UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

LOW-COST CHEMICALLY ACTIVATED COW BONE FOR FLUORIDE REMOVAL FROM DRINKING WATER: BATCH, FIELD-SCALE COLUMN AND BUSINESS MODEL STUDIES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

Degree of

DOCTOR OF PHILOSOPHY

By

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Norman, Oklahoma
2017

LOW-COST CHEMICALLY ACTIVATED COW BONE FOR FLUORIDE REMOVAL FROM DRINKING WATER: BATCH, FIELD-SCALE COLUMN AND BUSINESS MODEL STUDIES

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

BY

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I dedicate this dissertation to my late father, Lemma Yami Biratu, and my late sister, Etenesh Lemma Yami. Additionally, I would also like to dedicate this dissertation to my childhood friends (alive and dead) in Sululta, Ethiopia.

Acknowledgements

First of all, I would like to thank the almighty God for all His blessings and continued presence in my life during my graduate student years at the University of Oklahoma. My deepest gratitude is to Dr. David A. Sabatini for believing in me and giving me this graduate scholarship opportunity. This work would not have been possible without his continuous advice and guidance, and unrestrained support during my graduate years. Dr. Sabatini's positive criticism and approach were very important in developing my critical thinking ability and sharpening my writing skills. My special thanks are also to Dr. Elizabeth C. Butler for all her guidance and continued support as a co-advisor; I have benefited enormously from her positive outlook and critical comments. I would also like to thank my committee members Dr. Paul Spicer, Dr. Lowell Busenitz and Dr. Jim Chamberlain for their time, consideration, and support during my ten semesters at the University of Oklahoma. I would also like to especially express my deepest gratitude to Mrs. Frances K. Sabatini for her words of encouragement and kind support both to me and my family during my graduate student years.

I am also indebted to Dr. Preston Larson for SEM/EDS analysis, Dr. Andrew Madden for XRD and BET analytical assistance and Ms. Andria Hendricks (OU-HSC) for her support during zeta potential analysis. I would also like to thank my previous and current lab mates Laura Brunson, Linh Do, Chodchanok Attaphong, Junyi Du, Hayley Rickman, Anisha Nijahawan, Phaodee Parichat and Philip Deal for their encouragement and valuable discussions during my lab work. I would also like to thank my undergraduate lab assistants Rachel Rogers, Derrick Nguyen, and Ismael Dumutu for their help in the laboratory.

I would also like to thank the University of Oklahoma's Civil Engineering and Environmental Science department staff for their kind support during my five years' tenure in this department.

I would also like to acknowledge the University of Oklahoma's Water Technology for Emerging Regions (WaTER) Center, the Sun Oil Company Endowed Chair, the Ken Hoving Graduate College Fellowship and the National Science Foundation (CBET 1066425) for their financial support during this study.

Last but not least, I would like to thank my wonderful family; my wife Selamawit Aseffa, and my children Natanim, Melat, Daniel and Amen Teshome Lemma for their encouragement, understanding, unconditional love and sense of humor during my busy five academic years at the University of Oklahoma. Wife, without you, I would not have been able to accomplish this study; you are the MVP!!! Thanks for taking good care of our wonderful children and me during my graduate study years. I am grateful to the members of St. George Ethiopian Orthodox Church in Oklahoma City for their words of encouragement. I am also eternally thankful to my mother Gorfinesh Wondimagegn, my brothers Alemu Lemma, Tegenu Lemma and Birhanu Lemma, and my sister Genet Lemma for their continuous support and encouragements throughout my academic life. God bless you all!!

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Abstract

Excess fluoride concentrations in drinking water negatively impact the health of communities living in fluoride affected regions of the world by causing dental and skeletal fluorosis and other severe socio-economic problems. Thermally activated cow bone (bone char) is among the various adsorbents studied for removal of excess fluoride from drinking water. However, the fluoride removal capacity of bone char is low and needs to be enhanced. The goal of this study was to improve the fluoride adsorption capacity of cow bone using chemical activation in place of thermal activation, and to understand the mechanisms responsible for the increased fluoride removal of the chemically activated cow bone (CAB). Cow bone exposed to varying concentrations of chemical activating agents could achieve a four-fold higher fluoride adsorption than bone char both in laboratory batch studies conducted in the University of Oklahoma's WaTER Center and in field–scale column studies in the Ethiopian Rift Valley. X-ray diffraction analysis conducted on CAB media showed bassanite ($CaSO_4.0.5H_2O$) and monetite ($CaHPO_4$) minerals that were not present in bone char; these minerals were thought to be responsible for the high fluoride adsorption capacity of the media.

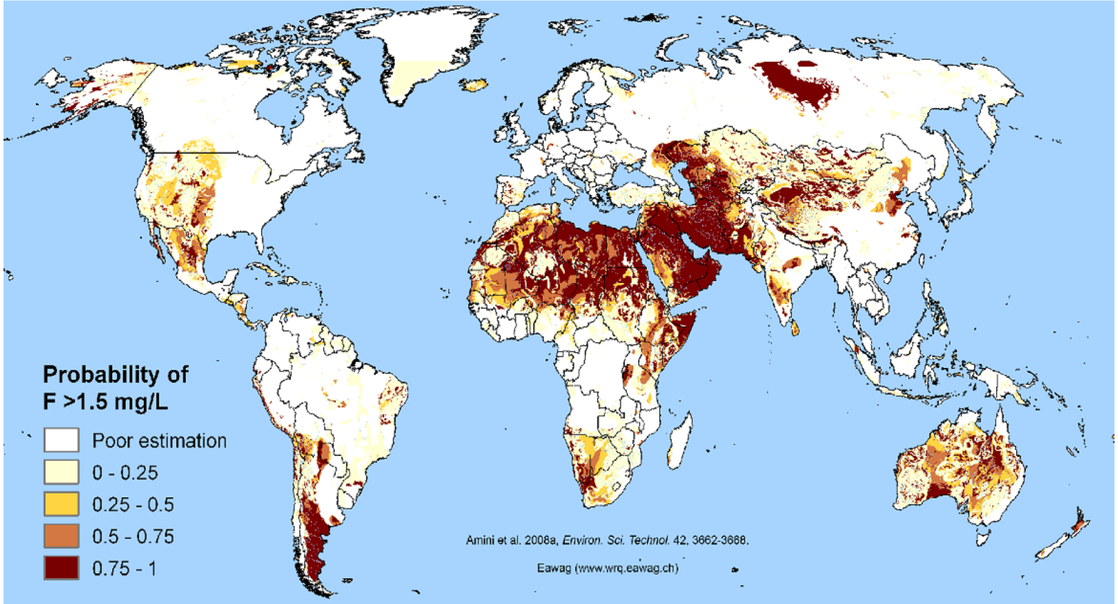
Monetite and bassanite samples were synthesized and evaluated for their ability to account for the increased fluoride adsorption capacity of the CAB media. A high purity (99.6%) monetite was thus prepared in the laboratory. The monetite had a three-fold higher adsorption capacity than CAB (the fluoride adsorption capacities at an equilibrium fluoride concentration of 1.5 mg/L ($Q_{1.5}$) were 20.26 mg/g and 6.4 mg/g for monetite and CAB, respectively), thus, validating that monetite can account for the increased capacity of CAB. The EGME specific surface area (SSA) of monetite (Ca/P ratio 1:0.43) is twice that of the CAB media (260 m^2/g vs. 134 m^2/g) and thus may account for a portion of the three-fold higher capacity of monetite versus CAB. The monetite's increased capacity can also be partly attributed to the high surface charge (zeta potential) measured on the monetite compared to CAB. In contrast, the bassanite prepared in the laboratory had negligible fluoride removal capacity and thus cannot account for the high adsorption capacity of the CAB media. Therefore, CAB and monetite media have been shown to be superior to bone char for mitigating the negative health impacts of excess fluoride concentrations in drinking water. Finally, this paper addresses how businesses models inform viability of different fluoride treatment technologies for developing countries as well as the pursuit of financial and operational sustainability. In this study, the investment cost of producing fluoride safe water, the annual revenues generated, and the net benefits obtained from different technologies were analyzed. The business model analysis indicated that access to safe water can lead to an average annual cost saving of $67 per person through averted medical costs and productivity losses. The study results validate the use of business models to help evaluate different technologies as a means of pursuing sustainable applications for safe drinking water.

Chapter 1: Introduction

1.1 Statement of problems

Groundwater constitutes 30.1% of total global freshwater (Gleick 1996) and is thus the single largest available supply of drinking water, especially in rural settings (WHO 2004). Consuming drinking water with excess fluoride concentrations remains a major health hazard and environmental problem in the 21st century. Fluoride in groundwater originates from geogenic sources (dissolution of fluoride-containing rock minerals and soils with which the groundwater comes into contact) and/or anthropogenic sources (application of fluoride containing phosphate fertilizers or sewage sludge or pesticides) (Apambire et al. 1997; Cronin et al. 2000; Jha et al. 2011; Roy & Dass 2013). High fluoride concentrations can occur in groundwater with long residence times in the host aquifers (Jagtap et al. 2012). Fluoride concentrations of up to 68 mg/L have been detected in groundwater wells located north of Lake Abijata, in the Rift Valley of Ethiopia (Rango et al. 2012). Globally, more than 200 million people consume water above the World Health Organization's guideline threshold of 1.5 mg/L (Amini et al. 2008) (see Figure 1.1 for global distribution of fluoride in groundwater). Therefore, solutions are needed to mitigate the sufferings of people affected by fluoride-induced health concern.

Excess fluoride concentration in drinking water is a significant contaminant of concern due to its short- and long-term effects on human health. Fluoride concentrations above the World Health Organization (WHO) maximum acceptable level of 1.5 mg/L threshold are harmful to human health (WHO 2011) causing dental, skeletal and/or crippling fluorosis depending on other factors such as nutritional status (Dissanayaka 1991; Fawell and Balley 2006). Beyond dental and skeletal concerns, fluorosis has significant socio-economic impacts stemming from the fact that persons who develop skeletal fluorosis suffer considerable hardship and have reduced productivity (Apambire et al. 1997; Frank et al 2011). Moreover, the prevalence of fluorosis and the related widespread health problems may stigmatize entire villages (McKnight et al. 1997). Although not life-threatening illnesses, dental and skeletal fluorosis often produces many adverse effects, including: added health costs, loss of labor, and significant psychological stress for affected populations (Apambire et al. 1997). Therefore, it is critical to treat excessive fluoride-rich groundwater or provide alternative water sources to at-risk communities.



Amini et al. 2008a, *Environ. Sci. Technol.* 42, 3662-3668.

Eawag (www.wrq.eawag.ch)

Figure 1.1: Modeled global probability of fluoride concentration in groundwater (adapted from Journal of Environmental Science and Technology, http://pubs.acs.org/doi/full/10.1021/es071958y).

1.2 Literature review

1.2.1 Fluoride removal technologies

Various treatment methods such as adsorption, ion-exchange, chemical precipitation, membrane processes (reverse osmosis), electrolytic defluoridation and Donnan dialysis have been investigated for removal of excess fluoride from drinking water (Mohapatra et al. 2004; Durmaz et al. 2005; Ndiaye et al. 2005; Fawell & Balley 2006; Meenakshi and Viswanathan 2007; Ayoob et al. 2008; Sehn 2008; Brunson and Sabatini 2009 and 2015). Of all these methods, the adsorption process has been commonly adopted for fluoride removal based on ease of operation, use of locally available materials, cost effectiveness of operation and maintenance, and potential for regeneration and reuse, and high water quality (Choy et al. 2004; Ho et al. 2004; Jagtap et al. 2012).

1.2.2 Fluoride adsorbents

Recently, adsorbents such as bone char, hydroxyapatite, zeolites and modified zeolites, ion exchange resins, and layered double oxides have been investigated for fluoride removal (Mohapatra et al. 2009; Tor et al. 2009; Ramdani et al. 2010; Du et al. 2014). Thermally activated cow bone, commonly known as bone char, is among the adsorbents used to remove excess fluoride due to its large surface area and the high fluoride affinity of hydroxyapatite, the main constituent of cow bone (Fawell and Balley 2006; Medellin-Castillo et al. 2007; Ayoob et al. 2008; Osterwalder et al. 2014). It is also widely available at low-cost in developing countries, e.g., in the Rift Valley area in Ethiopia (Mutheki et al. 2011), and Nakuru area in Kenya (Jacobsen and Muller 2007). Thermal activation of bone is a process of heating cow bones in a furnace to high temperature under restricted access of atmospheric oxygen, increases fluoride adsorption capacity by decreasing the organic matter content of the bone (Bhargava and Killedar 1991).

In terms of capacity, bone char's fluoride adsorption capacity at an equilibrium dissolved fluoride concentration of 1.5 mg/L ($Q_{1.5}$) has been shown to be on the order of 1 to 2 mg/g on average (Abe et al. 2004; Medellin-Castillo et al 2007; Brunson and Sabatini 2009). Although this bone char's $Q_{1.5}$ is better than the values reported for activated alumina ($Q_{1.5} = 0.85$ mg/g, Maliyekkal et al. 2008) and wood char ($Q_{1.5} = 0.5$ mg/g, Brunson and Sabatini 2014), respectively, there is still room for further improvement. Moreover, thermal activation is energy intensive, requiring carbonization temperatures above 400 ^{o}C (Lussier et al. 1994).

The fluoride removal mechanisms of bone char are direct adsorption of fluoride and ion exchange, where the fluoride exchanges with hydroxyl ion (Equation 1.1), carbonate ion, and phosphate ions (Bregnhøj and Dahi 1995; Abe et al. 2004; Kawasaki et al. 2009).

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6(F)_{2(s)} + 2OH^- \text{ ....Equation 1.1}$$

Fluoride adsorbents (e.g., bone char) eventually become exhausted (saturated) (Mjengera 1988). The exhausted media can either be replaced by virgin material or regenerated for reuse. Some of the benefits of regeneration and reuse of spent adsorbents include reduced operational cost, since media can be reused multiple times, and potentially minimizing negative environmental impacts associated with their manufacture and disposal (Yami et al. 2015). Fluoride saturated bone char has been regenerated through surface- coating, precipitation, and sodium hydroxide solutions (Christoffersen et al. 1991; Medellin-Castillo et al. 2007). NaOH regeneration of bone char has been performed using 1% - 8% NaOH solution converting fluoroapatite to hydroxyapatite (Christoffersen et al. 1991; Jacobsen and Muller 2007; Ayoob et al. 2008). The fluoride desorption reactions are the reverse of Equation 1.1.

Additionally, surface amendment, a process of dispersing aluminum salts into the matrix of the biomaterials (Tchomgui-Kamga et al. 2010), has been applied on thermally activated wood char (Brunson and Sabatini 2014). Dispersing these metals in a protective matrix can provide high fluoride adsorption capacity. Therefore, surface amendment using aluminum salts was evaluated for its impact on the fluoride adsorption capacity of bone char.

1.3 Effect of chemical activation

1.3.1 Chemical activation of carbonaceous materials

Based on a literature review, chemical activation of carbonaceous materials produces activated carbon with higher specific surface areas (SSAs) than thermal activation. For example, very large Brunauer-Emmett-Teller (BET) SSAs have been reported for chemically activated carbon materials; 2595 m^2/g using potassium hydroxide for corn cob (Tseng and Tseng 2005), and 2400 m^2/g for coconut shell (Hu et al. 2001). On the other hand, an SSA value of 1400 m^2/g for eucalyptus (Ngernyen et al. 2006) has been reported via thermal activation. This shows that higher SSAs can be achieved via chemical activation as compared to thermal activation. These high SSAs obtained during chemical activation of a range of different carbonaceous materials motivated us to evaluate chemical activation of bone to see if it would increase fluoride adsorption capacity of the CAB media. Another advantage to chemical over thermal activation is the small adsorbent mass losses upon activation (Srinivasakannan and Balasubramanian 2007; Zhang et al. 2010). The modification of adsorbent surface chemistry using chemical activation of carbonaceous materials appears to be a promising approach for developing novel cow bone-based adsorbents for defluoridation (Alagumuthu and Rajan 2010; Tchomgui-kamaga et al. 2010; Paudyal et al. 2011).

1.3.2 Chemical activation of cow bone

To our knowledge, chemical activation of cow bone has not been evaluated as an alternative to thermal activation for fluoride removal. In this dissertation, the process of chemical activation of carbonaceous materials was applied to cow bones to prepare chemically activated cow bones (CABs), evaluate its fluoride removal capacity, and investigate the mechanisms responsible for its increased fluoride removal capacity. Further, fluoride removal efficiency of CAB media produced in the laboratory was evaluated in the field and also it was attempted to produce the media in the field using locally available materials and field conditions.

1.4 Treated water quality

When highly fluoride impacted drinking water is treated using adsorbents, it is imperative to ensure that the universal drinking water standards are met in the produced water, considering not only fluoride but also other constituents. For example, Kawasaki et al. (2009) suggested that when using cow bone-based adsorbents for fluoride removal, the produced water should be analyzed for phosphate ion concentrations. Furthermore, other drinking water parameters such as taste, odor and color need to be assessed when using cow bone-based adsorbents since they may introduce objectionable taste and smell to treated water (Ayoob et al. 2008; Dahia 2015). Studies by Crapper et al. (1973), Davidson (1982) and Tanne (1983) have shown that animals exposed to residual aluminum concentrations have evidenced health effects (e.g., aluminum induces neurofibrillary degeneration in neurons of higher mammals). Bhattacharjee et al. (2014) investigated aluminum and its potential contribution to Alzheimer disease. Feasibility and efficiency of defluoridation systems depends on the level of dissolved residual aluminum concentration in treated water (Qureshi and Malmberg 1985; Mameri et al. 1998). Therefore, water quality analysis should be undertaken for a new adsorbent to prevent unintentional negative health impacts from the adsorbent.

1.5 Sustainability of fluoride treatment systems

1.5.1 Business model and sustainability of fluoride treatment systems

Fluoride treatment systems installed in developing countries have not been sustainable due to the lack of capacity to manage defluoridation systems, lack of chemical supply chains, high cost of chemicals, limited financial management skill, and lack of skilled labor to install and operate the treatment systems (Bregnhøj 1997; Brunson et al. 2013). This dissertation therefore, additionally aims at using business model approach to show how one can assess and compare viability of different fluoride treatment methods in the effort to avail safe and sustainable water supply services to the communities at- risk of fluoride induced health problems.

1.5.2 Environmental sustainability of fluoride treatment systems

Production of fluoride adsorbents emits contaminants that can affect human health and the environment although the extent of these impacts was unknown. In this dissertation, the environmental impacts of four low-cost and easy to use adsorbents such as activated alumina, aluminum oxide amended wood char, bone char and treated alum waste were evaluated. The environmental impacts of these adsorbents were evaluated using life cycle assessment (LCA). The life cycle stages considered were raw material acquisition, adsorbent manufacturing, and waste management. Eco-indicator and the Tool for Reduction and Assessment of Chemicals and other Environmental Impacts (TRACI) were used to interpret the environmental impacts.

The results indicated that the fluoride adsorption capacity of the adsorbent is a key determining factor for the impacts. Further, the environmental impacts of the adsorbents can be reduced by increasing their fluoride adsorption capacity and/or carefully selecting key process components. Regeneration and reuse of spent adsorbents has the potential to minimize impacts to ecosystem quality. A detail on the results of life cycle assessment of fluoride adsorbents is available in Appendix E[1].

1.6 Research objectives

The specific research objectives of this dissertation were; (1) prepare chemically activated cow bones (CABs), and evaluate their fluoride removal capacity (2) Install small and large –scale columns in the field and evaluate the fluoride removal capacity

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[1] This chapter or portions thereof has been published previously in *The International Journal of Life Cycle Assessment* in collaboration with Dr. Junyi Du, Dr. Laura R. Brunson, Dr. Jim F. Chamberlain, Dr. David A. Sabatini and Dr. Elizabeth C. Butler under the title “Life Cycle Assessment of Adsorbents for Fluoride Removal From Drinking Water”. Int. J. Life Cycle Assess. (2015), 20 (1277) DOI:10.1007/s11367-015-0920-9. The current version has been reformatted for this dissertation.

of CAB; (3) prepare monetite and bassanite and evaluate their effectiveness at fluoride removal; (4) Use business model tools to compare and evaluate sustainability/ viability of fluoride treatment systems as a business.

1.7 Outline of the dissertation

Chapter 2 focuses on production and evaluation of a more efficient (fluoride uptake) and effective (mass recovery) cow bone-based fluoride adsorbent using the process of chemical activation; a process of exposing cow bones to varying concentrations of chemical activating agents with the purpose of increasing the fluoride adsorption capacity of cow bones. In this chapter, the fluoride removal capacity of CAB was evaluated and its adsorption capacity was compared to bone char. Additionally, the effect of surface amendment (dispersion of aluminum salts onto the matrix of bone char) on its fluoride removal capacity was studied, the mechanisms responsible for the increased capacity of CAB media was analyzed, the cost of production of chemically activated cow bone and bone char along with the mass of product versus mass of starting material for each were analyzed.

To date, our laboratory studies have shown that chemically activated cow bone (CAB) using sulfuric acid demonstrated four-fold more effective than bone char for removal of excess fluoride concentrations from drinking water (Yami et al., 2016). CAB's high adsorption capacity was attributed to the presence of monetite ($CaHPO_4$) and bassanite ($CaSO_4.0.5H_2O$) produced during chemical activation of cow bone that was not present in thermally activated cow bone (bone char).

Based on these encouraging preliminary results, this dissertation next focused on conducting additional studies necessary to further evaluate the viability of CAB for field deployment. **Chapter 3** therefore, attempts to produce CAB media under field conditions, install small and large defluoridation columns in the field to evaluate CAB performance/ suitability (feasibility) for fluoride removal using fluoride impacted natural groundwater. Further, fluoride adsorption capacity of CAB and bone char using field column will be studied, the suitability of water treated using the CAB system in the field for public consumption will be assessed and the regeneration potential of CAB/ bone char will be evaluated. With these results the viability of CAB for fluoride removal from drinking water can be more fully assessed.

Chapter 4 focuses on the synthesis of monetite and bassanite shown during CAB production and evaluates their ability to account for the increased fluoride removal of the CAB media. A reverse micelles method by Wei et al. (2007) which produced sphere particles of 50 nm diameters was used to prepare monetite ($CaHPO_4$). Further, the effect of Ca/P ratio on the mineralogical composition of resulting monetite and its fluoride removal capacity was evaluated. Bassanite ($CaSO_4.0.5H_2O$) was prepared by dissolving $CaCl_2$ in methanol solution and adding an equimolar sulfuric acid using the method proposed by Tritschler et al. (2015). The mechanisms responsible for the increased fluoride removal of monetite and bassanite, and effect of co-existing competing anions in natural groundwater on their fluoride adsorption capacity were also evaluated.

Finally, and more broadly, it is becoming increasingly recognized that well designed business models have the potential to address prevailing global problems including sustainable development (Wilson & Post 2013). For example, Wüstenhagen & Boehnke (2006) demonstrated that barriers to sustainable energy can be addressed with innovative business models. **Chapter 5** thus focuses on evaluating the applicability of the business model approach as a tool to set up a sustainable market-based scale-up of defluoridation (fluoride removal) systems. To address this growing problem of safe water supply, this dissertation attempts to show how the use of business models can help lead to more sustainable fluoride solutions. Based on literature study, fluoride treatment systems installed in developing countries are not sustainable. Additionally, there is in no engagement of private sectors in the defluoridation processes. As a result, the fluoride removal technologies developed thus far have not proven sustainable. An example of this include that although more than 20 Nalgonda systems have been implemented in the Rift Valley of Ethiopia over the past 10 years, more than half are no longer functional with some of them have never been used (Osterwalder et al. 2014; Datturia et al. 2015). Therefore, the business model approach is evaluated in this study to address the fluoride affected water in the Rift Valley of Ethiopia as a pathway for considering the viability of such an approach throughout the developing world.

Chapter 6 summarizes key findings, discussions, and conclusions and recommendations drawn from this dissertation to help guide design and installation of sustainable fluoride treatment systems in developing countries and beyond.

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Chapter 2: Chemically Activated Cow Bone for Increased Fluoride Removal from Drinking Water[2]

Abstract

Thermally activated cow bone is widely utilized for treating fluoride impacted drinking water to meet the World Health Organization guideline value of 1.5 mg/L. However, the fluoride removal capacity of bone char is low, leaving room for further improvement. This study, therefore, strives to improve the fluoride adsorption capacity of cow bone by using chemical activation in place of thermal activation. Chemically activated cow bones (CAB) had, on average, a four-fold higher fluoride adsorption capacity than bone char. Characterization of the most effective CAB were made to explore potential reasons for the increased fluoride adsorption capacity. The X-ray diffraction pattern of the CAB showed formation of bassanite and monetite which may be responsible for the higher fluoride adsorption capacity. Chemical activation is also a lower-cost production process than the thermal activation of cow bone. Further, a higher mass of media was recovered per unit mass of starting material during chemical activation. Therefore, this research shows that increased fluoride removal capacity can be achieved with chemical activation of cow bone while reducing activation costs and greatly increasing product yield per unit mass of starting material, all of which support further evaluation and field testing of this material.

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[2] This chapter or portions thereof has been published previously in *Journal of Water, Sanitation and Hygiene for Development* in collaboration with Dr. Elizabeth C. Butler and Dr. David A. Sabatini under the title "Chemically Activated Cow Bone for Increased Fluoride Removal from Drinking Water". J. Water Sanit. Hyg. Dev. DOI:10.2166/washdev.2016.172. The current version has been reformatted for this dissertation.

Key words bassanite, chemical activation, cow bone, fluoride removal, low-cost adsorbent, monetite

2.1 Introduction

Consuming drinking water with excess fluoride concentrations remains a major health hazard and environmental problem in the 21st century. Globally, more than 200 million people consume water above the World Health Organization's guideline threshold of 1.5 mg/L (Amini et al. 2008). Fluoride concentrations above the 1.5 mg/L threshold are harmful to human health (WHO 1984) and can cause dental and skeletal fluorosis (Dissanayaka 1991; Fawell and Balley 2006). Although not life-threatening illnesses, dental and skeletal fluorosis often produces many adverse effects, including: added health costs, loss of labor, and significant psychological stress for affected populations (Apambire et al. 1997). Therefore, it is critical to treat excessive fluoride-rich groundwater or provide alternative water sources to at-risk communities. Various treatment methods such as adsorption, membrane processes, and electrolytic defluoridation have been investigated for removal of excess fluoride from drinking water (Mohapatra et al. 2004; Fawell & Balley 2006; Ayoob et al. 2008). Of all these treatment methods, adsorption is often the preferred option for fluoride removal due to its high efficiency and its low-cost of operation and maintenance (Jagtap et al. 2012).

Thermal activation of bone, a process of heating cow bones in a furnace to high temperature under restricted access of atmospheric oxygen, increases fluoride adsorption capacity by decreasing the organic matter content of the bone (Bhargava and Killedar 1991). Thermally activated cow bone, commonly known as bone char, is among the adsorbents used to remove excess fluoride (Fawell and Balley 2006; Medellin-Castillo et al. 2007; Ayoob et al. 2008) owing to its large surface area and the high fluoride affinity of hydroxyapatite, the main constituent of cow bone. It is also widely available at low-cost in developing countries, e.g., in the Rift Valley area in Ethiopia (Mutheki et al. 2011), and Nakuru area in Kenya (Jacobsen and Muller 2007). Initially, bone char was imported from Kenya to assess technical performance and user acceptance (Johnson et al. 2011) and subsequently a production facility was established in Ethiopia by Oromo Self Help Organization (OSHO) in 2011 (Osterwalder et al. 2014).

To our knowledge, chemical activation of cow bone has not been evaluated as an alternative to thermal activation for fluoride removal. Results in the literature indicate that thermally activated bone can achieve an average fluoride adsorption capacity ($Q_{1.5}$) of 1.5 mg/g at an equilibrium dissolved fluoride concentration of 1.5 mg/L (Abe et al. 2004; Brunson and Sabatini 2009). Although, the bone char's $Q_{1.5}$ is better than that of activated alumina ($Q_{1.5}$ = 0.5 mg/g) and wood char ($Q_{1.5}$ = 0.2 mg/g) (Brunson and Sabatini 2014), there is still room for further improvement. Moreover, thermal activation is energy intensive, requiring carbonization temperatures above 400 ^{o}C (Lussier et al. 1994).

Based on a literature review, chemical activation of carbonaceous materials produces activated carbon with higher specific surface areas (SSAs) than thermal activation. For example, very large Brunauer-Emmett-Teller (BET) SSAs have been reported for chemically activated carbon materials; 2595 m^2/g using potassium hydroxide for corn cob (Tseng and Tseng 2005), and 2400 m^2/g for coconut shell (Hu et al. 2001). On the other hand, an SSA value of 1400 m^2/g for eucalyptus (Ngernyen et al. 2006) has been reported via thermal activation. This shows that higher SSAs can be achieved via chemical activation as compared to thermal activation. These high SSAs obtained during chemical activation of a range of different carbonaceous materials motivated us to evaluate chemical activation of bone to see if it would increase fluoride adsorption capacity of the CAB media. Another advantage to chemical over thermal activation is the small adsorbent mass losses upon activation (Srinivasakannan and Balasubramanian 2007; Zhang et al. 2010).

Additionally, surface amendment, a process of dispersing aluminum salts into the matrix of the biomaterials (Tchomgui-Kamga et al. 2010), has been applied on thermally activated wood char (Brunson and Sabatini 2014). Dispersing these metals in a protective matrix can provide high fluoride adsorption capacity. Therefore, surface amendment using aluminum salts was evaluated for its impact on the fluoride adsorption capacity of bone char.

The overall goal of this work was to produce a more efficient (fluoride uptake) and effective (mass recovery) cow bone-based fluoride adsorbent. The research questions evaluated in this work were: (1) does the chemical activation process, which has proven to be effective in increasing the SSA of activated carbon and thereby increase its adsorption capacity, result in similar increase in fluoride uptake in cow-bone based adsorbents? and (2) does the chemical activation of cow bone lead to improved mass recovery of the starting materials as compared to thermal activation? To our knowledge, this research is the first to evaluate chemical activation of bone as an alternative to thermal activation for fluoride removal. The specific objectives of this study were (1) to investigate the fluoride adsorption capacity of CAB, (2) to compare the fluoride adsorption capacity of chemically activated and thermally activated cow bone, (3) to investigate the effect of surface amendment (dispersion of aluminum salts onto the matrix of bone char) on its fluoride removal capacity, (4) To investigate mechanisms for improved fluoride adsorption by assessing the chemical and structural properties of the CABs which proved most effective for fluoride removal, (5) to compare cost of production of chemically activated cow bone and bone char along with the mass of product versus mass of starting material for each.

