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The Control of Water Contaminants Assisted by Natural Materials

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The Control of Water Contaminants Assisted by Natural Materials

by

Wen Zhao

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering Science
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College of Engineering
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November 2, 2017

Keywords: Ion exchange, Adsorption, Ammonia, Fluoride

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DEDICATION

This dissertation is dedicated to the Lord my God, who has strengthened me, blessed me, and made my work possible through Jesus Christ.

To my beloved husband, Ran Rui.

To my families, especially my parents and grandparents in China.

To my church families, especially every brothers and sisters in the Tampa Chinese Student Christian Fellowship.
ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor, Dr. Norma A. Alcantar, who taking care of me and supporting me over the years. I’m so grateful to have such a patient and knowledgeable advisor who always encourages me. I would also like to thank my committee members. In particular, I would like to thank Dr. Sarina Ergas, who showed me the research paths when I went through my master’s degree at USF. I have learned a lot from you, especially your passion for science and for helping students. To Dr. Delcie Durham, thank you for your nice support throughout my dissertation progress. To Dr. Kebreab Ghebremichael, thank you for your vital contribution to the fluoride project. To Dr. Sylvia Thomas, thank you for your encouragement and lovely support throughout my work. To Dr. Qiong Zhang, thank you for building up my confidence to become a mature researcher.

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# TABLE OF CONTENTS

LIST OF TABLES iv  
LIST OF FIGURES vi  
ABSTRACT viii  

CHAPTER 1: INTRODUCTION 1  
1.1 Background 1  
1.2 Part I: Aquaculture Wastewater Treatment 2  
1.3 Part II: Drinking Water Treatment 5  

CHAPTER 2: FRAMEWORK 8  
2.1 Aquaculture Wastewater Treatment 8  
  2.1.1 Ammonia and Fish 8  
  2.1.2 Ammonia Removal Techniques 9  
2.2 Drinking Water Treatment 11  
  2.2.1 Biosand Filter (BSF) 11  
  2.2.2 Turbidity in Water 13  
  2.2.3 pH of Water 13  
  2.2.4 Fecal Indicator Bacteria in Water 14  
  2.2.5 Fluoride in Water 14  
  2.2.6 Fluoride Removal Techniques 15  
  2.2.7 Fluoride Adsorption by Aluminum Oxide Coated Pumice (AOCP) 16  

CHAPTER 3: AMMONIA REMOVAL IN AQUACULTURE WASTEWATER 19  
3.1 Aquaculture Wastewater Treatment 19  
3.2 Materials and Methods 20  
  3.2.1 Materials 20  
    3.2.1.1 Ion Exchanger 20  
    3.2.1.2 Chemical Neutralizer 21  
    3.2.1.3 Aquaculture Wastewater 21  
  3.2.2 Methods 22  
    3.2.2.1 Analytical Methods 22  
    3.2.2.2 Chabazite Characterization 23  
    3.2.2.3 Ammonia Accumulation Rate Determination 23  
    3.2.2.4 Ammonium Adsorption Kinetic Studies 24  
    3.2.2.5 Ammonium Adsorption Isotherm Studies 26  
    3.2.2.6 In-vitro Comparison of Ammonia Removal 28  
    3.2.2.7 In-vivo Comparison of Ammonia Removal 28
### 3.2.2.8 Toxicity Assessment

3.2.2.9 Chabazite Regeneration and Regeneration Efficiency Studies

3.2.2.10 Statistical Analysis

### 3.3 Results and Discussions

3.3.1 Ammonia Accumulation Rate Determination

3.3.2 Characterization of Chabazite

3.3.3 Ammonium Adsorption Kinetics

3.3.4 Ammonium Adsorption Isotherm Study

3.3.5 *In-vitro* Comparison of Ammonia Removal

3.3.6 *In-vivo* Comparison of Ammonia Removal

3.3.7 Toxicity Assessment

3.3.8 Cost Analysis

3.3.9 Regeneration Efficiency Studies of Ammosorb

### 3.4 Conclusions

### CHAPTER 4: FLUORIDE REMOVAL BY MODIFIED BIOSAND FILTER (BSF)

4.1 Introduction

4.2 Materials and Methods

4.2.1 Fluoride Adsorption Material

4.2.2 Fluoride Adsorption by AOCP

4.2.3 Fluoride Adsorption Isotherm and Kinetic Studies

4.2.4 Bench Scale BSF

4.2.5 Bench Scale BSF Operation

4.2.6 Analytical Methods

4.2.7 BSF Modeling

4.2.8 Statistical Analysis

4.2.9 BSF Regeneration

4.3 Results and Discussion

4.3.1 Fluoride Adsorption by AOCP

4.3.2 Fluoride Adsorption Kinetic Studies

4.3.3 Fluoride Adsorption Isotherm Studies

4.3.4 Bench Scale BSF Performance

4.3.4.1 Hydraulic Aspects

4.3.4.2 Turbidity Removal

4.3.4.3 pH

4.3.4.4 Fluoride Removal

4.3.5 BSF Modeling

4.3.6 BSF Regeneration

4.4 Conclusions

### CHAPTER 5: CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

5.2 Future Works

### DISCLOSURE
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1</td>
<td>Expected output water qualities in this dissertation</td>
<td>4</td>
</tr>
<tr>
<td>Table 3-1</td>
<td>Synthetic water constituents</td>
<td>22</td>
</tr>
<tr>
<td>Table 3-2</td>
<td>Non-linear and linear forms of Langmuir, Freundlich, Temkin, and Sips isotherm models</td>
<td>27</td>
</tr>
<tr>
<td>Table 3-3</td>
<td>The daily maximum dose of ammonia removal substance</td>
<td>29</td>
</tr>
<tr>
<td>Table 3-4</td>
<td>Ammonia production rate constant for different groups</td>
<td>32</td>
</tr>
<tr>
<td>Table 3-5</td>
<td>Chemical composition of chabazite based on SEM-EDS analysis</td>
<td>34</td>
</tr>
<tr>
<td>Table 3-6</td>
<td>Textural and physicochemical properties of chabazite</td>
<td>34</td>
</tr>
<tr>
<td>Table 3-7</td>
<td>Pseudo-second-order kinetic parameters for ammonium removal in both freshwater and seawater</td>
<td>40</td>
</tr>
<tr>
<td>Table 3-8</td>
<td>Diffusion kinetic parameters for ammonium removal in both freshwater and seawater</td>
<td>41</td>
</tr>
<tr>
<td>Table 3-9</td>
<td>The maximum ammonium adsorption capacity (q₀) data for chabazite from other literature</td>
<td>41</td>
</tr>
<tr>
<td>Table 3-10</td>
<td>Adsorption isotherms parameters estimated by linear and non-linear regression in freshwater</td>
<td>42</td>
</tr>
<tr>
<td>Table 3-11</td>
<td>Adsorption isotherms parameters estimated by linear and non-linear regression in seawater</td>
<td>43</td>
</tr>
<tr>
<td>Table 3-12</td>
<td>Ammonia removal efficiency comparison among AmmoSorb, commercial water conditioner (CC), and novel neutralizer (NN)</td>
<td>45</td>
</tr>
<tr>
<td>Table 3-13</td>
<td>LC₅₀ of commercial water conditioners (B.B.™ and P.S.™) and novel neutralizer (NN)</td>
<td>49</td>
</tr>
<tr>
<td>Table 3-14</td>
<td>Daily cost comparison between the AmmoSorb, the novel neutralizer (NN), and commercial water conditioner (CC)</td>
<td>51</td>
</tr>
<tr>
<td>Table 4-1</td>
<td>The daily charge of bench scale BSFs</td>
<td>59</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------</td>
<td>----</td>
</tr>
<tr>
<td>Table 4-2</td>
<td>BSF regeneration procedures for four different cycles</td>
<td>62</td>
</tr>
<tr>
<td>Table 4-3</td>
<td>Pseudo-second-order kinetic parameters for fluoride adsorption by AOCP</td>
<td>65</td>
</tr>
<tr>
<td>Table 4-4</td>
<td>Comparison of fluoride adsorption capacity (q_{max}, mg/g) by different types of pumice</td>
<td>68</td>
</tr>
<tr>
<td>Table 4-5</td>
<td>The experimental and calculated parameters of Bohart-Adams model and Thomas model</td>
<td>81</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

| Figure 3-1 | (a) Ammonia production as a function of time and (b) pH change as a function of time in seawater shrimp, seawater pinfish/pufferfish with Pogey-Croaker Saver™, freshwater bass with Better Baits™, and freshwater bass without Better Baits™ | 32 |
| Figure 3-2 | Chemical composition of exchangeable cations changes before and after modification | 35 |
| Figure 3-3 | XRD pattern comparison between natural chabazite (NC), freshwater modified chabazite (FC) and sodium chloride modified chabazite (SC) | 35 |
| Figure 3-4 | Ammonium removal efficiency in freshwater (left) and seawater (right) | 40 |
| Figure 3-5 | The ammonia excretion (top) and pH trend (bottom) of the freshwater specimen as the function of time | 48 |
| Figure 3-6 | The exchangeable ion comparison before and after AmmoSorb addition. | 49 |
| Figure 3-7 | Ammonia excretion (top) and pH trend (bottom) of the seawater specimen as the function of time | 50 |
| Figure 3-8 | Toxicity comparison among each ammonia removal substances (Spring water works as control) | 51 |
| Figure 3-9 | Ammonium adsorption equilibrium comparison between new chabazite and regenerated chabazite. | 52 |
| Figure 4-1 | Schematic of three biosand filter (BSF) designs | 58 |
| Figure 4-2 | Residual fluoride concentration after adsorbed by pumice (▲) and AOCP (●) as a function of time (adsorbent 20g/L, initial fluoride concentration 5 mg/L, contact time 24 h) | 66 |
| Figure 4-3 | Adsorption kinetics of fluoride onto AOCP: (a) pseudo-first-order plot; (b) pseudo-second-order plot | 66 |
| Figure 4-4 | Adsorption kinetics of fluoride onto AOCP analyzed by intraparticle diffusion model | 66 |
Figure 4-5  The variation of maximum filtration rate (MFR) as a function of days 73
Figure 4-6  The variation of initial head loss as a function of days 74
Figure 4-7  The variation of residual turbidity as a function of days 75
Figure 4-8  The variation of output pH as a function of days 76
Figure 4-9  The variation of residual fluoride concentration as a function of days 77
Figure 4-10  The plot of Bohart-Adam (BA) model and Thomas model as a function of BSF service time 80
Figure 4-11  The breakthrough time as a function of AOCP layer depth (BDST model) 81
Figure 4-12  The variance of maximum flow rate (MFR) of four bench scale BSFs during the regeneration cycles 85
Figure 4-13  The variance of pH of four bench scale BSFs during the regeneration cycles 86
Figure 4-14  The variance of turbidity of four bench scale BSFs during the regeneration cycles 87
Figure 4-15  The variance of fluoride concentration of four bench scale BSFs during the regeneration cycles 88
Figure 4-16  The raw water and output water mean *E. coli* concentration of four bench scale BSFs during the regeneration cycles 89
**ABSTRACT**

Natural materials can be used to remove water contaminants by applying proper physical, chemical, and biological water treatment processes. This study involves using natural materials, as they are considered to be more environmentally benign and cost-effective than synthetic materials. This dissertation concentrates on monitoring five major water quality parameters—ammonia, fluoride, turbidity, pH, and fecal indicator bacteria (FIB)—in two major applications where clean water is needed. The focus is on meeting the water quality requirements for each contaminant. The overall objective of this study is to control the levels of ammonia in aquaculture wastewater, and adjust fluoride, turbidity, pH, and FIB in drinking water by using natural materials. To accomplish this objective, this dissertation study is divided into two parts. Part I is about ammonia removal in aquaculture wastewater. Zeolite was the representative natural material that was used in this study. The methodologies presented include ion exchange and chemical neutralization processes. Part II is about fluoride, turbidity, pH and fecal indicator bacteria control in drinking water. Pumice stone was used in this study. The methodologies utilized in this work include biofiltration and adsorption.

In Part I, the methods of ion exchange and chemical neutralization as a function of ammonia removal efficiency, toxicity, and daily cost were compared. All these methods were found to remove ammonia by a simple drop-off system. Chabazite, a natural zeolite, was the ion exchanger source. Similarly, we compared the effectiveness of commercialized neutralizers versus a novel neutralizer prepared for this work. The ion exchanger (chabazite) had the highest ammonia removal in freshwater, but no significant ammonia removal in seawater was observed.
after *in-vivo* trials. However, for commercial water neutralizers, the *in-vivo* trials showed that they are not able to control ammonia levels in either freshwater or seawater. The novel neutralizer was found to have higher ammonia removal efficiencies in both freshwater and seawater. In terms of toxicity, the AmмоSorb can be considered non-toxic. To safely use the novel neutralizer, it is recommended to control its daily dose at 1 g/L/day followed by a two-thirds volume of water change every day. A comprehensive cost analysis also showed that the novel neutralizer was the least expensive ammonia remover.

In Part II, drinking water was treated by a bench-scale biosand filter system that included different filtration technologies, biological disinfection, and adsorption. The filtration technologies analyzed in this work include Aluminum Oxide Coated Pumice (AOCP) and sand. The AOCP also works as adsorption media to remove fluoride in water. As results, the AOCP imbedded biosand filter (BSF) can efficiently control fluoride, turbidity, and pH level to meet the WHO standards. In addition, the exhausted BSF can be regenerated by recoating the pumice with additional layers of aluminum oxide. The fluoride, turbidity, pH, as well as fecal indicator bacteria levels controlled by the regenerated BSF also meet the WHO standard for about one-month operation.

The overall contribution of this research is providing new methods to treat water at an affordable cost and an easy operational procedure with potential health benefits to the specific applications that require ammonia, fluoride, turbidity, pH, and *E. coli* levels to be controlled.
CHAPTER 1
INTRODUCTION

1.1 Background

Water sources can be contaminated for many reasons; therefore, water treatments are mandated to meet specific water quality standards. The decision of water treatment processes starts by considering the quality of the source water, desired water quality after treatment, and its application (Crittenden, Trussell, et al., 2005). In this dissertation, two water treatment applications: aquaculture wastewater treatment and drinking water treatment are discussed. The focused water quality parameters include ammonia, fluoride, turbidity, pH, as well as fecal indicator bacteria (FIB). To achieve the desired water quality, the proper treatment methods such as ion exchange, physicochemical adsorption, and biological filter were designed to use as a potential sustainable water treatment process. Natural materials are considered as ideal materials that can be involved in all of the aforementioned processes (Ghebremichael, 2004; Yusof, Keat, et al., 2010; Kallman, Oyanedel-Craver, et al., 2011; Intiaz, Anderson, et al., 1990; Cooney, Booker, et al., 1999; Gong, Qu, et al., 2012; Zhou and Boyd, 2014; Leyva-Ramos, Monsivais-Rocha, et al., 2010). Natural materials are naturally formed and extracted from the Earth, therefore it is easier to access. Instead of conventional water treatment technologies, natural materials are usually locally available. The other advantage of natural materials is their low cost. Therefore, they are especially suitable for water treatment applications for low-income communities. Many natural materials are environmentally benign, as they are obtained through sustainable practices and are biodegradable (Wegst and Ashby, 2004). When disposal is needed,
they are not hazardous (Wegst and Ashby, 2004). All of these properties make natural materials good options for water treatment applications. In spite of those advantages, there are a few knowledge gaps existing in the natural material related research. For example, few researches have applied natural materials into pilot or industrial applications as they were all in batch adsorption model (Ali, Asim, et al., 2012). Therefore, in this dissertation, we looked at two cases that natural materials are both worked in pilot cases. One was using natural materials in the real fish environment and the other one was applying natural materials into column adsorption system to purify drinking water. The overall objective of this dissertation study was to control the level of ammonia in aquaculture wastewater, and adjust fluoride, turbidity, pH, and FIB level in drinking water by using adequate natural materials.

To achieve this objective, this dissertation is divided into two parts. Part I is about ammonia removal in aquaculture wastewater. Part II is related to the fluoride, turbidity, pH and FIB control in drinking water. The expected output water qualities are listed in Table 1-1. This research will provide significant contributions to new methods to treat water at an affordable cost with potential health benefits to the specific applications that require ammonia, fluoride, turbidity, and FIB to be removed.

1.2 Part I: Aquaculture Wastewater Treatment

Ammonia is one of the major contaminants in wastewater, such as in fish storage and aquaculture water tanks. Production of ammonia during fish metabolism process is toxic to fish health (Levit, 2010). In a normal aquarium system, the ammonia can be controlled by biological process (i.e., nitrification) by maintaining high dissolved oxygen levels to promote aerobic bacterial activity. However, in fresh-caught fish systems or fish transportation systems, the ammonia accumulation rate is much faster than the ammonia oxidation rate by nitrification.
Therefore, ammonia is better removed directly from water by using physical or chemical processes. The physicochemical treatment process of ammonia removal includes ion exchange (IX), adsorption, chemical neutralization (CN), reverse osmosis, electrochemical reduction-oxidation, air stripping or precipitation (Boyer, 2014; Mook, Chakrabarti, et al., 2012; Peddie, van Teijlingen, et al., 2005; Bhatnagar and Sillanpää, 2011). Among them, ion exchange and chemical neutralization are two techniques that are suitable for fish storage and aquaculture water applications. Ion exchange has the advantages of being inexpensive, easy operational procedures, and renewable, especially using natural materials (Mumption and Fishman, 1977; Hedstrom, 2001; Emadi, Nezhad, et al., 2001). Chemical neutralization has the characteristics of easy operation and quick reaction rate (Crittenden, Trussell, et al., 2005). Zeolite is the most widely studied natural materials for ammonia removal (Hedstrom, 2001; Ivanova, Karsheva, et al., 2010). There are many kinds of zeolite in the world, such as clinoptilolite and chabazite. Chabazite was reported to have higher ammonia removal efficiency than clinoptilolite (Aponte-morales, 2015; Amini, Aponte-Morales, et al., 2017). Sodium bisulfate salt has been suggested to use as an ammonia neutralizer in aquaria for decades (Riche, Pfeiffer, et al., 2006; Harnish, Colotelo, et al., 2011; Kuhns, 1987). However, the side effects of ammonia neutralization products for fish or humans are still not well established. On the other hand, in terms of ion exchange method, the studies of ammonia removal in seawater are limited by in-vitro tests (Emadi, Nezhad, et al., 2001; Miladinovic, Weatherley, et al., 2004; Burgess, Perron, et al., 2004). Most literature suggests that the ammonia removal in saline water is not recommended in pond systems due to the effect of competing ions (Zhou and Boyd, 2014). The existing studies of ammonia removal by zeolite in freshwater vary by the zeolite type, size, dosage, pretreatment etc. The ammonia removal efficiency ranged from 18% to 94% (Ghasemi, Sourinejad, et al.,
If zeolite combined with the pH buffer will improve the ammonia removal performance is still unproven. Although chemical neutralization methods have been commercialized for decades, a removal efficiency and economic comparison against ion exchange is lacking.

