Enhanced Fluoride Removal in Biosand Filters Using Aluminum Oxide Coated Media and Modified Filter Design

Madison Leigh Rice
University of South Florida

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Enhanced Fluoride Removal in Biosand Filters
Using Aluminum Oxide Coated Media and Modified Filter Design

by

Madison Leigh Rice

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
Department of Civil and Environmental Engineering
College of Engineering
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Dedication

To Warren and my parents, thank you for your love and support.
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Abstract

In 2010, the UN formally stated that access to safe drinking water and sanitation is a human right. Yet, one in three people globally do not have access to safe drinking water. Contaminated drinking water can negatively impact the health of consumers. This is a challenge that disproportionally affects developing regions, where limited access to resources exacerbates the problem. One drinking water contaminant of concern is fluoride. Fluoride is often added in low concentrations to drinking water to enhance consumers’ dental health. However, when water with high concentrations of fluoride is consumed frequently, it can have negative health effects, such as dental and skeletal fluorosis.

Biosand filters (BSFs) are a point of use drinking water treatment system that is widely used in developing regions. BSFs utilize both mechanical and biological filtration to achieve excellent removal of bacteria and organic matter. Fluoride, however, is not removed effectively by BSFs. The goal of this research was to modify the already successful technology of the BSF with a new design, filter media, and media coating to make it able to remove fluoride.

Along with the traditional sand, pumice and biochar were used as BSF media. Batch fluoride adsorption experiments were carried out on aluminum oxide coated sand, pumice, and biochar. Coated sand removed 26% of fluoride, while coated pumice removed 54.4%. Neither sand nor pumice were able to achieve fluoride concentrations below the World Health Organization (WHO) limit of safe consumption (<1.5 mg/L). Aluminum oxide coated biochar, on the other hand, achieved concentrations well below the WHO limit and removed 97% of fluoride.
The new BSF design consisted of a two-stage system, where the first stage provided removal of organics and suspended solids and the second stage modified for fluoride removal. Sand and pumice were coated with aluminum oxide, a known adsorbent of fluoride. Five BSFs were constructed in the University of South Florida (USF) Botanical Gardens. Three contained uncoated sand, pumice, or biochar, in both the first and second stage. The remaining two filters contained uncoated media in the first stage and coated media in the second stage for sand and pumice. A new in-situ coating method was tested to coat the pumice and sand, resulting in the production of aluminum oxide gel in the filters.

The BSFs were operated five days per week for 38 days. Turbidity, UV$_{254}$, flow rate, and pH were measured daily while *E. coli* and aluminum concentrations were measured once per week. Fluoride was measured every other day. The coating method significantly reduced the flow rate of the sand from an average of 144 mL/min uncoated to an average of 83 mL/min coated, while the uncoated and coated pumice filters averaged 278 mL/min and 268 mL/min, respectively. The biochar filter and the uncoated sand filter had similar average flow rates of 152 mL/min and 144 mL/min, respectively. All filters had similar removal of turbidity (88-90%), except the coated pumice, which removed only 79%, possibly due to export of fine particles from the coating process. The product water of the coated sand and pumice filters had a higher pH than the influent water, likely due to the presence of aluminum. However, the pH has been showing a downward trend as of this writing. Effluent aluminum from the coated pumice filter was 0.66 mg/L during the first week of operation, then decreased to 0.07 mg/L in the third week. The coated sand showed a similar trend but had much lower concentrations of aluminum in the effluent. This evidence, along with the increased effluent turbidity and pH, showed that not all of the aluminum was effectively coated on the media, especially in the pumice filter.
The *in-situ* coating method consistently doubled the removal of UV$_{254}$ in both the sand and pumice filters (60% and 62%, respectively). However, the biochar filter still achieved the best removal of UV$_{254}$ (87%), displaying the high capacity of biochar to adsorb organic matter. As expected, the uncoated filters did not remove a significant amount of fluoride, while the aluminum oxide coated filters did. The coated sand filter initially achieved an effluent fluoride concentration of 0.86 mg/L, but had concentrations above the WHO limit of 1.5 mg/L after Day 10. The coated pumice filter showed a similar trend, but started at 0.61 mg/L and remained below the WHO limit until Day 31.
Chapter 1: Introduction

Contaminated drinking water can transmit diseases such as polio, dysentery, and typhoid. Many of these diseases are largely preventable with safely managed drinking water and sanitation services; yet, in 2017 over 600 million people still lacked even the most basic drinking water services (WHO 2019). Unsafe drinking water services are a challenge that disproportionately affects developing countries. In 2015, the United Nations (UN) set seventeen Sustainable Development Goals, with one objective dedicated to water, sanitation, and hygiene issues. Specifically, Goal 6 aims to achieve “Clean Water and Sanitation” using access to a safely managed water supply that is free of contamination as one of its indicators (United Nations 2019).

One contaminant of concern in drinking water is fluoride. Along with nitrate, lead, and others, fluoride is recognized by the World Health Organization (WHO) as one of the key chemical contaminants in drinking water causing wide-spread, acute health effects (WHO 2017). In many centralized treatment systems around the world, fluoride is added to drinking water before it is sent to consumers to enhance dental health. Typically, this water has a fluoride concentration near 0.7 mg/L, which is recommended by the U.S. Department of Health and Human Services (HHS) as the ideal concentration to aid dental health (HHS 2015). However, long-term consumption of fluoride at higher concentrations can pose serious health risks, such as dental and bone fluorosis, kidney failure, and growth retardation (WHO 2017). Populations in Africa, continental America, Asia, and the Middle East rely on drinking water containing concentrations higher than the WHO limit of 1.5 mg/L (WHO 2017). In 2019, over 95% of the water used in households in rural and small communities in Ghana was extracted from groundwater wells (Community Water and
Sanitation Agency 2019). However, this water often has elevated levels of fluoride of up to 11.6 ppm (Salifu, Petrusevski et al. 2012) with 20-30% of boreholes being affected (Community Water and Sanitation Agency 2019). A study in 2013 revealed that 62% of schoolchildren in Bongo, a Northeastern district of Ghana, had dental fluorosis (FIREMPONG, NSIAH et al. 2013).

