zeolite ($M_{exhausted}$) was computed with equation (4.6):

$$M_{exhausted} = \int_0^{V_{final}} (C_0 - C)dV \qquad \text{Eq (4.6)}$$

Where, C_0 is the influent ammonium concentration (mg N/L) in the NH_4Cl solution, C is the effluent ammonium concentration (mg N/L), and V is the volume of the ammonium feed (L).

4.3 Results and Discussions

4.3.1 Batch Studies

4.3.1.1 Effects pH on ammonia regeneration from exhausted zeolite

Figure 4.2 shows the regeneration efficiency of the exhausted zeolite and the ammonia transfer efficiency at different pH conditions with shaking at 200 rpm (Figure 4.2a) and air stripping (Figure 4.2b). At least 12 hours were required to achieve the maximum regeneration efficiency in the shaking experiments, as compared to only 2 hours in the air stripping experiments. As depicted in Figure 4.2a, the regeneration efficiency of shaking tests increased gradually from 68±3.2% to a maximum 99±0.8%, when the pH was increased from 9.5±0.4 to 12±0.5. The fraction of ammonia gas in the regenerated aqueous ammonia was only 26±0.5% after 6 days at pH 9.5±0.4, and slightly increased to 37±1.2% at pH 10±0.2. The ammonia transfer efficiency was raised from 37±1.2% to 68±1.1% when the pH was increased from 10 to 11, and reached the maximum level of 95±2.4% at pH 12±0.5 in 6 days. As shown in Figure 4.2b, although air stripping tests behaved similar to ammonia regeneration with shaking tests, the transfer efficiency using air was higher than that using mechanical mixing at all pH conditions, except for pH 12. The regeneration efficiency increased from 67±1.0% at pH 9.5±0.4 to 96±2.4% at pH 12±0.5 in less than two hours. The transfer efficiencies were 33±0.6%, 51±1.6%, and 80±2.4% at pH of 9.5±0.4, 10±0.2, and 11±0.5, respectively, over 24 hours. These results were 18%-38% higher than those observed during the shaking experiments. The difference of ammonia transfer efficiency between shaking and air stripping tests indicates that mass transfer of ammonia from a liquid to a gas phase can be the rate-limiting for ammonia recovery at pH from 9.5 to 11. However, the maximum ammonia transfer efficiency of about 96% was achieved at pH 12 for both shaking and air stripping methods.

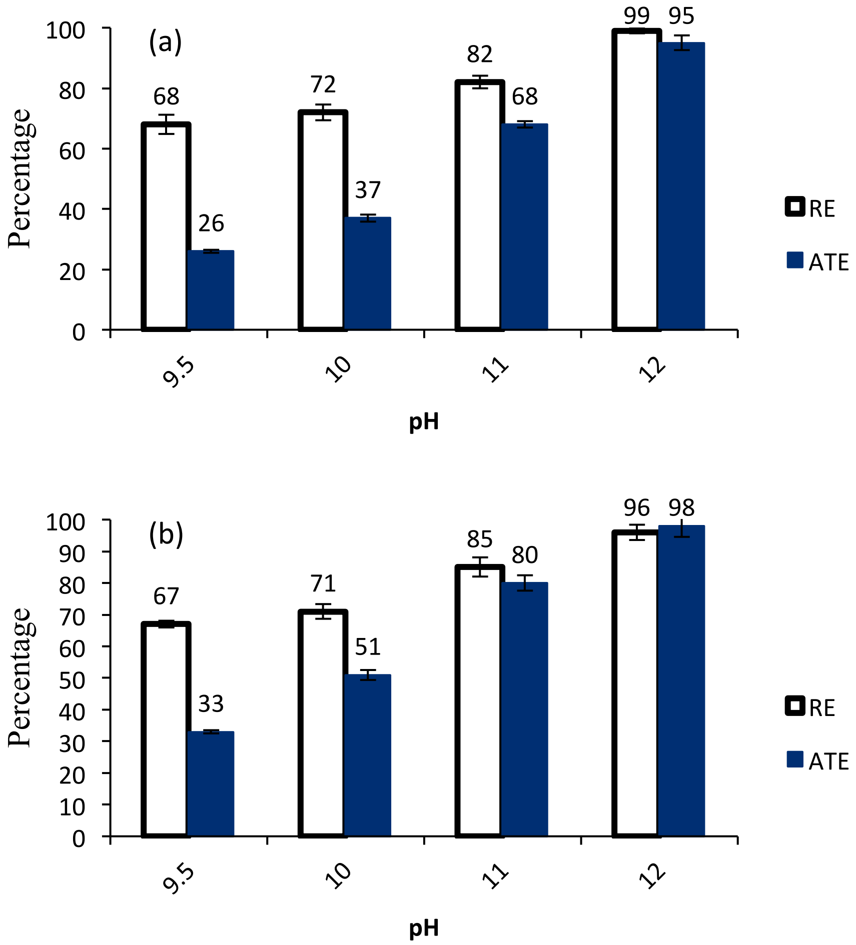


Figure 4.2. Ammonia regeneration efficiency (RE) and ammonia transfer efficiency (ATE) at different pH conditions (a) with 200 rpm shaking intensity in 6 days, and (b) with air stripping in 24 hours.

Control tests were conducted in duplicate with NH_4Cl solutions in the same pH range (without exhausted zeolite). A similar trend of ammonia transfer efficiency was observed: it increased with increasing pH for both shaking and air stripping tests, and the transfer efficiency in the control tests was higher than that with the exhausted zeolite, either with shaking or air stripping, at all pH conditions except pH 12 (Figure 4.3). This result clearly indicates that the ammonia dissolution rate from zeolite to bulk liquid would limit the ammonia recovery rate below pH 12; however, the concentration gradient of ammonia between liquid and gas would be enough to overcome the mass transport limitation of mechanical mixing at pH 12.

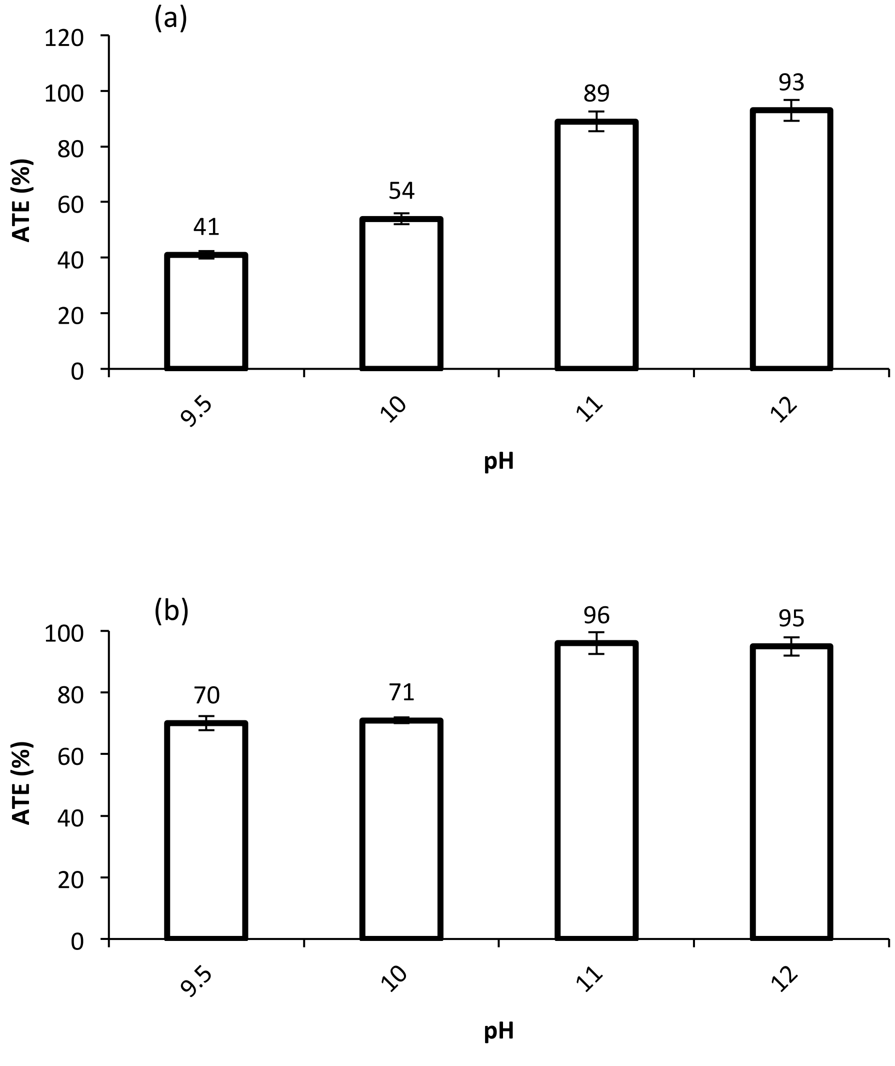


Figure 4.3. Ammonia Transfer efficiency (ATE) of the control experiments (without zeolite) at different pH conditions (a) with 200 rpm shaking intensity, and (b) with air stripping

The above-mentioned results reveal that pH has significant effects on regeneration efficiency and ammonia transfer efficiency. This trend agrees well with the previous studies (Table 4.2). Guo et al. reported that the ammonia transfer efficiencies increased from 80% to 92% when the pH was increased from 8 to 11. Gustin and

Marinsek-Logarb observed only 27% ammonia transfer to gaseous phase at pH 8.5, and the transfer efficiency rapidly rose to 92% at pH values of 11. Liao et al. observed the highest ammonia transfer efficiency, 90.3 %, at pH of 11.5 and 22°C. Norddahl et al. concluded that a pH of 11.5 yielded the best results in terms of ammonia mass transfer. Quan et al. reported that a pH of 11~12 is the optimum to promote the conversion of molecular ammonia in an aqueous solution. A few studies also report that temperature significantly affects ammonia transfer from the liquid to the gaseous phase; the optimum pH of ammonia stripping can be lower than 11 at higher temperatures. Gustin and Marinsek-Logarb reported that pH of 10 was sufficient for ammonia stripping if the temperature was increased to 70°C. Katehis et al. found that air stripping became pH insensitive at 75 °C. Bonmati and Flotats achieved an ammonia transfer efficiency of 87% at pH 9.5 when the temperature was 80°C, and they also concluded that the air stripping became independent of pH at a temperature of 80°C.