2.2 Materials and methods

2.2.1 Preparation of chemically activated cow bone

Cow bone was obtained from a ranch in LaRue, Texas, cut into smaller pieces and soaked in 12% NaOCl solution for 24 hours to remove impurities (Brunson and Sabatini 2009). The soaked cow bone was washed with deionized water to further remove organic matter, dried in an oven for 24 hours, and crushed manually using a metal mortar and pestle. The crushed bone was sieved using number 40/80 mesh sizes (180–425 μm). The fine powders were removed by rinsing with deionized water, oven dried again for 24 hours and stored for subsequent chemical activation.

The chemicals used for activation of cow bone were H_2SO_4 (Fisher scientific, 660 BAUME, Technical grade), H_3PO_4 (Fisher scientific, 85%, Certified ACS), KOH (EM science, pellets, solid), and $ZnCl_2$ (Fisher scientific, Technical grade, powder). The chemicals were chosen based on previous applications of chemical activation on carbonaceous materials which yielded high SSAs (see introduction section). $AlCl_3$ and

$Al_2(SO_4)_3$ were chosen for surface amendment of bone char based on their use in amending other biomaterials such as spruce wood (Tchomgui-Kamga et al. 2010).

2.2.2 Chemical activation of cow bone

The crushed, rinsed and oven-dried cow bones were chemically activated using H_3PO_4, H_2SO_4, $ZnCl_2$ and KOH solutions, each at 20, 30, and 50 wt %. The chemically activated cow bones are represented as HSCB, HPCB, ZnCB and KCB for H_2SO_4, H_3PO_4, $ZnCl_2$, and KOH activated cow bones, respectively. The experimental flow chart and procedures for chemical activation are shown in (Appendix A, Figure A.1.1). The preliminary screening tests conducted to identify parameters to be used in chemical activation indicated that a heating temperature of 50 ^oC, a heating duration of 3 hours, and a 1:1 media to activating agent ratio produced both a good quality and quantity of chemically activated cow bone. Activation parameters exceeding these values, i.e., heating temperatures higher than 50 ^oC, heating durations longer than 3 hours, and media to activating agent ratio lower than 1:1 dissolved the cow bones. The impact of activating agent concentration on mass recovery during activation was also evaluated. High mass recovery i.e., mass of media recovered per unit mass of starting material during chemical activation of bone was achieved for 20-30% HSCB and HPCB, and for 30-50% KCB activations.

After chemical activation, one sample from each kind of chemically activated cow bone was selected for further thermal treatment to study its effect on fluoride adsorption capacity. The effect of combined chemical and thermal activation of cow bone was investigated by heating the HSCB, KCB and ZnCB activated cow bones at 540 ^oC for 3 hours (referred to, for example, as HSCB-540). The CAB samples with the best adsorption capacity (HSCB and KCB), and the lowest adsorption capacity (ZnCB) were selected for characterization (i.e., to measure values of SSA and points of zero charge (PZC)); to identify morphology using scanning electron microscopy (SEM); to determine average elemental composition using energy dispersive X-ray spectroscopy (EDS); and to analyze structure using X-ray diffraction (XRD).

2.2.3 Surface amendment of bone char with aluminum salts

Bone char was amended using 1,000 and 2,000 ppm $AlCl_3$ and 500, 1,000 and 2,000 ppm $Al_2(SO_4)_3$ solutions in order to promote formation of an adsorbent aluminum (hydr)oxide phase. The amendment concentrations were created by adding the necessary quantities of $AlCl_3$ and $Al_2(SO_4)_3$ to a screw cap glass bottles and filling them with 200 mL Nano pure water (18.1 MΩ-cm) and adjusting the pH to 3.5 using 50 mM 2-(*N*-morpholino) ethanesulfonic acid **(**MES) and MES salt. Next, 12 g of bone char was added to the 200 mL glass bottle and the mixture was put on a shaker at 200 revolutions per minute for 5 days. The solution was then filtered, washed with deionized water, and oven dried overnight at 85 ^{o}C. The aluminum salts used for the amendment of bone char are soluble due to the low pH (i.e., pH 3.5) used in the amendment process.

2.3 Batch experiments

Chemically activated cow bone (0.5 g) was added to 50 mL polyethylene bottles containing initial fluoride concentrations ranging from 0 to 150 mg/L. The reactors were agitated on a shaker (Ping-Pong TM # 51504-00) at 200 revolutions per minute (rpm) for 24 hours (Brunson and Sabatini 2009). The pH of the adsorption experiment was fixed at 7.0 and confirmed by measurement, which is the pH of common natural water, by addition of 50 mM 2-[4-(2-hydroxyethyl) piperazin-1-yl] ethanesulfonic acid (HEPES) acid and salt. HEPES was utilized because it does not interfere with fluoride adsorption (Du et al. 2016). Furthermore, HEPES does not tend to complex with cations like Ca^{2+} (Good et al. 1966). After equilibration, each sample was filtered and the fluoride concentration was determined by ion selective electrode. Prior to analysis, both standards and samples were diluted with total ionic strength adjustment buffer (TISAB) on a 1:1 basis to reduce hydroxide interferences and the formation of HF, and maintain a constant pH and ionic strength during analysis (Larsen and Widdowson 1971). Calibration of the fluoride electrode and measurements of the fluoride concentrations were performed in triplicate. Experimental errors associated with the measurement of Q_e values were calculated using error propagation methods.

2.4 Adsorbent characterization

2.4.1 Measurement of specific surface area and point of zero charge

Specific surface area of the adsorbents was determined using the BET method. Additionally, the ethylene glycol monoethyl ether (EGME) method (Heilman et al. 1965) was employed for determining the SSAs of the chemically activated cow bones. The difference in the weight of samples before and after EGME coverage was used to calculate surface area. EGME analysis gives a more complete assessment of adsorbent surface area, because the BET method may measure only the external surface area of certain minerals (Yukselen and Kaya 2006), and because the aqueous medium in the EGME method may preserve pores that could collapse under the vacuum conditions applied during the BET method. The PZC of the chemically activated cow bone was determined using methods reported by Milonjić and Ilić (1983), Noh and Shwarz (1989), and Brunson and Sabatini (2009) (see Appendix A for measurement of PZC).

2.4.2 SEM/EDS and XRD analysis

SEM analysis was performed using a Zeiss NEON instrument operating at an accelerating voltage of 10 kV with an Iridium sputter coating. EDS analysis was performed to identify the average elemental composition of the chemically activated cow bone. Powdered X-ray diffraction was employed for structural characterization of the chemically activated cow bone using a Rigaku Ultima IV diffractometer and fitting with reference mineral patterns using materials data (MDI) JADE 2010 analytical software.

2.5 Results and discussion

2.5.1 Fluoride adsorption capacity of chemically activated cow bone

The HSCB and HPCB activated cow bone had much higher fluoride adsorption capacities than the thermally activated cow bone (Figure 2.1). The HSCB and HPCB equilibrium fluoride adsorption capacities ($Q_{1.5}$ fitted with the Freundlich isotherm) were four times higher than that of bone char (Table 2.1). Additionally, 30% and 50% KCB had higher adsorption capacities than bone chars (Figure 2.2) although their $Q_{1.5}$ values were not as high as those of HSCB and HPCB (Table 2.1). The ZnCB activation, on the other hand, led to a lower fluoride adsorption capacity than bone char (Figure 2.1, Table 2.1). The $Q_{1.5}$ obtained for bone char in this study is similar to values reported in the literature at pH 7 (Abe et al. 2004; Brunson and Sabatini 2009) (Table 2.1). Thus, these results clearly demonstrate that chemical activation of cow bone can achieve fluoride adsorption capacities of up to four times greater than those obtained via thermal activation.

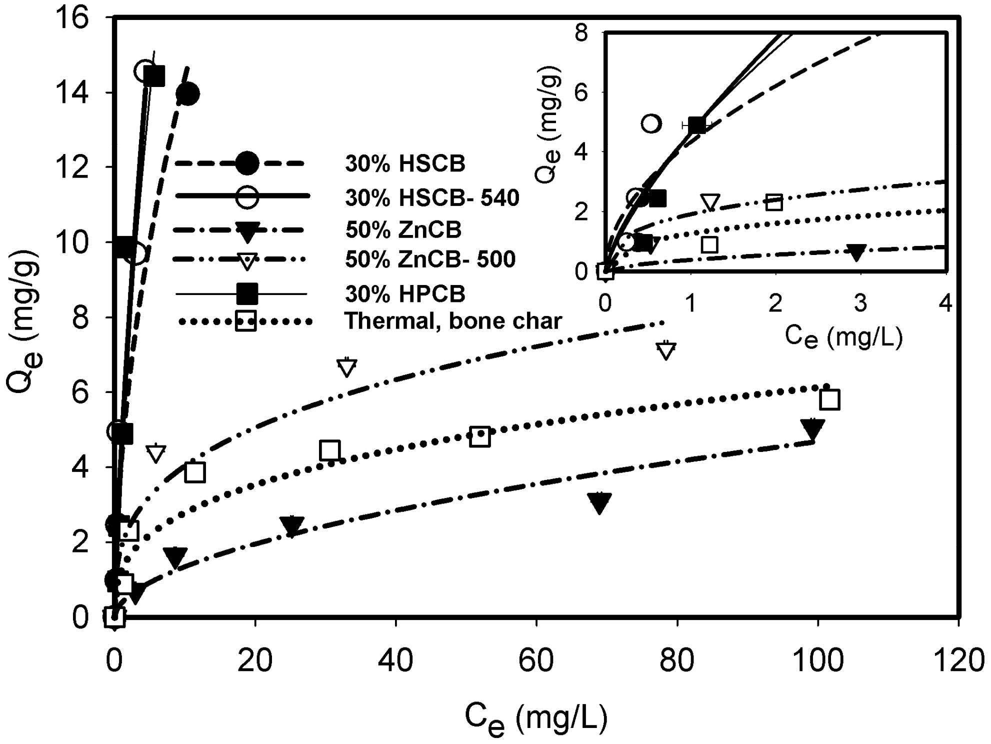

Figure 2.1: Fluoride adsorption fitting with Freundlich isotherms for chemically activated cow bone using sulfuric acid (30% HSCB), phosphoric acid (30% HPCB) and zinc chloride (50% ZnCB), and 30% HSCB and 50% ZnCB activated cow bone followed by thermal activation at 540 °C and 500 °C, respectively, and bone char. The inset panel indicates the fluoride adsorption at lower equilibrium fluoride concentrations. The error bars represent the standard deviations associated with Q_e and C_e calculated from triplicate measurements.

The effect of combined chemical and thermal activation of cow bone was investigated by heating the HSCB and KCB at 540 °C, ZnCB at 500 °C for 3 hours (referred to, for example, as HSCB-540). While the combined thermal-chemical activation process did significantly increase equilibrium fluoride adsorption capacity versus thermal activation alone (Figures 2.1 and 2.2), the adsorption parameters were not statistically different (95% CI) than chemically activated bone alone (see $Q_{1.5}$ values in Table 2.1). This makes a one-step chemical activation of cow bone generally preferable to a combined thermal and chemical activation, since thermal activation requires higher energy consumption than chemical activation (Lussier et al. 1994).

Surface amendment of bone char using $AlCl_3$ and $Al_2(SO_4)_3$ solutions produced lower $Q_{1.5}$ values than the fluoride removal capacity achieved through chemical activation of cow bone (Appendix A, Figure A.2.1) (Table 2.1). This is attributed to the already desirable adsorption properties of the bone char, and the potential for aluminum (hydr)oxide precipitates to block pores and limit access to internal surface area.

Table 2.1: Freundlich parameters of chemically activated cow bone and thermally activated cow bones.

	Freundlich constants				
Adsorbents	**k_f, $((mg/g)/(mg/L))^{1/n}$**	**1/n**	**$Q_{1.5}$[1] (mg/g)**	**pH**	**References**
Chemically activated cow bone					
30% HSCB[2]	4.6 ± 1.2	0.7 ± 0.0	6.1 ± 1.6	7	This study
30% HPCB[3]	4.3 ± 1.0	0.5 ± 0.0	5.4 ± 1.3	7	This study
50% ZnCB	0.4 ± 0.4	0.5 ± 0.4	0.5 ± 0.2	7	This study
30% KCB[4]	2.8 ± 0.8	0.4 ± 0.1	3.3 ± 1.4	7	This study
50% KCB	3.2 ± 0.9	0.4 ± 0.1	3.8 ± 0.3	6.9	This study
Thermally activated cow bone					
Bone char	1.3 ± 0.4	0.3 ± 0.1	1.4 ± 0.5	7	This study
Bone char	1.1	0.4	1.2	7	(Abe et al. 2004)
Bone char	0.8 ± 0.0	0.4 ± 0.0	0.9 ± 0.0	7.3	(Brunson & Sabatini 2009)
Bone char	1.8 ± 0.2	0.38	2.10	NR[7]	(Brunson & Sabatini 2014)
Chemical activation followed by thermal activation					
30% HSCB-540[5]	4.6 ± 0.8	0.7 ± 0.0	6.3 ± 1.1	7	This study
30% KBC-540	2.8 ± 0.6	0.4 ± 0.1	3.2 ± 0.8	7	This study
50% KBC-540	3.1 ± 0.7	0.4 ± 0.1	3.6 ± 0.9	7	This study
50% ZnCB-500[6]	1.9 ± 0.5	0.3 ± 0.1	2.2 ± 0.7	6.5	This study
Amended bone char					
1000 ppm $AlCl_3$- BC[7]	0.9 ± 0.3	0.6 ± 0.3	1.2 ± 0.7	6.9	This study
2000 ppm $AlCl_3$ - BC	0.9 ± 0.4	0.5 ± 0.4	1.2 ± 0.9	6.9	This study
500 ppm $Al_2(SO_4)_3$ -BC	1.3 ± 0.4	0.5 ± 0.3	1.6 ± 1.1	6.5	This study
1000 ppm $Al_2(SO_4)_3$ -BC	0.9 ± 0.3	0.6 ± 0.3	1.2 ± 0.7	6.5	This study
2000 ppm $Al_2(SO_4)_3$ -BC	0.9 ± 0.4	0.6 ± 0.3	1.2 ± 0.7	6.5	This study
Aluminum Impregnated BC	1.4 ± 0.1	0.42	1.66	NR[8]	(Brunson & Sabatini 2014)

The isotherm parameters (k_f and n) were obtained from Freundlich isotherm fitting using SigmaPlot 12.0 and the uncertainties in Q and 1/n are calculated using error propagation method.

Note:
1 $Q_{1.5}$ is Q at C_{eq} = 1.5 mg/L
2 Sulfuric acid activated cow bone
3 Phosphoric acid activated cow bone
4 Potassium hydroxide activated cow bone
5 Sulfuric acid activated bone char at 540 °C
6 Zinc chloride activated bone char at 540 °C
7 Aluminum chloride amended bone char at 540 °C
8 Not Reported

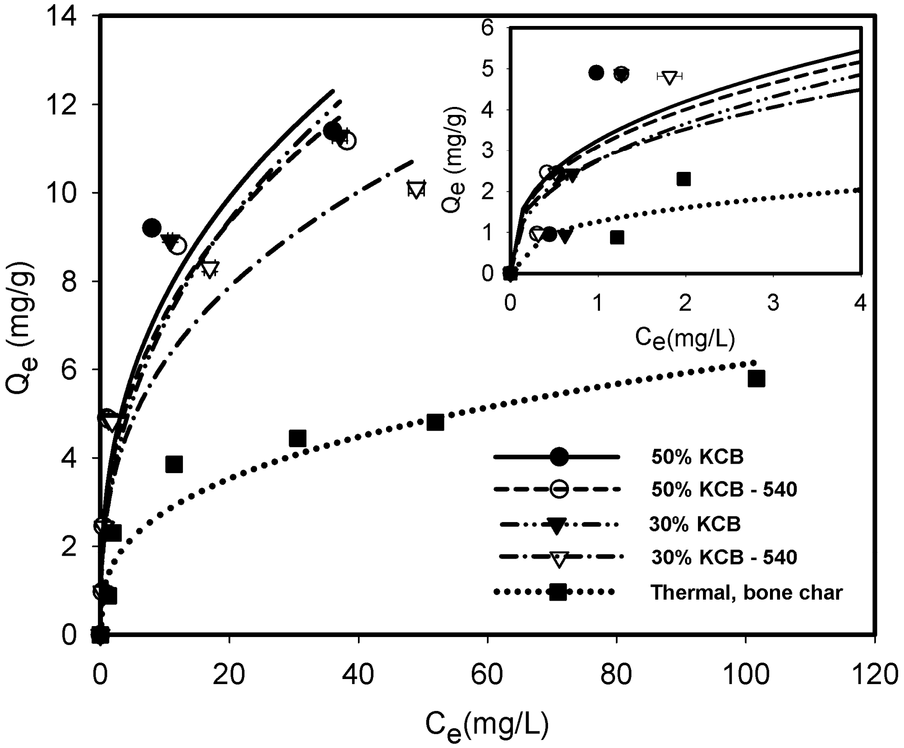

Figure 2.2: Fluoride adsorption fitting with Freundlich isotherms for chemically activated cow bone using potassium hydroxide (30% and 50% KCB), and 30% and 50% KCB chemically activated cow bone followed by thermal activation at 540 °C, and bone char. The inset panel indicates the fluoride adsorption at lower equilibrium fluoride concentrations. The error bars represent the standard deviations associated with Q_e and C_e calculated from triplicate measurements.

2.5.2 Characterization of the chemically activated cow bone

The BET SSAs of chemically and thermally activated cow bones ranged from 9 to 111 m^2/g (Table 2.2). By comparison, the BET SSA of bone char was reported as 104 m^2/g (Medellin-Castillo et al. 2007), and 110 m^2/g (Brunson and Sabatini 2009). The measured BET SSA of HSCB was a factor of ten lower (9 m^2/g) than the SSA measured by the EGME method (134 m^2/g), while the BET and EGME SSAs for 50% KCB and 50% ZnCB-500 °C differed by a factor of approximately two. The smaller BET SSA for

HSCB compared to the EGME BET may be due to the collapse of the mineral structure of the chemically activated cow bone during the vacuum stage of the BET process, suggesting that the EGME may be more representative in this case. Both the BET and EGME SSAs of the chemically activated cow bones showed an increasing trend of HSCB < ZnCB < KCB (Table 2.2), which does not correspond to the trend in adsorption capacity (Table 2.1). Generally, there was no clear relationship observed between either BET and EGME SSA and fluoride adsorption capacity of the chemically activated cow bones.

While chemical activation has been found to produce a much higher SSA for carbonaceous materials than thermal activation, this trend was not observed for chemically activated cow bone versus thermally activated bone (bone char). Rather, the BET SSA values were largely the same. And while the EGME surface area of bone char was not measured, the EGME and BET SSAs followed similar trends (Table 2.2). Thus, SSA can not account for the four times greater fluoride adsorption capacity of the chemically activated cow bone compared to the bone char. Additional characterization was therefore conducted to look for other possible explanations.

The PZC values for 30% HSCB, 50% KCB, and 50% ZnCB-500 are summarized in Table 2.2. The PZC value of 50% KCB was 8.4 (Appendix A, Figure A.3.1A) which is the same as the PZC value of bone char reported by Medellin-Castillo (2007) and Brunson and Sabatini (2009) (Table 2.2), yet the adsorption capacity of 50% KCB was significantly higher than that of bone char (Table 2.1). In addition, the PZC of 30% HSCB (6.6) (Appendix A, Figure A.3.1B and Table 2.2) was the lowest among those measured, and indicates a net negative charge at the pH of the experiments (pH

7), yet this adsorbent had the highest $Q_{1.5}$ of the three adsorbents for which PZC was measured (Table 2.1). Hence, the PZC also cannot account for four-fold increases in fluoride adsorption capacity of the chemically activated cow bone compared to bone char.

Table 2.2: Properties of chemically activated cow bone and amended bone char

Description of the adsorbent	**Specific surface area (m^2/g) (BET method)**	**Specific surface area (m^2/g) (EGME method)**	**pH_{PZC}**	**Reference**
30% HSCB	9	134	6.6	This study
50% KCB	111	258	8.4	This study
50% ZnCB-500°C	106	245	7.2	This study
Thermal, bone char	104	NR[a]	8.4	(Medellin-Castillo et al. 2007)
Thermal, bone char	110	NR	8.4	(Abe et al. 2004)
Thermal, bone char	99.1	NM[b]	NR	(Brunson & Sabatini 2014)
Aluminum impregnated bone char (AlBC)	91.8	NM[b]	NR	(Brunson & Sabatini 2014)

[a] NR – not reported
[b] NM- not measured

XRD analysis of 30% HSCB that exhibited the highest fluoride adsorption capacity showed the presence of the minerals bassanite ($CaSO_4 .0.5 H_2O$) and monetite ($CaHPO_4$) (Figure 2.3A) that were not present in bone char (only hydroxyapatite was found in bone char) (Figure 2.3B). This indicates that the phase change to bassanite and monetite occurred as a result of the chemical activation. The peaks of the chemically activated cow bone match the XRD pattern applied to bassanite crystals by Abriel and Nesper (1993), and monetite crystals by Frost et al. (2013). The CAB showed a mixture of elongated and rod-like crystals that could be bassanite and monetite, respectively (Figure 2.3C). The EDS elemental analysis of the CAB revealed the presence of higher percentage of calcium, and oxygen peaks (Figure 2.3D) compared to bone char. The CAB has additionally showed sulfur, magnesium and sodium peaks which were not present in the bone char. Furthermore, it was observed from the EDS analysis that chemical activation fully removed volatile and organic materials (no carbon was detected by the EDS), which are commonly responsible for bad odors in drinking water.

Abe et al. (2004), Masamba et al. (2005), and Ayoob et al. (2008) suggest that the presence of SO_4^{2-}, Ca^{2+}, and PO_4^{3-} enhances defluoridation capacity. Therefore, the presence of sulfate in bassanite and phosphate in monetite minerals may be responsible for the high fluoride removal capacity of the chemically activated cow bones versus thermally activated cow bone. The increased fluoride adsorption of the chemically activated cow bone may be due to an ion exchange of PO_4^{3-}, SO_4^{2-}, and OH^- by fluoride ions from aqueous solution. These concepts and the mechanisms responsible for the increased capacity of the chemically activated cow bone were further explored in chapter 4 of this dissertation.

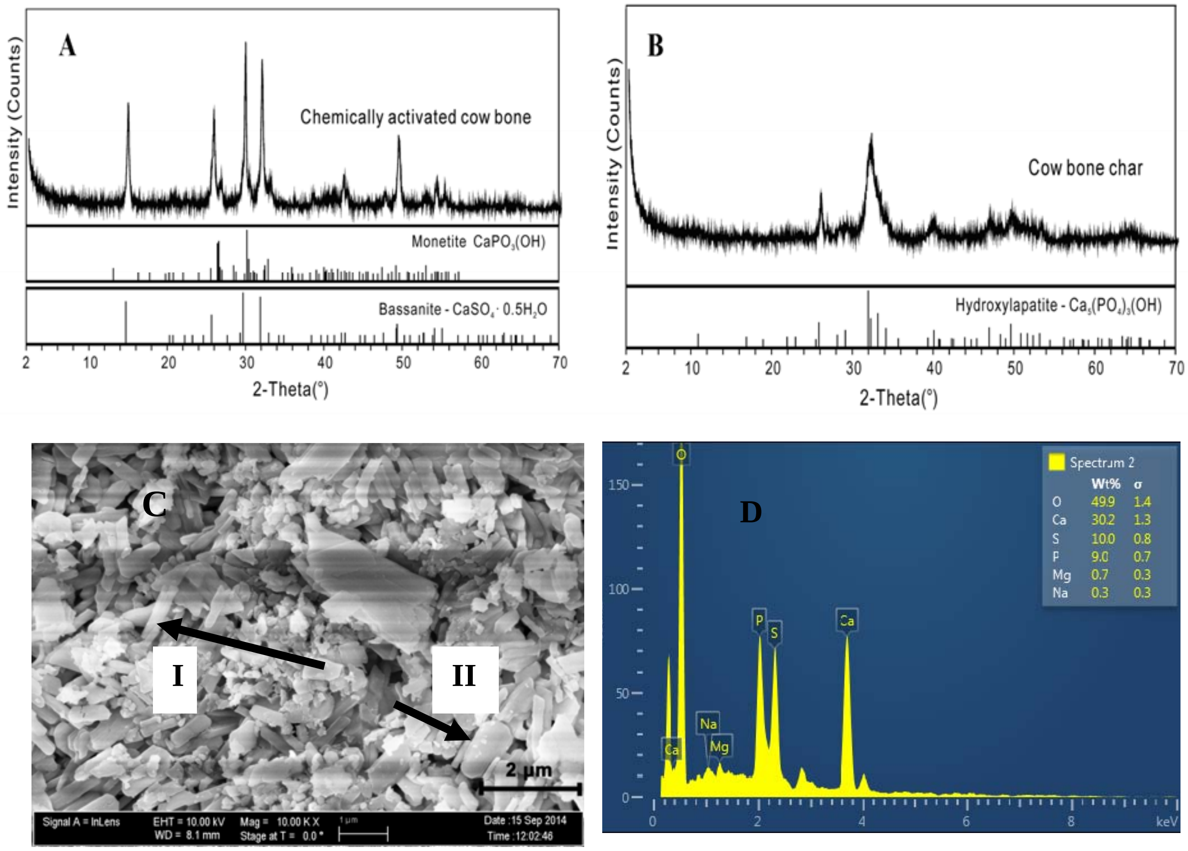

Figure 2.3: XRD result of sulfuric acid activated cow bone showing bassanite and monetite minerals (A) and bone char (B), SEM image (C), the dark arrow in panel shows the morphology of chemically activated cow bone (I and II shows bassanite and monetite crystals, respectively), and EDS analysis showing phosphorous, sulfur and calcium peaks (D).

2.5.3 Mass recovery during chemical activation

The chemical activation processes did not result in significant loss of the starting media as compared to losses measured during the thermal activation process (approx. 30% material loss versus approx. 80% loss, respectively, Appendix A, Table A.4.1). The media loss during chemical activation is negligible as compared to the loss during crushing of charred bones due to the significant quantity of fines and dust produced in the latter case. Bone charring produced about 45% loss during charring and 35% loss due to crushing. Hence, chemical activation produces higher mass recovery than the thermally activated bone char, in agreement with the results of Srinivasakannan and Balasubramaniam (2007), and Zhang et al. (2010). The combined benefits of higher adsorption capacity and higher efficiency of material production (mass recovery) makes chemically activated cow bone even more attractive than bone char.

2.5.4 Cost comparison of adsorbent production

The total costs of production of chemically and thermally activated cow bone were found to be \$0.30/ kg and \$0.83/ kg, respectively (Appendix A, Table A.5.1). The production of CAB (considering cost of the adsorbents per kg) is about eleven times cheaper than the thermal activation of cow bone (see calculations in Appendix A). Thus, chemical activation of cow bone is a very low-cost production process compared to thermal activation of cow bone.

2.6 Conclusions and recommendations

Comparison of the fluoride adsorption capacity of chemically activated cow bone showed on average about four-fold higher fluoride adsorption capacities than thermally activated cow bone. While chemical activation has been shown to produce a much higher SSA in carbonaceous materials in the formation of activated carbon, it did not likewise produce higher SSA when applied to cow bones. Likewise, the PZC values of CAB were found to be similar to those of bone char. Therefore, SSA and PZC were not able to explain this four-fold increase in fluoride adsorption capacity. Instead, the monetite formed during the process of chemical activation of cow bone was responsible for the high fluoride adsorption capacity of chemical activation of cow bone, while bassanite had negligible fluoride removal capacity and thus not deemed responsible for the high fluoride removal of the CAB media.

Compared to thermally activated cow bone, chemically activated cow bone achieved a higher mass recovery value than bone char due to fines lost during thermal activation. Chemical activation of cow bone was also found to be a more cost-effective production process than thermal activation. Therefore, chemically activated cow bone has proved to be a highly efficient and effective adsorbent in the laboratory. This shows that it has great potential to mitigate the negative health effects of fluoride impacted drinking water. The next chapter takes this research further by evaluating the effectiveness of chemically activated cow bone produced both in the laboratory and field through installation of small and large-scale field columns in the field.

2.7 Acknowledgment

This work was funded in part by The University of Oklahoma Water Technologies for Emerging Regions (WaTER) Center, the Sun Oil Company Endowed Chair, the Ken Hoving Graduate College Fellowship, and the National Science Foundation (CBET 1066425). The authors are highly indebted to Dr. Preston Larson for SEM /EDS analysis, Dr. Andrew Madden for XRD and BET analytical assistance, and Mr. Junyi Du for his assistance during sample characterization. The authors also extend special thanks to Ms. Rachel Rogers for her assistance in the lab, Ms. Jessica Johnston for reviewing the manuscript, and Dr. Laura Brunson for her valuable suggestions and provision of cow bones used in this study.

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Chapter 3: Using a High-Capacity Chemically Activated Cow Bone to Remove Fluoride: Field-Scale Column Tests and Laboratory Regeneration Studies[3]

Abstract

In this study, a novel material, chemically activated cow bone (CAB), was further evaluated for fluoride removal via laboratory batch and field column studies using fluoride impacted ground waters in the Rift Valley of Ethiopia. Regeneration of the exhausted CAB was evaluated using 0.05 M NaOH and 0.01 M $Ca(OH)_2$ solutions. Water quality parameters were analyzed to ensure that the CAB treated water is safe for human consumption. The study indicated that the CAB produced in the laboratory and field showed four-fold improvement in fluoride removal capacity versus bone char. The study also showed that more than 92% adsorption capacity of the exhausted CAB media can be regained using 0.05 M NaOH and 0.01 M $Ca(OH)_2$. The water quality analysis conducted on the highly fluoride impacted drinking waters treated using CAB media were found to be safe for public consumption. Therefore, these results reinforce that CAB media can be used to provide access to safe drinking water for communities living in the highly fluoride impacted areas in developing countries and beyond.

Key words: Chemical activation; Cow bone; Fluoride removal; Regeneration; Water quality

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[3] This chapter or portions thereof has been published previously in *Journal of Environmental Engineering* in collaboration with Dr. Jim F. Chamberlain, Dr. Elizabeth C. Butler and Dr. David A. Sabatini under the title "Using a High-Capacity Chemically Activated Cow Bone to Remove Fluoride: Field Scale Column Tests and Laboratory Regeneration Studies". J. Environ. Eng., DOI: 10.1061/(ASCE)/EE.1943-7870.0001169. The current version has been reformatted for this dissertation.

3.1 Introduction

Fluoride in groundwater occurs mainly from dissolution of natural minerals in the rocks and soils with which the groundwater comes into contact. Fluoride concentrations of up to 68 mg/L have been detected in groundwater wells located north of Lake Abijata, in the Rift Valley of Ethiopia (Rango et al. 2012). High fluoride concentrations can occur in groundwater with long residence times in the host aquifers (Jagtap et al. 2012). Fluoride concentrations above the World Health Organization (WHO) maximum acceptable level of 1.5 mg/L causes dental, skeletal and/or crippling fluorosis depending on other factors such as nutritional status. It is therefore of paramount importance to remove excess fluoride concentrations from drinking water.