To address these challenges, the objective of Part I is to control ammonia levels in aquaculture wastewater by using an ion exchange process and compare these results with a traditional chemical neutralization process. The major hypothesis of this research is that using natural materials to remove ammonia in fish wastewater will have the same or even better performance than chemical neutralization method. The following five tasks are designed to accomplish this objective.

Task 1: Determine the ammonia accumulation rate in stored fish systems.

Task 2: Understand ion exchange mechanisms of ammonium removal.

Task 3: Measure ammonia removal performance and establish a comparison between ion exchange and chemical neutralization.

Task 4: Analyze toxicity and cost between ion exchange and chemical.

Task 5: Describe the mechanisms involved in the ion exchanger regeneration.

Table 1-1 Expected output water qualities in this dissertation

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Output water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>&lt; Commercial water additive</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt;1.5 mg/L (WHO, 2011)</td>
</tr>
<tr>
<td>Turbidity</td>
<td>&lt; 5 NTU (WHO, 2011)</td>
</tr>
<tr>
<td></td>
<td>&lt;1 NTU (USEPA, 2017)</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-8.5 (WHO, 2011)</td>
</tr>
<tr>
<td>Fecal indicator bacteria</td>
<td>&lt;10 CFU/100 mL (WHO, 2011)</td>
</tr>
</tbody>
</table>
1.3 Part II: Drinking Water Treatment

Turbidity, pH, and fecal indicator bacteria (FIB) are major indicators of health in drinking water. The turbidity in water is caused by suspended particles that block light transmission through the water. Those suspended particles can be attached by microorganisms such as bacteria, viruses that are a threat to health (WHO, 2011). pH is an important water quality parameter. Improper pH might cause corrosion. Failure to control corrosion will result in the contamination of drinking water and the negative effect on its taste and appearance. E. coli is considered the most suitable indicator of fecal contamination in drinking water (WHO, 2011). In addition to these three basic parameters, fluoride concentration tends to attract the public’s attention in recent years, as the high fluoride intake will cause dental fluorosis and other toxic health effects, especially for children (U.S. Public Health Services, 1991). The World Health Organization (WHO) regulated 1.5 mg/L as the maximum level of fluoride in drinking water (Fawell, Bailey, et al., 2006). However, some developing countries such as India, have reported that the groundwater fluoride concentration was up to 19 mg/L, (reported in North-West India), which is much higher than the WHO standards (Yadav, Khan, et al., 1999; Fawell, Bailey, et al., 2006). Thus, the removal of fluoride in drinking water is necessary in communities that are susceptible to this kind of contamination. The control of fluoride, turbidity, pH, and FIB can be achieved by combing physical, chemical, and biological processes. Media filtration has been shown to be a simple but effective method for protecting drinking water from contamination especially for small communities (Dorea, Clarke, et al., 2004; WHO, 2011; Sobsey, Stauber, et al., 2008). The materials used in filtration are normally natural materials, such as sand, gravel, coal, or other substances (Bourke, Carty, et al., 1995). The filtration mechanisms usually include the biological action, adsorption, sedimentation, and straining (Bourke, Carty, et al., 1995). The
biosand filter (BSF) is highlighted as one of the most promising household water treatment technologies that are basically a sand and granular media filter (Sobsey, Stauber, et al., 2008). After reviewing 14 cases of BSF used in the field, the BSF’s performance averages 87% of E. coli removal and 78.9% of turbidity removal (Stauber, Printy, et al., 2012; Duke, Nordin, et al., 2006; Aiken, Stauber, et al., 2011; Stauber, Kominek, et al., 2012; Murphy, McBean, et al., 2010; Sobsey, Stauber, et al., 2008; Lukacs, 2002; Lynn, Wanjugi, et al., 2013). However, there is a major gap derived from the existing research publications (Noubactep, Temgoua, et al., 2012). A typical existing filtration system uses sand as the filtration media. Due to the low affinity of sand for inorganic compounds, it will be incapable of removing chemical contaminants such as fluoride in surface water by traditional BSF (Song, Kim, et al., 2005; Read, Lawless, et al., 1993; Murphy, McBean, et al., 2010). Accordingly, an alternative to conventional BSF should be worked on. Several materials, such as clay or activated alumina, have been well studied to remove fluoride, but using clay as the sorption medium of fluoride in column filter is only cost effective if the fresh clay is locally available (Padmasiri, 1997). The activated alumina is costly and also has high pH reduces potential (Ayoob, Gupta, et al., 2008).

To address these research gaps, the objective of Part II is to improve drinking water quality parameters, especially the fluoride, turbidity, pH, and fecal indicator bacteria by applying modified natural materials into the sand filter system. The major hypothesis of this study is that the natural material applied BSF has the capability to remove fluoride, turbidity, pH, and FIB and output water quality can meet the WHO drinking water standards. The following four tasks are designed to accomplish this objective.

*Task 1: Select filter material using fluoride adsorption batch tests.*
Task 2: Apply the chosen materials into bench scale BSFs and determine a proper filter configuration.

Task 3: Apply models to provide scale up parameters and conditions for a pilot scale BSF unit.

Task 4: Investigate a proper method to regenerate the exhausted BSF media.
CHAPTER 2
FRAMEWORK

2.1 Aquaculture Wastewater Treatment

2.1.1 Ammonia and Fish

Ammonia is present in water as two forms: free ammonia (NH\textsubscript{3}) and ammonium ion (NH\textsubscript{4}\textsuperscript{+}) (Durborow, Crosby, et al., 1992). Free ammonia (NH\textsubscript{3}) is toxic while the ammonium ion (NH\textsubscript{4}\textsuperscript{+}) is nontoxic. These two forms can convert to each other in water based on the following reaction:

\[
\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+ + \text{H}_2\text{O}
\]  

(2-1)

The proportion of NH\textsubscript{3} varies with water pH, temperature, pressure, and ionic strength. For example, at a temperature of 25°C, a pH is 7, there is almost no NH\textsubscript{3} in the water (USEPA, 1999). Ammonia can enter the aquaculture water by two main routes. The first route is decomposition of organic matter in the water. Proteins are highly abundant in fish and microorganisms. Each protein is made up of soluble building blocks called amino acids. Each amino acid contains an amino group that has NH\textsubscript{2} in it. Thus, degradation of protein will lead to the release of ammonia into the water (Helm, 2015). The second route involves the fishes’ digestion and assimilation of protein. During this process, some unused amino groups from the amino acid will be rejected back into the fish blood. From there, ammonia is excreted to the water via the gills (Helm, 2015). Fish excrete ammonia because of its toxicity. Excreted ammonia accumulates in the water over time. When ammonia levels are high enough in the water, the fish suffer ammonia burns, which affect the slime coating of fish to defend against infection and disease (Goldstein, 1985).
2.1.2 Ammonia Removal Techniques

The ammonia removal in aquaculture systems varies depending on the different types of water units. For fish ponds or culture systems, pumping fresh water into the pond is a common means to control the ammonia. However, this method is not economical nor practical for many fish farms. Maintaining high dissolved oxygen concentrations through aeration is also a good technique, but the efficiency is still low. In addition, temporarily reducing feed rates to the fish is recommended until the ammonia goes down to an ideal level (Durborow, Crosby, et al., 1992). In recent years, several advanced techniques have been developed for removing ammonia in aquaculture wastewater, and they can be divided into two categories: physicochemical and biological (Mook, Chakrabarti, et al., 2012). For instance, a wind-driven reverse osmosis system can remove about 92% of ammonia (Liu, Xia, et al., 2007), and a constructed wetland system (combination of free water surface and subsurface flow) can reach approximately 86-98% of ammonia removal (Lin, Jing, et al., 2002). Another type of aquaculture unit is a fish transportation or temporary storage system. Usually, this system includes a small volume of water, a closed lid bucket, and sometimes an aeration pump is provided. The limiting factors of this system include water temperature, water pH, fish loading density and transition or storage time. All of these factors will influence the mortality of fish that are stored in the system (Amend, Croy, et al., 1982). In addition, stress, or increased fish density will stimulate ammonia toxicity. Thus, stressed fish are more sensitive to ammonia than unstressed fish (Randall and Tsui, 2002). There is limited scientific research on fish transportation or temporary storage systems especially on ammonia removal (Emadi, Nezhad, et al., 2001; Kanyilmaz, Kocer, et al., 2014; Bower and Turner, 1982; Amend, Croy, et al., 1982). However, many commercial water
conditioners have been produced which claim that they can remove ammonia safely from the water.

Ammonia is more toxic to fish at a higher temperature and pH value (Levit, 2010; USEPA, 1999). Therefore, the way to control the ammonia level in the wastewater could be lowering the pH or decrease the temperature. Another way to remove ammonia is through ion exchange process. Ion exchange uses an ion exchanger such as zeolite to absorb NH$_4^+$ and release exchangeable ions such as Na$^+$ to the water. When NH$_4^+$ is removed, the reaction (Eq. 2-1) will go from left to right to rebalance. This will cause the decrease of concentration of toxic ammonia. The advantages of using an ion exchange process to remove ammonia include relatively low cost, high accessibility and easy operation (Weatherley and Miladinovic, 2004).

Using ion exchange technology for ammonia removal has been studied for several decades. The ammonia-containing wastewater varies from aquaculture wastewater, agriculture wastewater, domestic wastewater, human urine, composting leachate and, landfill leachate (Boyer, 2014). The main difference among those wastewater types in terms of the ammonia is the concentration. The value can range from 10 mg-N/L to >1000 mg-N/L (Boyer, 2014). In aquaculture wastewater, the ammonia concentration is usually around 0 mg-N/L to 50 mg-N/L depending on the fish species, the fish number, and the test duration (Bergero, Boccignone, et al., 1994; Lopez-Ruiz and Gomez-Garrudo, 1994; Silapajarn, Silapajarn, et al., 2006). At low concentrations of ammonia (0 to 50 mg-N/L), the ammonia removal efficiency by ion exchange improved as the ammonia concentration increased. This was due to the increase of mass transfer driving force between NH$_4^+$ and the ion exchanger (Sarioglu, 2005; Alshameri, Ibrahim, et al., 2014). Zeolite trapping of ammonia and toxic heavy metals in aquaculture wastewater has been intensively studied all around the world. Many factors such as zeolite type, the particle size of
zeolite, pretreatment, and wastewater type affect ammonia removal effectiveness (Ghasemi, Sourinejad, et al., 2016). Bower & Turner (1982) reported that as high as 20 g/L of clinoptilolite was used to reduce about 93% of ammonia in the freshwater during 24 h of simulated transport at stocking densities of 44 g-fish/L-water. Kanyilmaz (2014) reported that using clinoptilolite to treat sea bass wastewater during a 24 h transportation can achieve about 21% removal of ammonia.

Except for ion exchange, various commercially available water conditioners are using a chemical to neutralize free ammonia in aquaculture wastewater. One common chemical is alkali metal formaldehyde bisulfite (HOCH₂SO₃⁻) (U.S. Patent No. 4666610 A, 1987). The ammonia reaction of HOCH₂SO₃⁻ can be simply written as Equation 2 (Riche, Pfeiffer, et al., 2006). While the health effect of H₂NCH₂SO₃⁻ for fish species has not been determined, it is known to be less toxic than NH₃ as it can be further oxidized to nitrate by nitrifying bacteria (Riche, Pfeiffer, et al., 2006). This chemical has been used successfully on crustaceans and fish.

\[ \text{HOCH}_2\text{SO}_3^- + \text{NH}_3 \rightarrow \text{H}_2\text{NCH}_2\text{SO}_3^- + \text{H}_2\text{O} \]  (2-2)

2.2 Drinking Water Treatment

2.2.1 Biosand Filter (BSF)

Point-of-use treatment (POU) technology such as reverse osmosis (RO) and ultraviolet disinfection was recommended by the World Health Organization (WHO) as a post-collection water treatment process (WHO, 2005). It has high potential to improve household water quality after treated water distribution or transportation. Biosand filter (BSF) is a simple, inexpensive technology that can be built using locally available natural materials such as gravel, sand, and cement (Ngai, Coff, Baker, & Lentz, 2014). It has been reported that BSF can remove turbidity.
and *E. coli* in water efficiently (Ngai and Walewijk, 2003; Chiew, Sampson, et al., 2009; Fabiszewski De Aceituno, Stauber, et al., 2012; Aiken, Stauber, et al., 2011).

The mechanisms involved in the BSF include physical, chemical and biological process. The physical filtration acts in a way to strain out fine particles in the raw water. By this way, turbidity is removed. The fine particles to be trapped by sand bed follow transport mechanisms include interception, straining, diffusion, and sedimentation (Fewster, Mol., et al., 2004). Trapped particles must become attached to the sand grains so that they can stop moving forward. The attachment of particles undergoes physicochemical and molecular force. The bridge between particles is mainly responsible for the attachment between sand bed and particles in the raw water (Fewster, Mol., et al., 2004). The biological activity occurs in the BSF contributes to the removal of bacteria and even pathogens. As most of the solid particles are removed by physical filtration within the top 0.5-2.0 cm of sand in BSF, the area develops a biological film called *schmutzdecke* as well as a biological activity zone. The word *schmutzdecke* comes from German for ‘dirty layer’. This film acts a role to remove fine colloidal particles in the raw water. The *schmutzdecke* film also acts as an initial zone of biological activity. The *schmutzdecke* film merges with a deeper biological layer, where biological actions happen in this zone. While the dominant process of purification at biological zone is still not clear, most literature suggested four processes which contribute to the purification: hostile environment, food scarcity, predation, and poisons excretion (Huisman and Wood, 1974). The combined effects result in the death and inactivation of many pathogens and indicator bacteria such as *E. coli*. However, one of the limitations of BSF is that they have limited removal of chemical contaminants such as arsenic, nitrite, nitrate, fluoride (Noubactep, Temgoua, et al., 2012; Ngai, Coff, et al., 2014). Therefore, a proper innovation of BSF is needed to improve the efficiency of conventional BSF. It has been
studied that a metallic iron amended BSF can remove arsenic at the efficiency of 93% (Ngai and Walewijk, 2003; Chiew, Sampson, et al., 2009).

2.2.2 Turbidity in Water

The turbidity is caused by the presence of suspended particles or colloidal matter in the water. They prohibit the light transmission through the water. It might be the result of the attachment of microorganisms to the particulates. The removal of turbidity will significantly reduce the threat of microbial contamination in water. In addition, the component of turbidity has been found to associate with total organic matter (TOC) in water (LeChevallier, Evans, et al., 1981). The TOC is likely to react with chlorine to form disinfection by-product such as trihalomethanes, which are known as carcinogenic (Wilkins III, Reiches, et al., 1979). Since BSF are often followed by chlorine disinfection, turbidity control is necessary as well to main the drinking water quality. Turbidity can also affect the human acceptability of water as the visible clouds. The aim of treated water turbidity should be less than 5 NTU and if at all possible, below 1 NTU (WHO, 2011).

2.2.3 pH of Water

The pH is an important water quality parameter. The normal range of pH for drinking water should be between 6.5 and 8.5. When the pH is too low, the water is acidic. Acidic water is corrosive. It may also cause aesthetic problems such as sour water taste. When the pH is too high, it could indicate that the water is hard. Although if hard water will cause some health issues such as epidemiological diseases is still under debate (Sengupta, 2013), it can also cause aesthetic problems including alkali taste of water, formation of scale deposits on dishes, and also keep soap from lathering.
2.2.4 Fecal Indicator Bacteria in Water

Fecal indicator bacteria (FIB) is a type of bacteria that is used to represent the level of fecal contaminations in the water throughout the world. The U.S Environmental Protection Agency (EPA) recommended using *Escherichia coli* (*E. coli*) as an indicator organism in freshwater bodies. *E. coli* is a gram-negative, facultatively anaerobic bacterium that is a subset of the total coliform bacteria group (Tenaillon, Skurnik, et al., 2010). It is present in the normal intestinal flora of humans and animals, where it is not harmful. However, in the other part of the body, *E. coli* can cause many diseases, such as acute diarrhea (WHO, 2011). The classes of enteropathogenic *E. coli* include enterohaemorrhagic *E. coli* (EHEC), enterotoxigenic *E. coli* (ETEC), enteropathogenic *E. coli* (EPEC), enteroinvasive *E. coli* (EIEC). There several other classes name, while the pathogenicity and prevalence of them are less well studied (WHO, 2011). The response of enteropathogenic *E. coli* to conventional water treatment and disinfection procedures are the same of other *E. coli* strains. Therefore, a test of *E. coli* can provide a proper indication for the enteropathogenic serotypes in drinking water (Nataro and Kaper, 1998; WHO, 2011). The WHO standard of *E. coli* is <10 CFU/100 mL.

2.2.5 Fluoride in Water

Fluoride is an essential element for human health. The U.S. Department of Health and Human Services recommends a level of 0.7 mg/L of fluoride in our daily drinking water. This is the level that prevents tooth decay and promotes good oral health (Division of Oral Health, 2010). Many communities add fluoride to their drinking water to promote dental health (United States Environmental Protection Agency, 2013). From 2011 to 2014, the fluoride detected level of drinking water in Tampa Bay Area was 0.15-0.7 mg/L (Water Department of City of Tampa Florida, 2013; Water Department of City of Tampa Florida, 2011; Water Department of City of
Although water overfluoridation is not a problem of United States now, it is a huge health concern in many developing countries. In South India, a concentration of fluoride ranged from 0.2 to 20 mg/L was reported (Agrawal, Vaish, et al., 1997). Also in Kenya and South Africa, the level of fluoride was reported exceed 25 mg/L (Susheela et al., 1999). The combination of arsenic and fluoride toxic in drinking water also reported in India, China, and Bangladesh (Barghouthi and Amereih, 2013; Chinoy et al., 2004; Nair et al., 2004). The EPA regulates the maximum contaminant level (MCL) of fluoride at 4 mg/L. The chronic health effects on people who drink water containing fluoride in excess of the MCL include bone diseases, dental fluorosis, skeletal fluorosis, and mottled teeth in children aged 8 years and younger (United States Environmental Protection Agency, 2002). The main source of high fluoride concentration in water is geological deposits. Some fluoride compounds, such as sodium fluoride and fluorosilicates can dissolve easily into groundwater when it moves through gaps and pores spaces between rocks. Fluoride also enters drinking water from the discharge of fertilizer or aluminum factories.