Conventional methods of removing fluoride from drinking water can be broadly divided into two categories: membrane processes and adsorption processes. Reverse Osmosis (RO) has been shown to remove up to 98% of fluoride; however, RO is expensive, has high energy demands, and produces waste concentrates that can be a disposal problem (Mohapatra, Anand et al. 2009). Nanofiltration utilizes larger pore sizes than RO, so its operational costs are lower due to lower pressure requirements and less frequent fouling. While RO and nanofiltration are effective at removing fluoride, they require expensive membranes that cannot be manufactured in developing world settings (Mohapatra, Anand et al. 2009). Adsorption techniques are generally more accessible and less expensive than membrane technologies for people in developing countries. The most common and accepted method of removing fluoride is the Nalgonda Technique, which utilizes aluminum sulfate and calcium carbonate to carry out the coagulation and precipitation of fluoride. However, this method has disadvantages such as high use of chemicals, toxic byproducts, and sludge disposal requirements (Loganathan, Vigneswaran et al. 2013). Several adsorbents have been studied with varying capacities to remove fluoride, but many are unacceptable due to high cost or extreme pH requirements (Bhatnagar, Kumar et al. 2011). Aluminum oxide effectively removes fluoride at a pH between 6 and 9, potentially removing the requirement for costly pH adjustment (Loganathan, Vigneswaran et al. 2013). By coating filter media with aluminum oxide, researchers have been able to improve fluoride removal performance in bench-scale studies (Salifu, Petrusevski et al. 2013, Zhao 2017).
Removing fluoride is one challenge associated with treating contaminated groundwater. It is also important to remove fecal indicator bacteria (FIB), turbidity, and organic matter. One technology that achieves this is the biosand filter (BSF). BSFs are widely used point-of-use drinking water treatment systems that are similar to slow sand filters used for centralized water treatment. According to the Center for Affordable Water and Sanitation Technology (CAWST), in 2013 BSFs were used in over fifty-five countries providing water for over four million people. Unlike traditional slow-sand filters, BSFs are small enough to be used within a home and do not require continuous flow (CAWST 2017). A layer of water is maintained above the sand at all times, which allows the growth of a beneficial biolayer, or schmutzdecke. As the biolayer grows, it enhances the filter’s ability to capture pathogens and small particles. Pathogens and small particles are removed through both mechanical and biological processes, including trapping, predation, and natural die-off (CAWST 2017). BSFs are traditionally made out of concrete or commercially-made plastic containers, such as the one shown in Figure 1.1. The BSF was invented in 1991 by Dr. David Manz and there have since been at least 10 design updates to improve performance and acceptability by users (Ngai, Baker et al. 2014). One of the most recent updates increased the pore volume to enhance the removal of FIB via trapping and die-off, but inadvertently decreased the product flow rate (Ngai, Baker et al. 2014). In order to make BSFs more desirable to users, their design must produce safe drinking water without compromising the product flow rate. An added benefit includes the option to construct BSFs out of locally available and inexpensive materials. A few BSFs made out of alternative materials have been created, but very little work has been done to test their performance (Smith 2013).
While BSFs have been shown to be highly efficient at removing the FIB and turbidity (Lynn, Wanjugi et al. 2013), dissolved contaminants, such as fluoride, are not effectively removed (Murphy, McBean et al. 2010). Studies have been done to combine the technology of the BSF with adsorptive materials to remove fluoride (Salifu, Petruievski et al. 2013, Zhao 2017), however, there is a lack of research on full-scale systems. Ahamed, and Davra (2011) conducted a full-scale study of BSFs containing a layer of iron oxide coating, a similar coating to aluminum oxide, to test the removal of FIB and turbidity. The BSF modified with iron oxide consistently removed 1-log$_{10}$ more *Escherichia coli* (*E. coli*) and fecal coliforms than the unmodified BSF and performed
the same with respect to turbidity removal, but no results were shown for dissolved contaminants (Ahammed and Davra 2011). Studies by Zhao (2017) showed that laboratory scale BSFs containing media coated with aluminum oxide were capable of removing 99% of fluoride.

Sand has a low porosity that results in a low pore volume. These characteristics contribute to undesirable effects when used in BSFs, such as low product flow rate and frequent clogging, that may reduce user satisfaction (Ghebremichael, Wasala et al. 2012). Pumice, a naturally occurring volcanic mineral, has been shown to produce greater flow rates while maintaining performance with respect to FIB removal and improving removal of turbidity in full-scale BSFs (Ghebremichael, Wasala et al. 2012). Pumice, like sand, shows very little capacity to remove fluoride and other dissolved contaminants, however, its high surface area makes it a good candidate for aluminum oxide coating. Laboratory scale batch studies have shown that aluminum-oxide coated pumice is capable of reducing fluoride concentrations from 5 mg/L to 1.5 mg/L in one hour (Salifu, Petrusevski et al. 2013). Biochar has also shown promising results as an adsorbent media (Mohan, Sharma et al. 2012). Biochar is the product of the pyrolysis of organic materials, such as wood or even agricultural waste products. Like pumice, biochar also has a high surface area which makes it a good candidate for aluminum oxide coating. Few studies have been done to investigate the removal of fluoride with aluminum oxide coated biochar (Chen, Peng et al. 2016).

The goal of this research was to re-design the traditional BSF using conventional 5-gallon buckets and enhance the performance of the traditional BSF by using alternative and/or modified filter media to target fluoride removal. Specific objectives were to:

1) Compare the hydraulic and water quality performance of uncoated sand, pumice, and biochar BSFs,
2) Compare the performance of coated and uncoated sand and pumice for the removal of multiple contaminants: fluoride, organic matter, and *E. Coli*.

3) Analyze the efficacy of an *in-situ* coating method for removing fluoride,

4) Compare the performance of “Bucket-BSFs” with traditional BSF designs.
2.1 Fluoride in Drinking Water

In many parts of the United States and Europe, fluoride is added to drinking water to improve oral health and prevent dental caries. However, this beneficial concentration of fluoride in drinking water is typically less than half of the WHO safe drinking water limit of 1.5 mg/L. When consumed above this safe limit, fluoride can cause dental and skeletal fluorosis (WHO 2017). Dental fluorosis typically occurs with long-term ingestion of drinking water with concentrations between 1.5 and 3 mg/L, and is characterized by discoloration of teeth. Between 4 and 8 mg/L, skeletal fluorosis begins to occur and bones become malformed and movement is difficult. Beyond 10 mg/L, consumers may be crippled by the effects of skeletal fluorosis, so much that they become immobile (Malago, Makoba et al. 2017). It is estimated that over 200 million people drink groundwater contaminated with fluoride with concentrations above 1.5 mg/L, with the majority occurring in developing areas (see Figure 2.1). In Northern regions of Ghana, groundwater samples revealed fluoride levels between 0 and 11.6 mg/L (Salifu, Petrusevski et al. 2012).

The most common cause of elevated concentrations of fluoride in groundwater is contact with rocks that are naturally rich in fluoride compounds such as apatite, micas, and amphiboles, but fluorite is usually the greatest contributor. The amount of fluoride that is dissolved into groundwater from the surrounding rock formations is highly dependent on a number of factors including pH, contact time, temperature, and the presence of potential coagulating ions (Apambire,
Fluoride is also commonly present in volcanic ash, as well as fly ash, a product of the combustion of fossil fuels (Brindha and Elango 2011). One notable case of this is the combustion of coal for brick burning in India. Brick kilns are widely used to make the popular and inexpensive building material, yet they contribute extensively to air pollution, including the release of fluoride into the air (Jha, Nayak et al. 2008). Fluoride in the air can deposit on the soil and subsequently end up in groundwater. Phosphate fertilizers can also be a significant source of fluoride contamination, though not as significant as underlying rock formations (Rao 1997).

Groundwater is frequently the most suitable source of drinking water in developing communities because it is less likely to be contaminated by pathogenic microorganisms. Simply switching water sources is often not feasible or desirable. Fluoride concentrations in groundwater change over time both horizontally and vertically and monitoring can be expensive (Maheshwari 2006). It is common for this groundwater to be used for drinking, cleaning dishes, or bathing without treatment or with minimal treatment due to lack of infrastructure and decentralized treatment. Fluoride exhibits no color, odor, or taste in drinking water so it is difficult to detect, especially where sophisticated analytical tools are not available (Brindha and Elango 2011).

2.2 Defluoridation

Given the significant risk to human health that fluoride poses, there are many technologies developed to remove it, such as membrane processes, coagulation/precipitation, and adsorption.