Adsorption, ion exchange, chemical precipitation, Donnan dialysis, and reverse osmosis are among the various methods that have been investigated to remove excess fluoride concentrations from drinking water (Durmaz et al. 2005; Ndiaye et al. 2005; Meenakshi and Viswanathan 2007; Ayoob et al. 2008; Sehn 2008; Brunson and Sabatini 2009 and 2015). The adsorption process has been commonly adopted for fluoride removal based on ease of operation, use of locally available materials, cost effectiveness, and potential for regeneration and reuse. Recently, adsorbents such as bone char, hydroxyapatite, zeolites and modified zeolites, ion exchange resins, and layered double oxides have been investigated for fluoride removal (Mohapatra et al. 2009; Du et al. 2014).

Adsorbent-based fluoride removal is generally implemented in packed-bed column systems. These systems are flexible and convenient in terms of design and operation (Bhargava and Killedar 1991; Ghorai and Pant 2004; Chen et al. 2011).

Furthermore, Brunson and Sabatini (2014) indicated the Rapid Small-Scale Column Tests (RSSCTs) scaling equations developed for activated carbon (Crittenden et al. 1991) are applicable for bone char removal for fluoride. The benefit of RSSCTs are the breakthrough curves can be obtained in a fraction of the time with a small volume of water, and costs are lower compared to pilot-scale studies (Crittenden et al. 2005). The bed-depth/service time analysis (BDST) model (Goel et al. 2005) and Thomas model (Thomas 1994) can also be used to analyze column performance.

Thermally activated cow bone (commonly known as bone char) has been widely used as an adsorbent for removal of excess fluoride although its fluoride removal capacity is low and thus need further enhancement. The fluoride removal mechanisms of bone char are direct adsorption of fluoride and ion exchange, where the fluoride exchanges with hydroxyl ion (Equation 3.1), carbonate ion, and phosphate ions (Bregnhøj and Dahi 1995; Abe et al. 2004; Kawasaki et al. 2009).

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6(F)_{2(s)} + 2OH^- \text{ ....Equation 3.1}$$

Fluoride adsorbents (e.g., bone char) eventually become exhausted (saturated) (Mjengera 1988). The exhausted media can either be replaced by virgin material or regenerated for reuse. Some of the benefits of regeneration and reuse of spent adsorbents include reduced operational cost, since media can be reused multiple times, and potentially minimizing negative environmental impacts associated with their manufacture and disposal (Yami et al. 2015). Fluoride saturated bone char has been regenerated through surface- coating, precipitation, and sodium hydroxide solutions

(Christoffersen et al. 1991; Medellin-Castillo et al. 2007). NaOH regeneration of bone char has been performed using 1% - 8% NaOH solution converting fluoroapatite to hydroxyapatite (Christoffersen et al. 1991; Jacobsen and Muller 2007; Ayoob et al. 2008). The fluoride desorption reactions are the reverse of Equation 3.1.

When highly fluoride impacted drinking water is treated using adsorbents, it is imperative to ensure that the universal drinking water standards are met in the produced water, considering not only fluoride but also other constituents. For example, Kawasaki et al. (2009) suggested that when using cow bone-based adsorbents for fluoride removal, the produced water should be analyzed for phosphate ion concentrations. Furthermore, other drinking water parameters such as taste, odor and color need to be assessed when using cow bone-based adsorbents since they may introduce objectionable taste and smell to treated water (Dahia 2015; Ayoob et al. 2008). Studies by Crapper et al. (1973), Davidson (1982) and Tanne (1983) have shown that animals exposed to residual aluminum concentrations have evidenced health effects (e.g., aluminum induces neurofibrillary degeneration in neurons of higher mammals). Bhattacharjee et al. (2014) investigated aluminum and its potential contribution to Alzheimer disease. Feasibility and efficiency of defluoridation systems depends on the level of dissolved residual aluminum concentration in treated water (Qureshi and Malmberg 1985; Mameri et al. 1998). Therefore, water quality analysis should be undertaken for a new adsorbent to prevent unintentional negative health impacts from the adsorbent.

The modification of adsorbent surface chemistry using chemical activation of carbonaceous materials appears to be a promising approach for developing novel cow bone-based adsorbents for defluoridation (Paudyal et al. 2011; Alagumuthu and Rajan

2010; Tchomgui-kamaga et al. 2010). Chemical activation is an alternative to thermal activation for producing activated carbon; we recently reported a study showing the effectiveness of chemical activation of cow bones for fluoride removal as an alternative to bone char in chapter 2 of this dissertation and Yami et al. (2016). Therefore, chemical activation of cow bones, a process of exposing cow bones to varying concentrations of chemical activating agents, was performed by Yami et al. (2016) (see chapter 2 above) with the purpose of increasing the fluoride adsorption capacity of cow bones. The high fluoride removal capacity of chemically activated cow bone (CAB) was developed in the laboratory under controlled conditions where the activation temperature was maintained constant using an electrical heater, high purity chemicals, and the CAB media was rinsed using deionized water. In this research, we produced CAB media under field conditions i.e., using wood as an energy source, rinsing the media using the local water supply, and using locally available chemicals and skilled personnel. Furthermore, in this research we used small and large columns in the field and conducted the defluoridation work using natural groundwater in the Rift Valley of Ethiopia. The small column was installed to provide preliminary evaluation of the performance of the CAB media produced in the laboratory and guide design and installation of the larger column in the field.

To date, our laboratory studies have shown that CAB is four times more effective than bone char for removal of excess fluoride concentrations from drinking water (Yami et al., 2016). Based on these encouraging preliminary results, the overall goal of this work is to conduct additional studies necessary to further evaluate the viability of CAB for field deployment. The Rift Valley of Ethiopia was selected for production and field testing of the CAB media due to the ongoing collaboration with Ethiopian Universities, government offices, and Non-Governmental Organizations working in fluoride removal from drinking water.

The specific objectives of this study are (1) to produce chemically activated cow bone in the laboratory and the field and install small and large defluoridation columns in the field to evaluate CAB performance/ suitability (feasibility) for fluoride removal using fluoride impacted natural groundwater in the Rift Valley of Ethiopia, (2) to compare the fluoride adsorption capacity of CAB and bone char using field column studies, (3) to assess the suitability of water treated using the CAB system in the field for public consumption, (4) to investigate the regeneration potential of CAB/ bone char and evaluate the fluoride removal capacity of the regenerated adsorbent. With these results the viability of CAB for fluoride removal from drinking water can be more fully assessed.

3.2 Materials and methods

3.2.1 Adsorbent media

For small-scale field columns, CAB was prepared in the University of Oklahoma's Water Technologies for Emerging Regions (WaTER) Center using cow bones obtained from La Ruhe, Texas, using varying concentrations of potassium hydroxide (30 % and 50%) solutions (details on preparation of CAB can be found in chapter 2 of this dissertation). For the large-scale field columns, CAB was produced at Oromo Self Help Organization (OSHO) in the town of Modjo in the Rift valley of Ethiopia using cow bones obtained from a slaughter house in Addis Ababa, Ethiopia. The crushed cow bone was rinsed using water from Modjo town water supply system, sun dried for two days, and sieved to remove organic matter and fine particles. The chemical activation of cow bones in the field was conducted using 50% potassium hydroxide (KOH) solutions and the resulting media is termed as CAB in this manuscript. The 50% KOH solution was selected for chemical activation in the field due to its effectiveness during the laboratory screening tests (Yami et al. 2016) and its local availability. The chemical (KOH) was purchased from Uni-Chem Chemicals and Reagents company in Addis Ababa (pellets and solid). The CAB produced in laboratory was used in batch studies (laboratory), and small-scale column studies in the field. The CAB produced in the field was used for large field column experiments, and batch studies in the laboratory. The laboratory and field column dimensions, and other parameters are provided in Table 3.1.

3.2.2 Water samples

For small-scale column studies conducted in the Rift Valley of Ethiopia, raw ground waters were collected from two existing fluoride impacted wells, namely Dodo Wadera and Woyo Gabriel -2 which are located 7 km north of Alemtena town and 12 km south of Meki town, respectively. They are designated as RW-1 and RW-2 in Table 3.2. For the large-scale column study, water from an existing raw water tanker (10,000 L capacity) filled from a groundwater well located 3 km north of Meki town was utilized and designated as RW-3 in Table 3.2. For the preparation of CAB media in the field, raw water from Modjo town water supply service with a fluoride concentration of 1.9 mg/L was used.

To undertake laboratory batch adsorption and regeneration studies, a 1000 mg/L fluoride stock solution was prepared by putting 4.42 g NaF (Fisher Scientific) into 2 L glass container and then filling it with 2 L of [4-(2-hydroxyethyl)-1-1 piperazineethanesulfonic acid (HEPES) acid and salt solution (50 mM) prepared using deionized water, and 36.21 g and 12.51 g HEPES acid and HEPES salt, respectively. Fluoride solutions of concentrations ranging from 0 to 150 mg/L were prepared by diluting the stock solution with the HEPES solution. The fluoride solutions prepared in the laboratory were also used to conduct the adsorption study of the bone char and CAB media after regeneration.

3.3 Experiments

3.3.1 Small- scale field column tests

The small-scale field columns were 1 cm diameter and 30.5 cm in length made of glass with Teflon end caps. Glass wool was packed into the bottom of the column to support the CAB media and 5 mm borosilicate glass beads were placed at the top of the glass wool to disperse the influent flow (Westerhoff et al. 2005). The CAB was sieved using number 40/80 mesh sizes (180–425 μm) and added to the column using funnel and DI water to flush down into the packed bed height (H) of 10 cm. The empty bed contact time (EBCT) of 7.9 minute was obtained from Equation 3. 2 with a flow rate of 1 mL/min:

$$\text{EBCT} = \frac{V}{Q} \quad \text{.................. Equation 3.2}$$

where V is the empty bed volume in the column (mL), and Q is the flow rate through the column (mL/min). The glass beads and glass wool were packed at the top of the CAB media to prevent migration with the effluent flow. The small-scale column tests were performed in the Meki- Catholic Secretariat guest house in Meki town in the Rift

Valley of Ethiopia using natural groundwater from Dodo Wadera and Woyo Gabriel-2 wells.

A mini-peristaltic pump with variable flow (Fisher scientific) was used to pump the raw water by operating the column in up flow mode. The amount of water treated, effluent fluoride concentration, and pH were measured every hour and recorded. The small-scale column parameters are summarized in Table 3.1.

3.3.2 Large- scale column study

A large column (23 cm diameter and 115 cm height) was produced locally in Modjo town in the Rift Valley of Ethiopia by manually rolling and welding the iron sheet into a cylindrical column shape (Figure B.2.1). The iron sheet was used in this study due to its local availability. The CAB column was installed next to the existing bone char based defluoridation system (Giraba Fila site, RW-3) to allow easy access to the raw water from the feed reservoir of 10,000 L capacity. Crushed stone aggregate was washed three times and packed at the bottom of the column and then the CAB media (0.4 mm mean diameter) was packed into the column. The column was sealed with a rubber washer and bolted metal cover at the top to prevent leakage. The column was backwashed to remove fine particles by operating the column in upflow mode. The column was operated during day light hours (10 hours a day) and stopped at dusk and overnight for security reasons. The outlet flow rates were controlled by a gate valve installed at the entrance to the column. The inflow and outflow from the column were operated using a 2 cm diameter orifice welded to the column. The treated water quantity, effluent water fluoride concentration, and pH were measured daily using standard procedures outlined by Hall et al. (1972). The column parameters and raw water characteristics for the large field column are summarized in Table 3.1 and Table 3.2.

3.3.3 Batch fluoride adsorption study

Batch fluoride adsorption studies were conducted in the laboratory using CAB media prepared both in the laboratory, and field (in the Rift Valley of Ethiopia) to compare batch and column results with the same media. A 0.5 g CAB media was added to 50 mL polyethylene bottles containing initial fluoride concentrations ranging from 0 to 150 mg/L. HEPES buffer (acid and salt) were used to control the pH to the common natural water of pH 7. The reactors were agitated on a shaker (Ping-Pong TM # 51504-00) at 200 revolutions per minute (rpm) for 24 hours, and the samples were filtered. The batch experimental parameters such as adsorbent dose and contact time were selected based on preliminary tests in the laboratory. The fluoride concentrations were determined using ion selective electrode (Orion, Thermo Scientific). The samples were diluted with total ionic strength adjustment buffer (TISAB) on a 1:1 basis to reduce hydroxide interferences and the formation of hydrogen fluoride, and to maintain a constant pH and ionic strength during analysis according to Larsen and Widdowson (1971).

3.3.4 Water quality

Water samples were collected from the CAB treated water (RW-1 and RW-2 for small-scale column study, and RW-3 for large column study) to evaluate for other potential chemicals of concern. Polyethylene containers (0.5 L) were used to collect the treated water samples. Nitric acid was used to adjust the pH to 2 and preserve the samples during shipment to Ana-Lab Corporation in Kilgore, TX, U.S.A for analysis. The water quality parameters tested were selected based on human health (primary standards), aesthetic (secondary standards) concerns, and their compositions of the adsorbent used in this study. Water quality parameters were analyzed using standard procedures.

3.3.5 Regeneration.

CAB produced in the laboratory was used to undertake studies on the regeneration potential of the media. CAB media (0.5 g) was added into a 50 mL polypropylene graduated centrifuge tube with an initial fluoride concentration of 100 mg/L which produces equilibrium fluoride concentration (C_e) values in the range of 10 - 25 mg/L which is in the range of typical fluoride levels in groundwater in the region. The solution pH was adjusted to 7 by addition of 50 mM 2-[4-(2-hydroxyethyl) piperazin-1-yl] ethanesulfonic acid (HEPES) acid and salt to undertake adsorption study. After equilibration for 24 hours, each sample was filtered and the fluoride concentration and pH were determined using an ion selective electrode (Orion, Thermo Scientific) and pH meter (Orion, 3 star). Regeneration studies of CAB and bone char were performed using varying concentrations; 0.025 M - 1 M NaOH and 0.001 – 0.01 M $Ca(OH)_2$ to evaluate the potential for reusability of these media. The adsorption cycle was followed by regeneration study after decanting the saturated fluoride solution and adding 50 mL NaOH and $Ca(OH)_2$ solutions. Both the adsorption and desorption process were performed by agitating it on a shaker (Ping-Pong TM # 51504-00) at 200 revolutions per minute (rpm) for 24 hours.

3.4 Results and discussion

3.4.1 Small- scale column studies

Figure 3.1 shows the fluoride concentrations exiting the column as a function of the number of bed volumes in small-scale column studies conducted using CAB and bone char adsorbents. Initially, most of the fluoride ions were adsorbed on to the CAB media; hence the fluoride concentration in the effluent water sample was negligible. As the fluoride adsorption continues, the adsorptive front (mass transfer zone) moves through the column and eventually the effluent fluoride concentration of CAB begins to rise until it reaches a breakthrough point i.e., reaches the WHO guideline value fluoride concentrations of 1.5 mg/L. The residence time for the small column ($EBCT_{sc}$) of 7.9 minute was obtained from Equation 3.2 with a flow rate of 1 mL/min, and the empty bed volume in this small-scale column was 7.9 mL. Beyond the breakthrough point, the effluent fluoride concentrations continue to rise until it exceeds 90% of the initial fluoride concentration, known as exhaustion. For bone char, the fluoride concentrations reached breakthrough sooner than the CAB media. For RW-1, breakthrough was experienced at 117 bed volumes for bone char and 400 for CAB, while for RW-2, bone char breakthrough was experienced at 125 bed volumes while for CAB it was 600 bed volumes. Thus, both ground waters demonstrated a four-fold increased fluoride adsorption capacity of CAB media versus bone char (Figure 3.1 and Table 3.2). The bone char's breakthrough (117 to 125 bed volumes) obtained in these column studies is similar to the 100 bed volumes reported by Dahi (1997).

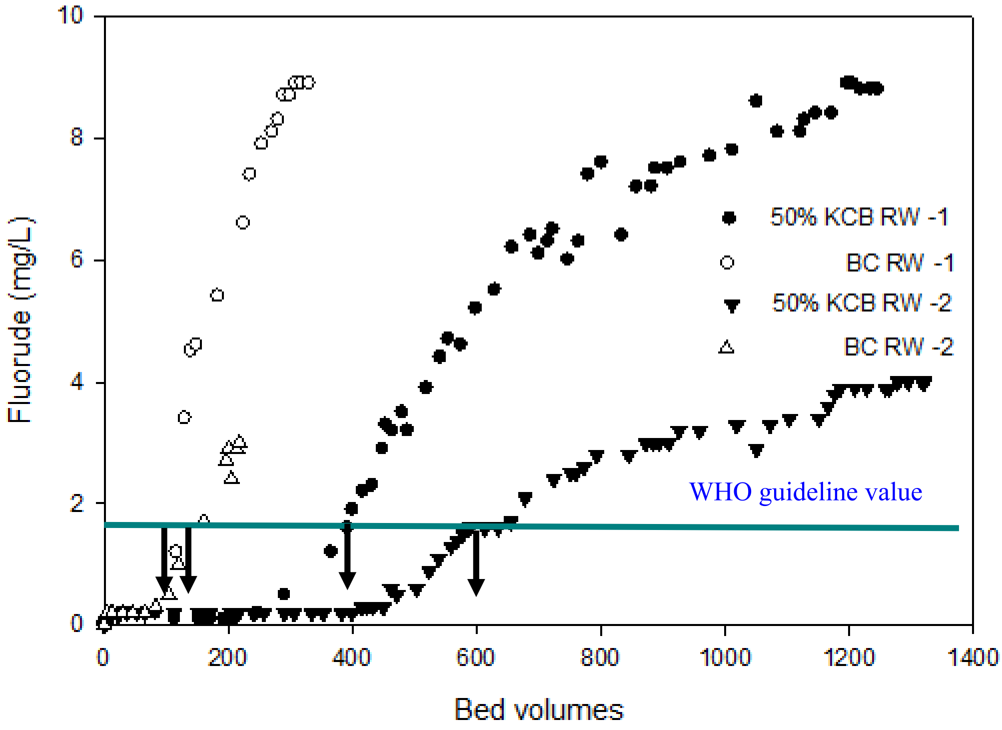

Figure 3.1: Small-scale column studies of chemically activated cow bone (potassium hydroxide, 50% KCB) and bone char (BC) using fluoride impacted natural water from Wells in the Rift Valley of Ethiopia (summer 2014) (RW- 1 and RW- 2 represents raw water from Well number 1 and 2, respectively). The column parameters are summarized in Table 3.1 and raw water characteristics are reported in Table 3.2.

The raw water sample from Well 2 (RW-2) with lower initial fluoride concentration of ($C_0 =$ 4.3 mg/L) achieved a larger number of bed volumes prior to the breakthrough point as compared to the RW-1 with the higher initial fluoride concentration (C_0 = 9.3 mg/L) for the same CAB media. This is attributed to the fact that the specific capacity ($Q_{1.5}$) is more rapidly achieved with higher initial fluoride concentrations. During the column operation, the pH entering and exiting the column was monitored for both the CAB media and bone char for the raw waters (RW-1 and

RW-2) considered in the small-scale column studies. For RW-1 the inlet pH of 8.3 was reduced and reached 6.2 as the number of bed volumes of treated water increased until a breakthrough point is attained and the average pH during column operation was about 7.5. The pH of the column operated using RW-2 also showed a similar decreasing pattern as RW-1 i.e., the pH gradually decreased from 7.8 to about 7.0. The decrease in pH during column operation might be due to the buffering capacity of the media during continuous column operation or could also be due to equilibration with atmospheric CO_2. The CAB packed in the small-scale column study on average produced about four times higher bed volumes to breakthrough compared to bone char which is similar to the batch adsorption study results conducted in the laboratory using the CAB media. These results further demonstrate that the CAB adsorbent is more suitable for the practical application in the field as compared to bone char.

Table 3.1: Parameters of small and large (field) column study using CAB media and bone char

Description	**Particle diameter (mm)**	**Column diameter (cm)**	**Packed bed height (cm)**	**Empty bed volume (mL)**	**In flow rate (mL/ min)**	**Surface loading rate (V), $cm^3/(cm^2.$ min)**	**EBCT[1] (min)**	**Column run (hr/day)**	**Volume of water treated (L/day)**
Small-scale column Tests[2]	0.18[4]	1.0	10	7.9	1.0	1.3	7.9	24	1.44
Large column[3]	0.4[5]	23	115	47,800	6,000	3.6	7.9	10[6]	3,600

Note: Column studies were conducted using fluoride impacted natural water in the Rift Valley of Ethiopia.

[1] EBCT – Empty Bed Contact Time

[2] Small-scale column tests using CAB media produced in the laboratory and bone char

[3] Pilot (large) column conducted using CAB media produced in t he field

[4] Particles passing mesh number 40 and retained on mesh 80

[5] particles retained on sieve number 40

[6] Not operated at night for safety reasons in the field

3.4.2 Field (large) column studies

Figure 3.2 shows the effluent fluoride concentrations versus bed volumes of the large column (23 cm diameter) using CAB produced in the Rift Valley of Ethiopia. The field column design parameters, such as the EBCT, column length, and particle size, are summarized in Table 3.1. The field column reached a breakthrough at 360 bed volumes (Figure 3.2) which was similar to the small-scale column result (400 bed volumes) for CAB (laboratory produced media) presented in Figure 3.1 and Table 3.2. The column was run for 10 hr per day and the influent water was discontinued overnight due to safety reasons of field operation. This mode of operation is similar to a typical village operation where the system would be operated by an individual operator (i.e., one shift per day). Resting the column at night allowed longer contact time which increased the extent of fluoride removal by the media. The pH variation at the start of the column run may have been due to the buffering capacity of the media and/ or the equilibration with atmospheric CO_2, as discussed above. The production cost of CAB media was estimated at $0.30/kg, compared to $0.83/kg for bone char (Yami et al. 2016) (see chapter 2 of this dissertation). A more comprehensive cost analysis for water treatment by CAB in the field was undertaken and provided in chapter 2, Appendix A.

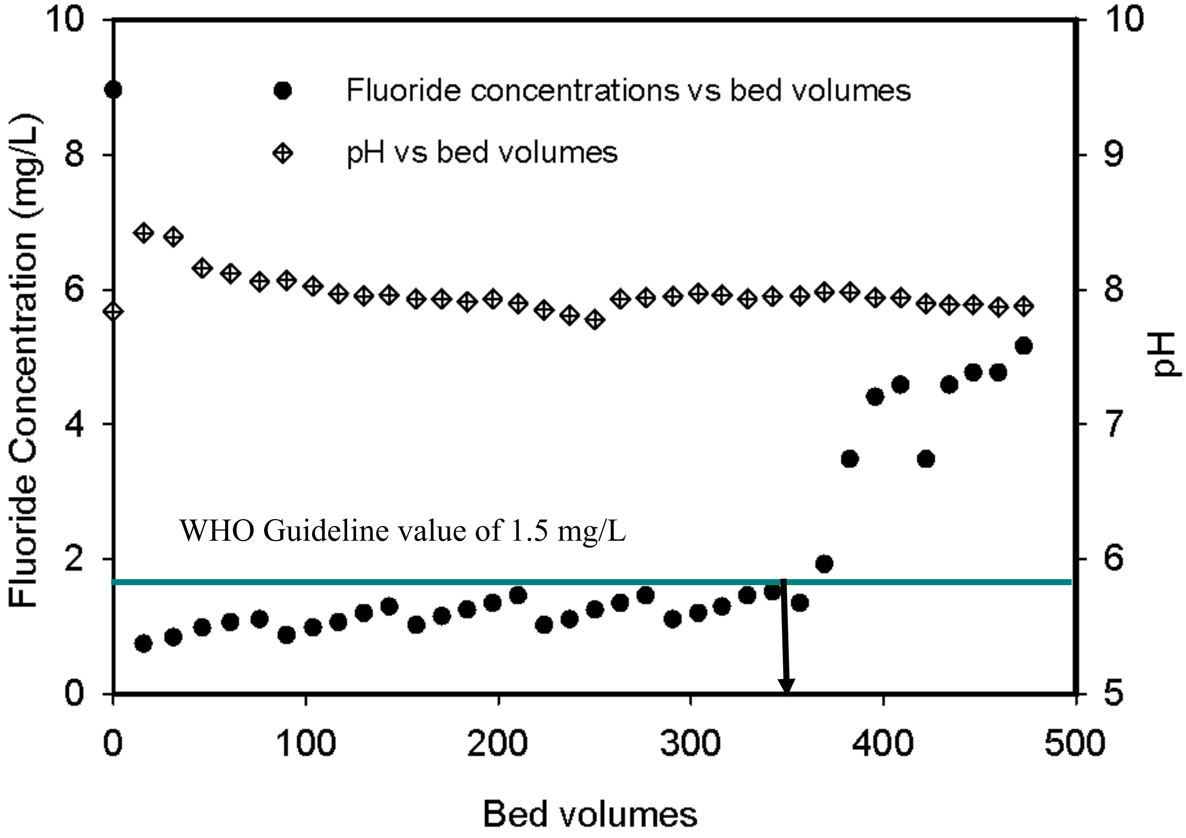

Figure 3.2: Large (23 cm diameter) field column study of potassium hydroxide activated cow bone (50 % KCB) produced in the Rift Valley of Ethiopia (summer 2015) using Giraba Fila Well (RW-3). The step function (inflection points) in this figure are because the system was not operated at night due to security reasons in the field i.e., longer contact time decreased the effluent fluoride concentration. Column parameters are summarized in Table 3.1.

Table 3.2: Raw water characteristics and results of column study using CAB media and bone char. Small-scale column study and large-scale column tests were conducted using natural water in the Rift Valley of Ethiopia (summer 2014 and 2015).

Description	Small columns				Large column
	CAB media[1]		Bone char		CAB media[2]
	RW1[3]	RW2[3]	RW1[3]	RW2[3]	RW3[3]
Initial fluoride concentration, C_0 (mg/L)	9.3	4.3	9.3	4.3	8.9
pH (raw water)	8.3	7.8	8.3	7.8	7.8
Average pH (treated water)	7.5	7.6	7.5	7.6	7.7
Bed volume at $C_e = 1.5$ mg/L	400	600	117	125	360
Bed volume at $C_e = C_0$ (mg/L)	1247	1321	331	218	NA[4]
Q_e column (mg/g) mass balance ($C_{in} = C_{eff}$)	4.6	2.5	1.2	1.14	NA[4]

Note: [1] CAB media developed in the lab

[2] CAB media developed in the field

[3] RW-1, RW-2 and RW-3- raw water from Well 1 (Dodo Wadera), Well 2 (Woyo Gabriel-2), and Well 3 (Giraba Fila)

[4] NA- parameters not analyzed (column was not run to exhaustion)

3.4.3 Batch adsorption studies (field media)

Figure 3.3 shows laboratory fluoride adsorption isotherms of CABs produced both in the laboratory and field, and bone char. These batch adsorption studies were conducted to compare the fluoride removal capacities of CAB media produced in the field versus the media produced in the laboratory. The CAB media prepared in the field (in the Rift Valley of Ethiopia) had higher fluoride adsorption capacity ($Q_{1.5} = 3.4$ mg/g) than bone char adsorbent (Figure 3.3). The batch equilibrium fluoride adsorption capacity of CAB media produced in the field ($Q_{1.5}$ fitted with the Langmuir isotherm) was statistically indistinguishable from the laboratory material (Table 3.3). This is quite encouraging as the field conditions of the media production were not yet optimal (e.g., maintaining constant activation temperature was difficult since heating to remove organic matter was accomplished with a wood fire, and the activation temperature varied from 40 – 70 °C). With further development of field process, improved fluoride adsorbent materials close to laboratory conditions can be produced. Nonetheless, the column studies showed similar bed volumes to breakthrough for small-scale column and large-scale field column studies (higher fluoride adsorption capacity compared to bone char was attained in both cases). Additionally, the comparison of the fluoride removal of CAB versus other adsorbents such as bone char and Aluminum amended bone char can be found in Yami et al. (2016). The raw water from Modjo town, with a fluoride concentration of 1.9 mg/L, was used to rinse the media. While this level of fluoride could potentially affect the fluoride uptake, the bed volumes of 400 (lab media) and 360 (field media) obtained in this study are similar suggesting that any impact on the column performance was minor. Thus, the results clearly show that CAB can be produced in the field and can achieve an increase in fluoride adsorption capacity compared to bone char. The next chapter further evaluates the reason for the high fluoride removal of CAB media via preparation of monetite and bassanite minerals shown during the chemical activation of cow bone.

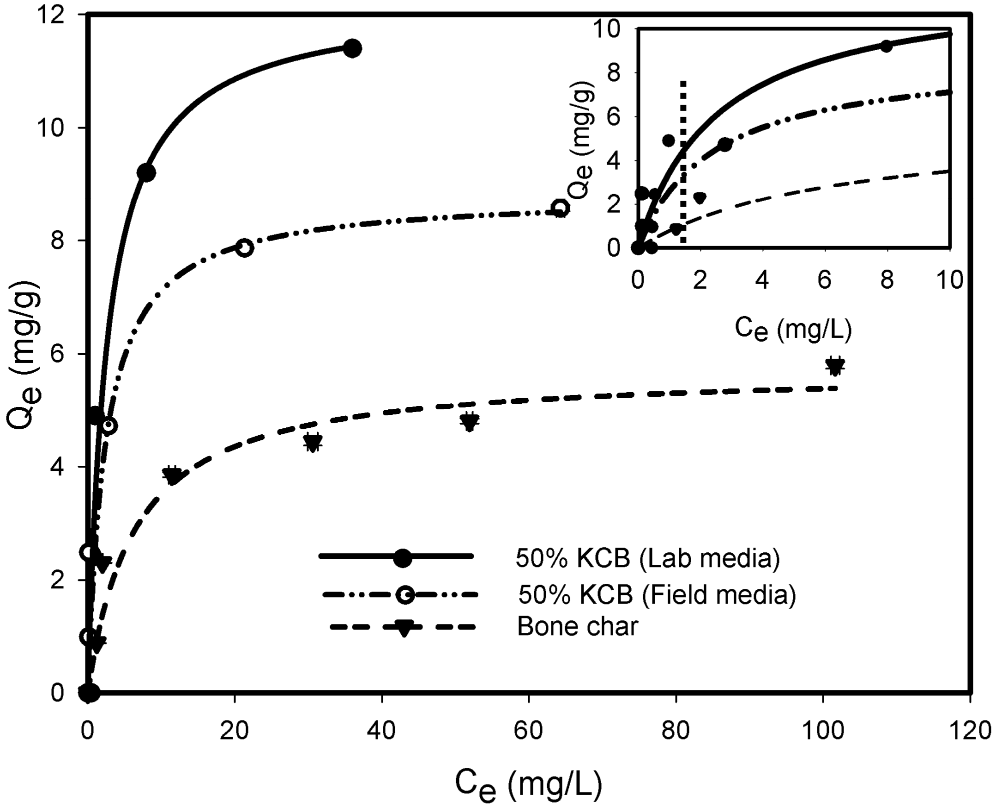

Figure 3.3: Fluoride adsorption data and Langmuir isotherms for potassium hydroxide (50% KCB) activated cow bone and bone char tested in the Rift Valley of Ethiopia. The error bars represent the standard deviations associated with Q_e and C_e calculated from triplicate measurements (If not visible error bars are same size as symbols). The vertical dashed line on inset panel indicates fluoride adsorption capacity (Q_e) at an equilibrium fluoride concentration (C_e) of 1.5 mg/L.