2.2.6 Fluoride Removal Techniques

The traditional BSF has little capability to remove dissolved chemical contaminants in the water, such as arsenic, iron, and fluoride. Therefore, it is reasonable to modify the existing BSF to enhance its removal of other chemical contaminants that drive health concerns. One of the removal mechanisms is adsorption. The arsenic biosand filter (ABF) has been developed for
many years to implement the BSF in arsenic affected area (Ngai and Walewijk, 2003). In the ABF, an arsenic removal layer was placed above the regular sand layer. When arsenic-contaminated water was poured into the ABF, the arsenic was rapidly absorbed into the arsenic removal layer, and the residual particles were flushed onto the underlying sand layer. The ABF was found to effectively remove 93% of arsenic, 64% of E. coli on average (Ngai and Walewijk, 2003). The idea of an ABF can also be applied to the fluoride removal scenario. To remove fluoride, adsorption is widely accepted as it gives satisfactory results. Meanwhile, the process is low cost, simple design, and operation (Mohapatra, Anand, et al., 2009; Bhatnagar, Kumar, et al., 2011). Some adsorbents for fluoride removal have been tested, such as manganese oxide coated alumina, bone charcoal, fired clay chips, pumice (Li, Wang, et al., 2001; Ayoob, Gupta, et al., 2008; Ali, Asim, et al., 2012; Salifu, Petrushevski, et al., 2013). Among them, clay chips had been used in the BSF to enhance the removal of fluoride, but the results showed that the clay chips are only cost-effective if fresh clay is locally available (Padmasiri, 1997). Activated alumina is the most studied adsorption material for fluoride but it is costly and also has high pH reduction potential (Ayoob, Gupta, et al., 2008; Bhatnagar, Kumar, et al., 2011). Replacing sand by pumice in BSF has been found to increase the filtration rate but keep the same turbidity and E. coli removal effectiveness (Ghebremichael, Wasala, et al., 2012). Therefore, in this study, a modified BSF was proposed where a part of sand media is replaced by pumice to enhance its water purification results.

2.2.7 Fluoride Adsorption by Aluminum Oxide Coated Pumice (AOCP)

Pumice was used as a base material for the aluminum ions because it has a rough surface and porous structure for the ions to attach to. Raw pumice was reported as not effective for fluoride removal. However, aluminum oxide coated pumice (AOCP) can reduce fluoride
concentration from 5 mg/L to 1.5 mg/L within 1 h when the adsorbent dose is 10 mg/L (Salifu, Petrusevski, et al., 2013). The X-ray fluorescence (XRF) and energy dispersive X-ray spectroscopy (EDX) analysis have indicated that the AOCP is incorporated with aluminum and oxygen not only at the surface but also penetrated inside of the pumice grain (Salifu, Petrusevski, et al., 2013).

The good affinity of fluoride (F\(^-\)) and aluminum (Al\(^{3+}\)) can be explained in accordance with the hard and soft acid and base (HSAB) concept. In the HSAB concept, F\(^-\) is categorized as a hard base, and Al\(^{3+}\) is a hard acid. The principle of HSAB concept is: soft like soft, hard like hard (Alfarra, Frackowiak, et al., 2004). The hard base means the donor atoms have a high electronegativity and a low polarizability. They can hold the valence electrons tightly. The hard acid means the acceptor atoms have a high positive charge density. They have a low electronegativity and a low polarizability and do not contain unshared pairs in their valence shells (Alfarra, Frackowiak, et al., 2004). A general reaction between F\(^-\) and Al\(^{3+}\) can be expressed as follows (Ku and Chiou, 2002):

\[
\text{Al}^{3+} + m\text{F}^- \leftrightarrow \text{AlF}^{3-m}
\] (2-3)

However, when the aluminum oxide surfaces are hydrated, it forms surface hydroxyl group with water (Rosenqvist, 2002; Salifu, Petrusevski, et al., 2013). The Al-OH complex can be written as (Ku and Chiou, 2002):

\[
\text{Al}^{3+} + m\text{OH}^- \leftrightarrow \text{Al(OH)}^{3-m}
\] (2-4)

The distribution of each complex can be calculated based on the mass balances of fluoride and aluminum with specific reaction constant (Morel and Hering, 1993). The result is strongly affected by the solution pH (Ku and Chiou, 2002). When pH is below 5.0, the surface of
AOCP is positively charged, because the pH$_{zpc}$ of AOCP is 5.2 (Salifu, Petrusevski, et al., 2013). The adsorption of fluoride is predominant by anionic/ligand exchange, such as:

$$\text{Al(OH)}^{2+} + \text{F}^- \leftrightarrow \text{AlF}^{2+} + \text{OH}^-$$

(2-5)

The main Al-F complexes in water are AlF$^{2+}$, AlF$_2^+$, and AlF$_3$ species at this range (Ku and Chiou, 2002). When pH is above pH$_{zpc}$, the surface of AOCP becomes negatively charged, the adsorption of fluoride is presumably due to the coulombic force of attraction between OH$^-$ and F$^-$, for instance:

$$\text{Al(OH)}^{2+} + 4\text{F}^- \leftrightarrow \text{AlF}_4^- + \text{OH}^-$$

(2-6)

At this range, the Al-F complex is dominant by AlF$_4^-$ and AlF$_3$. When pH is above 8.0, aluminum ions is preferable to form aluminum hydroxide complex, hence the fluoride adsorption is inhibited (Farrah, Slavek, et al., 1987; Bhatnagar, Kumar, et al., 2011; Ku and Chiou, 2002). In this study, the pH of water is between 7 and 8, thus, the adsorption of fluoride will be due to the coulombic force of attraction between OH$^-$ and F$^-$. 


CHAPTER 3
AMMONIA REMOVAL IN AQUACULTURE WASTEWATER

3.1 Aquaculture Wastewater Treatment

Ammonia is one of the major contaminants in fish wastewater. Production of ammonia during fish metabolism is toxic to fish health (Levit, 2010). In a typical aquarium or aquaculture system, the ammonia concentration can be controlled by nitrification by maintaining high dissolved oxygen levels and bioreactor configurations that promote aerobic biological activity. However, in fresh-caught fish or fish transportation systems, the ammonia accumulation rate is much faster than the ammonia oxidation rate by nitrification. Therefore, ammonia needs to be removed directly from the water using a physical or chemical process. Physicochemical treatment processes that have been used for ammonia removal include ion exchange (IX), adsorption, chemical neutralization (CN), reverse osmosis, electrochemical oxidation-reduction, air stripping and precipitation (Bhatnagar and Sillanpää, 2011; Boyer, 2014; Mook, Chakrabarti, et al., 2012; Khelifi, Kozuki, et al., 2002). Among them, IX and CN are the most suitable for fish wastewater applications. IX is inexpensive, easy to operate and renewable, especially if natural IX materials are used (Emadi, Nezhad, et al., 2001; Hedstrom, 2001). CN is easy to implement and has a fast reaction rate (Crittenden, Trussell, et al., 2005). Zeolites are the most widely studied natural ion exchangers for ammonia removal (Hedstrom, 2001; Ivanova, Karsheva, et al., 2010). There are many kinds of natural zeolite materials, such as clinoptilolite and chabazite. Aponte-Morales et al. (2016) reported that chabazite had a higher ammonia removal efficiency than clinoptilolite. Regarding CN, sodium bisulfate salt can react with free ammonia (NH$_3$) to
form an aminobisulfate salt that has been used as an ammonia neutralizer in aquariums for decades (Harnish, Colotelo, et al., 2011; Kuhns, 1987; Riche, Pfeiffer, et al., 2006). Therefore, it’s worth comparing these two methods in terms of the ammonia removal efficiency, toxicity, as well as financial cost. The objective of this research was to control ammonia levels in aquaculture wastewater by using an ion exchange process and compare these results with a traditional chemical neutralization process. The research design of this chapter includes five parts.

Task 1: Determine the ammonia accumulation rate in stored fish systems.

Task 2: Understand ion exchange mechanisms of ammonium removal.

Task 3: Measure ammonia removal performance and establish a comparison between ion exchange and chemical neutralization.

Task 4: Analyze toxicity and cost between ion exchange and chemical.

Task 5: Describe the mechanisms involved in the ion exchanger regeneration.

3.2 Materials and Methods

3.2.1 Materials

3.2.1.1 Ion Exchanger

As mentioned in section 2.2.1, chabazite was selected as the ion exchanger in this research. The chabazite was purchased from St. Cloud Mining Inc. (Winston, NM). The grain size range was 1-2 mm. All natural chabazite (NC) grains were washed with deionized (DI) water to remove extremely small particles and then dried in an oven set to 110 °C. Washed chabazite was stored in a sealed plastic bottle at room temperature. Freshwater modified chabazite (FC) was made from NC soaked in synthetic freshwater (Table 1) where the suspension was shaken for 24 hours. The FC particles were then washed with DI water and dried
at 110°C. Sodium chloride modified chabazite (SC) was made from NC soaked in 117g/L NaCl (2M) where the suspension was shaken for 24 hours. The SC particles were then washed with DI water and dried at 110°C.

AmmoSorb is the name of a product developed in our laboratory that is designed to remove ammonia by IX. AmmoSorb consisted of a mesh bag packed with color coated FC or SC with a phosphate buffer (Innophos™). Color coating of FC and SC was carried out by suspending it in an animal-friendly blue dye solution (Outdoor Water Solution™) for 24 hours. The blue color allows the user to know when AmmoSorb has been added to the water.

3.2.1.2 Chemical Neutralizer

Two categories of chemical neutralizer were used in this study. Commercial water conditioners (CC), Better Bait™ (abbr. B.B.™) was used in freshwater and Pogey-Croaker Saver™ (abbr. P.S.™) was used in seawater. The amount of water conditioners added was based on the directions provided by the manufactures. The other category is novel neutralizer (NN). It was composed of sodium formaldehyde bisulfite (Kuhns, 1987), blue dye (Outdoor Water Solution™), and cornstarch. Cornstarch was added to enhance the dispersion of sodium formaldehyde bisulfite as well as extend the long-term stabilization of NN. The total dose of NN was 1.0 g/L/day.

3.2.1.3 Aquaculture Wastewater

Both synthetic wastewater and natural wastewater were used in this research. The synthetic wastewater was prepared by injecting NH₄Cl (Fisher Scientific, Pittsburgh, PA) into the water at a rate calculated based on section 3.3.1. Freshwater was obtained from a pond at Simmons Park, located on the campus of the University of South Florida (average pH=8.49,
alkalinity=62.09 mg/L). Seawater was prepared based on the instructions of Instant Ocean™. The compositions of synthetic freshwater and seawater are shown in Table 3-1.

Natural wastewater used ammonia produced by live fish. All live fish were donated by Marine Metal Product, Inc. (MMP, Clearwater, FL). Bass and tilapia are two kinds of freshwater fish. Shrimp and pinfish are seawater fish representatives.

Table 3-1 Synthetic water constituents

<table>
<thead>
<tr>
<th>Ion</th>
<th>Synthetic freshwater (g/L) (Villavicencio, Urrestarazu, et al., 2011)</th>
<th>Synthetic seawater (g/L) (Orr, 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium (Na⁺)</td>
<td>0.075</td>
<td>10.780</td>
</tr>
<tr>
<td>Potassium (K⁺)</td>
<td>0.00312</td>
<td>0.42</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>0.024</td>
<td>1.32</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>0.193</td>
<td>19.290</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>0.043</td>
<td>0.400</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>-</td>
<td>0.056</td>
</tr>
<tr>
<td>Bicarbonate (HCO₃⁻)</td>
<td>0.0048</td>
<td>0.200</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>0.096</td>
<td>2.66</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0.310</td>
<td>0.241</td>
</tr>
</tbody>
</table>

3.2.2 Methods

3.2.2.1 Analytical Methods

The ammonia concentrations were measured using the salicylate method (HACH method 10023, Loveland, CO) and a high-performance ammonia ion selective electrode (Fisher
pH values were measured using a Denver Instrument Model 250 pH meter (Bohemia, NY). Cation concentrations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) were detected by Ion Chromatography (IC, Metrohm 850, Switzerland). Alkalinity was measured using Standard Method 2320B (Federation and Association, 2005).

3.2.2.2 Chabazite Characterization

The chemical composition of natural chabazite was investigated using a Scanning Electron Microscope with Electron Energy-dispersive X-ray spectroscopy (SEM-EDS, Hitachi, Japan). Chabazite was also characterized by comparing the chemical composition and crystalline structure before and after treatment. Chemical composition tests were performed in three 50 mL volumetric flasks. Flasks were filled with 50 mL DI water, synthetic freshwater and 2M NaCl, respectively. The chabazite was pretreated in each flask following the previously described pre-treatment procedure. When pre-treatment was completed, water was collected and filtered. The crystalline structure of chabazite before and after treatment was tested using X-Ray Diffraction (Panalytical, Westborough, MA).

3.2.2.3 Ammonia Accumulation Rate Determination

Experiments were carried out to determine accumulated ammonia concentration in a fresh-caught fish or fish transportation systems with both fresh and seawater species. All live fish and shrimp were donated by Marine Metal Product, Inc. (MMP, Clearwater, FL). Ten freshwater basses collected from Belleview CC East Course Pond (Belleair, FL) was contained in approximately 52L of freshwater. A second tank contained 3 marine pufferfish (Tetraodontidae) and 12 pinfish (Lagodon rhomboids) in approximately 55L of seawater. A third tank included 15 marine shrimp (Penaeid) in 10L of seawater. Specimens were maintained in the laboratory for 7 days until all fish and shrimp perished. Water samples were collected daily. The commercial
water conditioner was added on the first day of the experiment. A tablespoon (10.9 g) of B.B.™ was added to the large storage unit with 7 basses. Likewise, 21.4 g of P.S.™ was added to the pinfish/pufferfish unit. Concurrently, 3 basses were placed into a smaller unit (with 14 L of freshwater) and kept as a control (without water conditioner). Ammonia concentrations were measured using the salicylate method described previously and the accumulation rate ($k$) was calculated based on zero-order kinetics:

$$C = C_0 + kt$$  \hspace{1cm} (3-1)

where $C$ (mg/L) is the ammonia concentration at time $t$ (hour), and $C_0$ is the initial ammonia concentration (mg/L).

3.2.2.4 Ammonium Adsorption Kinetic Studies

Bench-scale kinetic studies were conducted at room temperature using four 1000mL containers filled with an ammonium solution. An air pump was used to simulate mixing conditions in fresh caught fish and transportation systems. Initial concentrations of NH$_4$Cl were 30, 75, 150, 300 mg/L. The NH$_4$Cl solution was prepared in either synthetic freshwater or seawater. The amount of chabazite was 30g in each container. Samples were taken every hour until equilibrium was observed.

Pseudo-first order and second-order kinetic models were used to analyze the data using the linear forms of Eq. 3-2 and Eq. 3-3 (Yusof, Keat, et al., 2010; Alshameri, Ibrahim, et al., 2014):

$$ln(q_e - q_t) = lnq_e - k_1 t$$  \hspace{1cm} (3-2)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$  \hspace{1cm} (3-3)

$$q_e = (C_0 - C_e)\frac{V}{m}$$  \hspace{1cm} (3-4)
where the variables $q_t$ and $q_e$, represent the amount of ammonium adsorbed (mg/g) at any time $t$ (min) and at equilibrium, respectively; $k_1$ (/min) and $k_2$ (g/mg·min) are the pseudo first-order and second-order adsorption rate constants, respectively; $V$ is the solution volume (L), and $m$ is the chabazite mass (g). The least squares method was applied to predict the best-fit linear solution and parameter values. If the adsorption kinetic follows the pseudo-second-order kinetic, the initial adsorption rate, $h$ (mg/g·min) at $t\rightarrow0$, can be defined as:

$$h = k_2q_e^2$$

The best fit model was chosen based on the determination coefficient ($R^2$). The fitness of the kinetic models to the experimental data was evaluated by the error index of Marquardt’s standard deviation percentage ($\Delta q$) which is written as (Ahmaruzzaman and Laxmi Gayatri, 2010):

$$\Delta q(\%) = \sqrt{\frac{\sum[(q_{e,exp} - q_{e,cal})/q_{exp}]^2}{n-1}} \times 100$$

where $n$ is the number of data points and $q_{e,exp}$ and $q_{e,cal}$ (mg/g) are the experimental and calculated adsorption capacity, respectively.

To better understand the dominant adsorption mechanisms involved in the adsorption process, it is necessary to use a molecular diffusion model. The kinetic data can be further fitted with the film diffusion model and a particle diffusion model (Moussavi, Talebi, et al., 2011):

**Film diffusion model:**

$$\ln \left(1 - \left(\frac{q_t}{q_e}\right)\right) = -k_f t$$

**Particle diffusion model:**

$$\ln \left(1 - \left(\frac{q_t}{q_e}\right)^2\right) = -2k_p t$$

where $k_f$ (hr) and $k_p$ (hr) are the film and pore rate constants, which are calculated from:

$$k_f = D_f \frac{c}{c_x} \text{ hr}$$

$$k_p = D_p \frac{c}{c_x} \text{ hr}$$
where the C (mg/g) is the initial NH$_4^+$-N in the solution, and C$_t$ (mg/g) is concentration of NH$_4^+$-N absorbed by chabazite. D is the diffusion coefficient (m$^2$/min), r is the grain radius of chabazite (m), and h is the thickness of film around chabazite particles ($10^{-6}$ m for poorly stirred solution).

The experimental adsorption kinetic data can also be analyzed using the Morris-Weber equation:

$$q_t = k t^{0.5} + C$$

where $k$ is the coefficient of particle diffusion (mg/g·min$^{0.5}$). By plotting this equation, we can also verify that if particle diffusion is the rate-limited step.

3.2.2.5 Ammonium Adsorption Isotherm Studies

Four isotherm models: Langmuir, Freundlich, Temkin, and Sips were studied to describe the solid-liquid adsorption data (Table 3-2). The parameters and the thermodynamic assumptions of these equations describe the sorption mechanisms, surface properties and affinities of the sorbents in detail (Ho, Chiu, et al., 2005).

In Table 3-2, $q_e$ is the equilibrium amount of ammonium adsorbed (mg/g), which is experimentally determined from the difference between the initial concentration, $C_0$ (mg/L), and the final NH$_4^+$-N concentrations, $C_e$ (mg/L), at equilibrium using Eq. (5), $q_0$ is the maximum monolayer adsorption capacity (mg/g), $b$ is the Langmuir adsorption constant of NH$_4^+$-N (L/mg) (Foo and Hameed, 2010). $K$ is the Freundlich adsorption capacity parameter ((mg/g)(L/mg)$^{1/n}$), $1/n$ is the Freundlich adsorption intensity parameter (unitless), $R$ is the universal gas constant (8.314 J/mole K), $T$ is the absolute temperature during the experiment (296K), $b_t$ is the Temkin constant (J/mole), and $A_t$ is the Temkin isotherm equilibrium binding constant (L/g) (Foo and
Hameed, 2010), $K_s$ and $a_s$ are the Sips isotherm model constant ($L/g$), and $\beta_s$ is the Sips model exponent (Foo and Hameed, 2010).

The least square method was used to calculate all isotherm parameters. In the linear regression model, a linear coefficient of determination, $R^2$, was used to examine the accuracy of the model fit. The non-linear regression was established by iterative non-linear least square fitting using the solver add-in in Microsoft Excel (Brown, 2001). The coefficient of determination, $R^2$, and chi-square, $\chi^2$ tests were used to evaluate the fit of the non-linear isotherm to the experimental data. The equivalent mathematical statement of chi-square is:

$$\chi^2 = \sum \frac{(q_{e,m} - q_e)^2}{q_{e,m}} \quad (3-12)$$

where $q_{e,m}$ is the equilibrium capacity obtained by the model (mg/g). If $\chi^2$ is a small number, the data from the model are similar to the experimental data; if $\chi^2$ is large, the model data are different from the experimental data (Ho, Chiu, et al., 2005).