Table: 4.2 Effect of pH and temperature on air stripping

	pH	**Temperature**	**ATE(%)**
Gustin and	8.5-11	50℃	27-92
Marinsek-Logarb	10	30-70℃	89-98
Guo et al.	8-11	23 ℃	80-92
Liao et al.	11.5	22℃	93
Norddahl et al.	11.5	25℃	92
Quan et al.	11-12	25℃	90
Katehis et al.	pH insensitive	75 ℃	90
Flotats	9.5	80 ℃	87

The previous results strongly support that the ammonia transfer efficiency depends on both the pH of the solution and the temperature. In general, at a temperature of 20℃ and a pH of 7 or below, only ammonium ions are present. As the pH increases above 7, the chemical equilibrium is gradually shifted to the left in favor of the ammonia gas formation. At a pH of about 11.5-12, only the dissolved gas is present. Figure 4.4 shows this relationship at 0, 20, and 40℃. As shown, the relative distribution of the dissolved NH_3 gas vs the NH_4^+ ions in true solution depends greatly on pH. The liquid temperature can also affect the ammonia transfer efficiency in two different ways. First, at a given pH, the percentage of ammonia nitrogen present as a dissolved gas increases with temperature as shown in Figure 4.4. Second, the solubility of ammonia gas increases with decreasing temperature. The greater the solubility, the greater the amount of air required to remove a given amount of ammonia gas. Therefore, if the operating efficiency must be maintained as high in the winter as in the summer, a substantial increase of air flow must be provided. [Gustin and Marinsck-Logarb, 2011; Norddahl et al., 2006; Quan et al., 2009]

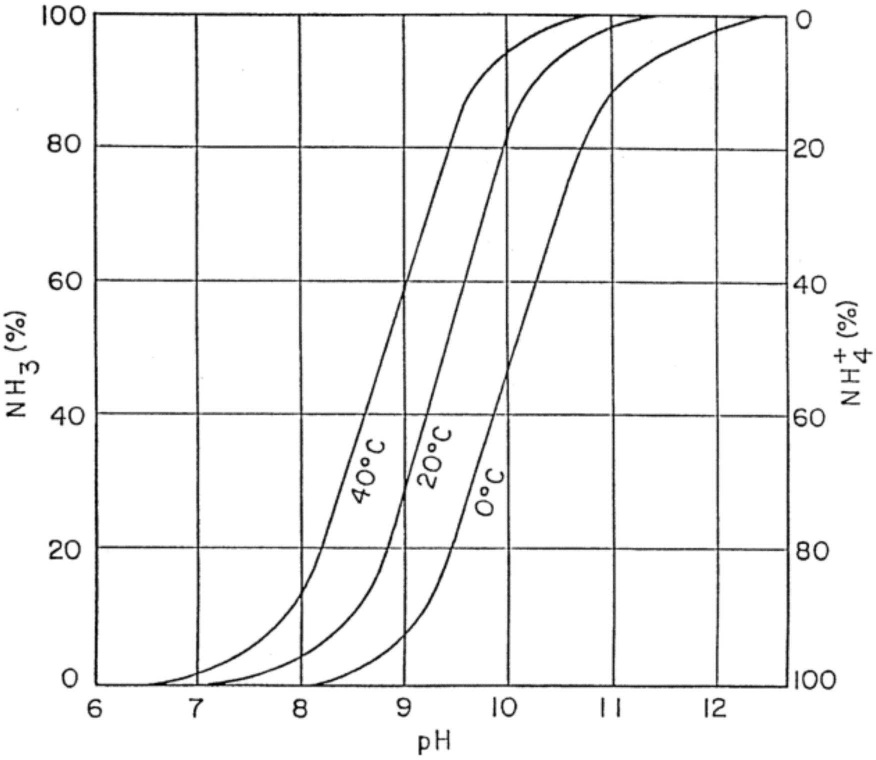


Figure 4.4 Effects of pH and temperature on the distribution of ammonia and ammonium ion in water (Huang, 2009)

4.3.1.2 Effect of air flow on ammonia transfer efficiency

Figure 4.5a shows the ammonia transfer efficiency with shaking and air stripping at pH 12±0.5, with exhausted zeolite. 98±2.1% of aqueous ammonia was stripped as ammonia gas in 24 hours when air stripping was used, while it took at least 5 days to achieve the same ammonia transfer efficiency in the shaking tests (200 rpm). These results indicate that air stripping is superior to shaking in the field of dissolved ammonia transferring to gaseous ammonia.

The literature commonly shows that the equilibrium between ammonium ions (NH_4^+) and dissolved NH_3 mainly depends on both of pH and the temperature (Table 4.2). In addition to converting all the ammonia to the dissolved gas phase, efficient ammonia stripping requires proper conditions to facilitate a rapid transfer of the dissolved gas from the liquid phase to the air. To remove ammonia from water, the dissolved NH_3 molecules must move from the bulk liquid solution to the air–water interface then to the stripping air flow [Water Environment Federation, 2010]. The transportation of the dissolved NH_3 from the bulk liquid solution to the air–water interface can be easily achieved by turbulent mixing, and the limiting factor of ammonia stripping is always the step of transfer from air–water interface to the gaseous phase. The transfer of ammonia from the liquid to the atmosphere occurs when the partial pressure of the dissolved gas in the water is greater than that of the gas in the atmosphere near the air-liquid interface, until equilibrium of partial pressures is reached in accordance with Henry's law [Idelovitch, 1977]. The ratio of ammonia at equilibrium in the liquid phase (C_l) to the ammonia in the gaseous phase (P_g) is shown as:

$$H_c = \frac{P_g}{C_l} \qquad \text{Eq (4.7)}$$

where H_c is Henry's constant of ammonia. The difference in the ammonia partial pressures between the liquid and the gaseous phases is actually the driving force causing the interfacial gas transfer [Monteny and Lamaker, 1997; Ruxton, 1995]. The maximum transfer rate will occur when a maximum difference in the partial pressures exists. With a given ammonia concentration, the partial pressure in the liquid phase is constant. The ammonia partial pressure in the gaseous phase can be minimized by supplying an ample amount of air flow to dilute the concentration of the ammonia released into the gaseous phase. As a result, the supply of air can accelerate the ammonia gas transfer rate.

The ammonia transfer from water to air is considered to be proportional to the concentration of ammonia nitrogen in solution; it was experimentally proved to be a first-order reaction:

$$\ln (C_t)=-kt+\ln (C_0) \qquad \text{Eq (4.8)}$$

where C_0 is the initial ammonia concentration in liquid phase, t is the reaction time, C_t is the residual ammonia concentration at time t, and k is reaction rate constant (depending on pH, temperature, air velocity, and surface turbulence). Figure 4.5b shows the kinetics of ammonia transfer with shaking and air stripping. From the data obtained, the reaction rate constants were calculated as follows:

k=0.019/hr for shaking at a mixing intensity of 200 rpm and room temperature of

22±3°C(R^2=0.94).

k=0.153/hr for air stripping at a air flow rate of 30 L/hr and room temperature of 22±3°C (R^2=0.998).

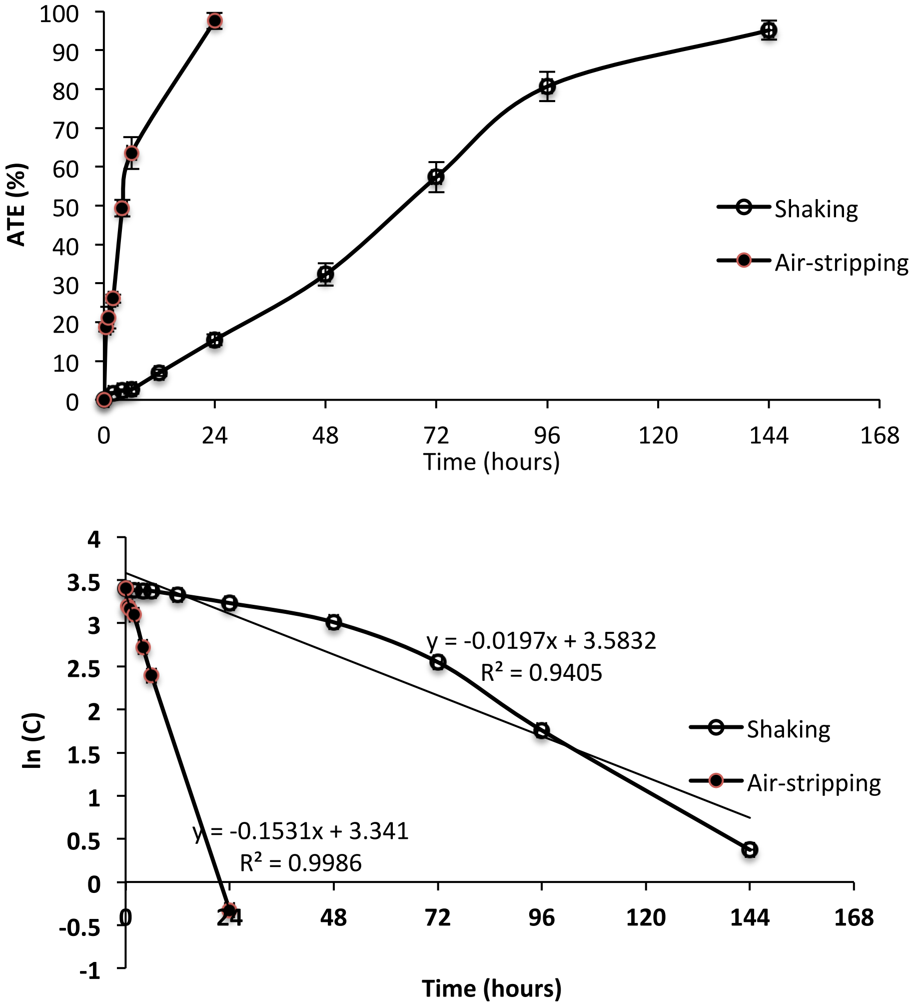


Figure 4.5. (a) Ammonia transfer efficiency, (b) ammonia transfer rate using shaking and air stripping at pH 12.