Table 3.3: Comparison of laboratory and field produced CAB media based on laboratory fluoride adsorption capacity (Q_e) (fitted with Langmuir isotherm) using batch isotherm studies of media developed in the laboratory and field. The uncertainties in Q_{max} and k are calculated using the error propagation method (see Figure 3.3).

Adsorbent	**Q_{max} (mg/g)**	**k (L/mg)**	**$Q_{1.5}$ (mg/g) at C_e = 1.5 mg/L F^-**	**Remark**
CAB media (lab produced)	12.3 ± 1.2	0.4 ± 0.2	4.5 ± 1.8	Yami et al. (2016)
CAB media (field produced)	8.8 ± 0.9	0.4 ± 0.2	3.4 ± 1.9	This study

3.4.4 Water quality

Table 3.4 presents the results of water quality analysis conducted on treated water of the field scale column. The water quality parameters tested were selected based on human health (primary standards), aesthetic (secondary standards) concerns, and the composition of the adsorbent used in this study. The high fluoride concentration water in the Rift Valley of Ethiopia that was treated using CAB complied with the WHO (2011) drinking water guideline values (see results in Table 3.4). The potassium level of 24.6 mg/L in treated water is approximately equal to the average background concentration of 22.7 mg/L in the natural groundwater in the Rift Valley of Ethiopia reported by Rango et al. (2010). The CAB media was rinsed three times before being packed into the column to reduce leaching during the column operation. Therefore, the high fluoride impacted water in the Rift Valley of Ethiopia treated using CAB was found to be safe for human consumption and this adsorbent can thus be used to expand installation of CAB-based defluoridation systems in place of bone char which has low adsorption capacity. It should be noted that aluminum was not analyzed since bone's main constituent (hydroxyapatite) does not contain aluminum, and aluminum was not present in the regeneration solutions. Furthermore, energy dispersive X-ray spectroscopy (EDS) conducted on CAB did not show aluminum in its elemental composition (Yami et al. 2016).

Table 3.4: Treated[1] and raw water quality parameters (water samples collected from the pilot project sites in the Ethiopian Rift Valley and tested in Ana-Lab Corp., Kilgore, TX, U.S.A)

Water Quality Parameters	**Unit**	**Raw water quality of the study area[2]**	**Treated water**			**Guide-line values**
			RW1- (Dodo Wadera)	**RW- 2 (Woyo Gabriel - 2)**	**RW3- (Giraba Fila)**	
pH	-	8.0	7.5	7.6	7.7	6.5 – 8.5
Fluoride	mg/L	9.2	1.5	1.5	1.5	1.5[3]
Arsenic, Total	mg/L	0.021	0.0016	0.0101	<0.0005	0.01 MCL[3]
Chloride	mg/L	170	65	230	150	250[3]
Sulfate	mg/L	94.4	9.0	32	<1.5	500[3]
Phosphate	mg/L	NA[4]	<0.301	<0.100	3.98	No limit listed
Potassium	mg/L	22.7	NA[4]	NA[4]	24.6	82[5]
Calcium	mg/L	25.7	19.4	26.5	6.85	50[6]
Magnesium	mg/L	69.8	2.13	12.9	7.12	50[6]
Total Hardness as $CaCO_3$	mg/L	352	57.3	119.0	46.4	500[6]

Note: [1] The anion concentrations seem higher than the cations since only parameters of potential health concerns in connection with the use of cow bone and the chemical activating agent are considered.
[2] The data in this column were from Rango et al. (2010), except for fluoride and pH which were measured as part of this study.
[3] WHO (2011), [4] Parameters not analyzed
[5] http://apps.who.int/iris/bitstream/10665/70171/1/WHO_HSE_WSH_09.01_7_eng.pdf
[6] Canadian Health act safe drinking water regulation BC Reg 230/92, & 390, Sch 120, 2001

3.4.5 Regeneration study

Thermally activated cow bone (bone char). The regeneration potential of bone char was investigated to establish a baseline for comparison with CAB regeneration and also for screening of the concentrations of regeneration solutions to be used. The regeneration was conducted using varying concentrations of NaOH and $Ca(OH)_2$

solutions. From Figure 3.4, it is observed that of the studied solutions, 0.1 M NaOH produced, on average, 73% effluent fluoride concentration (desorption) of the previously adsorbed fluoride over three regeneration/adsorption cycles. In this study, the subsequent regeneration processes are called R1, R2 and R3, the corresponding adsorption processes are called A1, A2 and A3, and the sequence of events is A1, R1, A2, R2, A3, R3. Using 0.1 M NaOH, the amount of fluoride adsorbed during cycles A2 and A3 (Figure 3.4, panel A) corresponding to the previous desorption cycles (R1 and R2) (Figure 3.4, panel B) was 93% on average (i.e., the Q_e for A2 (4.3 mg/g), after the first regeneration cycle, was 93% of the Q_e for A1 of 4.6 mg/g, see Table B.1.1). This adsorption capacity after regeneration is higher than the 71% and 89% adsorption capacity recoveries reported for bone char by (Kaseva 2006) and (Kanyora et al. 2015), respectively. This shows high regeneration capacity of bone char was achieved using 0.1 M NaOH solution in this study.

Regeneration of bone char by 0.01 M $Ca(OH)_2$ desorbed, on average, about 40% of the fluoride adsorbed in each cycle (Figure 3.4, panel B). However, for the 0.01 M $Ca(OH)_2$ regeneration solution, on average more than 92% of the fluoride adsorption capacity was regained (i.e., Q_e for A2 (4.2 mg/g) was 92% of the A1 Q_e value of 4.5 mg/g) which is in excess of the average desorbed amount of 40%. The increase in adsorption capacity upon regeneration may have been because the addition of $Ca(OH)_2$ resulted in supersaturation of the solution with respect to the mineral fluorapatite ($Ca_5(PO_4)_3F$), and thereby appreciably increasing the fluoride removal capacity, as highlighted by Ayoob et al. (2008). Furthermore, the extra fluoride uptake capacity could be due to reactive sites of the adsorbent exposed after each regeneration cycle.

The quantitative amount of fluoride adsorbed/desorbed (Q_e values) at each adsorption/ regeneration cycle is summarized in Table B.1.1 and the comprehensive regeneration test results, which illustrate the effectiveness of additional concentrations of NaOH and $Ca(OH)_2$, are shown in Figure B.2.2. Therefore, the study indicated that 0.1 M NaOH and 0.01 M $Ca(OH)_2$ solutions are promising for regeneration of the exhausted bone char media.

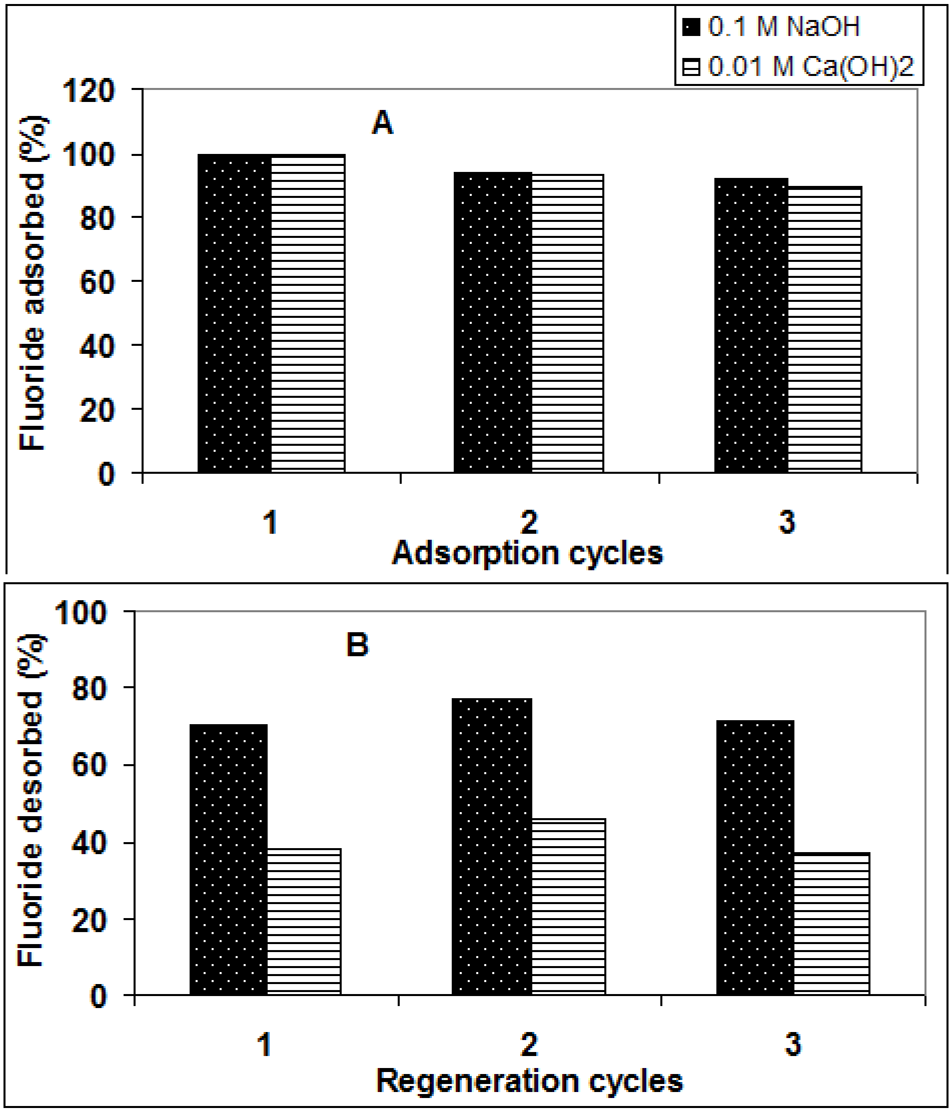

Figure 3.4: Regeneration of saturated bone char (BC) using 0.1 M NaOH and 0.01 M $Ca(OH)_2$ solutions. Panels A and B show the adsorption and regeneration cycles, respectively.

Chemically activated cow bone (CAB). Figure 3.5 shows regeneration results of CAB media. The CAB media regenerated using 0.05 M NaOH solution led to removal of at least 40% of the fluoride adsorbed in cycle 1 (Figure 3.5, panel B). Specifically, the amounts of fluoride desorbed in R1, R2, and R3 were 40%, 60% and 75% of the fluoride adsorbed in A1, A2, and A3, respectively. For example, the Q_e for A2 was 7.0 mg/g, which is 82% of the Q_e for A1, which was 8.5 mg/g (Table B.1.1). When using 0.01 M $Ca(OH)_2$ as a regenerant for CAB, a smaller amount of fluoride desorption was observed at all the three regeneration cycles compared to 0.05 M NaOH (Figure 3.5 panel B). However, a high adsorption capacity recovery (94%) (i.e., Q_e of 8.4 mg/g for A2 compared to 8.9 mg/g for A1 (Table B.1.1) was obtained for A2 (Figure 3.5, panel A) despite the corresponding low desorption amount in R1. This high adsorption capacity can be attributed to exposure of adsorbent reactive sites during multiple regenerations, and formation of fluoroapatite when $Ca(OH)_2$ was added. The average adsorption capacity regained for CAB media using 0.1 M $Ca(OH)_2$ is 92% of the Q_e for A1 (Table B.1.1). From these results, it is suggested that the CAB media can be regenerated and reused for at least three cycles without significant loss of fluoride removal capacity. The regeneration of the CAB media can be conducted at water treatment site by suitably trained technicians by removing the exhausted CAB media from the column, soaking it in 0.05 M NaOH or 0.01 M $Ca(OH)_2$ solutions and sun drying the media. Comparison of the regeneration of CAB media could not be made since no similar studies had been conducted by other researchers. Thus, this study showed that CAB has the potential for regeneration using 0.05 M NaOH and 0.01 M $Ca(OH)_2$, which when coupled with its higher fluoride adsorption capacity compared to bone char makes it even more viable for fluoride treatment. Future research should build on this initial work and further develop the regeneration of CAB media.

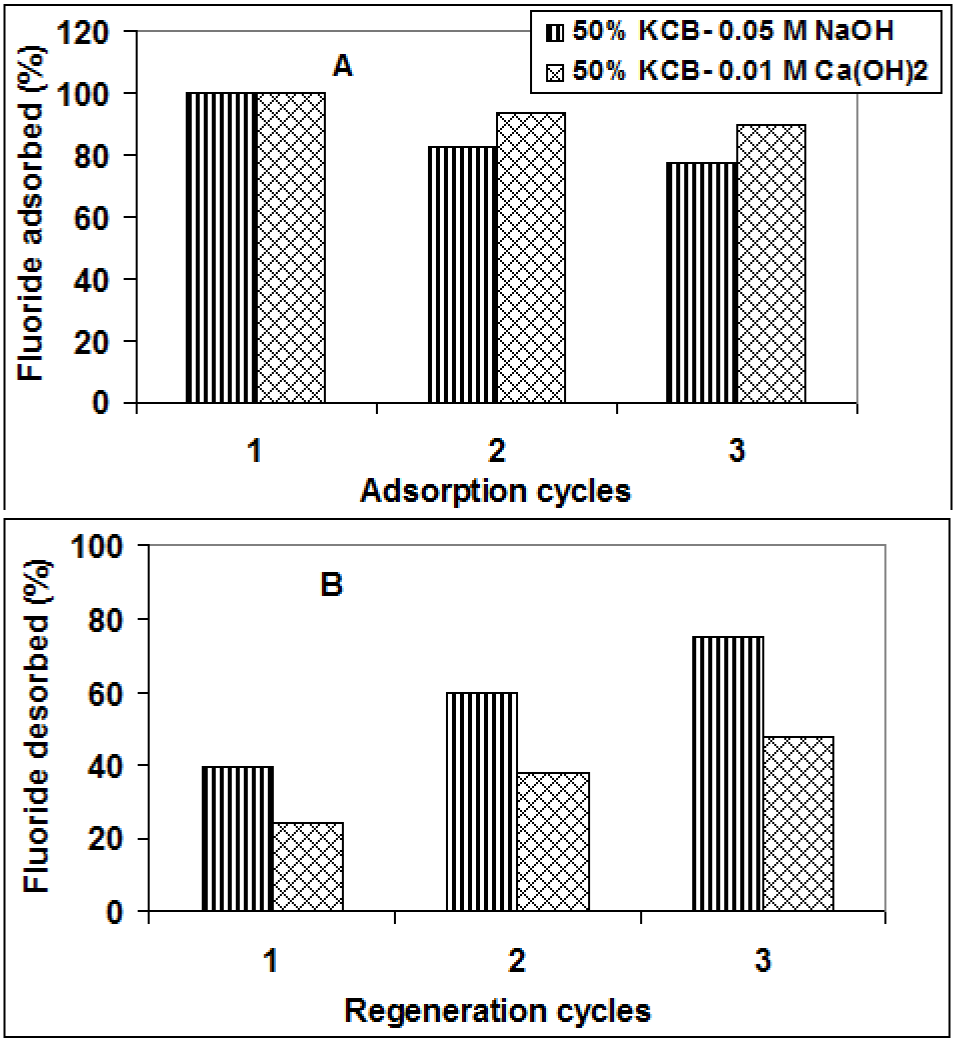

Figure 3.5: Regeneration of potassium hydroxide (50% KCB) activated cow bone using 0.05 M NaOH and 0.01 M $Ca(OH)_2$ solutions. Panels A and B show the adsorption and regeneration cycles, respectively.

3.5 Conclusions

Results of the research demonstrate that chemically activated cow bone (CAB) can be produced in the field using locally available raw materials and equipment. Laboratory batch adsorption studies conducted on CAB produced both in the laboratory (Yami et al., 2016) and the field (this work) had four-fold higher fluoride removal capacities compared to bone char. Likewise, small-scale and large-scale column studies conducted using CAB produced both in the laboratory and field, using natural water in the Rift Valley of Ethiopia, achieved approximately 400 bed volumes prior to breakthrough (versus approximately 100 bed volumes for bone char). Again, this is four-fold fluoride removal capacity compared to bone char both in batch and column (small-scale and large column) studies. The water quality analysis conducted on samples collected from CAB treated water meets the WHO guidelines for drinking-water quality (WHO 2011). The 0.01 M $Ca(OH)_2$ is found to be a better regenerant since it produced higher adsorption capacity (on average 92% of the Q_e at A1) compared to 0.01 M NaOH which was 80% on average. Therefore, this research further validates CAB as a potential media for the removal of high fluoride concentrations from drinking water in developing countries and beyond.

3.6 Acknowledgment

The authors would like to thank Oromo Self Help Organization (OSHO), Dr. Feleke Zewge (Addis Ababa University, College of Natural Sciences, Ethiopia), Catholic Relief Service/ Meki-Catholic Secretariat, and National Fluorosis Mitigation Project Office (Ministry of Water, Irrigation and Electricity, Ethiopia) for facilitation of field works in the Rift Valley of Ethiopia. This work was funded in part by The University of Oklahoma Water Technologies for Emerging Regions (WaTER) Center, the Sun Oil Company Endowed Chair, the Ken Hoving Graduate College Fellowship, the National Science Foundation (CBET 1066425), and the Norman Noon Rotary Club, District 5770, Oklahoma. The authors also thank Philip Deal for reviewing the manuscript.

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Chapter 4: Preparation and Evaluation of Monetite as a High-Capacity Adsorbent for Fluoride Removal from Drinking Water[4]

Abstract

Chemically activated cow bone (CAB) had four-fold higher fluoride removal capacity compared to bone char both in laboratory batch studies and field–scale column studies in the Ethiopian Rift Valley. The CAB media showed bassanite ($CaSO_4.0.5H_2O$) and monetite ($CaHPO_4$) minerals that were not present in bone char; these minerals were thought to be responsible for the high fluoride adsorption capacity of the media. The overall objective of this study was to investigate the fluoride adsorption capacity of monetite and bassanite to see if they are effective at fluoride adsorption. High purity (99.6%) monetite was prepared in the laboratory and showed a three-fold higher adsorption capacity than CAB (the fluoride adsorption capacities at an equilibrium fluoride concentration of 1.5 mg/L ($Q_{1.5}$) were 20.0 mg/g and 6.4 mg/g for monetite and CAB, respectively), which illustrates the significant adsorption capacity of monetite. The EGME specific surface area (SSA) of monetite (Ca/P 1:0.43) was twice that of the CAB media (260 m^2/g vs 134 m^2/g) and thus may account for a portion of the three-fold higher capacity of monetite versus CAB. The increased capacity of monetite (Ca/P ratio 1:0.43) can also be partly attributed to the high surface charge (zeta potential) on the monetite compared to CAB (27.1 mV and 7.5 mV, respectively, measured at pH 7). In contrast to monetite, bassanite had negligible fluoride removal capacity. Therefore,

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[4] This chapter or portions thereof has been submitted to *Journal of Environmental Engineering* in collaboration with Dr. Elizabeth C. Butler and Dr. David A. Sabatini under the title “Preparation and Evaluation of Monetite as a High-Capacity Adsorbent for Fluoride Removal from Drinking Water”. It is currently in review.

monetite is found to be promising for fluoride removal to mitigate the negative health impacts of excess fluoride concentrations in drinking water.

Key words: adsorption; bassanite; chemically activated cow bone; cow bone; fluoride; monetite

4.1 Introduction

Groundwater constitutes 30.1% of total global freshwater (Gleick 1996) as the single largest available supply of drinking water, especially in rural settings (WHO 2004). Fluoride in groundwater originates from geogenic sources (dissolution of fluoride-containing minerals) and/or anthropogenic sources (e.g., application of pesticides) (Apambire et al. 1997; Jha et al. 2011; Roy & Dass 2013). The dominant factor controlling the levels of fluoride in water are the amount of clay minerals present, pH, the concentration of calcium and phosphate, and the levels of exchangeable sodium (Chhabra et al. 1980). Furthermore, anions like SO_4^{2-} and PO_4^{3-} positively affect fluoride removal since they react with Ca^{2+} to form precipitates of $CaSO_4$, $CaHPO_4$ and $Ca_3(PO_4)_2$, depending on solution pH (YangM et al. 1999). Fluorite (CaF_2) precipitation in the presence of Ca^{2+} ion provides new adsorption sites and thereby enhances the fluoride removal (Fan et al. 2003).

Excess fluoride in drinking water is a significant concern primarily because it has both short- and long-term effects on human health. Fluoride concentrations above the 1.5 mg/L threshold are harmful to human health (WHO 2011). Beyond dental and skeletal concerns, fluorosis has significant socio-economic impacts stemming from the fact that persons who develop skeletal fluorosis suffer considerable hardship and have reduced productivity (Apambire et al. 1997; Frank et al 2011). Moreover, the prevalence of fluorosis and the related widespread health problems may stigmatize entire villages (McKnight et al. 1997). For instance, more than 8 million people living in the Rift Valley of Ethiopia consume groundwater with high fluoride concentrations (range: 1.1 to 68 mg/L) (Rango et al. 2012). Therefore, solutions are needed to mitigate the suffering of those people affected by fluoride-induced health concerns.

To date, various treatment methods have been investigated to remove excess fluoride from drinking water. For example, bone char, activated alumina, red mud, quartz, fly ash, hydroxyapatite, zeolites and modified zeolites, ion exchange resins, and layered double hydroxides are among the adsorbents studied for fluoride removal from drinking water (Mohapatra et al. 2009; Tor et al. 2009; Ramdani et al. 2010; Du et al. 2014). Bone char is among the adsorbents widely used to remove excess fluoride from drinking water in developing countries such as Ethiopia, Kenya, and Tanzania due to its large specific surface area, high affinity for fluoride (Medellin-Castillo et al. 2007; Ayoob et al. 2008; Osterwalder et al. 2014), and its local availability at low-cost in developing countries (Mutheki et al. 2011). However, bone char has a relatively low fluoride removal capacity.

Chemical activation of carbonaceous materials has been shown to produce very high specific surface areas (SSA). Therefore, Yami et al. (2016) evaluated the chemical activation process used for carbonaceous materials for chemical activation of cow bone in an attempt to increase its fluoride adsorption capacity. Chemically activated cow bone (CAB) prepared using sulfuric acid demonstrated four-fold higher fluoride removal capacity versus bone char (Yami et al. 2016), with the high adsorption capacity being attributed to the presence of monetite ($CaHPO_4$) and bassanite ($CaSO_4.0.5H_2O$) produced during chemical activation of cow bone that were not present in bone char, which is mainly hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Medellin-Castillo et al. 2007). Therefore, in this chapter, monetite and bassanite minerals were prepared in the laboratory and their effectiveness at fluoride removal was investigated.

From the literature, various methods have been utilized to synthesize monetite. For example, Sutter et al. (1971), Ball and Casson (1973) and Louati et al. (2005) prepared monetite by dehydrating brushite ($CaHPO_4.2H_2O$) in H_3PO_4, in a static air atmosphere over a range of temperature of 200-250 ^oC, and slowly evaporating an aqueous solution of $Ca(NO_3).4H_2O$ and $NH_4H_2PO_4$ mixture at 80 ^oC, respectively. However, these dehydration techniques yield large particle sizes (15-40 μm), a major limitation compared to commercially available monetite (Tas 2009). A reverse micelle solution of water, cyclohexane containing cetyltrimethylammonium bromide (CTAB) surfactant and n-pentanol as co-surfactant was used by Wei et al. (2007) to produce spherical particles of 50 nm diameters. Well-crystallized monetite nanoparticles with various morphologies were obtained in CTAB reverse micelles solution (Wei et al. 2007). Therefore, the reverse micelle method was used in this study to prepare monetite at a Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18. The Ca/P ratios of the components ($CaCl_2$ and $(NH_4)_2HPO_4$) affect the composition and crystal phases of the resulting monetite (Raynaud et al. 2001). For example, the surface area of the product decreased with increase in Ca/P molar ratio, and XRD pattern of synthesized powder showed hydroxyapatite at higher Ca/P ratio and monetite at lower Ca/P ratio (Raynaud et al.

2001). Therefore, the effect of Ca/P molar ratio on the resulting monetite was considered in this study.

Bassanite ($CaSO_4.0.5H_2O$) is commonly formed by dehydration of gypsum ($CaSO_4. 2H_2O$) (Hunt et al. 1966; Kinsman et al. 1969; Arakel 1980; Mees 1998). A mixed phase of gypsum and bassanite was prepared by (Yang et al. 2010) by dissolving $CaCl_2$ in ethanol at 35 ºC. Tritschler et al. (2015) prepared pure bassanite by dissolving $CaCl_2$ in methanol solution and adding an equimolar sulfuric acid, and this method is adopted here to prepare bassanite.

The objectives of this research work are as follows:

1. To produce monetite and bassanite and investigate their fluoride removal capacity as compared to CAB;
2. To evaluate the effect of Ca/P ratio on the mineralogical composition of resulting monetite and its fluoride removal capacity;
3. To investigate the mechanisms/properties of fluoride removal of monetite media;
4. To study the impact of competing anions present in natural groundwater on the fluoride removal capacity of monetite.

4.2 Materials and methods

4.2.1 Materials

The starting materials used in the preparation of monetite ($CaHPO_4$) were $CaCl_2$ (anhydrous) (Fisher Scientific, Fair lawn, NJ), $(NH_4)_2HPO_4$ (98% grade) (Strem Chemicals, Newburyport, MA), cetyltrimethylammonium bromide (CTAB) (MP

Biomedicals, LLC, Solon, OH), cyclohexane (99+% grade) as a continuous oil phase (Across Organics, Fair Lawn, NJ), and co-surfactant, n-amyl alcohol (Fisher Scientific, Nazareth, PA). All the starting chemicals used in this study are reagent grade. De-ionized water (DI) was used in the preparation of the media. The effect of competing ions on the fluoride removal of monetite was studied using potassium salts: K_2SO_4 (Across Organics, Fair Lawn, NJ), $KHCO_3$ (Alfa Aaeser, Ward Hill, MA), KCl (EM Science, Darmsadt, Germany), and KNO_3 (EMD, Gibbstown, NJ).

4.2.2 Preparation of monetite and bassanite

To prepare monetite two separate reverse micelles containing calcium and phosphate were prepared by adding calcium and phosphate solutions into the CTAB containing cyclohexane and n-pentanol. The following experimental parameters were kept constant throughout the preparation of monetite: 0.1 M CTAB in cyclohexane and 1 M $CaCl_2$, while the $(NH_4)_2HPO_4$ concentration was varied as 0.25 M, 0.5 M and 1 M, respectively, to prepare monetite at Ca/P ratio of 1:0.43, 1:0.68, 1:1.18 (considering 0.18 M H_3PO_4, 85% grade, (Fisher Scientific, Fair Lawn, NJ) added for pH adjustment). The molar ratio between n-pentanol and CTAB was 3 and the molar ratio between water and CTAB was 5 as per the procedure highlighted in Wei et al. (2007). Both solutions (one solution containing calcium and CTAB with cyclohexane and n-pentanol, and another containing phosphate and CTAB with cyclohexane and n-pentanol) were placed on a magnetic stirrer for 30 minutes, and then the two reverse micelle solutions were rapidly mixed and stirred for another 30 minutes. Abbona et al. (1993) suggested that an acidic environment can possibly drive the formation of monetite, while the basic aqueous environment can change synthesized monetite into hydroxyapatite with sufficient supply of OH^- (Da Silva et al. 2001). The pH of maximum formation of monetite was thus estimated using computer software, MINEQL+ version 4.6 (A Chemical Equilibrium Modeling System- Environmental Research Software, Hallowell, ME) for monetite prepared at Ca/P ratio of 1:0.43 (Figure 4.1). Additionally, model calculations were done for the other Ca/P ratios (1:0.68 and 1:1.18) and showed the same trend in pH of monetite formation. The input data (component totals and solids) considered in MINEQL+ modeling is shown in Table C.1.1. The pH of maximum formation of monetite was found to be pH 3, so the pH of the solution containing the mixture of the two reverse micelles (containing Ca^{2+} and PO_4^{3-}) was adjusted to 3 using phosphoric acid. The resulting mixture was aged for two weeks at room temperature, centrifuged for 5 minutes at 5,000 revolutions per minute (Thermo Scientific IEC centrifuge, CL 10, Waltham, Massachusetts) to remove the supernatant. The product was placed on a glass beaker with a filter (Whatman No. 42 paper) and washed three times using ethanol to remove organic components. The sample was subsequently washed using 400 mL deionized water and oven dried at 100 ^{o}C for 24 hours.

Bassanite was prepared using the procedure by Tritschler et al. (2015) by dissolving 10 mM $CaCl_2$ in 50 mL methanol, adding an equimolar amount of H_2SO_4, and adding 2.11% water (by volume). The resulting product was isolated by centrifugation, filtered using Whatman No. 42 paper, washed using 400 mL of deionized water and dried at 100 ^{o}C for 24 hours.

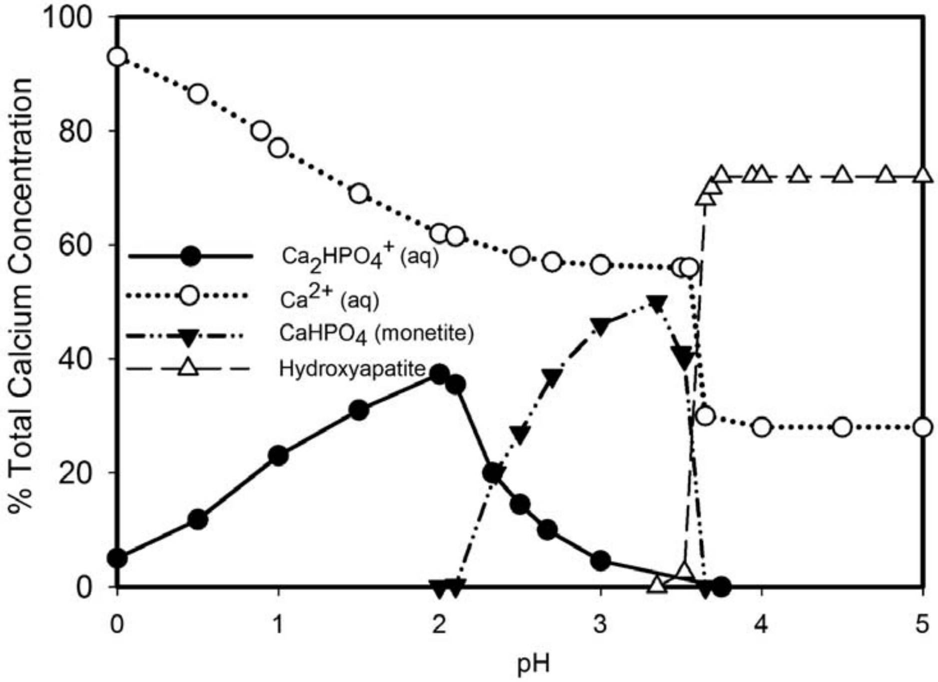

Figure 4.1: Solubility diagram for preparation of monetite based on MINEQL+ software. The component totals and solids considered are given in Table C.1.1.