Table 3-2 Non-linear and linear forms of Langmuir, Freundlich, Temkin, and Sips isotherm models

<table>
<thead>
<tr>
<th></th>
<th>Non-linear form</th>
<th>Linear form</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td>$q_e = \frac{q_0 \cdot b \cdot C_e}{1 + b \cdot C_e}$</td>
<td>$c_e = \frac{1}{q_0} \cdot C_e + \frac{1}{q_0 \cdot b}$</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>$q_e = K \cdot C_e^{\frac{1}{n}}$</td>
<td>$\log q_e = \log K + \frac{1}{n} \cdot \log C_e$</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td>$q_e = \frac{RT}{b_t} \ln(A_t \cdot C_e)$</td>
<td>$q_e = \frac{RT}{b_t} \ln A_t + \frac{RT}{b_t} \ln C_e$</td>
</tr>
<tr>
<td><strong>Sips</strong></td>
<td>$q_e = \frac{K_s \cdot C_e^{\beta_s}}{1 + a_s \cdot C_e^{\beta_s}}$</td>
<td>$\beta_s \ln C_e = -\ln \left( \frac{K_s}{q_e} \right) + \ln(a_s)$</td>
</tr>
</tbody>
</table>
3.2.2.6 In-vitro Comparison of Ammonia Removal

The in-vitro study was performed in two fish aeration systems. Each system included a 13L container and an air pump. Each system was filled with 10L of synthetic water. An NH₄Cl solution was pumped into each system at a specified rate based on the ammonia accumulation rate experiment described above. The ammonia removal agent (AmmoSorb, CC or NN) was added into one aeration system. The other one was set up as a control. Samples were taken every hour for 24 hours. During this study, ammonia concentrations were measured using an ammonia ion selective electrode as described previously.

3.2.2.7 In-vivo Comparison of Ammonia Removal

The in-vivo study was approved by the Institutional Animal Care and Use Committee (IACUC). Tilapia and pinfish were selected as representative fish species that live in freshwater and seawater environments, respectively. Tilapia were collected at a freshwater lake in Bellaire, Florida, U.S.A. Pinfish was collected from a mangrove coastal seawater site at the same location as the tilapia. Within 1 hour of catch, live fish were transported to the laboratory and stored in the dark without feeding, while oxygen was supplied using air stones. The tilapia (7.97 ± 1.15 lb; N=15) were stored in five 75L coolers with three tilapias in each cooler with 50L of fresh water. The pinfish (0.07 ± 0.02 lb; N=200) were maintained in five 38L buckets with approximately 30 pinfish in each bucket with 27L of seawater. The water temperature ranged from 22°C to 23°C. The pH of freshwater and seawater were 7.19 ± 0.19 and 7.48 ± 0.02, respectively. All five coolers or buckets were different study groups - control group, CC added, NN added, AmmoSorb (FC or SC) added, and combined AmmoSorb (FC or SC) and NN added. The water was sampled every hour for 24 hours. According to the requirement of Institutional Animal Care
and Use Committee (IACUC), fish that showed endpoint signs (i.e., inactive, not eating, surface breathing) were euthanatized using the approved protocol (USF IACUC protocol IS00003131).

3.2.2.8 Toxicity Assessment

The toxicity test was adapted from EPA method EPA-821-R-02-012 (USEPA, 2002). *Daphnia Magna* neonates (age < 24 h) were used as the test species. The tests were conducted at 23°C. Ten neonates were placed in a 100-mL transparent plastic beaker with triplicates for each group. The number of dead neonates was recorded at 24 and 48 hours after the initiation of the test. The test water included spring water (control), CC added water, NN added water, or AmmoSorb added water. The concentration of each conditioner was the daily maximum dose designed to be added to the water (Table 2). The LC<sub>50</sub> of NN and CC was also tested. The LC<sub>50</sub> refers to the concentration of a substance that is lethal to 50% of the animals in the toxicity test (Boyd, 2005). The exposure periods were 24 and 48 hours. Five concentrations were tested from 0 to 2 g/L.

Table 3-3 The daily maximum dose of ammonia removal substance

<table>
<thead>
<tr>
<th>Substances</th>
<th>Daily maximum dose (g/L/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.B.™</td>
<td>1.0</td>
</tr>
<tr>
<td>P.S.™</td>
<td>1.0</td>
</tr>
<tr>
<td>NN</td>
<td>1.0</td>
</tr>
<tr>
<td>AmmoSorb (FC)</td>
<td>4.6</td>
</tr>
<tr>
<td>AmmoSorb (SC)</td>
<td>8.8</td>
</tr>
</tbody>
</table>
3.2.2.9 Chabazite Regeneration and Regeneration Efficiency Studies

All used chabazite was oven dried, mixed and stored separately in covered containers. During the regeneration process, 30g of used chabazite was immersed in 200 mL of NaCl solution with pH controlled at 7. The NaCl concentrations were 0 g/L (RE₀), 40 g/L (RE₄₀), and 80 g/L (RE₈₀), respectively. The suspension was shaken for 6 hours and then separated from the supernatant. Aqueous samples were collected from the supernatant to measure desorbed NH₄⁺-N concentrations. Each test was performed in triplicate. Regenerated chabazite was washed with DI water and then dried at 110°C before use.

The regeneration efficiency (RE) of chabazite was calculated using Eq. (3-13):

\[ RE \, (\%) = \frac{q_{e'}}{q_e} \times 100 \]  

(3-13)

where \( q_{e'} \) (mg/g) is the amount of ammonium absorbed by the regenerated chabazite at equilibrium.

3.2.2.10 Statistical Analysis

All samples in ammonia accumulation studies were taken once per time. The in-vitro and in-vivo experiments were taken in triplicate. The results of concentration and pH were present as the mean with max/min values. The data analysis of linear regression was performed in Microsoft Excel 2013, with results presented as a slope with uncertainty. A student t-test was used to determine if the results from the ammonia removal efficiency studies were statistically significant at an alpha value of 0.05.

3.3 Results and Discussions

3.3.1 Ammonia Accumulation Rate Determination

Ammonia accumulation as a function of time for the four units is shown in Figure 3-1. Ammonia accumulated much faster in the unit containing shrimp. The pH of the water had a
noticeable decrease when the fish were added to the water. The values decreased from 8.35 to 6.83 in the unit containing bass and from 7.77 to 6.86 in the unit containing pinfish/pufferfish. No significant differences were found when CC was added (p-value 0.1 in freshwater, p-value 0.6 in seawater). Both fish and shrimp started to die after 80 hours, which coincided with NH$_3$-N concentrations higher than 10.3 mg/L in the bass control group, 12.4 mg/L in the bass with B.B.$^\text{TM}$, 36.7 mg/L in the pinfish/pufferfish unit, and as high as 41.2 mg/L in the shrimp unit. It was also observed that the pH in all four units started to increase at this point. These findings confirm that non-ionized ammonia production will increase with small increases in pH. This also verifies that the mechanism for the two water conditioners used in these experiments is not chemical or physical removal of non-ionized ammonia. Ammonia accumulation rates (Table 3-4) were calculated based on a zero-order kinetic model, in which the accumulation rate (mg NH$_3$-N/fish/h) is the same as the slope. Since fish started to perish after 80 hours, the ammonia accumulation by living fish was calculated based on the first 80 hours. The results show that the $k$ of freshwater bass with B.B.$^\text{TM}$ added (1.14 ± 0.14 mg NH$_3$-N/fish/h) is about two times higher than the $k$ calculated from the bass in control group (0.61 ± 0.08 mg NH$_3$-N/fish/h). However, the results were not significantly different (p-value was 0.82). Therefore, the water conditioner has no effect on the ammonia removal. The value of $k$ in the control was similar to the results in the literature, where the C. Karachi can produce 0.94 ± 0.36 mg NH$_3$-N/fish/h (Danulat and Kempe, 1992). In seawater, the pinfish/pufferfish group excreted approximately 1.57 ± 0.53 mg NH$_3$-N/fish/h when P.S.$^\text{TM}$ is added, while shrimp produced about 0.34 ± 0.02 mg NH$_3$-N/shrimp/h. From other literature, the average ammonia excretion rate of seawater blue crab is 0.57 mg NH$_3$-N/fish/h (Kormanik and Cameron, 1981), which is close to the shrimp group.
Figure 3-1 (a) Ammonia production as a function of time and (b) pH change as a function of time in seawater shrimp, seawater pinfish/pufferfish with Pogey-Croaker Saver™, freshwater bass with Better Baits™, and freshwater bass without Better Baits™.

Table 3-4 Ammonia production rate constant for different groups

<table>
<thead>
<tr>
<th>Water type</th>
<th>System</th>
<th>$k$ (mg NH$_3$-N/specimen/h)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>B.B.™</td>
<td>0.17 ± 0.02</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>0.21 ± 0.03</td>
<td>0.97</td>
</tr>
<tr>
<td>Seawater</td>
<td>P.S.™</td>
<td>0.40 ± 0.05</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>0.81 ± 0.17</td>
<td>0.94</td>
</tr>
</tbody>
</table>

3.3.2 Characterization of Chabazite

Analysis of the chemical composition of chabazite showed that the chabazite used in this study was sodium-dominated (Table 3-5). Table 3-6 lists the textural and physicochemical
properties of the chabazite obtained from the manufacturer. The reported ion exchange capacity can be as high as 2.5 mg/g.

The chemical compositions of cations before and after modification is shown in Figure 3-2. In natural zeolite, Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) are exchangeable cations and these cations balance the negative charges by isomorphic substitution of the Al atoms in the framework (Leyva-Ramos, Monsivais-Rocha, et al., 2010). Natural chabazite (NC) has the highest weight percentage of Na\(^+\) in the framework compared to other cations. After being modified with synthetic freshwater (FC), the concentration of Na\(^+\) decreased from 7.19% to 1.9%. Meanwhile, Ca\(^{2+}\) also decreased from 0.8% to 0.3%, Mg\(^{2+}\) had a slight reduction (~0.16%), and there were almost no changes in K\(^+\) between NC and FC (<0.1%). This phenomenon can be explained by the ion exchange reaction. Ion exchange commonly occurs between liquid and solid phases when there is ion sharing. The process is determined by the ion selectivity and the ion concentrations in both phases (Colella, 1996). The ion selectivity is a function of both the hydrated radius of the ions in solution and the magnitude of the charge (Boyd, Schubert, et al., 1947; Colella, 1996). Since the external ion strength in freshwater is low, the ion exchange process is mainly determined by the cationic affinity. The cationic affinity sequence for chabazite is commonly written as K\(^+\)>Na\(^+\)>NH\(_4\)^+>Ca\(^{2+}\)>Mg\(^{2+}\) (Breck, 1973; Barrer, Davies, et al., 1969; Colella, 1996). Therefore, in FC, Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) ions are exchanged during the modification process. This change probably created more residual negative charges on the chabazite framework. The effect of treatment with NaCl solution also showed the same trend as treatment with synthetic freshwater; the only difference was the increase in Na\(^+\) in the SC. As the Na\(^+\) in the liquid phase is much higher than any other ions in the solid phase, Na\(^+\) is easily exchanged. Ca\(^{2+}\) decreased to almost zero in this case. This result is reasonable because Na\(^+\) and Ca\(^{2+}\) have a lower cationic
affinity with the chabazite framework. XRD patterns of chabazite before and after modification are shown in Figure 3-3. The chabazite used in this study has the same characteristic peaks as described previously (Treacy, 1986), and those peaks are consistent among NC, FC, and SC. Although SC has a relatively high intensity at 2θ value of 42.6, this peak still matched with the peak lists of chabazite (Treacy, 1986).

Table 3-5 Chemical composition of chabazite based on SEM-EDS analysis

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>31.65 ± 1.33</td>
</tr>
<tr>
<td>Al</td>
<td>9.04 ±0.35</td>
</tr>
<tr>
<td>Ca</td>
<td>0.83 ± 0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>0.54 ± 0.05</td>
</tr>
<tr>
<td>Na</td>
<td>7.19 ± 0.61</td>
</tr>
<tr>
<td>K</td>
<td>1.02 ± 0.13</td>
</tr>
</tbody>
</table>

Table 3-6 Textural and physicochemical properties of chabazite

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>460 m²/g</td>
</tr>
<tr>
<td>Ion exchange capacity</td>
<td>2.5 mg/g</td>
</tr>
<tr>
<td>Density</td>
<td>1.73 g/cm³</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.468 cm³/g</td>
</tr>
</tbody>
</table>
Figure 3-2 Chemical composition of exchangeable cations changes before and after modification

<table>
<thead>
<tr>
<th>Relative intensity</th>
<th>Natural chabazite (NC)</th>
<th>Freshwater modified chabazite (FC)</th>
<th>Seawater modified chabazite (SC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position [°2 Theta]</td>
<td>0  10  20  30  40  50  60</td>
<td>0  10  20  30  40  50  60</td>
<td>0  10  20  30  40  50  60</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-3 XRD pattern comparison between natural chabazite (NC), freshwater modified chabazite (FC) and sodium chloride modified chabazite (SC)
3.3.3 Ammonium Adsorption Kinetics

A pseudo-second-order relation had the best correlation with the experimental kinetic data in both freshwater and seawater. This finding is the same as most published literature (Yusof, Keat, et al., 2010; Karadag, Koc, et al., 2007). Table 3-7 lists the results of pseudo-second-order kinetics constants and coefficient data for both freshwater and seawater. The value of Δq is very small, which confirms that the pseudo-second-order kinetic model is the best fit to the experimental data.

From both freshwater and seawater data, we see some similar trends. The adsorption capacity (\(q_{e,exp}\)) increased with increasing initial ammonium concentration. The high initial concentration of ammonium provided a powerful driving force to overcome mass transfer resistance from solution to the adsorbent; therefore, adsorption of a higher number of ammonium molecules onto a given amount of chabazite will increase the adsorption capacity (Tsai, Hsien, et al., 2009; Moussavi, Talebi, et al., 2011). In comparison with freshwater, \(q_{e,exp}\) in seawater was about half of \(q_{e,exp}\) in freshwater. The cations in seawater also interacted with the zeolite, decreasing the ability of ammonium ions to bind freely (Burgess, Perron, et al., 2004). Another important finding from Table 3-7 is that the rate constant, \((k_2)\), decreased, while the initial adsorption rate \((h)\) increased with increasing initial ammonium concentration. This also shows that the mass transfer rate of ammonium ions improved with increasing initial ammonium concentration (Moussavi, Talebi, et al., 2011).

The third finding can be combined with the equilibrium removal of ammonium (Figure 3-4). The kinetic studies were conducted for 270 mins, but only 30 mins were needed for an equilibrium concentration to be achieved. The same phenomena can be found in other literature (Burgess, Perron, et al., 2004; Huang, Xiao, et al., 2010; Alshameri, Ibrahim, et al., 2014;
The most probable explanation is that ammonium diffused onto the external surface of the chabazite, which was followed by pore diffusion into the intraparticle surfaces to attain equilibrium. The key driving force, in this case, is the difference in the adsorbed concentration of ammonium at chabazite surface \( q_e \) and the solution \( q_t \) (Ho, Chiang, et al., 2005; Alshameri, Ibrahim, et al., 2014). The ion exchange capacity is proportional to the number of active ion exchange sites at chabazite (Wen, Ho, et al., 2006; Alshameri, Ibrahim, et al., 2014). The pseudo-second-order kinetic model involves three steps of ion exchange. In the first step ammonium ions diffuse from the liquid phase to the liquid-solid interface (film diffusion), and then the ammonium ions move from the liquid-solid interface to the solid phase of the adsorbent (intraparticle diffusion). Finally, the ammonium ions adsorbed onto the solid phase (mass action) (Badruzzaman, Westerhoff, et al., 2004). The last step is usually very quick, so if we want to consider the rate-limited step of adsorption, this step is negligible (Suresh and Sundaramoorthy, 2014).

A plot of the Morris-Weber equation (Eq.3-11) confirmed that the sorption processes include both film diffusion and particle diffusion (Moussavi, Talebi, et al., 2011; Vadivelan and Vasanth Kumar, 2005). The contribution of each step can be further studied by looking at the value of the particle diffusion coefficient \( D_p \) and film diffusion coefficient \( D_f \) (Table 3-8). The value of \( D_p \) for freshwater is higher than the value of \( D_f \), but opposite relations are observed in the seawater. This shows that in freshwater, film diffusion is the dominant mechanism in the adsorption rate. In seawater, particle diffusion dominated the rate of sorption. For the sorption process, film diffusion controls when the system has poor mixing, and dilute adsorbate concentration. In contrast, particle diffusion controls the sorption process when the adsorbate has
low affinity for the adsorbent (Vadivelan and Vasanth Kumar, 2005). Na\(^+\) has a relatively lower affinity than K\(^+\), therefore it is reasonable to have greater particle diffusion in seawater.

3.3.4 Ammonium Adsorption Isotherm Study

The study of adsorption isotherms can aid in the design and operation of ammonia removal systems. The obtained values for the isotherm model parameters using linear and non-linear regression in freshwater are listed in Table 3-10. All non-linear regressions had a better fit than the linear regressions (with higher R\(^2\)). This is reasonable because the alterations of the linear regression form have the tendency to create a higher error distribution (Karadag, Koc, et al., 2007; Foo and Hameed, 2010). The highest correlation was found in non-linear regression in the Sips isotherm, with an R\(^2\) value of 0.99 and \(\chi^2\) value of 0.01. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms (Foo and Hameed, 2010). It is used to predict the heterogeneous adsorption systems by avoiding the limitations of the Freundlich isotherms (Günay, Arslankaya, et al., 2007; Foo and Hameed, 2010). From the previously obtained adsorption kinetic result, we find that the ammonium adsorption onto chabazite was not a simple monolayer adsorption. The transmigration of ammonium ions happened on the surface of chabazite. Therefore, the Langmuir isotherm (monolayer adsorption isotherm (Dada, Olalekan, et al., 2012; Karadag, Koc, et al., 2007; Foo and Hameed, 2010)) is not the best isotherm model to predict this adsorption phenomenon. The Sips isotherm confirms that the ammonium adsorption onto modified chabazite under freshwater is a complex process that a simplified isotherm model is not able to predict the results.