2.2.1 Membrane Processes

Membrane processes used to remove fluoride from drinking water include reverse osmosis (RO) and nanofiltration. Reverse osmosis (RO) is the process of forcing feed water through a semipermeable membrane at high pressure. RO membranes work by excluding ions based on their size as well as charge (Maheshwari 2006). Nanofiltration (NF), like RO, utilizes a semipermeable
Figure 2.1 Regions with Groundwater Concentrations of Fluoride Above 1.5 mg/L ([BGS © UKRI: https://www.bgs.ac.uk/research/groundwater/health/fluoride.html](Edmunds and Smedley 2013)

membrane but has lower pressure requirements. These membranes have larger pore sizes and thus do not have as much rejection of contaminants, but do not have the same energy requirements as RO (Maheshwari 2006). NF and RO both can have a high selectivity for fluoride removal due to charge repulsion (Damtie, Woo et al. 2019, Yadav, Kumar et al. 2019). RO has been shown to remove up to 98% of fluoride in laboratory bench-scale studies, while NF has slightly lower performance (Mohapatra, Anand et al. 2009, Damtie, Woo et al. 2019). While both RO and NF exhibit excellent fluoride removal, they also remove other minerals from drinking water that are necessary for human health, creating the requirement for re-mineralization. In addition, water passed through these membranes loses alkalinity and may require pH adjustment (Yadav, Kumar et al. 2019). A portion of the water treated with membranes gets wasted as brine, which becomes
a disposal problem. A solar-powered nanofiltration plant studied by Bouhadjar et al. (2019), while highly effective at achieving product water within WHO guidelines, only had on average a 12% recovery of permeate. RO and NF membranes can also be quite costly and they cannot be manufactured locally in most developing regions (Maheshwari 2006).

2.2.2 Coagulation/Precipitation

Aluminum sulfate (alum) and calcium hydroxide (lime) can be used to coagulate and precipitate fluoride, which can then be filtered out of water. Alum acts as a flocculent for fluoride, and lime is added to maintain a neutral pH and promote quick settling. The Nalgonda Technique, one of the most popular methods of defluoridation, involves these two chemicals and can be used on the household or community level (Mohapatra, Anand et al. 2009). This method is able to remove approximately 70% of fluoride (Yadav, Kumar et al. 2019). While the Nalgonda Technique has been widely accepted in India and much of Asia, areas with higher alkalinity and fluoride concentrations require greater amounts of alum and lime (Alfredo, Lawler et al. 2014, Yadav, Kumar et al. 2019). In addition to the possible prohibitive cost of materials, the Nalgonda Technique has been shown to produce harmful byproducts in excess of WHO safe limits such as sulfate, aluminum, and aluminum-fluoride complexes along with sludge that must be disposed of (Mohapatra, Anand et al. 2009, Dubey, Agarwal et al. 2018). Users of this method to remove fluoride also tend to dislike the taste of the treated water, and the monitoring required to select the correct amount of chemicals to add can be difficult (Maheshwari 2006).

A modification on the traditional coagulation method is electrocoagulation. In traditional coagulation, the coagulant is an added chemical. In electrocoagulation, the coagulant is generated in-situ using a sacrificial anode and electrolytic oxidation induced by an external charge (Mollah, Schennach et al. 2001). Studies performed using sacrificial electrodes made of aluminum and a
hydraulic retention time of five minutes were able to achieve 93% fluoride removal with initial concentrations between 4 and 6 mg/L (Khatibikamal, Torabian et al. 2010). Electrocoagulation removes the need for continuous chemical supplies needed for traditional coagulation techniques, and requires relatively simple equipment. However, sacrificial electrodes are used up in the process and require replacement and the requirement for electricity may not be feasible in many developing regions (Mollah, Schennach et al. 2001).

### 2.2.3 Adsorption

Adsorption methods, along with coagulation/precipitation methods, are generally regarded as the most suitable ways to treat fluoride in developing regions. Adsorption is favorable due to its relatively low cost, ease of operation, ability to regenerate media, and high capacity (Mohapatra, Anand et al. 2009, Yadav, Gupta et al. 2018). Adsorption is a process where the adsorbate, in the liquid phase, undergoes mass transfer and accumulates on the surface of the adsorbent, the solid phase. There are three steps to adsorption: mass transfer of fluoride ions from the bulk liquid solution to the surface of the adsorbent, then adsorption of fluoride ions onto the surface, and finally the fluoride ions move to the inner surfaces of the adsorbent or exchange with its structural elements (Habuda-Stanić, Ravančić et al. 2014). Loganathan (2013) listed five mechanisms that describe how fluoride can be adsorbed: 1) van der Waals forces, 2) ion exchange, 3) hydrogen bonding, 4) ligand exchange, and 5) chemical modification of adsorbent surface. Neither van der Waals forces nor ion exchange are preferable to remove fluoride, as they are not selective to fluoride. Hydrogen bonding tends to occur with organic adsorbents while ligand exchange occurs with inorganic adsorbents (Loganathan, Vigneswaran et al. 2013). Fluoride exists in solution as fluorine ions (F⁻), which have a high tendency to act as ligands and exchange with OH⁻ molecules.
to form metal complexes. Equations 2.1 and 2.2 show examples of potential ligand exchange mechanisms with aluminum as the adsorbent.

\[
\text{AlOH}_2^+ + F^- \rightarrow \text{AlF} + \text{H}_2\text{O} \quad (2.1)
\]

\[
\text{AlOH} + F^- \rightarrow \text{AlF} + \text{OH}^- \quad (2.2)
\]

Many different adsorbents have been studied to remove fluoride, ranging from expensive ion exchange resins to commonly available waste products (Habuda-Stanić, Ravančić et al. 2014). The feasibility of an adsorbent depends on a number of factors, including adsorption capacity, fluoride ion selectivity, cost, availability, and regenerability (Habuda-Stanić, Ravančić et al. 2014). The solution chemistry and operating conditions also play a role in the effectiveness of an adsorbent, as adsorption of fluoride depends on pH, initial concentration, temperature, adsorbent dose, and contact time (Yadav, Gupta et al. 2018). In developing areas where resources are limited, it is preferable to limit the amount of pH adjustment required as well as the adsorbent dose to minimize costs. Other considerations include availability, hydraulic properties, and ease of regeneration.

Natural adsorbents, such as found materials or waste products, have been investigated for their capacity to remove fluoride as they exemplify many of the previously mentioned characteristics, such as local availability and affordability. However, their efficiency at removing fluoride is limited. Devi et al. (2008) studied full-scale household sand filters modified with a layer of crushed brick with an influent fluoride concentration of 5 mg/L. Residual fluoride values of 0.72 mg/L were observed after 10 hours, but breakthrough began to occur after 12 hours. Many of the results outlined in Table 2.1 were obtained via batch experiments under laboratory conditions. The capacity of the media to adsorb fluoride is shown in units of mg F⁻/g media and it is solely a measure of the maximum amount that can be adsorbed.
Adsorption capacity depends heavily on the reactor conditions, such as shaking speed, pH, temperature, and even type of source material. Decreasing the grain size, modifying the pH, and increasing the ratio of sorbent to solution have been shown to improve the performance of most natural materials (Craig, Stillings et al. 2015). However, reducing grain size may require a significant amount of manual labor, especially for large quantities of media. Also, as discussed previously, pH adjustment is typically costly, as it often requires that chemicals be purchased and shipped. Given that many natural materials have unsatisfactory performance alone, many studies have been done with various types of modifications such as crushing, pyrolysis, and burning to enhance performance (Sinha, Pandey et al. 2003, Biswas, Dutta et al. 2016, Chen, Peng et al. 2016, Vázquez-Guerrero, Alfaró-Cuevas-Villanueva et al. 2016). While these modifications do increase the barrier of entry for adsorbent materials, their benefits may out-weigh their difficulties.

