UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

AN INVESTIGATION OF SUSTAINABLE FLUORIDE WATER TREATMENT TECHNOLOGIES WITH A FOCUS ON ETHIOPIA

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

Degree of

DOCTOR OF PHILOSOPHY

By

LAURA R. BRUNSON
Norman, Oklahoma
2014

AN INVESTIGATION OF SUSTAINABLE FLUORIDE WATER TREATMENT TECHNOLOGIES WITH A FOCUS ON ETHIOPIA

A DISSERTATION APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

BY

Dr. David A. Sabatini, Chair

Dr. Lowell Busenitz

Dr. Elizabeth C. Butler

Dr. Robert C. Knox

Dr. Robert Nairn

This dissertation is dedicated to the women and children around the world that spend countless hours each day walking to collect water for their families.

Acknowledgements

None of this work would have been possible without the advice, support, encouragement, teaching, and mentoring of Dr. David Sabatini. Dr. Sabatini has served as my graduate adviser for over eight years. He encouraged me to come to OU for my graduate work and to pursue graduate degrees in Environmental Science even though I did not come from a science or engineering background. From Dr. Sabatini, I have learned technical aspects about engineering and science, as well as writing, leadership, and how to be a better human being. I will utilize the lessons I have learned from Dr. Sabatini throughout the rest of my life.

I would also like to thank Mrs. Frances Sabatini who has been a constant cheerleader throughout my graduate school experience. Thanks to Peggy Sabatini, who has been a graduate assistant in the lab for many years, and after our travels to Ethiopia, is like a little sister to me. Peggy and Frances have both provided countless laughs and encouragement.

Thank you to the additional committee members for this dissertation – Dr. Elizabeth Butler, Dr. Lowell Busenitz, Dr. Robert Knox, and Dr. Robert Nairn. These four faculty members have spent hours teaching me, both in their classes and through additional questions and paper reviews. I thank them for their time and guidance towards making the research stronger and making this a better dissertation.

I thank Dr. Andy Madden who trusted me to spend many hours in his lab using several pieces of characterization and measurement equipment. I thank him for his time teaching me how to use them. Thanks to Dr. Nairn and Dr. Zaman for the use of their microwave digestion equipment and high temperature oven, respectively.

I am very grateful for funding from the following sources: the Sun Oil Company Endowed Chair, the National Science Foundation Graduate Fellowship Program, the

Environmental Projection Agency Science To Achieve Results Fellowship Program, the OU WaTER Center, the Graduate College at the University of Oklahoma, and the College of Engineering at the University of Oklahoma.

I appreciate the helpful and generous assistance with funding paperwork, enrollment, logistics and much more from Molly Smith, Brenda Clouse, Susan Williams and Audre Carter in the College of Engineering.

The work done in rural Ethiopia could not have been done without the generous help of Catholic Relief Services Ethiopia, the Meki Catholic Secretariat, the Oromo Self Help Organization, CARE Ethiopia, Dr. Feleke Zewge, Teshome Lemma, Esayas Samual, Bekele Abaire, and most of all, Meseret Desalegn who was with us every step of the way during the several months of continuous flow column studies.

Many thanks to the undergraduate lab assistants who went above and beyond providing help with lab work which included endless washing of glassware and batch test bottles. I thank them also for their friendship and entertainment. Over the years my wonderful lab assistants were Peggy Sabatini, Tessa Blanchard, Erik Tichansky, Aislinn McLeod, Katie Heitman, and Peter Everest.

I am so appreciative of the support and encouragement and teaching that came from lab mates over the years. I learned so much from all of them in various ways about research and writing, lab equipment, and how to do posters and research presentations. Thanks to “Oat” Witthayapanyanon, Tri Pham, Linh Do, “Mink” Attaphong, Chris Cope, Hayley Ryckman, Damon Webster, Teshome Lemma, Junyi Du, Sezin Kadioglu, Anisha Nijhawan and others that came to visit for a short time, for the learning, fun and friendship-building times in the lab.

In great part, this PhD was made possible by the friends and family who prayed for me through presentations, papers, exams, and the final defense. I would like to specifically thank Virginia Tackett and Elda Shafer who were grandmas that weren’t here to see this dissertation come to a conclusion, but who provided numerous prayers during the years when they were still here. To my “Carla Mom”, Carla Walker who provides such thoughtful support, I thank you.

It is impossible to adequately thank the many friends and family that were with me throughout some or all of my graduate work. These loved ones provided laughs and fun, put up with my erratic schedule and lack of socializing, invited me for home-cooked meals, shared their homes and sometimes their kids (“Auntee Laura’s kids”), made me take research breaks, commiserated during failures or frustrations, celebrated successes, encouraged me, shared their lives with me and overall were there for me day and in day out for years. I am deeply grateful for the love, support and friendship of this wonderful group of people and I am lucky to have them in my life.

Table of Contents

Page

ACKNOWLEDGEMENTS..iv

TABLE OF CONTENTS……………………………………………………………vii

LIST OF TABLES……………………………………………………………........x

LIST OF FIGURES…………………………………………………………….xii

ABSTRACT…………………………………………………………………...xvi

CHAPTER 1 Introduction…………………………………………………...…1

Safe Drinking Water and Fluoride………………………………………………1

Fluoride Removal Technologies…………………………………………………2

Goal and Objectives……………………………………………………………..7

Overview of Chapters……………………………………………………………8

References……………………………………………………………………...10

CHAPTER 2 In Pursuit of Sustainable Water Solutions in Emerging Regions………16

Abstract……………………………………………………………………….....16

Introduction………………………………………………………………….....16

Implementation Challenges…………………………………………….............17

Sustainable Development………………………………………………………21

Social and Cultural Assessment………………………………………………..23

Market-based Implementation………………………………………………......26

Technology Development……………………………………………………...31

Sustainability Tools…………………………………………………………......32

Practical Implications………………………………………………………......33

Conclusion……………………………………………………………………...34

Acknowledgements…………………………………………………………......35

References……………………………………………………………………...35

CHAPTER 3 The Role of Surface Area and Surface Chemistry during an Investigation of Eucalyptus Wood Char for Fluoride Adsorption from Drinking Water……………………………………………………………………………43

Abstract…………………………………………………………………………43

Background……………………………………………………………………..44

Materials and Methods…………………………………………………………49

Results and Discussion…………………………………………………………52

Conclusion……………………………………………………………………...64

Acknowledgements…………………………………………………………….65

References……………………………………………………………………...66

CHAPTER 4 Practical Considerations, Column Studies and Natural Organic Material Competition for Fluoride Removal with Bone Char and Aluminum Amended Materials in the Main Ethiopian Rift Valley……..…………………………72

Abstract…………………………………………………………………………72

Introduction…………………………………………………………………….73

Methods………………………………………………………………………...78

Results and Discussion…………………………………………………………81

Conclusion……………………………………………………………………...95

Acknowledgements…………………………………………………………….96

References……………………………………………………………………...96

CHAPTER 5 Methods for Optimizing Activated Materials for Fluoride Removal from Drinking Water Sources…...104

Abstract…104

Introduction...…105

Materials and Methods…..110

Results and Discussion…..114

Conclusion…135

Acknowledgements…...136

References…137

CHAPTER 6

Conclusions..…142

APPENDICES

Appendix A: Fluoride Removal by Bone and Wood Chars…..149

Appendix B: Competing Ions…151

Appendix C: Iron Oxide Amendments…..152

List of Tables

Page

2.1 Examples of water projects in developing countries and possible improvements that could increase sustainability. Text in grey indicates projects with a high level of success……………………………………..19-20

2.2 Tasks that fall into each component of synergistic research towards developing sustainable research and water access or treatment implementations…………………………………………………………..23

3.1 Freundlich constants calculated from batch tests investigating fluoride removal of aluminum amended and unamended wood and bone chars………..54

3.2 Specific surface area and pH_{PZC} of aluminum amended, reducing agent modified and unamended eucalyptus wood and bone chars at various charring temperatures………………………………………………………..…56

3.3 Freundlich constants calculated from batch tests investigating fluoride removal of bone and wood chars modified with reducing agents and amended with aluminum or unamended. In all cases 1/n values have been forced to a common values so K_f constants can be statistically compared…….61

4.1 Q_e data for six media evaluated in batch isotherm studies……………………..82

4.2 Q_e in mg of fluoride removed per gram of material calculated based on the amount of fluoride removed during the continuous flow column study run to saturation ($C_{effluent} = C_{influent}$). The bed volumes to $C_{eff} = 1.5$ mg/L obtained using the data presented in 4.1. Using the Langmuir equation both the Langmuir Qm and the Q_e value at 8.6 equilibrium fluoride concentration are presented…………………………………………………….86

4.3 Results of batch isotherms studying fluoride removal with and without the presence of sulfate and natural organic material in solution……………….93

5.1 Freundlich and Langmuir Constants and $Q_{e1.5}$ data obtained using batch isotherm data for wood char alone and metal oxide amended wood char…………………………………………………………………..116

5.2 Freundlich and Langmuir Constants obtained using batch isotherm data for untreated, amended and pretreated wood chars……………………...119

5.3 Metal loading, specific surface area and surface chemistry characteristics of all materials tested…………………………………………………………124

C-1: Results of preliminary iron oxide amendment tests conducted on wood char with variations in amendment time, concentration and method…..……..…………152

List of Figures

Page

2.1 Diagram showing the three discussed areas crucial to successful implementation, their overlap where a sustainable outcome should be obtained, and their embedding in a broader systems perspective (the enabling environment)……………………………………………………….22

3.1 The equilibrium fluoride concentration, C_e, in mg/L (x-axis) versus mg of fluoride removed per gram of material, Q_e, (y-axis) for both aluminum amended and unamended eucalyptus wood chars……………………………...55

3.2 Bar graph shows specific surface area (m^2/g) (left y-axis) and line graph shows the pH_{PZC} (right y-axis) while charring temperature for both aluminum amended and unamended eucalyptus wood chars is shown on the x-axis.…………………………………………………………...57

4.1 Results of continuous flow columns studies where the x-axis shows bed volumes and the y-axis shows effluent fluoride concentrations in mg/L. 4.1A. Lab studies where the influent pH (unadjusted) was approximately 6.0 and the solution was fluoride in deionized water. 4.1B. Field studies using native groundwater with an influent pH of approximately 8.2 ......………………83-84

4.2 Graph shows results of continuous flow columns studies where the x-axis shows bed volumes and the Y axis shows effluent fluoride concentration in mg/L. Influent fluoride concentration was 8.6 mg/L and pH and competing ions vary as stated in the key…………………………………………………...89

4.3 Graph shows results of rapid small scale column tests where the x-axis shows bed volumes and the y-axis shows effluent fluoride concentration in mg/L. Columns have volumes of 34.9 and 7.9 cm3 and average particle sizes of 637 and 302 µm , for large and small scale respectively. Starting concentration and flow rate were equivalent for both at 8.6 mg/L fluoride and 1.2 ml/min……………………………………………………………94

5.1 Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars. Q_e, the mg of fluoride removed per gram of media is plotted against C_e, the equilibrium concentration of fluoride in mg/L……………………………………………..115

5.2 Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars with and without pretreatment (KM = potassium permanganate, HP = hydrogen peroxide). Figure 5.2A shows results of wood char treated with aluminum sulfate and Figure 5.2B shows results of wood char treated with iron (III) chloride. Q_e, the mg of fluoride removed per gram of media is plotted against C_e, the equilibrium concentration of fluoride in mg/L…………..117-118

5.3 Results of material analysis where 5.3A shows metal loading percentages, 5.3B shows point of zero charge values and 5.3C shows specific surface area data. Numbers above the bars in each graph note the $Q_{e1.5}$ values for that media……………………………………………………...……122-123

5.4 Data shows the fluoride removal capacities of untreated wood char and metal oxide amended wood chars (WC), with and without pretreatment, (KM = potassium permanganate, HP = hydrogen peroxide) normalized by metal content. 5.4A shows results of wood char treated with aluminum sulfate, 5.4B shows wood char treated with aluminum chloride, 5.4C shows wood char treated with iron (III) nitrate with the inset graph showing the data only up to C_e = 5 and 5.4D shows wood char treated with iron (II) chloride. The y-axis shows, Q_e/metal %, the mg of fluoride removed per gram of media normalized by metal content, and is plotted against C_e, the equilibrium concentration of fluoride in mg/L……………….……...127-129

5.5 Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars normalized by both specific surface area and metal content. Q_e, the mg of fluoride removed per gram of media is normalized by specific surface area and metals content (mg fluoride * g char/g metal * m^2) and plotted against C_e, the equilibrium concentration of fluoride in mg/L………………..134

A-1 Graph shows adsorption isotherms of fluoride removal by *Ximenia americana* (XA) and *Eucalyptus robusta* (EU) wood chars amended with aluminum oxides, plotting fluoride levels adsorbed by the chars (Q_e, mg fluoride/g wood char) versus equilibrated aqueous fluoride concentration (C_e, mg/L)……………………………………….…149

A-2 Graph shows adsorption isotherms of fluoride removal by fish and bone chars and aluminum oxide amended fish and bone chars, plotting fluoride levels adsorbed by the chars (Q_e, mg fluoride/g wood char) versus equilibrated aqueous fluoride concentration (C_e, mg/L)…………….....150

B-1 Adsorption isotherms of fluoride on fish bone char (FBC), with competing ions sulfate (SO_4) and phosphate (PO_4) present in some systems as noted in the legend. The y-axis shows fluoride levels adsorbed by the fish bone char (Q_e, mg fluoride/g fish bone char) and the x-axis shows equilibrated aqueous fluoride concentration (C_e, mg/L)…....151

.

Abstract

Human consumption of unsafe drinking water from an unimproved source is a global issue affecting approximately 748 million people worldwide. While this number has been decreasing in recent years, an additional 1.2 billion people are estimated to lack access to water that is consistently free from health risks. This dissertation begins with a literature review investigating drinking water improvement initiatives around the world and a discussion of reasons why these initiatives often fail. Resources are provided for researchers and practitioners working on drinking water treatment implementations and examples of implementations that have failed or succeeded are discussed. The conclusion from this review is that global drinking water solutions will be more effective when designed and implemented by personnel from multiple disciplines. For example, people in several fields, including: social sciences, engineering and business, should collaborate and share ideas and expertise. Ideally this collaboration should start at the genesis of a project and continue through implementation and follow up. There is hope that the synergistic efforts of multidisciplinary teams will help to increase the number of successful water initiatives.

Next the dissertation focuses on the problem of elevated fluoride concentrations in drinking water. Naturally occurring fluoride is the second largest issue contributing to the global water crisis. It is estimated that globally over 200 million people are affected by elevated concentrations of fluoride in drinking water. The goal of the technical portion of this dissertation is to investigate locally available and sustainable materials that can be used to remove fluoride from drinking water, with a focus on Ethiopia and eastern Sub-Saharan Africa. Bone char is very effective as an adsorptive material, but is not always accepted by communities due to religious or cultural beliefs. Therefore, this research evaluated methods to improve the fluoride removal capacity of bone char as well as investigated materials that might serve as a replacement for bone char in appropriate communities. Eucalyptus trees are prevalent in Ethiopia where a large fluoride problem exists, and thus, eucalyptus wood char was investigated as a potential substitute for bone char. This dissertation studied wood char produced from *Eucalyptus robusta* as an adsorption material to remove fluoride from water, thereby making it safe for consumption. Although the use of eucalyptus wood char alone removed minimal fluoride, when it was amended with aluminum and iron oxides it evidenced much higher fluoride removal capacities. Metal oxides, produced from starting materials such as aluminum sulfate and iron (III) nitrate, were used to amend the wood char. Metal amendments resulted in fluoride removal capacities ranging from 3 to 50 times higher than wood char without amendment. The combination of wood char and metal oxide amendment is synergistic because the wood char provides a matrix with a high specific surface area for the metal oxides to adhere to while the metal oxide amendment increases the electrostatic attraction of the char surface for fluoride. Additionally, wood char was pretreated with oxidizing agents such as hydrogen peroxide and potassium permanganate prior to metal amendment. These pretreated and metal amended chars were found, in most cases, to have increased metal loading rates and, in some cases, higher fluoride removal capacities.

This dissertation also looked at ways to improve the adsorption effectiveness of bone char for communities where bone char is an acceptable material for drinking water treatment. Amending bone char with aluminum nitrate showed an increase in fluoride removal at high equilibrium concentrations but not at low equilibrium concentrations close to the WHO recommended value for fluoride (1.5 mg/L). Select fluoride removal materials, including aluminum impregnated wood char, activated alumina, bone char and aluminum amended bone char, were studied in the field using groundwater from a well in a rural Ethiopian community. Field results suggested that the combination of elevated groundwater pH along with competing ions such as sulfate (both common in ground waters of the Ethiopian Rift Valley) affected the fluoride removal capacities of the materials studied, particularly the aluminum impregnated wood char. Finally, this research tested the validity of the Rapid Small Scale Column Tests (RSSCT) principles for bone char adsorbing fluoride from water. These experiments indicated that RSSCT principles are applicable for bone char; use of this approach can result in large time and cost savings to researchers and implementers. Overall, this dissertation provides several conclusions that are practically helpful to researchers in the field and also foundational research on which future studies can build to continue efforts to find sustainable and appropriate fluoride removal technologies.

CHAPTER 1

Introduction

Safe Drinking Water and Fluoride

Lack of safe drinking water is a key global issue. The World Health Organization (WHO) and the United Nations International Children's Emergency Fund (UNICEF) estimate that 748 million people currently lack access to an improved water source (WHO and UNICEF, 2014). Onda et al. (2012) suggested that in addition to the 748 million people without an improved water source, another 1.2 billion people may be consuming water from sources that are improved but still at risk for microbial contamination. Lack of safe water is further exacerbated by the reality that 1.4 billion people are estimated to live on less than $1.25 (US) per day (Chen and Ravallion, 2008). In addition, water-related health issues contribute to concerns such as lack of education, gender equity and economic development. To mitigate these drinking water issues, sustainable, inexpensive and locally available water treatment technologies must be developed, improved and implemented.

After pathogens, the largest issue contributing to lack of safe drinking water is naturally occurring fluoride, which is estimated to affect 200 million people globally (Amini et al., 2008). The WHO recommended fluoride limit in drinking water is 1.5 mg/L (World Health Organization, 2011). Fluoride is naturally occurring in the groundwater of many areas of the world including: the Rift Valley of Africa, portions of China and India and parts of the southwestern United States (Brindha et al., 2010; Fewtrell et al., 2006; Meenakshi and Maheshwari, 2006; Nigussie et al., 2007).

Although fluoride is naturally occurring in groundwater, it can also occur due to anthropogenic processes such as aluminum smelting and fertilizer production (Hem, 1985; Hudak, 2008). Fluoride is an example of an element where the dose consumed determines whether it is beneficial or toxic. In low doses fluoride helps to prevent dental carries and, thus, improves the health of teeth (Fawell et al., 2006; Schamschula and Barmes, 1981). However, consumption of higher concentrations can be harmful as it causes dental and skeletal fluorosis (Fawell et al., 2006; Gazzano et al., 2010). Dental fluorosis results in darkening or mottling of teeth, which, while not physically debilitating, can cause social and financial issues due to the stigma of mottled teeth. Skeletal fluorosis can cause bones to become deformed or stiff which can limit mobility and/or cause pain (Kaseva, 2006; Meenakshi and Maheshwari, 2006). Therefore, many researchers are investigating fluoride removal technologies (Abe et al., 2004; Ayoob et al., 2008; Gwala et al., 2011; Nigussie et al., 2007).

Fluoride Removal Technologies

Water treatment methods frequently investigated for fluoride removal include: precipitation, ion exchange, electrocoagulation, and adsorption (Brunson and Sabatini, 2009; Gwala et al., 2011; Kamble et al., 2007; Meenakshi and Maheshwari, 2006; Rao, 2003; Tchomgui-Kamga et al., 2010). For rural regions in developing countries, techniques should be inexpensive, sustainable and use locally available materials for treating water containing high concentrations of fluoride. The Nalgonda technique utilizes alum and lime to produce aluminum oxide precipitates that sorb and settle fluoride ions. This technique is popular because of its low cost and use of chemicals that are easily obtained. However, the Nalgonda technique requires frequent addition of chemicals, produces copious amounts of waste sludge, and is not efficient for fluoride removal when the starting concentration is high (Fawell et al., 2006; Nigussie et al., 2007). While electrocoagulation can effectively remove fluoride, it requires some form of electricity (Gwala et al., 2011). Activated alumina is an adsorptive material frequently used in filtration systems. Adsorption can be helpful for fluoride removal because it operates using gravity flow, and, depending on the sorptive material, can be effective at treating water to meet the WHO fluoride standard. Activated alumina can be effective, but is a manufactured material that may be prohibitively expensive to obtain in rural developing regions. Therefore, research evaluating less expensive and locally available adsorptive materials is desirable in an effort to respond to the limitations of techniques discussed above.

Bone char has been widely investigated as an adsorptive material for removal of fluoride and several trace metals (Bhargava and Killedar, 1991; Kaseva, 2006; Larsen et al., 1994; Thomson et al., 2003). Bone char is primarily composed of hydroxyapatite (70-76%) and carbon (8-11%) and is currently produced in several developing countries from waste bones, which makes it relatively inexpensive (Medellin-Castillo et al., 2007; Müller, 2007; Purevsuren et al., 2004; Wilson et al., 2003). Charring animal bones removes organic matter from the bone structure, producing a large specific surface area which is helpful for high adsorption capacity (Chidambaram et al., 2004; Kaseva, 2006). For example, Medellin-Castillo et al. (2007) reported a specific surface area of 104 m^2/g for their tested bone char. This is similar to levels reported by others, such as 150 m^2/g (Chen et al., 2008) and 105 m^2/g (Brunson and Sabatini, 2009). Variations in specific surface area can be attributed to char source, type of bones and preparation method. Bone char also exhibits favorable surface chemistry with Medellin-Castillo et al. (2007) and Brunson and Sabatini (2009) both finding the point of zero charge (pH_{PZC}) of bone char to be close to 8.3. In solutions with pH values below the pH_{PZC}, the bone char surface will exhibit a positive charge, while at solution pH values above the pH_{PZC} the material will exhibit a negative charge. Thus, for fluoride removal occurring in groundwater with near neutral pH values, a material with a high pH_{PZC} will evidence a positive surface charge which will attract negatively charged fluoride ions. Despite its favorable surface chemistry and effective fluoride removal, bone char is not accepted in some communities due to religious and cultural reasons or poor quality of char production (Fawell et al., 2006), leading to the need for alternate materials.

New research investigating the potential for using a carbon-based material, such as wood char, as an adsorption material is helpful for locations where bone char is not accepted. Wood is typically composed of carbon (50%), oxygen (44%), hydrogen (6%) and trace amounts of metals (Pettersen, 1984; Rowe and Conner, 1979). However, the chemical composition and other characteristics of wood can vary based on location, soil type, season, age and type of wood (Pettersen, 1984). The specific surface area of wood char is shown to differ greatly depending on charring conditions, wood type and location of wood growth. For example, James et al. (2005) showed wide ranges of specific surface area for wood chars produced in laboratory conditions, ranging from 1.0 to 397 m^2/g, and different kinds of wood charred in nature, ranging from 1.7 to 85 m^2/g. Although wood char in some cases exhibits a high surface area, a study by Abe et al. (2004) showed that bone char has a much higher fluoride removal capacity than several tested wood chars. Therefore, methods are needed to improve the fluoride removal capacity of wood chars.

Metal amendments have shown promise as one way to improve the fluoride removal capacity of wood chars. For example, studies have shown promising results for removing fluoride with aluminum or iron-based precipitates. Levya-Ramos et al. (1999) found that impregnating activated carbon with aluminum greatly improved the fluoride removal capacity. A material produced from aluminum and iron was studied by Biswas et al. (2007) and results showed a maximum removal value of 18 mg of fluoride removed per g of material as calculated by the Langmuir equation. The success of fluoride adsorption by metal amendments is attributed to the attraction between the negatively charged fluoride ions and the positively charged metal oxide surfaces, resulting in ion exchange between fluoride and hydroxide ions on the material surface. While bone char has previously shown a high fluoride removal capacity, it is not reaching the removal effectiveness of some of the aluminum/iron based materials discussed above, which means it may be useful to investigate ways of enhancing fluoride uptake with bone char.

A final approach of interest is pretreating charred media with either oxidizing or reducing agents to alter their surface chemistry. Pretreatment methods could be invaluable for their effects on surface chemistry. Polovina et al. (1997) suggested this is one of the most important aspects of an adsorption material. There are several potential effects of pretreating char media. One is that pretreatment of media with reducing agents may remove some acidic functional groups from the surface of the materials, which would increase the basicity of the media and, thus, increase the pH_{PZC} values.

This change in pH_{PZC} should increase the attraction between the media and fluoride ions without the requirement of metal amendments. Minimal work has been done in this area. One study was conducted where activated carbon was treated with iron ammonium sulfate and sodium dithionite to enhance removal of hexavalent chromium from water. While the study by Han et al. (2000) did not show success with increased hexavalent chromium removal, their preliminary work laid the foundation for the current research seeking to enhance fluoride removal. A second potential effect is that pretreating the materials with oxidizing agents may add acidic functional groups to the surface. This should enhance the loading of metals onto the chars and potentially increase fluoride removal. A few researchers have evaluated oxidation pretreatment with various carbon-based materials. One study was done to assess whether treatment with oxidizing agents could alter the lead adsorption capacity of coconut-based activated carbon (Song et al., 2010). The results demonstrated that lead adsorption onto the treated activated carbon increased significantly while the surface area changed minimally and the pH_{PZC} decreased. It was shown that oxidation using boiling nitric acid increased the acidic oxygen-based functional groups, such as carboxyl and phenol, on the surface of activated carbon in work done by Liu et al. (2007) and Polovina et al. (1997). This increase in acidic functional groups is likely the cause of the decrease in pH_{PZC} resulting from oxidation pretreatment. One impetus for the idea that pretreatment with oxidizing agents will increase metal loading comes from a study where a lignite-based activated carbon was modified with iron and then used to remove arsenic (Hristovski et al., 2009). In this study, two methods for treating the starting material were compared. One method used an alcohol and iron mixture and the other utilized pretreatment with an oxidizing agent, potassium permanganate, followed by iron amendment. The material pretreated with potassium permanganate resulted in both higher iron loading and a higher arsenic removal capacity (Hristovski et al., 2009).

Goal and Objectives

The goal of this dissertation is to investigate fluoride removal technologies in both laboratory and field settings in order to contribute new information to the area of fluoride removal for greater availability of safe drinking water and water point sustainability. Based on previous work and gaps in research the objectives of this dissertation are to:

1. Present a review of the global failure in implementing safe drinking water initiatives that exhibit long-term viability and develop ideas for increasing the sustainability of these initiatives (Chapter 2).
2. Assess the possibility of wood char as a fluoride adsorption substitute for bone char (Chapters 3 and 5).
3. Investigate ways to improve the fluoride removal capacity and implementation of bone char (Chapters 3 and 4).
4. Conduct continuous flow field tests on amended and unamended bone and wood chars (Chapter 4).
5. Evaluate methods for amending wood char with aluminum and iron oxides and assess the subsequent fluoride removal capacities (Chapters 3, 4, and 5).
6. Test the hypothesis that pretreating wood char with oxidizing agents will decrease the pH_{PZC} and increase metal loading onto the char (Chapter 5).

Overview of Chapters

Chapter 2 reviews literature on the lack of long-term sustainability in water treatment or supply systems implemented in the developing world. This chapter discusses past successes and failures and recommends resources to help researchers and practitioners within the water community achieve sustainable solutions. The chapter concludes with the suggestion that development and implementation of water treatment and supply points should not be done only by engineers or, for that matter, any individual field of study, but instead should be a collaborative effort among diverse groups such as engineers, business people and social scientists. This collaboration allows a multitude of ideas, methods and areas of expertise to synergistically develop solutions that are more sustainable over time.

Chapter 3 presents an investigation of wood char, specifically *Eucalyptus robusta,* as a possible substitute for bone char as an adsorption material for areas not amenable to using bone char. Eucalyptus wood was charred at temperatures ranging from 300 – 600 °C and fluoride removal capacity was tested to find the most effective charring temperature. While the results showed that 600 °C was the most effective charring temperature for fluoride removal, all of the wood chars were minimally effective despite the high specific surface area and pH_{PZC} values, approximately 320 m^2/g and 9.6, respectively, at 600 °C. Several experiments were conducted to assess the potential to improve the fluoride removal capacity of the wood char. In one test wood char was amended with aluminum nitrate and in another it was pretreated with reducing agents. The early-stage work with reducing agents did not show promising results and thus, this was not further investigated. On the other hand, the aluminum nitrate amendment resulted in over 400 % improvement from the low starting fluoride removal capacity of the wood char alone, although still not reaching the removal capacity of bone char.

Chapter 4 delved further into aluminum amendment of wood char and also added the study of iron oxide amendment in pursuit of wood chars with higher fluoride removal capacities. Both aluminum and iron oxide amendment of wood char were found to increase the fluoride removal capacities while decreasing the pH_{PZC}. One of the iron oxide amendments provided the largest increase in fluoride removal; however, it also showed the largest decrease in specific surface area after amendment and therefore, was the least efficient when fluoride removal was normalized by metal loading. This research also assessed pretreatment of wood char with oxidizing agents and found that in several cases, pretreatment increased metal loading onto wood char and, for some pretreated and amended chars, fluoride removal capacities also increased.

Chapter 5 evaluated fluoride uptake by several materials, including two discussed in Chapter 3, one produced by an alternative aluminum impregnation method, and one that is prevalently used for fluoride removal. Based on isotherm batch tests, these materials were selected for field study in the Rift Valley of Ethiopia. This field work was done to determine and better understand any differences between material performance in a realistic field setting versus a laboratory setting. These studies utilized both batch and continuous flow column studies and assessed whether natural organic matter in groundwater would compete with fluoride for removal on adsorption materials. Competing ions and groundwater pH were shown to impact fluoride removal capacities. In addition, the Rapid Scale Small Column Test approach was shown to apply for fluoride uptake with bone char.

Chapter 6 reviews the key findings of this dissertation relative to technologies for fluoride removal from drinking water and implementation of safe water initiatives in a sustainable way.

References

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., and Tanada, S. (2004). "Adsorption of fluoride ions onto carbonaceous materials." *J. Colloid Interf. Sci.* 275(1), 35–39.

Amini, M., Mueller, K., Abbaspour, K., Rosenberg, T., Afyuni, M., Møller, K., Sarr, M., and Johnson, A. (2008). "Statistical modeling of global geogenic fluoride contamination in groundwaters." *Environ. Sci. Technol.* 42(10), 3662–3668.

Ayoob, S., Gupta, A. K., and Bhat., V.T. (2008). "A conceptual overview on sustainable technologies for the defluoridation of drinking water." *Crit. Rev. Environ. Sci. Technol.* 38(6), 401–470.

Bhargava, D., and Killedar, S. (1991). "Batch studies of water defluoridation using fishbone charcoal." *Res. J. Water Pollut. Control Fed.* 63(6), 848–858.

Biswas, K., Saha, S., and Gosh, U. (2007). "Adsorption of fluoride from aqueous solution by a synthetic iron(III)−aluminum(III) mixed oxide." *Indust. Eng.Chem. Res.* 46(16), 5346–5356.

Brindha, K., Rajesh, R., Murugan, R., and Elango, L. (2010). "Fluoride contamination in groundwater in parts of nalgonda district, Andhra Pradesh, India." *Environ. Monitor. Assess.* 172(1-4), 481–492.

Brunson, L.R., and Sabatini, D.A. (2009). "An evaluation of fish bone char as an appropriate arsenic and fluoride removal technology for emerging regions." *Environ. Eng. Sci.* 26(12), 1777–1784.

Chen, S., and Ravallion, M. (2008). *The developing world is poorer than we thought, but no less successful in the fight against poverty*. Policy Research Working Paper, World Bank Development Research Group, Washington, D.C.

Chen, Y., Chai, L., and Shu, Y. (2008). "Study of arsenic (V) adsorption on bone char from aqueous solution." *J. Hazard. Mater.* 160(1), 168–172.

Chidambaram, S., Ramanathan, A., and Vasudevan, S. (2004). "Fluoride removal studies in water using natural materials." *Water SA*, 29(3), 339–344.

Fawell, J., Bailey, K., Chilton, J., and Dahi, E. (2006). *Fluoride in Drinking-Water*. World Health Organization, Geneva, Switzerland.

Fewtrell, L., Smith, S., Kay, D., and Bartram, J. (2006). "An attempt to estimate the global burden of disease due to fluoride in drinking water." *J. Water Health*, 4(4), 533–542.

Gazzano, E., Bergandi, L., Riganti, C., Aldieri, E., Doublier, S., Costamagna, C., Bosia, A., and Ghigo, D. (2010). "Fluoride effects: the two faces of Janus." *Current Med. Chem.* 17(22), 2431–2441.

Gwala, P., Andey, S., Mhaisalkar, V., Labhasetwar, P., Pimpalkar, S., and Kshirsagar, C. (2011). "Lab scale study on electrocoagulation defluoridation process optimization along with aluminium leaching in the process and comparison with full scale plant operation." *Water Sci. Technol.* 63(12), 2788–2795.

Han, I., Schlautman, M., and Batchelor, B. (2000). "Removal of hexavalent chromium from groundwater by granular activated carbon." *Water Environ. Res.* 72(1), 29–9.

Hem, J. D. (1985). *Study and interpretation of the chemical characteristics of natural water*. U.S. Geological Survey, Reston, VA.

Hristovski, K., Westerhoff, P., Moller, T., and Sylvester, P. (2009). "Effect of synthesis conditions on nano-iron (hydr) oxide impregnated granulated activated carbon." *Chem. Eng. J.* 146(2), 237–243.

Hudak, P. (2008). "Elevated fluoride and selenium in west Texas groundwater." *Bull. Environ. Contam. Tox.* 82(1), 39–42.

James, G., Sabatini, D., Chiou, C., Rutherford, D., Scott, A., and Karapanagioti, H. (2005). "Evaluating phenanthrene sorption on various wood chars." *Water Res.* 39(4), 549–558.

Kamble, S., Jagtap, S., Labhsetwar, N., Thakare, D., Godfrey, S., Devotta, S., and Rayalu, S. (2007). "Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan." *Chem. Eng. J.* 129(1-3), 173–180.

Kaseva, M. (2006). "Optimization of regenerated bone char for fluoride removal in drinking water: A case study in Tanzania." *J. Water Health*, 4(1), 139–147.

Larsen, M., Pearce, E., and Ravnholt, G. (1994). "The effectiveness of bone char in the defluoridation of water in relation to its crystallinity, carbon content and dissolution pattern." *Arch. Oral Biol.* 39(9), 807–816.

Levya-Ramos, L. R., Ovalle-Turrubiartes, J., and Sanchez-Castillo, M. A. (1999). “Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon.” *Carbon*, 37(4), 609–617.

Liu, S. X., Chen, X., Chen, X. Y., Liu, Z. F., and Wang, H. L. (2007). “Activated carbon with excellent chromium(VI) adsorption performance prepared by acid-base surface modification.” *J. Hazard. Mater.* 141(1), 315–319.

Medellin-Castillo, N., Leyva-Ramos, R., Ocampo-Perez, R., Garcia de la Cruz, R., Aragon-Piña, A., Martinez-Rosales, J., Guerrero-Coronado, R., and Fuentes-Rubio, L. (2007). “Adsorption of fluoride from water solution on bone char.” *Indust. Eng. Chem. Res.* 46(26), 9205–9212.

Meenakshi, and Maheshwari, R. C. (2006). “Fluoride in drinking water and its removal.” *J.Hazard.Mater.* 137(1), 456–463.