Nevertheless, the Langmuir isotherm still fits with experimental data with a high R\(^2\) value of 0.99 and low \(\chi^2\) value of 0.03. The \(q_o\) value was determined to be 11.1 mg/g, which is smaller than the \(q_o\) reported in other literature (Table 3-9). One probable reason for the low maximum ion
adsorption capacity in this study was the testing protocol. In prior literature, batch reactors had constant mixing (Lahav and Green, 1998; Cyrus and Reddy, 2011) or were mixed 3-4 times daily (Leyva-Ramos, Monsivais-Rocha, et al., 2010). In this study, the mixing energy of chabazite and water was provided by water turbulence generated from aeration only, which is weaker compared with constant shaking. The second probable reason was the diversity of particle size. It has been found that smaller particle size would have higher ammonium adsorption capacity (Hedstrom, 2001; Cyrus and Reddy, 2011; Wen, Ho, et al., 2006).

Table 3-11 lists the obtained isotherm parameters using linear and non-linear regression in seawater. Non-linear models were better than linear models in this case. Under seawater conditions, both Temkin and Sips isotherms fit the experimental data, with an $R^2$ value of 0.94 and a $\chi^2$ value of 0.01. The Temkin isotherm includes a factor that takes into account the interaction of adsorbent and adsorbate (Dada, Olalekan, et al., 2012). In consideration of the characteristics of the Sips and Temkin isotherms, it is clear that the ammonium adsorption in seawater is complex. The non-linear Langmuir isotherm also had a relatively good fit with the $R^2$ of 0.92 and a $\chi^2$ of 0.03. The maximum ammonia adsorption capacity ($q_o$) in seawater was 7.80 mg/g. This low value also reveals that strong competing ion competition occurred during the adsorption process in seawater. Zeolite used to remove ammonia is seldom studied in marine water due to the competing ions present. However, in this study, the ammonium removal efficiency was $48.6 \pm 5.91\%$, which is much higher than $18.1 \pm 2.47\%$ reported by Miladinovic et. al. (Miladinovic, Weatherley, et al., 2004) and $18\%$ reported by Burgess et. Al.(Burgess, Perron, et al., 2004). Emadi et al. also reported an ammonium removal efficiency of $58.8\%$ when the initial $\text{NH}_4\text{Cl}$ was $5 \text{ mg/L}$ (Emadi, Nezhad, et al., 2001); however, in their study, $\text{NaCl}$
was used instead of synthetic seawater. This will eliminate many other competing ions such as 
$\text{Ca}^{2+}$, $\text{K}^+$, and $\text{Mg}^{2+}$.

<table>
<thead>
<tr>
<th>Water type</th>
<th>NH$_4^+$-N (mg/L)</th>
<th>Pseudo-second-order</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k$_2$ (g/mg·min)</td>
<td>h (mg/g·min)</td>
<td>q$_{e,exp}$ (mg/g)</td>
<td>q$_{e,cal}$ (mg/g)</td>
<td>R$^2$</td>
<td>Δq (%)</td>
<td></td>
</tr>
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<td>Freshwater</td>
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<td>12.59</td>
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<td>0.30</td>
<td>1.00</td>
<td>0.17</td>
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<td></td>
<td>30</td>
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<td>0.36</td>
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<td>0.91</td>
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<td>1.00</td>
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<tr>
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<td>2.77</td>
<td>2.74</td>
<td>1.00</td>
<td>0.35</td>
</tr>
<tr>
<td>Seawater</td>
<td>10</td>
<td>2.11</td>
<td>0.07</td>
<td>0.18</td>
<td>0.17</td>
<td>0.99</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.51</td>
<td>0.09</td>
<td>0.41</td>
<td>0.40</td>
<td>0.99</td>
<td>1.03</td>
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</table>
Table 3-7 (Continued)

<table>
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<tr>
<th>Water type</th>
<th>NH$_4^+$-N concentration (mg/L)</th>
<th>Film diffusion coefficient, D$_f$ (m$^2$/min)</th>
<th>Particle diffusion coefficient, D$_p$ (m$^2$/min)</th>
<th>Particle diffusion rate constant, k (mg/g·min$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>10</td>
<td>$2.39 \times 10^{-11}$</td>
<td>$8.58 \times 10^{-10}$</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$2.74 \times 10^{-11}$</td>
<td>$9.97 \times 10^{-10}$</td>
<td>0.0109</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$2.14 \times 10^{-11}$</td>
<td>$7.75 \times 10^{-10}$</td>
<td>0.0116</td>
</tr>
<tr>
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<td>100</td>
<td>$2.69 \times 10^{-11}$</td>
<td>$1.05 \times 10^{-9}$</td>
<td>0.0271</td>
</tr>
<tr>
<td>Seawater</td>
<td>10</td>
<td>$2.38 \times 10^{-7}$</td>
<td>$4.08 \times 10^{-15}$</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$6.08 \times 10^{-8}$</td>
<td>$1.28 \times 10^{-15}$</td>
<td>0.0082</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$6.13 \times 10^{-8}$</td>
<td>$1.46 \times 10^{-15}$</td>
<td>0.0067</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>$5.12 \times 10^{-8}$</td>
<td>$1.36 \times 10^{-15}$</td>
<td>0.0201</td>
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Table 3-8 Diffusion kinetic parameters for ammonium removal in both freshwater and seawater

<table>
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<th>Water type</th>
<th>NH$_4^+$-N concentration (mg/L)</th>
<th>Film diffusion coefficient, D$_f$ (m$^2$/min)</th>
<th>Particle diffusion coefficient, D$_p$ (m$^2$/min)</th>
<th>Particle diffusion rate constant, k (mg/g·min$^{0.5}$)</th>
</tr>
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<tbody>
<tr>
<td>Freshwater</td>
<td>10</td>
<td>$2.39 \times 10^{-11}$</td>
<td>$8.58 \times 10^{-10}$</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$2.74 \times 10^{-11}$</td>
<td>$9.97 \times 10^{-10}$</td>
<td>0.0109</td>
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<tr>
<td></td>
<td>50</td>
<td>$2.14 \times 10^{-11}$</td>
<td>$7.75 \times 10^{-10}$</td>
<td>0.0116</td>
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<tr>
<td></td>
<td>100</td>
<td>$2.69 \times 10^{-11}$</td>
<td>$1.05 \times 10^{-9}$</td>
<td>0.0271</td>
</tr>
<tr>
<td>Seawater</td>
<td>10</td>
<td>$2.38 \times 10^{-7}$</td>
<td>$4.08 \times 10^{-15}$</td>
<td>0.0042</td>
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<tr>
<td></td>
<td>30</td>
<td>$6.08 \times 10^{-8}$</td>
<td>$1.28 \times 10^{-15}$</td>
<td>0.0082</td>
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<tr>
<td></td>
<td>50</td>
<td>$6.13 \times 10^{-8}$</td>
<td>$1.46 \times 10^{-15}$</td>
<td>0.0067</td>
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<tr>
<td></td>
<td>100</td>
<td>$5.12 \times 10^{-8}$</td>
<td>$1.36 \times 10^{-15}$</td>
<td>0.0201</td>
</tr>
</tbody>
</table>

Table 3-9 The maximum ammonium adsorption capacity ($q_0$) data for chabazite from other literature

<table>
<thead>
<tr>
<th>Size</th>
<th>Modification</th>
<th>Water type</th>
<th>$q_0$ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2 mm</td>
<td>Freshwater</td>
<td>Freshwater</td>
<td>11.10</td>
<td>Current study</td>
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Table 3-9 (Continued)

<table>
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<th>Size</th>
<th>Type</th>
<th>Source</th>
<th>Linear</th>
<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18 mm</td>
<td>No</td>
<td>-</td>
<td>32.20</td>
<td>(Leyva-Ramos, Monsivais-Rocha, et al., 2010)</td>
</tr>
<tr>
<td>0.18 mm</td>
<td>NaCl</td>
<td>-</td>
<td>37.24</td>
<td>(Leyva-Ramos, Monsivais-Rocha, et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Secondary wastewater</td>
<td>41.50</td>
<td>(Lahav and Green, 1998)</td>
</tr>
<tr>
<td>1 mm</td>
<td>No</td>
<td>Swine wastewater</td>
<td>10.84</td>
<td>(Cyrus and Reddy, 2011)</td>
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<tr>
<td>2-4 mm</td>
<td>No</td>
<td>Swine wastewater</td>
<td>10.28</td>
<td>(Cyrus and Reddy, 2011)</td>
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Table 3-10 Adsorption isotherms parameters estimated by linear and non-linear regression in freshwater

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Linear</th>
<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>q₀</td>
<td>10.83</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>χ²</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K</td>
<td>0.85</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.63</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>χ²</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Temkin</td>
<td>bₜ</td>
<td>1195.21</td>
<td>1195.20</td>
</tr>
<tr>
<td></td>
<td>Aₜ</td>
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<td>0.94</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.97</td>
<td>0.97</td>
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Table 3-10 (Continued)

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<tr>
<th>Sips</th>
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<th>0.847</th>
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<td></td>
<td>$a_s$</td>
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<td>0.061</td>
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<tr>
<td>$K_s$</td>
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<td>0.92</td>
<td>0.829</td>
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<tr>
<td>$R^2$</td>
<td></td>
<td>0.98</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>$\chi^2$</td>
<td></td>
<td>-</td>
<td>0.01</td>
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Table 3-11 Adsorption isotherms parameters estimated by linear and non-linear regression in seawater

<table>
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<th>Isotherm</th>
<th>Parameters</th>
<th>Linear</th>
<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
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<tr>
<td></td>
<td>$b$</td>
<td>0.001</td>
<td>0.006</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.024</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K$</td>
<td>0.027</td>
<td>0.11</td>
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<tr>
<td></td>
<td>$1/n$</td>
<td>1.038</td>
<td>0.72</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.92</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>-</td>
<td>0.06</td>
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<tr>
<td>Temkin</td>
<td>$b_t$</td>
<td>1674.68</td>
<td>1674.70</td>
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<tr>
<td></td>
<td>$A_t$</td>
<td>0.082</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>-</td>
<td>0.01</td>
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</table>
Table 3-11 (Continued)

<table>
<thead>
<tr>
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<th>$\beta_s$</th>
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<th>1.86</th>
</tr>
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<td></td>
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<td>0.001</td>
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<tr>
<td></td>
<td>$K_s$</td>
<td>0.08</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.92</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3.3.5 **In-vitro Comparison of Ammonia Removal**

In preliminary *in-vitro* experiments carried out in our lab, no ammonia removal was observed when only phosphate buffer was added. In addition, if AmmoSorb was only added once at the beginning of an experiment, there was no ammonia removal after 24 hours (data not shown). This can be explained by observing the data obtained from the ammonium adsorption study using chabazite (Aponte-morales, 2015). The majority of ammonium adsorption by using chabazite only takes places during the first hour. After that, ammonium adsorption is slow.

To enhance ammonia removal performance, the AmmoSorb was added to the containers every three hours, the same as CC and NN. The result of ammonia removal efficiency at the end of 24 hours under *in-vitro* conditions is shown in Table 3-12. In freshwater conditions, the average $k$ in control group is $0.38 \pm 0.07$ mg/L/h, while the $k$ of AmmoSorb amended tanks is as low as $0.25 \pm 0.02$ mg/L/h (p-value 0.0025). Therefore, at the end of 24 hours, AmmoSorb had the highest ammonia removal efficiency compared with CC and NN. In seawater conditions, due to the competing ions in the seawater, the ammonia removal efficiency of AmmoSorb was lower than for freshwater ($24.56 \pm 1.85\%$). In seawater, NN had the highest removal efficiency. These results reveal that both IX and CN methods are capable of removing ammonia in simulated fish
conditions. Meanwhile, adding the ammonia removal agent more frequently can potentially enhance the ammonia removal efficiency.

Table 3-12 Ammonia removal efficiency comparison among AmmoSorb, commercial water conditioner (CC), and novel neutralizer (NN)

<table>
<thead>
<tr>
<th></th>
<th>Ammonia removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freshwater</td>
</tr>
<tr>
<td>AmmoSorb</td>
<td>39.25 ± 1.27</td>
</tr>
<tr>
<td>CC</td>
<td>0.00</td>
</tr>
<tr>
<td>NN</td>
<td>17.44 ± 0.55</td>
</tr>
</tbody>
</table>

3.3.6 *In-vivo* Comparison of Ammonia Removal

Results from the *in-vivo* experiment for the freshwater specimen is shown in Figure 3-5. Figure 3-5(a) shows the concentration of NH$_3$-N per fish over time (h). Figure 3-5(b) shows the pH change over time (h). No fish died during the experiments, however, significant differences were observed among each group. In the control group, the ammonia accumulation rate was 4.68 ± 0.38 mg/kg fish/h ($R^2 = 0.97$). While in the CC group, the ammonia accumulation rate was slightly higher than the control ($k = 4.98 ± 0.49$ mg/kg fish/h, $R^2 = 0.95$, $p$-value 0.0041). This result was consistent with the *in-vitro* experiment result, where the commercial water conditioner had no effect on ammonia removal. The $k$ in the NN group was 4.37 ± 0.40 mg/kg fish/h ($R^2 = 0.95$) and in AmmoSorb group was 3.42 ± 0.36 mg/kg fish/h ($R^2 = 0.94$). These results also confirmed the data in the *in-vitro* experiment. IX may have better ammonia control capacity than CN ($p$-value 0.09). A combined AmmoSorb and NN group was found had the lowest ammonia accumulation rate ($k = 2.23 ± 0.32$ mg/kg fish/h, $R^2 = 0.90$, $p$-value 2E-10). By normalizing the data, we found that the high ammonia removal efficiency of combined group (AmmoSorb + NN)
was caused by a simple superposition phenomenon. The total amount of NH$_4^+$ removed in combined group was generally equal to the sum of NH$_4^+$ removed by AmmoSorb and NN (p-value:0.32).

Ammonia removal by the IX process occurs when NH$_4^+$ is exchanged by other changeable ions (Na$^+$, Mg$^{2+}$, and Ca$^{2+}$) in the zeolite which shifts the equilibrium from left to right in Eq. 2-1. Figure 3-6 shows the exchangeable ion concentration before and after the in-vivo experiment. The increase in Na$^+$ and Mg$^{2+}$ is attributed to the IX process; when the NH$_4^+$ is taken up by the AmmoSorb, Na$^+$ and Mg$^{2+}$ are released. The order of ion selectivity for chabazite is K$^+ >$ NH$_4^+ >$ Na$^+ >$ Ca$^{2+} >$ Mg$^{2+}$ (Aponte-Morales, 2015; Hedstrom, 2001). The sharp increase in K$^+$ was caused by the addition of phosphate buffer. The decrease in Ca$^{2+}$ was most likely due to the formation of calcium phosphate precipitates.

Because the average pH of the bulk water in all five groups was 6.81 ± 0.19, the major fraction of ammonia was NH$_4^+$ (USEPA, 1999). Therefore, the CN reaction (Eq. 2-2) is limited; however, the IX process (Eq. 2-1) can proceed. The combination of AmmoSorb and NN had the lowest ammonia accumulation rate ($k = 2.23 ± 0.31$ mg/kg fish/h, $R^2 = 0.90$). In terms of the pH, the lowest water pH was found in the NN group (pH= 6.46), but this pH is still fish friendly (Stevens, 2009).

The in-vivo experiment results for the seawater specimen are shown in Figure 3-7. The results indicate that the $k$ in CC group ($k = 9.59 ± 0.32$ mg/kg fish/h, $R^2 = 0.99$) is much higher than the control group ($k = 6.68 ± 0.24$ mg/kg fish/h, $R^2 = 0.99$, p-value 7.90E-10). The reason for this phenomenon is unknown, but we can combine the results from the freshwater experiment to conclude that the commercial water conditioner (CC) does not remove ammonia from the water. In seawater, the AmmoSorb ($k = 6.38 ± 0.37$ mg/kg fish/h, $R^2 = 0.98$) is less effective than
the NN \((k = 4.89 \pm 0.20 \text{ mg/kg fish/h}, R^2 = 0.99, \text{ p-value 1.5E-09})\), which is consistent with the results of the \textit{in-vitro} experiment. The high \(\text{Na}^+\) ion concentration reduces the effectiveness of the IX process (Miladinovic, Weatherley, et al., 2004). The \(k\) in the combined AmmoSorb and NN group is the lowest \((k= 4.61 \pm 0.26 \text{ mg/kg fish/h}, R^2 = 0.98)\), which is consistent with the freshwater result. The normalization results also showed that the lowest ammonium removal performance was caused by the superposition phenomenon (p-value 0.52). The average pH in the NN group was 6.68, which is also a safe pH range for fish health.

Figure 3-7 (bottom) shows the exchangeable ion concentrations in seawater before and after AmmoSorb addition. The decreasing \(\text{Na}^+\) concentration is most probably due to the IX process since \(\text{Na}^+\) is the dominant cation in the liquid phase (Colella, 1996). The increase in \(\text{K}^+\) was caused by the addition of phosphate buffer. By considering the ion selectivity of \(\text{K}^+\) and \(\text{Na}^+\), it is recommended that sodium phosphate buffer is used instead of potassium phosphate buffer in future studies. The slightly increasing \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) concentration might be explained by the poor IX process by AmmoSorb in seawater.

3.3.7 Toxicity Assessment

Results from the toxicity tests are shown in Figure 3-8. \textit{Daphnia Magna} is the regulated species by USEPA Toxic Substance Control Act (TSCA) for toxicity tests (Hayes, 2007). According to EPA guidelines, the survival percentage of \textit{Daphnia Magna} in the control group should be equal to or higher than 90\% at the end of testing time (USEPA, 2002). This criterion was fulfilled in this experiment. After 24 hours, B.B.™ had the lowest survival rate, which was 80 ± 5\%. After 48 hours, the survival rate decreased to 33 ± 9\%. The 48-hour toxicity of the NN group was found to be the highest of all the test groups. The AmmoSorb and P.S.™ can be considered nontoxic to \textit{Daphnia Magna} neonates.
LC₅₀ results are tabulated in Table 3-13. After 24 hours, the lethal concentration of NN for *Daphnia Magna* neonates was 1.32 g/L, which is higher than the daily maximum dose (1.0 g/L). Thus, if the daily dose of NN that is used to remove ammonia does not exceed the daily maximum dose (1.0 g/L), the NN is relatively safe to *Daphnia Magna* neonates. In addition, replacing two third of fresh water daily is also recommended to minimize the effect of toxic ammonia.