Metal oxides have been widely studied for their removal of fluoride from drinking water (Tripathy, Bersillon et al. 2006, Ganvir and Das 2011, Salifu, Petrushevski et al. 2013, Craig, Stillings et al. 2015, Chen, Peng et al. 2016, Amalraj and Pius 2017). The main mechanism that occurs when fluoride is adsorbed onto metal oxides is ligand exchange (Loganathan, Vigneswaran et al. 2013). Iron oxide, aluminum oxide, and especially activated aluminum have shown favorable results for fluoride removal from drinking water (Kumar, Bhatnagar et al. 2009, Salifu, Petrushevski et al. 2013, Craig, Stillings et al. 2015, Zhao 2017). Craig et al. (2015) found that activated alumina adsorbed 92-95% of fluoride at a pH of 7.5. Granular iron hydroxide was found to remove 95% of fluoride within ten minutes during laboratory batch experiments conducted by Kumar et al. (2009). Activated alumina is the most commonly studied material, but it is relatively expensive and has a tendency to reduce pH (Bhatnagar, Kumar et al. 2011). Evaluating and comparing these adsorbents is difficult given that most experiments were performed under different conditions that can have
significant effects on fluoride adsorption such as pH, initial concentration, contact time, and adsorbent dose.

Table 2.1 Fluoride Removal of Some Natural Adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Capacity (mg F/g media)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered Biomass (Tinospora Cordifolia)</td>
<td>7</td>
<td>25</td>
<td>(Pandey, Pandey et al. 2012)</td>
</tr>
<tr>
<td>Common Water Hyacinth (Eichhornia crassipes)</td>
<td>-</td>
<td>4.4</td>
<td>(Sinha, Pandey et al. 2003)</td>
</tr>
<tr>
<td>Lemon leaves (Citrus Limonum)</td>
<td>2-8</td>
<td>0.07</td>
<td>(Pandey, Pandey et al. 2012)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>6</td>
<td>1.73</td>
<td>(Balouch, Kolachi et al. 2013)</td>
</tr>
<tr>
<td>Coal Cinder</td>
<td>-</td>
<td>0.52</td>
<td>(Li, Liu et al. 2014)</td>
</tr>
<tr>
<td>Soil*</td>
<td>-</td>
<td>0.18</td>
<td>(Li, Liu et al. 2014)</td>
</tr>
<tr>
<td>Mahabir colliery shale</td>
<td>7</td>
<td>0.008</td>
<td>(Biswas, Dutta et al. 2016)</td>
</tr>
<tr>
<td>Sonepur Bazari colliery shale</td>
<td>7</td>
<td>0.011</td>
<td>(Biswas, Dutta et al. 2016)</td>
</tr>
<tr>
<td>Red Mud</td>
<td>5.5</td>
<td>1.9</td>
<td>(Çengeloğlu, Kir et al. 2002)</td>
</tr>
<tr>
<td>Common Duckweed (Spirodela polyrrhiza)</td>
<td>-</td>
<td>0.91</td>
<td>(Pandey, Pandey et al. 2012)</td>
</tr>
<tr>
<td>Fish Bone Char (500 °C)</td>
<td>-</td>
<td>4.85</td>
<td>(Brunson and Sabatini 2009)</td>
</tr>
<tr>
<td>Cow Bone Char (400 °C)</td>
<td>-</td>
<td>5.96</td>
<td>(Brunson and Sabatini 2009)</td>
</tr>
</tbody>
</table>

* Soil was collected near the Chinese Academy of Sciences

The affordability of adsorption processes depends heavily on their regeneration. No matter the capacity of the adsorption media used, it will require regeneration once it becomes saturated with fluoride or other anions. Studies have been done on the performance of adsorptive media after regeneration as it is imperative to understand long-term performance. Zhao (2017) performed regeneration experiments on bench-scale BSFs by re-coating the medium with aluminum oxide.
after it became saturated. Regeneration was successful at enhancing fluoride removal, however, it took 5-10 days for the BSFs to return to neutral pH after a sharp pH increase. In addition, aluminum residuals in the product water were not monitored in this study. Tripathy et al. (2006) performed desorption and resorption studies on aluminum oxide impregnated activated alumina and found that the removal efficiency of the media decreased significantly, from 92% to 84% removal. Salifu (2017) regenerated saturated media by re-coating it with aluminum oxide and reported that although the media was partially regenerated, it was not restored to its initial adsorption capacity.

2.3 Aluminum Oxide

Aluminum oxide (Al$_2$O$_3$), also known as aluminum (III) oxide, is a promising adsorbent for fluoride (Loganathan, Vigneswaran et al. 2013) and it was chosen as the adsorbent for this research.

2.3.1 Physical and Chemical Characteristics

The hard-soft-acid-base (HSAB) concept can be used to explain why aluminum oxide is a favorable adsorbent for fluoride. Al$^{3+}$ is classified as a hard acid, and F$^{-}$ is classified as a hard base. The HSAB concept states that hard acids and bases attract each other, therefore Al$^{3+}$ has a good affinity for F$^{-}$ (Salifu, Petrushevski et al. 2013). Another important factor that characterizes the efficiency of an adsorbent is its point of zero charge (pH$_{PZC}$). Ghorai et al. (2005) found that thermally treated aluminum oxide, called activated alumina, exhibits maximum removal of fluoride at a pH of 7. Below a pH of 7, harmful alumino-fluoro complexes are formed and leave with the product water. Above a pH of 7, other ions seem to be preferred by the activated alumina (Ghorai and Pant 2005). Salifu (2017) found the pH$_{PZC}$ of aluminum oxide coated pumice to be 5.2. At or below the pH$_{PZC}$ the surface charge is expected to be positive, which contributes to non-specific adsorption of fluoride ions via columbic forces (Sujana, Pradhan et al. 2009). Despite this
low pH$_{PZC}$, the aluminum oxide coated pumice exhibited the best fluoride removal at a pH of 6, showing that fluoride uptake was not only dictated by non-specific adsorption, but by specific adsorption mechanisms such as ligand exchange (Salifu 2017).

### 2.3.2 Media Coating

Aluminum oxide has been studied a great deal as media coating to remove contaminants from water. Coating media enhances its ability to remove dissolved contaminants that the media otherwise would not be able to remove, such as fluoride and arsenic, while still maintaining the filtration properties of the media (Heidari, Moattar et al. 2011). Salifu et al. (2013) coated pumice with aluminum oxide and observed a decrease in fluoride concentration from 5 mg/L to 1.5 mg/L in one hour with an adsorbent concentration of 10 g/L. These batch adsorption experiments were carried out at neutral pH, which confirms that aluminum oxide coating can be effective for drinking water treatment without pH adjustment. Zhao (2017) also performed experiments with aluminum oxide coated pumice, but used laboratory scale BSFs. This experiment included three BSFs: one with only sand, one with half coated pumice and half sand with the pumice layer on top, and the third with coated pumice sandwiched between two layers of sand. Both of the filters with the aluminum oxide coating had average residual fluoride concentrations of approximately 0.04 mg/L until they experienced breakthrough (Zhao 2017). Other natural adsorbents, such as rice husk ash, spent mushroom biochar, pine sawdust, and activated carbon prepared from bark, have been coated with aluminum oxide and achieved enhanced fluoride removal (Ganvir and Das 2011, Chen, Peng et al. 2016, Vázquez-Guerrero, Alfaro-Cuevas-Villanueva et al. 2016, Amalraj and Pius 2017).