Müller, K. (2007). “CDN’s experiences in producing bone char.” P. Jacobsen, ed. CDN Water Quality and Eawag, Switzerland.

Nigussie, W., Zewge, F., and Chandravanshi, B. S. (2007). “Removal of excess fluoride from water using waste residue from alum manufacturing process.” *J. Hazard. Mater.* 147(3), 954–963.

Onda, K., LoBuglio, J., and Bartram, J. (2012). “Global access to safe water: Accounting for water quality and the resulting impact on MDG progress.” *Int. J. Environ. Res. Public Health*, 9(3), 880–894.

Pettersen, R. (1984). “The chemical composition of wood.” *The Chemistry of Solid Wood*, R. M. Rowell, ed. American Chemical Society, Washington D.C.

Polovina, M., Babić, B., Kaluderović, B., and Dekanski, A. (1997). “Surface characterization of oxidized activated carbon cloth.” *Carbon*, 35(8), 1047–1052.

Purevsuren, B., Avid, B., Narangerel, J., Gerelmaa, T., and Davaajav, Y. (2004). “Investigation on the pyrolysis products from animal bone.” *J. Mater. Sci.* 39(2), 737–740.

Rao, N. C. R. (2003). “Fluoride and environment - a review.” *Proceedings of the Third International Conference on Environment and Health*, Chennai, India, 386–399.

Rowe, J. W., and Conner, A. H. (1979). *Extractives in eastern hardwoods - a review*. Forest Products Laboratory - U.S. Department of Agriculture, Madison, WI.

Schamschula, R. G., and Barmes, D. E. (1981). “Fluoride and health: dental caries, osteoporosis, and cardiovascular disease.” *Ann. Rev. Nutr.* 1(1), 427–435.

Song, X., Liu, H., Cheng, L., and Qu, Y. (2010). “Surface modification of coconut-based activated carbon by liquid-phase oxidation and its effects on lead ion adsorption.” *Desalination*, 255(1-3), 78–83.

Tchomgui-Kamga, E., Alonzo, V., Nanseu-Njiki, C. P., Audebrand, N., Ngameni, E., and Darchen, A. (2010). “Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water.” *Carbon*, 48(2), 333–343.

Thomson, B. M., Smith, C. L., Busch, R. D., Siegel, M. D., and Baldwin, C. (2003). “Removal of metals and radionuclides using apatite and other natural sorbents.” *J.Environ. Eng.* 129(6), 492–499.

World Health Organization and UNICEF. (2014). *Progress on drinking water and sanitation - 2014 update*. World Health Organization, Geneva, Switzerland.

Wilson, J. A., Pulford, I. D., and Thomas, S. (2003). "Sorption of Cu and Zn by bone charcoal." *Environ. Geochem. Health*, 25(1), 51–56.

CHAPTER 2

In Pursuit of Sustainable Water Solutions in Emerging Regions[1]

Abstract

While lack of access to consistent safe drinking water is estimated to affect nearly 2 billion people worldwide, many of the efforts to solve this crisis have proven to be unsustainable. This paper discusses some of the reasons for these challenges and suggests interdisciplinary practices that could be integrated from the very beginning of a water intervention to achieve long-term success. Of key importance for sustainable water implementation is an enabling environment that incorporates aspects such as funding, potential for market development, and supportive governance. While this enabling environment is acknowledged, the focus of this work is on the integration of three key areas: (i) social and cultural assessment of behavior and preferences; (ii) market-based implementation approaches that draw on this knowledge; and (iii) technology development for these markets.

Introduction

The World Health Organization (WHO) and United Nations International Children's Emergency Fund (UNICEF) estimate that 780 million people lack access to improved water sources (WHO and UNICEF, 2012). WHO and UNICEF (2012) also acknowledge that not all water from improved sources is safe for consumption; an estimated 1.2 billion people consuming water from improved sources are still exposed

---

[1] Brunson, L.R., Busenitz, L., Sabatini, D.A. and Spicer, P.G. (2013) "In Pursuit of Sustainable Water Solutions in Emerging Regions." J. Water, Sanitation Hygiene for Development. 3(4), 489 – 499.

to potential health risks from water (Onda et al., 2012). Pursuit of safe drinking water is further complicated by the fact that 1.4 billion people are living on less than US$1.25 per day, thus increasing the challenge of getting safe drinking water to many communities (United Nations, 2009).

The focus of this paper is on the development and implementation of sustainable drinking water solutions for emerging regions. While there are some important overlaps with sanitation, we focus here on safe drinking water since the proposed market solutions we explore are, to some extent, unique to this issue. We acknowledge that improved sanitation plays an important role in access to safe drinking water and that some of the ideas and tools presented in this work are equally applicable to sanitation but because of boundary and space constraints, we only address safe drinking water issues here. We encourage others to extend the ideas presented here to the sanitation sector.

Implementation Challenges

In response to the lack of safe drinking water, numerous governmental, university and humanitarian organizations have attempted to implement solutions ranging from point-of-use (POU) household treatment systems to piped community-scale projects. Despite these good intentions, sustainable water solutions are often not realized and many challenges still remain. Furthermore, global data on long-term successes and failures are frequently unavailable because of the expense and challenge of achieving high-quality, long-term monitoring (Onda et al., 2012;

WHO and UNICEF, 2012). Nevertheless, available data and observations indicate that the water issue is far from solved, in part because of the premature failure of water schemes (Foster, 2012; Hunter et al., 2010). For example, over the past 20 years an estimated US$1.2 billion have been ‘lost’ because of wells that have failed prematurely in sub-Saharan Africa (Schouten and de Jong, 2009).

There are many reasons why water systems fail in developing countries. One reason is that solutions may not be culturally appropriate or are not selected based on local preferences and practices, which makes it unlikely that the community will readily adopt and/or sustain them (Hokanson et al., 2007; Skinner, 2009). For example, if a society believes drinking warm water causes illness then setting up a system that, intentionally or unintentionally, results in warm drinking water may produce water that is safe but is deemed unacceptable by the community (Wellin, 1955; Rogers, 2003). Some problems are technology related such as when hardware fails or a filter clogs (Hankin, 2001; Mackintosh and Colvin, 2003; Burr et al., 2012). Another common cause of failure is missing or ineffective supply chains for breakable parts, necessary chemicals, or replacement filtration media, or when there is a lack of human capital for maintenance and repairs (Diergaardt and Lemmer, 1995; Oyo, 2006; Clasen, 2009; Hirn, 2012). Other frequently mentioned causes of failure include lack of education on the importance of the safe water scheme (Hokanson et al., 2007), minimal capacity and ownership of the intervention in the community (Breslin, 2003; Skinner, 2009), aesthetic issues such as taste or smell of the treated water (Diergaardt and Lemmer, 1995; Hoque et al., 2004; Wood et al., 2012), disruption of daily routine (e.g. time or inconvenience) (Hoque et al., 2004; Gupta et al., 2008;

Sobsey et al., 2008), costs to consumers (Carter et al., 1999; Gupta et al., 2008; Sobsey et al., 2008; Wood et al., 2012), and lack of accountability or follow through between stakeholders such as government, community and NGOs (Carter et al., 1999; Harvey and Reed, 2006; Hunter et al., 2010). Table 2.1 summarizes examples of water projects, primarily failures but also a few successes, along with reasons for success or failure and suggestions for improvement.

Table 2.1: Examples of water projects in developing countries and possible improvements that could increase sustainability. Text in grey indicates projects with a high level of success.

Projects[a]	**Reasons for failure or success**[b]	**Possible improvements**[c]	**Sources**
Wells in Africa (nearly 200,000 wells)	• Lack of funding for repairs/maintenance and overall lack of physical repairs and maintenance (Reasons implied but not specifically stated in source documents; overall statistic comes from many different projects and various reasons for failure likely exist)	• Market-based solutions to encourage supply chains and repair networks • Social and cultural assessment research to ensure community acceptance and buy-in	• (Breslin, 2010) • (Schouten and de Jong, 2009)
Water boiling behavior change in Peru	• Community members associated warm boiled water with sick people and were therefore, in many cases, unwilling to boil water for drinking, despite the health education provided	• Attention to cultural assessment and local information to inform treatment choice	• (Wellin, 1955) • (Rogers, 2003)
Household water chlorination in Kenya	• Intervention was conducted with the help of trusted local nurses • Social marketing was utilized for chlorine • Culturally appropriate education messages • Initial interventions were conducted by local NGOs and then later followed up	• Follow up education from nurses or local project staff • Address concerns that the health clinic visitors may not be representative of the total local community and engage in education initiatives outside the health clinic	• Parker et al., 2006

Projects[a]	Reasons for failure or success[b]	Possible improvements[c]	Sources
Chlorination project in Namibia	• Lack of consistent supply chain for chlorine • Taste of water after chlorination was not palatable for users	• Assess user preferences through social science assessment prior to technology implementation • Test a business model for sustaining a consistent supply of chlorine for water treatment	• (Diergaardt and Lemmer, 1995)
Bone char use to remove fluoride from drinking water in Ethiopia	• Community unwilling to use bone char for cultural reasons • Lack of education for communities on system and effectiveness	• Social marketing campaign to raise awareness and encourage use and purchase of treatment technology • Quality control and additional research on producing high-quality bone char for water filtration	• (Abaire et al., 2009)
Public water points were partially broken or completely broken at rates of 44% and 24%, respectively, in Sierra Leone	• Lack of supply chain for replacement parts • Lack of trained persons to do repairs • Lack of active management of water point	• Ensure active management of water point • Set up market-based models for supply chain and repair mechanics • Increase local ownership of wells	• (Hirn, 2012)
Water filtration and safe storage for HIV/AIDS population in Zambia	• Implementation in a population already highly aware of health issues • Provision of safe water storage containers to provide a storage option for filtered water	• Inclusion of a broader population beyond those that were referred by health clinics	• (Peletz et al., 2012)
Intervention to improve safe water access through sale of PUR sachets in Guatemala	• Time required for use of water treatment product • Cost (a possible but less supported cause)	• More technology development to reduce time required for treatment • Reduce costs • Marketing strategy based on more than health outcomes	• (Luby et al., 2008) • (Jones, Christensen and Thomas, 2008)
Ceramic water filters for point-of-use water treatment in Cambodia	• Broken ceramic filter components • Filters were considered slow • Concern that filter life had expired	• Technology development to reduce breakage rates • Increased supply chain access and knowledge of where the supply chain exists • Increased education in user households • Amend expectations for life of the filters	• (Brown et al., 2009)

[a] Most examples listed here are not of complete failure but partial (e.g. 200,000 wells failed in Africa though some are still functioning and 69% of ceramic water filters are no longer operational while 31% are still in use). Shading indicates water interventions that were primarily successful.

[b] Reasons for failure are stated or implied by the source document.

[c] Possible improvements are in part suggested in the original source documents and in part suggested by the authors of this work based on insights gleaned from reviews of failed and successful projects.

Sustainable Development

The failure to achieve sustainable safe water solutions is well known, but much remains unknown about how to move forward. Breslin (2010) argues for increased attention to monitoring, including a focus on realistic success metrics over the long term, transparency and accountability, and assessing where funding comes from and how it is leveraged. Hokanson et al. (2007) studied several specific water purification technologies and several geographic regions and made suggestions including: appropriate technologies should be used, community training should be increased, and more efforts should be made to improve community buy-in. Building on these important efforts, we argue that formulation and implementation of sustainable water solutions requires the blending of social science (to understand the human dimensions), business and economic capacity (to aid in market-based implementation and assuring a consistent supply chain), and science and engineering (to aid in technology development). These three components of the system are often discussed individually but rarely integrated in the literature. Indeed, social and cultural assessments are often quite hostile to market-based solutions (e.g. Goldman, 2006). While a number of water system approaches provide safe water, the ideas presented in this work apply primarily to POU and community-scale safe water systems. Figure 2.1 shows how the overlapping disciplines might look when working together within a given enabling environment, as discussed below. This collaborative effort is proposed not as a one-time occurrence in initial product development, but instead as something that should occur throughout the duration of each initiative.

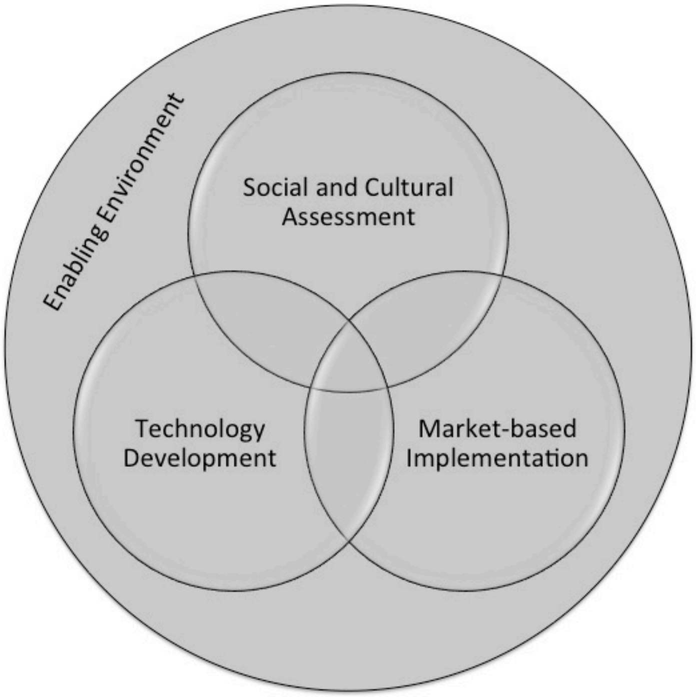


Figure 2.1: Diagram showing the three discussed areas crucial to successful implementation, their overlap where a sustainable outcome should be obtained, and their embedding in a broader systems perspective (the enabling environment).

Mihelcic and Trotz (2010) argued that the “Application of sustainability to engineering projects thus requires more emphasis on integrating and balancing human and societal considerations with technological and economic consideration.” We build on this position and assert that the integration of disciplines should be conceptualized not as three separate sub-projects working in one area, but instead as three distinct areas of thought and expertise working collaboratively on one project with a common goal of building a sustainable solution. Table 2.2 suggests tasks that fall into each aspect of this integrated approach. We propose an integrative vision of these solutions by embedding them in the enabling environment, which incorporates aspects such as politics, economics, available resources, legal frameworks, and funding opportunities. In order for projects to be successful an enabling environment must exist that is conducive to sustainable safe water supply solutions. This cannot, of course, be presumed, but in this paper we assume that such an enabling environment exists and we focus on the other key elements to achieving sustainable water solutions. We focus here on local context, but we expect that this will lead to a more comprehensive approach that will consider these local systems in a global context that includes donor communities and governments (Breslin, 2010; Hunter et al., 2010).

Table 2.2: Tasks that fall into each component of synergistic research towards developing sustainable research and water access or treatment implementations.

Social and cultural assessment	**Market-based implementation**	**Technology development**
• Assessment of local practices regarding drinking water • Assessment of willingness to pay • Assessment of drinking water aesthetic preferences • Values inventory • Determination of health needs, goals, beliefs, and behavior	• Business models research • Market research • Economic assessment • Implementation through social entrepreneurship • Cost assessment using life cycle costs approach • Supply chain analysis and support	• Lab testing • Field technology assessment • Improved or new technology development • Life-cycle assessment • Assessment of locally available materials and processing capabilities

Social and Cultural Assessment

Critiques of development initiatives abound within the social sciences (e.g. Ferguson, 1994; Scott, 1999; Goldman, 2006) especially criticisms of the failure to consider local social and cultural realities. Unfortunately, these critiques have seldom been applied in improving development initiatives such as access to safe water.

Understanding the social and cultural context in which people may care about drinking water quality is an obvious, but often neglected, dimension of any sustainable safe water scheme. In a development context, technological and market-based approaches presume certain forms of social and cultural orientation, which may not always be warranted. For example, Mary Douglas, a social anthropologist, points out that sometimes apathy of communities, often caused by helplessness and an inability to envisage a way out of the current life situation, can be a major deterrent to implementation and success of development projects (Douglas, 2004). When properly designed and implemented, social and cultural assessment should help us better understand the human system in which an initiative is attempting to intervene.

Social and cultural assessment is commonly conducted by anthropologists, sociologists, or psychologists (and at times engineers) using methods such as observations, surveys, interviews and focus groups. Huber et al. (2011) discuss a method that can be used to conduct this research and McConville and Mihelcic (2007) provide a sample list of information to gather. These tools can reveal where people get affirmation or criticism of their behaviors, what beliefs cause people to accept or reject ideas, and information about attitudes, preferences, aspirations, and other factors that influence current and potential behavior. Formative research is needed to assess needs as well as community wishes. This process can be daunting and several helpful sources of information are available that offer guidelines and approaches for this. The Participatory Hygiene and Sanitation Transformation (PHAST) approach is one method for working with a community to plan a project and a helpful guide is available from WHO titled *PHAST step-by-step guide: A participatory approach for the control of* *diarrheal disease*. *Safe Water Systems for the Developing World: A Handbook for Implementing Household-Based Water Treatment and Safe Storage Projects* from the Centers for Disease Control and Prevention offers information about how to conduct a focus group and includes sample questions. Knowledge, Attitudes and Practice (KAP) studies are another method for gathering data: Two helpful resources, though not specific to water, are ‘The KAP Survey Model’ from Médecins du Monde and ‘A Guide to Developing Knowledge, Attitude and Practice Surveys’ from WHO.

A growing number of water researchers have gravitated toward cognitive and behavioral theories of behavioral change, often derived from health psychology, to understand problems in international water development (e.g. Heierli, 2008). Others have found the inductive community-based approaches of anthropology to be central to their efforts (e.g. Mihelcic et al., 2007; Ramaswami, et al., 2007). Thus, social and cultural assessment plays a key role in safe water development because the research in this area assesses community knowledge, beliefs, behaviors and desires and then influences the education, information sharing, and motivational tools for health behavior change that have been argued to be a critical component of water treatment projects as a whole (Hokanson et al., 2007). Health behavior change is a difficult topic at times because it can seem paternalistic or offensive. However, it is possible to motivate, as opposed to force, positive health-related behavior modification with a minimum level of community change or invasiveness if researchers and practitioners gain a solid understanding of the community and its history and beliefs, and follow ethical development guidelines (e.g. Gasper, 2004, 2012; the International Development Ethics Association “http://secure.pdcnet.org/idea/About-Us).

Social and cultural assessment, if well done, should also inform both market analysis and technology selection and development. If we take seriously the idea that a community or family should be able to have a voice in selecting their water treatment technology or water source, social sciences are essential to cultivate this participation (McConville and Mihelcic, 2007; Skinner, 2009). Heierli suggests one of the most important things to do in determining implementation methods for a community is to gain a thorough understanding of the culture and values of the community in which practitioners and researchers are working (Heierli, 2008). Rogers (2003) suggests new technologies are better disseminated if the change in behavior required is minimal when compared with previous behavior; thus, understanding patterns of behavior, behavior stimuli, and habits of the community members is key. In direct relation to water, we know that household water treatment technologies are more likely to be accepted and used if they are easy to use and require minimal time (Sobsey et al., 2008). Thus, social and cultural information gathering and assessment is a critical aspect of an integrated water implementation. The knowledge gained about local communities is crucial to understanding the local markets that should inform the selection or design of technologies.

Market-based Implementation

There are growing signals that market-based solutions may be an important avenue through which sustainable drinking water issues can be addressed. For example, Prahalad (2009) noted that there are millions of people living in poverty that are becoming viable consumers of scalable consumer items sold through sales techniques and appropriate marketing. For the world's 4 billion poorest people, the water market is approximately $20 billion (Hammond et al., 2007). Thus, in the larger ecosystem, utilizing market approaches can be beneficial for poverty reduction and global economic growth along with increased sustainability of access to safe water.

There are several areas where an entrepreneurship perspective contributes to water research and implementation. The process of analyzing how the various pieces of a business model could work or how they need to be adjusted to better facilitate the customer value proposition, the inter-workings of the various exchange partners and how money flows, can be highly constructive (McGrath, 2010). Rural Water Supply Network (2010) and Foster (2012) suggest that exploration and testing of market-based solutions for rural safe water in developing countries is helpful for addressing water sustainability concerns. Markets readily benefit people by offering competition, which drives down prices and encourages continued innovation based on customer demand (Wolff, 2012). Furthermore, market-based systems provide strong encouragement to maintain, repair and upgrade existing systems as individual livelihoods depend on ongoing operations. The use of market-based models for water implementation also has the potential to solve issues such as missing supply chains, willingness to use technologies, and marketing concerns (Foster, 2012). Skinner (2009) suggests it is helpful to have a viable market that ensures availability of a repair person(s) and replacement supplies to encourage fair pricing and options for consumers. And Oyo (2006) indicates that, while private operation of supply chains for well and pump spare parts in Africa is not currently the norm nor always the best option, it could be the ideal option for sustainability if certain operating criteria are met.

While market-based implementation is certainly gaining traction, constraints include political instability, corruption, and lack of literacy (Hokanson et al., 2007). Government or NGO projects often run out of funding because of political or economic shifts, thereby jeopardizing the success of the project (Banerjee et al., 2007). In contrast, market-based solutions that are financially self-sustaining have the potential to be much more enduring without concerns about donor or government funding. In market-based systems, including POU or community scale, financial concerns must be addressed to remain operational. The means of economic exchange and payment systems between suppliers and users must also be accommodating and fluid. Therefore, aside from studying business model alternatives, business experts on water research teams need to understand what can add value for customers, how it can be delivered in a way that meets the needs and wants of customers, and cost/payment mechanisms. Fonseca et al., (2011) and Burr et al., (2012) offer an in-depth discussion of the life cycle costs approach and suggest that it takes into consideration water point/treatment costs including minor operations and maintenance and major capital maintenance, capital investment and both direct and indirect support. Fonseca et al. (2011) provide information on accounting strategies and guidance on how to conduct a life cycle cost assessment.

There is increasing movement towards charging water consumers enough such that full cost recovery becomes a viable option, but in many cases users do not have the ability to pay at this level (Banerjee and Morella, 2011; Foster, 2012). Thus, subsidies may be needed to complement local systems in certain cases (Banerjee et al., 2007; Kremer et al., 2010; Foster, 2012). Due to the diversity of funding sources and the complexities of implementation, options such as hybrid organizations, subsidies from governments or NGOs, paying in installments, and other creative solutions could be explored for the implementation of some market-based solutions (Gupta et al., 2008). Further discussion of issues with willingness to pay, costing and potential options for private water business can be found in Foster (2012) and Kols (2011) and there is an ongoing need for research on private sector water options (Harvey and Reed, 2006).

Market-based solutions can improve sustainability of water supply as well as benefit communities by employing local people and expanding markets. However, it is important to acknowledge that market-based approaches are not ideal in every situation. For example, willingness to pay for water treatment in some areas can be quite low, and it was reported by Null et al. (2012) that the short-term uptake of water treatment options was much higher if items were given away free or were very inexpensive, thus not supporting a market-based approach. However, Baumann (2006) suggests that the market for boreholes in Africa is massive and increasingly the private sector, in particular indigenous drilling companies, are best suited for meeting this need. Additional research on payment options is needed to inform market-based solutions and the 'best option' no doubt depends on local culture, habits, preferences, markets, etc.

Related to these market-based approaches is social marketing. Social marketing is the application of marketing principles to influence social behaviors and accomplish a social good (Andreasen, 1994). Furthermore, social marketing seeks to benefit the target market and even society as a whole, not the marketer as done in commercial marketing. Kotler & Zaltman (1971) were among the first to characterize social marketing as 'A bridging mechanism which links the behavior scientist's knowledge of human behavior with the socially useful implementation of what that knowledge allows'. With public health issues, social marketing has been employed to help implement programs aimed at broad-based behavioral change (Andreasen, 1994; Rogers, 2003).

Social marketing is a tool that allows us to consider ways of combining social and cultural assessment with market-based implementation and dissemination of treatment technologies or safe water sources. Social marketing can be powerful when used by the private sector or by NGOs, such as Population Services International, for marketing safe water solutions based on careful social and cultural assessment, though it should not necessarily be considered a complete substitution for other behavior change activities (Banerjee et al., 2007; Foster, 2012; Wood et al., 2012). Sometimes combining more than one health-related initiative together can be beneficial. For example, Peletz et al. (2012) found that implementing household water treatment filters with HIV-positive mothers who had young children resulted in an 82% use rate and improved drinking water quality, confirmed by bacteriological improvements. The authors suggest this may have resulted from an increased awareness of health-based concerns in HIV-positive populations, thus, leading to an increased willingness to use health improvement interventions (Peletz et al., 2012).

Good market-based approaches have the best chance of success when they are built on a solid assessment of the culture. Furthermore, to have water treatment products that are effective, efficient and culturally acceptable is imperative for developing market-based systems. At the same time, social and cultural assessment and market analysis are useless without sustainable technology, to which we now turn.

Technology Development

The ability to supply or treat water is essential to addressing the safe water availability issue, which is the focus of this paper. But if we are to take seriously the critiques of water development that formed the motivation for this essay, it is clear that technology development is just one piece of the interdisciplinary effort. There are two key aspects to a discussion of technology in the framework of building sustainable water solutions.

First, technology research, development, and assessment can be more effective and powerful when guided by information learned through social and cultural assessment (i.e. local cultures and taboos) and when, in consideration of the local economy, technology’s place in local markets is taken into consideration. As mentioned in Table 2.1, sometimes projects fail because a technology is not appropriate for the local community. For example, research using bone char to remove harmful fluoride in a community that has a cultural preference against animal bones is not appropriate, even if the approach is technically viable (Abaire et al., 2009). Assessment of community preferences should guide technology selection/development with the assumption that a community or family may be responsible for funding operations and maintenance as well as physically collecting/treating water. Selection of locally produced versus imported technology is often a discussion of cost and availability of materials, but it is imperative to also consider community members’ preferences as they will influence what technologies will actually be utilized. Additionally, depending on what the local market situation is, the ‘best’ answer may be one that does the most to facilitate not only increased access to safe water but also to boost the local economic market.

A second key aspect of research and selection of technologies is that in some cases the necessary technologies either do not exist or would benefit from continued research for improvements. The literature presents some cases where projects fail as a result of technical issues or where technologies could be improved to make them more user-friendly, sturdy, effective, etc. For example, Hokanson et al. (2007) point out that UV disinfection is highly effective for pathogen removal, but that there are several drawbacks including: the necessity of a power source, the requirements for quality of the source water, and the fact that no visible change occurs during the treatment process. Gupta et al. (2008) suggest the need for additional engineering to make chulli water filters more durable and reliable, and Baumann (2006) suggests that decreasing the cost and increasing the efficiency of borehole production, specifically in Africa, would improve access to safe water in Africa.

Sustainability Tools

A number of tools can guide the kind of integrations we propose here. The work by McConville and Mihelcic (2007), which develops a framework for looking at factors that affect sustainable development of water and sanitation projects, provides practical steps to be utilized – specifically Table 1 which suggests helpful tasks within five life stages of a project. The Triple-S (Sustainable Services at Scale) initiative website, led by the International Water and Sanitation Center, contains tools, ideas, case studies, and training options and is available at http://www.waterservicesthatlast.org. Finally, Skinner (2009) discusses ways to make Africa's waterpoints more sustainable including focusing on quality control of implemented technology, waterpoint management and ownership, and use of local markets to support maintenance and repairs. This work offers a table containing 30 elements that are suggested as necessary for success for sustainable safe water in African communities.

Practical Implications

There are many lessons to be learned from the individual disciplines discussed above, but more important than the individual disciplines learning from one another in isolation is the synergistic impact of collectively designing, evaluating and implementing sustainable solutions for access to safe water. We have argued for the importance of including at least the three disciplines (social science, business and technology) into a safe drinking water initiative from the very inception of the project in order to ensure that each step of the process is influenced by all areas. We argue that failure to collectively include multiple areas from the onset will lead to suboptimum solutions. For example, through this literature review the importance of conducting a thorough market analysis of the target communities or households has emerged.

This type of analysis could be done in isolation, but to be most effective requires a solid social and cultural understanding of human behavior, desires and motivations, the willingness/ability to pay for safe water, and social marketing to better inform the targeted populations. At the same time, social and cultural assessment could be done by a social scientist who does not fully understand the business/supply chain/entrepreneurial elements and thus would fail to incorporate critical information necessary to assess these aspects. Finally, this step, even if forged by both of these disciplines, may lack knowledge of what technologies might be available or feasible. We strongly encourage researchers and practitioners to fully adopt this integrated approach into their program design, implementation and assessment, and have provided a number of tools that can facilitate these processes in most initiatives, even in the absence of specialized expertise on a team. We further suggest that funders and government organizations look for these elements in project proposals or evaluations and consider funding and supporting activities in part based on evidence showing careful consideration of these aspects of sustainable development.

Conclusion

Identifying a successful solution that is appropriate for each context is certainly a challenge. While a multitude of excellent organizations have been implementing solutions to the water crisis for decades, an alarming number of past projects are not demonstrating long-term sustainability. We argue that it is imperative that researchers and practitioners work to find best practices, integrate skills and ideas from many fields, and put them together to research and create synergistic solutions for safe water needs in communities around the world. We posit that the combination of social and cultural assessments, market-based solutions and technology development can provide a powerful approach for achieving sustainable safe water solutions by allowing each approach to bring unique tools and methods to the project that inform and influence the direction and outcome of the project as well as the actions of the other disciplines. Future research on the methods and outcomes of designing, implementing and assessing this integrated approach will be helpful to the water community as it seeks ways to further improve sustainability of water supply/treatment implementation.

Acknowledgements

The authors gratefully acknowledge partial funding from the US Environmental Protection Agency and the US National Science Foundation that contributed to this work. This publication was developed under STAR Fellowship Assistance Agreement no. 91731301 awarded by the US Environmental Protection Agency (EPA). This work has not been formally reviewed by EPA, and the views expressed in this paper are solely those of the authors and the EPA does not endorse any products or commercial services mentioned in this publication. The authors also wish to acknowledge partial funding from the OU WaTER Center and the University of Oklahoma in support of this work.

References

Abaire, B., Zewge, F., and Endalew, M. (2009). “Operation experiences on small-scale community defluoridation systems.” In *Water, Sanitation and Hygiene: Sustainable Development and Multisectoral Approaches - 34th WEDC International Conference*, May 18-22, 2009, Addis Ababa.

Andreasen, A. (1994). “Social marketing: its definition and domain.” *J. Public Pol. Mkt.* 13(1), 108–114.

Banerjee, A., McFarland, D. A., Singh, R., and Quick, R. (2007). “Cost and financial sustainability of a household-based water treatment and storage intervention in Zambia." *J. Water Health,* 5(3), 385–394.

Banerjee, S.G. and Morella, E. (2011). *Africa's water and sanitation infrastructure: access, affordability, and alternatives*. World Bank, Washington, DC.

Baumann, E. (2006). *Cases studies of operating conditions for local drilling entrepreneurs in rural water supply in Africa*. Water and Sanitation Program, Washington, DC.

Breslin, E. (2003). The demand-responsive approach in Mozambique why choice of technology matters. *WATERfront* 16, 9-10, 12.

Breslin, E. (2010). "Rethinking hydrophilanthropy: smart money for transformative impact." *J. Contemp. Water Res. Edu.* 145(1), 65–73.

Brown, J., Proum, S., and Sobsey, M. (2009). Sustained use of a household-scale water filtration device in rural Cambodia. *J. Water Health* 7(3), 404–412.

Burr, P., Fonseca, C., Moriarty, P., and McIntyre, P. (2012). *The recurrent expenditure gap: failing to meet and sustain basic water services - executive summary*. International Water and Sanitation Centre, The Netherlands.

Carter, R., Tyrrel, S., and Howsam, P. (1999). The impact and sustainability of community water supply and sanitation programmes in developing countries. *Water. Environ. J.* 13(4), 292–296.

Clasen, T. (2009). *Scaling up household water treatment among low-income populations.* World Health Organization, Geneva, Switzerland.

Diergaardt, G. and Lemmer, T. (1995). Alternative disinfection methods for small water supply schemes with chlorination problems. *Water Suppl,y* 13(2), 309–312.

Douglas, M. (2004). In: *Culture and public action,* V. Rao, and M. Walton, eds. Stanford Social Sciences, Stanford, CA

Ferguson, J. (1994). *Anti - politics machine: development, depoliticization, and bureaucratic power in Lesotho*. University of Minnesota Press, Minneapolis, MN.

Fonseca, C., Franceys, R., Batchelor, C., McIntyre, P., Klutse, A., Komives, K., Moriatry, P., Naafs, A., Hyarko, K., Pezon, C., Potter, A., Reddy, R., and Snehalatha, M. (2011). *Briefing note 1a life-cycle costs approach*. International Water and Sanitation Centre, The Netherlands.

Foster, T. (2012). *Private sector provision of rural water services: a desk study for Water for People*. Water for People, Colorado.

Gasper, D. (2004). *The ethics of development*. Edinburgh University Press, Edinburgh, United Kingdom.

Gasper, D. (2012). Development ethics - Why? What? How? A formulation of the field. *J. Global Ethics,* 8(1), 117–135.

Goldman, M. (2006) *Imperial nature: the World Bank and struggles for social justice in the age of globalization*. Yale University Press, New Haven, Connecticut.

Gupta, S., Islam, M., Johnston, R., Ram, P., and Luby, S. (2008). The chulli water purifier: acceptability and effectiveness of an innovative strategy for household water treatment in Bangladesh. *Am. J. Trop. Med. Hyg.* 78(6), 979–984.

Hammond, A., Karmer, W., Katz, R., Tran, J., and Walker, C. (2007). *The next 4 billion: market size and business strategy at the base of the pyramid*. World Resources Institute and International Finance Corporation, Washington DC.

Hankin, P. (2001). The afridev handpump - problems and solutions. In *People and Systems for Water, Sanitation and Health - 27th WEDC Conference,* Lusaka, Zambia.

Harvey, P. and Reed, R. (2006). Community- managed water supplies in Africa: sustainable or dispensable? *Community Dev. J.* 42(3), 365–378.

Heierli, U. (2008). *Marketing safe water systems.* Employment and Income Division and Social Development Division - Swiss Agency for Development and Cooperation, Berne, Switzerland.

Hirn, M. (2012). *Sierra Leone waterpoint report*. Sierra Leone Ministry of Energy and Water Resources, Sierra Leone.

Hokanson, D., Zhang, Q., Cowden, J., Troschinetz, A., Mihelcic, J., and Johnson, D. (2007). Challenges to implementing drinking water technologies in developing world countries. *Environ. Engineer: Appl. Res. Pract.* 1, 31–38.

Hoque, B., Hoque, M., Ahmed, T., Islam, S., Azad, A., Ali, N., Hossain, M., and Hossain, M.S. (2004). Demand-based water options for arsenic mitigation: an experience from rural Bangladesh. *Pub. Health*, 118(1), 70–77.

Huber, A. C., Bhend, S., and Mosler, H. J. (2012). Determinants of exclusive consumption of fluoride-free water: a cross-sectional household study in rural Ethiopia. *J. Pub. Health*, 20(3), 269-278.

Hunter, P. R., MacDonald, A. M., and Carter, R. C. (2010). Water supply and health. *PLoS Medicine*, *7*(11), e1000361.

Jones Christensen, L. and Thomas, J. (2008). *Procter & Gamble's Pur water purifier:*

the hunt for a sustainable business model (Teaching Case). Kenan-Flagler Business School - University of North Carolina, Chapel Hill, North Carolina.

Kols, A. (2011). *PATH safe water project's monitoring and evaluation framework: testing market-based solutions in four countries*. PATH, Seattle, WA.