![NH₃-N and pH trend](image)

**Figure 3-5** The ammonia excretion (top) and pH trend (bottom) of the freshwater specimen as the function of time.
Table 3-13 LC$_{50}$ of commercial water conditioners (B.B.$^{\text{TM}}$ and P.S.$^{\text{TM}}$) and novel neutralizer (NN)

<table>
<thead>
<tr>
<th></th>
<th>24h</th>
<th>48h</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.B.$^{\text{TM}}$</td>
<td>2.64 g/L</td>
<td>0.52 g/L</td>
</tr>
<tr>
<td>P.S.$^{\text{TM}}$</td>
<td>3.57 g/L</td>
<td>1.98 g/L</td>
</tr>
<tr>
<td>NN</td>
<td>1.32 g/L</td>
<td>0.73 g/L</td>
</tr>
</tbody>
</table>

Figure 3-6 The exchangeable ion comparison before and after AmmoSorb addition. Freshwater (top); Seawater (bottom)
3.3.8 Cost Analysis

Table 3-14 shows the daily cost comparison between the AmmoSorb, NN, and CC. The cost of NN was calculated based on the maximum recommended dosage (1 g/L). The cost of AmmoSorb and CC was calculated based on the dose used in the in-vivo experiment (Table 3-3). The source of each component price comes from the company quote or commercial vendors. The daily cost of NN was the lowest.
Table 3-14 Daily cost comparison between the AmmoSorb, the novel neutralizer (NN), and commercial water conditioner (CC)

<table>
<thead>
<tr>
<th></th>
<th>AmmoSorb ($/day)</th>
<th>NN ($/day)</th>
<th>CC ($/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>3.53</td>
<td>0.90</td>
<td>1.23</td>
</tr>
<tr>
<td>Seawater</td>
<td>3.53</td>
<td>0.34</td>
<td>2.09</td>
</tr>
</tbody>
</table>

3.3.9 Regeneration Efficiency Studies of Ammosorb

Figure 3-9 shows the ammonium adsorption capacity comparison between original and regenerated chabazite. In the case of freshwater, the ammonium adsorption capacity ($q_e'$) was decreased after regeneration. The regeneration efficiency (RE) of RE$_{40}$ was $80.03 \pm 5.40\%$ and the RE of RE$_{80}$ was $66.25 \pm 16.69\%$. In terms of seawater, the ammonium adsorption started to have an interesting change. When regenerated chabazite was used to remove 10 mg/L NH$_4^+$-N, ammonium desorption occurred. The most probable reason is the presence of competing ions in
seawater. Since seawater has a very high concentration of Na\(^+\), the ion exchange process went from right to the left (Eq. 3-16) and caused more release of NH\(_4^+\)-N. It was calculated that the RE of RE\(_{40}\) was 80.24 ± 38.82\% in seawater which is close to the result in freshwater. The RE of RE\(_{80}\) was 87.99 ± 29.39\% in seawater. In consideration of the amount of NaCl used as well as the regeneration efficiency, it is recommended to use 40g/L NaCl to regenerate the exhausted chabazite. The average RE is 80.14 ± 25.74 \% in both freshwater and seawater.

\[
\text{Chabazite} - \text{Na}^+ + \text{X}^+ \leftrightarrow \text{Chabazite} - \text{X}^+ + \text{Na}^+ \quad (3-14)
\]

Figure 3-9 Ammonium adsorption equilibrium comparison between new chabazite and regenerated chabazite. Left: freshwater; Right: seawater

### 3.4 Conclusions

This study compared the effectiveness of ion exchange and chemical neutralization methods as a function of ammonia removal, toxicity as well as daily cost. All these methods were found to remove ammonia by a simple drop-off system. The chabazite was selected as the ion exchanger. A commercialized chemical neutralizer and a novel neutralizer were compared as well. Characterization of chabazite shown that there were no structural changes of chabazite after
being modified. Experimental kinetic data suggest that ammonium removal follows a pseudo-second-order reaction model. The diffusion model showed that film diffusion is the dominant in the ammonium sorption in freshwater, while pore diffusion dominated ammonium sorption in seawater. The isotherm studies showed that non-linear regression had the best fit for ammonia removal in both freshwater and seawater. The Sips isotherm indicated that the ammonium adsorption is not a simple process that can be described by only one simplified isotherm. In terms of the ammonia removal efficiency, the AmmoSorb showed noticeable ammonia removal in both freshwater and seawater in in-vitro trials. However, in in-vivo trials, AmmoSorb was found to only works in freshwater and was ineffective in seawater. For commercial water neutralizer, both in-vitro and in-vivo trials showed that they are not able to control ammonia levels in both freshwater and seawater. The novel neutralizer was found to have high ammonia removal efficiency in both freshwater and seawater. Regarding chabazite regeneration, it is recommended to use 40g/L NaCl to regenerate the exhausted chabazite. In terms of toxicity, the AmmoSorb can be considered non-toxic. To safely use the novel neutralizer, it is recommended to control its daily dose at 1 g/L/day followed by a two-thirds volume of water change every day. The cost analysis also showed that the novel neutralizer had the lowest cost.
CHAPTER 4

FLUORIDE REMOVAL BY MODIFIED BIOSAND FILTER (BSF)

4.1 Introduction

The United States has one of the world’s safest drinking water supplies. However, in 2015, 663 million people in the world still lacked improved drinking water sources (UNICEF and World Health Organization, 2015). Biosand filters (BSFs) is simple and low cost household drinking water treatment facilities that has been widely applied in many water crisis areas such as South Africa, South America, and Asia (Stauber, Printy, et al., 2012; Duke, Nordin, et al., 2006; Murphy, McBean, et al., 2010; Aiken, Stauber, et al., 2011; Stauber, Kominek, et al., 2012). The BSF can generally remove turbidity and microorganisms such as E. coli from the water. The pH of treated water can also be maintained at a neutral level. Besides that, a modified type of BSF can also enhance its water treatment ability, such as for arsenic or fluoride removal (Ngai and Walewijk, 2003). In this chapter, a modified type of BSF is proposed to remove turbidity, pathogens, and fluoride at the same time. Fluoride is a common element that is widely present in minerals. The WHO guideline limits the fluoride level in drinking water to 1.5 mg/L, as excess fluoride may cause dental fluorosis. However, in some parts of the world, such as India, a concentration up to 38.5 mg/L has been reported by the UNICEF in 1999. Also in Kenya and South Africa, the level of fluoride was reported to exceed 25 mg/L (Susheela, Mudgal, et al., 1999).

Traditional BSFs use sand as the filtration media. The sand can be obtained easily from local materials. However, some field studies have shown that the BSF is not capable of removing
dissolved compounds such as fluoride, iron, nitrite or arsenic (Murphy, McBean, et al., 2010; Dangol and Spuhler, 2010; Noubactep, Temgoua, et al., 2012). Hence, modification of traditional BSF is needed to enhance its removal capacity. The overall objective of this chapter is to improve drinking water quality parameters, especially fluoride, turbidity, pH, and *E. coli* by modifying the traditional BSF system. The research design of this chapter includes four parts.

*Task 1: Select filter material using fluoride adsorption batch tests.*

*Task 2: Apply the chosen materials into bench scale BSFs and determine a proper filter configuration.*

*Task 3: Apply models to provide scale-up parameters and conditions for a pilot scale BSF unit.*

*Task 4: Investigate a proper method to regenerate the exhausted BSF media.*

### 4.2 Materials and Methods

#### 4.2.1 Fluoride Adsorption Material

As mentioned in section 2.2.6, pumice is an ideal natural material that can enhance the water filtration rate but keep the same output water quality as sand media. Previous research also found that aluminum hydroxide coated pumice (AOCP) was effective for fluoride removal and had better removal efficiency compared to activated alumina (Salifu, Petruşevski, et al., 2013). Therefore, pumice was selected as fluoride adsorption material in this study.

The pumice was purchased from Charles B. Chrystal Co., Inc. (Mamaroneck, NY). It was sieved to get the effective diameter ($D_{10}$) of 0.3 mm. The $D_{10}$ means 10% of the media mass that can pass through a certain sieve size. A recommended $D_{10}$ value of a BSF is 0.15-0.3 mm based on the slow sand filter studies (Lynn, Wanjigi, et al., 2013). Once the pumice was received, it was washed with deionized (DI) water and dry at room temperature. Pumice was pretreated to
enhance its fluoride removal capacity. The pumice pretreatment procedure was obtained from Salifu et al.’s (2013). Dry pumice was soaked in 0.5M $\text{Al}_2(\text{SO}_4)_3$ for 1.5 hours under continuous mix up and air dried at room temperature. Then the dried pumice was soaked in 3M $\text{NH}_4\text{OH}$ to neutralize the pH. The coated pumice was washed with DI water again to remove loosely bonded aluminum ions. The coated pumice is called AOCP.

4.2.2 Fluoride Adsorption by AOCP

Batch scale fluoride adsorption experiments were carried out to verify the results obtained by Salifu et al. (2013). Raw pumice (20g) and AOCP (20g) were simultaneously added to 1000 mL of fluoride injected water. Fluoride concentrations were measured at times 0, 1, 3, 5, 10, and 24 hours. The water was obtained from the Simmons Park at the University of South Florida, FL (Average pH=8.49, alkalinity=62.09 mg/L). The sodium fluoride (5 mg/L) was spiked into it.

4.2.3 Fluoride Adsorption Isotherm and Kinetic Studies

Batch fluoride adsorption isotherm experiments were carried out by adsorbing different concentrations (0, 1, 5, 10, 15, 20, 25 mg/L) of fluoride with 4g of AOCP for 48 hours in 250 mL Erlenmeyer flasks. The flasks were covered with parafilm and placed on a shaker table for 48 hours. Fluoride concentrations were measured at the beginning and end of the experiment.

The fluoride adsorption kinetic experiment was performed under the same conditions as isotherm experiment. However, 5mg/L of fluoride was adsorbed by 4g of AOCP for 96 hours. Samples were collected at different times (0, 0.5, 1, 2, 4, 6, 10, 24, 48, 96h). The data were evaluated using the pseudo-first and second order models as described in the previous section (3.2.2.4).
4.2.4 Bench Scale BSF

A series of bench-scale BSFs were designed in this study. The bench-scale design would help understand fluoride removal performance in a BSF and provide a model to predict a full-scale BSF in the future research. The component of bench scale BSF follows a traditional full-scale BSF but forty times size down (CAWST, 2012; Noubactep, Temgoua, et al., 2012).

The bench-scale BSFs were constructed of PVC plastic pipe (Mcmaster-Carr, Atlanta, GA) with 7.62 cm internal diameter. The filter media were prepared according to the BSF construction manual (CAWST, 2012). The D_{10} of both sand and AOCP was 0.3 mm. The size ranges of separation and drainage gravel were 0.7-6 mm and 6-12 mm. The bed porosity of sand layer and AOCP layer was 0.43 and 0.7, respectively. The design of bench scale BSF had three types. BSF-A was a control BSF, which contained 18 cm sand. BSF-H was a half-half design included 9 cm AOCP on top and 9 cm sand on the bottom. The BSF-S was a sandwich type with 6 cm AOCP in the middle and 6 cm sand on top and bottom side. The depths of separation and drainage gravel were 3 cm in each in all three designs. The outlet pipe was 0.5 cm above the filter media. This was designed to keep the standing water 0.5 cm depth during the resting time to protect biological layers in the BSF (Figure 4-1). A diffuser plate was placed on top of the filter. It can protect the top sand from moving around and also evenly distribute the water charge.

4.2.5 Bench Scale BSF Operation

Raw water was collected from Lake Behnke at University of South Florida (Tampa, FL) and stored in the fridge. The raw water was spiked with ~3mg/L of fluoride ions from NaF. Water was well mixed before being charged into the BSF. The daily charge volume was separated into three steps (Table 4-1). The increased charging volume at Step 2 is used to match the full-scale BSF manual, which was one-fortieth of the full-scale BSF charge volume (Lynn,
Wanjugi, et al., 2013; CAWST, 2012). The system would overflow if charge more than 200 mL, so in Step 3 the total daily charge was 200 mL first and 100 mL right after the water level returned to the elevation of the diffuser plate. When the maximum flow rate (MFR) was lower than 18 mL/min, the BSF was stirred on the top 6 cm media layers. The pause period varies between 20 to 24 hours, sometimes 48 hours during the weekend. The BSF operational procedure was stopped when the outlet fluoride concentration was higher than the breakthrough point ($C_b=0.125$ mg/L), which was 5% of the inlet fluoride concentration.

Figure 4-1 Schematic of biosand filter (BSF) designs. (a) BSF-A: all sand media; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP is located between two sand layers. (Gravel layer: 6cm; Sand/AOCP+Sand /Sand+AOCP+Sland layer=17.9cm; Standing water: 1 cm; Diameter: 7.62 cm)

58
Table 4-1 The daily charge of bench scale BSFs

<table>
<thead>
<tr>
<th>Step</th>
<th>Charge volume</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130 mL</td>
<td>1-44</td>
</tr>
<tr>
<td>2</td>
<td>200 mL</td>
<td>45-61</td>
</tr>
<tr>
<td>3</td>
<td>300 mL</td>
<td>62-90</td>
</tr>
</tbody>
</table>

4.2.6 Analytical Methods

The fluoride concentrations were determined using a high-performance fluoride ion selective electrode (9609BNWP, Thermo Scientific, Beverly, MA). The turbidity, fluoride concentration, pH, and maximum filtration rate (MFR) were measured daily. The turbidity was measured by a portable turbidimeter (2100Q, HACH, Loveland, CO). The fluoride concentration was measured by the high-performance fluoride ion selective electrode (9609BNWP, Thermo Scientific, Beverly, MA). The pH was measured by the pH meter (Denver Instrument Model 250, Bohemia, NY). The MFR was measured by the volume of collected water in 3 mins right after the initial charge. The *E. coli* was measured monthly in the regeneration study by using EPA Method 1603.

The clean-bed head loss was calculated based on the Ergun Equation (Kubare and Haarhoff, 2010):

\[
\frac{h}{L} = \left[ \frac{150 \cdot \mu \cdot (1-\varepsilon)^2}{\rho \cdot g \cdot d^2 \cdot \psi^2 \cdot \varepsilon^3} \right] \cdot V + \left[ \frac{1.75 \cdot (1-\varepsilon)}{g \cdot d \cdot \psi \cdot \varepsilon^3} \right] \cdot V^2
\]  

(4-1)

where the \(h\) was the clean-bed head loss (m), \(L\) was the depth of media bed (m), \(V\) was the filtration rate (m/s), \(\varepsilon\) was the media bed porosity, \(\psi\) was the average surface area sphericity, \(d\) was the geometric grain diameter (m), \(g\) was the gravitational acceleration (m/s\(^2\)), \(\rho\) was the water density (kg/m\(^3\)), \(\mu\) was the dynamic viscosity of water (kg/m·s).
The calculation using the above equation shows that the first term (Laminar term) was much larger than the second term (Turbulent term) in BSF systems. Thus, the second term can be neglected. Since the BSF-H and BSF-S have two different media types, a transformed Ergun Equation is (Kubare and Haarhoff, 2010):

\[ h = \left[ \frac{150 \mu (1-e)^2 \cdot L \cdot V}{\rho \cdot g \cdot d^2 \cdot \phi^2 \cdot \varepsilon^3} \right] \cdot \sum_{i=1}^{n} \frac{a_i}{d_i^2} \]  

(4-2)

where the \( n \) was the number of size fraction, \( a \) was the fraction of the total media depth, \( d \) was the geometric mean of the diameter of each fraction.

4.2.7 BSF Modeling

The modeling of bench scale BSF was necessary to provide quantified parameters to design pilot scale BSFs. To optimize the design and operational conditions of BSF especially in terms of the fluoride removal, a proper mathematical model is necessary. Fluoride removal in BSF can be seen as an intermittent fix-bed adsorption system. Thus, two widely used fix-bed adsorption models: Bohart-Adams (BA) model and Thomas model were selected to predict the dynamic performance of BSFs in terms of the fluoride removal. The mathematical expression of the BA and Thomas model can be written as (Chu, 2010):

BA model: \[ \ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{K_{BA} N_0 Z}{u} - K_{BA} C_0 t \]  

(4-3)

Thomas model: \[ \ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{K_T q_0 M}{Q} - K_T C_0 t \]  

(4-4)

where \( C_0 \) was the input fluoride concentration (mg/L), \( C_t \) was the output fluoride concentration (mg/L), \( K_{BA} \) was the BA rate constant (L/mg·min), \( N_0 \) was the adsorption capacity per unit volume of AOCP layer (mg/L), \( Z \) was the total AOCP layer depth (m), \( u \) was the linear velocity of filtration (m/min) and \( t \) was the service time (min). In the Thomas model, the \( K_T \) was the Thomas rate constant (L/mg·min), \( q_0 \) was the adsorption capacity (mg/g), \( M \) was the mass of
AOCP (g), and Q was the flow rate (L/min). In the two models, $K_{BA}$, $N_0$, $K_T$, and $q_0$ are four unknowns that need to be calibrated by non-linear regression of the experimental data.

The analytical solution of BA model was given as (Chu, 2010):

$$\frac{C_0}{C_t} = \frac{\exp(\alpha)}{\exp(\alpha) + \exp(\beta) - 1}$$  \hspace{1cm} (4-5)

with

$$\alpha = K_{BA}C_0t; \quad \beta = \frac{K_{BA}N_0Z}{u}$$

The BA model can be rearranged to a form with related to bed depth ($Z$) and service time ($t$) given by Eq. (4-6):

$$t = mZ + c$$  \hspace{1cm} (4-6)

where $m = \frac{N_0}{C_0u}$, $c = -\frac{1}{K_{BA}C_0} \ln\left(\frac{C_0}{C_t} - 1\right)$.

This equation is also named the bed depth service time (BDST) model. By plotting $Z$ vs. $t$, a linear relationship can be used to predict the performance of AOCP layer depth associated with the service time.

The Thomas model can be written as (Balkaya and Cesur, 2008):

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_Tq_0M}{q - K_TC_0t}\right)}$$  \hspace{1cm} (4-7)

All the model curves and the parameters were plotted and fitted using MATLAB.

4.2.8 Statistical Analysis

All samples in the fluoride adsorption studies were collected and measured in triplicate. A student t-test was used to compare if the residual fluoride concentration was statistically significant. The test was performed at a confidence level of 95%.

In the BSF performance studies, samples were collected once per day. Raw water turbidity and fluoride concentration were measured weekly. Arithmetic mean and standard
deviations were calculated to represent the raw water qualities. A student t-test was used to compare if the MFR, turbidity, pH, and fluoride concentrations were statistically different in each BSF design. The test was performed at a confidence level of 95%.

In BSF regeneration studies, samples were collected in triplicate daily. Arithmetic mean and standard deviations were calculated for turbidity, fluoride concentration, and pH.

4.2.9 BSF Regeneration

The exhausted BSF was regenerated in situ by recoating Al$_2$(SO$_4$)$_3$ into the system. One modification was made on BSF-S as the AOCP layer was increased to 0.09 m, which was the same as BSF-H. This modification was used to verify if the biological layer growth on the AOCP layer would hinder the fluoride adsorption. The turbidity, fluoride concentration, pH, maximum filtration rate (MFR) were measured daily. *E. coli* were measured monthly. In this study, BSFs were regenerated four times. The whole experiment lasted 180 days. Each time the regeneration procedure was slightly different. The detailed regeneration procedure was described in Table 4-2.