It is apparent from the literature that aluminum oxide coating is effective at removing fluoride and is worth further investigation. Aluminum oxide coatings may also assist with the removal of other contaminants, such as FIB, viruses, and arsenic (Lukasik, Farrah et al. 1996,
Chen, Truesdail et al. 1998, Truesdail, Lukasik et al. 1998, Lukasik, Cheng et al. 1999, Lee, Park et al. 2010). Lukasik et al. (1999) investigated the effect of coating sand with aluminum oxide on the removal of *E. Coli*. Coating sand with a 0.5 M aluminum sulfate solution resulted in a 3.50 log10 reduction in *E. Coli*, while the log10 reduction was only 0.62 for uncoated sand (Lukasik, Cheng et al. 1999). Chen et al. (1998) observed significant removal of arsenic, a dissolved contaminant also persistent in groundwater, with aluminum oxide coated pumice.

**2.4 Point of Use Drinking Water Treatment**

In urban areas in developed regions, drinking water is usually treated in centralized treatment plants and then sent to citizens through extensive piping networks. While centralized treatment can be very effective at making water safe to drink, it is not feasible for all communities. If homes are very spread out or the local government lacks the funds for the required infrastructure, centralized treatment will be unobtainable (Pooi and Ng 2018). In situations like these, people may have access to improved water sources, such as covered wells or public taps, instead of piped water from a centralized source. However, even if the source is protected from contamination, the water may still be contaminated during transport or storage via unhygienic containers (WHO 2007). One possible solution to this problem is point of use (POU) drinking water treatment. POU treatment consists of methods used to treat water at the place where it will be consumed, such as a home or a school. By providing treatment at home, these systems reduce the risk of contamination between the source and the point of use (Murphy, McBean et al. 2010). POU systems are often inexpensive, simple to operate, and durable. However, they must be designed, operated, and maintained properly so that they can be effective at removing drinking water contaminants (Pooi and Ng 2018). POU design and operation will be most effective if it addresses the contamination of the drinking water source.
POU treatment can refer to any method used to treat water at the point of consumption, such as disinfection, coagulation, or filtration. The focus of this thesis will be on one POU method: biosand filtration. Biosand filters, unlike traditional slow sand filters commonly used for centralized treatment, are operated on a batch basis so users have the freedom to add water when needed or convenient. Figure 2.2 presents a schematic of a typical BSF. Users pour a volume of raw water equal to approximately the pore volume of the filter in through the top, and it slowly enters the media through the diffuser. As the water moves down through the filter via gravity, the water added during the previous charge essentially gets pushed out through the outlet pipe, where the user collects the treated water. BSFs are typically 70-90 centimeters tall by 20-30 centimeters wide filters and consist of three layers: gravel, separation gravel, and sand. An important part of the BSF is its elevated outlet pipe that maintains a layer of water above the sand at all times, keeping the sand saturated. This also allows the growth of a beneficial biolayer within the top 2 cm of the sand called the schmutzdecke. As the biolayer grows, it improves the quality of the treated water by removing pathogens and organic matter (Pooi and Ng 2018). Organic matter is biodegraded by the schmutzdecke and pathogens are removed through trapping, predation, competition and natural die-off (CAWST 2017). However, as the schmutzdecke grows, clogging occurs and the outlet flow rate decreases and the filter must be cleaned lest the flow rate drop to unacceptable levels and dissuade users (CAWST 2017). BSFs are cleaned using the “Swirl and Dump” method as outlined in CAWST BSF Construction Manual. The user swirls the standing water above the media, detaching some of the biolayer, then removes the dirty standing water by scooping it out with a cup (CAWST 2012). BSFs can be purchased from commercial sources or constructed from locally available materials, such as concrete.
BSFs have been widely employed in developing regions, with an estimated 650,000 implemented in over 55 countries as of 2013 (CAWST 2017). Many studies have been done to investigate the performance of these systems with regards to parameters such as turbidity, organic matter, and *E. coli* removal (Duke, Nordin et al. 2006, Murphy, McBean et al. 2010, Lynn, Wanjugi et al. 2013, Pooi and Ng 2018). Removal of *E. coli* and other fecal indicator bacteria (FIB) depends heavily on the ripening of the filter, creating dramatic differences in efficiency (Murphy, McBean et al. 2010). BSFs can successfully treat water with a variety of turbidities, but they are not recommended for water with turbidity above 50 NTU (Ngai, Baker et al. 2014). Lynn et al. (2013) found that BSFs operated over a 4-month period were able to reduce turbidity from 7.5 NTU to 1.1 NTU, and remove 27% of total organic carbon (TOC).

### 2.5 Alternate Biosand Filter Media

While BSFs have been deployed all over the world and positively impacted thousands of lives, they can still be improved. As BSFs go through a period of “ripening”, or growing their schmutzdecke, removal of turbidity and FIB increases and the flow rate decreases until it becomes unacceptable to the user (Lynn, Wanjugi et al. 2013). Subsequently, the BSF must be cleaned and the ripening process begins again. Users satisfaction would increase if head loss were decreased, pore volume were increased, and filtration rates increased, as they would be able to filter more water in each batch (Ghebremichael, Ergas et al. 2016). One way that these problems can be addressed is by using alternate filter media.
2.5.1 Pumice

Pumice is a naturally occurring volcanic mineral that is relatively inexpensive and available. This mineral is mainly found in areas with volcanic activity. For instance, in Africa pumice can be found in the Atlantic Islands, northeastern Morocco, and the East African Rift System (Smedley and Dickson 2019). Pumice has a high surface area and is very porous, having a greater surface area than sand by 5-15 m$^2$/g (Kitis, Kaplan et al. 2007). Raw pumice has very little ability to remove fluoride, but modifying it with aluminum oxide coatings has had favorable results, as discussed in 2.4.2 (Salifu, Petrushevski et al. 2013, Zhao 2017). The porosity of pumice makes it a good candidate for aluminum oxide coating, but it also makes it a favorable filter media. Studies by Ghebremichael et al. (2012) demonstrated that BSFs, when modified with pumice
media, had enhanced performance. Laboratory scale BSFs with pumice and sand were run for four months. The pumice filters demonstrated 24% higher volumetric production per cycle, similar *E. coli* removal, and greater turbidity removal than the sand filters (Ghebremichael, Wasala et al. 2012). Pumice BSFs exhibited better hydraulic performance than sand, which can make them more desirable for users without compromising product water quality.

### 2.5.2 Biochar

Biochar is the product of the pyrolysis of organic materials. Because of this, it can be very diverse and tailored to the area where it is being used. Research shows that biochar and its activated forms have the ability to remove FIB, heavy metals, arsenic, phosphate, and fluoride (Gwenzi, Chaukura et al. 2017). Biochar has commonly been used as a soil amendment to enhance soil, but it has also been studied in the context of drinking water treatment.