4.2.3 Batch study

Batch studies of fluoride adsorption using monetite and bassanite were conducted by preparing a 1,000 mg/L stock solution by adding 4.42 g NaF (Fisher Scientific, Fair Lawn, NJ) into 2 L glass container and filling it with 2 L of 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) acid and salt solution (50 mM) prepared using deionized water, and 36.21 and 12.51 g HEPES acid and HEPES salt, respectively. A total of 0.5 g of the media was added into 50 mL polyethylene bottles containing initial fluoride concentration ranging from 0 - 150 mg/L prepared by diluting the fluoride stock solution using HEPES (Sigma, Saint Louis, Missouri) to fix the solution pH at 7 in the adsorption experiments. The reactors were agitated for 24 hours at 200 revolutions per minute on a shaker (Ping-Pong TM # 51540-00, Cole-

Parmer, Vernon Hills, Illinois). The samples were then filtered and the fluoride concentrations in solution were determined using an ion-selective electrode (Orion, Thermo Scientific, Beverly, Massachusetts). Before measurement, samples were diluted with an equal volume of total ionic strength buffer (TISAB) to reduce interferences and maintain constant pH and ionic strength during the analysis (Larson and Widdowson, 1971). The fluoride adsorption studies were conducted in triplicate to estimate the errors associated with experimental measurements.

4.2.4 Competing ion studies

The impact of co-existing anions on fluoride adsorption was investigated by performing fluoride adsorption experiments with an initial fluoride concentration of 25 mg/L and solution pH of 7. The molar concentrations of competing ions were 5 mM and 10 mM based on average concentrations of these ions in the Rift Valley of Ethiopia (Rango et al. 2010). The mass concentration of monetite in this experiment was 4 g/L with initial fluoride concentration of 25 mg/L (in duplicate) and the sample was shaken, equilibrated, and measured as described above.

4.3 Sorbent characterization

The monetite samples prepared in this study were characterized using a Rigaku (Tokyo, Japan) Ultima IV powder X-ray diffractometer (XRD) and fitting with reference mineral patterns using materials data (MDI) JADE 2010 analytical software. Powder samples for the XRD analysis were first pulverized, micronized and sprinkled onto a single-crystal sample holder to form a thin layer. The X -ray diffractometer was operated at 40 kV with a 44 mA current by using monochromated CuKα radiation. XRD data were collected over a range of 2º - 70º 2θ using counting 2 s per 0.02º 2θ at each step. The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were performed using a Zeiss NEON instrument (Oberkochen, Germany) operating at an accelerating voltage of 10 kV with iridium sputter-coating before imaging, to impart surface conductivity to the samples. The SEM analysis was performed to determine the surface morphology and EDS analysis was performed to identify the average elemental composition of the monetite.

The specific surface area (SSA) of the monetite was measured according to Brunauer-Emmett-Teller (BET) method using Quantachrome Autosorb (Boynton Beach, Florida) with a Beckman (Brea, California) Coulter SA -3100 surface area analyzer and N_2 gas adsorption. Additionally, the ethylene glycol monoethyl ether (EGME) method (Heilman et al. 1965; Cerato and Lutenegger 2002) was employed for determining the SSA of the monetite. The difference in the weight of samples before and after EGME coverage was used to calculate surface area. EGME analysis gives a more complete assessment of adsorbent surface area, because the BET method may measure only the external surface area of certain minerals (Yukselen and Kaya 2006), and because the aqueous medium in the EGME method may preserve pores that could collapse under the vacuum conditions applied during the BET method. The monetite zeta potential was measured using a ZetaPALS zeta potential analyzer (Brookhaven Instruments Corporation, Holtsville, NY). Zeta potentials were measured in triplicate to estimate the uncertainties in the experimental measurements.

4.4 Results and discussion

4.4.1 Fluoride adsorption capacity of monetite and bassanite- batch study

Figure 4.2 shows fluoride adsorption isotherms of monetite prepared under several conditions (Ca/P ratios of 1:0.43, 1:0.68, 1:1.18) as well as fluoride adsorption on sulfuric acid (30% HSCB) chemically activated cow bone (CAB). The adsorption data were well fitted to the Langmuir isotherm. The monetite prepared at Ca/P ratio of 1:0.43 had higher fluoride removal capacity compared to the Ca/P ratios of 1:0.68 and 1:1.18. The fluoride adsorption at an equilibrium fluoride concentration of 1.5 mg/L ($Q_{1.5}$) of monetite prepared at Ca/P ratio of 1:0.43 was found to be 2.5 and 10 times higher than monetite prepared at Ca/P ratios of 1:0.68 and 1.18, respectively (Figure 4.2 and Table 4.1). Additionally, monetite prepared at a Ca/P ratio of 1:0.43 had three-fold higher fluoride removal capacity compared to CAB (30% HSCB) (Table 4.1).

The chemically activated cow bone using 30% H_2SO_4 (termed as 30% HSCB) had bassanite in it. In contrast, the bassanite prepared in this study had negligible fluoride adsorption capacity compared to monetite (data not shown). Therefore, the bassanite mineral produced during the chemical activation of cow bone is deemed not be the reason for the fluoride removal capacity of CAB media.

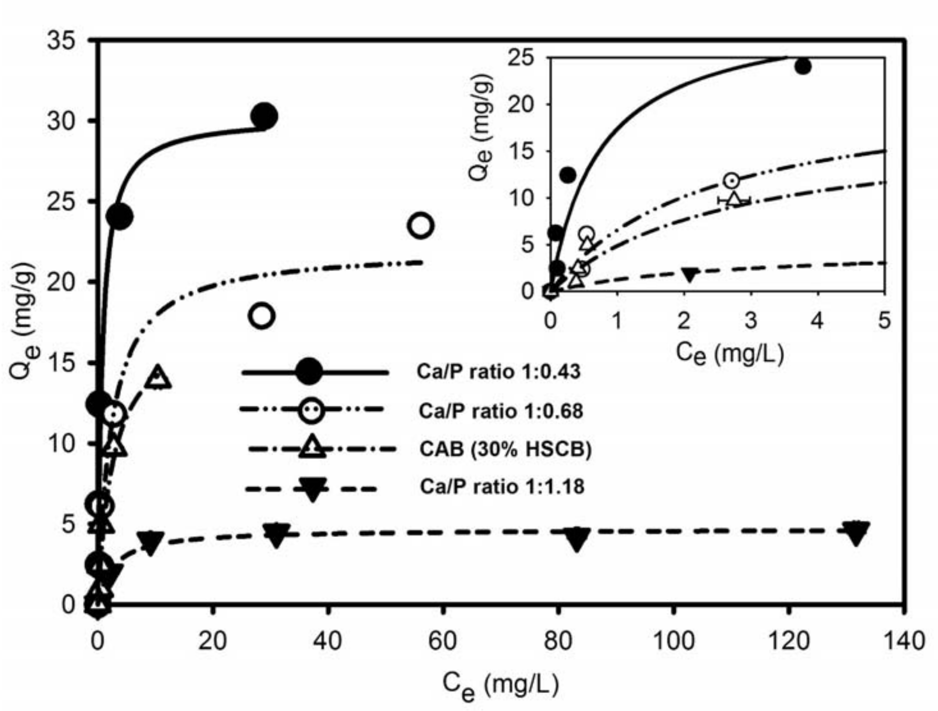

Figure 4.2: Fluoride adsorption fitted with Langmuir isotherm for synthesized monetite at Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18, and sulfuric acid activated cow bone (30% HSCB, data taken from Yami et al. 2016). The inset panel shows the fluoride adsorption at lower equilibrum fluoride concentrations. The error bars represent the standard deviation associated with Q_e and C_e calaculated from triplicate measurements.

Table 4.1: Langmuir parameters for synthesized monetite and chemically acid activated cow bone (CAB) at pH 7.

Adsorbent	**$Q_{1.5}^{a}$ (mg/g)**	**Q_{max} (mg/g)**	**K (L/mg)**	**References**
Ca/P ratio 1:0.43	20.0 ± 1.2	30.3 ± 3.4	1.3 ± 0.6	This study
Ca/P ratio 1:0.68	7.5 ± 2.6	20.1 ±1.7	0.4 ± 0.1	This study
Ca/P ratio 1:1.18	1.8 ± 0.6	4.2 ± 0.2	0.5 ± 0.2	This Study
CAB (30% HSCB^{b})	6.4 ±1.8	17.7 ± 2.9	0.4 ± 0.1	Yami et al. (2016)

The isotherm parameters (K) was obtained from Langmuir isotherm fitting using sigmaplot 13.0 and the uncertainties in Q_e and C_e are calculated using error propagation method.

[a] $Q_{1.5}$ is Q at C_e = 1.5 mg/L.

[b] Sulfuric acid activated cow bone

4.4.2 Fundamental properties of monetite

In an effort to understand the high fluoride adsorption capacity of monetite, several fundamental properties of the media were assessed. The BET specific surface areas (SSAs) of the monetite prepared at various Ca/P ratios were all approximately equal to 4 m^2/g (Table 4.2), which is less than half of the BET SSA of sulfuric acid activated cow bone (CAB) (9 m^2/g, Yami et al. 2016). Thus, the monetite's BET SSA is not able to account for either the higher fluoride adsorption capacity of monetite versus CAB, or the variation in adsorption between the three monetite species. However, the EGME SSA of monetite (Ca/P ratio 1:0.43) is twice that of the CAB media (260 m^2/g vs 134 m^2/g) (Table 4.2), and this increased surface area can account for a portion of the three-fold increase in fluoride removal capacity of monetite compared to CAB but not the variation in fluoride adsorption within the monetite samples. The smaller BET SSA values for the monetite samples compared to the EGME SSAs (Table 4.2) may be due to the collapse of monetite pores during the vacuum stage of the BET process; higher SSA values have previously been observed using the EGME versus the BET method by Yuskelen and Kaya (2006), who reported EGME to BET SSA ratios of 2 to 4 for kaolinte and zeolite, and 15 to 35 on average for montmorillonite samples. In addition, the EGME SSAs had a slightly decreasing trend (260 m^2/g, 256 m^2/g and 247 m^2/g for monetite prepared at Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18, respectively) (Table 4.2). These relatively small differences in EGME SSA, however, do not explain the significant difference in fluoride uptake by the three monetite samples with different Ca/P ratios.

Zeta potential, on the other hand, was found to vary significantly between the samples (Table 4.2). Thus, the high fluoride adsorption capacity of monetite prepared at a Ca/P ratio of 1:0.43 versus the other ratios could be due to its higher positive zeta potential of 27.1 mV compared to 8.3 and -8.0 for Ca/P ratios of 1:0.68 and 1:1.18, respectively (Table 4.2). The result indicates that the surface of monetite prepared at a Ca/P ratio of 1:0.43 achieved higher positive charge density and consequently increased the uptake of the negatively charged fluoride ion through electrostatic attraction. The decrease in fluoride adsorption capacity of monetite prepared at Ca/P ratios of 1:0.68 and 1:1.18 compared to that prepared at a Ca/P ratio of 1:0.0.43 (Figure 4.2) could be due a greater abundance of phosphate at the sorbent surface, decreasing the surface charge and reducing fluoride uptake. This is consistent with Raynaud et al (2001) who explained Ca/P ratios affect the composition, crystal phases and characteristic of the resulting monetite. It is also in agreement with Zhou et al. (2015), who indicated that when the Ca/P ratio reaches 1/3 during preparation of monetite, excessive PO_4^{3-} can precipitate in the reaction. It is further noted that the monetite sample with a zeta potential closest to CAB (Ca/P ratio 1:0.68) also has the most similar $Q_{1.5}$ value (Table 4.2).

Monolayer adsorption of fluoride onto monetite was estimated considering a hydrated radius of fluoride ion as 3.5 Å (Conway 1981) and the EGME SSA values for monetite reported in Table 4.2. Assuming monolayer coverage, the average maximum fluoride adsorption capacity is 21 mg/g, which approaches but is less than the experimental Q_{max} value (30.3 mg/g) for monetite (Ca/P ratio 1:0.43) (Table 4.1). Thus, although monolayer coverage can account for a large portion of the fluoride removal capacity of the monetite, additional processes (e.g., formation of calcium and fluoride co-precipitates) may also contribute to fluoride removal.

Table 4.2: Properties of synthesized monetite and sulfuric acid activated cow bone

Description	**BET Specific surface area (SSA, m^2/g)**	**EGME[a] (SSA, m^2/g)**	**Zeta potential (mV)**	**% monetite of prepared media**	**($Q_{1.5}$, mg/g)[b]**
Monetite ($CaHPO_4$)					
Ca/P ratio 1:0.43	4.0	260 ± 1.8	27.1 ± 2.3	99	20.0 ± 1.2
Ca/P ratio 1:0.68	4.0	256 ± 2.1	8.3 ± 1.4	94	7.5 ± 2.6
Ca/P ratio 1:1.18	3.9	247 ± 1.5	-8.0± 1.1	89	1.8 ± 0.6
Chemically activated cow bone (CAB)					
CAB (30% HSCB)[c]	9.0	134	7.5 ± 2.1	58	6.4 ± 1.8

[a]EGME- ethelene glycol monoethyl ether
[b]Fluoride adsorption capacity at C_e = 1.5 mg/L
[c]NM- not measured
[d]data taken from Yami et al. (2016)

The XRD patterns of monetite prepared at various Ca/P ratios and the reference patterns are displayed in Figure 4.3. The XRD pattern of the monetite prepared in this study matches that of the reference pattern as well as Djošić et al. (2009) and Frost et al. (2013). The XRD pattern acquired for the high fluoride adsorption capacity monetite, Ca/P ratio 1:0.43, demonstrated that pure (99.6%) monetite (CaHPO4) obtained from whole pattern fitting is the primary phase present, with 0.4% being hydroxyapatite ($2\theta = 33^{o}$). Whole pattern fitting of the XRD patterns of the media prepared at Ca/P molar ratios of 1:0.68 and 1:1.18 also showed the presence of hydroxyapatite. The monetite synthesized at Ca/P ratio of 1:1.18 also showed biphosphammite peaks (at $2\theta = 17^{o}$, 24^{o}, 28.6^{o}, 34^{o}, 38^{o}, 40^{o}, 45.5^{o}, 53^{o}) which was not present in monetite prepared at Ca/P ratio of 1:0.43 or 1:0.68. The biphosphammite may have precipitated at the higher ammonium phosphate concentrations used to prepare monetite at Ca/P ratio of 1:1.18.

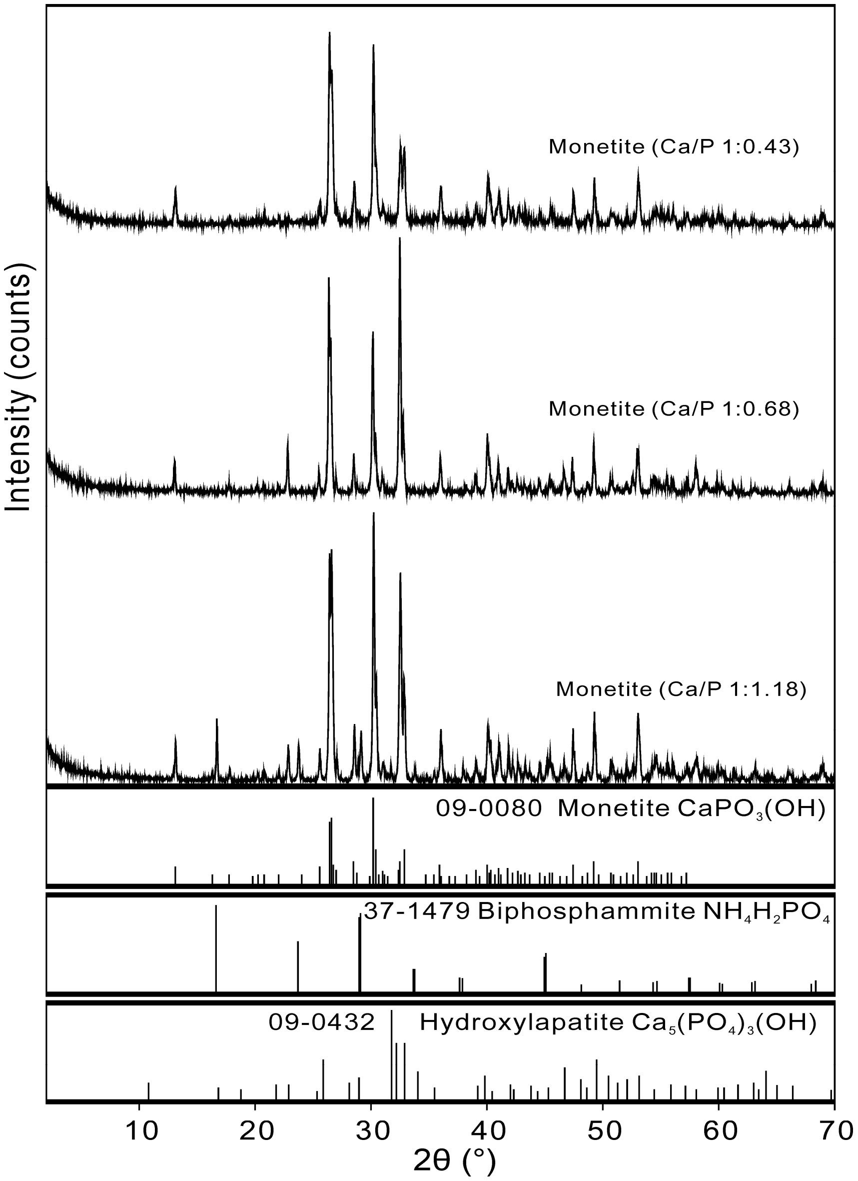

Figure 4.3: XRD pattern of synthesized monetite at Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18

This excess ammonium phosphate could have affected the surface chemistry of the monetite by release of ammonium or phosphate in a way that would hinder the fluoride adsorption capacity. To investigate this possibility, excess ammonium phosphate compared to $CaCl_2$ (1.18 M PO_4^{3-}, equivalent to the amount added to prepare monetite at Ca/P ratio of 1:1.18) was added to monetite containing fluoride solution and the fluoride adsorption capacity was tested. The result indicated that the additional PO_4^{3-} significantly reduced the fluoride adsorption capacity of the monetite originally prepared at Ca/P ratio of 1:0.43 (Figure 4.4). Therefore, excess phosphate could be the reason for the lower fluoride removal capacity of monetite prepared at a Ca/P ratio of 1:1.18 compared to that prepared at a Ca/P ratio of 1:0.43. The excess phosphate may have sorbed to the surface, reducing the zeta potential (Table 4.2), and hindering fluoride removal.

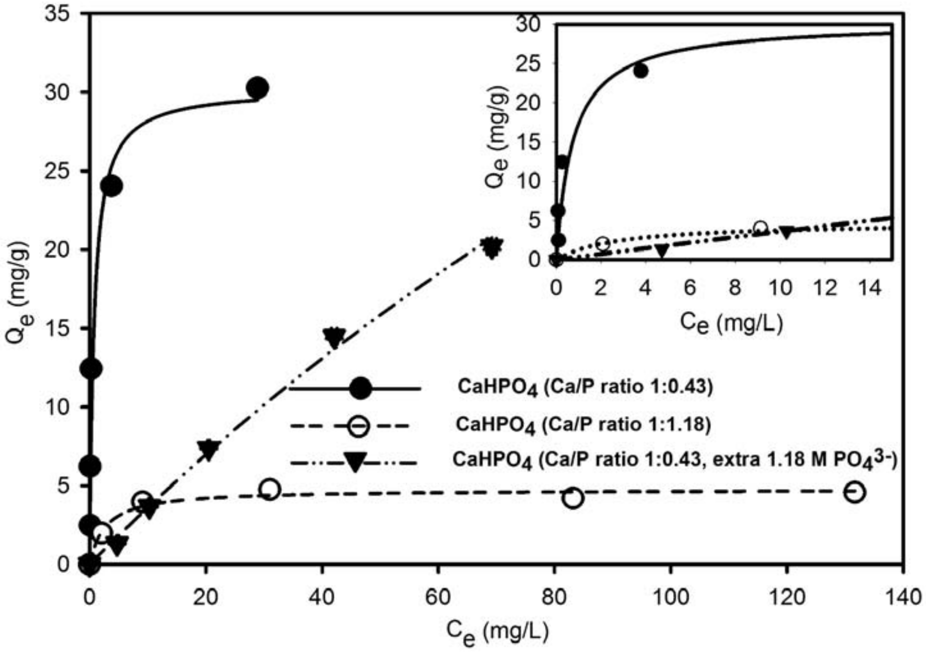

Figure 4.4: Isotherm showing effect of extra (1.18 M phosphate) added to monetite (prepared at Ca/P ratio of 1:0.43) containing fluoride solution.

Figure 4.5 shows the morphology of the monetite synthesized at Ca/P ratios of 1:0.43 (panel A, I and II), 1:1.18 (panel C, I and II) and the monetite after fluoride adsorption (Ca/P ratio 1:0.43 panel B, I). For the fluoride adsorbed sample, the initial fluoride concentration, equilibrium adsorption capacity (q_e), and equilibrium fluoride concentration (C_e) were 100 mg/L, 24 mg/g and 3.8 mg/L, respectively. All samples of monetite had micrometer-scale crystals. The monetite synthesized at Ca/P ratios of 1:0.43 and 1.18 had similar bundles of elongated and tabular crystal shapes (Figure 4.5, A and C). The fluoride adsorbed monetite had spikes on the surfaces of the crystals (Figure 4.5, panel B). Thus, Figure 4.5 A and B (monetite prepared at Ca/P ratio of 1:0.43, before and after fluoride adsorption) demonstrate the morphology changes that can occur upon sorption of fluoride.

Figure 4.5, (panel B'**)** shows EDS spectra of the monetite prepared at Ca/P ratio of 1:0.43 after fluoride adsorption. The EDS analysis had shown the presence of fluoride, demonstrating that fluoride had been adsorbed on the media. Additionally, the detection of more than 1% by weight fluoride indicates more than monolayer coverage i.e., not just adsorption.

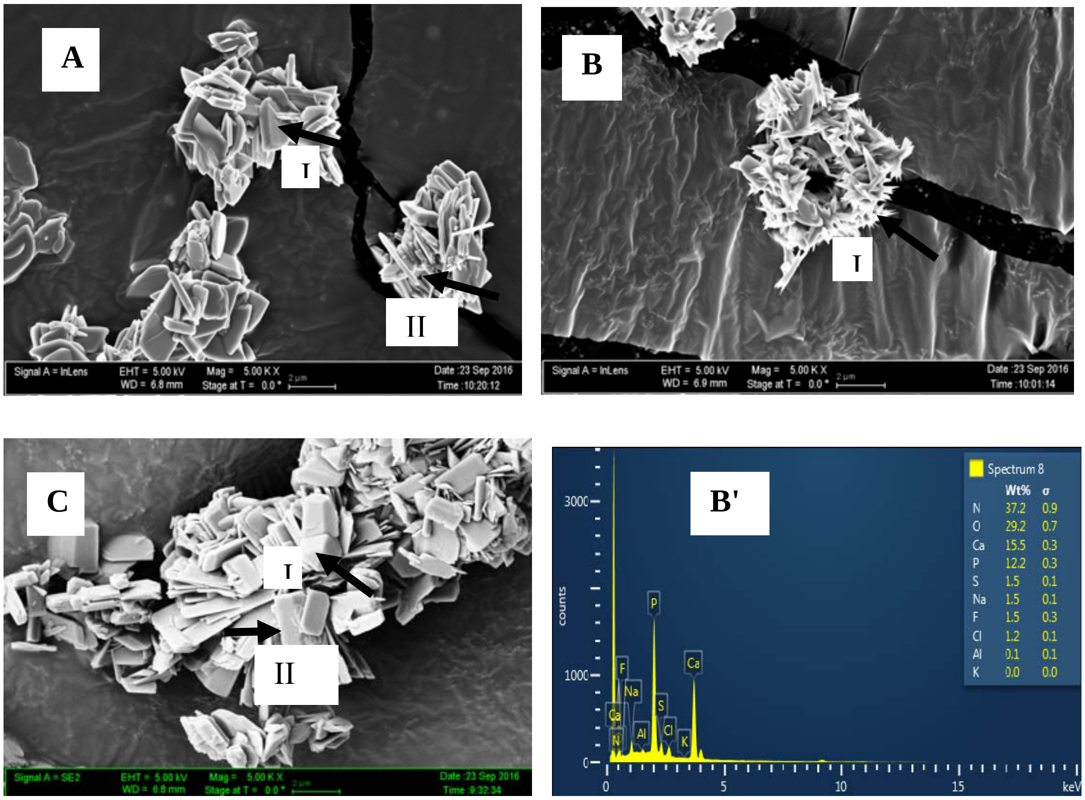

Figure 4.5: SEM images for monetite synthesized at Ca/P ratio of 1:0.43 and 1:1.18 (panel A and C, respectively) before fluoride adsorption, and panel B for Ca/P 1:0.43 after fluoride adsorption. Panel B´ shows Energy Dispersive X-ray Spectroscopy (EDS) for monetite prepared at Ca/P ratio of 1:0.43 (after fluoride adsorption). The dark arrows in panels A, B and C show the shape and morphology of the synthesized monetite (I and II), and EDS analysis showing N, O, Ca, P, S, Na, F, and Cl peaks.

4.4.3 Effects of competing ions on fluoride removal capacity of monetite

Figure 4.6 shows the effect of competing ions on the fluoride removal of monetite. The competition study was conducted at pH 7. The major anions reduced the fluoride adsorption capacity of monetite in the order of HCO_3^-, NO_3^-, SO_4^{2-} and Cl^-. Of all the competing ions considered, HCO_3^- completely inhibited the fluoride removal capacity of monetite (data not shown). In this study, it was observed that HCO_3^- raised the pH of the solution during the adsorption process to 7.6, while the pH of the remaining competing ions was 7.02 on average. This phenomenon is in agreement with Onyango et al. (2004) who discussed how bicarbonate raises the solution pH and thus diminishes the affinity of the active sites for fluoride. Other competing ions such as nitrate, sulfate and chloride reduced the fluoride adsorption capacity up to 30% on average (Figure 4.6). Chloride (Cl^-) had less impact on the fluoride adsorption capacity as compared to NO_3^- and SO_4^{2-}. Tor et al. (2006) suggested that Cl^- forms outer-sphere complex, while SO_4^{2-} forms outer-sphere and inner-sphere complexes with surface active sites, which could account for the difference in extent of competition of these anions for the adsorption site with fluoride.

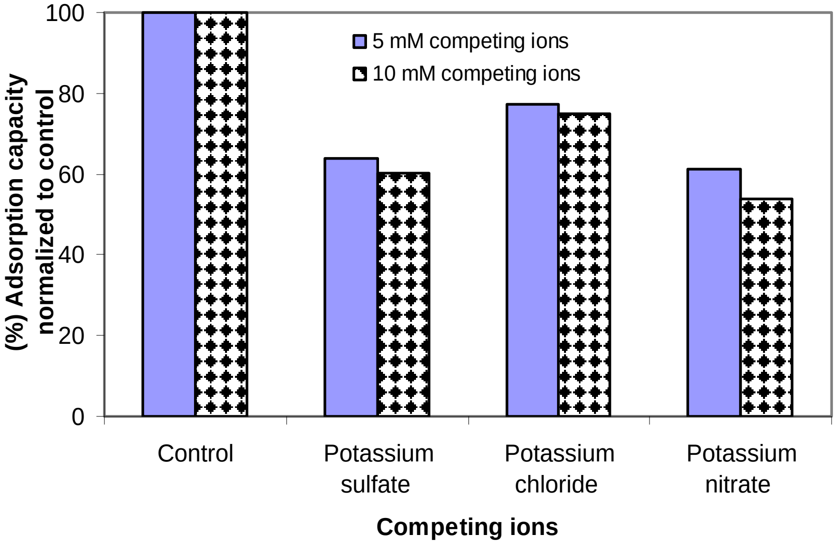

Figure 4.6: Effect of competing ions on the fluoride removal capacity of synthesized monetite. The control shows the monetite's adsorption capacity without addition of competing ions. The error bars are not seen since their magnitudes are small.

4.5 Conclusion and recommendations

The high-purity (99.6%) monetite ($CaHPO_4$) prepared in this study demonstrated a three-fold higher fluoride adsorption capacity than chemically activated cow bone, CAB (the fluoride adsorption capacities at an equilibrium fluoride concentration of 1.5 mg/L ($Q_{1.5}$) were 20.0 mg/g and 6.4 mg/g for monetite and CAB, respectively). This shows that monetite is an active component of CAB in terms of fluoride removal, and is itself a promising fluoride sorbent. In contrast, bassanite had negligible fluoride removal capacity and thus does not contribute to the adsorption capacity of CAB prepared with sulfuric acid. The Ca/P ratio of the chemical reagents was found to significantly affect the fluoride removal capacity of resulting monetite ($Q_{1.5}$ = 20.0 ± 1.2, 7.5 ± 2.6 and 1.8 ± 0.6 for Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18, respectively). The EGME specific surface area (SSA) of monetite (Ca/P 1:0.43) is twice that of the CAB media (260 m^2/g vs 134 m^2/g) and thus may account for a portion of the three-fold higher capacity of monetite versus CAB, but cannot explain the variation in fluoride uptake across the monetite media prepared with different ratios of Ca to P. The increased capacity of monetite (Ca/P ratio 1:0.43) compared to CAB can also be partly attributed to its higher zeta potential (27.1 mV and 7.5 mV, respectively). The presence of potassium bicarbonate completely inhibited the fluoride removal capacity of monetite while potassium nitrate, potassium sulfate and potassium chloride reduced the fluoride adsorption capacity of monetite up to 30% on average. In summary, monetite shows significant fluoride removal capacity and potential for mitigating the negative health impacts of excess fluoride in drinking water. The next chapter uses business model tool to evaluate the sustainability and viability of fluoride treatment systems as a business.

4.6 Acknowledgment

This work was funded in part by The University of Oklahoma Water Technologies for Emerging Regions (WaTER) Center, the Sun Oil Company Endowed Chair, and the Ken Hoving Graduate College Fellowship. The authors are highly indebted to Dr. Andrew Madden for XRD and BET analytical assistance, Dr. Preston Larson for SEM /EDS analysis, Ms. Andria Hedrick for zeta potential analysis, and Dr. Junyi Du for his assistance during sample characterization.