4.3.1.3 Ammonia air stripping at different conditions

The ammonia transfer efficiency was evaluated at pH 12±0.5 under different operating conditions, i.e., different initial ammonia concentrations (50 and 500 mg N/L), different temperatures (22 and 50°C), and different working volumes (250 and

500 mL). At an ammonia concentration of 50±3.2 mg N/L, the ammonia transfer efficiency increased to 70±3.5% in the first 6 hours and reached 95±2.6% after 24 hours. When the ammonia concentration was increased to 500±15 mg N/L, the ammonia transfer efficiency increased much slower, and was only 40±4.2% after 6 hours. After 24 hours, the transfer efficiency increased to 88±3.9%, which was only slightly lower than that at low concentration (95±2.6%), as shown in Figure 4.6a. These results revealed ammonia stripping is more feasible at low ammonia concentration. However, the mass of ammonia transferred from liquid to gaseous phase showed the different trend comparing with ammonia transfer efficiency (Figure 4.7a). At an ammonia concentration of 50±3.2 mg N/L (250 mL), the mass of ammonia transferred was only 8.5±0.4 mg N after 6 hours and reached 11.9±0.5 after 24 hours. When the ammonia concentration was increased to 500±15 mg N/L (250 mL), the ammonia mass transfer increased to 49.4±2.3 mg N only in 6 hours, and reached 110.6±4.7 mg N after 24 hours; it was 10 times more than that at an ammonia concentration of 50 mg N/L. These results suggested that although the ammonia transfer efficiency increased slowly, the overall ammonia mass transferred from liquid to gaseous phase was much higher at a high ammonia concentration.

The temperature showed a stronger influence on ammonia stripping than ammonia concentration. At a temperature of 22±3°C, the ammonia transfer efficiency was only about 19±2.0% over 24 hours shaking at 200 rpm. When the temperature was increased to 50±5°C, the ammonia transfer efficiency was 93±3.3% after 24 hours

(Figure 4.6b). Heating is an alternative for the improvement of ammonia transfer efficiency; however, the cost of energy is considerable. In previous studies [11,14,15], the optimal temperature was always fixed at 25~55℃ for ammonia stripping, and the cost of heating could be the predominant part of the operation and maintenance costs when the temperature is lower than 25℃. Therefore, the low temperature could be a barrier to the high latitude area.

The effects of the working volume were investigated with 250 mL and 500 mL serum bottles. When using 500 mL working volume, the ammonia transfer efficiency was 44±3.7% over 24 hours. If the working volume was lessened to 250 mL, the ammonia transfer efficiency doubled to 89±3.9% (Figure 4.6c). Figure 4.7b shows the relationship between mass of ammonia transferred and working volume. When using 500 mL working volume (500 mg N/L), the mass of ammonia transferred from liquid to gaseous phase was 110 mg N after 24 hours. When the working volume was lessened to 250 mL (500 mg N/L), the ammonia mass transferred was almost the same as that of 500 mL after 24 hours; however, the ammonia mass transferred was much quicker when the working volume was lessened, especially in the first 6 hours.

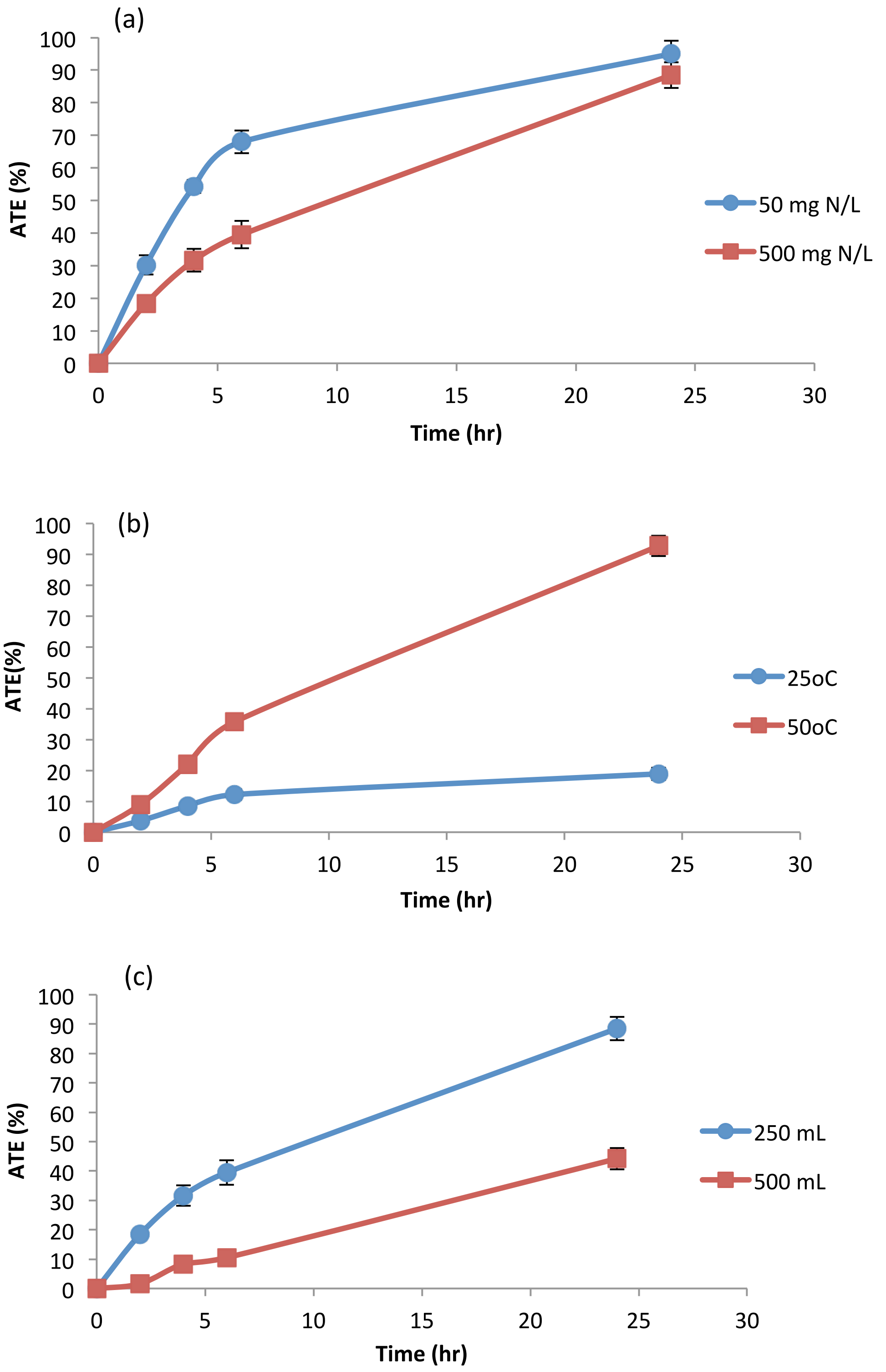


Figure 4.6. Ammonia transfer efficiency (ATE) at different (a) initial ammonia concentration, (b) temperature, and (c) working volume.

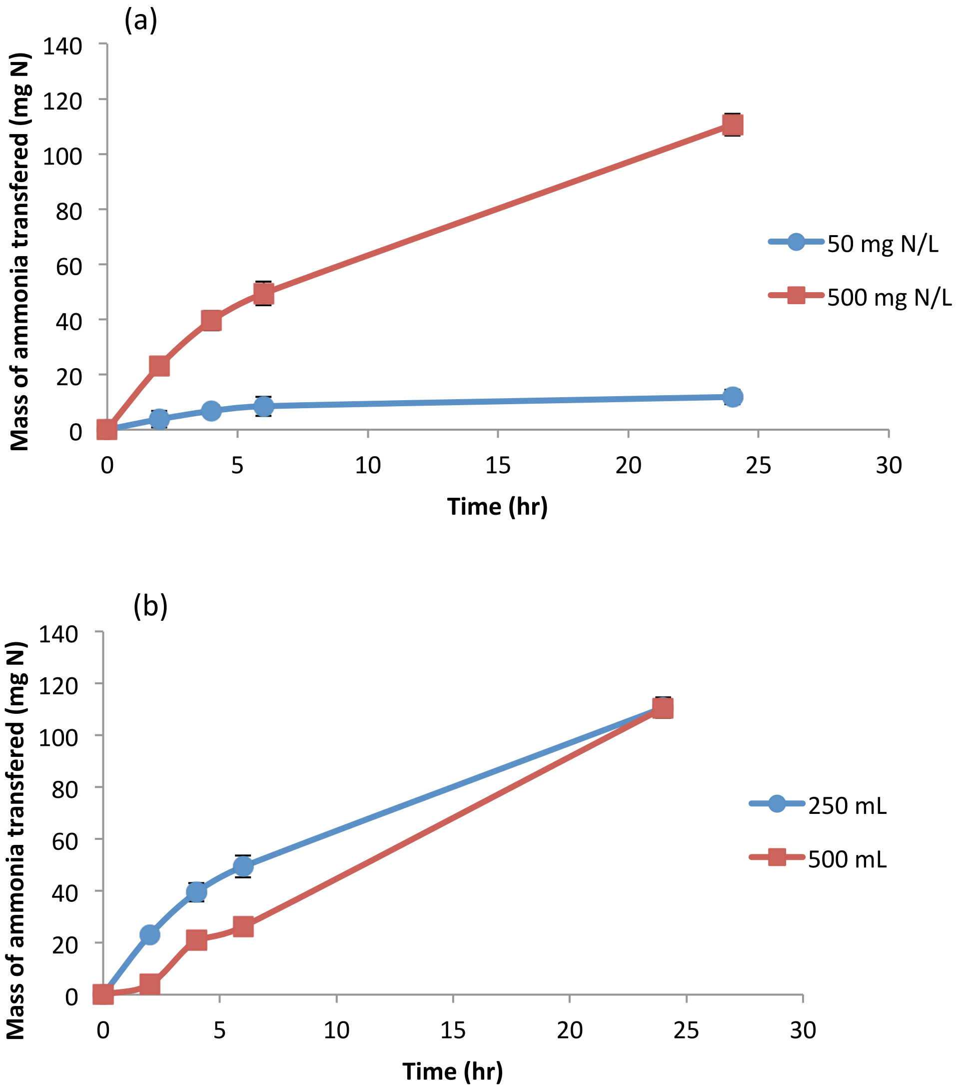


Figure 4.7. Mass of ammonia transfered at different (a) initial ammonia concentration, (b) working volume.

4.3.2 Column Studies

Figure 4.8a shows the regeneration efficiencies and the ammonia transfer efficiencies at five different liquid circulation rates ranging from 1.5 to 32.4 L/hr. The pH was 12±0.5, and the air flow rate is fixed as 6 L/hr. The dissolved ammonia left in the regenerant and ammonia absorbed in the acid were measured after one day. All the data are reported in the form of average results from duplicate experiments. As shown in Figure 4.8a, the liquid circulation rate did not have a significant effect on the regeneration efficiency; the regeneration efficiency was about 81%-85%. In comparison, the average ammonia transfer efficiency was as low as 1.8±0.29% for all liquid circulation rates, which means that the mass transfer rate of ammonia from the liquid to the gas phase was the limiting factor of ammonia stripping.