Table 4-2 BSF regeneration procedures for four different cycles

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Days</th>
<th>BSF-A</th>
<th>BSF-A-RE</th>
<th>BSF-H</th>
<th>BSF-S</th>
</tr>
</thead>
</table>
| 1     | 1-49 | No change | 1. Pour 500ml 0.5M Al$_2$(SO$_4$)$_3$ and let it recirculate 5 times  
2. Add 500 ml 3M NH$_4$OH to neutralize the pH.  
3. Back wash. (Due to precipitation)  
4. Add 100mL0.1M HCl to dissolve leftover precipitation  
5. Add 200mL tap water to wash. |
Table 4-2 (Continued)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Days</th>
<th>BSF-A</th>
<th>BSF-A-RE</th>
<th>BSF-H</th>
<th>BSF-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-49</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6. Add extra AOCP or sand if media lost during previous steps</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>7. Tap water flush 5 times</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50-115</td>
<td>No change</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. Drain out the columns</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2. Install the outlet pipe</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3. Pour in 0.5M Al$_2$(SO$_4$)$_3$ until it overflows.</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>4. Let it sit overnight.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5. Drain out the Al$_2$(SO$_4$)$_3$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6. Wash with 1000mL tap water.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7. Wash with 500mL 3M NH$_4$OH.</td>
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<td></td>
<td></td>
<td></td>
<td>8. Wash with 1000mL tap water.</td>
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<td></td>
<td></td>
<td></td>
<td>9. Install the outlet pipe.</td>
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<td></td>
<td></td>
<td></td>
<td>10. Start to run the column.</td>
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<tr>
<td>3</td>
<td>120-162</td>
<td>No change</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. Add 500ml 0.5M Al$_2$(SO$_4$)$_3$ to each BSF</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2. Let it sit overnight.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3. Wash with 1000mL tap water.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4. Add 500mL 3M NH$_4$OH.</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>5. Wash with tap water until output water pH was higher than 6.</td>
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</tr>
<tr>
<td>4</td>
<td>166-180</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>1. Drain out the columns</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. Install the outlet pipe</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. Pour in 0.5M Al$_2$(SO$_4$)$_3$ until it overflows.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>4. Let it sit overnight.</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>5. Drain out the Al$_2$(SO$_4$)$_3$</td>
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<td></td>
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<td></td>
<td>6. Wash with 3000 mL tap water.</td>
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<td></td>
<td></td>
<td></td>
<td>7. Wash with 3M NH$_4$OH.</td>
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<td></td>
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</tbody>
</table>
Table 4-2 (Continued)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Days</th>
<th>BSF-A</th>
<th>BSF-A-RE</th>
<th>BSF-H</th>
<th>BSF-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>166-180</td>
<td>No change</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8. Wash with 3000 mL tap water.
9. Install the outlet pipe.
10. Start to run the column.
11. Back wash if precipitation still happened

4.3 Results and Discussion

4.3.1 Fluoride Adsorption by AOCP

Figure 4-2 shows the residual fluoride concentration (mg/L) with respect to time (h) during a 24-hour adsorption experiment. Compared with AOCP, raw pumice has no capacity to remove fluoride (p-value 0.04). A slight increase in residual fluoride concentration at times 3, 5, and 10 hour may have been due to measurement error. The calculated fluoride removal efficiency of AOCP was approximately 96% at the end of 24 hours. This result was consistent with previous researchers who found that the fluoride removal efficiency varied from 55.7% to 97.8% (Salifu, Petrusevski, et al., 2013). It also verifies the adsorption mechanisms discussed in section 2.2.7 because no free aluminum ions are bounded in the raw pumice. Another finding of this study was that most of the fluoride was adsorbed at the first 2 hours. This lead to the subsequent study of adsorption kinetics.

4.3.2 Fluoride Adsorption Kinetic Studies

The fluoride adsorption process was fit into the pseudo-first-order and pseudo-second-order kinetic models by using the linear forms of Eq. 3-2 and Eq. 3-3. By fitting the experimental data into both pseudo-first-order and pseudo-second-order models, the fluoride adsorption process was found to have the best correlation with the pseudo-second-order kinetic model.
(Figure 4-3). The calculated parameters are summarized in Table 4-3. This finding agrees with all the other published literature related to the fluoride adsorption by pumice, which indicated that the fluoride adsorption by modified pumice follows the pseudo-second-order kinetics (Asgari, Roshani, et al., 2012; Sepehr, Sivasankar, et al., 2013; Mahvi, Heibati, et al., 2012; Salifu, Petrusevski, et al., 2013). As mentioned in Chapter 3, the pseudo-second-order kinetics model involves three steps: film diffusion, pore diffusion, and mass action (Liao, Ismael, et al., 2012; Wang, Shu, et al., 2011; Alshameri, Ibrahim, et al., 2014). Therefore, an intraparticle diffusion model was applied to help explain the phenomenon. The mathematical equation of intraparticle diffusion model was listed Chapter 3, Eq. 3-11. The plot of intraparticle diffusion model helped to understand which step is the dominant steps. Basically, if the initial phase of adsorption had a good linearization, it will be intraparticle diffusion controlled (Ofomaja, 2010).

From Figure 4-4, there are apparently three stages involving in the fluoride adsorption process. Stage 1 (0-1 h) had a good linear fit which represented the external surface adsorption. Stage 2 (1-6 h) was where the intraparticle diffusion controlled. The diffusion process reached to equilibrium when the concentration gradient reached zero (Stage 3, 6-96 h) (Sun and Yang, 2003; Wu, Tseng, et al., 2009; Chen, Zhang, et al., 2010). The calculated intraparticle diffusion coefficient for each stage were 0.11 ± 0.07 mg/g·min$^{0.5}$, 0.04 ± 0.02 mg/g·min$^{0.5}$, and 0.0045 ± 0.0024 mg/g·min$^{0.5}$. These values also confirmed that when the fluoride concentration in solution decreased, the diffusion rate decreased as well.

Table 4-3 Pseudo-second-order kinetic parameters for fluoride adsorption by AOCP

<table>
<thead>
<tr>
<th>F (mg/L)</th>
<th>k_2 (g/mg·min)</th>
<th>h (mg/g·min)</th>
<th>q_{e,exp} (mg/g)</th>
<th>q_{e,cal} (mg/g)</th>
<th>R^2</th>
<th>Δq (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>0.08</td>
<td>0.19</td>
<td>0.20</td>
<td>0.20</td>
<td>0.99</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure 4-2 Residual fluoride concentration after adsorbed by pumice (▲) and AOCP (●) as a function of time (adsorbent 20g/L, initial fluoride concentration 5 mg/L, contact time 24 h)

Figure 4-3 Adsorption kinetics of fluoride onto AOCP: (a) pseudo-first-order plot; (b) pseudo-second-order plot.

Figure 4-4 Adsorption kinetics of fluoride onto AOCP analyzed by intraparticle diffusion model. (AOCP 20g/L, initial fluoride concentration 5 mg/L, contact time 96 h)
4.3.3 Fluoride Adsorption Isotherm Studies

The adsorption isotherm study was used to help understand the fluoride adsorption mechanisms. The data were evaluated by non-linear regression using Langmuir, Freundlich, Sips, and Temkin isotherm models as described in the previous section (3.2.2.5). The mathematical types of each model are discussed in Chapter 3, Table 3-2. Based on the correlation coefficient $R^2$ and $\chi^2$, the Freundlich and Sips isotherm were best fitted to the experimental data. The Sips isotherm was a modified Langmuir-Freundlich isotherm that can describe both the Langmuir-type and Freundlich-type adsorption behavior (Jeppu and Clement, 2012). At low fluoride concentration, the adsorption process tends to follow the Freundlich isotherm, while at high fluoride concentration, it was more likely to follow a Langmuir isotherm. In this study, the parameters calculated from the Sips isotherm was the same as Freundlich isotherm, which is consistent with the above-mentioned theory. The Freundlich isotherm was a widely accepted isotherm that is usually used to describe heterogeneous adsorption. When the slope of Freundlich isotherm ($1/n$) was close to zero, the adsorption surface was more heterogeneous. Whereas, a value below 1 implies a chemical adsorption processes (Foo and Hameed, 2010). In this study, the calculated slope of the Freundlich isotherm was 0.63, therefore, the fluoride adsorption by AOCP can be classified as chemical adsorption dominated. In addition, the mechanism of Al and F bonding discussed in section 2.2.7 also explained the chemical adsorption process (Geankoplis, 2003; Crittenden, Trussell, et al., 2005). The maximum adsorption capacity of AOCP can be calculated from the Sips model as well (Al-qaradawi and Salman, 2002), which was 22.64 mg/g.

Table 4-4 compares fluoride adsorption capacity by different types of pumice. The reasons for the high adsorption capacity in this study might be due to the high ionic bonding
energy between Al and F as well as the error distribution of linear regression (Foo and Hameed, 2010; Karadag, Koc, et al., 2007).

Table 4-4 Comparison of fluoride adsorption capacity \(q_{\text{max}}, \text{mg/g}\) by different types of pumice

<table>
<thead>
<tr>
<th>Pumice type</th>
<th>(q_{\text{max}} \text{ (mg/g)})</th>
<th>Isotherm model</th>
<th>Regression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide modified pumice (HMP)</td>
<td>11.77</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Sepehr, Sivasankar, et al., 2013)</td>
</tr>
<tr>
<td>Magnesium chloride modified pumice (MGMP)</td>
<td>5.56</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Sepehr, Sivasankar, et al., 2013)</td>
</tr>
<tr>
<td>Natural Pumice</td>
<td>4.53</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Sepehr, Sivasankar, et al., 2013)</td>
</tr>
<tr>
<td>Natural Pumice</td>
<td>0.31</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Katsou, Malamis, et al., 2011)</td>
</tr>
<tr>
<td>Surfactant modified pumice (SMP)</td>
<td>41.65</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Asgari, Roshani, et al., 2012)</td>
</tr>
<tr>
<td>Acid-treated pumice</td>
<td>13.51</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Mahvi, Heibati, et al., 2012)</td>
</tr>
<tr>
<td>AOCP</td>
<td>7.87</td>
<td>Langmuir</td>
<td>Linear</td>
<td>(Salifu, Petrusevski, et al., 2013)</td>
</tr>
<tr>
<td>AOCP</td>
<td>22.64</td>
<td>Sips</td>
<td>Non-linear</td>
<td>This study</td>
</tr>
</tbody>
</table>
4.3.4 Bench Scale BSF Performance

4.3.4.1 Hydraulic Aspects

The maximum filtration rate (MFR) was monitored daily with respect to the hydraulic performance of the BSF (Figure 4-5). The initial filtration rate started to increase in the first 7 days (Phase I). The extremely low flow rate in the Phase I may have been caused by the air locking. When air bubbles got trapped in the media, it forms stationary air pockets within the filter media. These pockets prevented water from accessing to media surfaces locked by the air bubbles. Once airlocking was removed by continued water flow, the filtration rate started to increase (Phase II). In this phase, the *schmutzdecke* layer was building up. In general, the ripening period of BSF ranges from 7 days to several months, depending on the charging water temperature, turbidity, as well as its nutrient level (Barrett, Bryck, et al., 1991). Once the system ripened, the filtration rate tended to decrease slowly. At day 45, the filtration rate started to increase again (Phase III). This was due to the charge volume increase. The BSF operation was suspended when the residual fluoride concentration of BSF-H reached to the breakthrough point ($C_b=0.125$ mg/L). The average MFR of BSF-A was $16.19 \pm 4.45$ mL/min, which was lower than the BSF-H ($17.49 \pm 4.33$ mL/min, p-value 0.07) and BSF-S ($17.56 \pm 4.90$ mL/min, p-value 0.07). However, the p-value higher than 0.05 indicated that the filtration rate differences had no statistical significance. Similarly, no significant difference was found between the BSF-H and BSF-S (p-value 0.92). At day 77, BSF-S had a slight increase. This was caused by the cleaning of BSF-S columns. No clogging was observed on all BSFs during the 90 days operation time. The main reason was the low inlet water turbidity ($5.19 \pm 5.21$ NTU) as well as the small amount of daily charge (130–300 mL/day).
The change of clean-bed head loss of each BSF with respect to filter running days was shown in Figure 4-6. Basically, the water charge causes the water level in the filter increase by a height (cm), that represents the clean-bed head loss or initial head loss. The trend of initial head loss change was similar to the filtration rate, but the values were different. Among them, BSF-A had the highest head loss while BSF-H was lowest. Taking in consideration of the Ergun Equation (Eq. 4-1), the first term represents the laminar term while the second term represents the turbulent term. Based on the calculation, the laminar term was dominant. This means that the flow regime of all BSFs can be considered as laminar flow. Based on Eq.4-2, it was observed that the initial head loss was a function of filtration rate, media bed porosity (ε) as well as the fraction of the total media depth (α). Since the resistance of bed to the flow was inversely proportional to the porosity, decreasing the porosity increases the bed resistance to the flow (Farizoglu, Nuhoglu, et al., 2003). Therefore, the high porosity of the pumice bed (BSF-H and BSF-S) resulted in a lower initial head loss than BSF-A. Due to the high porosity of pumice, BSF-H and BSF-S can potentially retain more suspended solids than BSF-A. It can be expected that, ignoring the fluoride removal efficiency, BSF-H and BSF-S should clog slowly and have longer use period than BSF-A.

4.3.4.2 Turbidity Removal

The average residual turbidity as a function of filter running days is shown in Figure 4-7. The average raw water turbidity was 5.19 ± 5.21 NTU. In general, all three BSF designs were able to meet WHO drinking water turbidity standards (<5 NTU), but BSF-A did not meet the EPA standards (< 1 NTU). The average treated water turbidity in BSF-A was 1.16 ± 0.87 NTU, which was higher than BSF-H (0.55 ± 0.13 NTU, p-value 1.46E-08) and BSF-S (0.54 ± 0.12 NTU, p-value 5.30E-09). Therefore, the pumice modified BSF was found to have higher
turbidity removal efficiency than a regular BSF. This result was consistent with the results reported in other literature (Ghebremichael, Wasala, et al., 2012; Farizoglu, Nuhoglu, et al., 2003). Since the pumice bed had a greater porosity, it had a greater possibility to capture solid particles in water. As smaller particles were deposited inside the pumice pores, the filtration bed can be used more efficiently (Farizoglu, Nuhoglu, et al., 2003). No significant difference was found between the BSF-H and BSF-S (p-value 0.55).

Another finding from Figure 4-7 was that approximately 10 days start-up period was needed for BSF-A, but only 5 days were needed for BSF-H and BSF-S. The better performance of pumice modified BSF than regular BSF should also due to higher bed porosity of pumice. This will create higher surface area and capture more particles than sand (Farizoglu, Nuhoglu, et al., 2003; Ghebremichael, Wasala, et al., 2012). In addition, since microbial contamination was likely to attach to the suspensions in water, the higher removal of turbidity can potentially reduce more pathogens substance in water (LeChevallier and Norton, 1992; Momba and Kaleni, 2002; WHO, 2011).

4.3.4.3 pH

The pH of input and output water was essential in this study because pH will significantly affect the fluoride adsorption efficiency. As mentioned previously, the adsorption of fluoride by AOCP was a process of chemisorption as well as physical adsorption. The pH not only affects the surface charge of AOCP but also the speciation and degree of ionization of fluoride (Salifu, Petrucevski, et al., 2013). AOCP was found exhibit good fluoride adsorption within the pH range 6-9, in this study, the average raw water pH was 7.02 ± 0.29. Therefore, both BSF-H and BSF-S were expected to have good fluoride adsorption efficiency.
The output water pH was stable during the operating period (Figure 4-8). The average outlet pH of BSF-A, BSF-H, and BSF-S were 7.44 ± 0.04, 6.82 ± 0.40, and 7.13 ± 0.19, respectively, which all meet WHO drinking water standard. The slightly decrease of final pH in BSF-H and BSF-S may have been due to the ion exchange between AOCP surface sites and fluoride ions (Salifu, Petrushevski, et al., 2013).

4.3.4.4 Fluoride Removal

Figure 4-9 shows the residual fluoride concentration as a function of filter running days. BSF-A had a slight fluoride removal in the first 5 days. This might have been due to the physical adsorption by the sand bed. Physical adsorption mainly happens on the surface of adsorbate as a result of van der Waals forces, which was likely to quickly lower the adsorbent concentration (Tsai, Hsien, et al., 2009). However, the adsorption equilibrium was easily reached within 10 days. BSF-H and BSF-S could both remove fluoride constantly. In Phase I, the residual fluoride concentration slightly increased. This may have been caused by air locking in the columns, as discussed previously. As air bubbles get trapped in the filter, it causes channeling or short-circuiting of water in the filter bed, which results in partial usage of the filter media. Eventually, some AOCP area was wasted. Once air locking was solved, the output fluoride concentration started to remain in a constant value (Phase II-III). Both BSF-H and BSF-S can be seen as packed bed adsorption systems in considering fluoride removal. Therefore, the BSF operation was suspended when the output fluoride concentration was higher than the breakthrough point, which was 5% of the initial fluoride concentration (Ct=0.125 mg/L). It was observed that BSF-H reached the breakthrough point at day 90, while BSF-S breakthrough occurred at day 66. The average outlet fluoride concentrations in BSF-H and BSF-S were 0.03 ± 0.03 mg/L and 0.04 ± 0.02 mg/L, respectively, which is far below the WHO regulation (Table 1-1). This result also
showed that the fluoride adsorption by AOCP was a combined physical and chemical adsorption processes. Physical adsorption generally occurred among all solid-liquid interfaces, while chemical adsorption requires chemical interaction between adsorbent and adsorbate. In the chemical adsorption process, chemisorbed fluoride ions were tightly bonded to the surface and active centers of AOCP particles without freely moving (Ayoob, Gupta, et al., 2008).

Figure 4-5 The variation of maximum filtration rate (MFR) as a function of days. Phase I (0-10 days): air locking, Phase II (10-44 days): 130 mL initial charge, Phase III (45-90 days): 200mL initial charge. (a) BSF-A: All sand media BSF; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP was located between two sand layers.
Figure 4-6 The variation of initial head loss as a function of days. Phase I (0-10 days): air locking, Phase II (10-44 days): 130 mL initial charge, Phase III (45-90 days): 200mL initial charge. (a) BSF-A: All sand media BSF; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP was located between two sand layers.
Figure 4-7 The variation of residual turbidity as a function of days. (a) BSF-A: All sand media BSF; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP was located between two sand layers.
Figure 4-8 The variation of output pH as a function of days. (a) BSF-A: All sand media BSF; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP was located between two sand layers.
Figure 4-9 The variation of residual fluoride concentration as a function of days. Phase I (0-10 days): air locking, Phase II-III (11-90 days). (a) BSF-A: All sand media BSF; (b) BSF-H: half layer of AOCP and half layer of sand; (c) BSF-S: AOCP was located between two sand layers.
4.3.5 BSF Modeling

Figure 4-10 (a-d) shows plots of Bohart-Adam(BA) and Thomas models in terms of BSF-H and BSF-S. To have an accurate prediction, the service period ended when the residual fluoride concentration was 0.8 mg/L. It took about 1000 mins for BSF-H to reach the target concentration, while approximately 800 mins were required for BSF-S. Since the total weight of AOCP in BSF-H was 10g more than BSF-S, it was worth noting that more AOCP imbedded BSF should have a longer operating period.