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Chapter 5: Using Business Models in Designing Market-Based Solutions: The Case of Fluoride Treatment Systems[5]

Abstract

This paper addresses how businesses models inform viability of different fluoride treatment technologies for developing countries as well as the pursuit of financial and operational sustainability. Excess fluoride concentrations in drinking water supplies negatively impact the health of communities living in fluoride affected regions of the world by causing dental and skeletal fluorosis and other severe socio-economic problems. Given that fluoride mitigation solutions have proven elusive, we apply business model logic to compare fluoride removal technologies to examine the financial sustainability of water service provisions. We analyze the investment cost of producing fluoride safe water, the annual revenues generated, and the net benefits obtained from different technologies. Furthermore, the reduced medical costs and productivity losses averted due to access to fluoride safe water can lead to an average annual cost saving of $67 per person. Our results validate the use of business models to help evaluate different technologies as a means of pursuing sustainable applications for safe drinking water.

Key words: Business models, Technological and economic sustainability, Chemically activated cow bone, Electrolytic defluoridation Fluoride, Nalgonda

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[5] This chapter or portions thereof has been accepted in *Journal of Water, Sanitation and Hygiene for Development* in collaboration with Dr. David A. Sabatini and Dr. Lowell W. Busenitz under the title "Using Business Models in Designing Market-Based Solutions: The Case of Fluoride Treatment Systems". J. Water Sanit. Hyg. 2017 (accepted). The current version has been reformatted for this dissertation.

5.1 Introduction

The global need for sustainable solutions to provide basic human needs (e.g., safe drinking water) has never been greater. As human needs mount, it is becoming increasingly apparent that entities such as governments, foreign aid and non-governmental organizations are unable to meet these mounting needs. Getting to viable solutions is increasingly being connected with business models to implement sustainable solutions that incentivize key input providers to the final users. A business model describes the system of interdependent activities that are performed by the firm and its partners, and the mechanisms that link these activities to each other to deliver value (Chesbrough 2010; Zott & Amit 2010). For example, Wüstenhagen & Boehnke (2006) demonstrated that barriers to sustainable energy can be addressed with innovative business models. More broadly, it is becoming increasingly recognized that well designed business models have the potential to address prevailing global problems including sustainable development (Wilson & Post 2013).

This chapter focuses on the sustainable supply of safe drinking water in developing countries. To address this growing problem of high fluoride concentrations in drinking water, our purpose is to show how the use of business models can help lead to more sustainable fluoride solutions. More specifically, we address the fluoride affected water in the Rift Valley of Ethiopia as a pathway for considering the viability of such an approach throughout the developing world. The business model is used as a tool to set up a sustainable market-based scale-up of defluoridation (fluoride removal) systems so that safe drinking water can become the norm rather than the exception in these areas. Our objectives are the following:

1. To extend the use of business models into social needs where market-based solutions and sustainability are becoming increasingly valued; we specifically address the safe drinking water issue.
2. To show the relevance of business models in evaluating alternative approaches to a given business activity; specifically to the application of defluoridation of drinking water.
3. To compare viability of fluoride treatment technologies as a business venture.

By using the businesses model approach, we show how one can assess and compare viability of different fluoride treatment methods. This has significant implications for financial and operational sustainability. In discussing the business model logic and its principal components, we are able to show relevance to the operations of safe water supply services where unsafe levels of fluoride are a major problem. We explicitly address fluoride challenges instead of other water contaminants because fluoride is one of the most pervasive problems in developing countries. This sets up the viability of business models in addressing fluoride challenged areas as a template for many other safe drinking water issues.

5.2 Business model logic

Business models seek to address fundamental questions such as – who are the customers, what do they value, how the business deploy its assets, and how value can be delivered to the customer at an appropriate cost (Osterwalder et al. 2005; Zott & Amit 2010). Business models consist of both a quantitative assessment of how it makes a financial return and a narrative of how the business works. Business sustainability depends on the quality of services it offers to the customers, its focus on addressing the unmet needs, value-additions, and the ability to link technical and socio-economic issues relevant for delivering value to customers (Chesbrough 2010).

While business models were first explicitly applied to electronic commerce (online shopping), they are now utilized in most industries including markets in developing countries (Brown et al. 2009). By extension, our assumption is that applying business model logic to safe drinking water needs in developing countries has great potential. The development of business models and the creative thinking that they encourage are likely to be critical for the development of sustainable services involving basic human needs in developing countries. The use of business model logic can be very instrumental in better articulating how basic human services and needs, such as water, can be met in a more sustainable manner.

5.3 Business models for safe water supply services

Small-scale private water service providers are emerging as a common and reliable deliverer of water in areas with significant population. With the efficient utilization of resources, private water treatment systems are able to achieve sustainability and make an adequate return to continue with services (Kariuki & Schwartz 2005). However, publicly owned services tend to be intermittent in their provisions of water and they usually need subsidies to continue operations (Guidthai 2008). The delivery of water purchased from boreholes and water kiosks to end users has been documented in places such as Onitisha, Nigeria (Whittington et al. 1991), peri-urban areas of South America, urban areas of Sub-Saharan Africa (Solo 1999), and Mumbai, India (Angueletou-Marteau 2007). Private water service providers are increasingly proving effective for areas that historically have not had access to safe water. By extension, we assume that suitably designed business models can help address existing problems related to safe water supply services, even in the more rural areas of developing countries.

Significant efforts have been made to examine and reform water delivery in populated areas of developing countries over the past several decades. Unfortunately, only very limited attention has been focused on rural water supply services and virtually no attention has been given to the scaling of the defluoridation of water. Sustainability of safe water supply schemes is constrained by social, technical, financial, institutional and environmental issues (Brikké & Bredero 2003). Some of the common problems faced by safe water supply services in Ethiopia include availability of spare parts, chemicals, operation and management capacity, tariff collection, and water quality issues (Israel & Habtamu 2007). As a result, the non-functionality rates of the developed safe water supply schemes are high (Abebe & Deneke 2008).

This paper argues that business models can help identify and correct the prevailing sustainability challenges faced by safe-water supply services. More specifically, since safe-water technologies are central and the early step in addressing this huge need, we address the technology side of business models in seeking sustainability socially and economically. This is foundational to the development of sustainability of the safe water supply services.

Drinking water fluoride concentrations in the Ethiopian Rift Valley range from 1 to 33 mg/L with an average value of 5 mg/L (Haimanot et al. 1987). Beyond dental and skeletal concerns, fluorosis has significant socio-economic impacts stemming from the skeletal fluorosis (Apambire et al. 1997; Frank et al. 2011). Moreover, the prevalence of fluorosis and the related health problems is very prevalent and has stigmatized entire villages (Mcknight et al. 1997; Frank et al. 2011). One community-based survey revealed 65.7% skeletal fluorosis among adults (Tekle-haimanot et al. 2006). While our experience here is connected to the fluoride affected areas in the Rift Valley of Ethiopia, the implication of this paper will likely have considerable applicability throughout the developing world. The business model concept is used to set up a sustainable market-based scale-up of defluoridation systems so that safe drinking water can be more widely obtained.

5.4 *Defluoridation technologies*

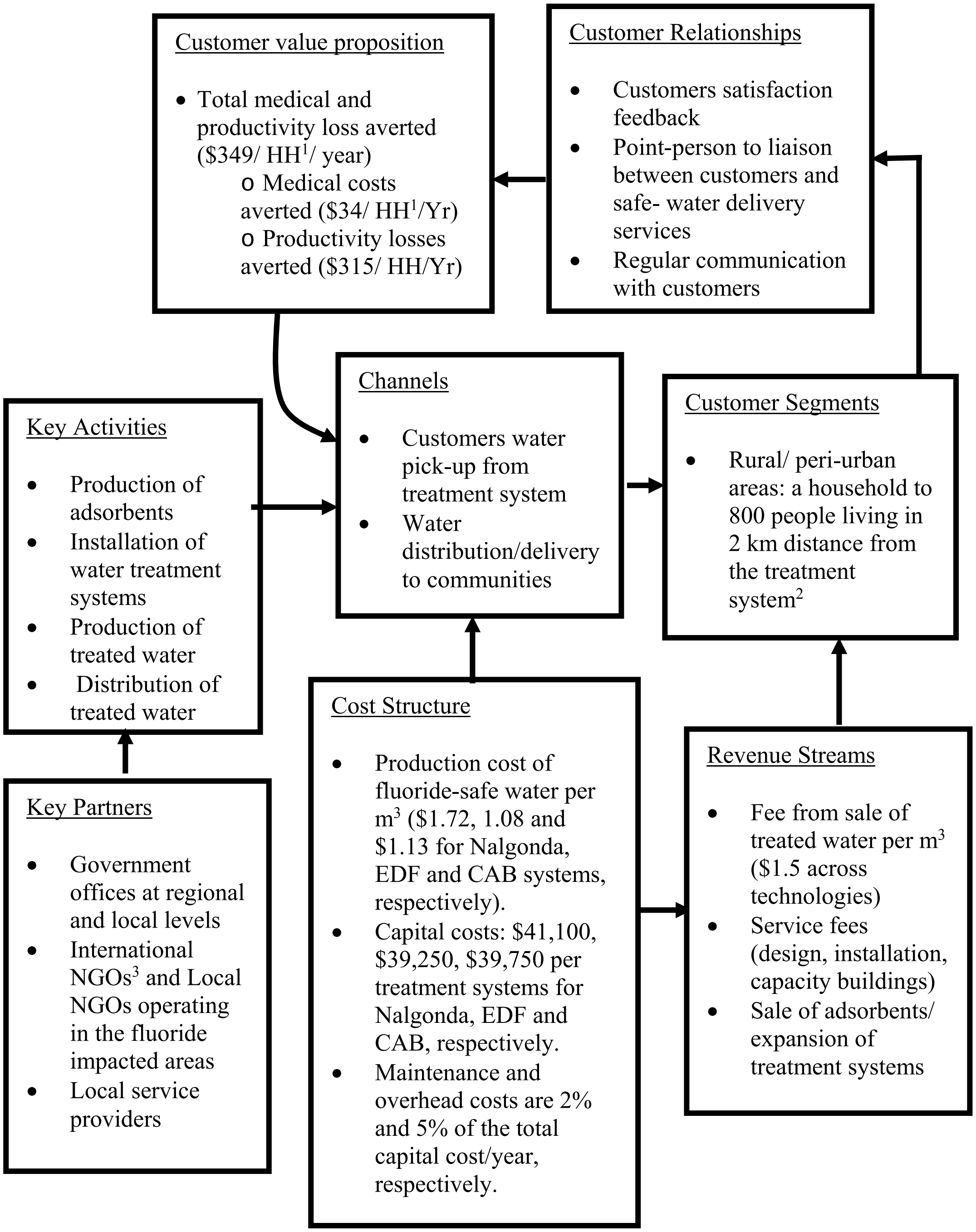
Among various technologies developed and implemented to remove excess fluoride concentrations from drinking water supplies, the Nalgonda and bone char techniques have most commonly been implemented in developing countries such as Kenya, Tanzania, Ethiopia and India (Ayoob et al. 2008; Frank et al. 2011; Osterwalder et al. 2014). The Nalgonda technique, the process of aluminum sulfate based coagulation-flocculation-sedimentation, was developed and adapted in India for fluoride removal. The cow bone-based treatment system uses thermally treated cow bone (bone char) for fluoride removal. However, the low fluoride removal capacity of bone char needs further enhancement. Recently, a high fluoride removal capacity chemically activated cow bone (CAB) media has been developed by Yami et al. (2016). A pilot study conducted in the Rift Valley of Ethiopia by the University of Oklahoma's Water Technology for Emerging Regions (WaTER) Center in summer 2014 and 2015 indicated that CAB had about four-fold higher fluoride removal compared to bone char. Electrolytic defluoridation systems (EDF) use aluminum electrodes that release Al^{3+} ions by an anodic reaction with subsequent aluminum precipitation; the fluoride removal occurs at the precipitate surface and settles out of solution with the precipitate. In this study the Nalgonda, chemically activated cow bone (CAB), and electrolytic defluoridation techniques were considered for comparison using business model tools.

5.4.1 Challenges faced by existing defluoridation systems

Very limited effort is currently focused on addressing the fluorosis problems in developing countries (Frank et al. 2011). For example, defluoridation of drinking water in the Ethiopian context has been impractical because it is also expensive, technically unattainable by technologies evaluated, and unsustainable for large populations. However, defluoridation systems can be considered at the household and small community levels. Defluoridation systems in Wonji-Shoa Irrigation scheme in Ethiopia used activated alumina which was expensive and had logistical constraints with operations and maintenances (Teklehaimanot et al. 2006). Reasons for poor sustainability of past fluoride treatment systems include the lack of capacity to manage defluoridation systems, lack of chemical supply chains, high cost of chemicals, limited financial management skill, and lack of skilled labor to install and operate the treatment systems (Bregnhøj 1997; Brunson et al. 2013). In addition, there is no engagement of private sectors in the defluoridation processes. As a result, the fluoride removal technologies developed thus far have not proven sustainable.

5.4.2 Business model for defluoridation of drinking water

The defluoridation technologies considered in this study are the Nalgonda system (uses aluminum sulfate and lime), EDF (uses aluminum electrode), and CAB (uses cow bone activated using acid and base chemicals). The business models proposed for fluoride removal from drinking water supplies (Figure 5.1) is expected to help entrepreneurs evaluate where the challenges are with each water technology and which ones are the most likely to get to sustainability.



Customer value proposition

- Total medical and productivity loss averted (\$349/ HH^1/ year)
  - Medical costs averted (\$34/ HH^1/Yr)
  - Productivity losses averted (\$315/ HH/Yr)

Customer Relationships

- Customers satisfaction feedback
- Point-person to liaison between customers and safe- water delivery services
- Regular communication with customers

Key Activities

- Production of adsorbents
- Installation of water treatment systems
- Production of treated water
- Distribution of treated water

Channels

- Customers water pick-up from treatment system
- Water distribution/delivery to communities

Customer Segments

- Rural/ peri-urban areas: a household to 800 people living in 2 km distance from the treatment system^2

Key Partners

- Government offices at regional and local levels
- International NGOs^3 and Local NGOs operating in the fluoride impacted areas
- Local service providers

Cost Structure

- Production cost of fluoride-safe water per m^3 (\$1.72, 1.08 and \$1.13 for Nalgonda, EDF and CAB systems, respectively).
- Capital costs: \$41,100, \$39,250, \$39,750 per treatment systems for Nalgonda, EDF and CAB, respectively.
- Maintenance and overhead costs are 2% and 5% of the total capital cost/year, respectively.

Revenue Streams

- Fee from sale of treated water per m^3 (\$1.5 across technologies)
- Service fees (design, installation, capacity buildings)
- Sale of adsorbents/ expansion of treatment systems

Note:

[1] HH stands for household

[2]The East Shewa Zone (where defluoridation systems are currently installed) average population density of 181.7 persons/km^{2}s (CSA -2005 National Statistics, Table B.3 & B.4) was used to estimate the customers

[3]NGOs stands for Non-Governmental Organizations

Figure 5.1: Proposed business model for provision of fluoride-safe water services

In this study, five principal components of business models are considered and discussed.

Customer Value Proposition. Value proposition is the value created or the benefits offered to customers (Chesbrough 2007). Fluoride removal technologies in developing countries may provide substantial cost saving advantage through averting costs incurred due to the negative health impacts associated with excess fluoride concentrations in drinking waters. Communities living in developing countries are exposed to dental and skeletal fluorosis thereby incurring medical costs despite their meager income. Furthermore, crippling skeletal fluorosis exposes communities to wage and productivity losses due to restricted mobility.

The proposed business model thus provides findings from the analysis made on cost savings that can be achieved in providing fluoride-safe water to the communities. Based on this analysis, the fluoride removal technologies provide an annual average cost saving of $349 per household due to averted medical cost and productivity loss (Figure 5.1, Table D.1.1).

Customers. The target customers are women, men and children (11 Million people) living in the Rift Valley of Ethiopia and beyond. Additionally, public institutions such as schools and health posts are among the target customers. The proposed customers for the fluoride treatment systems are rural and peri-urban areas with a population ranging from one household to 800 persons living within 2 km of the treatment systems.

Cost Structure. Costs include key activities such as manufacturing and installation of components of defluoridation systems, production of adsorbents, distribution of adsorbents and/or treated water, and other marketing and customers' capacity building costs.

Revenue generation mechanism(s). Revenue refers to how the firms are compensated for the value offered sustainably (Lindgardt at al. 2009). The revenue generation mechanism in this business model is the fee collected from sale of fluoride-safe water and adsorbents to the customers, and expansion of treatment systems into adjacent communities. Additional revenue is expected to be generated from services costs such as design, installation, and capacity building training offered to customers and local government offices.

Value network and strategy to remain competitive. A value network analysis is a means to evaluate and improve the capability of a business to convert assets into other forms of value to realize greater value (Allee 2008). Continuous innovations in a business model, considering changing markets, technologies, and legal structures can help achieve advantages by creating unique and hard to replicate products and services. Further, correct design of business model, implementation and refining are key factors in success and sustainability of businesses (Teece 2010). To remain competitive, the business model strategy is framed around offering sustainable services through provision of safe- treated water which meets the WHO Standards of 1.5 mg fluoride/L guideline value by supporting local government offices and communities to participate in monitoring and evaluation of the water quality. Additionally, creation of a customer data base and communicating with them regularly are among the strategies proposed to establish a successful fluoride- safe water based business. A trained point-person will be deployed to facilitate communication with customers.

The planning of the defluoridation systems envisages working and aligning with existing government and international and local non-governmental organizations (NGOs) plans to expand safe water supply services to the community. Identification of additional funding sources besides the government, such as local and international NGOs, is important. Suppliers of raw materials/ inputs and key partners including private firms will be identified and capacity building trainings will be provided to enhance their engagement in the expansion of defluoridation systems. A central adsorbent production facility will be established by private firm(s). Local service providers participate in supply of raw materials and chemicals. Water distribution will be conducted by trained local service providers at the water point/kiosk. Local donkey/horse carts, bajaj (three-wheeled motorcycle), and small truck owners participates in the distribution of treated water to communities living far from the water point/kiosk.

Figure 5.2 shows details of the processes involved in delivering a fluoride- safe water enterprise (FSWE) in partnership with local service providers and local government offices to undertake design, production and installation of fluoride treatment systems. FWSE additionally undertakes production of treated water and capacity building works to local government and local service providers. Local service providers participate in supply of raw materials and chemicals, and distribution of treated water. The shaded boxes in Figure 5.2 indicate activities performed by FSWE in partnership with local service providers, local NGOs and government offices, and the white boxes are the activities performed by FSWE.

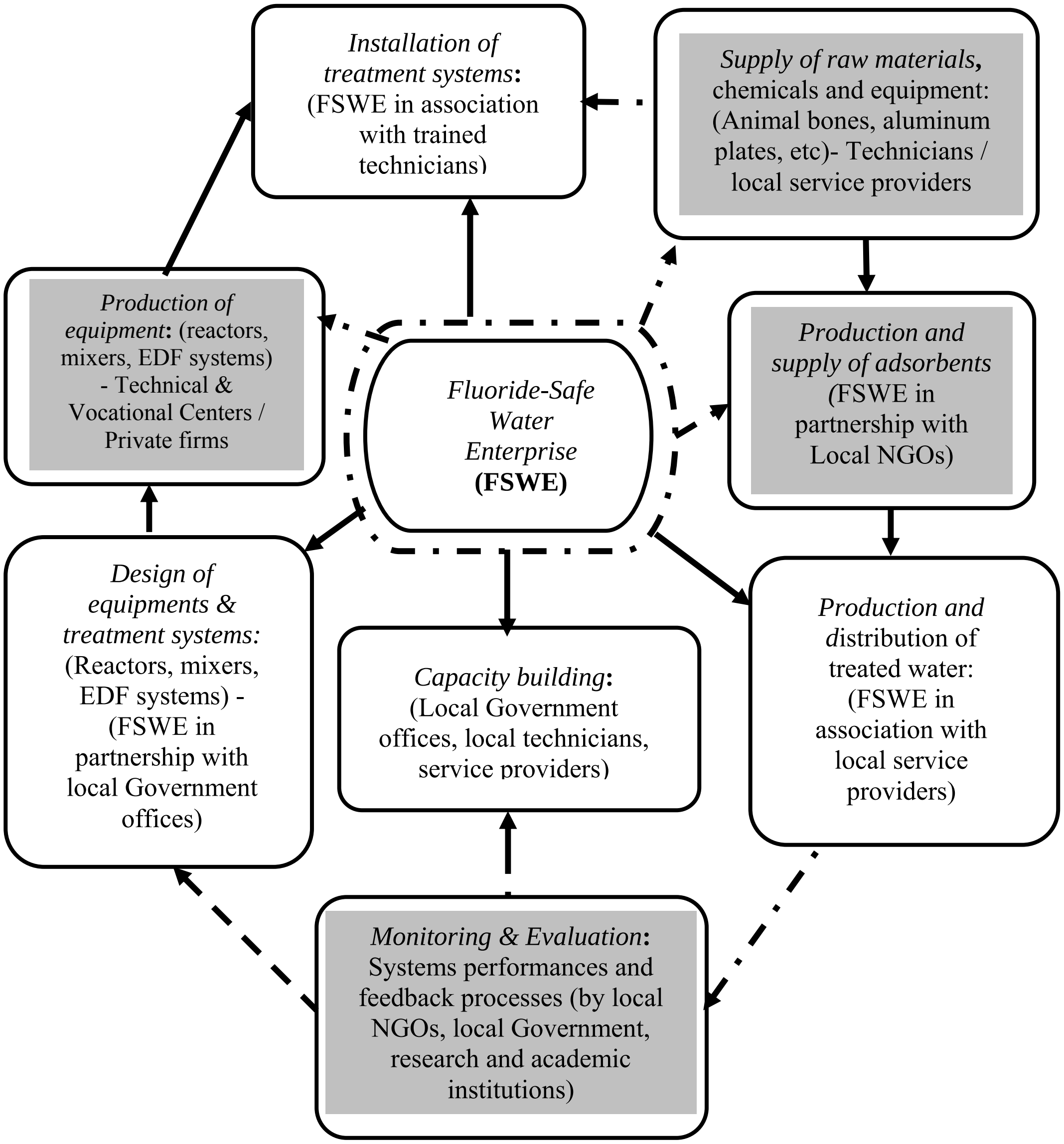


Figure 5.2: Processes involved in production and distribution of fluoride- safe water

5.5 Building blocks

The following building blocks and assumptions were made in development of the business model:

- Cost of infrastructure development i.e., well development, installation of casing and pump, and electromechanical equipment that are common to the Nalgonda, EDF and CAB- based systems were not considered in this analysis/comparison. These costs were assumed to be covered by the government and/ or NGOs.
- Maintenance cost for main systems components such as wells, pumps and generators maintenance or replacement were assumed to be covered by the government and/ or NGOs.
- \$ 1.5 per m^3 of treated water was considered uniformly for all the three technologies as a cost of water to determine the total revenue generated from the sale of treated water based on the discussion made during summer 2014 with the communities living in the Rift Valley of Ethiopia on the affordability and willingness to pay.
- Routine maintenance cost was assumed to be 2% of the water treatment system cost.
- Operational costs include chemicals, labor cost (salaries, perdiems and systems washing and replacement of chemicals), fuel, and overhead cost of firms responsible for operating the safe water supply systems. Overhead costs were assumed to be 5% of the total water treatment systems cost.

- Dodo Wadera, Woyo Gabriel and Berta Semi communities in the Rift Valley of Ethiopia were considered as target communities in this study (Table D.1.1), using data from these communities to set up a value proposition, analyze costs incurred in the water treatment processes, and corresponding revenues generated from the proposed safe water supply systems.

5.6 Results and discussions

5.6.1 Results

Figure 5.1 shows the business model developed to address the prevailing problems of fluoride treatment systems in developing countries and beyond. Table 5.1 shows comparison of three fluoride removal technologies namely, Nalgonda, EDF, and CAB using economic criteria and the business model concepts. The Nalgonda, EDF, and CAB systems have an average production cost of \$1.72, \$ 1.08, and \$1.13 per m^3 of treated water, respectively (Table 5.1 and Table D.1.2). It can be observed from Table 5.1 and Table D.1.3 that the total revenue generated from sale of treated water for each system is \$ 9,855. Cost of production of treated water per year is \$ 11,300, \$ 7,100 and \$ 7,400 for Nalgona, EDF and CAB, respectively (Table 5.1 and Table D.1.3). A total cost saving of \$349 per household (HH) per year (\$34/HH/Yr and \$315/ HH/Yr for medical and productivity losses averted, respectively) can be achieved due to the use of fluoride-safe water (Figure 5.1). Table 5.1 shows a net-profit per year of (\$1,445), \$2,755, and \$2,455 for Nalgonda, EDF and CAB, respectively. Table D.1.4 shows a comparison of the three fluoride treatment systems: Nalgonda, EDF and CAB using technical, economical and operation and management aspects. The comparison of the performance of these treatment technologies are made based on the analysis of the information collected from field works in the Rift Valley of Ethiopia and literature study. The data used in this comparison are summarized in Tables 5.1 and Table D.1.4.

Table 5.1: Economic criteria for comparison of defluoridation systems (see supplemental data for detailed calculations).

	Fluoride removal technologies		
Description	**Nalgonda**	**Electrolytic Defluori-dation**	**Chemically activated cow bone (CAB)**
Production cost of treated water (\$/ m^3)	1.72	1.08	1.13
Total cost of production of treated water (\$/year) per treatment system	11, 300	7,100	7,400
Total revenue generated from sale of treated water (\$/ year)	9,855	9,855	9,855
Net profit per treatment system (\$/year)	(1,445)	2,755	2,455
Considering 50 treatment systems operated per year, net benefit (\$/year)	(72,250)	137,750	122,750

5.6.2 Discussions

This study shows that EDF and CAB are more cost effective than Nalgonda system due to relatively lower production, installation and operation and management costs of these systems. Furthermore, the EDF and CAB offer significantly higher net annual benefit (profit) than the Nalgonda system (Table 5.1). The EDF and CAB have better fluoride removal capacity, and less daily operational requirements than the Nalgonda system. Additionally EDF system produces much lower sludge compared to the Nalgonda system, and CAB media does not produce sludge.

Currently, communities in the Rift Valley of Ethiopia typically pay \$ 1 per m^3 of water at the water point even though the treated water does not meet the WHO guideline value of 1.5 mg/L (WaTER center baseline survey, 2014). The baseline survey additionally indicated that communities have high demand for fluoride safe-water and are willing to pay more for fluoride safe water; their ability to do so is reflected by the observation that they have been paying up to \$ 4 per m^3 from distant sources when water is not available in their area. The profitability of fluoride-safe water system coupled to the averted medical and productivity losses may raise government interest to support expansion of fluoride treatment systems and also attract private-firms to participate in the adaption of the business model.

The existing fluoride related health problems and poor sustainability of treatment systems highlighted by Bregnhøj (1997) and Brunson et al. (2013) are the main drivers for business model entrepreneurship opportunities for defluoridation of drinking water identified in this study. Comparisons of defluoridation systems of drinking water were performed using the business model as a tool to help identify technologies that can be sustainably utilized by the local community. Socio-cultural aspects, customer demand, marketing and distribution, and access to financial sources were given due consideration in comparing the viability of defluoridation systems to deliver value in line with Chesbrough (2010). The business model developed in this study clearly stipulated the partners involved, identified key resources leading to success, customer segments and costs associated and the revenue generated from the fluoride- safe water supply services. The comparison of the business models is made considering cost savings achieved due to access to fluoride- safe water, cost of water treatment, annual revenue and benefits generated.

Business models focus attention on the potential of ventures that will be responsible for the production of treatment systems in partnership with local service providers, installation of the system, and treatment of fluoride impacted water, distribution of treated water, and over all operation and management of treatment systems (Figure 5.1). Business models bring together a system of interdependent activities to deliver value as developed by Chesbrough (2010) and Zott & Amit (2010). This study demonstrated that a business model is a useful tool to address the prevailing challenges encountered by safe water supply services. Business models can help develop and expand safe-water technologies that strive to realize both social and financial returns, and thereby ensure sustainability of the safe water supply services.

Understanding the existing challenges, working with local government, non-governmental organization and communities, and involving academic and research institutions will help facilitate scaling up of a market-based solutions to the existing safe- water supply crisis. The private sector/ local service providers play a significant role in the scale up of defluoridation technologies by actively engaging in production and installation of treatment systems, and supply of equipment and chemicals. Additionally, the private sector/ service providers can produce adsorbents, treat fluoride impacted water, and distribute treated water and undertake operation and management works. However, incentive mechanisms to private sectors (e.g., provision of tools such as plumbing, masonry and carpentry) need to be put in place to maintain their continuous engagement in scale up of the treatment systems. Capacity building to local private firms i.e., technical, financial and business management are also key in sustaining the business. We also suggest that governments concerned with safe-water supply provisions need to develop policies that can enhance participation of private sectors in expansion of defluoridation systems e.g. provision of credit mechanisms.

5.7 Conclusions and recommendations

This study indicates that significant cost savings can be achieved from the fluoride- safe water service provision due to the medical costs and productivity losses averted amounting up to $349 per household per year. We have shown how the business model can be an effective tool in evaluating different technologies for the provision of fluoride -safe water supply services by solving the existing constraints of equipments and chemicals supply for defluoridation systems. The inclusion of business model logic in this domain also brings attention to technology and economic sustainability issues for those involved with getting safe water to end-users. By comparing the viability of the various treatment technologies for fluoride removal, we show how the business model can be used as a tool to examine differences. In this study, EDF and CAB- based fluoride treatment systems produced fluoride-safe water at lower cost, more manageable maintenance and generated higher profit compared to the Nalgonda system.

5.8 Acknowledgment

This work was funded in part by The University of Oklahoma Water Technologies for Emerging Regions (WaTER) Center, the Sun Oil Company Endowed Chair, and the Ken Hoving Graduate College Fellowship.

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Chapter 6: Conclusions

The purpose of this chapter is to summarize key findings and knowledge gained from the individual chapters of this dissertation. Major conclusions from the works conducted in each chapter are provided and future recommendations are enumerated at the end. The overall goal of this dissertation was to prepare, evaluate and characterize the chemically activated cow bone (CAB) and monetite for fluoride removal from drinking water. Various chemicals and conditions of preparation of CAB and monetite were evaluated in this dissertation to formulate an efficient and effective fluoride adsorbent. Additionally, the effectiveness of the CAB media produced in the lab was evaluated using natural groundwater in the Rift Valley of Ethiopia.

In Chapter 2, the CAB media was prepared in the laboratory and the fluoride removal capacity was evaluated. The comparison of the fluoride adsorption capacity CAB media showed on average about four-fold higher fluoride adsorption capacities than thermally activated cow bone (bone char). The formation of the bassanite and monetite minerals during chemical activation of cow bone was thought to be responsible for the high fluoride adsorption capacity. Further, the CAB media achieved a higher mass recovery value than bone char due to fines lost during thermal activation. Chemical activation of cow bone was also found to be a more cost-effective production process than thermal activation.