Figure 4.8b shows the regeneration efficiency and the ammonia transfer efficiency at eight different air flow rates from 0 to 360 L/hr, at the same pH of 12±0.5 and a constant liquid circulation rate of 6 L/hr. The fractions of dissolved ammonia left in the regenerant and gaseous ammonia absorbed in acid were measured after one day. All the data are reported in the form of averaged results of duplicate experiments. As shown in Figure 4.8b, the air circulation rate did not have significant effect on the regeneration efficiency (80%-85%). However, the air flow rate significantly affected the ammonia transfer efficiency. The ammonia transfer efficiency was trivial without an air flow, but it reached 95±2.9% with an air supply rate of 360 L/hr. A linear correlation between the ammonia transfer efficiency and the air circulation rates was observed, as shown in Figure 4.8c.

A higher air flow rate can reduce mass transfer resistance and promotes stripping of ammonia [Arogo et al., 1999]. The general form of the equation for the rate of mass transfer across the gas/liquid interface is:

$$\frac{dM}{dt} = KA_0*(C_l-C_g) \qquad \text{Eq (4.9)}$$

where M is the mass of the ammonia , K is the overall mass transfer coefficient of ammonia, A_0 is the interfacial surface area, C_l is the concentration of dissolved ammonia, C_g is the concentration of ammonia gas, and t is the reaction time. The resistance to the rate of mass transfer is given by $R_t = \frac{1}{K}$, and is estimated by summing the resistances offered by the liquid- and gas-phase boundary layers, R_l and R_g, respectively:

$$R_t = \frac{1}{K} = R_l + R_g \qquad \text{Eq (4.10)}$$

For extremely volatile compounds, with high Henry's constants, the overall rate of transfer would therefore be controlled by the transfer rate at the liquid-phase boundary. However, ammonia is a soluble gas with a low Henry's law constant; the overall mass transfer resistance in the air stripping largely lies on the gas film side [Matter-Muller et al., 1981], and the resistance can be reduced by increasing the air flow rate [Quan, 2009]. On the other hand, as Henry's law shown (Eq. 4.7), the difference in the ammonia pressures between the liquid and gaseous phases (C_l-C_g) is the force for ammonia to transfer from the liquid to the air flow, an ample supply of air flow will dilute the concentration of the ammonia released thereby reducing its partial pressure in the gaseous phase and maximizing the ammonia release rate. Furthermore, a higher air flow rate can produce larger shear stress which causes the breakage of water drops into fine drops or mist so the contact area (A_0) between the liquid and the gaseous phase is expanded [Katehis et al., 1998; Bonmati and Flotats, 2003].

Huang and Shang (2006) reported that the amount of air required to achieve a given degree of ammonia removal can be determined from the following analysis of the material balance [Huang and Shang, 2006]:

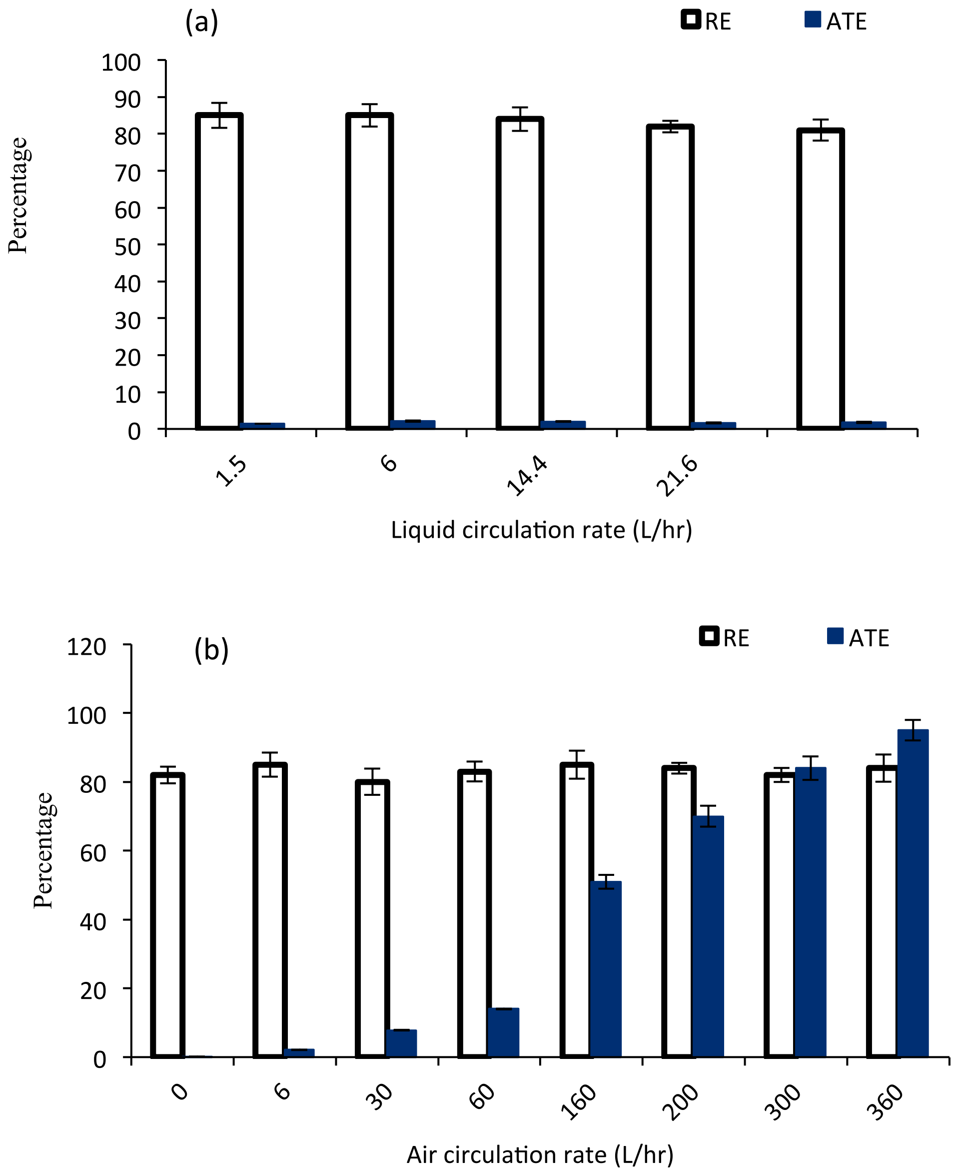
$$L_q (x_1 - x_2) = G (y_1 - y_2) \qquad \text{Eq (4.11)}$$

where L_q is the liquid flow rate (moles water/hr), x_1 is the inlet water ammonia concentration (moles ammonia/mole water), x_2 is the outlet water ammonia concentration (moles ammonia/mole water), G is the air flow rate (moles air/hr), y_1 is the outlet air ammonia concentration (moles ammonia/mole air), and y_2 is the inlet air ammonia concentration (moles ammonia/mole air). If it is assumed that the water leaving and the air entering have a zero ammonia concentration, then Eq. (4.11) can be rewritten as:

$$G/L_q = x_1/y_1 \qquad \text{Eq (4.12)}$$

That is, the amount of air requirement per unit volume of water, G/Lq, is equal to x1/y1, the concentration of ammonia in the inlet water divided by the ammonia concentration in the outlet air. At a given temperature and atmospheric pressure, the molar ratio of ammonia saturated in the outlet air and in the inlet water can be assumed to remain constant according to Henry's law, which can thus be used to determine the respective moles of ammonia in a mole of air as a function of the moles of ammonia in a mole of water. Tchobanoglous has prepared a set of curves showing the equilibrium distribution of ammonia in air and water at various temperatures under the condition of atmospheric pressure (Figure 4.9). Using Eq (4.12) and Figure 4.9, the theoretical requirement of air for the ammonia stripping operation can be calculated.

Figure 4.8d shows the regeneration efficiency and the ammonia transfer efficiency at a fixed air flow rate and liquid circulation rate (Q_{air}=300 L/hr and Q_{liquid}=6 L/hr) under four different pH conditions. The fractions of dissolved ammonia left in the regenerant and gaseous ammonia absorbed in acid were measured after one day. All the data are reported in the form of averaged results of duplicate experiments. The regeneration efficiency and the ammonia transfer efficiency were only 9.2±1.0% and 54±2.1%, at pH 9.5±0.4, respectively. When the pH was increased from 9.5 to 10, the regeneration efficiency was almost the same (9.4±0.9%), but the ammonia transfer efficiency increased significantly to 85±1.9%. As shown in Figure 4.8d, when the pH was increased from 10 to 11 and 12, no significant change observed in the ammonia transfer efficiency; it ranged from 85±1.9% to 92±3.7%. However, the regeneration efficiency changed dramatically when the pH was increased, and the regeneration efficiency reached its maximum of 84±3.7% at pH 12±0.5. This result clearly showed the significant effect of the pH on both the regeneration efficiency and the ammonia transfer efficiency. The pH should be higher than 11 for an efficient ammonia stripping, and pH 12 is the optimal pH for the ammonia recovery using an ion exchange-air stripping system.