Kotler, P. and Zaltman, G. (1971). Social marketing: an approach to planned social change. *J. Mkt.* 35(3), 3–12.

Kremer, M., Ahuja, A., and Peterson-Zwane, A. (2010). *Providing safe water: evidence from randomized evaluations* (Discussion Paper 23). Harvard Environmental Economics Program, Cambridge, MA.

Luby, S., Mendoza, C., Keswick, B., Chiller, T., and Hoekstra, R. (2008). Difficulties in bringing point-of-use water treatment to scale in rural Guatemala. *Am. J. Trop. Med. Hyg.* 78(3), 382–387.

Mackintosh, G. and Colvin, C. (2003). Failure of rural schemes in South Africa to provide potable water. *Environ.Geol.* 44(1), 101–105.

McConville, J. and Mihelcic, J. (2007). Adapting life-cycle thinking tools to evaluate project sustainability in international water and sanitation development work. *Environ. Eng. Sci.* 24(7), 937–948.

McGrath, R. G. (2010). Business models: A discovery driven approach. *Long Range Plann.* 43(2-3), 247–261.

Mihelcic, J. and Trotz, M. (2010). Sustainability and the environmental engineer: implications for education, research, and practice. *Environ. Engr. Appl. Res. Pract.* 10, 1-10.

Mihelcic, James R., Zimmerman, J. B., and Ramaswami, A. (2007). Integrating developed and developing world knowledge into global discussions and strategies for sustainability. 1. Science and technology. *Environ. Sci. Technol.* 41(10), 3415–3421.

Null, C., Kremer, M., Miguel, E., Hombrados, J., Meeks, R., and Zwane, A. (2012). *Willingness to pay for cleaner water in less developed countries: a systematic review of experimental evidence*. International Initiative for Impact Evaluation, Washington, DC.

Onda, K., LoBuglio, J., and Bartram, J. (2012). Global access to safe water: accounting for water quality and the resulting impact on MDG progress. *Intl. J. Environ. Res. Pub. Heal. 9*(3), 880–894.

Oyo, A. (2006). *Spare part supplies for handpumps in Africa*. Water and Sanitation Program, Switzerland.

Peletz, R., Simunyama, M., Sarenje, K., Baisley, K., Filteau, S., Kelly, P., and Clasen, T. (2012). Assessing water filtration and safe storage in households with young children of HIV-positive mothers: a randomized, controlled trial in Zambia. *PLoS ONE* **7**(10), e46548.

Prahalad, C. (2009). *The fortune at the bottom of the pyramid, 5th Edition: eradicating poverty through profits*. Prentice Hall, Upper Saddle River, NJ.

Ramaswami, A., Zimmerman, J. B., and Mihelcic, J. R. (2007). Integrating developed and developing world knowledge into global discussions and strategies for sustainability. 2. Economics and governance. *Environ. Sci. Technol.* 41(10), 3422–3430.

Rogers, E. (2003). *Diffusion of Innovations*, 5th ed. Free Press, New York.

Schouten and De Jong, D. (2009). Source Bulletin No. 56. IRC International Water and Sanitation Centre, The Hague, Netherlands.

Scott, J. (1999). *Seeing like a state: how certain schemes to improve the human condition have failed*. Yale University Press, New Haven, Connecticut.

Skinner, J. (2009). *IIED Briefing*. International Institute for Environment and Development, London, United Kingdom.

Sobsey, M., Stauber, C., Casanova, L., Brown, J., and Elliott, M. (2008). Point of use household drinking water filtration: A practical, effective solution for providing sustained access to safe drinking water in the developing world. *Environ. Sci. Technol.* 42(12), 4261–67.

United Nations Department of Economic and Social Affairs (2009). *Rethinking poverty: report on the world social situation 2010*. United Nations, New York.

Water and Sanitation Program. (2010). *Myths of the rural water supply sector*. World Bank, Washington D.C.

Wellin, E. (1955). Water boiling in a Peruvian town. In: *Health, culture and community: case studies of public reactions to health programs*, B. Paul, ed. Russell Sage Foundation, New York, NY.

World Health Organization and UNICEF (2012). *Progress on drinking water and sanitation 2012 update*. World Health Organization and UNICEF, New York, NY.

Wolff, J. (2012). Start me up: the effectiveness of a self-employment programme for needy unemployed people in German. *J. Small Bus. Entrepr.* 25(4), 499–518.

Wood, S., Foster, J., and Kols, A. (2012). Understanding why women adopt and sustain home water treatment: Insights from the Malawi antenatal care program. *Soc. Sci. Med.* 75(4), 634–642.

CHAPTER 3

The Role of Surface Area and Surface Chemistry during an Investigation of Eucalyptus Wood Char for Fluoride Adsorption from Drinking Water[2]

Abstract

This work studied the use of eucalyptus wood char as an adsorption material for fluoride removal from drinking water and investigated options to improve the removal capacity of bone char to increase availability of safe water. Upon increasing charring temperature, the specific surface area of the eucalyptus wood char increased from 0.9 to 327 m^2/g; however, the fluoride removal capacity of the unamended eucalyptus wood char was negligible for all charring temperatures. Amendment of the wood char with aluminum oxides increased the fluoride removal capacity to 1.6 mg/g, demonstrating a significant improvement relative to the unamended wood char. Although this adsorptive capacity is not yet as high as values reported for bone char, it is higher than the capacity of other media currently in use in some locations. Thus, the aluminum oxide modified eucalyptus char may be a helpful alternative for fluoride removal in areas where bone char is not a viable option. This work also studied the possibility of altering the pH_{PZC}, initially 9.6 and 8.2 for wood and bone chars, respectively, to enhance the electrostatic

---

[2] Brunson, L.R., and Sabatini, D.A. (2014). "The Role of Surface Area and Surface Chemistry during an Investigation of Eucalyptus Wood Char for Fluoride Adsorption from Drinking Water." *J. Environ. Enr.* Accepted.

attraction between the media and fluoride in water. The use of reducing agents actually lowered the pH_{PZC} to less than 8 for both types of char but increased the fluoride adsorption capacity of the bone char by approximately 25% while causing minimal change to the wood char capacity.

Background

Naturally occurring fluoride is a major drinking water quality concern contributing to the global water crisis; worldwide an estimated 200 million people are affected, including many living in the Rift Valley of Africa (Coetzee et al., 2004; Nigussie et al., 2007; Fawell et al., 2006) as well as people living in India, China, and several areas of the United States (Amini et al., 2008; McGill, 1994). When fluoride is consumed at levels above the World Health Organization (WHO) standard of 1.5 mg/L, dental and skeletal fluorosis can occur (World Health Organization, 2011). Beyond discoloration of teeth, fluorosis can cause tooth sensitivity and pain, stiffness and defomities in bones and joints (Fawell et al., 2006; Fewtrell et al., 2006; Malde et al., 2011). Not only is this a significant health issue, but social and financial impacts can result from the social stigma of dental fluorosis as well as from physical disabilities that impact subsistence farmers and wage earners (McGill, 1994; Tonguc et al., 2011).

Water treatment methods investigated for fluoride removal include: ion exchange, electrolytic defluoridation, filtration, and precipitation (Abe et al., 2004; Fawell et al., 2006; Ayoob et al., 2008; Gwala et al., 2011). Adsorptive filters are one of the most commonly used methods, due in large part to the ability to operate filters without any stirring or mechanical requirements once water is pumped from the ground (Daifullah et al., 2007).

Commonly used fluoride adsorptive materials include activated alumina, bone char, and clays (Fawell et al., 2006; Ayoob et al., 2008; Mlilo et al., 2010). Activated alumina is a high surface area removal material that functions best at low pH values and is suggested to have a field removal effectiveness of 1 mg of fluoride per gram of material (Fawell et al., 2006; Ayoob et al., 2008). Activated alumina is not commonly produced in many developing countries and would therefore need to be imported, which would likely increase the cost of water filtration. Clays are locally available in many locations, but their chemical compositions are highly variable and removal capacities are typically low, much less than 1 mg/g (Coetzee et al., 2004; Fawell et al., 2006). Bone char, widely investigated for adsorptive removal of fluoride, can be produced in developing regions from waste animal bones, is relatively inexpensive, and is composed primarily of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (70-76%), carbon (8-11%), and calcium carbonate (7-9%) (Larsen et al., 1994; Wilson et al., 2003; Kaseva, 2006; Medellin-Castillo et al., 2007). The fluoride removal capacity of bone char has been attributed to several mechanisms including: the exchange of fluoride for hydroxyl ions due to their similar charge and hydrated radii (3.52 and 3.00 Å, respectively) (Nightingale, 1959; Fan et al., 2003; Kaseva, 2006) and exchange of carbonate for fluoride (Bhargava and Killedar, 1991).

Charring animal bones is helpful because it produces a large specific surface area. Medellin-Castillo et al. (2007) found the bone char surface area to be 104 m^2/g which is comparable to the 150 m^2/g found by Chen et al. (2008) and the 98 – 112 m^2/g

shown by Brunson and Sabatini (2009). Variations in the surface area are found based on bone type, charring temperature and preparation method. Another measurable characteristic of bone char is its point of zero charge (pH_{PZC}) which Medellin-Castillo et al. (2007) found to be 8.4, consistent with the 8.2 pH_{PZC} found by Brunson and Sabatini (2009). In solutions with pH values below the pH_{PZC} the surface of a material will be positively charged, further increasing in charge with any additional lowering of solution pH. In contrast, for pH values above the pH_{PZC}, the surface of a material will have a net negative charge. Therefore, a material with a high pH_{PZC} is expected to work best for removing negatively charged fluoride ions from water because it will have a strong positive surface charge at typical groundwater pH values (ranging from 6.0 to 8.5).

In some communities, for religious or cultural reasons, people are not amenable to using bone char for water treatment (Fawell et al., 2006). A potential alternative is to use a carbon-based material, such as wood char. Wood is primarily composed of lignin (18-35%) and carbohydrates (65-75%) (Pettersen, 1984). However, chemical composition and other characteristics of wood and wood chars vary based on location, soil type, season, age and type of wood (Pettersen, 1984). James et al. (2005) showed that the specific surface areas of several types of wood naturally charred in forest fires ranged from 1.7 to 85 m^2/g, while woods charred under laboratory conditions at varying temperatures had specific surface areas in the range of 1.0 to 397 m^2/g. This suggests that surface area is highly variable based on wood type, location, and charring temperature and method. Previous studies on spruce wood (Tchomgui-Kamga et al., 2010) and unspecified wood types (Abe et al., 2004) suggested that unmodified wood char has merit for study, but may not be as effective at removing fluoride as bone char.

Abe et al. (2004) found in a study of twelve char materials, that the three different wood chars exhibited higher fluoride removal than charcoals or petroleum coke but much less than that of bone char (e.g. 13% removal for a wood char versus 82% removal for bone char).

Several approaches can be tested for improving the fluoride removal capacity of wood char. Based on the success of aluminum-based materials, one potential way to improve fluoride removal of wood char is to amend it with aluminum oxides. Levya-Ramos et al. (1999) impregnated coconut shell-based activated carbon with aluminum nitrate and found that the fluoride removal capacity increased 3 to 5 times after aluminum amendment. Tchomgui-Kamga et al. (2010) tested the potential to remove fluoride by impregnating spruce wood with aluminum chloride. Their work suggested that the best results, approximately 3.8 times better than charred spruce alone, were obtained when wood was impregnated with both aluminum and iron. Based on these two studies, further study of aluminum amendment on wood char for fluoride removal is helpful.

Another option for enhancing the fluoride removal capacity of wood char may be to alter the pH_{PZC} of the char. The suggestion is that if the pH_{PZC} is raised, then the stronger positive charge on the sorbent surface at typical groundwater pH values will improve fluoride removal. Treating activated carbon type materials with reducing agents may remove acidic functional groups from the surface, which would therefore, increase the basicity and raise the pH_{PZC}. Han et al. (2000) treated granular activated carbon (GAC) with two reducing agents, iron ammonium sulfate and sodium dithionite, with the intention to enhance removal of hexavalent chromium by altering the surface chemistry of the GAC. In this case, removal of chromium was not improved after treatment with reducing agents; the treatment effects on characteristics such as pH_{PZC} and specific surface area were not reported. Thus, to date, research has not fully evaluated the concept of using reducing agents to alter the pH_{PZC} of charred media, making this a fruitful area of study.

Based on previous research, two key items that make media effective at fluoride removal are high specific surface area (often resulting from materials with high internal porosity) into which fluoride can be sorbed and a surface chemistry that attracts fluoride. Thus, the goal for this work is to assess whether wood char can be produced that has both high specific surface area and desirable surface chemistry that is conducive to fluoride removal, preferably approaching or exceeding the effectiveness of bone char. Two key hypotheses were tested to gain traction towards this goal. The first is that amending wood char with aluminum nitrate will improve the fluoride removal capacity due to the attraction between negatively charged fluoride ions and the positively charged metal oxides. The second is that treatment with reducing agents will remove oxygen from the surface, which will reduce the amount of acidic functional groups and, therefore, increase the surface basicity of the sorbent and the pH_{PZC}. It is hoped that raising the pH_{PZC} will increase the fluoride removal capacity due to the resulting positive surface charge at groundwater pH levels. This work is unique due to the study of aluminum amendment using aluminum nitrate with eucalyptus wood charred at a range of charring temperatures and investigation of altering the wood char pH_{PZC} through the use of reducing agents. Another key factor this work addresses is the importance of looking for solutions that are locally available and inexpensive for fluoride removal in developing regions. Eucalyptus wood is prevalent throughout Ethiopia, a country with a high prevalence of fluoride in ground water, where it grows quickly and can continue growing even in marginal conditions (Dessie and Erkossa, 2011). Therefore, eucalyptus wood (*Eucalyptus robusta*) is the biomaterial that was charred in this work to allow for assessment of the effects of charring temperature on specific surface area and surface chemistry and of the potential for utilizing wood char or amended wood char as an alternative to bone char for fluoride removal.

Materials and Methods

Materials

Eucalyptus robusta was purchased from Mezozoic Landscapes, Inc. in Lake Worth, Florida and fish bone meal was purchased from Peaceful Valley Farm & Garden Supply in Grass Valley, California. Raw media were charred at temperatures ranging from 300 °C to 600 °C for four hours based on previous charring work by Brunson and Sabatini (2009). For charring, media were placed in clean and unglazed porcelain containers with lids and placed in a temperature controlled Thermolyne oven. After charring, media were cooled to room temperature, crushed with a mortar and pestle, and sieved to achieve a size range of 180 – 425 µm. Materials were rinsed with deionized water to remove fines and stored in clear, sealed plastic bags.

Surface Modification

A 175 mg/L aluminum solution (0.0065 molar) was prepared using aluminum nitrate and the pH was adjusted to 3.5 with 4-Morpholineethanesulfonic acid based on work done by Levya-Ramos et al. (1999). The solution, 417 mL, was combined with 25 grams of charred media in a glass container and shaken for five days. After shaking, media were filtered, dried at 100 °C, rinsed with deionized water until the pH of the solution was consistent and then dried again. Treatment of media by using reducing agents was conducted based on a modified method from Han et al. (2000) where 0.1 mM solutions of sodium dithionite or iron ammonium sulfate were prepared in deionized water. The solutions were mixed with 25 grams of charred material and shaken for 24 hours. Media was then filtered from solution, dried, and rinsed with continuously flowing deionized water until pH readings were consistent.

Batch Isotherms

Batch tests were conducted by placing 0.5 grams of material in jars and adding fluoridated solutions with concentrations ranging from 0 to 100 mg/L to the jars. Jars were then placed on a shaker table and shaken at 200 shakes per minute for 24 hours; preliminary tests showed 24 hours allows equilibrium to be reached. Solutions were filtered through Whatman 15 cm ashless paper into clean jars and sealed until pH and fluoride measurements were taken. Batch studies were run in triplicate to allow for statistical analysis and all solutions used, unless otherwise specified, were adjusted with NaCl to an ionic strength of 0.05 molar. Batch tests were conducted at room temperature (approximately 22 °C) and, unless otherwise specified, starting pH values, which were not controlled or adjusted, ranged from 5.5 to 7.0.

Material Characterization

Surface area and pore size distribution measurements were conducted using a Quantochrome 2000E instrument. Specific surface area was determined using a five point measurement system at 77 °K based on the theory of Brunauer, Emmett, and Teller (Brunauer et al., 1938). Pore size distribution was assessed using a twenty point measurement, including both adsorption and desorption, with P/P_0 values ranging from 0.25 to 0.99 and the Density Functional Theory method. Media pH_{PZC} values were tested using the drift method (Babic, 1999). Media were added at 0.2 grams per bottle to sets of 12 bottles containing 50 mL solutions that had been pH adjusted to values ranging from 2.5 to 12. After media were added the bottles were sealed and shaken for 24 hours. After 24 hours the final pH was tested. Final versus initial pH values were graphed and the plateau was assessed to determine the pH_{PZC} (Babic, 1999). Tests were conducted in triplicate.

Analysis

Fluoride samples were combined in a one to one ratio with Total Ionic Strength Adjustment Buffer, composed of cyclohexylenedinitrilotetraacetate, sodium hydroxide, sodium chloride, and glacial acetic acid and mixed with samples prior to analysis to ensure consistent ionic strength and pH for accurate readings. Measurements were conducted using a fluoride specific electrode connected to an Orion pH/ISE meter. A HACH HQ30d pH and Multi-Parameter Meter was used to measure pH values.

Isotherm data were analyzed using the Freundlich equation as shown in Equation 3.1 where C_e is the equilibrium concentration after an isotherm test, Q_e is the amount of chemical removed per mass of media, K_f is related to adsorption capacity and 1/n suggests the adsorption intensity (Fan et al., 2003; Kamble et al., 2007). SigmaPlot (Version 12.0) was used to performed regression analysis in order to calculate K_f and 1/n to $p = 0.05$.

$$Q_e = K_f C_e^{1/n} \qquad \text{Equation 3.1}$$

The Freundlich isotherm assumes a heterogeneous media surface accounting for the nonlinear nature of the adsorption. The equilibrium fluoride concentrations studied, which are of environmental relevance, did not achieve an adsorption plateau and thus the data were not analyzed by the Langmuir isotherm.

Results and Discussion

Material Charring

This is one of the first research efforts to assess the ability of eucalyptus wood char to remove fluoride from drinking water. Results of batch isotherms show that unamended eucalyptus wood, charred between 300 and 600 °C, demonstrates negligible fluoride adsorption (Table 3.1); the highest Freundlich adsorption value, K_f=0.02, was obtained at the charring temperature of 600 °C. Table 3.1 also shows the fluoride removal capacity of bone char compared with unamended wood char. For example, at $Q_{e,10}$ (where C_e equals 10 mg/L in the isotherm), values are 0.11 (600 °C wood char) and 3.9 (500 °C bone char) mg/g. The most likely reason for the significant difference in fluoride removal capacity between wood and bone chars is the favorable chemical composition of the bone char, primarily hydroxyapatite, versus wood char, which is primarily carbon (Benaddi et al., 2000; Wilson et al., 2003; Medellin-Castillo et al., 2007). This interpretation is reinforced by the fact that the wood char, while exhibiting much less fluoride adsorption, actually has a higher surface area than the bone char as discussed in a later section. The minimal fluoride removal capacity of unamended wood char, even for a range of charring temperatures, is consistent with the work of Levya-Ramos (1999) who found the maximum fluoride adsorption capacity of activated carbon produced from coconut shells to be 0.5 mg/g. Additonally, Abe et al. (2004) found that out of six tested activated carbon type materials, the highest fluoride adsorption value obtained was 0.34 mg/g. Ayoob et al. (2008) offered that fluoride has a high affinity for metals, which means that the nonmetallic sites on materials such as carbon-based media have low affinities for fluoride even when these media have very high surface areas.

Aluminum Amendment

In an effort to improve the surface chemistry of the eucalyptus chars they were amended with aluminum with the starting material being aluminum nitrate. Table 3.1 and Figure 3.1 show the results of batch isotherms for wood char amended with aluminum oxides (Al wood char) at a range of charring temperatures. Adding aluminum increased the fluoride removal capacity by approximately 6 times, from 0.11 to 0.72 mg/g at C_e=10 mg/L.

Table 3.1: Freundlich constants calculated from batch tests investigating fluoride removal of aluminum amended and unamended wood and bone chars.

Freundlich Constants						
Media		K_f (mg/g)/(mg/L)$^{1/n}$	1/n	r^2	$Q_{e1.5}$ at C_e = 1.5 mg/L	Q_{e10} at C_e = 10 mg/L
300 °C	Wood Char*	Not quantifiable	Not quantifiable	-	-	-
400 °C	Wood Char*	Not quantifiable	Not quantifiable	-	-	-
500 °C	Wood Char	<0.01 ± 0.03	1.35 ± 0.03	0.99	0.00	0.01
600 °C	Wood Char	0.02 ± 0.01	0.60 ± 0.12	0.92	0.04	0.11
500 °C	Bone Char	1.80 ± 0.20	0.33 ± 0.04	0.97	2.10	3.90
300 °C	Al Wood Char	0.04 ± 0.02	0.58 ± 0.11	0.99	0.05	0.14
400 °C	Al Wood Char	0.04 ± 0.01	0.74 ± 0.08	0.98	0.06	0.24
500 °C	Al Wood Char	0.12 ± 0.04	0.48 ± 0.05	0.99	0.24	0.61
600 °C	Al Wood Char	0.15 ± 0.02	0.69 ± 0.04	0.94	0.20	0.72
500 °C	Al Bone Char	1.40 ± 0.10	0.42 ± 0.02	0.99	1.70	3.08
_500 °C_	_Wood Char**_	_<0.01 ± ≤0.01_	_0.98**_	_0.97_	_0.00_	_0.02_
_500 °C_	_Al Wood Char**_	_0.02 ± ≤0.01_	_0.98 **_	_0.73_	_0.04_	_0.24_
_600 °C_	_Wood Char**_	_0.02 ± ≤0.01_	_0.65 **_	_0.92_	_0.03_	_0.10_
_600 °C_	_Al Wood Char**_	_0.17 ± ≤0.01_	_0.65 **_	_0.99_	_0.23_	_0.77_

*These chars removed such small quantities of fluoride that the Freundlich constants could not be calculated.

**For this data the 1/n Freundlich values have been forced to a common value so that the K_f values can be directly compared. Due to process of forcing the 1/n values to a common number there is no error for these 1/n values.

As can be seen from the higher Q_e values in Figure 3.1, the wood chars amended with aluminum oxides (Al wood char) are much more effective at fluoride removal at all charring temperatures than unamended wood char even at the highest charring temperature (and thus highest specific surface area). Figure 3.1 shows that Q_e values go from highest to lowest along with charring temperature in the order of 600 °C > 500 °C > 400 °C > 300 °C. Based on the data in italics in Table 3.1, the bottom four rows where the 1/n constants have been forced to a common value to allow for direct comparison of K_f, it is clear that the eucalyptus wood char amended with aluminum oxides is more effective at removing fluoride than unamended wood char. When comparing wood chars with and without aluminum amendment at 600° C the difference in fluoride removal results is statistically significant at $p = 0.05$.

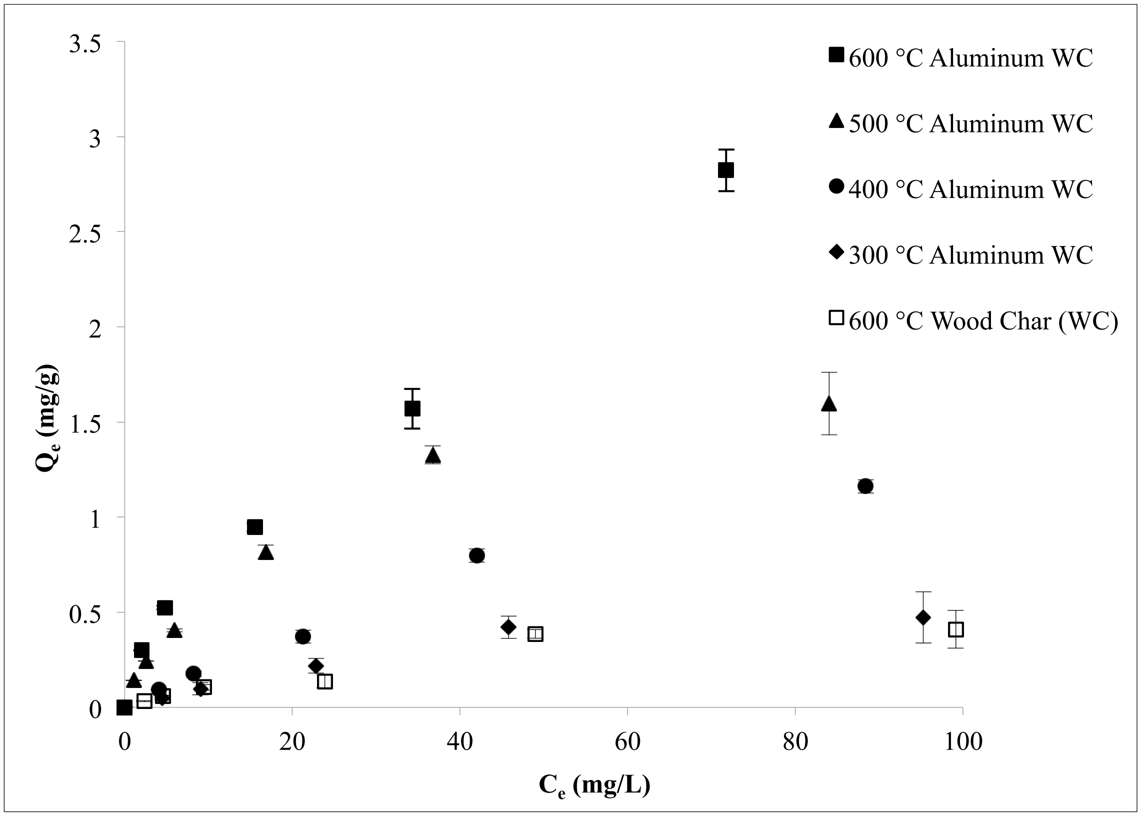


Figure 3.1: The equilibrium fluoride concentration, C_e, in mg/L (x-axis) versus mg of fluoride removed per gram of material, Q_e, (y-axis) for both aluminum amended and unamended eucalyptus wood chars.

Specific Surface Area

Brunson and Sabatini (2009) showed that charring temperature has a marked effect on the specific surface area and the fluoride adsorptive capacity of bone char. Other researchers have confirmed that the specific surface area of wood chars changes as a result of charring temperatures (James et al., 2005; Zhou et al., 2010). The results of this work show that for eucalyptus wood char a similar trend can be seen where charring temperature affects both surface area and fluoride adsorption capacity. Table 3.2 and Figure 3.2 show that charring eucalyptus wood has a pronounced effect on the specific surface area of the resulting chars and that specific surface area increases as charring temperature increases. Abe et al. (2004) suggested that fluoride adsorption by carbonaceous materials improves with increasing specific surface area and that it is dependent on pore size distribution. The data for wood char matches the trend shown by

Table 3.2: Specific surface area and pH_{PZC} of aluminum amended, reducing agent modified and unamended eucalyptus wood and bone chars at various charring temperatures.

Treated and Untreated Wood and Bone Char Parameters				
Charring Temperature/ Pretreatment	Material	Amendment	Specific Surface Area (m^2/g)	pH_{PZC}
300 °C	Wood Char	None	0.90 ± 0.1	5.8 ± 0.2
400 °C	Wood Char	None	13.5 ± 1.3	7.2 ± 0.5
500 °C	Wood Char	None	149 ± 2.6	8.9 ± 0.2
600 °C	Wood Char	None	327 ± 7.0	9.6 ± 0.4
500 °C	Bone Char	None	99.1 ± 0.8	8.2 ± 0.4
300 °C	Wood Char	Aluminum	0.70 ± 0.1	4.0 ± 0.2
400 °C	Wood Char	Aluminum	17.1 ± 0.3	4.3 ± 0.1
500 °C	Wood Char	Aluminum	151 ± 6.4	5.5 ± 0.4
600 °C	Wood Char	Aluminum	256 ± 9.1	5.7 ± 0.2
500 °C	Bone Char	Aluminum	93.2 ± 6.8	7.0 ± 0.1
$(NH_4)_2Fe(SO_4)_2$/600 °C	Bone Char	None	94.1 ± 3.0	7.5 ± 0.1
$(NH_4)_2Fe(SO_4)_2$/600 °C	Wood Char	None	319 ± 3.6	8.0 ± 0.6
$Na_2S_2O_4$/600 °C	Bone Char	None	96.0 ± 1.2	6.8 ± 0.2
$Na_2S_2O_4$/600 °C	Wood Char	None	315 ± 3.3	6.8 ± 0.6

Abe et al. (2004) - while virtually no fluoride removal was observed for wood charred at 300 °C with a specific surface area of 0.90 m^2/g, the adsorption increased slightly at 500 °C (0.01 mg/g at C_e=10 mg/L) where the specific surface area was 149 m^2/g and the highest fluoride removal capacity was achieved at 600 °C (0.11 mg/g at C_e=10 mg/L) with a surface area of 327 m^2/g. Nonetheless, the fact that the wood char was minimally effective at fluoride adsorption regardless of charring temperature or surface area suggests that the surface chemistry of wood char is not conducive to attracting negatively charged fluoride ions.

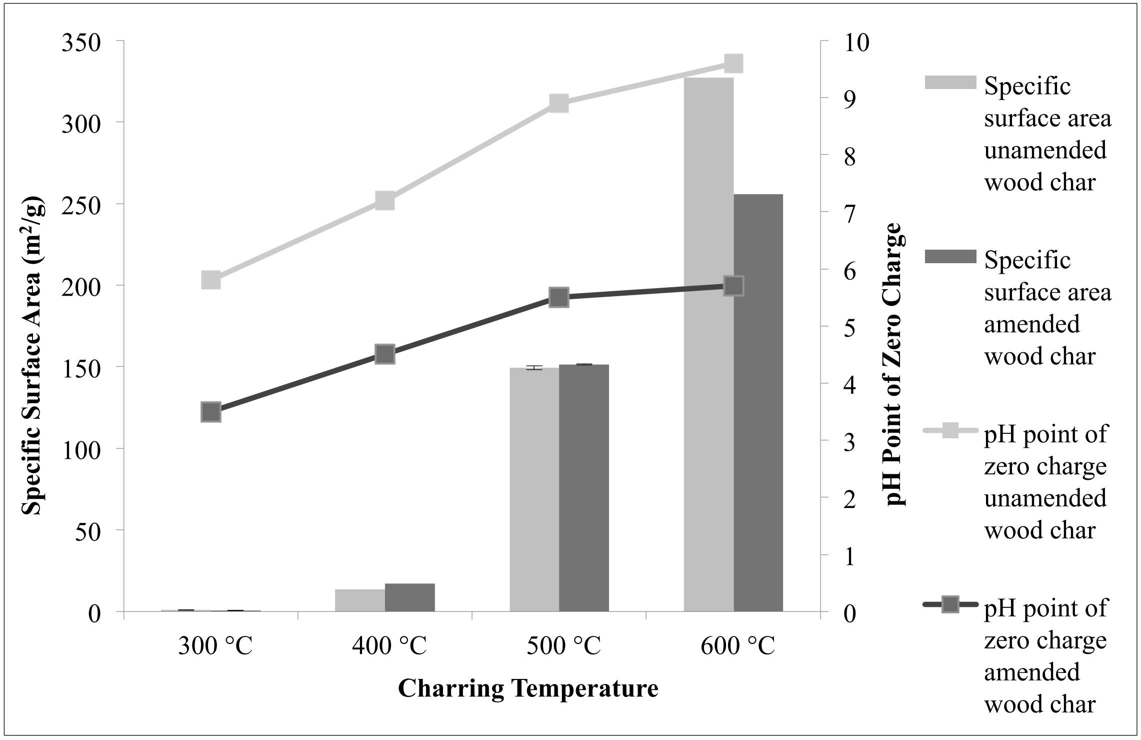


Figure 3.2: Bar graph shows specific surface area (m^2/g) (left y-axis) and line graph shows the pH_{PZC} (right y-axis) while charring temperature for both aluminum amended and unamended eucalyptus wood chars is shown on the x-axis.

Wood chars amended with aluminum oxides exhibit similar specific surface areas to those of the unamended chars and show the highest surface areas at 600 °C and the lowest at 300 °C. The low level of aluminum oxides incorporated into the media during treatment (approximately 0.25% aluminum by weight) was enough to greatly increase the adsorption capacity of the media but not to cause a significant change in the specific surface area (some samples, 600 °C, show a slight decrease while others, 400 °C, do not). Any decrease in specific surface area due to amendment with aluminum oxides is offset by the improved surface chemistry as noted by the large increase in the fluoride removal capacity. The fact that the 500 °C bone char has a lower surface area (99 versus 327 m^2/g) relative to the 600 °C wood char and yet evidences a much higher fluoride adsorption supports the suggestion that the chemical composition, with its resulting change in surface chemistry, of adsorption materials is important as discussed above.

Point of Zero Charge

Another property of interest is the $pH_{PZC,}$ a characteristic of media assessed to determine the surface charge at different water pH levels. Figure 3.2 and Table 3.2 show that both charring temperature and aluminum amendment affect the pH_{PZC}. For example, at 300 °C the pH_{pzc} of wood char was 5.8 while at 600 °C it was 9.6. When the aluminum amendment is taken into account, results show that at 600 °C the pH_{pzc} values are 9.6 and 5.7 for unamended and amended, respectively (Table 3.2). Chingombe et al. (2005) stated that thermal treatment of activated carbon based materials has been known to produce more basicity on the surface of media. In this case, a higher charring temperature resulted in a higher pH_{PZC}, which is likely due to the removal of oxygen atoms on the surface that in turn reduced the acidic functional groups and raised the pH_{PZC} (Hao et al., 2004). Work done by other authors has shown the pH_{PZC} of activated carbon-based materials to fall in the range of 9 – 10 (Han et al., 2000; Song et al., 2010; Gonzalez and Pliego-Cuervo, 2013). Research on bone char also supports this finding that higher charring temperatures tend to increase the pH_{PZC} or residual pH at equilibrium (Larsen et al., 1994; Mwaniki and Nagelkerke, 1990). It is interesting to note, as shown in Table 3.2, that the pH_{PZC} of the wood char actually decreases when chars are amended with aluminum oxides. The fact that the pH_{PZC} decreases to below 6 is a surprising result given the increased fluoride removal. However, this is a feasible result as the pH_{PZC} values of aluminum oxides range from 4.5 to 9.8 (Smit and Holten, 1980; Sposito, 1996). A decrease in pH_{PZC} also results in a decrease in the pH of solution at equilibrium when fluoride is removed with aluminum amended wood char. Residual solution pH values for untreated wood char at 600 °C averaged 7.38 while the aluminum amended wood char averaged 6.18. This decrease in solution pH value through use of aluminum amended wood char may have played a role in the fluoride adsorption capacity since some pH values fell below the pH_{PZC}.

Surface Modification

Activated carbon surfaces can exhibit acidic, basic, or neutral characteristics depending on the surface functional groups; treatment with oxidizing or reducing agents can alter the surface functional groups and thus surface characteristics such as the pH_{PZC} of media (Daifullah et al., 2007; Liu et al., 2007; Song et al., 2010). Table 3.2 shows the specific surface area and pH_{PZC} of chars treated with reducing agents, sodium dithionite ($Na_2S_2O_4$) and iron ammonium sulfate [$(NH_4)_2Fe(SO_4)_2$]. It was hypothesized that treatment with reducing agents would increase the pH_{PZC} by making the surface of the media more basic, likely through removal of oxygen atoms. This work did not confirm the hypothesis. For example, when wood char was treated with iron ammonium sulfate the pH_{PZC} of the wood char decreased from 9.6 to 8.0. Additionally, treatment with sodium dithionite evidenced even larger changes with both eucalyptus wood and bone chars exhibiting a final pH_{PZC} of 6.8, much lower than their starting values of 9.6 and 8.2, respectively (see Table 3.2 for pH_{PZC} values). Han et al. (2000) found that treatment with strong reducing agent sodium dithionite also did not improve the chromium removal capacity of activated carbon. They speculated that the activated carbon surface may have a buffering capacity, due to its ability to oxidize reducing agents without significant changes in the media surface, that makes it resistant to change from reducing agents. This may, in part, explain why the pH_{PZC} was not altered in the expected direction in the case of the eucalyptus char.