### 2.5.3 Modified Media

As discussed previously, aluminum oxide amended media has been shown to be a promising way to remove fluoride from drinking water in batch experiments. Similar coating methods and metal amendments have been applied to full-scale BSFs to remove different dissolved contaminants, such as arsenic and FIB. Arsenic biosand filters (ABF) have been designed to remove arsenic by adding a layer of adsorbent material above the conventional sand layer, called a Kanchan filter. Ngai et al. (2003) utilized an adsorbent layer of iron nails within the diffuser plate of a traditional BSF and recorded, on average, 93% removal of arsenic, 58% of total coliforms, and 64% of *E. Coli* over three months. By modifying a traditional BSF in this way researchers were able to remove arsenic with the use of locally available and inexpensive materials.
2.6 Biosand Filter Design Modifications

The traditional design of the BSF, as discussed in section 2.1.1, consists of one container, either commercially or locally made, with three layers of media. Locally made BSFs are typically constructed with concrete, as outlined by the CAWST BSF construction manual (CAWST 2012). However, BSFs can be made from any number of materials, such as injection molded plastic, PVC, ceramic containers, large plastic drums, and 20 L buckets (Ngai, Baker et al. 2014). Concrete BSFs weigh roughly 91 kg and require molds, which can also be too heavy to easily move (Smith 2013). This may not be a challenge for aid organizations, but for small developing communities it can be a limiting factor. For this reason, it would be beneficial to design a new BSF that is not only made from locally found materials, but light weight and easy to transport. One promising design modification is the Sandstorm BSF by Smith (2013). Sandstorm consists of a cylindrical galvanized iron (GI) shell, only weighing 23 kg, and an inverted jerry can. The inverted jerry can feeds the water into the GI shell and provides a constant head of 7 cm above the filter media. While the Sandstorm BSF design seems promising, no research has been done on scaling up the system or over long periods of time.
Chapter 3: Materials and Methods

Batch experiments were performed for aluminum oxide coated sand, pumice, and biochar to study their fluoride adsorption capacity and inform future experiments. A new full-scale BSF design, called the “Bucket-BSF”, was constructed and operated for 20 days. Section 3.1 lists the materials used, Section 3.2 describes the filters and their operation, Section 3.3 outlines the in-situ coating method used, and Section 3.4 reviews the analytical methods used.

3.1 Materials

3.1.1 Media

Table 3.1 summarizes information about the three different types of media used: sand, pumice, and biochar. The D10 is a common parameter used to evaluate media for BSFs and other filters and it represents the mesh size at which 10% of the media is allowed to pass through. Studies by Lynn et al. (2013) identified a D10 between 0.14 mm and 0.26 mm as ideal for BSFs.

Table 3.1 Sand, Pumice, and Biochar Media Characteristics

<table>
<thead>
<tr>
<th>Media</th>
<th>Source</th>
<th>Brand Name</th>
<th>Bulk Density (g/mL)</th>
<th>D10 (mm)</th>
<th>Porosity</th>
<th>Feed Stock</th>
<th>Pyrolysis Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>Seffner Rock and Gravel (Tampa, FL)</td>
<td>Concrete Sand</td>
<td>1.20</td>
<td>0.22</td>
<td>0.37</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Pumice</td>
<td>Hess Pumice (Malad City, Idaho)</td>
<td>Hess Grade 2</td>
<td>0.80</td>
<td>0.27</td>
<td>0.56</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Biochar</td>
<td>Biochar Supreme Inc. (Everson, WA)</td>
<td>Environmental Ultra</td>
<td>0.18</td>
<td>1</td>
<td>0.69</td>
<td>Wood</td>
<td>900-1,000</td>
</tr>
</tbody>
</table>
3.1.2 Solutions

Both the batch and field experiments utilized a 1000 mg/L (0.053 M) fluoride stock solution for the creation of feed water as well as standards for calibrations. This stock solution was created by first drying sodium fluoride (NaF) (99+% for analysis, ACROS Organics, Geel, Belgium) for at least two hours in an oven set to 105 °C. Once the NaF powder was dried, 2.21 grams were added to a 1-liter volumetric flask and filled with deionized (DI) water until it reached 1 liter (the solubility of NaF is 43 g/L at 23 °C). The solution was then covered with an air-tight seal and stirred until all of the NaF dissolved. This stock solution was re-made weekly to ensure freshness. The stock solution was also stirred for at least 10 minutes prior to any use.

The batch and in-situ aluminum oxide coating methods both required the use of 0.5 M aluminum sulfate and 3 M ammonium hydroxide solutions. The aluminum hydroxide solutions were made with aluminum sulfate hydrate (Al₂(SO₄)₃·xH₂O), also called alum (97+% Alfa Aesar, Ward Hill, MA, U.S.A.), and the ammonium hydroxide (NH₄OH) solutions were made with 28.0% to 30.0%, BAKER ANALYZED™ A.C.S. Reagent (J.T. Baker, Phillipsburg, NJ, U.S.A.). Prior to making the alum solutions, the exact degree of hydration was determined via the Eriochrome Cyanine R Method (see Table 3.5 for more detail on this method) to ensure the accuracy of the concentration. Early analysis resulted in a degree of hydration of 14, which was used for the remainder of the research. For each batch experiment, 250 mL of 0.5 M alum solution was prepared by adding 74.29 g of alum to a 250 mL volumetric flask and gradually filling to the line with DI water while stirring to completely dissolve the alum (the solubility of alum is 86.9 g/100 mL). Detailed information about the batch coating method can be found in Section 3.4. For the full-scale in-situ coating method, 2.25 kg of alum was slowly added to approximately 1.9 L of DI water and stirred while the volume of water was gradually increased up to 7.6 L. The ammonium
hydroxide solutions were made with the same volumes of 250 mL and 7.6 L for the batch and full-scale experiments, respectively. The ammonium hydroxide stock solution was assumed to be 28%, therefore 104.30 mL were added to a 250 mL volumetric flask and filled to the line with DI water while under a fume hood. For the full-scale in-situ coating method, 3.16 L of ammonium hydroxide were added to 7.6 L of DI water while under a fume hood. More detailed information about the subsequent steps of the full-scale coating method can be found in section 3.5. Table 3.2 provides a summary of all the solutions required for the experiments performed and how they were made.

Table 3.2 Summary of Required Solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration of Solution</th>
<th>Chemical</th>
<th>Amount of Chemical Added per Liter of DI Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride Stock</td>
<td>0.053 M</td>
<td>NaF (99+%%)</td>
<td>2.21 g</td>
</tr>
<tr>
<td>Alum</td>
<td>0.5 M</td>
<td>Al₂(SO₄)₃·14H₂O</td>
<td>297.17 g</td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>3 M</td>
<td>NH₄OH (28-30%)</td>
<td>417.21 mL</td>
</tr>
</tbody>
</table>

3.1.3 Filter Construction and Design

Six Bucket-BSFs were constructed in the USF Tampa Botanical Gardens. Materials included 5-gallon plastic buckets, PVC pipe, and fittings. A complete list of supplies used for construction is provided in Table 3.3. Figure 3.1 shows the design of the Bucket-BSF. This design acts as two small BSFs in series, but the bottom bucket includes a valve below the outlet to facilitate regeneration of the adsorptive media. The first bucket contains a diffuser plate and acts as a pre-filter to reduce the turbidity and load of organic matter entering the second bucket. Each filter was also followed by a covered collection bucket to capture the effluent and prevent re-contamination. Each of the six buckets had a different media combination, as shown in Table 3.4. While each bucket either contained sand, biochar/sand mixture, or pumice, their gravel layers
remained constant and were prepared according to the CAWST Biosand Filter Construction Manual (2012). Figure 3.1 shows the configuration of the media and gravel within each bucket of the Bucket-BSF.