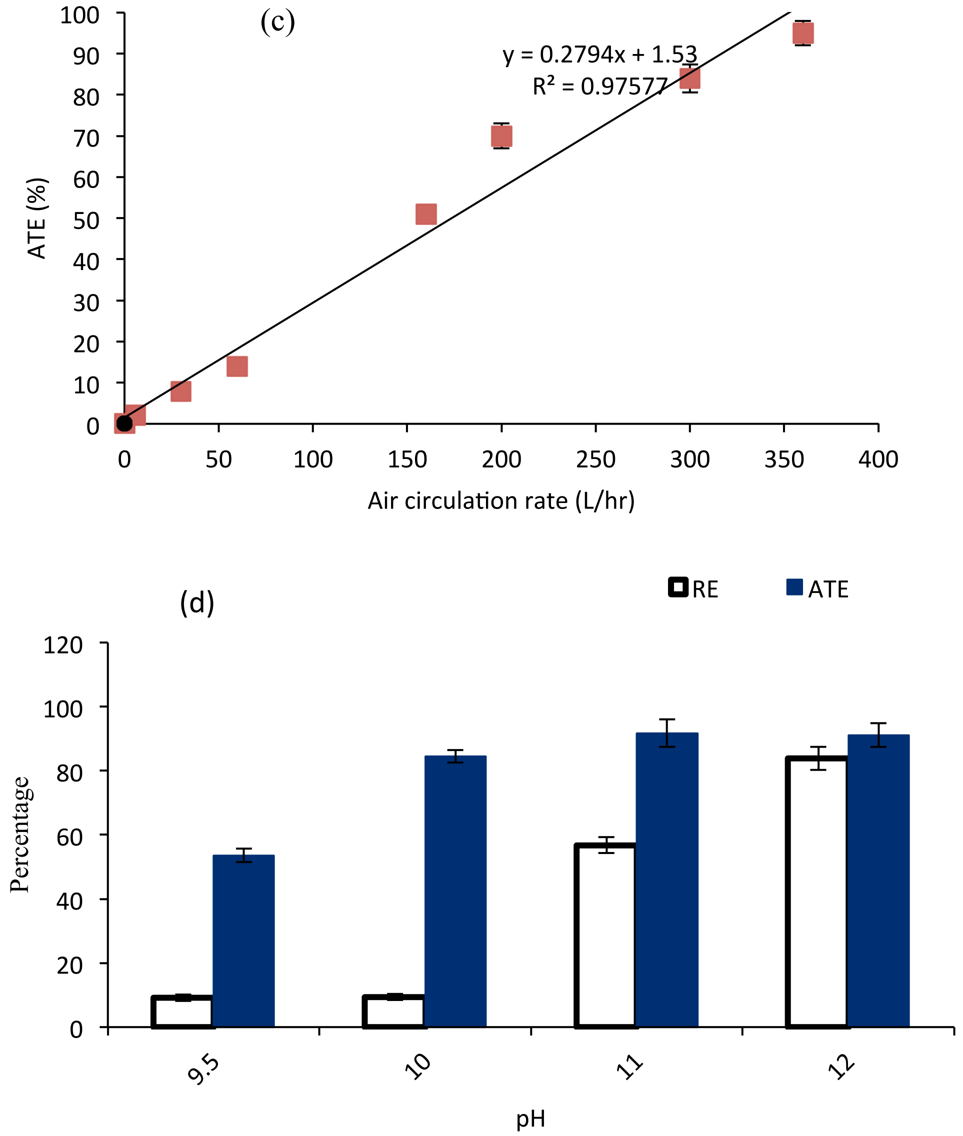


Figure 4.8. a) Ammonia fractions at different liquid circulation rates, b) Ammonia fractions at different air flow rates, c) Correlation between air circulation rate and ATE, d) Ammonia fractions at different pH conditions

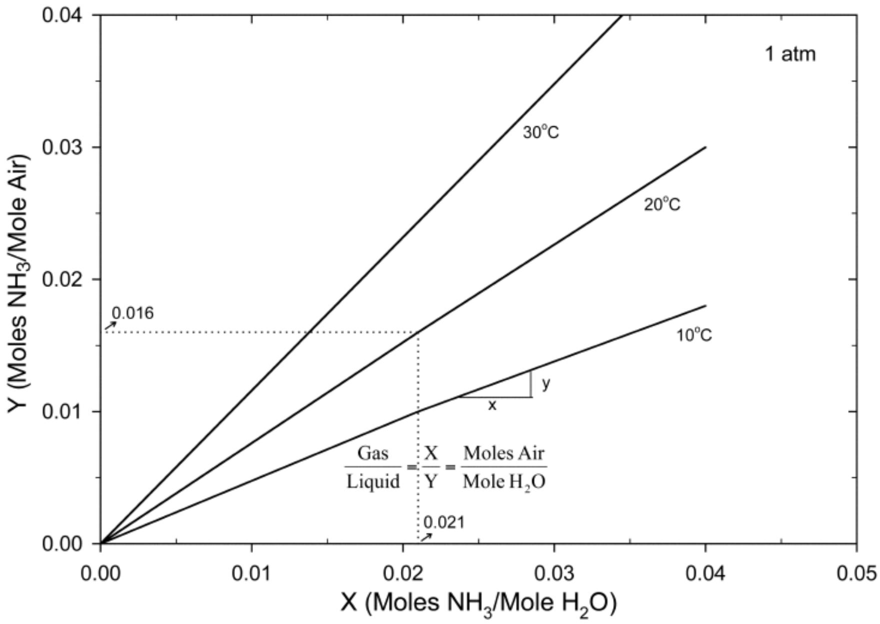


Figure 4.9. Equilibrium distribution of ammonia in air and water under one atmospheric condition (Tchobanoglous, 1970)

4.4 Conclusion

Based on the results of this study, the following points can be concluded:

- Air stripping can be considered an advanced and supplementary process for ammonia regeneration of the zeolite exhausted during ion exchange.
- A linear correlation between the ammonia transfer efficiency (ATE) and the air flow rate is observed; the liquid circulation rate did not affect the ATE.
- pH has a significant effect on both the regeneration efficiency and the ammonia transfer efficiency; it should be higher than 11.
- The integrated system can successfully be used for zeolite's regeneration and ammonia recovery. The regeneration efficiency of the exhausted zeolite is 80% to 85%, and the recovery of ammonia gas by acid in the stripping process can be higher than 90%. Hence, the proposed technology provides a feasible means of nitrogen control and recovery.

Chapter 5 Conclusions

5.1 Summary of results

Ammonium ion exchange using natural zeolite can be a feasible method for removing and recovering nitrogen from the permeates of anaerobic membrane bioreactors (AnMBRs). The mass ratio of Na^+ to Zeolite-NH_4^+-N is significant for improving the regeneration efficiency, and substantial NaCl amounts are needed to achieve high regeneration efficiency in the continuous column tests. To decrease the NaCl dose, a high pH regeneration method using an NaCl 10 g/L solution at pH 12 (the mass ratio of 4.2), which achieved a regeneration efficiency of 85%, is developed.

In continuous column operation, the ammonium exchange performance of the regenerated zeolites was significantly reduced as chemical regeneration was repeated: The breakthrough ammonium uptake (BAU) decreases 50% after 10 times reuse, 70% after 20 times reuse, and 80% after 24 times reuse of the exhausted zeolite.

Air stripping can be considered as an advanced and supplementary process for recovering ammonia from the exhausted zeolite followed ion exchange. The pH of the regenerant must be kept higher than 11 for the alkaline regeneration and the air stripping. The regeneration efficiency of the exhausted zeolite is 80% to 85%, and the adsorption of ammonia gas by acid in the stripping process can be higher than 90%. Furthermore, the absorbed ammonia gas forms ammonium sulfate with sulfuric acid, which can be used as fertilizer.

The ion exchange-air stripping system presented in this study may be considered as an innovative and applicable process for treating the permeate from AnMBRs. However, some challenges still need to be addressed. Firstly, the optimal temperature is 25-55°C for the ammonia stripping, and the cost of heating could be a predominant part of the operation and maintenance costs when temperatures are lower than 25°C. Therefore, low temperatures can be thought as a problem at high latitudes. Secondly, precipitation and attrition may happen under alkaline conditions during the regeneration and air stripping process; the precipitation and attrition will reduce the regeneration efficiency and the ammonium uptake during repetitive use of zeolite. Moreover, other valuable compounds exist in the permeate from AnMBR, such as dissolved methane and phosphorus, but cannot be recovered in this process. The IE-AS process should be preceded by additional treatments for the recovery of those compounds.

5.2 Recommendations

Based on the results of this research, following recommendations are proposed for further studies:

- A pilot-scale IE-AS system should be developed for ammonia recovery from the AnMBR permeate.
- Regeneration efficiency should be improved by supplementary manners or technologies.

- The replacement of reused zeolite should be investigated in the repetitive ion exchange process.
- The method for regular cleaning of the zeolite column should be developed to remove precipitates.
- Pre- or post-treatment should be investigated for the removal and recovery of dissolved methane and phosphorus.

References

Aiyuk, S., Amoako, J., Raskin, L., van Haandel, A., Verstraete, W., Removal of carbon and nutrients from domestic wastewater using a low investment, integrated treatment concept. Water Res. 38 (13) (2004), 3031–3042.

Bott, C.B., Murthy, S.N., Spano, T.T., Randall, C.W., WERF workshop on nutrient removal: how low can we go and what is stopping us from going lower? Alexandria, VA, WERF, 2007.

Ames L.L. Jr., Zeolite cation selectivity. *Canadian Mineralogist* 8 (1965), 325-333

Arogo, J., Zhang, R.H., Riskowski, G.L., Christianson, L.L., and Day, D.L., Mass transfer coefficient of ammonia in liquid swine manure and aqueous solutions. J. Agric. Eng. Res. 73 (1999), 77-86.

Ashrafizadeh S.N. and Khorasani Z., Ammonia removal from aqueous solutions using hollow-fiber membrane contactors, Chemical Engineering Journal 162 (2010) 242–249

Atkins, P. F., Jr., and Scherger, D. A., ‘‘A review of physicalchemical methods for nitrogen removal from wastewaters.’’ Progress in Water Technol., 8(1997), 713–719.

Beler Baykal, B., Guven, D.A., Performance of clinoptilolite alone and in Combination with sand filters for the removal of ammonia peaks from domestic wastewater. Water Sci. Technol. 35 (7) (1997), 47–54.

Bergero, D., Boccignone, M., Di Natale, F., Forneris, G., Palmegiano, G.B., Roagna, L. and Sicuro B., Ammonia removal capacity of European natural tuffs: application to aquaculture waste water. Aquaculture and Fisheries Management 25(8) (1994), 813-821

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

Bonmati, A. and Flotats, X., Air stripping of ammonia from pig slurry: characterisation and feasibility as pre- or post-treatment to mesophilic anaerobic digestion, Waste Manage. 23 (2003), 261 – 272.

Celik M.S., Ozdemir B., Turan M., Koyuncu I., Atesok G., and Sarikaya H.Z., Removal of ammonia by natural clay minerals using fixed and fluidized bed column reactors. J. Water Sci. Tec., 1(1)(2001): 81-88

Chiayvareesajja, S. and Boyd, C.E., Effects of zeolite, formalin, bacterial augmentation and aeration on total ammonia nitrogen concentrations. Aquaculture 116(1) (1993), 33-45.

Colella, C., Ion exchange equilibria in zeolite minerals. Mineralium Deposita 31 (1996), 554-562.

Cooney I., Booker A., Shallcross C. and Stevens W., Ammonia Removal from Wastewaters Using Natural Australian Zeolite. II. Pilot-Scale Study Using Continuous PackedColumn Process', Separation Science and Technology, 34: 14 (1999), 2741-2760

Corbitt R.A., Standard handbook of environmental engineering. New York, McGraw-Hill, 1999

Culp L. R., Wesner George Mack and Culp G.L., Handbook of Advanced Wastewater Treatment. 2nd Ed. Van Nostrand Reinhold Co., NY. 1978

Demir A., Gunay A. and Debik E.，Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite，Water SA Vol. 28 No. 3 (2002), 329-336

Dimirkou, A., Doula, M.K., Use of clinoptilolite and an Fe-overexchanged clinoptilolite in Zn^{2+} and Mn^{2+} removal from drinking water. Desalination 224 (1-3) (2008), 280–292.