Despite the decrease in pH_{PZC} between untreated wood and bone chars and chars treated with reducing agents, the equilibrium solution pH values were similar for both untreated and pretreated. For example, solution pH values after reaching equilibrium with wood and bone chars alone were in the range of 7.09 to 7.75 and 7.33 to 7.74, respectively, while for all chars treated with reducing agents the equilibrium solution pH values ranged from 7.15 to 7.69. The K_f values for fluoride removal with amended materials shown in Table 3.3 can be directly compared because the 1/n values were forced to the same value for each material. These K_f values demonstrate that for unamended wood and bone chars, the use of reducing agents increased the fluoride removal capacity minimally (e.g., the K_f value for bone char increased from 1.82 to 2.28 when treated with sodium dithionite) despite the decrease in pH_{PZC}, 8.2 to 6.8 for bone char. Treatment with reducing agents caused no significant change to specific surface area of materials. Therefore, this change in fluoride removal cannot be explained by removal of organics, significant change in solution pH, or increase in surface area.

Table 3.3: Freundlich constants calculated from batch tests investigating fluoride removal of bone and wood chars modified with reducing agents and amended with aluminum or unamended. In all cases 1/n values have been forced to a common values so K_f constants can be statistically compared.

Freundlich Constants						
Charring Temp.	Pretreatment	Amendment	Material	K_f $(mg/g)/(mg/L)^{1/n}$	$1/n^{**}$	r^2
600 °C	None	None	Wood Char	0.04 ± ≤0.01	0.50	0.91
600 °C	$Na_2S_2O_4$	None	Wood Char	0.05 ± ≤0.01	0.50	0.96
600 °C	$(NH_4)_2Fe(SO_4)_2$	None	Wood char	0.05 ± ≤0.01	0.50	0.99
600 °C	None	Aluminum	Wood Char	0.18 ± ≤0.01	0.64	0.99
600 °C	$(NH_4)_2Fe(SO_4)_2$	Aluminum	Wood Char	0.09 ± ≤0.01	0.64	0.99
500 °C	None	None	Bone char	1.82 ± 0.09	0.33	0.97
500 °C	$Na_2S_2O_4$	None	Bone Char	2.28 ± 0.25	0.33	0.97
500 °C	$(NH_4)_2Fe(SO_4)_2$	None	Bone Char	2.23 ± 0.10	0.33	0.98
500 °C	None	Aluminum	Bone char	5.31 ± 0.18	0.40	0.99
500 °C	$(NH_4)_2Fe(SO_4)_2$	Aluminum	Bone Char	2.29 ± 0.09	0.40	0.98

**For this data the 1/n Freundlich values have been forced to a common value so that the K_f values can be directly compared. Due to process of forcing the 1/n values to a common number there is no error for these 1/n values.

Therefore, an alternative possibility is that while not increasing the pH_{PZC}, the treatment with strong reducing agents altered the surface functional groups on the chars in a way that made the surface more attractive to the negatively charged fluoride. Conversely, Table 3.3 shows that when bone and wood char were pretreated with reducing agents and then amended with aluminum sulfate, the fluoride removal actually decreased as compared with aluminum amendment but no pretreatment (e.g. K_f for iron ammonium sulfate reduced aluminum modified bone char was 2.29 while the K_f for aluminum amended bone char was 5.31). This decrease in fluoride removal may be due to the decrease in acidic functional groups caused by treatment with reducing agents which would in turn decrease media uptake of aluminum and therefore, reduce fluoride removal from the aqueous solution. Song et al. (2010) found that pretreatment with oxidizing agents added acidic functional groups to the surface which enhanced the attraction of an activated carbon-based material to lead, another metal. Therefore, removing acidic functional groups from the surface should decrease the attractive forces between aluminum oxides and the material surface. These findings suggest that pretreatment of chars with reducing agents as tested here is not a helpful method for increasing fluoride removal capacity.

Comparison between Wood and Bone Chars

A motivation for this work was to find an alternative to using bone char for fluoride removal that may be more acceptable in select communities. In this research, eucalyptus wood char has proven to be a viable fluoride removal option only if it is amended with aluminum oxides. Despite the high specific surface area, the wood char requires amendment to approach the removal capacity of the bone char. Chemical composition, hydroxyapatite versus carbon for bone and wood chars, respectively, was discussed above as one of the key differences between the two chars. Due to the limited fluoride removal of carbon alone, the wood char benefits from the addition of aluminum oxides which provides a mechanism by which fluoride forms a bond with the aluminum present on the char, likely through ion exchange, motivating the adsorption. Another factor which could cause an adsorption difference between bone and wood chars is pore size distribution. If pore size distribution is different for bone and wood chars it could cause size exclusion when adsorption of fluoride or aluminum oxides occurs in the material with smaller pores. However, in this case, except for wood charred at 600 ˚C, all the pores in both wood and bone chars were found to be mesopores (20 - 500 Å). The wood charred at 600 ˚C had 40% of its total pore size as micropores (<20 Å). Therefore, since the hydrated radii of aluminum and fluoride have been reported to be 4.75 and 3.52 Å, respectively (Nightingal, 1959), no size exclusion of these dissolved ions should have occurred. Nonetheless, the size of colloidal aluminum oxide precipitates would be orders of magnitude higher and thus could experience size exclusion in the smaller pores. It is anticipated that the micropores present in the 600 ˚C char explain why it was the only temperature at which the aluminum amendment caused a significant change to the specific surface area. This is due to the aluminum oxides blocking some of the micropores during the amendment process. The pH_{PZC} values of both materials are diverse as unamended bone char is 8.2 while unamended wood char is 9.6 and the aluminum amended versions are 7.0 and 5.7 for bone and wood, respectively (shown in Table 3.2). This suggests that while the pH_{PZC} is a helpful characteristic to understand about media surfaces, it is not the only indicator of the fluoride removal capacity. This research demonstrated that despite the pH_{PZC} values for bone char and aluminum amended wood char being lower than those of other materials, the fluoride removal capacities were higher.

Conclusion

Although bone char has been proven as an effective fluoride adsorption material due to surface chemistry and specific surface area, in some areas it may not be suitable for use to remove fluoride from drinking water based on cultural reasons. Therefore, this work assessed the potential for eucalyptus wood char to be a substitute adsorptive material for bone char. In spite of the fact that the wood char exhibited higher specific surface area values at charring temperatures of 500 and 600 °C than bone char, it evidenced negligible fluoride removal capacity due to the unfavorable surface chemistry and chemical composition. Amending the wood char with aluminum oxides significantly increased fluoride uptake – this material having both desirable surface area and surface chemistry. The pH_{PZC} of the wood char increased with higher charring temperatures, which is likely due to the increased basicity of the surface after charring at higher temperatures. When amended with aluminum nitrate, the wood char, due in part to the strong attraction between aluminum and fluoride in water, exhibited a statistically significant increase in fluoride removal capacity despite the decrease in the pH_{PZC}. Unstudied until now, treatment with reducing agents, intended to raise the pH_{PZC}, actually lowered the pH_{PZC} but did not greatly alter the equilibrium pH values in solution. Treatment with reducing agents, while minimally increasing the fluoride removal capacity of unamended chars, did not cause enough change to make this a useful research area to pursue further at this time. Helpful to this line of inquiry towards finding a suitable substitute for bone char would be an investigation into other methods of amending wood chars with positively charged metals, such as iron and aluminum, to see if it is possible to get a higher percentage metal loading on the media and in doing so to increase the fluoride removal capacity. Additionally helpful would be to assess whether these types of surface area and surface chemistry amendments are equally or even more effective for other types of locally available materials such as bamboo, coconut waste, coffee production waste, or other wood chars.

Acknowledgements

The authors gratefully acknowledge the U.S. Environmental Protection Agency and the U.S. National Science Foundation that contributed partial funding to this work. This publication was developed under STAR Fellowship Assistance Agreement no. 91731301 awarded by the U.S. Environmental Protection Agency (EPA). This work has not been formally reviewed by EPA, and the views expressed in this paper are solely those of the authors and the EPA does not endorse any products or commercial services mentioned in this publication. The authors also wish to acknowledge partial funding from the OU WaTER Center and the University of Oklahoma in support of this work.

References

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., and Tanada, S. (2004). "Adsorption of fluoride ions onto carbonaceous materials." *J. Colloid Interf. Sci.* 275(1), 35–39.

Amini, M., Mueller, K., Abbaspour, K., Rosenberg, T., Afyuni, M., Møller, K., Sarr, M., and Johnson, A.C. (2008). "Statistical modeling of global geogenic fluoride contamination in groundwaters." *Environ. Sci. Technol.* 42(10), 3662–3668.

Ayoob, S., Gupta, A. K., and Bhat., V.T. (2008). "A conceptual overview on sustainable technologies for the defluoridation of drinking water." *Crit. Rev. Environ. Sci. Technol.* 38(6), 401–470.

Babic, B.M., Milonjic, S.K., Polovina, M., and Kaludierovic, B. (1999). "Point of zero charge and intrinsic equilibrium constants of activated carbon cloth." *Carbon*, 37(3), 477–481.

Benaddi, H., Bandosz, T. J., Jagiello, J., Schwarz, J. A., Rouzaud, J. N., Legras, D., and Beguin, F. (2000). "Surface functionality and porosity of activated carbons obtained from chemical activation of wood." *Carbon*, 38, 669–674.

Bhargava, D., and Killedar, S. (1991). "Batch studies of water defluoridation using fishbone charcoal." *Res. J. Wat. Poll. Control Fed.* 63(6), 848–858.

Brunauer, S., Emmett, P.H., and Teller, E. (1938). "Adsorption of Gases in Multimolecular Layers." *J. Am. Chem. Soc.* 60(2), 309-319.

Brunson, L.R, and Sabatini, D,A. (2009). “An evaluation of fish bone char as an appropriate arsenic and fluoride removal technology for emerging regions.” *Environ. Eng. Sci.* 26(12), 1777–1784.

Chen, Y., Chai, L., and Shu, Y. (2008). “Study of arsenic (V) adsorption on bone char from aqueous solution.” *J.Hazard. Mater.* 160(1), 168–172.

Chingombe, P., Saha, B., and Wakeman, R. (2005). “Surface modification and characterization of a coal-based activated carbon.” *Carbon*, 43, 3132–3143.

Coetzee, P., Coetzee, L., Puka, R., and Mubenga, S. (2004). “Characterization of selected South African clays for defluoridation of natural waters.” *Water SA,* 29(3), 331–338.

Daifullah, A., Yakout, S., and Elreefy, S., (2007). “Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw.” *J. Hazard. Mater.* 147(1-2), 633–643.

Dessie, G. and Erkossa, T. (2011). *Planted forests and trees working paper: eucalyptus in East Africa socio-economic and environmental issues*. Forestry Department Food and Agriculture Organization of the United Nations, Rome, Italy.

Fan, X., Parker, D., and Smith, M. (2003). “Adsorption kinetics of fluoride on low cost materials.” *Water Res.* 37(20), 4929–4937.

Fawell, J., Bailey, K., Chilton, J., and Dahi, E. (2006). *Fluoride in drinking-water*. World Health Organization, Geneva, Switzerland.

Fewtrell, L., Smith, S., Kay, D., and Bartram, J. (2006). “An attempt to estimate the global burden of disease due to fluoride in drinking water.” *J. Water Health,* 4(4), 533–542.

Gonzalez, P., and Pliego-Cuervo, Y. (2013). “Physicochemical and microtextural characterization of activated carbons produced from water steam activation of three bamboo species.” *J. Anal. Appl. Pyrol.* 99, 32–39.

Gwala, P., Andey, S., Mhaisalkar, V., Labhasetwar, P., Pimpalkar, S., and Kshirsagar, C. (2011). “Lab scale study on electrocoagulation defluoridation process optimization along with aluminum leaching in the process and comparison with full scale plant operation.” *Water Sci. Technol.* 63(12), 2788–2795.

Han, I., Schlautman, M., and Batchelor, B. (2000). “Removal of hexavalent chromium from groundwater by granular activated carbon.” *Water Environ. Res.* 72(1), 29–39.

Hao, X., Quach, L., Korah, J., Spieker, W., and Regalbuto, J. (2004). “The control of platinum impregnation by PZC alteration of oxides and carbon.” *J. Mol. Catalysis A: Chem.* 219(1), 97–107.

James, G., Sabatini, D., Chiou, C., Rutherford, D., Scott, A., and Karapanagioti, H. (2005). “Evaluating phenanthrene sorption on various wood chars.” *Water Res.* 39(4), 549–558.

Kamble, S., Jagtap, S., Labhsetwar, N., Thakare, D., Godfrey, S., Devotta, S., and Rayalu, S. (2007). “Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan.” *Chem. Engr.* 129(1-3), 173–180.

Kaseva, M E. (2006). “Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania.” *J. Water Health* 4(1), 139–147.

Larsen, M., Pearce, E., and Ravnholt, G. (1994). “The effectiveness of bone char in the defluoridation of water in relation to its crystallinity, carbon content and dissolution pattern.” *Arch. Oral Bio.* 39(9), 807–816.

Levya-Ramos, L. R., Ovalle-Turrubiartes, J., and Sanchez-Castillo, M. (1999). “Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon.” *Carbon*, 37(4), 609–617.

Liu, S., Chen, X., Chen, X., Liu, Z., and Wang, H. (2007). “Activated carbon with excellent chromium(VI) adsorption performance prepared by acid-base surface modification.” *J. Hazard. Mater.* 141(1), 315–319.

Malde, M., Scheidegger, R., Julshamn, K., and Bader, H. (2011). “Substance flow analysis: a case study of fluoride exposure through food and beverages in young children living in Ethiopia.” *Environ. Health Perspect.,* 119(4), 579–584.

McGill, P. E. (1994). “Endemic fluorosis.” *Baillieres Clin. Rheumataology*, 9(1), 75–81.

Medellin-Castillo, N., Leyva-Ramos, R., Ocampo-Perez, R., Garcia de la Cruz, R., Aragon-Piña, A., Martinez-Rosales, J., Guerrero-Coronado, R., and Fuentes-Rubio, L. (2007). “Adsorption of fluoride from water solution on bone char.” *Ind. Engr. Chem. Res.* 46(26), 9205–9212.

Mlilo, T., Brunson, L.R, and Sabatini, D,A. (2010). “Arsenic and fluoride removal using simple materials.” *J. Environ. Eng.* 136(4), 391–398.

Mwaniki, D., and Nagelkerke, N. (1990). “Sorption kinetics of fluoride in drinking water by bone charcoal columns.” *Front. Med. Biological Engr.* 2(4), 303–308.

Nightingale Jr., E. (1959). “Phenomenological theory of ion solvation. Effective radii of hydrated ions.” *J. Phys. Chemi.* 63(9), 1381–1387.

Nigussie, W., Zewge, F., and Chandravanshi, B. (2007). “Removal of excess fluoride from water using waste residue from alum manufacturing process.” *J. Hazard. Mater.* 147(3), 954–963.

Pettersen, R. (1984). “The chemical composition of wood.” *The chemistry of solid wood*, R.M. Rowell, ed. American Chemical Society, Washington D.C.

Smit, W., and Holten, L. (1980). “Zeta-potential and radiotracer adsorption measurements on EFG –α-Al2O3 single crystals in NaBr solutions.” *J. Colloid Interf. Sci*. 78(1), 1 - 14.

Song, X., Liu, H., Cheng, L., and Qu, Y. (2010). “Surface modification of coconut-based activated carbon by liquid-phase oxidation and its effects on lead ion adsorption.” *Desalination,* 255(1-3), 78–83.

Sposito, G., ed. (1996). *The environmental chemistry of aluminum*. CRC Press, Boca Raton, FL.

Tchomgui-Kamga, E., Alonzo, V., Nanseu-Njiki, C., Audebrand, N., Ngameni, E., and Darchen, A. (2010). “Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water.” *Carbon*, 48(2), 333–343.

Tonguc, M., Ozat, Y., Sert, T., Sonmez, Y., and Kirzioglu, F. (2011). “Tooth sensitivity in fluorotic teeth.” *European J. Dentistry,* 5(3), 273–280.

Wilson, J.A., Pulford, I., and Thomas, S. (2003). “Sorption of Cu and Zn by bone charcoal.” *Environ. Geochem. Health*. 25(1), 51–56.

World Health Organization. (2011). *Guidelines for drinking-water quality - 4th edition*. World Health Organization, Geneva, Switzerland.

Zhou, Z., Shi, D., Qiu, Y., and Sheng, D. (2010). “Sorptive domains of pine chars as probed by benzene and nitrobenzene.” *Environ. Pollut.* 158(1), 201–206.

CHAPTER 4

Practical Considerations, Column Studies and Natural Organic Material Competition for Fluoride Removal with Bone Char and Aluminum Amended Materials in the Main Ethiopian Rift Valley.[3]

Abstract

This work investigated the fluoride removal capacities of materials including: bone char (BC), aluminum oxide coated bone char (ACBC) and aluminum oxide impregnated wood char (AIWC) and activated alumina (AA). Materials were investigated in batch and column studies, including comparisons between synthetic and natural groundwater. Results suggest that in all cases the laboratory column results exhibited higher fluoride removal efficiencies than the field studies conducted in the Ethiopian Rift Valley. Further studies indicate that the reduced effectiveness in the field was likely due to a combination of the high pH of the groundwater (8.2) and the presence of competing ions (sulfate). Batch studies testing potential competition with natural organic material (NOM) showed no statistical evidence of competition for adsorption on BC between fluoride and NOM and minor evidence of competition when using ACBC and AIWC. To provide evidence for using Rapid Scale Small Column Test (RSSCT) principles for fluoride adsorption by BC, two different column volume and

---

[3] Brunson, L.R., and Sabatini, D.A. (2014). "Practical considerations, column studies and natural organic material competition for fluoride removal with bone char and aluminum amended materials in the Main Ethiopian Rift Valley." *Sci. Tot. Environ.* 488-489, 580–587.

particle sizes were tested. The results indicate that RSSCT scaling equations, developed for activated carbon, are applicable for BC removal of fluoride. These results provide valuable insights for utilizing fluoride adsorption materials for water treatment in a field setting.

Introduction

Lack of access to an improved source of drinking water is a global health issue affecting approximately 780 million people worldwide (WHO and UNICEF, 2012). Not considered in this statistic are an estimated 200 million people who potentially drink groundwater containing fluoride concentrations above the World Health Organization (WHO) guideline value of 1.5 mg/L (Amini et al., 2008; World Health Organization, 2011). Elevated fluoride concentrations occur in numerous groundwater formations globally, including areas of India, China, and the Rift Valley of Africa which includes the Main Ethiopian Rift Valley (MER) (Amini et al., 2008; Fawell et al., 2006; Fewtrell et al., 2006; Rango et al., 2010, 2012). Human consumption of elevated fluoride concentrations is problematic because dental and skeletal fluorosis can result (Li et al., 2001; Meenakshi and Maheshwari, 2006; Sivasamy et al., 2001). Dental fluorosis manifests itself as discoloration and pitting of the teeth, resulting in physical and economical effects, while skeletal fluorosis can cause pain and restriction of movement, which can impair the livelihood of those dependent on subsistence farming or other manual activities (Fewtrell et al., 2006; Meenakshi and Maheshwari, 2006; Tonguc et al., 2011).

When harvesting rainwater or using alternative water supplies is not practical, fluoride removal from drinking water is the most viable option for obtaining safe water. Treatment options that have been investigated include: electrolytic defluoridation (Gwala et al., 2011; Mameri et al., 2001), reverse osmosis and membrane processes (Arora et al., 2004; Meenakshi and Maheshwari, 2006), precipitation (Yadav et al., 2006), and adsorption (Abe et al., 2004; Ayoob et al., 2008; Brunson and Sabatini, 2009; Medellin-Castillo et al., 2007; Mlilo et al., 2010). Many of these options have proven viable for fluoride removal, but also exhibit aspects which make them less than ideal for rural developing areas. For example, electrolytic defluoridation requires an energy source, and reverse osmosis and membrane processes can require large capital costs and produce large volumes of waste solution (Gwala et al., 2011; Jagtap et al., 2012). The Nalgonda technique is a process by which aluminum sulfate and lime are added to water to cause co-precipitation of fluoride and aluminum hydroxides. Nalgonda has been used with some success, including in Ethiopia, but has constraints including the production of large amounts of waste sludge and the requirement of daily operational and chemical addition (Fawell et al., 2006; Meenakshi and Maheshwari, 2006; Yadav et al., 2006).

Adsorption is a helpful fluoride removal option because it can be implemented using gravity flow (no need for a power source), and is helpful in terms of cost and ease of use (Bhatnagar et al., 2011). Researchers have extensively studied activated alumina (AA), a material well known for fluoride adsorption. It has been found that AA works best at low pH values (< 5) and that it has a fluoride removal capacity ranging from 4 - 15 mg of fluoride per gram of AA for laboratory studies and 1 mg/g in a field study;

fluoride removal values for AA tend to vary based on water pH, competing ions and the nature of the study (Fawell et al., 2006; Ghorai and Pant, 2005; Hao and Huang, 1986; Tang et al., 2009). A number of activated carbon materials showed minimal fluoride removal capacities despite their high specific surface areas (Abe et al., 2004; Ayoob et al., 2008). Bone char (BC) has demonstrated a much higher fluoride removal capacity than activated carbon, which can be attributed to its dual properties of a high specific surface area [111 m^2/g (Brunson and Sabatini, 2009), 100 m^2/g (Cheung et al., 2005) and 104 m^2/g (Medellin-Castillo et al., 2007)] and desirable surface chemistry, a surface that exhibits a net positive charge at typical groundwater pH values so that it will attract fluoride ions. Researchers have shown that BC can remove fluoride and arsenic simultaneously with minimal competition, which is helpful in situations where they coexist; several MER locations have been suggested to have both fluoride and arsenic in the groundwater (Rango et al., 2010). Further, BC can be produced using local materials in rural areas of Ethiopia, Kenya and Tanzania (Abaire et al., 2009; Brunson and Sabatini, 2009; Mjengera and Mkongo, 2002). In some cases, BC is culturally unacceptable, therefore, alternative materials with similar properties to BC must be evaluated.

When considering the practicalities of removing fluoride from groundwater it is necessary to account for possible competition from other ions in water. Often phosphate and sulfate in groundwater compete with fluoride for adsorption by commonly used adsorbents. (Jagtap et al., 2012). Natural organic material (NOM) in the groundwater should also be considered as it sometimes competes with other adsorptive processes, particularly adsorption onto activated carbon, and is found in all groundwater sources

(Newcombe et al., 1997), generally at concentrations of 0.5 – 10 mg/L (Genz et al., 2008). NOM is composed of humic and fulvic acids and typically has negatively charged surface functional groups (Redman et al., 2002), which suggests it has the potential to compete with fluoride for removal on adsorption media in the same way that negatively charged phosphate and sulfate ions are known to compete. It does not appear that NOM competition has previously been studied in relation to fluoride adsorption onto bone or wood chars and competing ion studies have not been conducted on several of the materials studied in this work.

Continuous flow column studies are important to assess the ability of a sorbent to remove fluoride in a setting similar to a point-of-use (POU) or community scale system. Continuous flow tests capture kinetic effects, such as mass transfer and intraparticle diffusion, in a way not possible in batch tests. Ma et al. (2008) conducted batch and column studies and suggested that BC is more effective than AA at fluoride removal and that reducing the bed depth or increasing the flow rate of a column study decreased the bed volumes until breakthrough.. Minimal work to date has evaluated the fluoride removal potential of bone and wood chars in continuous flow studies, particularly in a field setting utilizing a natural water source (Ayoob and Gupta, 2007; Kloos and Haimanot, 1999).

Assessing filtration technologies for use in community scale systems can be costly and time consuming. One way to reduce these issues is through the use of Rapid Small Scale Column Test (RSSCT) principles which are helpful for reducing the amount of water and media required, the time needed to conduct studies, and the cost of such studies while producing results representative of full scale systems (Crittenden et al., 1986; Badruzzaman et al., 2004). RSSCT calculations use dimensionless scaling principles based on mass transfer and hydraulic flow conditions as in Equations 4.1 and 4.2, where EBCT is the empty bed contact time, d is the particle diameter of the sorbent, ν is superficial velocity, and SC and LC stand for small-scale and large-scale, respectively (Badruzzaman et al., 2004; Trussell et al., 2005).

$$EBCT_{SC}/EBCT_{LC} = [d_{SC}/d_{LC}]^{\wedge 2} \qquad \text{Equation 4.1}$$

$$\nu_{SC}/\nu_{LC} = d_{LC}/d_{SC} \qquad \text{Equation 4.2}$$

RSSCT equations were used to calculate particle size, flow rate and bed volumes for use in two column studies to evaluate the validity of this approach for the use of BC for fluoride removal (Trussell et al., 2005). The use of these equations for the RSSCT approach assumes that BC is homogenous at different particle diameters and that surface diffusivity is constant across different particle sizes (Westerhoff et al., 2005). RSSCTs can be valuable in scaling from small scale laboratory column systems, that can be tested in a few weeks, to full scale systems, which require multiple months (Badruzzaman et al., 2004; Westerhoff et al., 2005). Theoretically, if the RSSCT model is applicable, two columns of different sizes that are accurately scaled should have the exact same breakthrough curves, all other things equal (Westerhoff et al., 2005). To date the RSSCT method, first developed for activated carbon and later validated for arsenic removal on iron oxide based media, based on reviewed literature, has not been evaluated for BC adsorption of fluoride (Westerhoff et al., 2005).

The purpose of this work is to assess the ability of several materials (wood char, aluminum coated wood char, aluminum impregnated wood char, bone char, and aluminum coated bone char) to remove fluoride in a continuous flow system utilizing groundwater with elevated fluoride concentrations from the MER. Continuous flow tests will also be conducted in a laboratory setting to compare the relative fluoride removal capacities between laboratory and field systems. There are two hypotheses being tested in this work. The first is that, based on the relatively homogenous nature of the BC material, the RSSCT approach will be validated for BC, which would allow for quicker and easier scale up of systems intended to remove fluoride from water using bone char. This work also aims to assess the practical question of whether or not NOM will negatively affect the fluoride removal capacity of several materials. Thus, the second hypothesis is that NOM will have an effect on fluoride removal due to its negative charge.

Methods

Materials Preparation

Eucalyptus robusta was obtained from Mezozoic Landscapes, Inc. in Florida while fish bone meal was purchased from Peaceful Valley Farm & Garden Supply in California. Chars were prepared by placing raw material in a glaze-free covered porcelain container and charring them in an oven at 500 or 600 °C, bone and wood, respectively, for four hours. Materials were crushed and sieved to a size range of 180 – 425 μm in diameter and rinsed in deionized water to remove fines. Aluminum oxide coating was achieved by first using 4-Morpholineethanesulfonic acid hydrate, a biological pH buffer, in deionized water to obtain a solution pH of 3.5. Aluminum nitrate was then added at 175 mg/L along with 25 grams of char material, based on the work of Levya-Ramos et al. (1999), to 500 mL flasks. This mixture was shaken for 5 days and then char materials were filtered, rinsed, dried at 100 °C and stored in sealed plastic bags. Aluminum oxide impregnated wood char (AIWC) was prepared based on the work of Tchomgui-Kamga et al. (2010) where small pieces of raw eucalyptus wood were boiled for 1.5 hours in a 1 molar aluminum chloride solution. Char was then left to cool in solution for 2 hours, air-dried for 2 hours, and oven dried at 100 °C. Dried wood pieces were charred at 600 °C for 1 hour, crushed, sieved, rinsed, dried and stored as described above.

Analysis

Fluoride in the field was analyzed with an Extech Pocket Fluoride Tester (FL700) portable fluoride meter using Total Ionic Strength Adjustment Buffer (TISAB) reagent tablets. The Extech Pocket Fluoride Tester has an accuracy of ± 3% and a range from 0.1 to 9.99 mg/L. Fluoride and pH analyses in the laboratory were conducted using an Orion pH/ISE meter (model 710a) and fluoride was measured using equal amounts of sample and TISAB.

$$Q_e = K_f C_e^{1/n} \qquad \text{Equation 4.3}$$

$$Q_e = (C_e Q_m b)/(1+C_e b) \qquad \text{Equation 4.4}$$

Freundlich and Langmuir isotherm equations (Equations 4.3 and 4.4, respectively) were used to analyze the batch test data, where C_e is the fluoride concentration at equilibrium, Q_e is the adsorption of fluoride per gram of sorbent, K_f is the adsorption capacity, $1/n$ is the adsorption intensity, Q_m is the maximum fluoride adsorption per gram of media and b is a measure of adsorption affinity (Chen et al., 2011; Leyva-Ramos et al., 2010; Ma et al., 2008). SigmaPlot Version 11.0 software was used to perform regression analyses and statistical assessments of the data fitted to these two models.

Batch Studies

Batch tests were conducted by placing 0.5 grams of media in 250 mL HDPE Nalgene bottles with 50 mL of prepared fluoride solution. Sodium fluoride was used to make a 1,000 mg/L stock solution which was diluted with deionized water containing 0.05 molar sodium chloride (to provide a constant ionic strength) as needed to make solutions. Initial batch concentrations ranged from 2.5 - 100 mg/L fluoride. NOM was added to select batch studies as either Pahokee Peat humic acid (PPHA) or Nordic Aquatic fulvic acid (NAFA), purchased from the International Humic Substances Society, selected due to the fact that they are representative of a range of naturally occurring NOM. Sodium sulfate or organic buffers (MES, HEPES, TAPS), to test for competition or adjust the pH, respectively, were added to select systems. Sealed bottles were shaken at 200 shakes per minute for 24 hours to reach equilibrium. At that point, solutions were allowed to settle, then filtered using Whatman 11 micron filters to remove media, and tested for fluoride concentrations and pH values.

Column Tests

All column studies, with one exception, were conducted utilizing a glass column size 1 x 10 cm (empty bed volume of 7.9 mL) with a flow rate of 1.2 mL/min. While, due to availability, the particle diameter for AA was 125 µm, the diameter for the other materials was an average of 302 µm. In order to test RSSCT principles with BC, a second BC column was run using different column and paticle sizes. This study used a glass column size 2.5 x 7.1 cm (empty bed volume of 34.9 mL) with an average media size of 637 μm selected based on Equation 4.1. In this case, in order to avoid high head loss often experienced with high superficial velocities, Equation 4.2 was validated for use by verifying that the product of the Reynolds and Schmidt numbers was in the range of 160 to 40,000, which is acceptable in cases where dispersion is not the primary mechanism (Trussell et al., 2005). At the base of the column, glass beads and glass wool were placed to enhance even solution distribution and keep the media contained, with the same arrangement in reverse above the column. Water was pumped through the column from the bottom at approximately 1.2 mL/min using variable-flow peristaltic pumps from Fischer Scientific. Columns were packed with wet media to ensure that media was uniformly packed in the column without an excess of air. Samples were taken periodically throughout the column run and tested for pH and fluoride concentration until complete saturation ($C_{effluent} = C_{influent}$) occurred. For field studies water was collected from a community in the MER near Meki, Ethiopia. For laboratory studies, synthetic fluoride solutions were made using deionized water and fluoride. In select cases, the water was pH adjusted to 8.2 using TAPS organic buffer or 250 mg/L of sodium sulfate was added.

Results and Discussion

Screening of Media for Column Studies: Batch Results

Batch isotherms were used to compare the removal capacities of novel materials in order to select the best sorbent for column studies. Five materials were considered in the batch tests including: wood char (WC), aluminum oxide coated wood char (ACWC), aluminum oxide impregnated wood char (AIWC), bone char (BC), and aluminum oxide coated bone char (ACBC). Adsorption isotherm data for these five novel materials and activated alumina (AA) are shown in Table 4.1.

Table 4.1: Q_e data for six media evaluated in batch isotherm studies

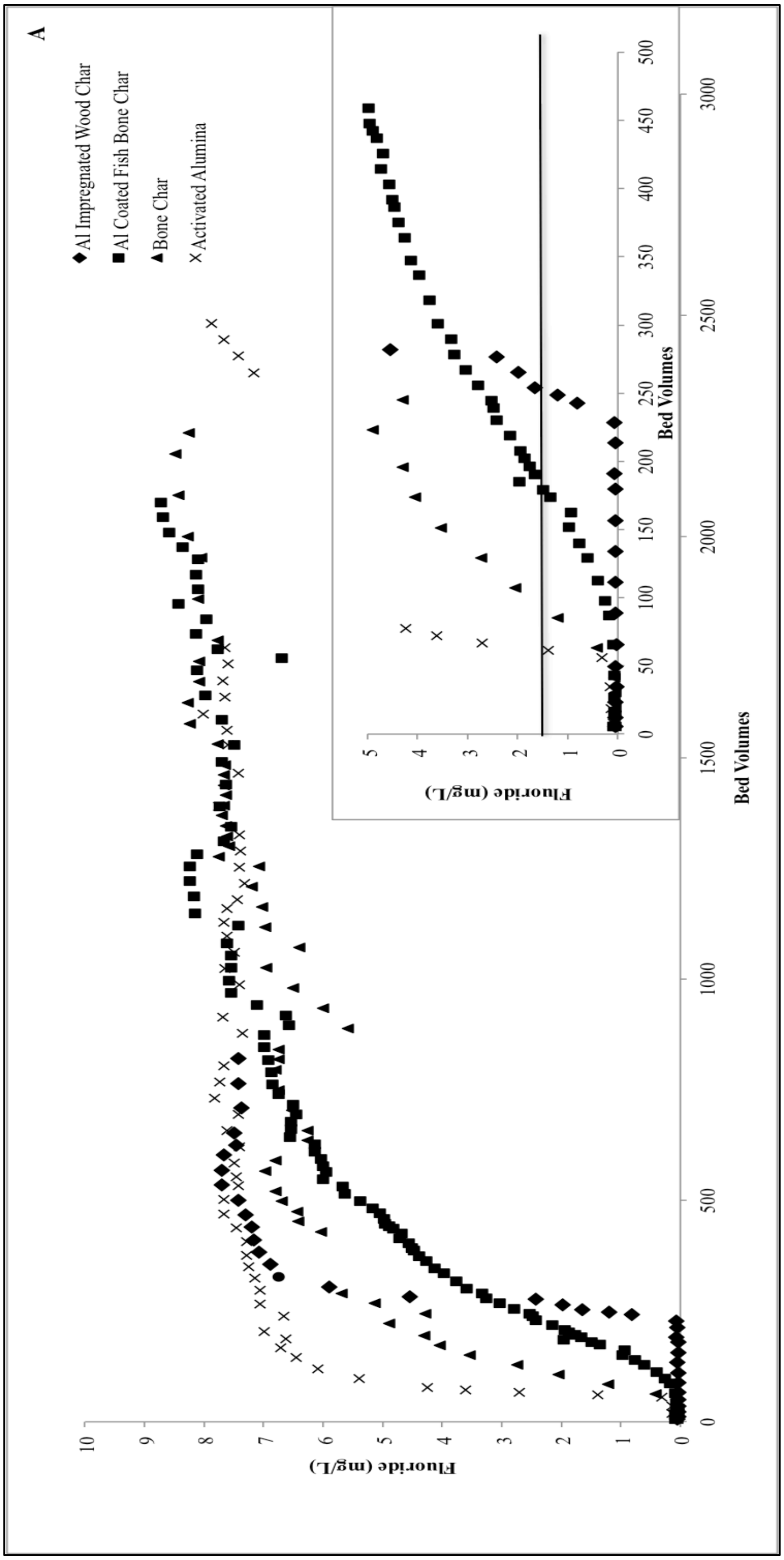
Material	**K_f (mg/g)(mg/L)$^{1/n}$**	**1/n**	**Langmuir Q_m (mg/g)**	**Q_e (mg/g) at C_e= 1.5 mg/L F**	**Q_e (mg/g) at C_e= 10 mg/L F**
Wood Char	<0.1 ± 0.0	0.82	NA*	0.2	0.1
Al Coated Wood Char	0.2 ± 0.0	0.69	NA*	0.2	0.7
Bone Char	1.8 ± 0.2	0.38	6.1 ± 0.4	2.1	3.9
Aluminum Coated Bone Char	1.4 ± 0.1	0.42	11.4 ± 0.9	1.7	3.5
Aluminum Impregnated Wood Char	4.6 ± 0.6	0.61	16.8 ± 5.8	6.0	18.8
Activated Alumina (AA)	0.4 ± 0.1	0.48	4.1 ± 0.9	0.5	1.2

***NA – not applicable – the data did not approach a plateau thus making the Langmuir isotherm inappropriate.**

Note: R-squared values for all Freundlich and Langmuir data in this table are in the range of 0.95 to 0.99

For WC and ACWC only Freundlich parameters are shown, as the isotherms exhibited such low removal capacities that a plateau was not exhibited and thus, Langmuir interpretation is not appropriate. The Freundlich isotherm can be indicative of a heterogeneous material and has been used in the literature to evaluate coal-based sorbents, BC, and pine wood char (Brunson and Sabatini, 2009; Mohan et al., 2012; Sivasamy et al., 2001). In looking at the results in Table 4.1, K_f values should be compared only if 1/n values are equal. Since values in Table 4.1 show a wide range of values for 1/n, the Freundlich equation is used to calculate Q_e values at C_e = 1.5 and C_e = 10 mg fluoride/L to compare the adsorption capacity at a constant C_e value (driving force for adsorption). For remaining materials the Langmuir isotherms were calculated and Q_m data, which suggest the maximum adsorption capacity of the material for that sorbate, are compared. AA, BC, ACBC, and AIWC were selected for further study.