Table 3.3 Materials Required to Construct a Bucket-BSF

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Gallon Plastic Buckets*</td>
<td>2</td>
<td>Home Depot, Atlanta, GA, U.S.A.</td>
</tr>
<tr>
<td>3/4” Sch-40 PVC Pipe</td>
<td>1 meter †</td>
<td>Charlotte Pipe, Charlotte, NC, U.S.A.</td>
</tr>
<tr>
<td>5-Gallon Bucket Lid</td>
<td>2</td>
<td>Home Depot, Atlanta, GA, U.S.A.</td>
</tr>
<tr>
<td>Sch-40 PVC Tee 3/4” Slip x 1/2” Threaded x 3/4” Slip</td>
<td>2</td>
<td>Charlotte Pipe, Charlotte, NC, U.S.A.</td>
</tr>
<tr>
<td>1/2” MIP x 1/4” Plastic Hose Barb</td>
<td>3</td>
<td>Ace Hardware, Oak Brook, IL, U.S.A.</td>
</tr>
<tr>
<td>7/16” OD 5/16” ID Clear Vinyl Tubing</td>
<td>1 meter †</td>
<td>Ace Hardware, Oak Brook, IL, U.S.A.</td>
</tr>
<tr>
<td>Rain Barrel Kit Replacement Seals for 3/4 in. Pipe</td>
<td>2</td>
<td>EarthMinded LLC, IN, U.S.A.</td>
</tr>
<tr>
<td>Sch-40 3/4” Slip x 3/4” MPT PVC Street Elbow</td>
<td>1</td>
<td>Charlotte Pipe, Charlotte, NC, U.S.A.</td>
</tr>
<tr>
<td>Sch-40 3/4” PVC tee</td>
<td>1</td>
<td>Charlotte Pipe, Charlotte, NC, U.S.A.</td>
</tr>
<tr>
<td>3/4” PVC Solvent Ball Valve Full Port</td>
<td>1</td>
<td>Mueller, Collierville, TN, U.S.A.</td>
</tr>
<tr>
<td>1 mm mesh screen</td>
<td>200 cm² ‡</td>
<td>N/A</td>
</tr>
<tr>
<td>Zip Ties</td>
<td>2</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* The dimensions of each 5-gallon bucket used were approximately 36.8 cm tall, with a top diameter of 30.5 cm and a bottom diameter of 26.2 cm.

† Dimensions are estimated
Table 3.4 Configuration of Media in Each Bucket-BSF

<table>
<thead>
<tr>
<th>BSF Name</th>
<th>Top Bucket Media</th>
<th>Bottom Bucket Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/S</td>
<td>Sand</td>
<td>Sand</td>
</tr>
<tr>
<td>P/P</td>
<td>Pumice</td>
<td>Pumice</td>
</tr>
<tr>
<td>B/B*</td>
<td>Sand/Biochar Mixture</td>
<td>Sand/Biochar Mixture</td>
</tr>
<tr>
<td>S/CS</td>
<td>Sand</td>
<td>Coated Sand</td>
</tr>
<tr>
<td>P/CP</td>
<td>Pumice</td>
<td>Coated Pumice</td>
</tr>
</tbody>
</table>

* The sand/biochar mixture was 20% biochar by volume, 3% by mass

3.2 Fluoride Adsorption Batch Experiments

The fluoride adsorption capacities of sand, pumice, and biochar were investigated along with the effect of coating with aluminum oxide on their capacities. Separate batch experiments were performed for sand, pumice, and biochar using the aluminum oxide coating method described
by Salifu et al. (2013). Prior to the batch experiments, the media was washed thoroughly with deionized (DI) water and dried in an oven at 105 °C. For the biochar batch experiment, two different grain sizes were tested: crushed through a 0.30 mm sieve, or uncrushed 1 mm D10 biochar. A portion of the media was then soaked in two volumes of 0.5 M aluminum sulfate solution for 1.5 hours while being stirred at 200 RPM. Excess aluminum sulfate solution was poured off and the media was dried in an oven at 105 °C overnight. The dried media was subsequently soaked in two volumes of 3 M ammonium hydroxide to neutralize and precipitate the aluminum oxide from solution. The solution was stirred at 200 RPM for 30 minutes, then excess liquid was poured off and the media was thoroughly washed with DI water buffered to a pH of 7.00 +/- 0.1 using 0.1 M NH₄OH. The coated media was dried and stored until its use. Prior to batch experiments the coated media was separated into the necessary masses and volumes.

Batch experiments were carried out with varying volumes of media and 250 mL of water from Lake Behnke at USF spiked with 1000 mg/L fluoride solution until it reached a fluoride concentration of 5.00 +/- 0.2 mg/L. Table 3.5 provides a matrix of the different volumes and masses of sand, pumice, and biochar used in each batch experiment. The lake water was buffered to a pH of 7.0 +/- 0.1 and added to 250 mL glass bottles along with either uncoated media or coated media. The bottles were then sealed and stirred at 100 RPM for 24 hours. Once the stirring was finished, each sample was immediately filtered through 0.45 µm membrane filters to prevent further adsorption of fluoride.
Table 3.5 Masses and Volumes of Uncoated and Coated Sand, Pumice, and Biochar Used in Adsorption Batch Experiments

<table>
<thead>
<tr>
<th>Media Used in Batch Experiment</th>
<th>Sand</th>
<th>Pumice</th>
<th>Biochar</th>
<th>Coated</th>
<th>Uncrushed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Added (mL)</td>
<td>25 5 25</td>
<td>25 5 25</td>
<td>19.9 2.4 10.4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Mass Added (g)</td>
<td>40.75 8.15 40.75</td>
<td>20 4 20</td>
<td>2.5 0.5 2.5 2.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Media Concentration (g/L)</td>
<td>163 33 163</td>
<td>80 16 80</td>
<td>10 2 10</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

3.3 Full-Scale Media Coating

The second buckets of the P/CP and S/CS filters were coated using a novel *in-situ* coating method derived from the method used during the batch experiments (Salifu, Petrusevski et al. 2013). Biochar was not coated due to unexpected results of the full-scale sand and pumice coating discussed in Chapter 4. First, the media was drained of all water using the valve (see Figure 3.1) and the media was back-filled with well water from the USF Tampa Botanical Gardens and drained three times. The bucket was drained once again, then back-filled with 0.5 M aluminum sulfate solution until the media was completely saturated and there was solution above the media. The solution was then recirculated through the media at 720 mL/min for 1.5 hours using a Cole Parmer Masterflex Easy-Load II peristaltic pump (Cole Parmer, Vernon Hills, IL, U.S.A.). Figures 3.2 and 3.3 show the full-scale coating set up and the coated sand and pumice filters after coating. The buckets were then drained and left covered with mesh for 24 hours to dry the media. After the drying period, the buckets were back-filled with 3 M ammonium hydroxide until the media was saturated and the solution was above the media. The solution was then recirculated through the media at 720 mL/min for 30 minutes. Using the valve, the ammonium hydroxide was drained from the bucket. Once all of the solution was drained, the filters were covered with mesh and left to dry for 24 hours. Prior to using the filters, the coated sand and pumice buckets were back-filled with
well water and drained three times to clean out excess ammonium hydroxide solution and any loosely bound aluminum.

Figure 3.2 Full-Scale Coating Setup with Peristaltic Pump

Figure 3.3 Coated Pumice and Sand Filters After the Full-Scale Coating Process
3.4 BSF Operation

Bucket-BSFs were fed daily (24 +/- 4 hours) five days per week with 6 liters of lake water from Lake Behnke at the USF Tampa Botanical Gardens. This charge volume was chosen because it is equivalent to the pore volume of one stage of the filter. The lake water was spiked with 1000 mg/L fluoride stock solution until it reached 5 +/- 0.2 mg/L. Spiked lake water was poured into the pre-filter of each BSF through a diffuser plate made out of a plastic bowl. Five minutes after charging the BSF, the flow rate was measured by collecting the effluent in a graduated cylinder for 30 seconds. Composite grab samples were collected from the storage vessel after half of the charge volume was collected. Samples were then immediately filtered through 0.45 µm membrane filters to prevent further adsorption of fluoride prior to analysis.