Djebbar Y. and Naraitz R.M., Improved Onda correlations for mass transfer in packed towers, Water Sci. Technol. 38 (6) (1998) 295–302

Doyle, J.D. and Parsons, S.A., Struvite formation, control and recovery. Water Res. (2002), pp. 3925-3940.

Du, Q., Liu, Z., Cao, Z., Wang, Y., Ammonia removal from aqueous solution using natural Chinese clinoptilolite. Sep. Purif. Technol. 44 (3) (2005), 229–234.

Englert A. H., Rubio J., Characterization and environmental application of a Chilean natural zeolite, Int. J. Miner. Process 75 (2005) 21–29

Farkas, A., Rozic, M., Barbaric-Mikocevic, Z., Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. J. Hazardous Mater. B 117 (2005), 25–33.

Ferreiro Almeda, S., García García, R., Feberero Castejón, A. and López Ruiz, J.L., Effects of a zeolitic product (Zestec-56) on ammonium production in a rainbow trout Oncorhynchus mykiss (Walbaum) fry culture, Aquaculture Research 26 (1995), 859-860

FRTR, Remediation Technologies Screening Matrix and Reference Guide, Version

4.0, 4.48 Ion Exchange, http://www.frtr.gov/matrix2/section4/4-49.html

Gómez, X., Morán, A., Cuetos, M.J., Sánchez, M.E., The production of hydrogen by dark fermentation of municipal solid wastes and slaughterhouse waste: a two-phase process. J. Power Sources 157 (2006), 727–732.

Guo J., Abbas A.A., Chen Y., Liu Z, Fang F., Chen P., Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process, Journal of Hazardous Materials 178 (2010), 699–705

Gustin S. and Marinsek-Logarb R., Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent, Process Safety and Environmental Protection 89 (2011), 61 – 66

Haralambous A., Maliou E., and Malamis M., The use of zeolite for Ammonium uptake. Water Sci. Tec. **25**(1)(1992): 139-145

Hasanoglu A., Romero J., Pérez B., Plaza A., Ammonia removal from wastewater streams through membrane contactors: Experimental and theoretical analysis of operation parameters and configuration, Chemical Engineering Journal 160 (2010), 530–537

Hawkins, D.B., Occurrence and availability of natural zeolites: in Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture, Pond, W.G. and Mumpton, F.A., eds., Westview Press, Colorado, 1983 pp. 69-78.

Hedström, A. Ion exchange of ammonium in zeolites: a literature review. Journal of environmental engineering, 127(8) (2001), 673-681

Hlavay, J., Vigh, G., Olaszi, V., and Inczedy, J.,‘‘Investigations on natural Hungarian zeolite for ammonia removal.''Water Res., 16(4) (1982), 417–420.

Ho, J., Sung, S., Anaerobic membrane bioreactor treatment of synthetic municipal wastewater at ambient temperature. Water Environ Res. 81 (9) (2009), 922-928.

Horsh, C.M. and Holway, J.E.,Use of clinoptilolite in salmon rearing. In: Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture, Pond, W.G. and

Huang, H., Xiao, X., Yan, B., Yang, L., Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. J. Hazard. Mater. 175 (1-3) (2010), 247–252.

Huang J.C. and Shang C., Advanced physicochemical treatment processes, Humana Press, 2006

Mumpton, F.A., eds., Westview Press, Colorado, 1983 pp. 229-239.

Idelovitch E. and Michail M., Nitrogen Removal by Free Ammonia Stripping from High pH Ponds, Journal (Water Pollution Control Federation), Vol. 53, No. 9, Annual Conference Issue (1981), pp. 1391-1401

Jama, M., Yücel, H. Equilibrium Studies of Sodium-Ammonium, Potassium-Ammonium, and Calcium-Ammonium Exchanges on Clinoptilolite Zeolite. Sep. Sci. Technol.24 (1989), 1393-1416.

Jorgensen, S.E., Libor, O., Graber, K.L. and Barkacs, K., Ammonia removal by use of clinoptilolite. Water Research 10 (1976), 213-224.

Jorgensen S.E., Libor O., Barkacs K., and Kuna L., Equilibrium and capacity data of clinoptilolite, Water Res. 13 (1979) 159–165.

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

Johnston, A.E. and Richards, I.R., Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manage (2003), pp. 45-49.

Johnson, P.W. and Sieburth, J. McN., Ammonia removal by selective ion exchange, a backup system for microbiological filters in closed system aquaculture. Aquaculture **4** (1974**)**, 61-68.

Jung, J., Chung, Y., Shin, H., Son, D., Enhanced ammonium nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. Water Res. 38 (2004), 347–354.

Kabdasli, I., Tunay, O., Islek, C¸, Erdinc¸, E., Huskalar, S., and Tatli, M.B., Nitrogen recovery by urea hydrolysis and struvite precipitation from anthropogenic urine, *Water Science and Technology,* 53 (2006b), 305–312

Katehis, D., Diyamandoglu, V., and Fillos, J., Stripping and recovery of ammonia from concentrate of anaerobically digested biosolids at elevated temperature, Water Environment Research 70 (2) (1998), 231–240.

Kessler, K., Analysis of nitrogen loading reductions for wastewater treatment facilities and non-point sources in the Great Bay Estuary watershed. New Hampshire Department of Environmental Services, USA, 2010.

Kim, H. and Pagilla K.R., Verification of enhanced phosphate removal capability in pure cultures of Acinetobacter calcoaceticus under anaerobic/aerobic conditions in a SBR. Biotechnol. Bioproc. Eng. 7 (2002): 335-339.

Kim J., Kim K., Ye H., Lee E., Shin C., McCarty P.L., Bae J., Anaerobic fluidized bed membrane bioreactor for wastewater treatment, Environ. Sci. Technol., 45 (2011), pp. 576–581

Kim, J.H., Rene, E.R., Park, H.S., Performance of an immobilized cell biofilter for ammonia removal from contaminated air stream. Chemosphere 68 (2) (2007), 274–280.

Klieve, J.R. and Semmens, M.J., An evaluation of pre-treated natural zeolites for ammonium removal. Water Research 14 (1980), 161-168.

Kiss, K., Nemestóthy, N., Gubicza, L., Bélafi-Bakó, K., Vacuum assisted membrane bioreactor for enzymatic hydrolysis of pectin from various agrowastes. Desalination 241 (2009), 29–33.

Koon J.H. and Kaufman W.J., Ammonia Removal from Municipal Wastewaters by Ion Exchange, Water Pollution Control Federation, Vol. 47 (1975), No. 3, Part I, pp.448-465

Koyuncu I., Topacik D., Turan M., Celik M.S., and Sarikaya H.Z., Application of the membrane technology to control ammonia in surface water, Water Science and Technology: Water Supply Vol 1(2001) pp 117–124

Kim, B.U., Lee, W.H., Lee, H.J., and Rim, J.M., Ammonium nitrogen removal from slurry type swine wastewater by pre-treatment using struvite crystallization for nitrogen control of anaerobic digestion, *Water Science and Technology,* 49(2004), 215–222

Laurenson, S., Bolan, N., Smith E., McCarthy, M., Changes in the cation composition of a Barossa Chromosol irrigated with wastewaters of contrasting monovalent cation concentrations. 19th World Congress of Soil Science, Soil Solutions for a Changing World, Brisbane, Australia, 2010.

Lee, H.S., Rittmann, B.E., Significance of biological hydrogen oxidation in a continuous single-chamber microbial electrolysis cell. Environ. Sci. Technol. 44 (2010), 948–954.

Li, M., Zhu, X., Zhu, F., Ren, G., Cao, G., Song, L., Application of modified zeolite for ammonium removal from drinking water. Desalination 271 (1-3) (2011) 295–300.

Liao, B.Q., Kraemer, J.T., Bagley, D.M., Anaerobic membrane bioreactors: Applications and research directions. Critical Reviews in Environmental Science and Technology 36 (6) (2006), 489-530.

Liao, P.B. and Lin, S.S., Ion exchange systems for water circulation. Journal World of the Mariculture Society **12**(1) (1981), 32-39.

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

Liberti, L., Boari, G., Peteruzzelli, D., and Passino, R., 'Nutrient removal and recovery from wastewater by ion exchange, Water Res.,15 (1981), 337–342.

Lin, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Liss, S.N., Liao, B.Q., Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). Water Res. 43 (15) (2009), 3827–3837.

Logan B, Regan J. Feature Article: microbial fuel cellschallenges and applications. Environ Sci Technol (2006);40(17): 5172e80.

Maekawa, T., Liao, C.M., and Feng, X.-D., Nitrogen and phosphorus removal for swine wastewater using intermittent aeration batch reactor followed by ammonium crystallization process, Water Research (1995), 29, 2643–2650

Marking, L.L. and Bills, T.D., Factors affecting the efficiency of clinoptilolite in removing ammonia from water, Progressive Fish-Culturist 44(1982), 187-189

Matter-Muller C., Gujer W., and Giger W., Transfer of volatile substances from water to the atmosphere, Water Res. 15 (1981) 1271–1279.

McLaren, J.R. and Farquhar, G.J., Factors affecting ammonia removal by clinoptilolite. *Journal of the Environmental Engineering Division,* **99**(4) (1973), 429-446.

Milán, Z., Montalvo, S., de Las Pozas, C., Monroy, O., Sánchez, E., Borja, R., The effects of hydraulic loading and NaCl concentrations on the regeneration of exhausted homoionic natural zeolite. J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng. 46 (6) (2011), 596-600.

Miles, A.E., and Ellis, T.G., Recovery of nitrogen and phosphorus from anaerobically wastes using struvite precipitation. Proceedings of the National Conference on Environmental Engineering, Water Resources and the Urban Environment. Chicago, Illinois (1998), p. 61.

Monteny G.J. and Lamaker E. J., Factors influencing air velocity in and ammonia volatilization from a slurry pit in cubicle houses for dairy cows. In: International Symposium on Ammonia and Odour Control from Animal Production Facilities, Vinkeloord, Netherlands, 1997

Mumpton, F.A., Natural zeolites. In: Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture, Pond, W.G. and Mumpton, F.A, eds., Westview Press, Colorado, 1983, pp. 33-43.

Neethling, J.B and Benisch M., Struvite control through process and facility design as well as operation strategy. Water Sci. (2004), pp. 191-199.