In Chapter 3, the CAB media produced in the laboratory was tested using natural groundwater in the Ethiopian Rift Valley. Additionally, CAB media was produced in the field using locally available chemicals and equipment and its fluoride removal capacity was evaluated using small and large field columns. The results demonstrated that the CAB media can be produced in the field using locally available raw materials and equipment. Laboratory batch adsorption studies and small-scale and large-scale column studies conducted on CAB produced both in the laboratory and the field had four-fold higher fluoride removal capacities compared to bone char. The water quality analysis conducted on samples collected from CAB treated water meets the WHO guidelines for drinking-water quality. Additionally, it was found out that the CAB media can be regenerated using 0.01 M $Ca(OH)_2$ solutions.

In Chapter 4, as it was discussed in chapter 2 above, the high fluoride removal capacity of the CAB media was attributed to bassanite and monetite minerals shown during the process of chemical activation of cow bone. In this chapter, monetite ($CaHPO_4$) and bassanite ($CaSO_4.0.5H_2O$) minerals were prepared in the laboratory and their fluoride removal capacity was evaluated. The high-purity (99.6%) monetite ($CaHPO_4$) prepared in this study demonstrated a three-fold higher fluoride adsorption capacity than the CAB media. This shows that monetite is an active component of CAB in terms of fluoride removal, and is itself a promising fluoride sorbent. In contrast, bassanite had negligible fluoride removal capacity and thus does not contribute to the adsorption capacity of CAB. The Ca/P ratio of the chemical reagents used in preparing the monetite was found to significantly affect the fluoride removal capacity of resulting monetite. The higher EGME specific surface area and higher zeta potential of the monetite prepared at Ca/P ratio of 1:0.43 versus the CAB media may account for a portion of the three-fold higher capacity of monetite versus CAB media. The presence of potassium bicarbonate completely inhibited the fluoride removal capacity of monetite.

In Chapter 5, the viability of fluoride treatment systems were evaluated using business model tool. Previous studies indicated that fluoride treatment systems installed in developing countries have either not been used or are non-functional. In this dissertation, business model tool was used to evaluate the viability of fluoride treatment systems. Furthermore, by comparing the viability of the various treatment technologies for fluoride removal, it was attempted to show how the business model can be used as a tool to examine differences. In this dissertation, electrolytic defluoridation system (EDF), CAB, and Nalgonda based fluoride treatment systems were compared using business model tool and it was found that the EDF and CAB produced fluoride-safe water at lower cost, more manageable maintenance and generated higher profit compared to the Nalgonda system. Additionally, the result indicated that significant cost savings can be achieved from the fluoride- safe water service provision due to the medical costs and productivity losses averted amounting up to $349 per household per year.

In summary, high capacity chemically activated cow bone and monetite media were successfully prepared and evaluated in this dissertation. This highly efficient and effective CAB and monetite media have great potential to mitigate the negative health effects of fluoride impacted drinking water in developing countries and beyond. Additionally, it was learned that the business model can be an effective tool in evaluating different technologies for the provision of fluoride-safe water supply services by solving the existing constraints of equipments and chemicals supply for defluoridation systems.

Finally, from these significant findings and knowledge, future recommendations and potential applications have been proposed as follows:

- Chemically activated cow bone has been produced and evaluated for the fluoride adsorption capacity both in the laboratory and field. Likewise, preparation and evaluation of monetite should be undertaken in the field to assess its effectiveness using natural groundwater and local conditions.
- This dissertation demonstrated that chemically activated cow bone and monetite had significantly higher fluoride removal capacity compared to bone char. It is thus recommended to evaluate the potential of both chemically activated cow bone and monetite to remove contaminants from wastewater, e.g., removal of phosphate from wastewater and re-using it as a potential fertilizer.
- Future research should also focus on further enhancing the fluoride removal capacity of the CAB and monetite media, e.g., using metal amendment of these media.
- In this dissertation, it was learned that business model is a very useful tool to evaluate the viability of fluoride treatment systems as a business. It is recommended that a privately managed pilot fluoride treatment system is installed in the field and its practical applicability and acceptance by the local communities should be evaluated to pave the way to implement a sustainable/viable business model.

Appendix A: Supplementary Materials for Chapter 2

A.1 **Preliminary screening for chemical activation cow bone (CAB) media**

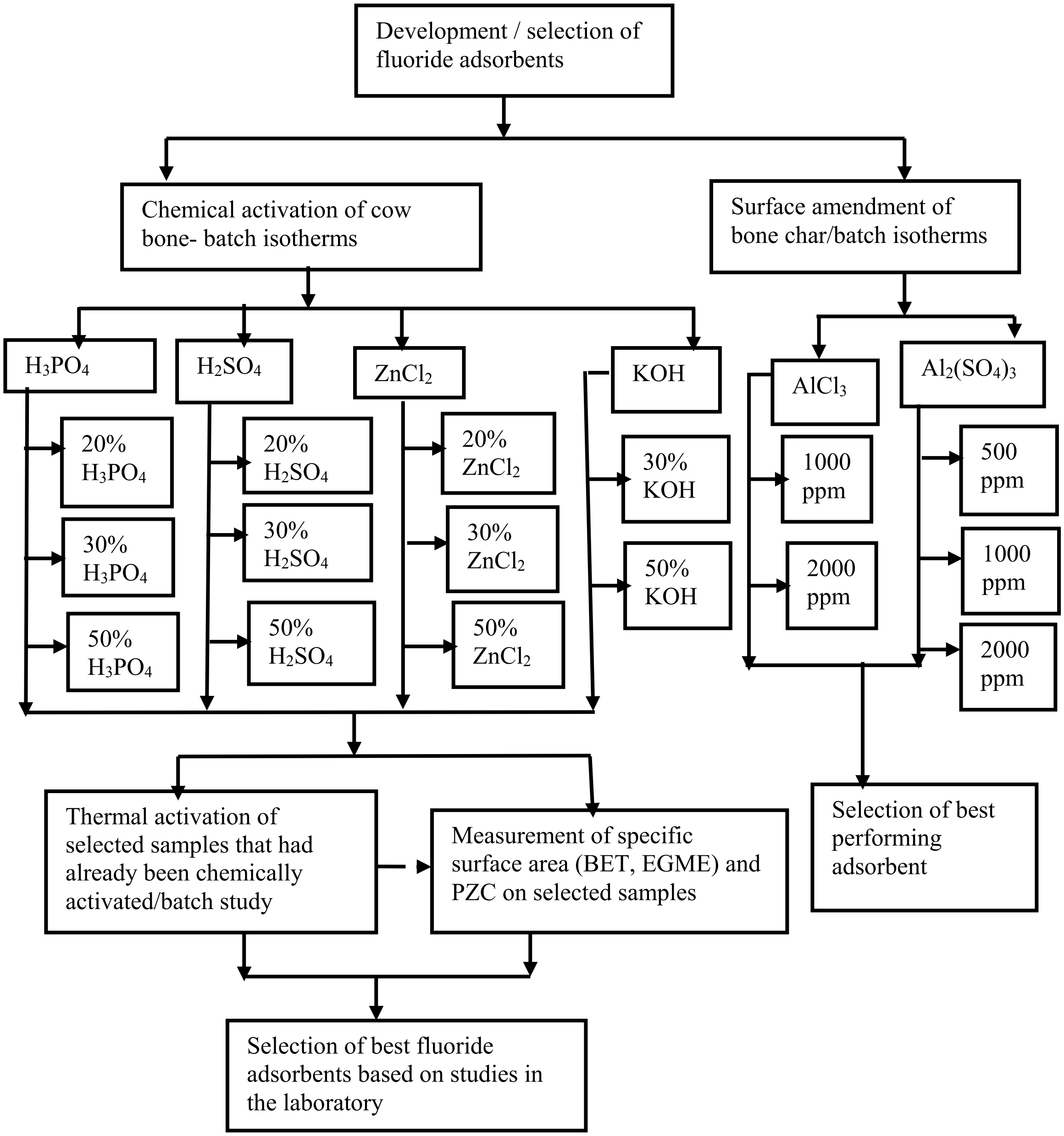

Figure A.1.1: Experimental flow chart for chemical / thermal activation and surface amendment of cow bone/ bone char and fluoride adsorption studies. The H_3PO_4, H_2SO_4, $ZnCl_2$ and KCB activated cow bones are presented as HPCB, HSCB, ZnCB, and KCB, respectively in the main manuscript and SI.

A.2 The additional results for the metal amendment of bone char

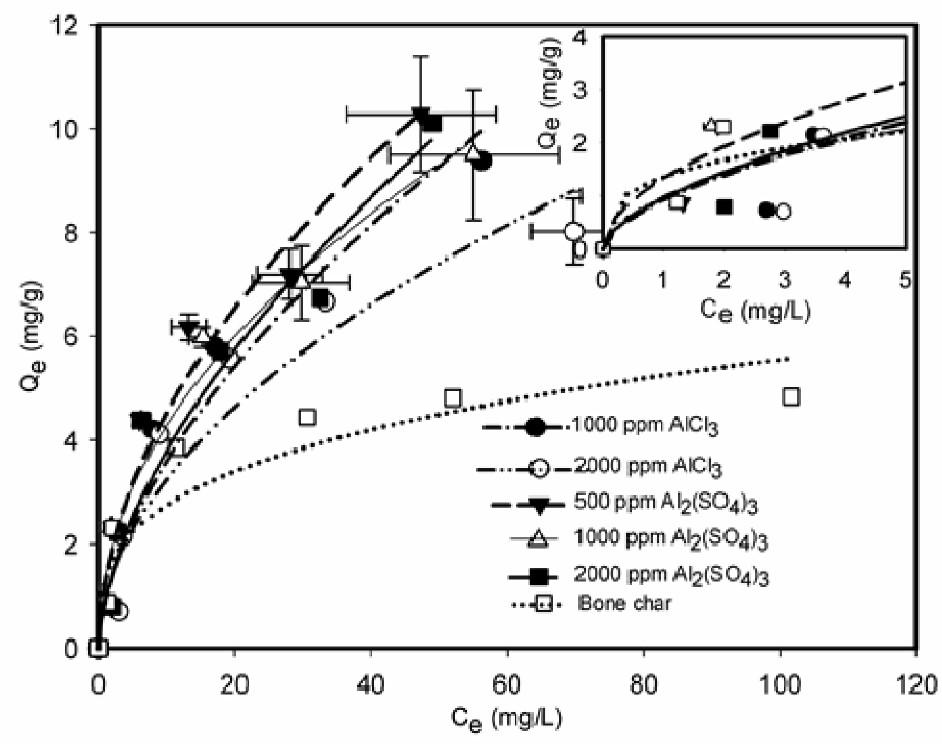

Figure A.2.1: Fluoride adsorption fitting with Freundlich isotherms of aluminum chloride ($AlCl_3$) and aluminum sulfate ($Al_2(SO_4)_3$ amended bone char. The inset panel indicates the fluoride adsorption at lower equilibrium fluoride concentrations. The error bars represent the standard deviations associated with Q_e and C_e calculated from triplicate measurements.

A.3 The additional results from characterization (pH_{PZC}) of CAB media

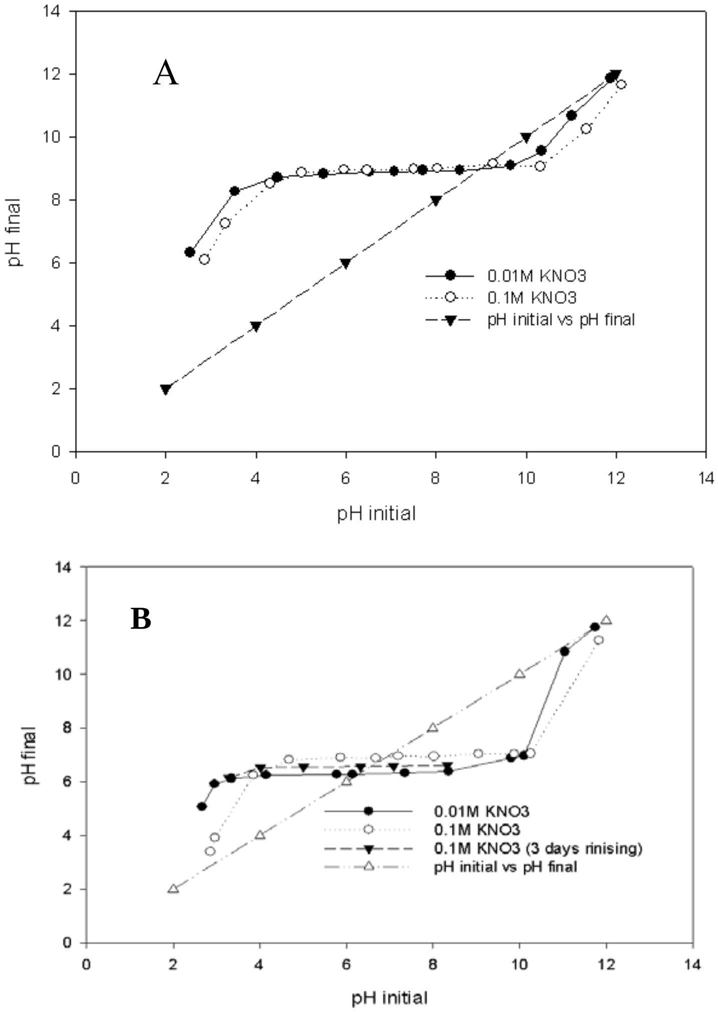

Figure A.3.1 pH PZC of 50% KCB (A), and 30% HSCB (B)

Measurement of PZC

The PZC of the chemically activated cow bone was determined using methods reported by Noh and Shwarz (1989), Milonjic et al. (1983), and Brunson and Sabatini (2009) where 50 mL solutions of 0.01 and 0.1 KNO_3 were poured into a series of vials and N_2 gas was bubbled into the solution for 10 minutes to avoid the interference of CO_2. The pH in the vials was adjusted to values ranging from 2.5 to 13 using 0.1 M KOH and 0.1 M HNO_3. Then 0.2 g of the chemically activated cow bone was added to each vial and samples were put on a shaker at 200 rpm for 24 hours to allow the cow bone to equilibrate with the pH adjusted solution. The final pH of the solution in each vial was measured and plotted against the initial pH values. The PZC of the cow bone adsorbent was taken to be the value at which the final pH plateaued.

A.4 The quantity of materials recovered from chemical activation and raw data for calculations of the quantity of materials recovered

Table A.4.1: Quantity of material recovered from chemical and thermal activation of cow bone

Adsorbent	Mass before activation (g)	Mass recovered after activation (g)	Percentage of mass recovered (%)	Percentage of mass lost due to activation (%)
30% HSCB	70	48	69	31
30% HPCB	20	14.2	71	29
30% KCB	70	49	70	30
50% KCB	70	52	74	26
30% HSCB-540	20	4	20	80
30% KBC-540	20	3.5	17	83
50% KBC-540	20	4	20	80
50% ZnCB-500	18	3	16	84
Thermal, bone char	70	15.4	22	78

A.5 The cost of production of bone char and chemically activated cow bone, assumptions and data for production cost calculations

Table A.5.1: Cost summary for production of 1 kg bone char and chemically activated cow bone

Description	Unit	Quantity	Unit price ($)	Total cost ($)
A.1 Bone char				
Material and utility cost				
Purchase of cow bone	kg	3.5	0.025	0.0875
Kerosene for ignition	Liter	0.007	1.057	0.0074
Charcoal for facilitation of bone charring	kg	0.47	1.195	0.564
Power cost for bone charring	kg	1	0.014	0.014
Labor costs				
Bone charring	kg	1	0.026	0.026
Supervision of bone charring	kg	1	0.029	0.029
Bone crushing (crusher operator)	kg	1	0.0046	0.0046
Sieving and washing	kg	1	0.013	0.013
Supervision crushing and sieving	kg	1	0.0069	0.0069
			Sub-total	**0.72**
			Administration cost at 15%	**0.11**
			Total cost to produce 1kg bone char	**0.83**
A.2 Chemically activated cow bone				
Material and utility cost				
Purchase of cow bone	kg	1.46	0.025	0.037
Sulfuric acid	kg	0.552	0.36	0.193
Power for bone crushing raw bone	kg	1	0.006	0.006
Labor costs				
Labor cost for chemical activation	kg	1	0.01	0.01
Bone crushing (crusher operator)	kg	1	0.0005	0.0005
Sieving and washing (3 persons)	kg	1	0.006	0.006
Supervision cost for crushing and sieving	kg	1	0.0069	0.0069
			Sub-total	**0.26**
			Administration cost at 15%	**0.04**
			Total cost to produce 1kg chemically activated cow bone	**0.3**

Calculations

Cost analysis data

- The quantity of cow bone needed to produce 1 kg of bone char and chemically activated cow bone is considered as 3.5 kg and 1.46 kg, respectively (based on our experimental result),
- Cost of 1 kg cow bone is \$0.025 (Personal communication, Esayas 2014).
- For bone char production, 10 liters of kerosene is required to ignite and burn 5,000 kg of bone (Jacobson and Műller 2007; Arrenberg 2010).
- Unit price of sulfuric acid is \$280-\$350 per ton, (Alibaba.com, sulfuric acid 2014).
- Bone crushing machine produces 200-600 kg/hr with a power rating of 11-15 kW, (Modern Butchery Supply 2014).

Assumptions

The following assumptions were made to calculate and compare the production costs of bone char and chemically activated cow bones:

- The adsorbent with the highest fluoride removal capacity, HSCB, was considered in this cost analysis.
- To chemically activate 40 g of cow bone, 40 mL of 30% H_2SO_4 is needed, considering an optimum media to activating agent ratio of 1:1 (wt.%), and 30% concentration sulfuric acid, based on our experiments. It was assumed that the same recipe as the laboratory is applied in the field and the associated costs were calculated.

- An average bone crusher capacity of 300 kg/hr and a power rating of 13 kW were considered for the cost analysis.
- Labor cost for charring, crushing, sieving, and supervision works were calculated considering the labor rates in the Rift Valley of Ethiopia.
- An administrative cost of 15% was assumed for salaries of administration, finance, procurement, utilities and other project management related expenses.
- Infrastructure common for production of the adsorbents such as crushing machine, sieves, and washing basins were not included in the cost analysis.
- The average fluoride concentration of groundwater in the Rift Valley of Ethiopia is 10 mg/L (Rango et al. 2010). Assuming a per capita treated water demand of 5 liters per day, and assuming 2,000 users, the total volume of water to be treated per day is 10,000 liters. The total mass of adsorbent needed to treat 10,000 liters (based on $Q_{1.5}$ values of 30% HSCB and bone char in Table A.5.1, and C_0 = 10 mg/L and C_e = 1.5 mg/L) was calculated to compare the production costs of the adsorbents (see calculations below).

Cost of production of bone char and chemically activated cow bone

Calculations of production of bone char and chemically activated cow bone was made based on the cost data and assumptions above. Summary of the cost calculation is provided in Table A.5.1.

Masses of adsorbents required were calculated using Equation A.5.1 below:

$$Qe = \frac{(Co - Ct)\, X\, V}{M} \quad \text{……….. Equation A.5.1}$$

Where, C_0 (mg/L) is the initial fluoride concentration and C_i 9mg/L) is the equilibrium fluoride concentration, Q_e (mg/g) is the fluoride adsorption capacity at an equilibrium fluoride concentration of 1.5 mg/L and M (g) is the mass of the adsorbent.

Therefore, mass of 30% HSCB needed considering its $Q_{1.5}$ of 6 mg/g is,

$$= \frac{(10mg/L - 1.5mg/L)X10{,}000L}{6mg/g} = 4.3 \text{ kg}$$

Similarly mass of bone char needed considering $Q_{1.5}$ of bone char as 1.5 mg/g is,

$$= \frac{(10mg/L - 1.5mg/L)X10{,}000L}{1.5mg/g} = 58.2 \text{ kg}$$

Therefore, multiplying these masses by their respective costs per kg (Table A.5.1) and taking their ratios illustrates that chemically activated cow bone is about eleven fold cheaper than bone char.

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Appendix B: Supplementary Materials for Chapter 3

B.1 The additional results of adsorption and desorption data for CAB and bone char media

Table B.1.1: Quantitative amount of fluoride adsorbed and desorbed at each regeneration cycles

Adsorbent	Concentration of regeneration solution	Amount of fluoride adsorbed (mg/g)			Amount of fluoride desorbed (mg/g)		
		A1	A2	A3	R1	R2	R3
CAB	0.05 M NaOH	8.50	7.00	6.60	3.30	4.20	4.90
	0.01 M $Ca(OH)_2$	8.90	8.40	8.00	2.20	2.40	3.80
Bone char	0.1 M NaOH	4.56	4.30	4.18	3.20	3.30	2.95
	0.01 M $Ca(OH)_2$	4.50	4.20	4.10	1.70	1.90	1.30

Note:

A1, A2 & A3 – Adsorption cycles

R1, R2, & R3 – Regeneration cycles

B.2 The picture showing large field- column installed in the Rift Valley of Ethiopia


[redacted]

Figure B.2.1: Large-scale column installed in the Rift Valley of Ethiopia (Photo: by Teshome L. Yami).

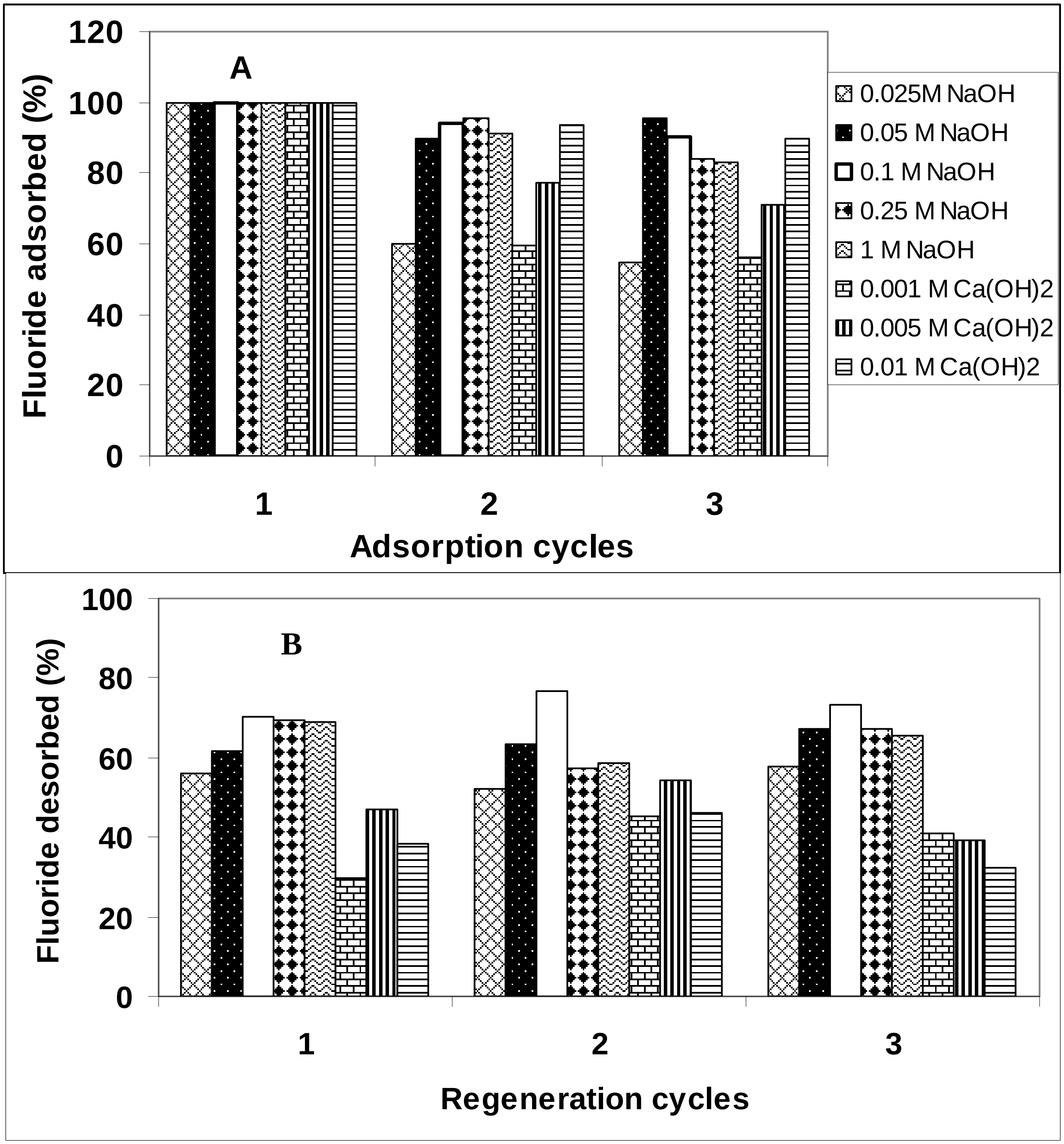

Figure B.2.2: Comprehensive regeneration test results of saturated bone char using varying concentrations of NaOH and $Ca(OH)_2$ solutions. Panels A and B show the adsorption and regeneration cycles, respectively.

Appendix C: Supplementary Materials for Chapter 4

C.1 The additional data used for modeling the solubility of monetites

Table C.1.1: Input data used for preparation of monetite media at Ca/P ratio of 1:0.43, 1:0.68 and 1:1.18.

Component selected	**Concentrations (moles)**		
	Ca/P ratio 1:0.43[b]	**Ca/P ratio 1:0.68**[b]	**Ca/P ratio 1:1.18**[b]
$CaCl_2$	1	1	1
Ca^{2+}	1	1	1
Cl^-	2	2	2
$(NH_4)_2HPO_3$	0.25	0.5	1
$NH4^+$	0.5	1	2
PO_4^{3-}	0.25	0.5	1
H_3PO_4 (pH adj.)[a]	0.18	0.18	0.18
Total (PO_4^{3-})	0.43	0.68	1.18
CTAB	0.1	0.1	0.1
CTA^+	0.1	0.1	0.1
Br^-	0.1	0.1	0.1
NaOH (pH adj.)[c]	1	1	1
Na^+	0.0125	0.0125	0.0125

[a] 5 ML, 85% grade H_3PO_4

[b] solids selected were lime, portlandite, $Ca_4H(PO_4)_3.3H_2O$, $CaHPO_4.2H_2O$, Hydroxyapatite, $CaHPO_4$ and $Ca_3(PO_4)_2$ Beta

[c] 5 mL, 1 M NaOH in 400 mL solution

Appendix D: Supplementary Materials for Chapter 5

D.1 The additional data used for cost of fluoride treatment systems calculations

Table D.1.1 Data used for the cost calculations of fluoride treatment systems[1]

Description	Unit	Quantity
Number of users per treatment systems per village	HH[2]	60
Number of villages using the treatment system	each	6
Average number of persons per household	each	5
Total number of persons using one treatment system	each	1800
Population growth rate for the Rift Valley area	%	3
Design period	years	15
Projected number of users	Persons	2800
Treated water demand for drinking and cooking (liters per person per day)	Liters	6.5
Total quantity of water treated per day	Liters	18,000

Note: [1] The data summarized in Table S1 are based on the household survey conducted by the University of Oklahoma (OU) Water Technologies for Emerging Regions (WaTER Center) in summer 2014 in the Rift Valley of Ethiopia

[2] HH stands for household

Calculations

Cost analysis data

- The total mass of aluminum sulfate (alum) required to remove 1mg of fluoride is 150 mg. The mass of lime required is 50% of the mass of the alum. The cost of alum and lime were considered as \$0.51/ kg and \$0.17/ kg, respectively (WaTER Center survey data, 2014).
- The quantity of cow bone needed to produce 1 kg of chemically activated cow bone is 1.46 kg (Yami et al. 2016).
- Cost of 1 kg cow bone is \$0.025 (Personal communication, Esayas 2014).
- The cost of aluminum plate used for the electrolytic defluoridation system is \$15/ kg (WaTER Center survey data, 2014).
- Average unit price of sulfuric acid is \$285 per ton, (Alibaba.com, sulfuric acid 2014).
- Bone crushing machine produces on average 300 kg/hr with an average power rating of 13 KW, (Modern Butchery Supply 2014).

Assumptions

The following assumptions were made to calculate cost of production of treated water using the Nalgonda, Electrolytic defluoridation (EDF), and chemically activated cow bone (CAB).

- In this study, three aluminum (Al) plates of 120 cm x 80 cm x 2 mm size with a 1 mm distance between plates were considered per tanker of the EDF treatment system.

- Labor cost for charring, crushing, sieving, and supervision works were calculated considering the labor rates in the Rift Valley of Ethiopia.
- The maintenance and overhead costs were considered as 2% and 5% of the water treatment system component works, respectively.
- Infrastructure common for production of the adsorbents such as crushing machine, sieves, and washing basins were not included in the cost analysis. Additionally, costs associated with the Well development i.e., Well drilling, casing, pumps and electromechanical installations were considered to be covered by the government or non-governmental organizations and thus excluded from this analysis.
- The average fluoride concentration of groundwater in the Rift Valley of Ethiopia is 10 mg/L (Rango et al. 2010). Assuming a per capita treated water demand of 6.5 liters per day, and assuming an average 2,800 users, the total volume of water to be treated per day is 18,000 liters.

1. Cost of treated water: In this section, the production cost of fluoride safe-water using three treatment systems is analyzed; Nalgonda, electrolytic defluoridation and chemically activated cow bone.

1.1 Nalgonda based treatment system

- ***Volume of the reactor***

Two reactors with 5000 liter capacity (per batch) were required for the production of treated water. A total of four treatment batches are required to meet the total daily treated water demand of 18,000 liters (see Table D.1.1).

Chemical dosage

The average raw water fluoride concentration in the Rift Valley of Ethiopia, C_0 = 10 mg/L, (Rango et al. 2010) and an equilibrium fluoride concentration of C_e = 1.5 mg/L, (WHO 2011) were used to determine the quantity of chemicals required to treat the daily water demand.