Column Studies



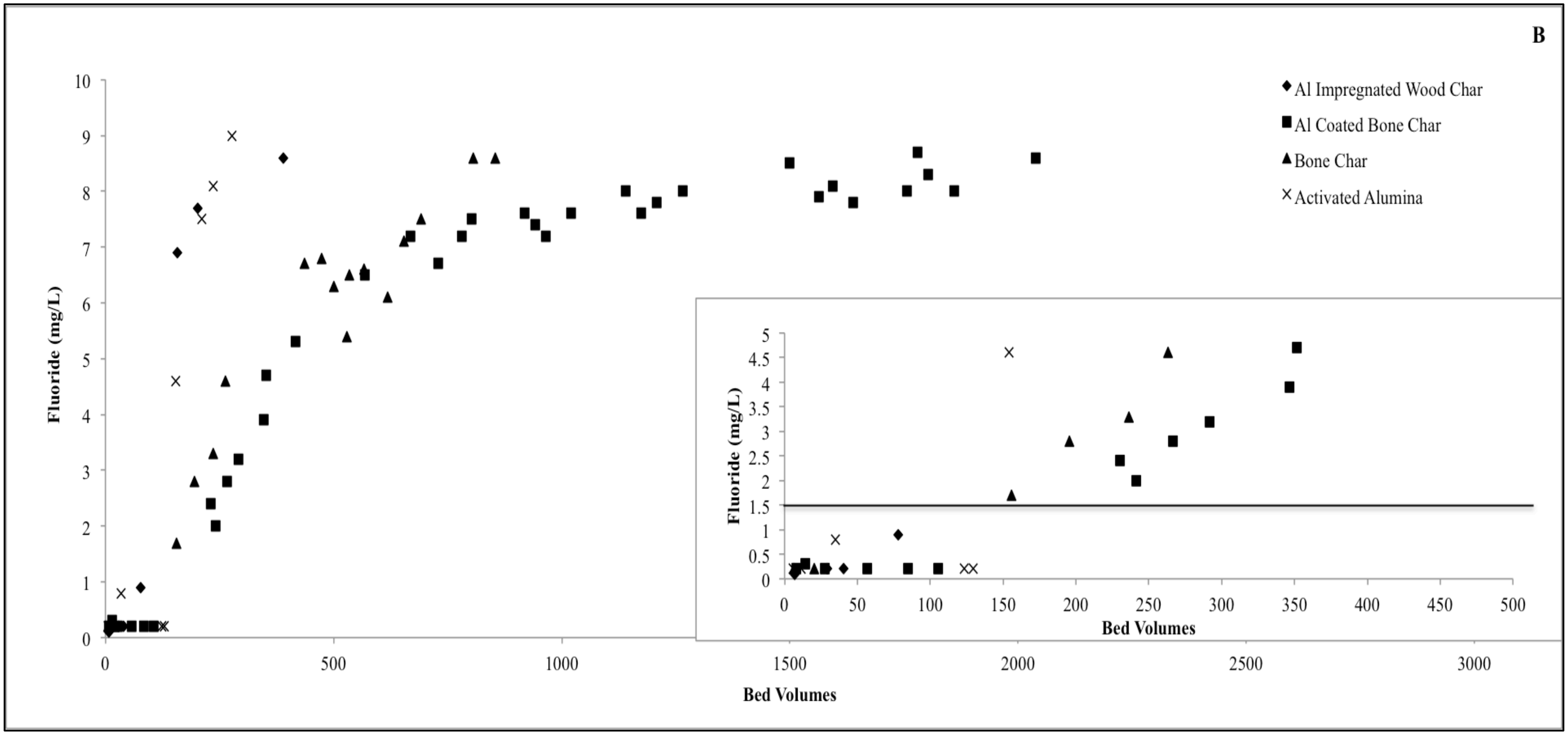


Figure 4.1: Results of continuous flow columns studies where the x-axis shows bed volumes and the y-axis shows effluent fluoride concentrations in mg/L. A. Lab studies where the influent pH (unadjusted) was approximately 6.0 and the solution was fluoride in deionized water. B. Field studies using native groundwater with an influent pH of approximately 8.2

Fluoride removal capacities were evaluated in laboratory column studies. Investigation of Figure 4.1 and Table 4.2 offers several interesting findings. The first observation is that the same sorption trends shown in the batch studies are also shown in laboratory column studies: AIWC > ACBC > BC > AA (compare bed volumes to reach 1.5 mg/L in Figure 4.1(A) and Table 4.2 with Q_m values in Table 4.1). It is interesting to note the variation in specific surface areas for these materials as the AIWC was found to be 284 ± 5.9 m^2/g, whereas BC and ACBC are 99.1 ± 0.8 and 91.8 ± 3.0 m^2/g, respectively, and the AA is 185 m^2/g based on manufacturer information. This higher specific surface area could indicate one key reason why the AIWC exhibits a larger fluoride removal capacity than the other media. All columns were run with the same bed volume size and volume of column output was measured, therefore it is feasible to compare fluoride removal capacities based on bed volumes across materials.

A mass balance of the columns was conducted to determine the weight of fluoride adsorbed per gram of media at exhaustion (when $C_{effluent} = C_{influent} = 8.6$ mg/L); these values are summarized in Table 4.2. In all cases, except for AA, the column study $Q_{exhaustion}$ values ($C_{eff} = C_{inf}$) were found to be less than the batch Langmuir Q_m, which is expected since Q_m can occur at C_e values much higher than the $C_e = 8.6$ mg/L selected as representative of groundwater in the MER. This is consistent with other findings in the literature that compared batch and column studies such as Ayoob and Gupta (2007) who found that for alumina cement granules being used to remove fluoride, the Q_{column} was 5.90 mg/g while the Langmuir Q_m was 10.22 mg/g.

Table 4.2: Q_e in mg of fluoride removed per gram of material calculated based on the amount of fluoride removed during the continuous flow column study run to saturation ($C_{effluent} = C_{influent}$). The bed volumes to C_{eff} = 1.5 mg/L were obtained using the data presented in Figure 4.1. The Langmuir equation was used and both the Langmuir Q_m and the Q_e value at 8.6 equilibrium fluoride concentration are presented.

	Batch	**Column Bed Volumes to Reach 1.5 mg/L Fluoride Effluent**		**Column Mass Balance $Q_{exhaustion}$ Values C_{inf} = 8.6 mg/L**	
Material	**Langmuir Q_m (mg/g)**	**Lab Fig 1(A)**	**Field Fig 1(B)**	**Lab (mg/g)**	**Field (mg/g)**
Activated Alumina	4.1	70	135	5.9	1.2
Bone Char	6.1	100	143	5.7	3.0
Aluminum Coated Bone Char	11.4	187	180	6.3	4.8
Aluminum Impregnated Wood Char	16.8	253	89	8.3	1.7

In both laboratory and field column studies (Figure 4.1A and 4.1B, respectively) the breakthrough curves of the AIWC and the AA are steeper than the other media, which suggests they have smaller mass transfer zones (less diffusion limited). For the AA this is attributed to its particle size (125 μm), which is smaller than all the other studied media. Smaller particle size results in shorter intraparticle diffusion distances and thus, a smaller mass transfer zone; nonetheless its lower fluoride removal capacity causes its breakthrough curve to occur earlier. The other materials all had the same particle size (approximately 302 μm), which suggests particle size is not the cause of the steeper breakthrough curve for AIWC. Instead, the sharp breakthrough curve of the AIWC can potentially be attributed to less mass transfer limitations due to intraparticle-limited diffusion - reasons for this are unclear at this time, but one possibility is that most of the adsorbing surfaces are near the outer region of the sorbent, which would reduce the amount of internal diffusion required. It should be noted that in the case of the laboratory results for AIWC, the breakthrough curve is still sharp, but the material showed the largest amount of bed volumes at low fluoride concentrations before the relatively steep breakthrough curve occurred, thus making it the most successful material at meeting the WHO standard.

In all cases, the $Q_{exhaustion}$ values calculated from the continuous flow data were higher in the laboratory setting than in the field setting (Table 4.2). This is expected due to constituents in the natural groundwater that can reduce adsorption; e.g. higher pH values, the potential for competing ions, and possible competition from NOM in the groundwater. Each potential effect is evaluated in a subsequent section. These findings are consistent with those of Kamble et al. (2007) who found that fluoride removal with another media (lanthanum-modified chitosan) was significantly higher when tested with distilled water and fluoride, than when field water samples were used; they attributed this to the pH (approximately 7) and the presence of competing anions in the field water. The BC and ACBC both show a similar percentage change (less than 65%) in $Q_{exaustion}$ between field and laboratory results of (e.g., 5.7 for lab and 3.0 mg/g for field for BC), which is similar to the approximately 67% difference shown by Kamble et al. (2007) for lanthanum-modified chitosan at an equilibrium value of 8 mg/L between field and synthetic samples. However, the AA and AIWC both show a difference in $Q_{exhaustion}$ greater than 130% between laboratory and field groundwater. Due to this large difference, it is helpful to further investigate the causes for this because it is clear that AIWC has potential to be a valuable fluoride removal material, but only if its ability to remove fluoride effectively in the field is understood.

Effects of pH

The higher pH in the field groundwater (8.2) than in the laboratory (6.0) likely accounts for some of the reduced effectiveness of the materials used in field columns. This is important because BC and AA are known to show improved fluoride removal as the pH decreases until pH 4, a value which is unlikely in most natural or pH adjusted systems (Abe et al., 2004; Medellin-Castillo et al., 2007; Tang et al., 2009). Therefore, it is expected that laboratory studies would show better fluoride removal than in the field with influent pH values of approximately 6.0 and 8.2, respectively. While in some cases pH adjustment would be considered in field applications to improve media performance, this was not implemented here in an effort to evaluate a simpler system appropriate for a remote area in Ethiopia. Decreased performance of AA in the field due to elevated pH has been documented by other researchers (Ghorai and Pant, 2005; Hao and Huang, 1986; Tang et al., 2009).

Thus, the focus here is on evaluating the effect of pH on AIWC in the field setting. Researchers have shown that elevated fluoride in the MER groundwater is typically accompanied by high salinity, high pH, and low calcium content (Fawell et al., 2006; Rango et al., 2009, 2012). The point of zero charge (PZC) for wood char alone is 9.6 ± 0.4 and for AIWC is 5.43 ± 0.25, showing a marked reduction in the PZC with the incorporation of aluminum into the material. The lower PZC of the AIWC suggests that this material should exhibit the best removal of negatively charged fluoride at system pH values below 5.43 and remove less fluoride as the system pH increases above the PZC.

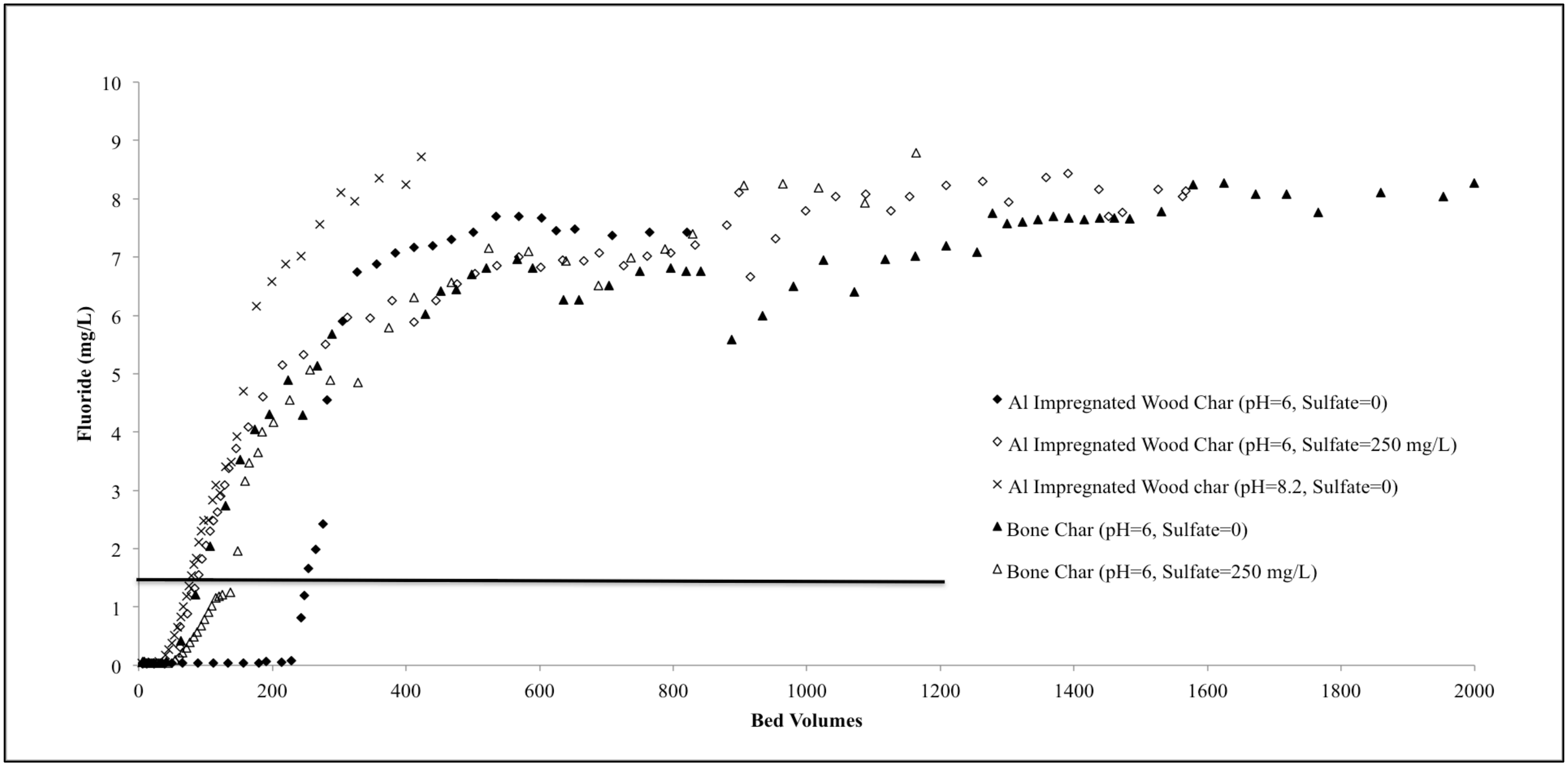


Figure 4.2: Results of continuous flow columns studies where the x-axis shows bed volumes and the y-axis shows effluent fluoride concentration in mg/L. Influent fluoride concentration was 8.6 mg/L and pH and competing ions vary as stated in the key.

Results of a column test assessing the fluoride removal capacity of the AIWC in a lab setting with the pH adjusted to 8.2 are shown in Figure 4.2. These results show that 78 versus 253 bed volumes passed prior to reaching C_{eff} = 1.5 mg/L for the field column with 8.2 pH influent as compared with unadjusted pH influent (approximately 6.0) and that the $Q_{exhaustion}$ values were 3.28 and 8.3 mg/g, respectively. This confirms batch test results leading to the conclusion that the AIWC removes fluoride more effectively at lower pH values and thus pH should be taken into consideration when setting up field treatment systems.

Sulfate Competition

Another potential cause of reduced fluoride removal capacity for AIWC is the effect of competing ions in the groundwater that were not present in the synthetic water. While elevated levels of phosphate are often found in conjunction with elevated levels of fluoride, in the case of MER, sulfate is the prevalent ion available that may provide competition for fluoride removal. A preliminary test from the field site suggested that the well water contained: sulfate = 60, phosphorous = 0.1, sodium = 490, potassium = 12 and calcium = 20 mg/L. These data are comparable to data of major ions in the MER waters presented in Rango et al. (2010), which showed that in samples from 24 MER groundwater well sources, the sulfate concentration ranged from below the detectable limit to 456 mg/L, the calcium concentration averaged 21.8 mg/L, and phosphate was not included in the data set of major ions. Table 4.3 shows the results of testing sulfate competition with BC and AIWC. Data on this table demonstrate, with 95% confidence, that there is no competition between sulfate and fluoride for removal by either BC or

AIWC for sulfate concentrations as high as 400 mg/L (4.2 mmol/L). However, it is difficult to make a final determination based on batch tests because the fluoride molarity in the vicinity of Q_m is 5.26 mmol, while in the column studies the fluoride was only 0.45 mmol. It is likely that at lower concentrations of fluoride there is more potential for sulfate to compete with fluoride for adsorption and thus removal. Therefore, a value of 250 mg/L sulfate (2.6 mmol), based on the EPA recommended limit, was selected to test in a column setting with BC and AIWC (U.S. EPA, 2012). Results of these tests can be observed in Figure 4.2. Comparing data from Figures 4.1 and 4.2 and Table 4.2 shows that approximate bed volumes passed to reach 1.5 mg/L fluoride were 142 and 100 for BC with and without 250 mg/L sulfate, respectively. The data also show that bed volumes passed to reach 1.5 mg/L fluoride for AIWC were 88 with 250 mg/L sulfate and 253 without. These results confirm the suggestion by batch tests that BC experiences minimal effects from the presence of sulfate in solution while the AIWC experienced a significant effect. Use of these materials in other locations where ions such as phosphate are high or the pH is low, would warrant additional testing to assess the fluoride removal capacity based on those changes.

Natural Organic Material

A further explanation for the reduction in the effectiveness of media in the field versus the laboratory could be the presence of NOM in the field groundwater. NOM is known to be widely occurring in groundwater sources in concentrations of 0.5 – 10 mg/L organic carbon (Genz et al., 2008), though it does not appear that competition in a field setting with fluoride adsorption has yet been investigated. The literature discussing water in the Main Ethiopia Rift did not yield specific types or concentrations of NOM, therefore, suggesting this is an area helpful for researchers to assess. However, Newcombe et al. (1997a) stated that NOM is present in all groundwater, which would include groundwater in the MER. Therefore, to assess the practical usefulness of these materials for fluoride removal it is helpful to determine whether or not NOM actually demonstrates competition with fluoride for these specific adsorptive materials. For this work, two NOM types were selected that are representative of a range of NOM based on molecular weight, functional groups and chemical composition. The functional groups of these two NOM types vary as Pahokee Peat humic acid (PPHA) contains 9.01 carboxylic meq/g of carbon as opposed to the 11.61 contained by the Nordic Aquatic Fulvic Acid (NAFA) and the PPHA contains 1.91 phenolic meq/g of carbon versus the 3.18 phenolic meq/g of carbon found in the NAFA (International Humic Substances Society, 2013a). The chemical composition also varies as PPHA and NAFA are partially composed of 37.34 and 45.12% oxygen and 3.69 and 0.68% nitrogen, respectively (International Humic Substances Society, 2013b). Results in Table 4.3 show that, with 95% confidence, the NOM causes no competition for fluoride removal with BC. NOM demonstrates minor competition with fluoride adsorption on AIWC and ACBC as exhibited by Q_m values in Table 4.3. Though no work has specifically been done investigating reasons for NOM adsorption on ACBC or AIWC, the addition of aluminum to the media may have an affect on NOM competition as Qualls et al. (2009) suggested that natural organic carbon can sorb to aluminum and thus block the pores for other ions to be removed. In this case, NOM minimally affects fluoride removal on the media tested.

Table 4.3: Results of batch isotherms studying fluoride removal with and without the presence of sulfate and natural organic material in solution.

Material	Competing Element	Amount (mg/L)	Amount (mmols/L)	Langmuir Q_m (mg/g)	Batch Q_e (mg/g) at C_e= 8.6* mg/L F
	Ion				
Bone Char	None	NA	NA	6.1 ± 0.4	4.8
Bone Char	Sulfate	50	0.5	5.9 ± 0.4	4.8
Bone Char	Sulfate	125	1.3	6.8 ± 0.6	4.6
Bone Char	Sulfate	400	4.2	6.9 ± 0.5	4.0
Al Impregnated Wood Char	None	NA	NA	16.8 ± 5.8	12.9
Al Impregnated Wood char	Sulfate	400	4.2	14.2 ± 3.3	7.6
	NOM				
Bone Char	None	NA	NA	6.1 ± 0.4	4.8
Bone Char	Nordic Aquatic	10	NA	5.8 ± 0.4	4.1
Bone Char	Pahokee Peat	10	NA	5.4 ± 0.5	3.8
Bone Char	Pahokee Peat	30	NA	6.1 ± 0.5	3.8
Al Impregnated Wood Char	None	NA	NA	16.8 ± 5.8	12.9
Al Impregnated Wood Char	Nordic Aquatic	10	NA	10.5 ± 0.8	10.2
Al Impregnated Wood Char	Pahokee Peat	10	NA	9.6 ± 0.8	9.3
Al Coated Bone Char	None	NA	NA	11.4 ± 0.9	3.5
Al Coated Bone Char	Nordic Aquatic	10	NA	7.1 ± 0.8	6.3
Al Coated Bone Char	Pahokee Peat	10	NA	8.6 ± 0.7	7.0

Note: For all results shown here tests were conducted using deionized water with the competing ion/NOM added and no additional buffering or solution manipulation was conducted.

*8.6 mg/L fluoride = 0.45 mmol/L. Thus, at 400 mg/L sulfate (nearly 10 moles of sulfate per mole of fluoride) competition, if present, would certainly be evidenced.

Rapid Scale Small Column Test – Scaling up to Field Scale

Figure 4.3 shows the breakthrough curves of columns that had different column volumes and particle sizes determined based on RSSCT concepts, using Equation 4.1. The results show that the breakthrough curves overlap, even though the large-scale column volume is nearly 5 times larger and the particle size is nearly twice as large.

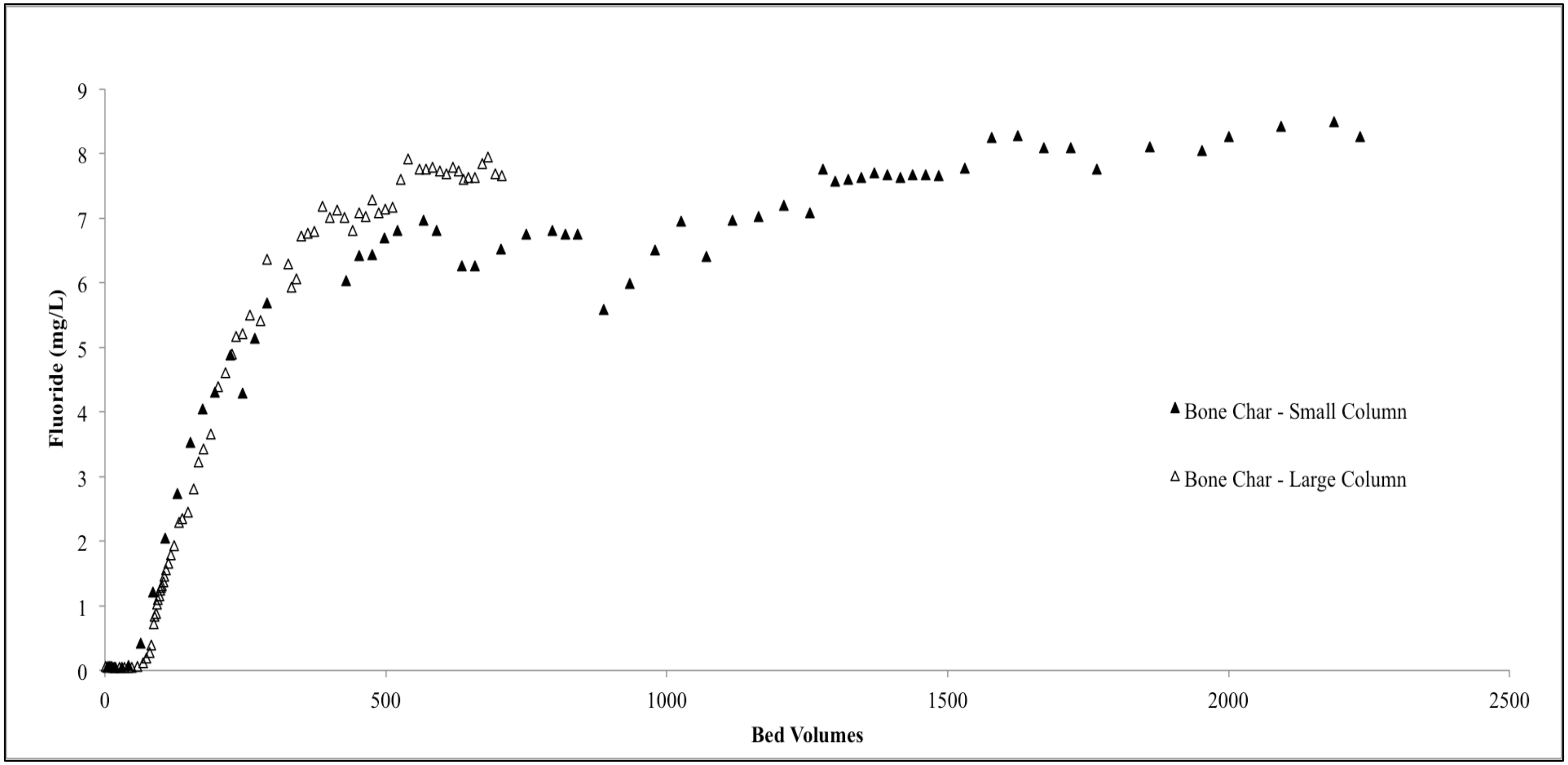


Figure 4.3: Graph shows results of rapid small scale column tests where the x-axis shows bed volumes and the y-axis shows effluent fluoride concentration in mg/L. Columns have volumes of 34.9 and 7.9 cm3 and average particle sizes of 637 and 302 µm , for large and small scale respectively. Starting concentration and flow rate were equivalent for both at 8.6 mg/L fluoride and 1.2 ml/min.

This suggests that it is possible to scale up fluoride removal using BC for a community scale system using RSSCT concepts, i.e. the data presented here could be scaled up for a larger scale field system at a community site. While this technique was developed for activated carbon (Crittenden et al., 1986), and Westerhoff et al. (2005) extended the validity of the RSSCT model for arsenic adsorption onto granular ferric hydroxide, based on literature review this is the first work to test and offer early stage validation of BC and fluoride. Future research should further validate the use of RSSCT equations for BC through repeat column tests and use of additional column and particle sizes (Westerhoff et al., 2005).

Conclusion

BC, ACBC and AIWC all proved to be effective fluoride adsorption technologies in batch tests, laboratory column studies and field studies conducted in the Ethiopian Rift Valley. The laboratory tests showed that each material removed fluoride more effectively than the often tested AA, and that the removal efficiency was AIWC > ACBC > BC. However, the field study resulted in the AIWC effectiveness being approximately 130% lower than in the laboratory columns. Additional batch and column studies suggest that this decrease in removal effectiveness was due to the presence of sulfate ions and the alkaline pH (8.2) in the field groundwater. This study also showed that two types of NOM, PPHA and NAFA, provided minimal competition with fluoride removal on the three novel media. A final piece of this study provided evidence that RSSCT principles can be applied to fluoride removal from water using bone char as the sorbent. Beyond this research, additional work will be helpful to assess options to improve media effectiveness, costs, local availability of materials and user acceptance of various technologies in the Main Ethiopian Rift.

Acknowledgements

The authors would like to thank Catholic Relief Services, the Meki Catholic Secretariat, CARE Ethiopia, and Addis Ababa University, organizations without which the work in Ethiopia could not have occurred. The authors gratefully acknowledge the U.S. Environmental Protection Agency and the U.S. National Science Foundation that contributed partial funding to this work. This publication was developed under STAR Fellowship Assistance Agreement no. 91731301 awarded by the U.S. Environmental Protection Agency (EPA). This work has not been formally reviewed by EPA, and the views expressed in this paper are solely those of the authors and the EPA does not endorse any products or commercial services mentioned in this publication. The authors also wish to acknowledge partial funding from the OU WaTER Center, the University of Oklahoma and the Rotary Club of Norman, Oklahoma in support of this work.

References

Abaire, B., Zewge, F. and Endalew, M. (2009). "Operation experiences on small-scale community defluoridation systems." In *Water, Sanitation and Hygiene: Sustainable Development and Multisectoral Approaches - 34th WEDC International Conference*, May 18-22, 2009, Addis Ababa.

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., and Tanada, S. (2004). "Adsorption of fluoride ions onto carbonaceous materials." *J. Colloid Interf. Sci.*, 275(1), 35–39.

Amini, M., Mueller, K., Abbaspour, K., Rosenberg, T., Afyuni, M., Møller, K., Sarr, M., and Johnson, A. C. (2008). "Statistical modeling of global geogenic fluoride contamination in groundwaters." *Environ. Sci. Technol.* 42(10), 3662–3668.

Arora, M., Maheshwari, R. C., Jain, S. K., and Gupta, A. (2004). "Use of membrane technology for potable water production." *Desalination*, 170(2), 105–112.

Ayoob, S., and Gupta, A. K. (2007). "Sorptive response profile of an adsorbent in the defluoridation of drinking water." *Chem. Eng. J.* 133, 273–281.

Ayoob, S., Gupta, A. K., and Bhat, V. T. (2008). "A conceptual overview on sustainable technologies for the defluoridation of drinking water." *Crit. Rev. Env. Sci.* 38(6), 401–470.

Badruzzaman, M., Westerhoff, P., and Knappe, D. R. U. (2004). "Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH)." *Water Res.* 38(18), 4002–4012.

Bhatnagar, A., Kumar, E., and Sillanpaa, M. (2011). "Fluoride removal from water by adsorption—a review." *Chem. Engr. J.* 171(3), 811–840.

Brunson, L. R. and Sabatini, D. A. (2009). "An evaluation of fish bone char as an appropriate arsenic and fluoride removal technology for emerging regions." *Environ. Eng. Sci.* 26(12), 1777–1784.

Chen, N., Zhang, Z., Feng, C., Li, M., Chen, R., and Sugiura, N. (2011). “Investigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud.” *Desalination*, 268(1-3), 76–82.

Cheung, C., Choy, K. K., Porter, J. F., and Mckay, G. (2005). “Empirical multicomponent equilibrium and film-pore model for the sorption of copper, cadmium and zinc onto bone char.” *Adsorption*, 11(1), 15–29.

Crittenden, J. C., Berrigan, J. K., and Hand, D. W. (1986). “Design of rapid small-scale adsorption tests for a constant diffusivity.” *J. Water Pollut. Con. Fed.* 58(4), 312–319.

Fawell, J., Bailey, K., Chilton, J., and Dahi, E. (2006). *Fluoride in drinking-water*. World Health Organization, Geneva, Switzerland.

Fewtrell, L., Smith, S., Kay, D., and Bartram, J. (2006). “An attempt to estimate the global burden of disease due to fluoride in drinking water.” *J. Water Health*, 4(4), 533–542.

Genz, A., Baumgarten, B., Goernitz, M., and Jekel, M. (2008). “NOM removal by adsorption onto granular ferric hydroxide: equilibrium, kinetics, filter and regeneration studies.” *Water Res*. 42(1), 238–248.

Ghorai, S., and Pant, K. (2005). “Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina.” *Sep. Purif. Technol.* 42(3), 265–271.

Gwala, P., Andey, S., Mhaisalkar, V., Labhasetwar, P., Pimpalkar, S., and Kshirsagar, C. (2011). “Lab scale study on electrocoagulation defluoridation process optimization along with aluminium leaching in the process and comparison with full scale plant operation." *Water Sci. Technol.* 63(12), 2788–2795.

Hao, O. J., and Huang, C. P. (1986). "Adsorption characteristics of fluoride onto hydrous alumina." *J. Environ. Eng.* 112(6), 1054–1069.

International Humic Substances Society. (2013a). "Acidic functional groups of IHSS Samples." *International Humic Substances Society*, <http://www.humicsubstances.org/acidity.html> (September 25, 2013).

International Humic Substances Society. (2013b). "Elemental compositions and stable isotopic ratios of IHSS samples." *International Humic Substances Society*, <http://www.humicsubstances.org/elements.html> (September 25, 2013).

Jagtap, S., Sneha, Yenkie, M. K., Labhsetwar, N., and Rayalu, S. (2012). "Fluoride in drinking water and defluoridation of water." *Chem. Rev.* 112(4), 2454–2466.

Kamble, S. P., Jagtap, S., Labhsetwar, N. K., Thakare, D., Godfrey, S., Devotta, S., and Rayalu, S. S. (2007). "Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan." *Chem. Eng. J.* 129(1-3), 173–180.

Kloos, H., and Haimanot, R. T. (1999). "Distribution of fluoride and fluorosis in Ethiopia and prospects for control." *Trop. Med. Intl. Health*, 4(5), 355–364.

Levya-Ramos, L. R., Ovalle-Turrubiartes, J., and Sanchez-Castillo, M. A. (1999). "Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon." *Carbon*, 37(4), 609–617.

Leyva-Ramos, R., Rivera-Utrilla, J., Medellin-Castillo, N. A., and Sanchez-Polo, M. (2010). "Kinetic modeling of fluoride adsorption from aqueous solution onto bone char." *Chem. Eng. J.* 158(3), 458–467.

Li, Y. H., Wang, S., Cao, A., Zhao, D., Zhang, X., Xu, C., Luan, Z., Ruan, D., Liang, J., and Wu, D. (2001). “Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes.” *Chem. Phys. Lett.* 350(5), 412–416.