Nelson, N.O., Mikkelsen, R.L. and Hesterberg, D.L, Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constants, Bioresour. Technol., 89 (2003), 229-236.

Norddahl B., Horn V.G., Larsson M., du Preez J.H., Christensen K., A membrane contactor for ammonia stripping, pilot scale experience and modeling, Desalination 199 (2006), 172–174

Nguyen M. L., Tanner C. C., Ammonium removal from wastewaters using natural New Zealand zeolites, New Zealand Journal of Agricultural Research 41 (1998) 427–446

Nunes S.P., Peinmann K.V., Membrane Technology, Wiley, New York, 2001

Ozturk I., Altinbas M., Koyuncu I., Arikan O., Gomec-Yangin C., Advanced physical-chemical treatment experiences on young municipal landfill leachates, Waste Manage. 23 (2003), 441–446

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

Odegaard, H., Rensing av avlopsvann, Tapir forlag, Trondheim, Norway, 1992 (in Norwegian)

Priestley, A.J., Cooney, E., Booker, N.A., and Fraser, I., Nutrients in wastewaters-Ecological problem or commercial opportunity? *Proceedings of the 17th Federal Convention of the Australian Water and Wastewater Association,* Melbourne, Australia, 1997, 340–346.

Quan X., Wang F., Zhao Q., Zhao T., Xiang J., Air stripping of ammonia in a water-sparged aerocyclone reactor, Journal of Hazardous Materials 170 (2009), 983–988

Rahmani, A.R., Mahvi, A.H., Mesdaghinia, A.R., Nasseri, S., Investigation of ammonia removal from polluted waters by Clinoptilolite zeolite. Int. J. Environ. Sci. Technol. 1(2) (2004), 125-133.

Rahmani, A.R., Samadi, M.T., Ehsani, H.R., Investigation of Clinoptilolite Natural Zeolite Regeneration by Air Stripping Followed by Ion Exchange for Removal of Ammonium from Aqueous Solutions. Iran. J. Environ. Health. Sci. Eng. 6 (3) (2009), 167-172.

Resch, C., Grasmug, M., Smeets, W., Braun, R., Kirchmayr, R., Optimised anaerobic treatment of house-sorted biodegradable waste and slaughterhouse waste in a high loaded half technical scale digester. Water Sci. Technol. 54 (2006), 231–236.

Roberts E., and Alley P. E., Water quality control handbook, McGraw-Hill, 2000

Ruxton G.D., Mathematical modeling of ammonia volatilization from slurry stores and its effect on Cryptosporidium oocyst viability. Journal of Agricultural Science, Cambridge (1995), 124, 55-56

Saddoud, A., Ellouze, M., Dhouib, A., Sayadi, S., Anaerobic membrane bioreactor treatment of domestic wastewater in Tunisia. Desalination 207 (1–3) (2007), 205–215.

Sarioglu M., Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite, Sep. Purif. Technol. 41 (2005) 1–11.

Schoeman, J.J., Evaluation of a South African clinoptilolite for ammonium-nitrogen removal from an underground mine water. Water SA 12 (2) (1986), 73-82.

Semmens, M., Klieve, J., Schnobrich, D., Tauxe, G. Modeling ammonia exchange and regeneration in clinoptilolite. Water Res. 15 (1981), 655-666.

Semmens, M.J., Booth, A.C. and Tauxe, G.W., Clinoptilolite column ammonia removal model. Journal of the Environmental Engineering Division, ASCE 104(2) (1978), 231- 245.

Semmens, M.J., Cation exchange properties of natural zeolites. In: Zeo- Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture, Pond, W.G. and Mumpton, F.A., eds., Westview Press, Colorado. 1983 pp. 45-53

Shen X.Y., Sun J.J., and Ma Z.Y., Effect of surfactant on the evaporation of BTEX from static water, Environ Sci. 26(2005): 122−126

Sirkecioglu, A., Senatlar, A., Removal of ammonium ions from wastewaters by Bigadiç clinoptilolite. Tr. J. of Eng. And Environ. Sci. 19 (1995), 399-405.

Stumm, W., Morgan, J.J., Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters. 3rd Ed. John Wiley & Sons, New York, USA, 1996, 219–221.

Sprynskyy, M., Lebedynets, M., Terzyk, A.P., Kowalczyk, P., Namiesnik, J., Buszewski, B., Ammonium sorption from aqueous solutions by the natural zeolite transcarpathian clinoptilolite studied under dynamic conditions. Colloid Interf. Sci. 284 (2005), 408–415.

Stumm W. and Morgan J.J., Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters, 3rd edn. John Wiley & Sons, New York, USA (1996), pp 219–221

Tan X.Y., Tan S.P., Teo W.K., Li K., Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water, J. Membr. Sci. (2006) 271

Tchobanoglous, G., F. L. Burton, and H. D. Stensel, Waste water Engineering: Treatment and Reuse. New York, NY: McGraw-Hill, 2003

Teo, L.R., Chen, T.W. and Lee, B.H., Packaging of the guppy, Poecilia reticulata, for air transport in a closed system. Aquaculture 78 (1989), 321-332

Tunay, O., Kabdas¸li, I., Orhon, D., and Kolcak, S., Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters, *Water Science and Technology,* 36(1997), 225–228.

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

Wang Y L., Treatment of ammonia nitrogen wastewater by ultrasonic stripping, Tech Equip Environ Pollut 2 (2001): 59–63

Wang, Y., Kmiya, Y., Okuhara, T., Removal of low-concentration ammonia in water by ion exchange using Na-mordenite. Water Res. 41 (2) (2007), 269 – 276.

Water Environment Federation: Design of Municipal Wastewater Treatment Plants: WEF Manual of Practice No. 8 ASCE Manuals and Reports on Engineering Practice

No. 76, Fifth Edition. Air Stripping for Ammonia Removal, McGraw-Hill Professional, 2010

Watten, B.J. and English, M.J., Effects of organic matter in aquacultural waste on the ammonium exchange capacity of clinoptilolite. Aquaculture 46(3) (1985), 221-235.

Weatherly, L.R., McVeigh, R.J., The Enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria. In: Proceedings of IEX 2000, Ion Exchange at The Millennium, 16–21 July, 2000, Cambridge, England, pp. 133–141.

Weatherley, L.R., Miladinovic, N.D., Comparison of the ion exchange uptake of ammonium ion onto NewZealand clinoptilolite and mordenite. Water Res. 38 (20) (2004), 4305–4312.

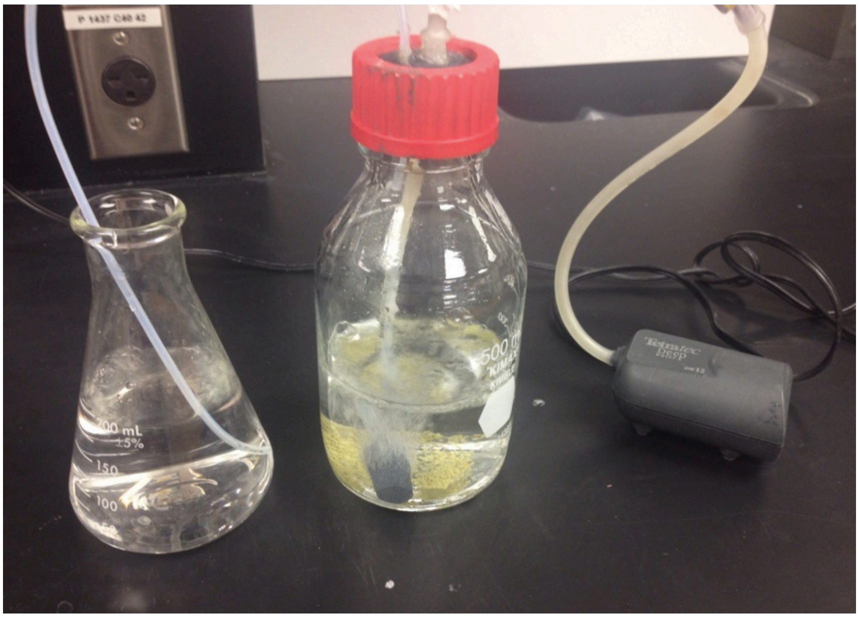
Woods, N.C., Daigger, G.T. and Sock, S.M., Sewage sludge reductions offered by phosphate recycling. CHIMICA Oggi/Chemistry today. (2000,) pp. 68-70.

Xu L.H. and Zhou Q., Ammonium removal from waste water by zeolite, Journal of China Water & Wastewater 19 (2003) 24–26.

Zhao, H., Vance, G.F., Ganjegunte, G.K., Urynowicz, M.A., Use of zeolites for treating natural gas co-produced waters in Wyoming, USA. Desalination 228 (1-3) (2008), 263–276