Mass of fluoride removed (mg/L) per day = (C_0 - C_e) x Total volume of water (L) treated per day (Equation D.1.1)

$$= (10\ mg/L - 1.5\ mg/L)\ X\ 18{,}000\ L = 153{,}000\ mg\ F^{-}/day$$

………Equation D.1.1

The total quantity of alum required to treat the daily water demand is calculated using Equation D.1.2,

$$= (153{,}0000\ mg\ F^{-}/day)\ X\ (150\ mg\ alum/mg\ F^{-})\ X\ (\frac{1\ kg}{10^6\ mg}) = 23\ kg\ alum/day$$

… Equation D.1.2

The mass of lime required is,

$$= 50\%\ (23\ kg/day) = 11.5\ kg\ \lim e/day$$ ….. Equation D.1.3

The costs of alum and lime are,

Cost of alum (\$/m^3)

$$= \left(\frac{mass\ of\ alum\ (kg/day)}{Volume\ of\ water\ treated\ (m^3/day)}\right)\ X\ (cost\ of\ alum,\ \$/kg)$$

$$= \left(\frac{23\ kg\ alum/day)}{18\ m^3/day}\right)\ X\ 0.51\ (\$/kg) = \$0.652/m^3 \text{ …. Equation D.1.4}$$

Cost of lime (\$/m^3)

$$= \left(\frac{mass\ of\ \lim e\ (kg/day)}{Volume\ of\ water\ treated\ (m^3/day)}\right)\ X\ (cost\ of\ \lim e,\ \$/kg)$$

$$= \left(\frac{11.5\ kg\ \lim e/day)}{18\ m^3/day}\right)\ X\ 0.17\ (\$/kg) = \$0.109/m^3 \text{ ….Equation D.1.5}$$

Therefore, the total cost of chemicals for the Nalgonda based treatment system is sum of cost of alum and lime is,

$$= \$0.652/m^3 +\ \$0.109/m^3 = \$0.769/m^3 \text{ ………………Equation D.1.6}$$

Infrastructure costs

Water system component works: The water treatment systems considered for the cost estimate includes reinforced concrete structure to support the raw water tanker, support structure for the reactor (column and slab), support for the treated water tanker, fiber glass raw water tanker (10 m^3), reactor tankers (iron sheet, 5 m^3), fiber glass treated water tankers (5 m^3), and chemical mixer and installation costs. Therefore, the total cost of the water system component works is estimated to be \$5,300. Considering, the water treatment systems have a life span of 10 years, the annual cost of the treatment systems is \$530.

Therefore, cost of water treatment component systems (\$/ m^3) is,

$$= \left(\frac{Cost\ of\ water\ treatment\ systems\ (\$/year)}{Volume\ of\ water\ treated\ (m^3/day) X (365\ days/year)}\right)$$

$$= \left(\frac{\$530/year}{18\ (m^3/day) X (365\ days/year)}\right) = \$0.0806/m^3$$ …….. Equation D.1.7

Operational costs

Personnel costs: Two persons, a tap attendant and a guard, were considered sufficient to operate the treatment system at \$40 per month per person. The total personnel cost is,

$$= \left(\frac{number\ of\ operators\ X\ salary\ (\$/month) X\ (1\ month/30\ days)}{amount\ of\ water\ treated\ (m^3/day)}\right)$$

$$= \left(\frac{2\ operators\ X\ (\$40/month)\ X\ (1\ month/30\ days)}{18\ m^3/day}\right) = \$0.148/m^3 \ldots.$$

Equation D.1.8

- *Diesel for water pumping:* Based on the data collected by the WaTER Center from the Nalgonda based treatment system in the Rift Valley of Ethiopia in summer 2014, 14.4 liters of diesel is required to pump 18 m^3 of water per day, and the cost of diesel is \$0.8 per liter. Therefore, the total cost of diesel needed to pump the daily water demand is,

$$Cost\ of\ diesel = \left(\frac{14.4L\ of\ diesel/day}{18\ m^3/day}\right) X (\$0.8/L\ diesel) = \$0.64/m^3 \ldots\ldots\ldots$$

Equation D.1.9

- *Cleaning reactor tanker:* Labor cost is calculated considering the labor rates in the Rift Valley of Ethiopia. One daily laborer washes the reactor once daily at \$1.5/day. The total cost for washing the reactor tanker is,

  $Labor\ \cos t = \frac{(1 person\ X\ \$1.5/person/day)}{18\ m^3/day} = \$0.083/m^3$ ……Equation D.1.10

  Therefore, total operational cost of the system is the sum of the costs indicated under (Equations D.1.9 –D.1.10).

  $= (\$0.148/m^3) + (\$0.64/m^3) + (\$0.083/m^3) = \$0.871/m^3$ … Equation D.1.11

- *Maintenance and overhead costs*: The total maintenance cost is,

  $= (2\%\ X\ \$\ 0.0806/m^3) = \$0.0016/m^3$ …………………… Equation D.1.12

  The total overhead cost is,

  $= (5\%\ X\ \$\ 0.0806/m^3) = \$0.0040/m^3$ …………..Equation D.1.13

  The cost summary for the Nalgonda based treatment system is provided in Table D.1.2.

1.2 Electrolytic Defluoridation (EDF) based treatment system

- ***Volume of the reactor***

  Four reactors each with 1000 liters capacity (per batch) were required for the production of treated water. The total daily treated water demand by the EDF unit is 18,000 liters (see Table D.1.1).

- ***Materials and chemicals:***

In this study, three Aluminum (Al) plates of 120 cm x 80 cm x 2 mm size with a 1 mm distance between plates were considered. The volume of the plates is,

$= 3\ plates\ X\ (1.2\ m\ X\ 0.8\ m\ X\ 0.002\ m) = 0.00576\ m^3$ ……….Equation D. 1.14

Weight of Al plates for four tankers is,

$= number\ of\ \tan\ker s\ X\ density\ of\ Al\ plate\ X\ volume\ of\ plates$

$= 4\ X\ (2700\ kg/m^3)\ X\ 0.00576\ m^3 = 62.21\ kg$ ………………..Equation D.1.15

Mass of Al dissolved in one tanker per day is,

= (C_0- C_e) (mg/L) x volume of one tanker (L) x Al/ F^- ratio at pH 6.5

$= (10\ mg/L - 1.5\ mg/L)\ X\ 1000\ L\ X\ 4 = 34\ g$ F^- per tank ……Equation D.1.16

Mass of Al dissolved in four tankers per day is,

$= 4\ X\ 34\ \frac{g\ F^-}{\tan k} = 136\ g$ ……….. …………………….Equation D.1.17

The total cost of aluminum plate (\$) per day = Total weight of Al plate dissolved per day (g) per treatment system x cost of plate per kg.

$$The\ \cos t\ of\ Al\ electrode = (\frac{136g}{day})X(\frac{1kg}{1000g})X(\frac{\$15}{kg}) = \$2.04\ \ per\ day$$ ......Equation D.1.18

The cost of Al electrode per volume of water treated daily is,

$$= Cost\ of\ Al\ electrode\ \ (\$/day)\ \ X\ \ volume\ of\ water\ treated\ \ (m^3/day)$$

$$= (\frac{\$2.04}{day})X(\frac{1day}{18000\ \ L})X(\frac{10^3\ \ L}{m^3}) = \$0.113/m^3$$ …………………. Equation D.1.19

- ***pH adjustment***: For pH adjustment, 1mmol H_2SO_4 is used. The average cost of sulfuric acid is \$0.285/ kg (Alibaba.com, sulfuric acid 2014).

The quantity of sulfuric acid needed for the pH adjustment is,

$$= \frac{0.001M}{L}\ X\ \frac{1000L}{m^3}\ X\ \frac{98}{M}\ g\ \ H_2SO_4\ \ X\ \ \frac{\$0.285}{kg}\ X\ \frac{1kg}{1000g} = \$0.0279/m^3$$ ….Equation D.1.20

- ***Solar panels and accessories:*** Installation of solar panels of 1500 Watt, 50 A and 24 Volt capacities together with its accessories were considered to be installed as a power source during electrolysis with an estimated total cost of \$4,000 including the labor costs.

Therefore, the total cost of solar panels and accessories (\$/ m^3 of treated water) is,

$$= (\frac{\$4000}{15year})X(\frac{1year}{365\ \ day})X(\frac{1day}{18m^3}) = \$0.0406/m^3$$

……………..Equation D.1.21

The total cost of materials and chemicals required for EDF system per m^3 of treated water is the sum of costs (Equation D.1.19-21), which is \$0.1815/m^3.

- **Infrastructure costs**

Water system component works: The water treatment systems considered for the cost estimate includes reinforced concrete structure to support the raw water tanker, support structure for the reactor (column and slab), support for the treated water tanker, fiber glass raw water tanker (10 m^3), reactor tankers (iron sheet, 5 m^3) for fiber glass treated water tankers (4 m^3), and installation costs. Therefore, the total cost of the system component works is estimated to be \$2,850. Considering, the water treatment systems to have a life of 15 years, the annual cost of the treatment system component works is \$190/ year.

Therefore, cost of water treatment component systems (\$/ m^3) is,

$$= \left(\frac{Cost\ of\ water\ treatment\ systems\ (\$/year)}{Volume\ of\ water\ treated\ (m^3/day)\,X\,(365\ days/year)}\right)$$

$$= \left(\frac{\$190/year}{18\ (m^3/day)\,X\,(365\ days/year)}\right) = \$0.0289/m^3 \text{ …..Equation D.1.22}$$

- **Operational costs**
  - *Personnel costs:* The personnel cost to operate the EDF system is the same as that of the Nalgonda system (\$0.148/m^3) (see Equation D.1.8
  - *Diesel for pumping water:* The total cost of the diesel needed to pump the daily water demand for the EDF system is same as that of the Nalgonda system (\$0.64/m^3) (see Equation D.1.9).

- *Washing reactor tanker:* The total labor cost for washing the EDF reactor tanker is same as that of the Nalgonda system (\$0.083/m^3) (see Equation D.1.10).

Therefore, total operational cost of the system is the sum of the costs indicated above,

$= (\$0.148/m^3) + (\$0.64/m^3) + (\$0.083/m^3) = \$0.871/m^3$ ……Equation D.1.23

Maintenance and overhead costs: The maintenance costs for the EDF system is,

$= (2\% \;\; X \;\; \$\; 0.0289/m^3) = \$0.00058/m^3$ …. ………………….Equation D.1.24

The total overhead cost is,

$= (5\% \;\; X \;\; \$\; 0.0289/m^3) = \$0.00145/m^3$ …………………….Equation D.1.25

The cost summary for the EDF based treatment system is provided in Table D.1.2.

1.3. Chemically activated cow bone (CAB) based treatment system

- *Water system component works:* The water treatment systems considered for the cost estimate includes reinforced concrete structure to support the raw water tanker, support structure for the reactor (column and slab), support for the treated water tanker, fiber glass raw water tanker (10 m^3), chemically activated cow bone reactor tankers (Roto tanker 2 m^3), for fiber glass treated water tankers (5 m^3), and installation costs. The total cost of the system component works is estimated to be \$4,000. Considering the water treatment system to have a life span of 10 years, the annual cost of the treatment system component works is \$400.

Therefore, cost of water treatment component systems ($\$/\ m^3$) is,

$$= \left(\frac{Cost\ of\ water\ treatment\ systems\ (\$/year)}{Volume\ of\ water\ treated\ (m^3/day) X (365\ days/year)}\right)$$

$$= \left(\frac{\$400/year}{18\ (m^3/day) X (365\ days/year)}\right)\ = \$0.061/m^3$$ …….Equation D.1.26

- ***Materials and chemicals:***
    - In this study, calculation of the various materials and chemicals needed for the production of the CAB media is conducted as per the assumptions and procedures highlighted by Yami et al. (2016). Accordingly, 1.46 kg of cow bone is needed to produce 1 kg CAB media. The cost of cow bone in the Rift Valley of Ethiopia is \$0.025 per kg (Personal communication, Esayas 2014).

Therefore, cost of cow bone to produce 1 kg of CAB media is,

$$= 1.46\ kg\ cow\ bone\ X\ \frac{\$0.025}{kg} = \$0.0365\ per\ kg\ of\ CAB\ media$$ …Equation D.1.27

Cost of chemicals: To activate 1 kg of cow bone, 200 mL of sulfuric acid (95% grade) is needed (Yami et al. 2016). Considering the average cost of sulfuric acid as \$0.285/ kg (Alibaba.com, sulfuric acid 2014), the cost of H_2SO_4 required to chemically activate 1 kg CAB media is,

$$= 200\ mL\ H_2SO_4\ X\ \left(\frac{1.84g}{mL}\right) X \left(\frac{1kg}{1000g}\right)\ X\ \left(\frac{\$0.285}{kg\ H_2SO_4}\right) = \$0.104\ per\ kg$$ ………

Equation D.1.28

- ***Labor cost for chemical activation:*** One semi-skilled person is required to undertake chemical activation of cow bone for 3 hours per batch. The salary of the semi-skilled person is \$200 per month. The cost of labor for 3 hours of chemical activation is,

$$= (\frac{\$200}{30 days}) X (\frac{1 day}{24 hr}) X 3\ hr = \$0.833$$ ....Equation D.1.29

Assuming one person produces 100 kg CAB media in 3 hrs, the cost of labor per kg is,

$$= \frac{\$0.833}{100\ kg\ CAB} = \$0.0083 / kg\ CAB\ media$$ ....Equation D.1.30

- ***Cost of crushing and washing cow bone:*** Considering a bone crushing machine with an average capacity of 300 kg/ hr and an average power rating of 13 kW (Modern Butchery supply 2014), the time required to crush 1.46 kg of cow bone required to prepare 1 kg of CAB media is,

$$= 1.46\ kg\ cow\ bone\ X\ \frac{1\ hr}{300\ kg} = 0.00487\ hr$$ ....Equation D.1.31

The cost of crushing 1 kg of cow bone considering the cost of electricity in Ethiopia as 8.0 US cents/ hr (WaTER Center's summer 2014 survey data) is,

$$= average\ power\ (kw)\ X\ crushing\ durtaion\ (hr)\ X\ \cos t\ of\ energy\ (US\ cents / hr)$$

$$= 13\ kw\ X\ \frac{0.00487\ hr}{1.46\ kg}\ X\ \frac{8.0\ US\ cents}{hr} X\ (\frac{\$}{100\ US\ cents}) = \$0.00347 / kg$$ .....

Equation D.1.32

- ***Labor cost for crushing bone:*** One daily laborer with a monthly salary of \$75 is required for the crushing the cow bone. The cost of labor for bone crushing is,

$$= \frac{\$75}{30 days} X \frac{1 day}{24 hr} X \frac{0.00487 hr}{1.46 \ kg \ cow \ bone} = \$0.00035 / kg \quad \ldots\ldots\ldots \text{Equation D.1.33}$$

- ***Labor cost for sieving and washing cow bone:*** Considering 2 persons can sieve and wash 100 kg cow bone per hour, the cost of sieving and washing cow bone is,

$$= \frac{\$75}{30 days} \ X \ \frac{1 day}{24 hr} \ X \ 2 \ \ persons \ X \ \frac{1 hr}{100 kg} = \$0.002 / kg \ \ldots\ldots\ldots\ldots \text{Equation D.1.34}$$

- *Supervision cost:* The supervision cost is calculated considering supervisor's monthly salary of \$200. The supervision cost is,

$$= \frac{\$200}{30 days} X \frac{1 day}{24 hr} X \frac{1 hr}{100 \ kg \ cow \ bone} = \$0.0028 / kg \ \ldots \text{ Equation D.1.35}$$

Therefore, the total cost of chemically activated cow bone (CAB) is the sum of cow bone, chemical, energy and labor costs required to produce 1 kg of CAB media (eq. 27 -35), which is, \$0.157/ kg CAB.

- ***Cost of CAB media (\$/ m^3 of treated water):*** The chemically activated cow bone has the fluoride adsorption capacity at an equilibrium fluoride concentration of 1.5 mg/L ($Q_{1.5}$) is 7.0 mg/g (Yami et al. 2016). Thus the mass of CAB media required to treat the daily water demand of 18,000 liter based on the $Q_{1.5}$ (mg/g) is determined from expression below,

$M = \dfrac{(C_0 - C_i)\ X\ V}{Q_{1.5}}$, where M is the mass of CAB media (g), V is the daily volume of water treated (liters), (mL) and C_0 and C_i are initial and equilibrium fluoride concentrations in (mg/L), respectively.

$M = \dfrac{(10mg/L - 1.5mg/L)}{7\ mg/g} X \dfrac{18{,}000L}{day} X \dfrac{1kg}{1000g} = 21.857\ kg\ CAB$ ….Equation D.1.36

The cost of CAB media (\$/m^3) is,

$= 21.857\ kg\ CAB\ X\ \dfrac{\$0.157}{kg\ CAB} X \dfrac{1day}{18m^3} = \$0.191/m^3$ …………Equation D.1.37

- **Operational costs**
    - *Personnel costs:* The personnel cost to operate the CAB system is same as that of the Nalgonda and EDF system (\$0.148/m^3) (see Equation D.1.8).
    - *Diesel for pumping water:* The total cost of the diesel needed to pump the daily water demand for the CAB system is same as that of the Nalgonda and EDF system (\$0.64/m^3) (see Equation D.1.9).
    - *Cleaning CAB column:* One person cleans CAB column at \$1.5 / day.

The CAB column cleaning cost is,

$= 1 person X \dfrac{\$1.5}{day} X \dfrac{1day}{18m3} = \$0.083/m3$…………………..Equation D.1.38

Therefore, total operational cost of the system is the sum of the costs indicated above,

$= (\$0.148/m^3) + (\$0.64/m^3) + (\$0.083/m^3) = \$0.871/m^3$ ……Equation D.1.39

Maintenance and overhead costs: The maintenance costs for the CAB system is,

$= (2\% \;\; X \;\; \$ \; 0.061/m^3) = \$0.00122m^3$ ……………………….Equation D.1.40

The total overhead cost is,

$= (5\% \;\; X \;\; \$ \; 0.061/m^3) = \$0.0033/m^3$ ……………………. Equation D.1.41

The cost summary for the CAB based treatment system is provided in Table D.1.2.

Table D.1.2 Summary of cost analysis for fluoride treatment systems

	Total cost ($ per m^3 of treated water)		
Description	**Nalgonda**	**EDF**	**CAB**
Water treatment component structures	0.0806	0.0289	0.0610
Materials and chemicals	0.7607	0.1815	0.1910
Operational costs	0.8710	0.8710	0.8710
Maintenance costs (2% of water treatment system costs)	0.0016	0.00058	0.00122
Overhead cots (5% of water treatment costs)	0.0040	0.00145	0.0033
Total cost of treated water ($/m^3)	**1.72**	**1.08**	**1.13**

2. Revenue generated from fluoride-safe water

Based on the WaTER Center's summer 2014 survey conducted in communities using the existing fluoride treatment systems (Nalgonda and bone char) in the Rift Valley of Ethiopia, the tariff for treated water is \$1.5/ m^3.

Therefore, the annual revenue generated from the treated water is,

$$= \frac{\$1.5}{m^3} X \frac{18m^3}{day} X \frac{365 days}{year} = \$9{,}855 / year \quad \text{……………………….Equation D.1.42}$$

The total cost annual cost of production of treated water using cost per m^3 of treated water summarized in Table D.1.2.

The cost of production of treated water and the corresponding revenue generated from sale of water is analyzed below.

***Nalgonda System*:**

$$Total\ annual\ \cos t\ of\ production\ of\ treated\ water = \frac{\$1.72}{m^3} X \frac{18m3}{day} X \frac{365days}{year} = \$11{,}300 / year$$

….Equation D.1.43

Electrolytic defluoridation system:

$$Total\ annual\ \cos t\ of\ production\ of\ treated\ water = \frac{\$1.08}{m^3} X \frac{18m3}{day} X \frac{365days}{year} = \$7{,}100 / year$$

….. Equation D.1.44

Chemically activated cow bone system:

$$Total\ annual\ \cos t\ of\ production\ of\ treated\ water = \frac{\$1.13}{m^3} X \frac{18m3}{day} X \frac{365days}{year} = \$7{,}400 / year$$

…. Equation D.1.45

The net revenue generated from the respective fluoride treatment system is summarized in Table D.1.3.

Table D.1.3 Net revenue generated from the sale of fluoride treatment systems[6]

Description	**Nalgonda**	**EDF system**	**CAB system**
Purchase cost of treated water per m^3	$1.5	$1.5	$1.5
Annual revenue from treated water per treatment system	$9,855	$9,855	$9,855
Annual cost of production of treated water (costs include pumping, labor, chemicals and equipments and O & M) (see Table D.1.2)[7].	$11,300	$7,100	$7,400
Net annual revenue per treatment system (annual revenue – annual cost of treated water production)[2]	**($1,445)**	**$2,755**	**$2,455**
Net annual revenue considering fifty treatment systems operated per year	**($72,250)**	**$137,750**	**$122,750**

3. Cost saving achieved using fluoride-safe water

In this section, the cost saving achieved due to utilization of fluoride safe drinking water supply is analyzed. The cost saving considered are medical and productivity losses.

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[6] Additional revenue that can potentially be generated from sale of raw water is not included in the revenue/cost calculations since the business model focuses on fluoride treated water.

[7] Cost of well development and associated activities were assumed to be covered by government and NGOs and thus not included in this cost analysis.

3.1 Medical costs

The average defluoridation system users of 2800 people in the Rift Valley of Ethiopia are considered in this analysis. According to the WaTER Center survey data (2014), individuals affected by dental and skeletal fluorosis make about 4 visits per year to seek medical help (dental and skeletal check up and treatment) at a cost of \$10 per person per visit. Thus the total medical check up and treatment cost is,

$$Annual\ medical\ \cos t = 4X\ \frac{\$10/year}{person} = \$40\ \ per\ person \quad \ldots\ldots\ldots \text{Equation D.1.46}$$

According to Frank et al. (2011), about 42% of the total number of people (= 42% x 2800 = 1,176 people) had painful dental and skeletal fluorosis in the Rift Valley of Ethiopia. About 40% of those who are suffering from painful dental and skeletal fluorosis (i.e., 470 people) seek medical check up and treatment (Tilahun, Dugda District water office, Interview, July 17, 2014).

Therefore, total cost of medical check up and treatment is,

$$Annual\ medical\ \cos t = 470\ \ persons\ X\ \ \frac{\$40/Year}{Person} = \$18{,}800 \ldots\ldots \text{Equation D.1.47}$$

The averted medical cost due to safe water supply per household per year is,

$$= \frac{\$18{,}800}{2{,}800\ \ personsX\ \ (\frac{1\ \ household}{5\, persons})} = \$34\ \ per\ \ /household/year \ldots\ldots \text{Equation D.1.48}$$

3.2 Productivity loss

The average household income in the Rift Valley of Ethiopia is \$100 per month (WaTER Center survey data, 2014). The average income per person per year is,

$$Average\ annual\ income\ (\$/household) = \frac{\$100}{(\frac{month}{household})}\ X\ \frac{12 month}{Year} = \$1200 \ldots\ldots\ldots$$

Equation D.1.49

Considering an average household size of 5 persons, the average annual income per person is,

$$Average\ annual\ income\ per\ person\ (\$/person) = \frac{\$1200}{household\ X\ \frac{5\ persons}{household}} = \$240$$

…..Equation D.1.50

According to WaTER Center survey data (2014), the average income loss per person is 50% of the total income (wage, farm income, and business losses) due to the burden of prevailing diseases in the Rift Valley of Ethiopia.

$Average\ annual\ income\ loss\ per\ person = 50\%\ X\ \$\ 240 = \$120$ ….. Equation D.1.51

Teklehaimanot et al. (2006) reported that 65.7% of the communities surveyed in the Rift Valley areas face skeletal fluorosis. According to the information obtained from the Dugda district water office, about 40% of the people with skeletal fluorosis encounter productivity losses.

Therefore, the total number of people with productivity loss is,

$$= \%\ of\ community\ with\ skeltal\ fluorosis\ X\ total\ number\ of\ users\ X\ \%\ of\ people\ facing\ productivity\ loss$$

$$Number\ of\ people\ facing\ productivity\ loss = 65.7\%\ X\ 2800\ persons\ X\ 40\% = 736$$

….. Equation D.1.52

The total annual productivity loss is,

$$= Average\ annual\ income\ per\ person\ year\ X\ number\ of\ people\ facing\ productivity\ loss$$

$$Annual\ productivity\ loss\ = \frac{\$240}{Person}\ X\ 736\ persons = \$176{,}640$$ ………..Equation D.1.53

The annual productivity loss per person of the total number of beneficiaries is,

$$Annual\ productivity\ loss\ per\ household = \frac{\$176{,}640}{2800\ persons}\ X\ \frac{5\ persons}{household} = \$315/household/year\ \ldots$$

…Equation D.1.54

The total annual medical and productivity loss is,

$$Total\ annual\ loss\ per\ year = Medical\ \cos t\ per\ year\ (eq.\ 47) + productivity\ loss\ per\ year\ (eq.\ 53)$$

$$Total\ annual\ loss\ per\ year = \$18{,}800 + \$176{,}640 = \$195{,}440$$ ………Equation D.1.55

Total annual medical and productivity loss per person is,

$$= \frac{Total\ annual\ loss\ per\ year}{Total\ number\ of\ beneficairies} = \frac{\$195{,}440}{2800\ persons} = \$70\ per\ person\ per\ year$$

….Equation D.1.56

The production cost of treated water (\$/ person/ year) considering an average production cost of water for Nalgonda, EDF and chemically activated cow bone as \$1.31/m^3 is,

$$\Pr oduction\ \cos t = \frac{\$1.31}{m^3}\ X\ \frac{6.5L}{(day/person)}\ X\ \frac{1m^3}{1000L}\ X\ \frac{365}{year} = \$3.108$$ ……Equation D.1.57

Therefore, cost saved due to water defluoridation is the difference of the cost of water production (\$/ person/ year) and the averted annual medical and productivity losses (\$/ person/ year), which is,

$$Total\ annual\ \text{cost}\ averted\ due\ to\ access\ to\ fluoride\ safe\ water = \$3.108 - \$70 = (\$67)\ \ per\ person............$$

.Equation D.1.58[8]

Table D.1.4 Comparison of fluoride treatment systems based on technical and social criteria (see supplemental data for more detailed costing information)

Description	Nalgonda	Electrolytic defluoridation (EDF)	Chemically activated cow bone (CAB)
System components	• Reactor tank 5 m^3 (quantity 1) • Reactor tank support (steel) • Electrical motor for mixing chemicals • Power source / Generator • Mixer/ stirrer and its shaft • Roto plastic treated water tanker (5 m^3)	• Reactors (4 compartment concrete structure, 1mx1mx1m each) • Power source/ Generator, control panel & DC current) • Roto plastic treated water storage (5 m^3)	• Reactor tanker 2 m^3 (quantity 2) • No power source needed (Gravity system) • Concrete sandwiched masonry treated water storage (4 m^3)
Treatment systems installation	• Large sludge disposal tanker (2m wide, 2.5m length, 1.5m depth) • Skilled labor to install electrical motor, chemical mixer & its shaft) • Cost of treatment system : \$41,100	• Small sludge tank (1.5 m wide, 1.5 m length, 1 m depth) • Semi- skilled labor to cut aluminum plates & place it in tanker • Cost of treatment system: \$39,250	• No sludge tank needed • Requires semi-skilled labor for system installation • Cost of treatment system: \$39,750
Input for system operations	• Aluminum sulfate, lime • Power source for mixing	• Aluminum plate • Power supply / AC to DC converter	• Cow bone • Bone charring • Regeneration chemicals (NaOH, $Ca(OH)_2$)
Maintenances: simplicity, skilled labor requirement	• Daily labor intensive tanker sludge removal • Daily chemical application & mixing is labor intensive (2 persons needed to clean tanker, and mix chemicals) • Requires continuous pH monitoring • Maintenance of electrical motor and stirrer requires skilled labor • Lubrication of gearbox every two weeks	• Cutting and placing aluminum electrode requires semi-skilled labor • Easy sludge removal (every three months) • Cleaning and replacement of aluminum electrodes (every three months)	• Chemically activated cow bone (CAB) packed into column (every 6 months) • Replacement of CAB (every six months)

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[8] The negative sign (bracket) indicates the cost saving achieved due to defluoridation.

Table D.1.4 Continued.

Description	**Nalgonda**	**Electrolytic defluoridation (EDF)**	**Chemically activated cow bone (CAB)**
Sustainability and quality of outputs: effectiveness of fluoride removal	• Suitable for fluoride level <10mg/L • Adsorbent not produced on site i.e. purchased from factory • Treated water is murky and less palatable taste (Meheshwari, 2006; Apparao & Karthikeyan, 1986). • No regeneration potential	• Suitable for (low-high) or >10mg/L F^- levels • High fluoride removal capacity (Andey et al. 2013) • Aluminum plate can be cut and installed on site • Palatable water taste • Spent aluminum plate can not be reused	• Suitable for (low-high) or >10mg/L F^- levels • High fluoride removal capacity (Yami et al. 2016) • Bone char media can be produced locally • Palatable water taste due to organic materials fully removed (Yami et al., 2016) • Easily regenerated using 0.1 M $Ca(OH)_2$ solution
Cost of treated water in USD per m^3	**1.72** • Water systems component works = \$0.081 / m^3 • Materials & chemicals =\$0.7607/ m^3 • Maintenance cost = 0.0016 \$/ m^3’ • Overhead cost 0.0041 \$/ m^3 • Operational cost = 0.871 \$/ m^3	**1.08** • Water systems component works = \$0.029 / m^3 • Materials & chemicals =\$0.1815/ m^3 • Maintenance cost = \$0.0006 / m^3 • Overhead cost \$0.0014 / m^3 • Operational cost = \$0.871 / m^3	**1.13** • Water systems component works = \$0.061 / m^3 • Materials & chemicals =\$0.1910/ m^3 • Maintenance cost = \$0.0012 / m^3 • Overhead cost= \$0.0012 / m^3 • Operational cost = \$0.871 / m^3

Note: Components common for the three technologies (water Well, pumps and generator, and pipes and fittings and raw water storage tankers) were excluded.

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Appendix E: Additional Research Publication

E.1. *Citations of the manuscript*

Yami, T.L., Du, J., Brunson, L.R., Chamberlain, J. F., Sabatini, D.A., & Butler, E.C., (2015). Life Cycle Assessment of Adsorbents for Fluoride Removal from Drinking Water in East Africa. *The International Journal of Life Cycle Assessment*, 20(9), 1277-1286.

Brief note on the manuscript [9]

The manuscript was prepared as part of the Sustainable Engineering (ENGR 4510 class project, lectured by Dr. Elizabeth Butler) where I was responsible to coordinate and lead the analysis and preparation of the manuscript.

The study evaluated the environmental impacts of four low-cost and easy to use adsorbents: activated alumina, aluminum oxide amended wood char, bone char and treated alum waste. The environmental impacts of these adsorbents were evaluated using life cycle assessment (LCA). Eco-indicator and the Tool for Reduction and Assessment of Chemicals and other Environmental Impacts (TRACI) were used to interpret the environmental impacts. The results indicated that the fluoride adsorption capacity of the adsorbent is a key determining factor for the impacts. Further, the environmental impacts of the adsorbents can be reduced by increasing their fluoride adsorption capacity and/or carefully selecting key process components. Regeneration and reuse of spent adsorbents has the potential to minimize impacts to ecosystem quality.

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[9] This manuscript was published in the *International Journal of Life Cycle Assessment* in collaboration with Dr. Junyi Du, Dr. Laura Brunson, Dr. Jim Chamberlain, Dr. David Sabatini & Dr. Elizabeth Butler under the title "Life Cycle Assessment of Adsorbents for Fluoride Removal from Drinking Water in East Africa". Doi: 10.1007/s11367-015-0920-9.