Table 4-5 lists all the experimental parameters as well as the calculated BA model and Thomas model constants. There are two findings from this table. First, the coefficient of determination ($R^2$) of the two models were the same ($R^2_{(BSF-H)} = 0.94$, $R^2_{(BSF-S)} = 0.93$). Second, the calculated BA rate constant ($K_{BA}$) and Thomas rate constant ($K_T$) for BSF-H are the same as well, which are both $0.0035 \pm 0.00031$ mg/L·min. Meanwhile, same results were found on BSF-S ($0.0060 \pm 0.00033$ mg/L·min). These two findings may indicate that BA model and Thomas model are mathematically equivalent to each other. A recent study also demonstrated that the two model parameters are interchangeable (Chu, 2010).

Another thing to notice from Table 4-4 was that the calculated fluoride adsorption capacity ($q_0$) for BSF-H was $1.77 \pm 0.028$ mg/g, which was slightly higher than the BSF-S ($1.68 \pm 0.024$ mg/g). Theoretically, the biofilm growth on top of the BSF-H may hinder the mass transfer efficiency of fluoride into the AOCP surfaces (Wang, Ho, et al., 2007; Sarti, Pozzi, et al., 2006; Hinder, Filipi, et al., 1994), therefore, $q_0$ of BSF-H should be lower than BSF-S. One possible reason for the contrary result might be due to the low raw water temperature. During the BSF operational period (0-90 days), raw water was stored in the refrigerator so that the water
temperature was maintained at 5°C. At low temperature, lower biofilm growth occurs (Van Loosdrecht, Eikelboom, et al., 1995).

The BDST model was plotted in Figure 4-11 to show the relationship between service time at breakthrough point ($t_b$) versus AOCP layer depth (m) with $R^2$ value equals to 0.98. The slope (m) of the BDST model represents the time needed for the fluoride to pass through a unit length of AOCP layer under the selected condition. In this case, when the average $C_0=2.51 \pm 0.61$ mg/L, the time was 8474.3 min/m.

Another function of the BDST model was to create a reference table that listed all the bed depth (m) with respect to the breakthrough time (min). It will directly help BSF designers to decide the height of AOCP layers when they know the initial fluoride concentration as well as how long the BSF was expected to be in use. The linear equation of BDST model (Eq.4-6) can also be developed to apply for another initial concentration ($C_0'$) based on:

$$m' = m \times \frac{C_0}{C_0'}$$  \hspace{1cm} (4-8)

$$c' = c \left( \frac{C_0}{C_0'} \right) \left[ \frac{\ln \left( \frac{C_0}{C_b} \right)}{\ln \left( \frac{C_0}{C_b} \right)} \right]$$  \hspace{1cm} (4-9)

However, in this study, only three BSF designs were experimentally verified in terms of the fluoride removal. It is recommended to perform at least 5 more BSFs with a variance of AOCP layer depths to validate the BDST model.
Figure 4-10 The plot of Bohart-Adam (BA) model and Thomas model as a function of BSF service time. The dot represents experimental data points, dash line represents model results. (a) BA model for BSF-H, (b) Thomas model for BSF-H, (c) BA model for BSF-S, (d) Thomas model for BSF-S.
Table 4-5 The experimental and calculated parameters of Bohart-Adams model and Thomas model

<table>
<thead>
<tr>
<th></th>
<th>BSF-H</th>
<th>BSF-S</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_0$ (mg/L)</td>
<td>2.51</td>
<td>2.51</td>
</tr>
<tr>
<td>$Z$ (m)</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>$M$ (g)</td>
<td>30.6</td>
<td>20.4</td>
</tr>
<tr>
<td>$Q$ (mL/min)</td>
<td>18.27</td>
<td>17.68</td>
</tr>
<tr>
<td><strong>BA model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{BA}$ (L/mg·min)</td>
<td>$0.0035 \pm 0.00031$</td>
<td>$0.0060 \pm 0.00033$</td>
</tr>
<tr>
<td>$W$ (mg)</td>
<td>52.96 ± 0.76</td>
<td>34.33 ± 0.56</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td><strong>Thomas model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_T$ (L/mg·min)</td>
<td>$0.0035 \pm 0.00031$</td>
<td>$0.0060 \pm 0.00033$</td>
</tr>
<tr>
<td>$q_0$ (mg/g)</td>
<td>1.77 ± 0.028</td>
<td>1.68 ± 0.024</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.94</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 4-11 The breakthrough time as a function of AOCP layer depth (BDST model)
4.3.6 BSF Regeneration

The BSFs that have reached the breakthrough point was regenerated for 4 cycles in situ. A BSF-A-RE was added to compare if the regeneration procedure affected the fluoride adsorption on sand layers at day 8. Figure 4-12 records the variance of maximum flow rate (MFR) of four BSFs. In general, there was no significant decrease in flow rate during the whole operational period. One main reason was the low average input water turbidity, 15.11 ± 4.38 NTU. The recommended source water turbidity was under 50 NTU (CAWST, 2012). Therefore, in this case, all BSFs clogged slowly. However, BSF-A was still backwashed when the output watercolor turned yellow (Day 85, 121, and 166). One possible source of the yellow color was dissolved organic matter. When the amount of microbial community accumulated on the top layers of BSF exceeded an optimal level, it had a high possibility that some microorganism in the biofilm may be sloughed (Morin and Camper, 1997). Backwashing can remove accumulated biomass. It has been found that backwashing can reduce nearly half of the attached biomass on the biofilm layer, followed by a 2 day recovery time (Kasuga, Shimazaki, et al., 2007; Liao, Chen, et al., 2015). Thus, backwashing can gently improve the output water flow rate as well as water quality. BSF-A-RE was backwashed when the sand had air pocket (Day 45) or when the system was clogged after regeneration (Day 169). Both BSF-H and BSF-S were backwashed after the 3rd and 4th regeneration cycle.

Figure 4-13 and 4-14 shows the variance of pH and turbidity during the whole experimental period. The regeneration procedure disturbed the pH and turbidity stability. Figure 4-13 (b)-(d) shows that pH had severe fluctuations right after each regeneration cycle. In general, pH increased first and then dropped to as low as 4. A possible reason for this phenomenon was the residual NH\textsubscript{4}OH as well as the formation of Al(OH)\textsubscript{3} gel. The Al(OH)\textsubscript{3} gel was a gelatinous
white precipitate. It formed from a simple chemical reaction between $\text{Al}_2(\text{SO}_4)_3$ and $\text{NH}_4\text{OH}$. The $\text{Al(OH)}_3$ gel dropped down the output water pH and increased the turbidity at the same time (Figure 4-14 (b)-(d)). The $\text{Al(OH)}_3$ gel was likely to form between pH 4 and 10 (Cardarelli, 2008). After the 1st and 2nd regeneration cycle, the breakout of pH and turbidity was likely to recover after 20 days. To shorten the recovery time, the 3rd regeneration cycle used 10L of tap water to flush the system until the output water pH was > 6 (Table 4-1). However, after a 24 hour pause period, the precipitation formed again, but the recovery time was decreased to 10 days. The 4th regeneration cycle used backwash to clean the gelatinous precipitate, which took approximately 5 days to recover. Another thing to point out is the breakout of pH and turbidity in BSF-H and BSF-S were stronger than BSF-A-RE. The days for BSF-A-RE to recover was 0~5 days. The main reason was the pore structure differences among sand and pumice. The high porosity of pumice likely to trap more $\text{Al(OH)}_3$ gels than sand.

Figure 4-16 shows the output water $E.\ coli$ concentration of each BSF during the regeneration cycle. The average raw water $E.\ coli$ level was $600 \pm 467.3$ $E.\ coli/100$ mL, which was variable due to different water conditions. After BSF treatment, all filters reduced the $E.\ coli$ level but did not always meet the WHO drinking water standards. The intervention of BSF-A reduced 98.41% of $E.\ coli$ (p-value = 0.02), but the average residual $E.\ coli$ level was still $9.5 \pm 14.2$ $E.\ coli/100$ mL which was close to the standard. The BSF-A-RE had average $E.\ coli$ level $57.1 \pm 82.7$ $E.\ coli/100$ mL, which does not meet the standard. One possible reason might be the first two regeneration cycles break the stability of biological layer. BSF-H and BSF-S can both accomplish 99.8-100% removal of $E.\ coli$ (p-value = 0.02). This result also indicated that a pumice bed had a greater porosity, so it can accumulate more particulate matter. As
microorganisms are likely to attach to the particulate matter, a higher reduction of microorganisms should be found on pumice imbedded BSFs.

Figure 4-15 shows the residual fluoride concentration change during the regeneration cycle. BSF-A was a control that was used to monitor the performance of a regular BSF, thus the output fluoride concentration was generally stable, which was the same as input fluoride concentration. Only at day 85, 121, and 166, the fluoride concentration slightly declined, which happened right after system backwash. As discussed previously, sand can adsorb fluoride through physical adsorption processes. Physical adsorption was mainly driven by van der Waals forces and was characterized by a relatively low energy of adsorption, which means that the fluoride was not bonded strongly to the sand surface (Ayoob, Gupta, et al., 2008).

In terms of BSF-A-RE, the output fluoride concentration dropped not only after backwashing but also after regenerating. The aluminum oxide coated sand can also remove fluoride at a certain point but will reach equilibrium in a very short period of time. This was also because sand media had much lower bed porosity (0.43) than pumice (0.7), which was less capable of bonding $\text{Al}^{3+}$ with the sand. The regenerated BSF-H and BSF-S showed a relatively high fluoride removal performance and a similar trend. The removal of fluoride in regenerated BSF can be explained as two reasons: adsorption occurred on the surface of re-coated pumice and adsorption by $\text{Al(OH)}_3$ gel. These two processes were likely happening the same time.
Figure 4-12 The variance of maximum flow rate (MFR) of four bench scale BSFs during regeneration cycles. (a) BSF-A: All sand media BSF. Backwashed at day 85, 121,166. (b) BSF-A-RE: Regenerated all sand media BSF. Regenerated at day 49,115,162. (c) BSF-H: half layer of AOCP and half layer of sand. Regenerated at day 49,115,162. (d) BSF-S: AOCP is located between two sand layers. Regenerated at day 49,115,162.
Figure 4-13 The variance of pH of four bench scale BSFs during regeneration cycles. (a) BSF-A: All sand media BSF. Backwashed at day 85, 121,166. (b) BSF-A-RE: Regenerated all sand media BSF. Regenerated at day 49,115,162. (c) BSF-H: half layer of AOCP and half layer of sand. Regenerated at day 49,115,162. (d) BSF-S: AOCP is located between two sand layers. Regenerated at day 49,115,162.
Figure 4-14 The variance of turbidity of four bench scale BSFs during regeneration cycles.  
(a) BSF-A: All sand media BSF. Backwashed at day 85, 121,166.  (b) BSF-A-RE: Regenerated all sand media BSF. Regenerated at day 49,115,162.  (c) BSF-H: half layer of AOCP and half layer of sand. Regenerated at day 49,115,162.  (d) BSF-S: AOCP is located between two sand layers. Regenerated at day 49,115,162.
Figure 4-15 The variance of fluoride concentration of four bench scale BSFs during regeneration cycles. (a) BSF-A: All sand media BSF. Backwashed at day 85, 121,166. (b) BSF-A-RE: Regenerated all sand media BSF. Regenerated at day 49,115,162. (c) BSF-H: half layer of AOCP and half layer of sand. Regenerated at day 49,115,162. (d) BSF-S: AOCP is located between two sand layers. Regenerated at day 49,115,162.
Conclusions

Pumice was selected as the fluoride adsorption material to remove fluoride in biosand filters (BSF). Raw pumice has no fluoride adsorption capacity. Therefore, aluminum oxide coated pumice (AOCP) was investigated to enhance its fluoride adsorption efficiency. After a 24-h bench scale adsorption study, the AOCP can remove approximately 96% of fluoride. The adsorption kinetic study showed that the fluoride adsorption by AOCP follows a pseudo-second-order reaction. The adsorption isotherms showed that Sips isotherm model has the best fit. The calculated maximum adsorption capacity of AOCP was 22.64 mg/g. The AOCP was then applied to two bench-scale BSFs. BSF-A was a traditional BSF which used sand as the main filtration media. BSF-H replaced half of the sand media to AOCP. BSF-S replaced one-third of the sand media and had the AOCP layer in the middle of the sand layers. After three months of operation, both BSF-H and BSF-S could remove fluoride efficiently (~99.9% removal). The BSF was suspended when the output fluoride concentration reached the breakthrough point. Regenerating

Figure 4-16 The raw water and output water mean *E. coli* concentration of four bench scale BSFs during regeneration cycles.
exhausted BSF was investigated as well. By re-coating aluminum hydroxide onto exhausted
pumice, the BSF can be regenerated, but with low efficiency. In the end, a pilot scale BSF design
reference table was calculated by applying Bohart-Adams (BA) model.
CHAPTER 5
CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

As presented in Chapter 1, the overall objective of this dissertation study was to control the level of ammonia in aquaculture wastewater and adjust fluoride, turbidity, pH, and FIB level in drinking water by using adequate natural materials. To achieve this objective, this dissertation study was divided into two parts. Part I was about ammonia removal in aquaculture wastewater, which was detailed discussed in Chapter 3. Part II was related to the fluoride, turbidity, pH and FIB control in drinking water, which was discussed in Chapter 4.

Relative to Part I study, all the five tasks were successfully accomplished.

Task 1: Determine the ammonia accumulation rate in stored fish systems.

After a five-day in-vivo experiment, the ammonia accumulation rate for both freshwater and seawater fish was calculated in Table 3-4.

Task 2: Understand ion exchange mechanisms of ammonium removal.

The chabazite was selected as the ion exchanger. Characterization of chabazite shown that there were no structural changes of chabazite after being modified. Experimental kinetic data suggest that ammonium removal follows a pseudo-second-order reaction model. The diffusion model shows that film diffusion was dominant in the ammonium sorption in freshwater, while pore diffusion dominated ammonium sorption in seawater. The isotherm studies showed that nonlinear regression has the best fit for ammonia removal in both freshwater and seawater. The
Sips isotherm indicates that the ammonium adsorption was not a simple process that can be described by only one simplified isotherm.

**Task 3: Measure ammonia removal performance and establish a comparison between ion exchange and chemical neutralization.**

In freshwater, the chabazite imbedded ammonia adsorption bag (AmmoSorb) can efficiently control ammonia accumulation rate in both *in-vitro* and *in-vivo* trials. However, in seawater, the efficiency of AmmoSorb was inhibited by the other competing ions. However, for commercial water neutralizers, the *in-vivo* trials showed that they are not able to control ammonia levels in both freshwater and seawater. The novel neutralizer was found had high ammonia removal efficiency in both freshwater and seawater.

**Task 4: Analyze toxicity and cost of ion exchange and chemical.**

In terms of toxicity, the AmmoSorb can be considered non-toxic. To safe use the novel neutralizer, it was recommended to control its daily dose at 1 g/L/day followed by a two-third volume of water change every day. The cost analysis also showed that the novel neutralizer had the lowest cost.

**Task 5: Describe the mechanisms involved in the ion exchanger regeneration.**

In consideration of the amount of NaCl used as well as the regeneration efficiency, it was recommended to use 40g/L NaCl to regenerate the exhausted chabazite.

In terms of Part II study, all the four tasks were accomplished as well and concluded below.

**Task 1: Select filter material using fluoride adsorption batch tests.**

Sand and pumice was selected as the filter media, but only aluminum oxide coated pumice (AOCP) had the capability to remove fluoride. Experimental kinetic data shows that
fluoride adsorption by AOCP follows a pseudo-second-order reaction model. The isotherm studies showed that non-linear Sips model regression has the best fit for fluoride removal.

**Task 2: Apply the chosen materials to bench scale BSFs and determine a proper filter configuration.**

The AOCP embedded BSFs have two designs. BSF-H was a half-half design include 9 cm AOCP on top and 9 cm sand on the bottom. The BSF-S was a sandwich type with 6 cm AOCP in the middle and 6 cm sand on top and bottom side. According to the output water quality discussed in section 4.3.4, both BSF-H and BSF-S are suitable for the fluoride removal.

**Task 3: Apply models to provide scale-up parameters and conditions for a pilot scale BSF unit.**

The Bohart-Adams (BA) and Thomas models are found mathematically equivalent to each other. Both of them can describe BSFs at high accuracy. The BDST model can be used to predict the bed depth (m) with respect to the breakthrough time (min). To validate this model, we should perform more BSF designs with variances of AOCP layer depth. This part of the research will be put into future work.

**Task 4: Investigate a proper method to regenerate the exhausted BSF media.**

The BSF regeneration procedure was described in section 4.2.9, which include six steps:

1) Drain out the BSF before regenerating the column.

2) A 0.5M Al₂(SO₄)₃ was added to the column until overflow and let it sit overnight.

3) Drain out the Al₂(SO₄)₃ and wash the column with tap water for 10 times.

4) Add 3M NH₄OH to neutralize the pH.

5) Wash the column with tap water for 10 times.

6) The BSF was regenerated for use.
This dissertation made a contribution to the field of water/wastewater treatment area where the low-cost materials are in needed. In terms of the aquaculture wastewater field, we developed two simple drop-off products that are easy operation but can potentially extend fish lifetime. In terms of the drinking water field, the modified bench scale BSF can meet the requirement for drinking water standards not only in turbidity, pH, FIB but also in fluoride. Since previous researches rarely applied natural materials into a pilot or industrial applications as they were all limited in batch adsorption model. This dissertation research made a step forward to fulfill this gap.

5.2 Future Works

In spite of those contributions, there are still some future works worthing to point out. In Part I study, the fish was transported and stored in closed systems with saturated oxygen in it. However, in some cases, the oxygen supply might be limited. One possible way to solve this issue is to add ice to the system. As the solubility of oxygen increase with the decrease of water temperature. However, the ion exchange kinetic was found to decrease with the decrease of temperature (Tsai, Hsien, et al., 2009). This controversy drove us to think if the kinetics of chemical neutralization processes also have the same trend as ion exchange. It is worth to do future research on how to control the ammonia level at lower temperature circumstance.

In Part II study, a possible work for future to do is the BDST model validation. In Figure 4-11, only three data points were collected, so the degree of freedom is one. To have a valid linear regression, the rule of thumb for the number of degree of freedom should be no less than five, so minimum seven data points are needed in the BDST model. To fulfill the seven data points, it is recommended to perform five more bench scale BSF designs with a variance of
AOCP layer depth. The validation of BDST model can provide a reference table for scaling up the bench scale BSF in terms of the AOCP bed depth versus filter running days.
DISCLOSURE

The authors would like to disclose that they have filed a patent application that contained part of the work included in this dissertation (14B165PRC_Alcantar - Ammonia Removal in Freshwater and Saltwater Systems). In addition, the University of South Florida has licensed part of this work to Marine Metal Products, INC. (Alcantar_LIC17157; 17A048).
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