Appendix A Photographs of Experimental Set-up

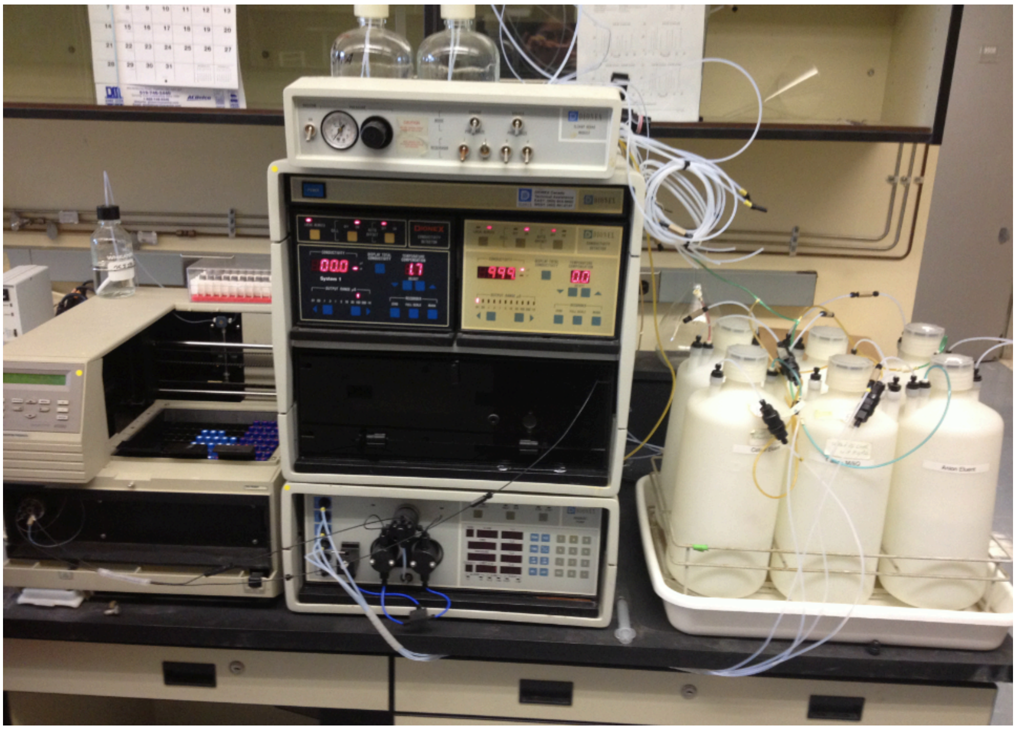
A1. Shaking batch tests



A2. Air stripping batch tests

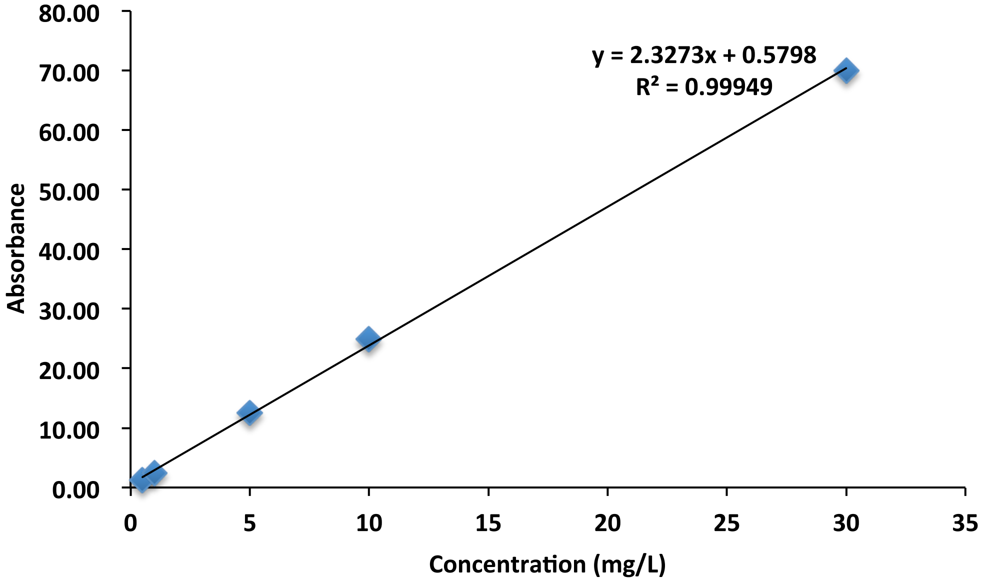
A3. Column regeneration system

A4. Bran-Luebbe Auto Analyzer 3 for ammonia measurement

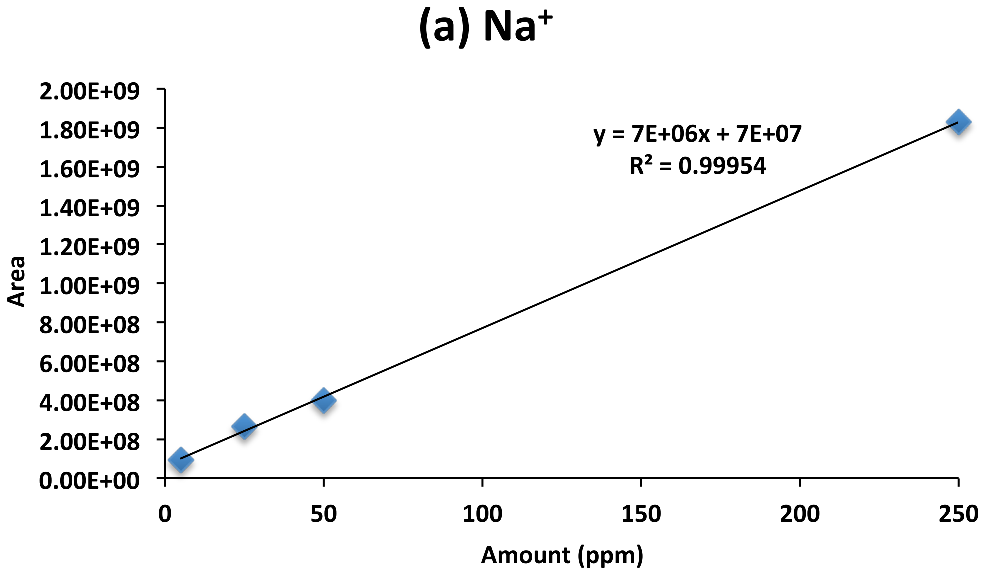


A5. IC for cations measurement

Appendix B Calibration Curves

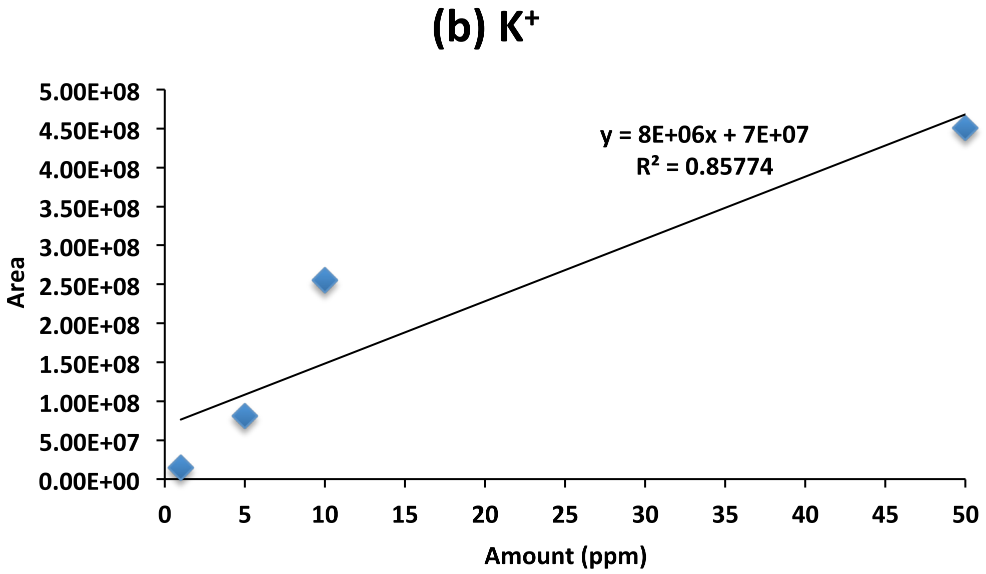


B1. Calibration curve for ammonium nitrogen



(a) Na^+

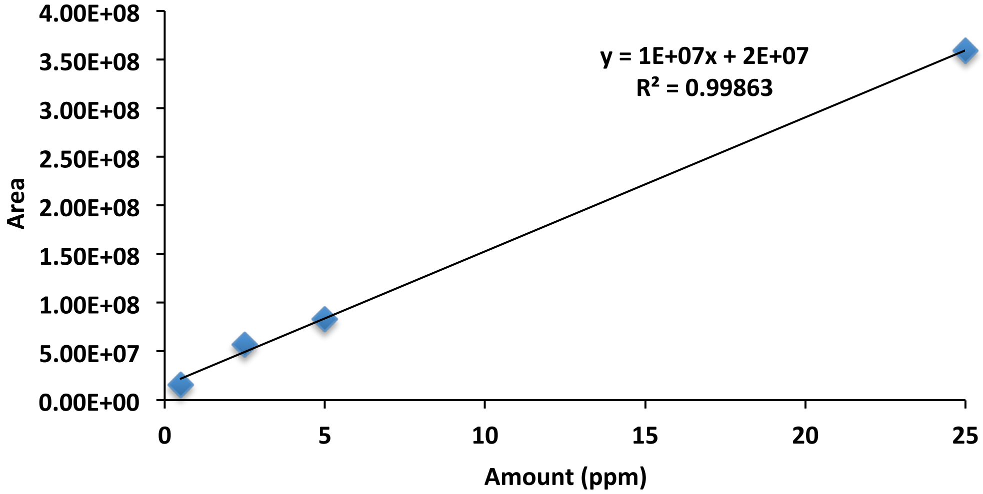
y = 7E+06x + 7E+07
R² = 0.99954
Area
2.00E+09
1.80E+09
1.60E+09
1.40E+09
1.20E+09
1.00E+09
8.00E+08
6.00E+08
4.00E+08
2.00E+08
0.00E+00
0
50
100
150
200
250
Amount (ppm)



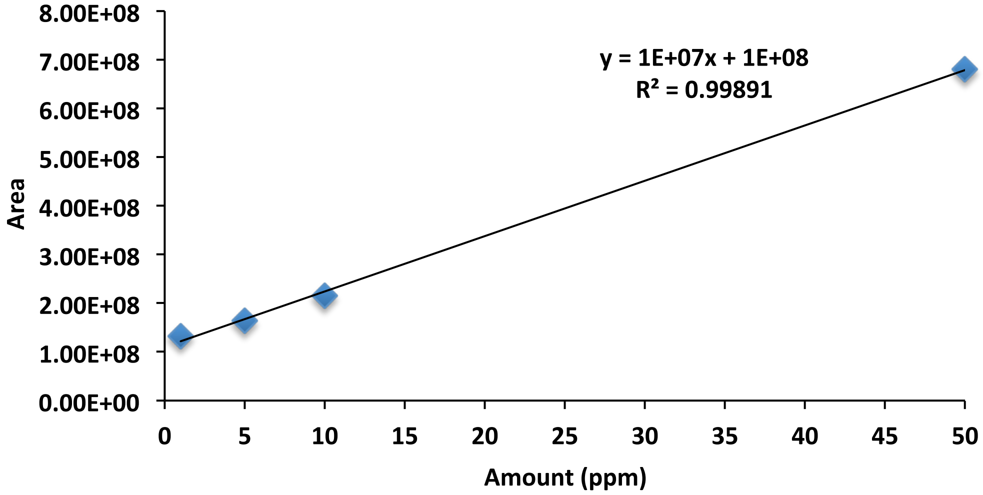
(b) K^+

y = 8E+06x + 7E+07
R² = 0.85774
Area
5.00E+08
4.50E+08
4.00E+08
3.50E+08
3.00E+08
2.50E+08
2.00E+08
1.50E+08
1.00E+08
5.00E+07
0.00E+00
0
5
10
15
20
25
30
35
40
45
50
Amount (ppm)

(c) Mg^{2+}



(d) Ca^{2+}



B2. Calibration curve for cations (Na^+, K^+, Mg^{2+}, and Ca^{2+})