Ma, W., Ya, F., Wang, R., and Zhao, Y. (2008). “Fluoride removal from drinking water by adsorption using bone char as a biosorbent.” *Intl. J. Environ. Technol. Manage.* 9(1), 59.

Mameri, N., Lounici, H., Belhocine, D., Grib, H., Piron, D. L., and Yahiat, Y. (2001). “Defluoridation of Sahara water by small plant electrocoagulation using bipolar aluminium electrodes.” *Sep. Purif. Techol.* 24(1), 113–119.

Medellin-Castillo, N., Leyva-Ramos, R., Ocampo-Perez, R., Garcia de la Cruz, R., Aragon-Piña, A., Martinez-Rosales, J., Guerrero-Coronado, R., and Fuentes-Rubio, L. (2007). “Adsorption of fluoride from water solution on bone char.” *Ind. Eng. Chem. Res.* 46(26), 9205–9212.

Meenakshi, and Maheshwari, R. C. (2006). “Fluoride in drinking water and its removal.” *J. Hazard. Mater.* 137(1), 456–463.

Mjengera, H., and Mkongo, G. (2002). “Appropriate defluoridation technology for use in fluorotic areas in Tanzania.” In 3rd WaterNet Symposium - Water Demand Management for Sustainable Development, October, 30-31, 2002, Dar es Salaam, Tanzania.

Mlilo, T. B., Brunson, L. R., and Sabatini, D. A. (2010). “Arsenic and fluoride removal using simple materials.” *J. Environ. Eng.* 136(4), 391–398.

Mohan, D., Sharma, R., Singh, V. K., Steele, P., and Pittman, C. U. (2012). “Fluoride removal from water using bio-char, a green waste, low-cost adsorbent:

equilibrium uptake and sorption dynamics modeling." *Ind. Eng. Chem. Res.* 51(2), 900–914.

Newcombe, G., Drikas, M., Assemi, S., and Beckett, R. (1997). "Influence of characterized natural organic material on activated carbon adsorption: I. characterization of concentrated reservoir water." *Water Res.* 31(5), 965–972.

Newcombe, G., Drikas, M., and Hayes, R. (1997). "Influence of characterized natural organic material on activated carbon adsorption: II. effect on pore volume distribution and adsorption of 2-Methylisoborneol." *Water Res.* 31(5), 1065–1073.

Qualls, R. G., Sherwood, L. J., and Richardson, C. J. (2009). "Effect of natural dissolved organic carbon on phosphate removal by ferric chloride and aluminum sulfate treatment of wetland waters." *Water Resour. Res.* 45(9), 9414–9423.

Rango, T., Bianchini, G., Beccaluva, L., and Tassinari, R. (2010). "Geochemistry and water quality assessment of Central Main Ethiopian Rift natural waters with emphasis on source and occurrence of fluoride and arsenic." *J. African Earth Sci.* 57(5), 479–491.

Rango, T., Colombani, N., Mastrocicco, M., Bianchini, G., and Beccaluva, L. (2009). "Column elution experiments on volcanic ash: geochemical implications for the Main Ethiopian rift waters." *Water, Air, Soil Pollut.* 208(1-4), 221–233.

Rango, T., Kravchenko, J., Atlaw, B., McCornick, P., Jeuland, M., Merola, B., and Vengosh, A. (2012). "Groundwater quality and its health impact: an assessment of dental fluorosis in rural inhabitants of the Main Ethiopian Rift." *Environ. Intl.* 43, 37–47.

Redman, A. D., Macalady, D. L., and Ahmann, D. (2002). "Natural organic matter affects arsenic speciation and sorption onto hematite." *Environ. Sci. Technol.* 36(13), 2889–2896.

Sivasamy, A., Singh, K. P., Mohan, D, and Maruthamuthu, M. (2001). "Studies on defluoridation of water by coal-based sorbents." *J. Chem. Technol. Biot.* 76(7), 717–722.

Tang, Y., Guan, X., Su, T., Gao, N., and Wang, J. (2009). "Fluoride adsorption onto activated alumina: modeling the effects of pH and some competing ions." *Colloid Surface A*, 337(1-3), 33–38.

Tchomgui-Kamga, E., Alonzo, V., Nanseu-Njiki, C. P., Audebrand, N., Ngameni, E., and Darchen, A. (2010). "Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water." *Carbon*, 48(2), 333–343.

Tonguc, M. O., Ozat, Y., Sert, T., Sonmez, Y., and Kirzioglu, F. Y. (2011). "Tooth sensitivity in fluorotic teeth." *Eur. J. Dent.* 5(3), 273.

Trussell, R. R., Tchobanoglous, G., Crittenden, J.C., Hand, D., and Howe, K. (2005). *Water treatment: principles and design; 2ND Ed*. John Wiley & Sons, Hoboken, New Jersey.

U.S. EPA. (2012). "Drinking Water Contaminants." <http://water.epa.gov/drink/contaminants/index.cfm#SecondaryList> (Apr. 19, 2012).

Westerhoff, P., Highfield, D., Badruzzaman, M., and Yoon, Y. (2005). “Rapid small-scale column tests for arsenate removal in iron oxide packed bed columns.” *J. Environ. Eng.* 131(2), 262–271.

World Health Organization and UNICEF. (2012). *Progress on drinking water and sanitation 2012 update*. New York, New York.

World Health Organization. (2011). *Guidelines for drinking-water quality - 4th edition*. World Health Organization, Geneva, Switzerland.

Yadav, A. K., Kaushik, C. P., Haritash, A. K., Kansal, A., and Rani, N. (2006). “Defluoridation of groundwater using brick power as an adsorbent.” *J. Hazard. Mater.* B128, 289–293.

CHAPTER 5

Methods for Optimizing Activated Materials for Fluoride Removal from Drinking Water Sources

Abstract

This paper presents results of amending eucalyptus wood char with the following aluminum and iron materials: aluminum sulfate, aluminum chloride, iron (II) chloride, and iron (III) nitrate. Results show that amending wood char with metal oxides increases the ability of the wood char to remove fluoride from drinking water. Wood char alone has a $Q_{e1.5}$ value of 0.04 mg/g, whereas the $Q_{e1.5}$ values of the metal amended wood chars range from 0.14 to 2.06 mg/g. Interestingly, the iron oxide amendments resulted in greater improvements to the fluoride removal capacity than the aluminum oxide amendments, with $Q_{e1.5}$ values of 2.06 and 0.76 mg/g for the two iron oxide amended chars and 0.57 and 0.14 mg/g for the aluminum oxide amended chars. Pretreating wood char with two oxidizing agents, potassium permanganate and hydrogen peroxide, increased both the metal loading and fluoride removal capacities in select instances. When wood char was pretreated with potassium permanganate and amended with aluminum sulfate, the $Q_{e\ 1.5}$ value increased from 0.14 to 0.40 mg/g and the metal loading from 0.05 to 0.65%. However, an increase in fluoride removal and metal loading was not observed for all pretreatments. Oxidation pretreatment of wood char reduced the point of zero charge and, for hydrogen peroxide only, decreased the specific surface area significantly (334 to 133 m^2/g). Thus, this work shows the

potential for using oxidizing agents and aluminum and iron amendments with wood char, and potentially other biochars, to improve their fluoride removal capacities.

Introduction

Fluoride in groundwater is a global concern as millions of people consume drinking water containing fluoride at concentrations above the 1.5 mg/L limit recommended by the World Health Organization (WHO) (World Health Organization, 2011; Jagtap et al., 2012). While fluoride is naturally occurring in the groundwater of over 30 countries, it can also occur anthropogenically through processes such as aluminum smelting and fertilizer production (Hem, 1985; Ayoob et al., 2008; Hudak, 2008). While in low doses fluoride helps prevent dental carries (Schamschula and Barnes, 2981; Fawell et al., 2006), high fluoride uptake from food or water can be harmful to human health, causing dental and skeletal fluorosis (Fawell et al., 2006; Gazzano et al., 2010). Dental fluorosis typically causes darkening or mottling of teeth, which can increase tooth sensitivity (Fawell et al., 2006; Tonguc et al., 2011). Skeletal fluorosis causes bone deformities or stiffness and, thus, pain and/or decreased mobility (Kaseva, 2006; Meenakshi and Maheshwari, 2006). In response, researchers globally are investigating methods for fluoride removal from drinking water (Fawell et al., 2004; Jagtap et al., 2012; Rao, 2003).

Methods frequently studied for removing fluoride from drinking water include: precipitation, ion exchange, electrocoagulation, membrane filtration, and adsorption (Pervov et al., 2000; Rao, 2003; Meenakshi and Maheshwari, 2006; Kamble et al., 2007; Tchomgui-Kamga et al., 2010; Gwala et al., 2011). For rural regions in developing countries it is helpful to investigate inexpensive, sustainable and locally available options for fluoride removal. Adsorption is an attractive approach because it can utilize gravity flow and thus, does not require electricity. Depending on the sorptive material, adsorption can be highly effective at removing fluoride from water to meet the WHO drinking water standard. Frequently utilized adsorption materials for fluoride removal include: bone char, activated alumina and clays or soils (Fawell et al., 2006; Ayoob et al., 2008; Brunson and Sabatini, 2014a). While activated alumina is an effective sorptive material, it is manufactured in select locations and may be prohibitively expensive to obtain in developing regions. Additionally, activated alumina performs best at pH values below normal groundwater (e.g., pH 5) (Fawell et al., 2006). While bone char is currently used in several countries, including Ethiopia and Kenya, bone char production must be done precisely or char quality is poor. Furthermore, some communities are not amenable to using an adsorption material made from animal bones for cultural or religious reasons. While most research evaluating clays and soils for fluoride removal has shown them to be minimally effective, materials that contain iron or aluminum hydroxides have often demonstrated higher removal capacities. Several researchers have investigated the potential for using wood char as a sorbent, but without amendment it has demonstrated poor fluoride removal ability thus far (Brunson and Sabatini, 2014b; Abe et al., 2004).

This paper investigates the potential to make wood char a more effective fluoride removal material by amending it with aluminum and iron oxides. Wood char is a carbon-based material typically composed of carbon (50%), oxygen (44%), hydrogen (6%) and trace amounts of metals (Pettersen, 1984). However, chemical composition and other characteristics of wood and wood chars, such as specific surface area, vary based on location, soil type, season, age and type of wood (James et al., 2005; Pettersen, 1984). Several studies have shown promising results for removing fluoride with aluminum and iron-based metal oxide materials. Biswas et al. (2007) demonstrated that an oxide made of aluminum and iron adsorbed fluoride with a Langmuir isotherm maximum adsorption value of 17.7 milligrams of fluoride per gram of material. This suggests an affinity between fluoride and metals such as aluminum and iron which can be attributed to the positive charge on the surface of these metal oxides and the negative charge of the fluoride ions in water at a neutral pH value. Additionally, Tchomgui-Kamga et al. (2010) investigated the ability of an aluminum–iron precipitate mixture to adsorb fluoride and the possibility of impregnating spruce wood with the precipitate mixture through a boiling process. Their work showed a Langmuir maximum adsorption of approximately 13.5 milligrams of fluoride per gram of material. These research efforts point to the potential for improving the fluoride removal capacity of wood char though metal oxide amendment.

Although previous studies have looked at different adsorption materials for fluoride removal and others have tested aluminum and iron amendments on various activated carbon materials, there is a lack of systematic studies of metal amended biochars. A systematic investigation should utilize the same starting material with multiple metal amendment processes and study fluoride removal capacity and surface properties to promote better understanding. Another aspect of interest is the potential to increase metal loading onto wood char by pretreating the wood char with oxidizing agents. Pretreatment methods are intended to alter the surface chemistry of the media which, according to Polovina et al. (1997), is one of the important characteristics of an adsorbent.

According to Song et al. (2010), both chemical and thermal techniques can be used to modify activated carbon surface functional groups, which include a range of acidic and basic groups. Thus, researchers have investigated the use of oxidizing agents as one chemical technique to alter the surface chemistry of activated carbon-based media. For example, Song et al. (2010) evaluated the use of oxidizing agents to alter the ability of coconut-based activated carbon to adsorb positively charged lead from water. Their research showed that the oxidation pretreatment process caused minimal change to the specific surface area of the activated carbon, lowered the point of zero charge, and resulted in increased lead removal, in some cases doubling the lead adsorption capacity of the media. Work done by Liu et al. (2007) and Polovina et al. (1997) showed that oxidation with boiling nitric acid increased the acidic oxygen-based functional groups on the surface of activated carbon. Hristovski et al. (2009) tested the ability of lignite-based activated carbon modified with iron to remove arsenic. Two procedures were tested for adding iron to activated carbon. The first involved an alcohol and iron mixture and the second utilized pretreatment of the activated carbon with potassium permanganate before amending it with iron. Their results concluded that samples pretreated with the oxidant, potassium permanganate, showed a higher percentage of iron in the activated carbon sample and a much higher arsenic removal capacity. Another test, conducted by Chen et al. (2007), assessed the ability of oxidation pretreatment to enhance iron loading onto activated carbons. They found that pretreatment with a nitric/sulfuric acid combination resulted in the highest level of iron loading onto the activated carbon. However, this oxidation procedure caused several activated carbons, wood-based ones in particular, to experience a significant loss of mass which made them unable to withstand the pressure and flow in a column study (Chen et al., 2007). These results suggest that oxidation pretreatment methods have the potential to improve metal loading onto charred or activated materials.

Thus, based on previously published work, the objectives of this research were to: (1) assess whether metal oxide amendment of wood char results in adsorbents with higher levels of fluoride uptake than unamended wood char, (2) determine whether pretreatment of wood char with oxidizing agents followed by metal oxide amendment improves the fluoride removal capacity as compared to that of metal amendment alone, and (3) investigate what, if any, effects on surface chemistry, metal loading, and surface area result from pretreatment and amendment with oxidizing agents and metal oxides that can help explain the results from objectives (1) and (2). The overall goal of this work is to assess which treatments can be applied to biochars to make them useful for absorbing fluoride from water in communities struggling with high concentrations of geogenic fluoride. The biochar selected for study in this work was Eucalyptus wood due to its prevalence in Ethiopia and ability to grow quickly in a variety of conditions (Dessie and Erkossa, 2011). To accomplish these objectives, one starting material, the wood char prepared from *Eucalyptus robusta*, was treated with several metal oxide amendment methods and two oxidation pretreatment methods. The use of a consistent starting material allows for equitable comparison of fluoride removal capacities, assessment of changes to the char characteristics occurring as a result of amendment and pretreatment, and formulation of recommendations for water treatment and future research in this area. This research approach advances previous work in this field in two ways: first, most work in this area has been done using an assortment of starting materials, thus making it difficult to draw comparative conclusions between amendment methods, and second, previous research has not included much investigation of fluoride removal in relation to oxidation pretreatment. Additionally, while considerable work has evaluated amending activated carbon materials with oxidizing agents, work has not yet been done to assess specifically the effects of treating wood char with oxidizing agents along with metal oxide amendments.

Methods and Materials

Media Preparation

Eucalyptus robusta was obtained from Mesozoic Landscapes, Inc. in Florida and was carbonized in a temperature controlled Thermolyne oven for 4 hours at 600 °C. After cooling, the media was crushed and sieved to capture particle sizes between 180 and 425 μm in diameter. Crushed char was rinsed to remove fines, dried at 100 °C and stored in sealed bags until used. Media pretreatment was achieved using two methods. In one method 1 liter of 15% hydrogen peroxide solution was mixed with 10 grams of wood char and heated to 90 °C in a reflux condenser for four hours (Song et al., 2010). A second method required combining a 0.1 molar permanganate solution with char in a ratio of 0.08 grams of char per milliliter of solution. The mixture was shaken for 15 minutes and then the char was filtered out of solution (Hristovski et al., 2009). In each case the residual char was rinsed in a continuous flow column with deionized water until the effluent showed a consistent pH and then media was dried and stored.

Amendment with Metal Oxides

The four metal amendment methods used in this research were selected due to having the highest fluoride removal capacity out of a larger group of amendment methods and method variations. One amendment method utilized a 500 mg/L (approximately 0.02 molar) aluminum sulfate solution. The pH was adjusted to 3.5 using 4-Morpholineethanesulfonic acid hydrate to keep the pH steady throughout the treatment process. The solution (417 milliliters) was combined with 25 grams of wood char, sealed in a glass container and shaken at 200 shakes per minute for five days. The char was then filtered out of the supernatant, dried at 100 °C, rinsed with deionized water and dried again. Aluminum chloride was used to make a 0.5 molar solution which was mixed at ratio of 1 gram per 25 milliliters of solution for 6 hours, then diluted in half and shaken for an additional 18 hours prior to rinsing and drying. Another method required preparing a 1 molar solution of iron (II) chloride that was pH adjusted to 4.2 – 4.5. The solution, 150 milliliters, was mixed with 10 grams of char for 24 hours, filtered, rinsed and dried at 80 °C for 4 hours (Gu et al., 2005). A final method involved mixing 25 grams of ferric nitrate nonahydrate with 150 milliliters of water (0.41 molar solution) and adding 10 grams of char. This combination was stirred for 20 minutes and then heated to 100 °C until dry with intermittent stirring throughout the drying process. Once dry the material was rinsed with deionized water and dried again (Vaishya and Gupta, 2003).

Surface Characteristic Assessment

Specific surface area was measured using a Quantochrome 2000E Surface Area and Pore Size Analyzer. Samples of 0.1 – 0.3 grams were degassed under vacuum at 100 °C for 24 hours. Nitrogen adsorption was evaluated at 77° K and five adsorption points were analyzed with the Brunauer, Emmett, Teller theory to calculate specific surface area. The drift method, based on the work of Babic (1999) was used to estimate the point of zero charge (pH_{PZC}) values. Potassium nitrate solutions, 0.1 M and 0.01 M, were prepared using deionized water and 50 mL of the solutions were placed in vials. Nitrogen gas was bubbled through the vials before and during pH adjustment to avoid atmospheric interferences. Adjusted pH values ranged from 3 to 12 and 0.1 molar KOH or HNO_3 were utilized to obtain this pH range. Next, 0.2 grams of material was added to each vial and vials were shaken to allow the media to equilibrate. After 24 hours, the pH values of the solutions were measured again and the starting pH values were graphed against final pH values to obtain the pH_{PZC} plateau.

Batch Adsorption Studies

Batch tests were conducted in triplicate to determine the fluoride adsorption capacity of each material. In these experiments the amount and type of media added was held constant (e.g., 0.5 g of media in 50 mL of solution), while the fluoride concentrations were varied (e.g. 2.5, 5, 10, 25, 50, 100 mg/L). Batch tests were shaken at 200 shakes per minute for 24 hours to reach equilibrium. Samples were filtered using Whatman 11 μm filter papers prior to analysis. All batch studies were conducted at a constant ionic strength of 0.05 molar NaCl.

Fluoride and Metals Quantification

Fluoride concentrations were measured using a fluoride specific electrode and an Orion pH/ISE meter, model 710A. Fluoride samples were treated with Total Ionic Strength Adjustment Buffer I prior to analysis to ensure equal ionic strength and pH. Samples to be analyzed for metals were digested and then analyzed on an ICP-MS.

Data Analysis

Data were analyzed using Freundlich and Langmuir isotherms. The Freundlich equation is shown in Equation 5.1, where Q_e represents the milligrams of fluoride removed per gram of material, C_e is the fluoride concentration at system equilibrium, and K_f and 1/n are empirical constants reflecting relative capacity and adsorption heterogeneity, respectively.

$$Q_e = K_f C_e^{1/n} \qquad \text{Equation 5.1}$$

$$Q_e = (C_e Q_m b)/(1+Q_m b) \qquad \text{Equation 5.2}$$

Equation 5.2 shows the Langmuir equation, where Q_e and C_e are the same as above, Q_m is the maximum possible fluoride removal value for that system and b is related to adsorption affinity. Regression analyses of data were conducted using SigmaPlot Version 12.0 software. In this work both Q_m and $Q_{e1.5}$ are utilized to discuss results. $Q_{e1.5}$ is the adsorption capacity exhibited by a material when the fluoride equilibrium concentration is 1.5 mg/L and is calculated using the Freundlich equation. While the Q_m values are interesting for research, the $Q_{e1.5}$ values are more relevant based on common environmental fluoride conditions and the WHO recommended fluoride concentration (1.5 mg/L).

Results and Discussion

Impact of Metal Oxide Amendment on Fluoride Removal

A primary objective of this research was to investigate whether amending wood char with metal oxides increases the fluoride removal capacity of the wood char. Additionally, if metal oxides do cause an increase in fluoride removal it is helpful to assess which metal oxide amendment method is most effective, which is possible because all amendments were tested using on a common starting material. The data in Figure 5.1 shows that amending wood char with metal oxides increases the fluoride removal capacity of the wood char (the unamended wood char [WC] evidenced the lowest Q_e values). Review of the Langmuir Q_m values for the metal amended chars (Table 5.1) shows that they range from 1.62 to 8.02 mg/g, as compared to the unamended wood char at 0.68 mg/g, thus confirming the helpful ability of metal oxide amendments to improve fluoride removal capacity of wood char. The $Q_{e1.5}$ value, the Q_e value resulting when $C_e = 1.5$ mg/L fluoride, of wood char alone is 0.04 mg/g, while the values of the metal oxide amended wood chars range from 0.14 mg/g, aluminum sulfate, to 2.06 mg/g, iron (III) nitrate. Iron (III) nitrate resulted in a fluoride removal capacity 50 times higher than wood char alone. Aluminum sulfate is a logical amendment material to use based on its availability in places such as Ethiopia that experience a high prevalence of fluoride in groundwater. However, the aluminum sulfate amendment, while improving the fluoride removal versus unamended wood char, does not demonstrate as much of a fluoride removal increase as the other metal amendments at $Q_{e1.5}$ values (shown in Table 5.1). Despite the fact that aluminum-based materials are more frequently evaluated for fluoride removal from drinking water than iron-based materials, this work demonstrates that iron amendments are also a viable option.

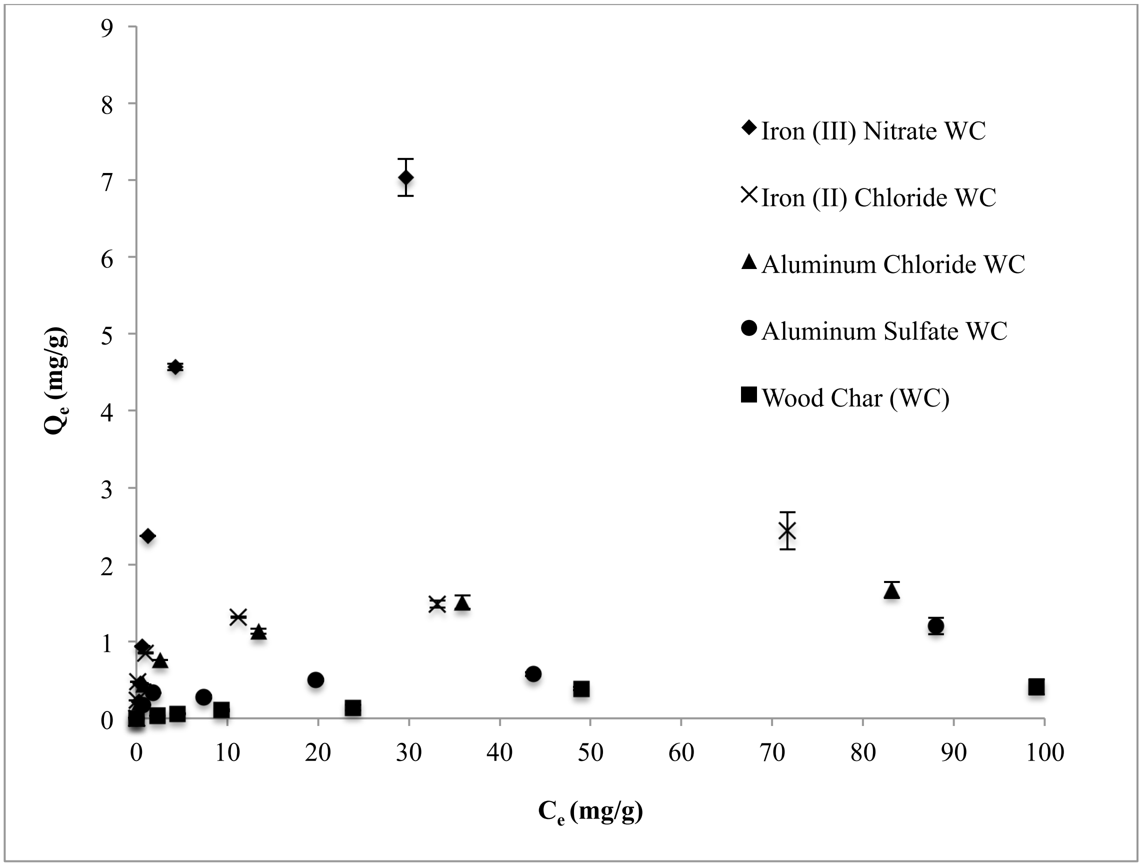


Figure 5.1: Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars. Q_e, the mg of fluoride removed per gram of media is plotted against C_e, the equilibrium concentration of fluoride in mg/L.

Table 5.1: Freundlich and Langmuir Constants and $Q_{e1.5}$ values obtained using batch isotherm data for wood char alone and metal oxide amended wood chars.

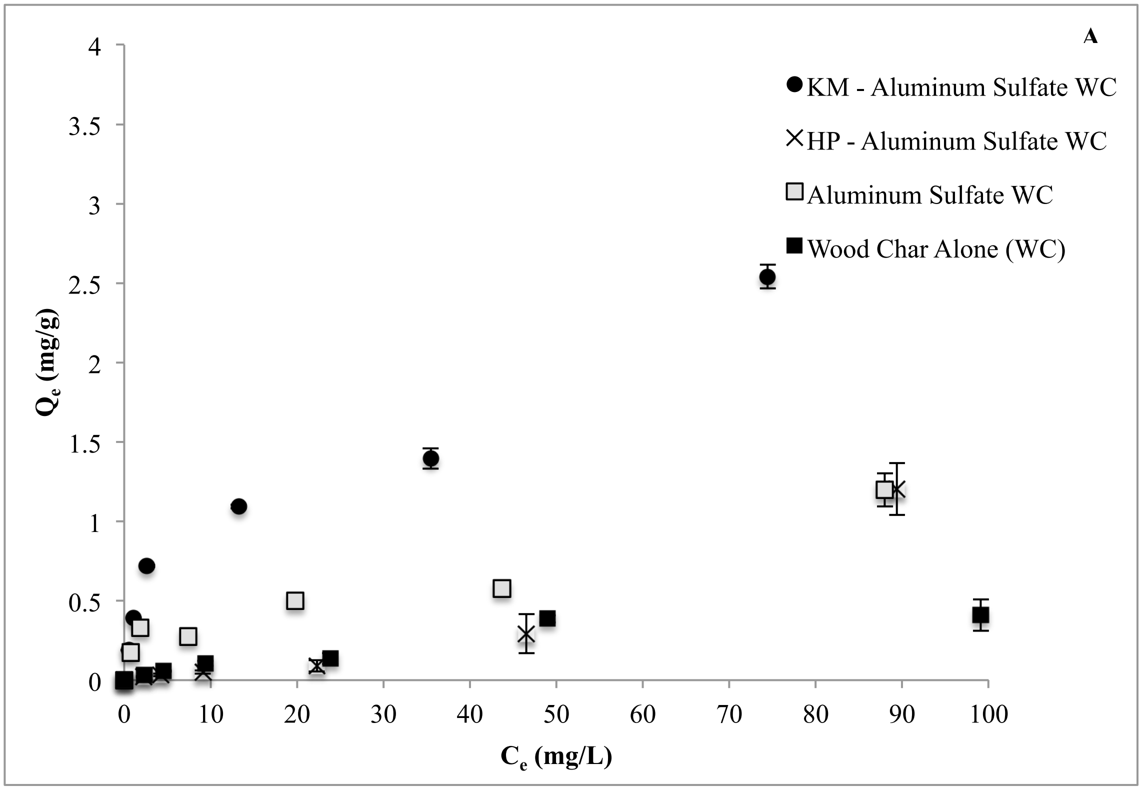
Freundlich and Langmuir Constants of Wood Char and Metal Oxide Amended Wood Char					
Pretreatment	**Metal Amendment**	**K_f (mg/g)(mg/L)$^{1/n}$**	**1/n**	**Q_e (mg/g) at C_e=1.5 mg/L F (Freundlich)**	**Langmuir Q_{max} (mg/g)**
None	None	0.03 ± 0.01	0.60	0.04	0.68 ± 0.18
None	Iron (III) Nitrate	1.73 ± 0.41	0.43	2.06	8.02 ± 0.49
None	Iron (II) Chloride	0.68 ± 0.10	0.27	0.76	1.83 ± 0.23
None	Aluminum Chloride	0.51 ± 0.06	0.28	0.57	1.62 ± 0.09
None	Aluminum Sulfate	0.12 ± 0.03	0.51	0.14	2.04 ± 1.13

This is consistent with the fact that fluoride is considered a hard base, and as such, has a strong attraction to multivalent metals, which include both iron and aluminum (Wu et al., 2007). Given the minimal exploration of using iron for fluoride removal, the results in Table 5.1 are particularly exciting for the field of fluoride removal from drinking water and should be further explored both in laboratory and field tests.

Effect of Pretreatment with Oxidizing Agents on Fluoride Removal

The second objective of this research was to assess the fluoride removal results when wood char was pretreated with oxidizing agents prior to metal oxide amendment. Results of these studies are shown in Figure 5.2 and Table 5.2. Figure 5.2 shows that, in some cases, pretreating the wood char with oxidizing agents increased the fluoride removal capacity. For example, in Figure 5.2A, the wood char that was pretreated with potassium permanganate (KM) and then amended with aluminum sulfate (KM – Aluminum Sulfate WC) shows a higher fluoride removal capacity than metal oxide amended wood char with no pretreatment (Aluminum Sulfate WC). The $Q_{e1.5}$ value

(Table 5.2) for aluminum sulfate amended wood char pretreated with potassium permanganate was 0.40 mg/g, while the aluminum sulfate with no pretreatment showed 0.14 mg/g. In contrast, Figure 5.2A and Table 5.2 show that hydrogen peroxide (HP) pretreatment combined with aluminum sulfate amendment had a calculated $Q_{e1.5}$ value of 0, lower even than the wood char alone at 0.04 mg/g. Figure 5.2B shows a similar trend for potassium permanganate pretreatment followed by iron (III) nitrate amendment when higher equilibrium concentrations are compared (Langmuir Q_m values of 10.6 and 8.02 mg/g for pretreated and not pretreated, respectively).



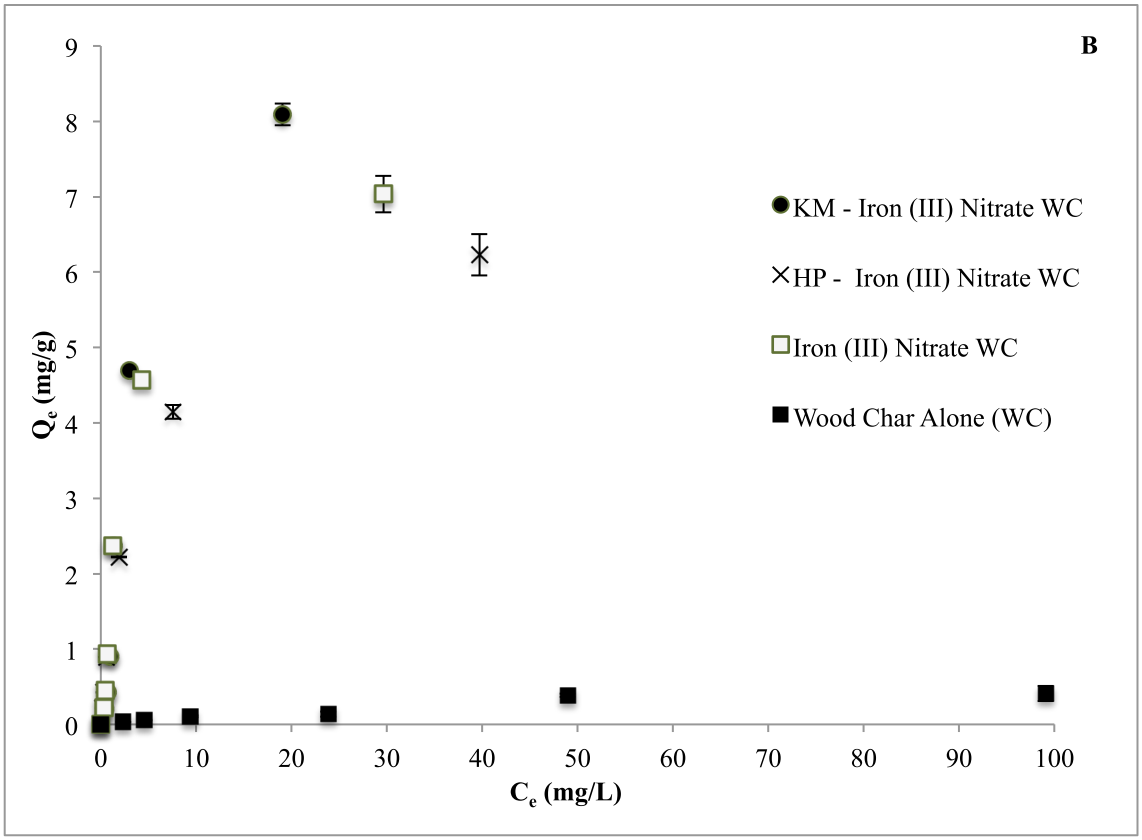


Figure 5.2: Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars with and without pretreatment (KM = potassium permanganate, HP = hydrogen peroxide). Figure 5.2A shows results of wood char treated with aluminum sulfate and Figure 5.2B shows results of wood char treated with iron (III) chloride. Q_e, the mg of fluoride removed per gram of media is plotted against C_e, the equilibrium concentration of fluoride in mg/L.

However, the drinking water relevant $Q_{e1.5}$ values show a different trend. At an equilibrium concentration of 1.5 mg/L, iron (III) nitrate amendment with no pretreatment results in a $Q_{e1.5}$ value of 2.06 versus 0.69 mg/g for potassium permanganate pretreated. Again, with iron (III) nitrate amendment, the hydrogen peroxide pretreatment lowered the fluoride removal capacity (Table 5.2).

Table 5.2: Freundlich and Langmuir constants obtained using batch isotherm data for untreated, amended and pretreated wood chars.

Treated and Untreated Wood and Freundlich and Langmuir Constants					
Pretreatment	**Metal Amendment**	**K_f (mg/g)(mg/L)$^{1/n}$**	**1/n**	**Q_e (mg/g) at C_e=1.5 mg/L F (Freundlich)**	**Langmuir Q_m (mg/g)**
None	None	0.03 ± 0.01	0.60	0.04	0.68 ± 0.18
Hydrogen Peroxide	None	0.01 ± 0.01	0.53	0.02	0.21 ± 0.07
Potassium Permanganate	None	0.03 ± 0.01	0.44	0.03	0.21 ± 0.04
None	Aluminum Sulfate	0.12 ± 0.03	0.51	0.14	2.04 ± 1.13
Hydrogen Peroxide	Aluminum Sulfate	0.00 ± 0.00	2.12	0.00	0.00 ± 0.00
Potassium Permanganate	Aluminum Sulfate	0.33 ± 0.08	0.46	0.40	3.04 ± 0.80
None	Aluminum Chloride	0.51 ± 0.06	0.28	0.57	1.62 ± 0.09
Hydrogen Peroxide	Aluminum Chloride	0.12 ± 0.02	0.82	0.17	11.1 ± 1.12
Potassium Permanganate	Aluminum Chloride	0.08 ± 0.09	0.63	0.27	1.57 ± 0.10
None	Iron (III) Nitrate	1.73 ± 0.41	0.43	2.06	8.02 ± 0.49
Hydrogen Peroxide	Iron (III) Nitrate	1.49 ± 0.26	0.40	1.76	6.84 ± 0.17
Potassium Permanganate	Iron (III) Nitrate	0.55 ± 0.46	0.55	0.69	10.6 ± 1.45
None	Iron (II) Chloride	0.67 ± 0.10	0.28	0.75	1.86 ± 0.25
Hydrogen Peroxide	Iron (II) Chloride	0.11 ± 0.02	0.42	0.13	078 ± 0.06
Potassium Permanganate	Iron (II) Chloride	0.78 ± 0.09	0.19	0.85	1.61 ± 0.06

Further study of Table 5.2 identifies additional interesting points. Oxidation pretreatment without metal amendment decreased the fluoride removal capacity of wood char. For example, hydrogen peroxide and potassium permanganate pretreated chars with no metal amendment both have a fluoride removal capacity (Q_m = 0.21

mg/g) below that of the wood char without pretreatment or amendment ($Q_{m} =$ 0.68 mg/g). Comparing the $Q_{e1.5}$ values in Table 5.2 shows that oxidizing agents have different effects depending on the metal oxide amendment with which they are paired. As discussed above, pretreatment with potassium permanganate resulted in higher fluoride removal when combined with aluminum sulfate than when aluminum sulfate amendment alone is used with wood char (Figure 5.2A and Table 5.2). On the other hand, aluminum chloride amendment with no pretreatment exhibits a $Q_{e1.5}$ value of 0.57 mg/g, whereas when a pretreatment step with potassium permanganate is added the results show a decrease in fluoride removal to 0.27 mg/g (Table 5.2). Similar trends are visible with the $Q_{e1.5}$ values shown in Table 5.2 for iron (II) chloride and iron (III) nitrate amended wood chars. Iron (II) chloride combined with potassium permanganate pretreatment resulted in an increase in fluoride removal while iron (III) nitrate combined with either oxidizing agent resulted in a lower $Q_{e1.5}$ values.

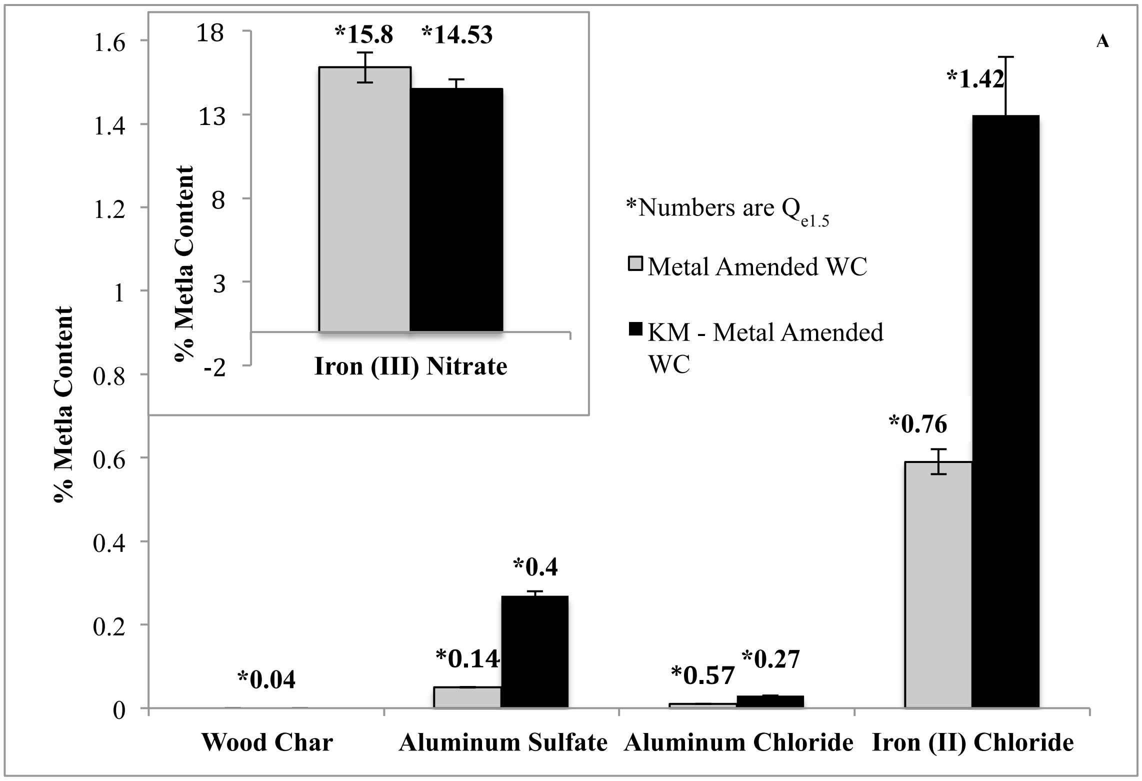
The Langmuir Q_m values offered in Table 5.2 offer additional insights into the fluoride removal capacity of the materials at higher equilibrium values. For example, the aluminum chloride amendment with no pretreatment exhibits a Q_m of 1.62 mg/g, whereas the wood char pretreated with hydrogen peroxide exhibits a Q_m of 11.13 mg/g (Table 5.2). This distinction between the $Q_{e1.5}$ values and the Langmuir Q_m values is important because the $Q_{e1.5}$ values reveal what is occurring at the WHO recommended drinking water fluoride guideline, whereas the Langmuir Q_m values suggest the highest amount of fluoride that can be removed by a specific material at higher fluoride water concentrations (potentially concentrations one to two orders of magnitude higher than the WHO guideline). Therefore, looking at the $Q_{e1.5}$ values is a more pragmatic indicator of what will be useful in a field setting to remove fluoride from drinking water in a community, while the Langmuir Q_m values are valuable from a research perspective to understand what might be possible with various material amendments

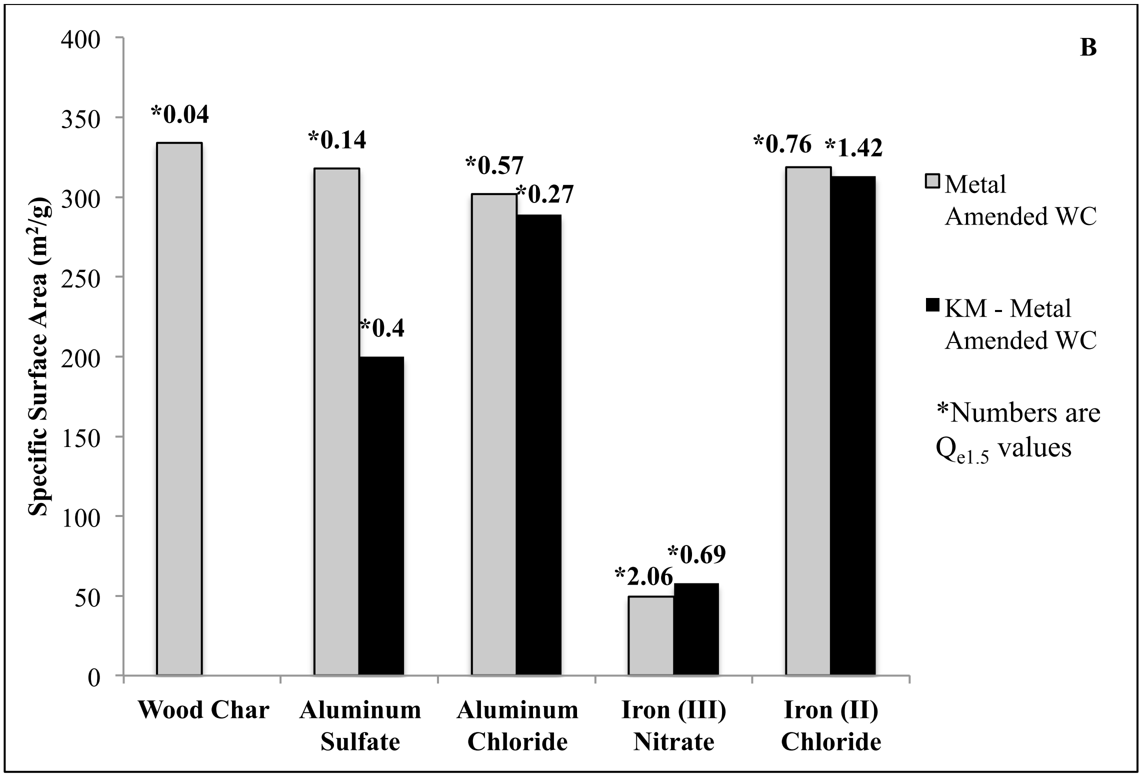
Given the goal of finding materials that offer high fluoride removal capacities for use in developing communities, it is helpful to compare the fluoride removal capacities of these amended materials with commonly used adsorption media, such as activated alumina and bone char. The work of Brunson and Sabatini (2014) offered $Q_{e1.5}$ values for activated aluminum and bone char of 0.5 and 2.1 mg/g, respectively. The data in table 5.2 show that many of the metal oxide amended and pretreated wood chars exhibit $Q_{e1.5}$ values greater than that of the activated alumina, such as the iron (II) chloride and potassium permanganate pretreated iron (II) chloride. While the metal amendments clearly improve the effectiveness of the unamended wood char, only the wood char amended with iron (III) nitrate (2.06 mg/g) approaches that of the bone char at the environmentally relevant $Q_{e1.5}$ value (Table 5.2). Thus, the metal oxide amended wood chars, particularly the iron (III) nitrate amended char, are helpful alternatives for communities not amenable to using bone char. It is also helpful to use something like wood char to provide a matrix for the metal oxides to adhere to so that water filtration is possible without filter clogging a filter (e.g., clogging would occur colloidal size metal particles).

Modifications caused by Metal Loading and Pretreatment with Oxidizing Agents

Metal Loading

The third objective of this work was to look for fundamental changes in surface properties (e.g. metal content, point of zero charge and specific surface area) that could account for the trends discussed above. Figure 5.3A shows that for all the metal oxide amendments except aluminum chloride, higher metal loading resulted in higher $Q_{e1.5}$ values. Looking first at metal amended wood chars with no pretreatment, the highest fluoride removal capacity clearly corresponds to the highest metal loading for iron (III) chloride with a $Q_{e1.5}$ value of 2.06 mg/g and a metal loading rate of 15.8%, both of which are much higher than wood char amended with other metals (ranging from 0.01 to 1.42 % metal loading, shown in Table 5.3 and Figure 5.3A).





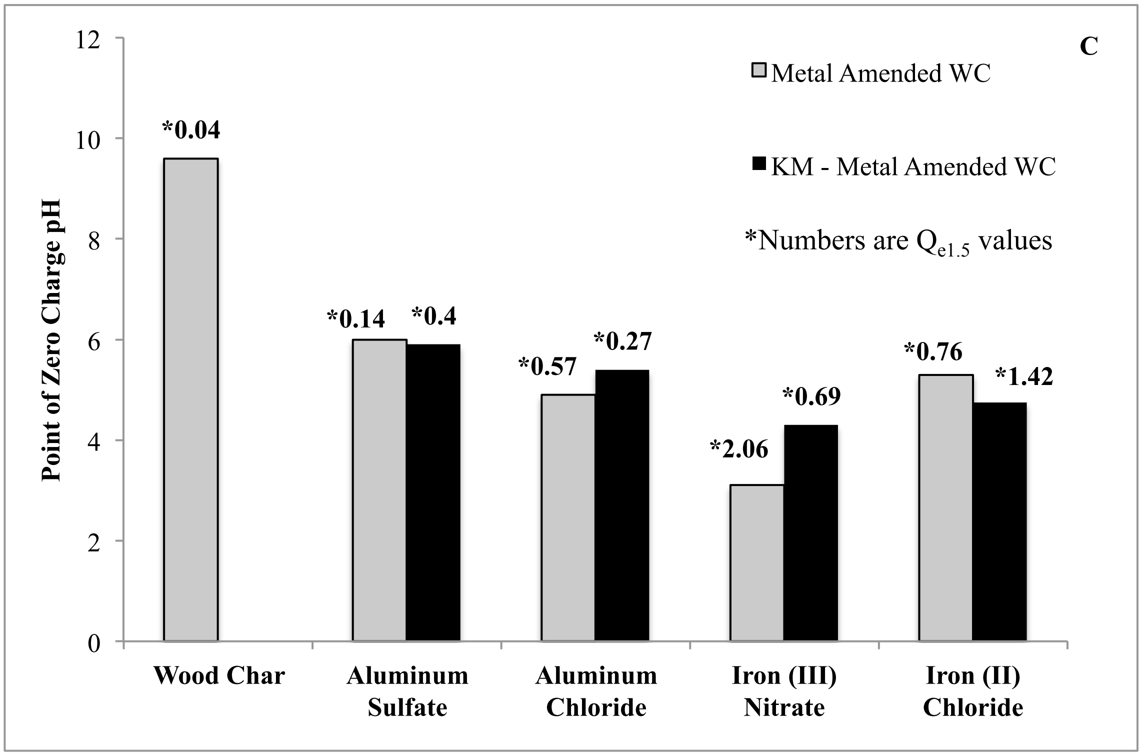


Figure 5.3: Char characteristic analysis where 5.3A shows metal loading percentages, 5.3B shows point of zero charge values and 5.3C shows specific surface area data.

Table 5.3: Metal loading, specific surface area and surface chemistry characteristics of all materials tested.

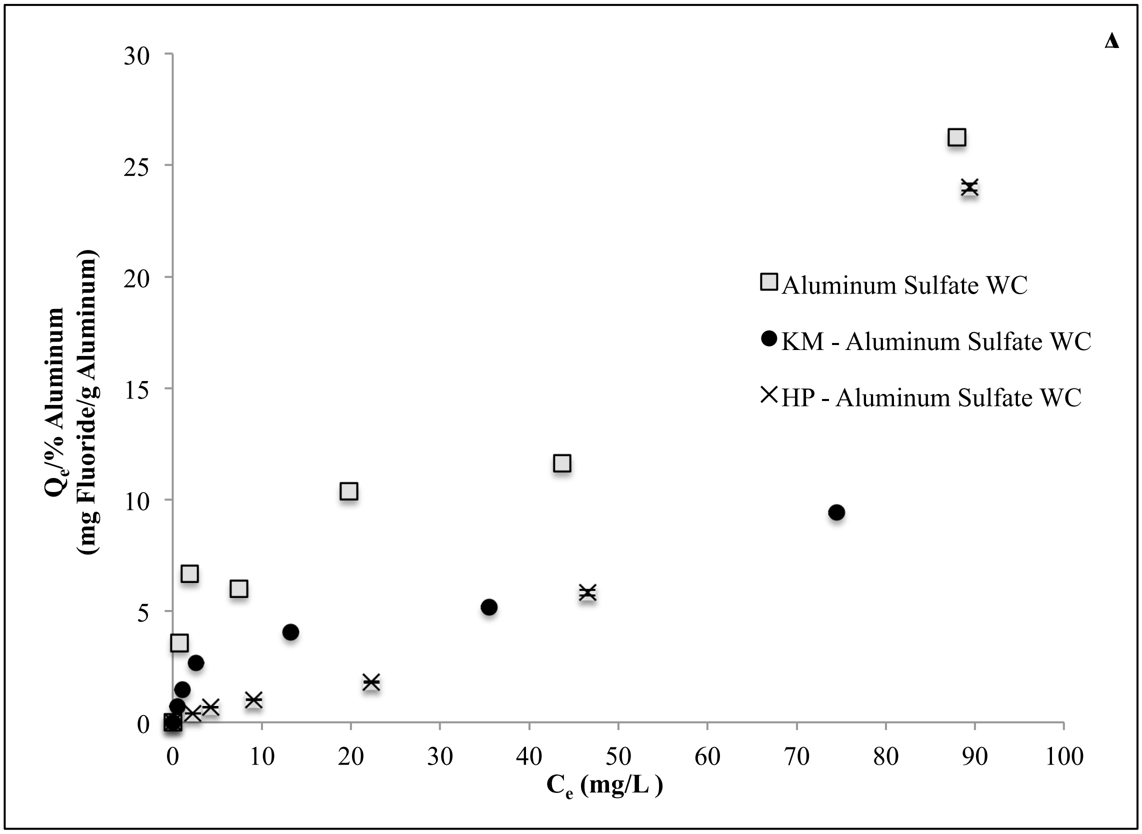
Treated and Untreated Wood Char Characteristics

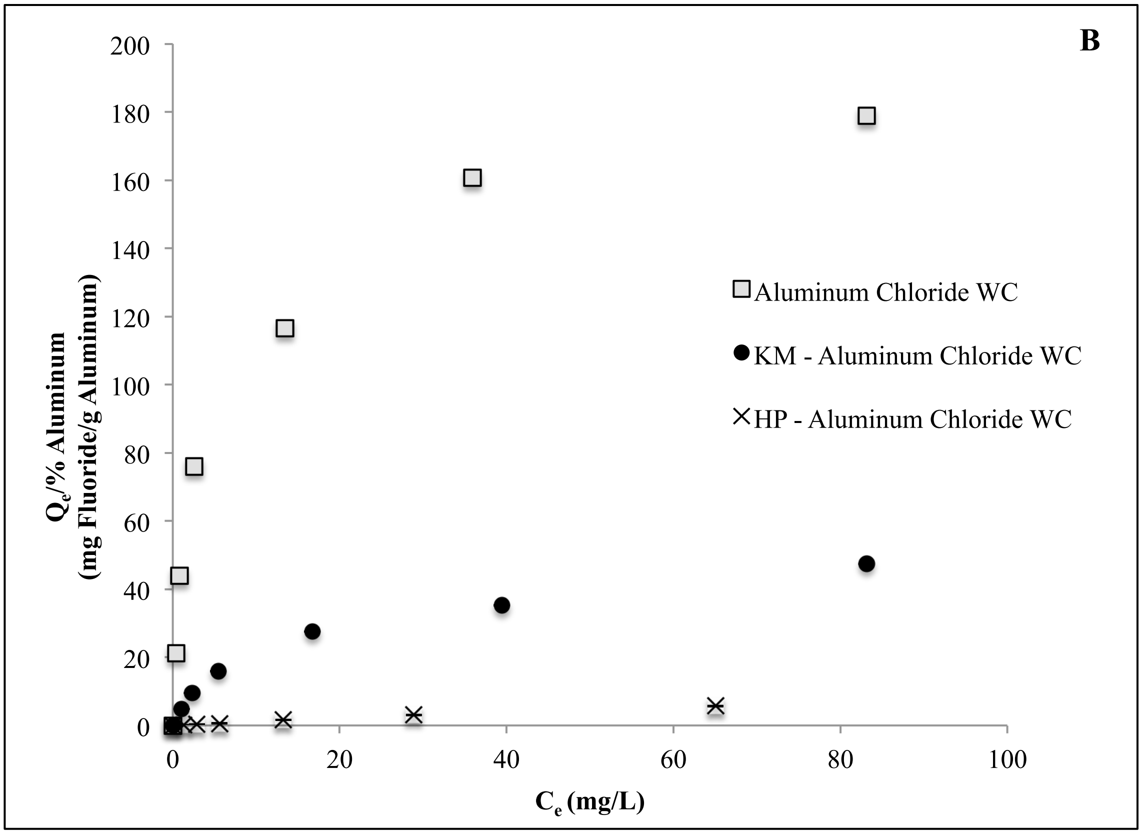
Pretreatment	**Metal Amendment**	**Percent Aluminum**	**Percent Iron**	**pH_{PZC}**	**Specific Surface Area (m^2/g)**
None	None	<0.01 ± 0	0.01 ± 0	9.4 ± 0.4	334 ± 5
Hydrogen Peroxide	None	<0.01 ± 0	0.01 ± 0	3.5 ± 0.2	133 ± 17
Potassium Permanganate	None	<0.01 ± 0	<0.01 ± 0	8.1 ± 0.3	300 ± 18
Pretreatment	**Metal Amendment**	**Percent Aluminum**		**pH_{PZC}**	**Specific Surface Area (m^2/g)**
None	Aluminum Sulfate	0.05 ± 0		6 ± 0.6	318 ± 22
Hydrogen Peroxide	Aluminum Sulfate	0.05 ± 0		3.5 ± 0.3	116 ± 9
Potassium Permanganate	Aluminum Sulfate	0.27 ± 0.01		5.9 ± 0.3	200 ± 45
None	Aluminum Chloride	0.01 ± 0.00		4.9 ± 0.6	302 ± 13
Hydrogen Peroxide	Aluminum Chloride	0.65 ± 0.01		4.6 ± 0.6	7 ± 1
Potassium Permanganate	Aluminum Chloride	0.03 ± 0.00		5.4 ± 0.6	289 ± 6
Pretreatment	**Metal Amendment**	**Percent Iron**		**pH_{PZC}**	**Specific Surface Area (m^2/g)**
None	Iron (III) Nitrate	15.8 ± 0.90		3.1 ± 0.3	49 ± 4
Hydrogen Peroxide	Iron (III) Nitrate	11.2 ± 0.53		3.3 ± 0.1	54 ± 9
Potassium Permanganate	Iron (III) Nitrate	14.5 ± 0.56		4.3 ± 1.3	58 ± 1
None	Iron (II) Chloride	0.59 ± 0.03		5.3 ± 0.4	319 ± 2
Hydrogen Peroxide	Iron (II) Chloride	0.70 ± 0.12		3.6 ± 0.1	105 ± 16
Potassium Permanganate	Iron (II) Chloride	1.25 ± 0.14		4.8 ± 0.5	313 ± 6

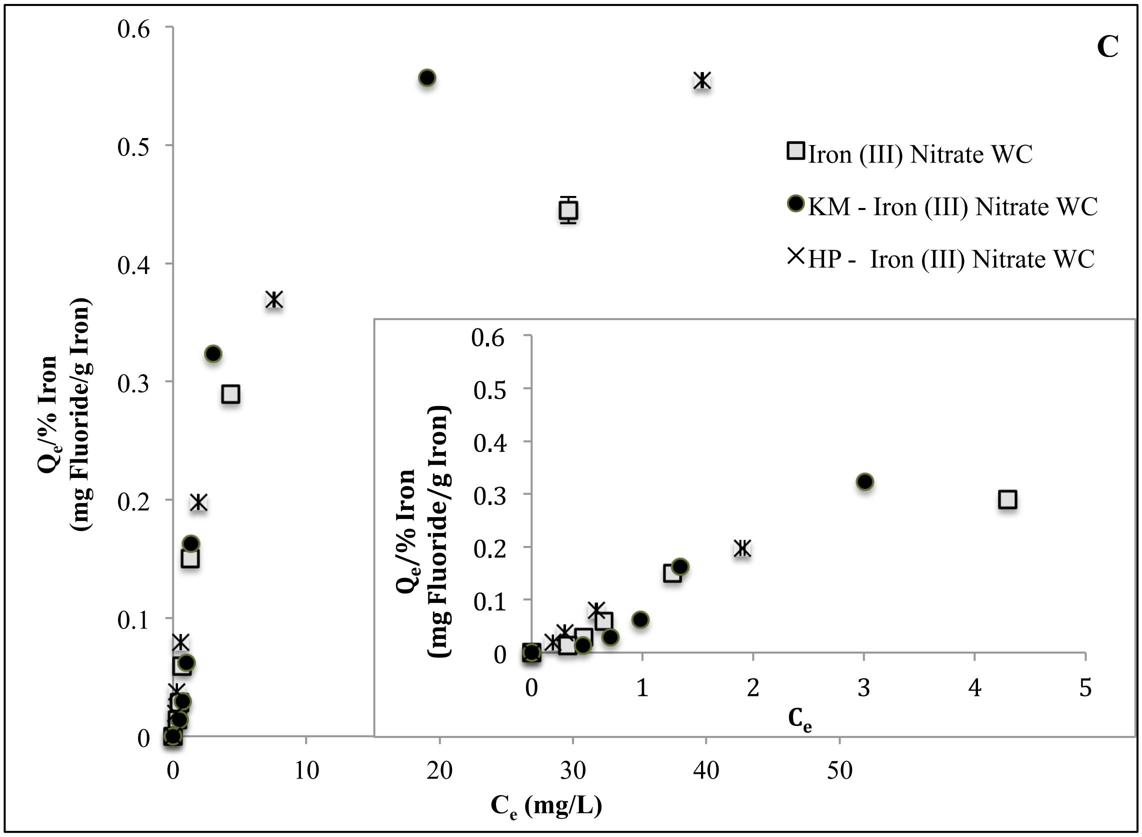
Additionally, iron (II) chloride and iron (III) nitrate, both with and without potassium permanganate pretreatment, exhibit the highest metal loading rates and the highest $Q_{e1.5}$ values among all the materials tested (Table 5.2). However, this trend of metal loading correlating with fluoride removal does not hold true for the entire set of treated materials. For example, the lowest metal loading, occurring with aluminum chloride amendment on untreated wood char, does not correspond with the lowest $Q_{e1.5}$ value, which is instead exhibited by aluminum sulfate amendment on untreated wood char (0.57 mg/g for aluminum chloride versus 0.14 mg/g for aluminum sulfate). Thus, while the general trend shown by this data is that metal loading equates with fluoride removal, there are exceptions.

Next it is helpful to assess the effect of oxidation pretreatment on metal loading. In all cases, except for the iron (III) nitrate amended wood char, pretreatment with potassium permanganate increased metal loading on the wood char above that of metal amendment without pretreatment (Figure 5.3A). For example, iron (II) chloride shows a 0.59 % iron loading without pretreatment and 1.25 % iron loading when pretreated with potassium permanganate (Table 5.3). Table 5.3 also shows that aluminum sulfate has 0.05 % aluminum loading on wood char with no pretreatment, 0.05% for the hydrogen peroxide pretreated wood char, and 0.27% for the potassium permanganate pretreated char. These data suggest that there is a relationship between the use of potassium permanganate pretreatment and higher metal loading, which subsequently increases fluoride removal capacity. However, pretreatment with hydrogen peroxide did not result in increased metal loading or higher fluoride removal (Table 5.3). An increase in metal loading on pretreated chars was expected due to previous research demonstrating that oxidation of activated carbon increases the oxygen content on the surface of the media, thus making it more acidic (Jia and Thomas, 2000). Jia and Thomas (2000) found a clear link between an increase in the oxygen content of the surface of coconut-based activated carbon and an increase in the adsorption of cadmium, a positively charged metal ion. However, Song et al. (2010) suggested there is still much to be learned about the methods by which activated carbons adsorb various metals. Interestingly, the metal loading of the aluminum oxide amended materials is negligible (< 0.65 %) compared to that of the iron oxide amendments (0.59 – 15.9 %) (Figure 5.3A and Table 5.3). Additionally, the order of metal concentrations in the starting solutions for metal amendment methods did not equate with the order of metal incorporated into the wood char. Starting metal concentrations in amendment solutions went from lowest to highest following the order of aluminum sulfate < iron (III) nitrate < aluminum chloride < iron (II) chloride, whereas the metal loading rates on wood char went in a different order of aluminum chloride < aluminum sulfate < iron (II) chloride < iron (III) nitrate. Thus, starting metal concentration in solution does not necessary equate with metal loading on the char material.

To provide more insight into the role of the metals in fluoride removal, the removal capacities were normalized by metal content. Inspection of Figure 5.4 shows that when the data are normalized, the aluminum chloride amended materials exhibit the highest fluoride removal capacity per gram of metal and the iron (III) nitrate amended materials exhibit the lowest capacity. This demonstrates that while iron (III) nitrate offers the highest overall fluoride adsorption based on its high iron loading, when normalized by metal loading it has the lowest adsorption efficiency. This suggests that only a fraction of the iron actually participates in fluoride adsorption, likely the exterior portion of the solid iron oxide. Specifically looking at the aluminum chloride amended chars, the hydrogen peroxide pretreated wood char (HP – Aluminum Chloride WC) exhibits the lowest fluoride removal effectiveness when normalized by aluminum content, while the aluminum chloride wood char with no pretreatment (Aluminum Chloride WC) proves to be the most effective (Figure 5.4B). This is consistent with Figure 5.3A which shows that hydrogen peroxide aluminum chloride amended char had the lowest aluminum loading, but with a $Q_{e1.5}$ value higher than several other tested materials.




B
Qe/% Aluminum (mg Fluoride/g Aluminum)
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
Ce (mg/L)
□ Aluminum Chloride WC
● KM - Aluminum Chloride WC
× HP - Aluminum Chloride WC


C
Qe/% Iron (mg Fluoride/g Iron)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Ce (mg/L)
□ Iron (III) Nitrate WC
● KM - Iron (III) Nitrate WC
× HP - Iron (III) Nitrate WC
Qe/% Iron (mg Fluoride/g Iron)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
Ce

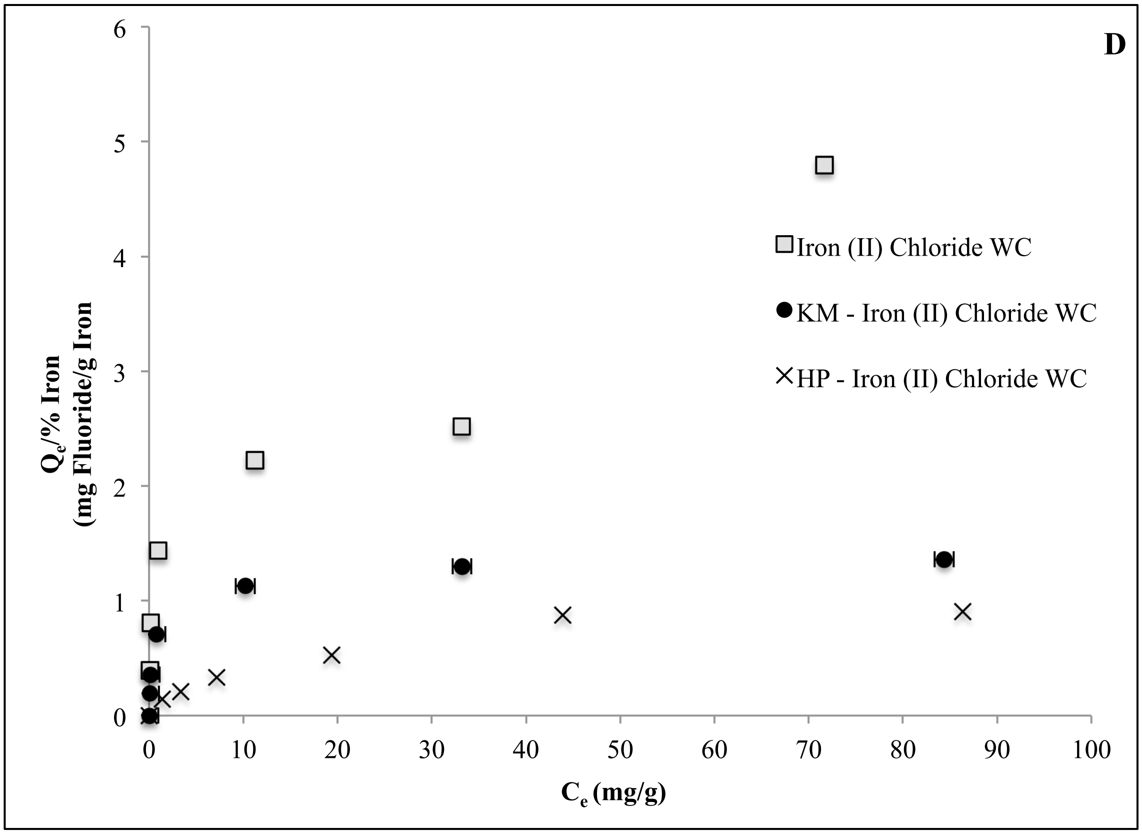


Figure 5.4: Data shows the fluoride removal capacities of untreated wood char and metal oxide amended wood chars (WC), with and without pretreatment, (KM = potassium permanganate, HP = hydrogen peroxide) normalized by metal content. The y-axis shows $Q_{e/}$metal %, the mg of fluoride removed per gram of media normalized by metal content, and is plotted against C_e, the equilibrium concentration of fluoride in mg/L. 5.4A shows results of wood char treated with aluminum sulfate, 5.4B shows wood char treated with aluminum chloride, 5.4C shows wood char treated with iron (III) nitrate with the inset graph showing data only up to C_e = 5 and 5.4D shows wood char treated with iron (II) chloride.

When normalized by metal loading, the aluminum chloride treated char performed best overall, which suggests there is potential to greatly improve fluoride removal capacity if a method is found that will increase aluminum chloride loading onto char materials.

Tests showed that neither increasing the starting aluminum chloride concentration or increasing the contact time between the starting aluminum chloride solution and the wood char increased fluoride removal. Other methods, such as temperature adjustment, method of shaking, and starting amendment solution pH, should be investigated in future research to increase metal loading. Future work should also be done with the aluminum based materials prior to using them in a field setting to ensure that only an acceptable level of residual aluminum is leaching into the drinking water supply during filtration due to the potential causative link between aluminum consumption and Alzheimer's disease (Walton, 2006).

Surface Chemistry

Another important media characteristic to assess is the pH_{PZC} (solution pH at which the surface of a material exhibits a net neutral charge). The pH_{PZC} can depict changes in the acidic and basic functional groups on the surface (Tchomgui-Kamga et al., 2010). The starting pH_{PZC} of the eucalyptus wood char was 9.4 and, as shown at the top of Table 5.3, in each case of oxidation pretreatment the pH_{PZC} decreased, to 8.1 for the potassium permanganate pretreatment and 3.5 for hydrogen peroxide. It was hypothesized that pretreating wood char with oxidizing agents would make the material surface more acidic through the oxidation of surface functional groups. The decrease in pH_{PZC} exhibited by the pretreated wood char affirms this hypothesis. A lower pH_{PZC} means that there is a much wider range (all solution pH values above the pH_{PZC}) in which the surface of the material will have a negative charge, which should be more effective for attracting positively charged metal oxides to the wood char.

The metal amendments also had an effect on the surface chemistry of the wood char. Figure 5.3B and Table 5.3 show that materials amended with iron have pH_{PZC} values ranging from 3.1 to 5.3 and those amended with aluminum range from 3.5 to 5.9. These are similar to results found by Tchomgui-Kamga et al. (2010) who obtained pH_{PZC} values ranging from 2.8 to 4.4 for their combined aluminum and iron impregnated spruce wood, depending on the charring temperature. There are aluminum oxides that have pH_{PZC} values of 4.5 to 9.5 and iron oxides that range from 6.3 to 9.8; values are variable based on crystalline structure and type of oxide (Sposito, 1995; Cornell and Schwertmann, 2003).

Most of the aluminum amended materials fall in the range of the expected aluminum oxide pH_{PZC} values, such as 6.0 for aluminum sulfate amended wood char, whereas, the iron (III) nitrate pH_{PZC} was lower than expected, at 3.1 (Table 5.3). It is possible that this occured because iron is a transition metal, which makes it a good oxidant and therefore, it may have served as an oxidizing agent for the wood char. If that is the case, the iron (III) nitrate would have added extra acidic functional groups to the surface of the char, thus further decreasing the pH_{PZC}. In the case of fluoride adsorption, ideally a material that exhibits a high pH_{PZC} value is preferred; a high pH_{PZC} leaves the surface of the sorbent positively charged at typical ground water pH values. For these experiments, the prepared fluoride solutions had starting pH values of 5.5 – 7 and ending equilibrium pH values varied based on the adsorbent used. Therefore, it is expected that any material with a pH_{PZC} value above 6 should perform better than those with lower pH_{PZC} values. However, in this work, the best performing materials, iron (III) nitrate and iron (II) chloride, exhibited pH_{PZC} values less than 6.0 (Table 5.3).

These unexpected results may be the outcome of ion exchange between the hydroxide ions, which are included in the metal oxides, and fluoride ions rather than the result of the amended wood char surface attracting the fluoride ions from water through electrostatic forces.

When investigating the effect of oxidation pretreatment it is difficult to see consistent trends in pH_{PZC} values. However, Figure 5.3B shows that, when comparing the potassium permanganate pretreated with the metal amendment without pretreatment, the metal treatment methods that exhibit the lowest pH_{PZC} values also offer the highest fluoride removal capacities. For example, the pH_{PZC} of aluminum chloride treated wood char with no pretreatment is 4.9 and for potassium permanganate pretreated is 5.4. The aluminum chloride with no pretreatment has the higher $Q_{e1.5}$ value of 0.57 versus 0.27 for the potassium permanganate pretreated. Future research should evaluate specific surface functional group changes on the wood char caused by the pretreatment and metal amendment methods to gain a better understanding of the fundamental processes occurring during treatment.

Surface Area

A final key media characteristic is specific surface area, which showed limited change through amendment and pretreatment in this research (Figure 5.3C and Table 5.3). The largest pretreatment change in specific surface area occurred when pretreatment was done with hydrogen peroxide, where the specific surface area decreased from 334 to 133 m^2/g (Table 5.3). This change is expected as specific surface area can decrease after oxidation pretreatment when strong oxidizing agents are used that can cause damage to the pore walls of an activated carbon material (Ania et al., 2002; Song et al., 2010). For nitric acid pretreatment, another common oxidizing agent used with activated carbon, Ania et al. (2002) found a significant decrease in the specific surface area with the use of nitric acid at 20% concentration or greater on a commercially available activated carbon. The wood char used in this study was found to experience a decrease in specific surface area even with just 2% nitric acid pretreatment, which suggests that *Eucalpytus robusta* char may be more friable than other activated carbon materials. The potassium permanganate exhibited minimal change in specific surface area (300 and 334 m^2/g for potassium permanganate pretreated and untreated wood char, respectively).

Treatment with metals in most cases did not greatly alter the specific surface area. For example, treatment with iron (II) chloride resulted in a specific surface area of 318 m^2/g compared with 334 m^2/g for unamended wood char (Table 5.3). However, in other cases metal amendment significantly reduced the surface area. For example, treatment with iron (III) nitrate reduced the specific surface area of all pretreated and untreated wood chars from a range of 133 to 334 m^2/g to between 47 and 59 m^2/g. Iron (III) nitrate also exhibited a much larger metal loading rate than any of the other amended materials, which suggests specific surface area was lost as a larger amount of metal was incorporated into the media. Metal amendments are expected to reduce the specific surface area, depending on metal loading, due to metal oxides blocking some of the internal pores. However, as shown in Figure 5.3C, the loss of surface area was not detrimental to the fluoride removal capacity of the iron (III) nitrate, as compared with all other treated media in this work.

Based on this large loss of specific surface area, it is interesting to see results when Q_e is normalized by both specific surface area and metal content. Figure 5.5 shows that when this double normalization is evaluated, the aluminum chloride amended wood char outperforms all the other tested media, suggesting that the best use of future research may be to find ways to enhance aluminum chloride amendment onto wood char for fluoride removal.

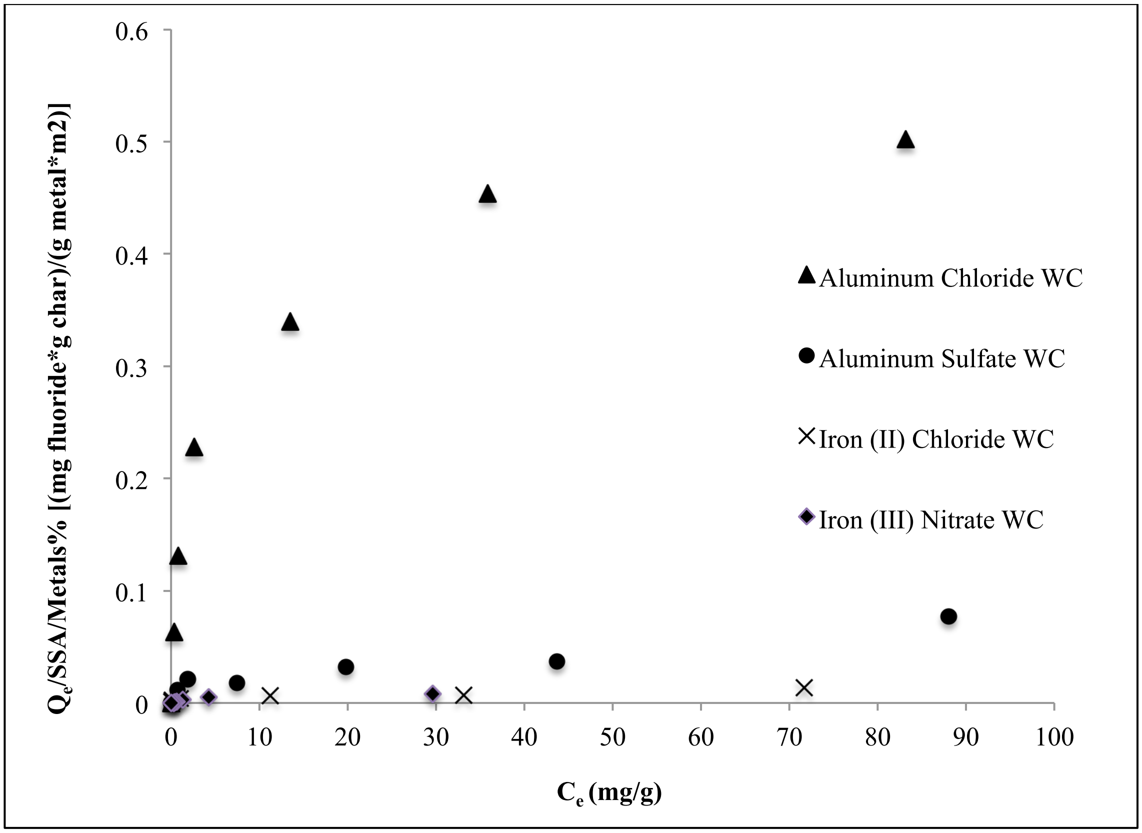


Figure 5.5: Results of batch isotherms showing the fluoride removal capacities of untreated wood char and metal oxide amended wood chars normalized by both specific surface area and metals content. Q_e, the mg of fluoride removed per gram of media is normalized by specific surface area and metals content [(mg fluoride * g char)/(g metal * m^2)] and plotted against C_e, the equilibrium concentration of fluoride in mg/L.

From a practical perspective, the aluminum chloride amendment is a simple procedure and, assuming chemicals are readily available, this is an easy way to improve the fluoride removal capacity of wood char.

Conclusion

This work offers several conclusions that provide new insights into increasing the fluoride removal capacity of wood char amended with metal oxides. This research demonstrates that aluminum oxide amendments, as well as the less studied iron oxide amendments, are effective at increasing fluoride removal by wood char. Although all four metal amendment methods showed statistically significant increases in fluoride removal above that of wood char alone, the iron oxide amendments actually resulted in higher fluoride adsorption than aluminum for all cases; the iron (III) nitrate showed a $Q_{e1.5}$ value over 50 times higher than that of wood char alone. Iron (III) nitrate amendment exhibited the highest metal loading and the largest fluoride update, but also demonstrated an inefficient use of iron when fluoride removal was normalized by metal loading. This result can likely be attributed to the reduced specific surface area caused by iron blocking the pore spaces in the wood char and preventing full use of pore space and iron content. In contrast, the aluminum chloride treated wood char showed the lowest metal loading but the highest efficiency when normalized by metal content and specific surface area. In all cases, pretreatment with oxidizing agents decreased the point of zero charge, and in most cases, potassium permanganate pretreatment increased metal loading and fluoride removal. Additionally, wood char, when treated with hydrogen peroxide or nitric acid (done in preliminary testing) was found to be less robust during the oxidation process than activated carbon used in oxidation tests conducted by other researchers. Therefore, the specific surface area decreased significantly with the stronger oxidation, pretreatment with hydrogen peroxide, but less with the potassium permanganate pretreatment. This suggests the weaker oxidation pretreatment is preferable for wood char. This work is one of the first to systematically study one starting material with several oxidizing agents and metal amendment processes. The conclusions from this work suggest that iron oxide amendment processes should be further explored for increased fluoride removal, particularly in geographic areas where iron amendment materials are readily available. Additionally, future work assessing fluoride removal mechanisms and surface functional group changes and investigating ways to enhance metal loading on wood char can be useful to the community working on fluoride removal from drinking water.

Acknowledgements

The authors gratefully acknowledge the U.S. Environmental Protection Agency and the U.S. National Science Foundation that contributed partial funding to this work. This publication was developed under STAR Fellowship Assistance Agreement no. 91731301 awarded by the U.S. Environmental Protection Agency (EPA). This work has not been formally reviewed by EPA, and the views expressed in this paper are solely those of the authors and the EPA does not endorse any products or commercial services mentioned in this publication. The authors also wish to acknowledge partial funding from the University of Okahoma WaTER Center and the Graduate College at the University of Oklahoma in support of this work

References

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., and Tanada, S. (2004). “Adsorption of fluoride ions onto carbonaceous materials.” *J. Colloid Interf. Sci.* 275(1), 35–39.

Ania, C. O., Parra, J., and Pis, J.J. (2002). “Influence of oxygen-containing functional groups on active carbon adsorption of selected organic compounds.” *Fuel Process. Technol.* 79(3), 265–271.

Ayoob, S., Gupta, A. K., and Bhat, V.T. (2008). “A conceptual overview on sustainable technologies for the defluoridation of drinking water.” *Crit. Rev. Environ. Sci. Technol.* 38(6), 401–470.

Babic, B.M., Milonjic, S.K., Polovina, M., and Kaludierovic, B. (1999). “Point of zero charge and intrinsic equilibrium constants of activated carbon cloth.” *Carbon*, 37(3), 477–481.

Biswas, K., Saha, S.K., and Gosh. U.C. (2007). “Adsorption of fluoride from aqueous solution by a synthetic iron(III)−aluminum(III) mixed oxide.” *Indust. Eng. Chem. Res.* 46(16), 5346–5356.

Brunson, L.R., and Sabatini, D.A. (2014a). “Practical considerations, column studies and natural organic material competition for fluoride removal with bone char and aluminum amended materials in the Main Ethiopian Rift Valley.” *Sci. Tot. Environ.* 488-489, 580–587.

Brunson, L.R., and Sabatini, D.A. (2014b). "The Role of Surface Area and Surface Chemistry during an Investigation of Eucalyptus Wood Char for Fluoride Adsorption from Drinking Water." *J. Environ. Enr.* Accepted.

Chen, W., Parette, R., Zou, J., Cannon, F.S., and Dempsey, B.A. (2007). "Arsenic removal by iron-modified activated carbon." *Water Res.* 41(9), 1851–58.

Cornell, R. M, and Schwertmann, U. (2003). *The iron oxides: structure, properties, reactions, occurrences, and uses*. Weinheim: Wiley-VCH, Weinheim, Germany.

Dessie, G., and Erkossa, T. (2011). Eucalyptus in East Africa: socio-economic and environmental issues. Forestry Department and Agricultural Organization of the United Nations, Rome, Italy.

Fawell, J., Bailey, K., Chilton, J., and Dahi, E. (2006). *Fluoride in drinking-water*. World Health Organization, Geneva, Switzerland.

Gazzano, E., Bergandi, L., Riganti, C., Aldieri, E., Doublier, S., Costamagna, C., Bosia, A., and Ghigo, D. (2010). "Fluoride effects: the two faces of Janus." *Curr. Med. Chem.* 17(22), 2431–2441.

Gu, Z., Fang, J., and Deng, B. (2005). "Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal." *Environ. Sci. Technol.* 39(10), 3833–3843.

Gwala, P., Andey, S., Mhaisalkar, V., Labhasetwar, P., Pimpalkar, S., and Kshirsagar, C. (2011). "Lab scale study on electrocoagulation defluoridation process optimization along with aluminum leaching in the process and comparison with full scale plant operation." *Water Sci. Technol.* 63(12), 2788–2795.

Hem, J.D. (1985). “Study and interpretation of the chemical characteristics of natural water”. Water Supply Paper 2254. U.S. Geological Survey, Reston, VA.

Hristovski, K.D., Westerhoff, P.K., Moller, T., and Sylvester, P. (2009). “Effect of synthesis conditions on nano-iron (hydr) oxide impregnated granulated activated carbon.” *Chem. Eng. J.* 146(2), 237–243.

Hudak, P.F. (2008). “Elevated fluoride and selenium in West Texas groundwater.” *Bull. Environ. Contam. Toxicol.* 82(1), 39–42.

Jagtap, S., Yenkie, M.K., Labhsetwar, N., and Rayalu, S. (2012). “Fluoride in drinking water and defluoridation of water.” *Chem. Rev.* 112(4), 2454–2466.

James, G., Sabatini, D., Chiou, C., Rutherford, D., Scott, A., and Karapanagioti, H. (2005). “Evaluating phenanthrene sorption on various wood chars.” *Water Res.* 39(4), 549–558.

Jia, Y. F., and Thomas, K. M. (2000). “Adsorption of cadmium ions on oxygen surface sites in activated carbon.” *Langmuir,* 16(3), 1114–1122.

Kamble, S., Jagtap, S., Labhsetwar, N., Thakare, D., Godfrey, S., Devotta, S., and Rayalu, S. (2007). “Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan.” *Chem. Engr.* 129(1-3), 173–180.

Kaseva, M E. 2006. “Optimization of regenerated bone char for fluoride removal in drinking water: A case study in Tanzania.” *J. Water Health,* 4(1), 139–147.

Liu, S., Chen, X., Chen, X., Liu, Z., and Wang, H. (2007). “Activated carbon with excellent chromium(VI) adsorption performance prepared by acid-base surface modification.” *J. Hazard. Mater.* 141(1), 315–319.

Meenakshi, and Maheshwari, R.C. (2006). “Fluoride in Drinking Water and Its Removal.” *J. Hazard. Mater.* 137 (1): 456–463.

Pervov, A.G., Dudkin, E.V., Sidorenko, O.A., Antipov, V.V., Khakhanov, S.A., and Makarov, R.I. (2000). “RO and NF membrane systems for drinking water production and their maintenance techniques.” *Desalination,* 132(1-3), 315–321.

Pettersen, R.C. (1984). “The chemical composition of wood.” In *The chemistry of solid wood*, Rowell, R. M. ed., American Chemical Society, Washington D.C.

Polovina, M., Babić, B., Kaluderović, B., and Dekanski, A. (1997). “Surface characterization of oxidized activated carbon cloth.” *Carbon,* 35(8), 1047–1052.

Rao, N.C.R. (2003). “Fluoride and environment - a review.” In *Proceedings of the Third International Conference on Environment and Health*, Chennai, India.

Schamschula, R. G., and Barmes D. E. (1981). “Fluoride and health: dental caries, osteoporosis, and cardiovascular disease.” *Ann. Rev. Nutr.* 1(1), 427–435.

Song, X., Liu, H., Cheng, L., and Qu, Y. (2010). “Surface modification of coconut-based activated carbon by liquid-phase oxidation and its effects on lead ion adsorption.” *Desalination,* 255(1-3), 78–83.

Sposito, G., ed. (1996). *The environmental chemistry of aluminum*. CRC Press, Boca Raton, FL.

Tchomgui-Kamga, E., Alonzo, V., Nanseu-Njiki, C., Audebrand, N., Ngameni, E., and Darchen, A. (2010). “Preparation and characterization of charcoals that contain dispersed aluminum oxide as adsorbents for removal of fluoride from drinking water.” *Carbon*, 48(2), 333–343.

Tonguc, M., Ozat, Y., Sert, T., Sonmez, Y., and Kirzioglu, F. (2011). “Tooth sensitivity in fluorotic teeth.” *European J. Dentistry,* 5(3), 273 - 280.

Vaishya, R.C., and Gupta, S.K. (2003). “Arsenic removal from groundwater by iron impregnated sand.” *J. Environ. Eng.* 129(1), 89–92.

Walton, J R. (2006). “Aluminum in hippocampal neurons from humans with Alzheimer’s Disease.” *Neurotoxicology,* 27(3), 385–394.

World Health Organization. (2011). *Guidelines for drinking-water quality - 4th edition*. World Health Organization, Geneva, Switzerland.

Wu, X., Zhang, Y., Dou, X., and Yang, M. (2007). “Fluoride removal performance of a novel Fe–Al–Ce trimetal oxide adsorbent.” *Chemosphere,* 69(11), 1758 – 1764.

CHAPTER 6

Conclusions

There is a global drinking water crisis affecting millions of people every day. Identifying successful solutions that work in specific contexts around the world is challenging. While a multitude of excellent organizations have been implementing solutions to the water crisis for decades, an alarming number of past projects are not demonstrating long-term sustainability. This dissertation began with a review of literature related to implementation of new water points and drinking water treatment technologies. The review provided examples of successes and failures in water scheme implementation and discussed causes of failure. For example, when a new well is drilled and implemented many things are needed to assure sustainability including: a supply chain for spare parts, money to buy spare parts, a reliable repair person and community buy-in for spending time or money for repairs. Lack of one or more of these elements is frequently the cause of water point failure. One possible solution is to incorporate business people into the research and implementation so they can evaluate whether a supply chain is available, how supply and repair systems can be set up, and develop a business model for financial viability of the water point or treatment system. Business model viability varies greatly based on community income levels, education, occupations, values, beliefs and more. To help understand some of these elements such as community values and beliefs, it is useful to incorporate social scientists into development and implementation so they can learn about the community and guide the technology selection, community training, implementation and business model. Finally, engineers and scientists play an integral role in developing and improving upon technologies, but their work should be influenced by the other fields of expertise on the team. The major conclusion of this review is that implementation of water treatment technologies and water access points can be more sustainable if multidisciplinary teams, specifically researchers and/or practitioners from different fields of expertise, work collaboratively on these implementations from the very beginning of a program to take advantage of strengths and ideas from multiple areas. This conclusion, along with the examples and resources provided, were offered in the hopes of assisting the water community in improving sustainable research and implementation of water treatment projects.

Building from this general foundation, the subsequent chapters in this dissertation focused on a specific water treatment challenge. Fluoride removal from water to make it safe to drink is an important area of research to assist with mitigation of the global water crisis. Research has shown that bone char is an effective fluoride adsorption material, due to favorable surface chemistry and high specific surface area. However, in some areas bone char is not suitable for use for fluoride removal from drinking water due to cultural or religious reasons. Therefore, this research, in addition to investigating several practical implementation aspects of bone char, assessed the potential for eucalyptus wood char to be a water treatment substitute for bone char. Results showed that the specific surface area and point of zero charge of wood char increased as charring temperature increased, and that the specific surface area of wood charred at 600 °C is approximately 3 times higher than that of bone char. However, despite the high specific surface area and high pH_{PZC} (9.6 at 600 °C), the wood char evidenced low fluoride removal capacity at any charring temperature. This is likely due to the unfavorable surface chemistry of eucalyptus wood char (despite the high ph_{PZC}) as compared to bone char that is caused by the difference in chemical composition between wood and bone. Amending eucalyptus wood char with aluminum oxides significantly increased fluoride uptake – this material having both desirable surface area and surface chemistry. When amended with aluminum nitrate the wood char exhibited a statistically significant increase in fluoride removal capacity, which is attributed to the strong electrostatic attraction between the aluminum oxide amendment and the fluoride. While this capacity is still lower than bone char it is nonetheless a significant improvement over untreated wood char. In an effort to further improve char materials they were treated with reducing agents – this was hypothesized to increase the pH_{PZC} values through the removal of oxygen containing functional groups on the surface of the media. However, results did not support this hypothesis and, though the fluoride removal capacity of chars treated with reducing agents increased slightly, the change was insufficient to make this a fruitful research area to further pursue.

Crucial to making this work practically useful was the study of selected materials using continuous flow studies that are more representative of how materials would be used in communities. Column studies were conducted in both the laboratory and the field with four materials including: bone char, aluminum oxide coated bone char, aluminum oxide impregnated wood char, and activated alumina. Results, not surprisingly, found that all four materials performed better in the laboratory than in the field. Further, the laboratory studies removed fluoride in the order of aluminum oxide impregnated wood char > aluminum oxide coated bone char > bone char > activated alumina. The change between laboratory and field results for the aluminum oxide impregnated wood char was particularly large with this material going from being the best performing to the worst performing in the laboratory and the field, respectively. From additional column and batch studies it was found that the high pH, 8.2, and the high sulfate concentration in the Main Ethiopian Rift Valley groundwater were key causes of the reduced effectiveness of the aluminum oxide impregnated wood char. Thus, both pH and competing ions (e.g., sulfate) should be tested for and taken into consideration when using adsorption materials for fluoride removal in new water sources. In order to assess the realistic use of several fluoride removal materials in communities, studies were done to assess whether natural organic matter offered any competition for fluoride removal by adsorption. These studies found no competition with fluoride removal on bone char at any equilibrium fluoride concentration and minimal competition using other fluoride removal materials at environmentally relevant fluoride concentrations (equilibrium values close to 1.5 mg/L). Another useful finding of this work is evidence to support the use of scale up principles that allow small scale laboratory studies to be used for design of community-scale systems through the use of dimensionless rapid small scale column test (RSSCT) principles. This, and the fact that bone char removal capacity can be improved by aluminum nitrate amendment to the bone char, are helpful conclusions for communities where bone char is an accepted treatment technology.

This research also investigated additional methods of amending wood char with positively charged metals, iron and aluminum, to assess possibilities for getting higher percentages of metals incorporated into the wood char and in doing so, increase the fluoride removal capacity. This line of inquiry resulted in several conclusions that offer insights into how the fluoride removal capacity of wood char can be increased by the use of metal oxide amendments and pretreatment with oxidizing agents. Batch experiments demonstrated that amendment with aluminum oxides and the less studied iron oxides is an effective way to increase fluoride removal by wood char. While the four tested metal amendment methods showed statistically significant increases in fluoride removal when compared to that of wood char alone, the iron oxide amendments resulted in higher fluoride adsorption than aluminum for all cases; iron (III) nitrated exhibited a $Q_{e1.5}$ value over 50 times higher than wood char alone. The iron (III) nitrate amendment, when compared with the other three metal oxide amendments, resulted in the highest metal loading on the wood char and the largest impact on fluoride removal. However, it also demonstrated an inefficient use of iron during the fluoride removal process, observed when fluoride removal capacities were normalized by metal loading. This inefficiency can likely be attributed to large amounts of iron particles blocking the wood char pores, thus preventing the full use of internal wood char pore space and access to iron oxides that may have incorporated into the wood char below the surface. In contrast, aluminum chloride amended wood char showed the lowest metal loading percentage yet had the highest removal efficiency when removal capacities were normalized by both metal contents and specific surface areas. These results suggest a helpful area of future research; investigating ways to further maximize fluoride removal capacity and efficient use of metal amendments for this purpose. Another hypothesis tested in this dissertation was that pretreating wood char with oxidizing agents would lower the pH_{PZC}, thus, increasing metal loading onto the wood char due to the increased electrostatic attraction between the char surface and the metal oxides. Results showed that pretreating wood char with oxidizing agents did lower the pH_{PZC}, and in most cases, when the oxidizing agent was potassium permanganate, the lower pH_{PZC} coincided with increased metal loading. However, when hydrogen peroxide was used as the oxidizing agent, the pH_{PZC} experienced a larger decrease, but this did not result in increased metal loading or improved fluoride removal in most cases. Wood char, when treated with strong oxidizing agents, hydrogen peroxide or nitric acid, lost a large portion of specific surface area, likely due to damage to the internal pore walls caused by strong oxidation. This research systematically studied one starting material with several oxidizing agents and metal amendment processes, which is helpful towards considering which area of study has the most merit for future work. The conclusions from this work suggest that iron oxide amendment processes should be further explored for fluoride removal, particularly in geographic areas where iron amendment materials are readily available. Additionally, future work assessing fluoride removal mechanisms and investigating ways to enhance metal loading onto wood char can be useful to the community working on fluoride removal from drinking water. Specific studies should be done to determine the optimal way to amend wood char, or other biochars, with iron oxides to efficiently use the iron oxides and gain maximum fluoride removal. Additionally, surface functional groups should be assessed for each amendment or pretreatment method to better understand the interactions occurring at each step in order to determine the best method (that is also feasible in developing regions) to produce highly effective fluoride removal materials.

When combined together, the research reported in this dissertation contributes to the body of knowledge surrounding technologies for removing fluoride from drinking water. The technologies and ideas that were evaluated focused on improving knowledge about existing sustainable and inexpensive fluoride adsorption technologies. This dissertation both assessed new options for fluoride removal and evaluated methods for improving an existing one (bone char). In particular this work offered the following: RSSCT principles showed promise for scale up and design of bone char systems, wood char can be effective for fluoride removal when amended with aluminum or iron oxides, iron oxide amendments proved effective for fluoride and should be further evaluated, and pretreatment with oxidizing agents, while not necessarily practical in the field, is an option that can alter surface chemistry and metal loading of wood char, potentially for the benefit of fluoride removal. While this dissertation offered many helpful conclusions for researchers and practitioners, there is still considerable work to be done to advance the field of fluoride removal and alternative water supply to mitigate the issue of 200 million people around the world consuming elevated fluoride concentrations in drinking water.

Appendix A: Fluoride Removal by Bone and Wood Chars

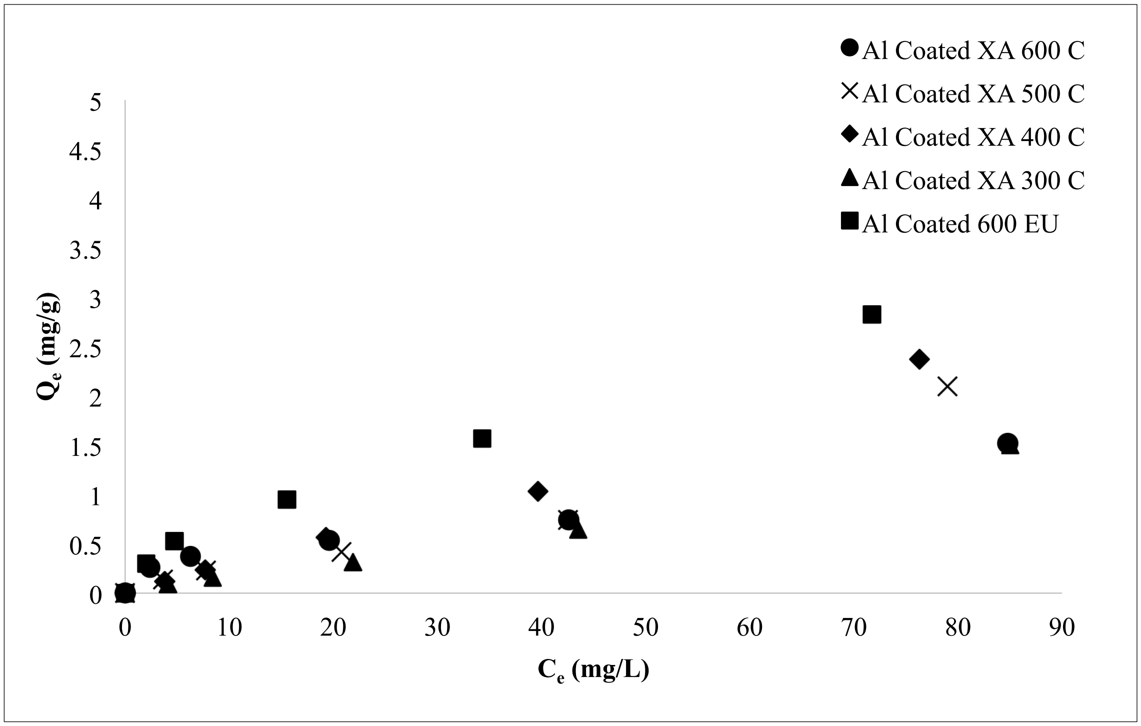


Figure A-1: Graph shows adsorption isotherms of fluoride removal by *Ximenia americana* (XA) and *Eucalyptus robusta* (EU) wood chars amended with aluminum oxides, plotting fluoride levels adsorbed by the chars (Q_e, mg fluoride/g wood char) versus equilibrated aqueous fluoride concentration (C_e, mg/L).

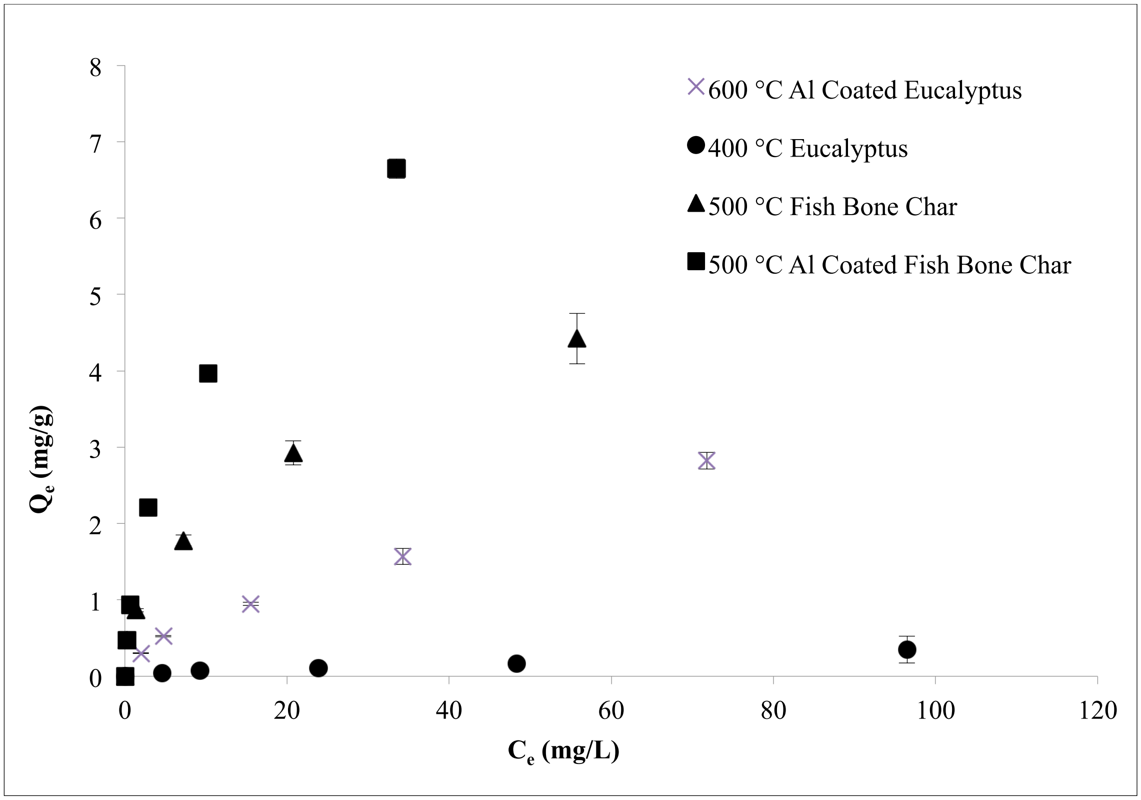


Figure A-2: Graph shows adsorption isotherm of fluoride removal by fish and bone chars and aluminum oxide amended fish and bone chars, plotting fluoride levels adsorbed by the chars (Q_e, mg fluoride/g fish bone char) versus equilibrated aqueous fluoride concentration (C_e, mg/L).

Appendix B: Competing Ions

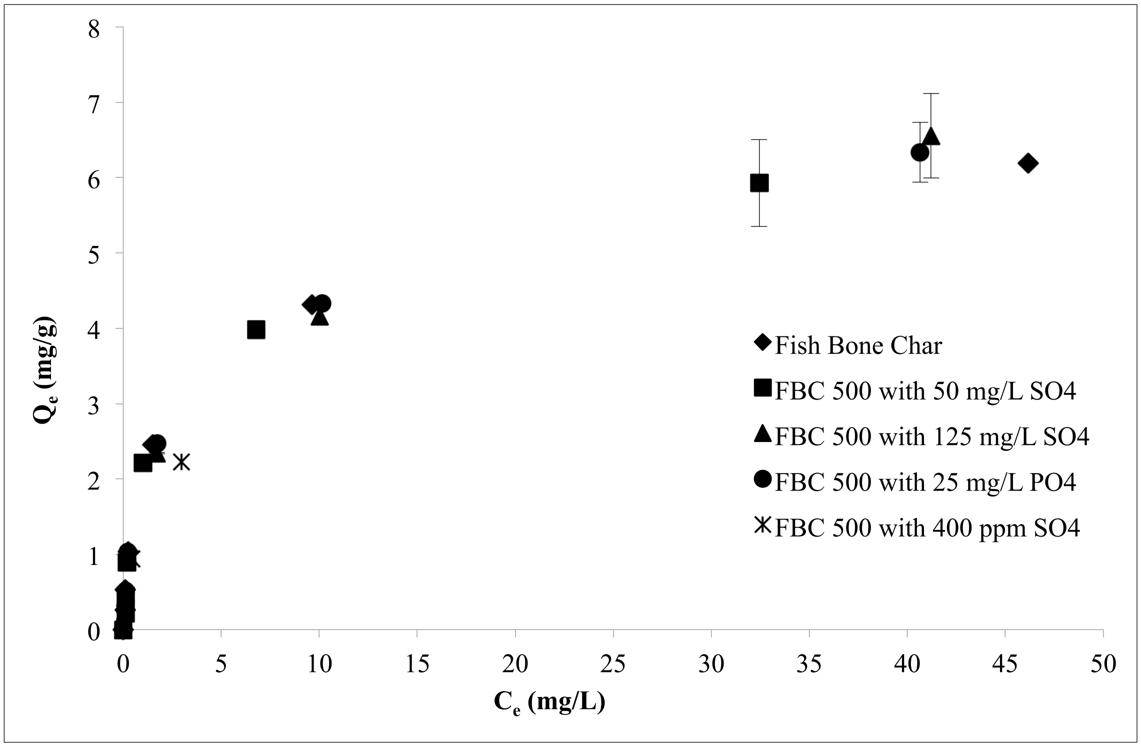


Figure B-1: Adsorption isotherms of fluoride on fish bone char (FBC), with competing ions sulfate (SO_4) and phosphate (PO_4) present in some systems as noted in the legend. The y-axis shows fluoride levels adsorbed by the fish bone char (Q_e, mg fluoride/g fish bone char) and the x-axis versus equilibrated aqueous fluoride concentration (C_e, mg/L).

Appendix C: Iron Oxide Amendments

Table C-1: Results of preliminary iron oxide amendment tests conducted on wood char with variations in amendment time, concentration and method.

Amendment	**Metal Concentration**	**Amendment Time (hours)**	**Starting Fluoride Concentration**	**Fluoride removal (mg/g)**	**Initial Method Source**
Iron oxide	7.5%	24	10	0.41	Li et al. (2010)
Iron oxide	7.5%	2	10	0.41	Li et al. (2010)
Iron oxide	30%	24	10	0.6	Li et al. (2010)
Iron oxide	30%	2	10	0.99	Li et al. (2010)
Iron oxide	0.5 molar	24	10	0.26	Gu et al. (2005)
Iron oxide	1.0 molar	24	10	0.48	Gu et al. (2005)
Iron oxide	3.0 molar	24	10	0.66	Gu et al. (2005)