3.5 Analytical Methods

All analysis was done in the USF Environmental Engineering Laboratory. Fluoride, flow rate, temperature, pH, and ultra violet absorbance at 254 nanometers (UV254) were measured daily for the influent and effluent of each filter. E. coli, Total Organic Carbon (TOC), and Al3+ were measured weekly, along with the other parameters at the effluent of each Bucket-BSF as well as the effluent of each pre-filter. Table 3.5 contains a summary of each analysis method along with instruments used.

3.6 Statistical Analysis

Statistical significance between results was analyzed using T-tests with 95% confidence values and α = 0.05, assuming equal variance. Data analysis was performed using Microsoft Excel Data Analysis Tools.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>Method Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate</td>
<td>Graduated Cylinder</td>
<td>CAWST BSF Construction Manual (2012)</td>
</tr>
<tr>
<td>pH</td>
<td>Hanna Instruments pH/ORP/ISE HI98191 Meter &amp; HI72911 pH Probe</td>
<td>Standard Method 4500-H^+B (Rice, Baird et al. 2017)</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Hach 2100Q Portable Turbidimeter</td>
<td>Standard Method 2130 (Rice, Baird et al. 2017)</td>
</tr>
<tr>
<td>UV_{254}</td>
<td>Thermo Electron Corporation Genesys 10-S UV-Vis Spectrophotometer</td>
<td>Standard Method 5910B (Rice, Baird et al. 2017)</td>
</tr>
<tr>
<td>TOC</td>
<td>Shimadzu TOC-V_{CSH} TOC Analyzer</td>
<td>Standard Method 5310 (Rice, Baird et al. 2017)</td>
</tr>
<tr>
<td>E. coli</td>
<td>N/A</td>
<td>EPA Method 1603: Escherichia coli (E. coli) in Water by Membrane Filtration Using Modified membrane-Thermotolerant Escherichia coli Agar (Modified mTEC)</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>Hach DR2800 Spectrophotometer</td>
<td>Hach Eriochrome Cyanine R Method 8236, derived from Standard Method 3500-Al (Rice, Baird et al. 2017)</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Hanna Instruments pH/ORP/ISE HI98191 Meter &amp; Orion Products 9609BNWP Combination Fluoride Electrode</td>
<td>Standard Method 4500-F^- (Rice, Baird et al. 2017)</td>
</tr>
</tbody>
</table>
Chapter 4 Results and Discussion

4.1 Aluminum Oxide Coating Batch Experiments

Twenty-four hour fluoride adsorption batch experiments were performed to verify that we could reproduce the coating method carried out by others (Salifu, Petrusevski et al. 2013, Zhao 2017). Sand, pumice, and biochar were coated according to the method outlined in Section 3.1. Two different masses of each media were tested as outlined in Table 3.5 to compare adsorption per mass of adsorbate. Biochar was also tested to see if crushed or uncrushed material would be the most effective at removing fluoride. The results are shown in Figure 4.1.

As shown in Figure 4.1, uncoated pumice did not adsorb a significant amount of fluoride (p>0.05) and this result agrees with those of Salifu et al. (2013) and Zhao (2017). Both studies, however, observed that coated pumice removed 90-96% of fluoride after 24 hours. This study found that 16 g/L of coated pumice removed 31.6% of fluoride and 80 g/L of coated pumice removed 54.4%, which is not a significant difference (p>0.05). This result agrees with that of Salifu et al. (2013) as they found that increasing the adsorbent dose above 10 g/L did not have a significant effect on fluoride removal. The discrepancy between the removals of this study and previous studies may be accounted for in properties of the pumice used, such as surface area.

To the author’s knowledge previous studies have not been carried out to test the capacity of aluminum oxide coated sand to adsorb fluoride. Like pumice, sand does not have the capacity to remove fluoride without modification. As shown in Figure 4.1, 24 g/L of coated sand reduced the fluoride concentration by 13% while 120 g/L reduced it by 26%. Unlike coated pumice, there
was a significant (p<0.05) difference between the two doses of sand. Further studies would need to be done to determine the optimum dose of aluminum oxide coated sand to adsorb fluoride. The discrepancy between the fluoride removals observed with coated sand and coated pumice may be due to the surface areas of the two media. Pumice generally has a much greater surface area (5-15 m²/g) than sand, making it a better candidate for coating (Kitis, Kaplan et al. 2007). Neither the coated pumice or sand from this study were able to achieve concentrations below the WHO limit of 1.5 mg/L (WHO 2017).

Fluoride adsorption batch studies were also carried out on biochar. Figure 4.1 shows the results of this study on 40 g/L of uncoated biochar and 8 g/L and 40 g/L of coated biochar, and 40 g/L of uncrushed coated biochar. Like sand and pumice, uncoated biochar does not have the capacity to adsorb fluoride. There was a significant increase in fluoride removal (p<0.05) between 8 g/L and 40 g/L of coated biochar. Uncrushed biochar performed significantly better (p<0.05) than crushed, removing 97% of fluoride after 24 hours and treating the water to below the WHO fluoride limit of 1.5 ppm (WHO 2017). It is hypothesized that crushing the biochar reduced the pore volume by destroying the complex structure of the media.
Figure 4.1 Aluminum Oxide Coating 24 Batch Adsorption Studies for (A) Pumice, (B) Sand, and (C) Biochar
4.2 Full-Scale Field Experiments

4.2.1 Uncoated Sand, Pumice, and Biochar BSF Performance

The uncoated sand, pumice, and biochar BSFs, S/S, P/P, and B/B, respectively, were compared for their hydraulic properties as well as water quality performance over 24 days. Parameters measured included flow rate, turbidity, pH, TOC, UV$_{254}$, and *E. coli*. Figures 4.2-4.4 show changes in turbidity, UV$_{254}$, and flow rate over time. The average influent turbidity over the course of the experiment was 9.22 +/- 6.07 NTU (n=18) while the average effluent of S/S was 0.91 NTU (n=16), of P/P was 0.89 NTU (n=16), and the average effluent of B/B was 0.73 NTU (n=16). The performance of S/S and P/P did not significantly differ (p >0.05). This is contrary to the findings of Ghebremichael et al. (2012) and Zhao (2013) in their laboratory-scale studies comparing the performance of sand and pumice BSFs with average influent turbidities of 8.70 +/- 4.09 NTU and 5.19 +/- 5.21 NTU, respectively. Their BSFs containing pumice consistently achieved higher turbidity removal than sand, with Ghebremichael et al. reporting approximately 98.5% removal. This discrepancy may be accounted for in the scale of the filters and the conditions in which they were tested. Studies performed on full-scale BSFs under real operating conditions typically have an average of 86% removal of turbidity (Duke, Nordin et al. 2006, Lynn, Wanjugi et al. 2013). The differences in performance of B/B and S/S or P/P were not significant (p>0.05). S/S, P/P, and B/B were consistently able to meet the WHO (<5 NTU) standard for turbidity in drinking water (WHO 2017).

P/P achieved 36% removal of UV$_{254}$ on average while S/S achieved an average of 30% removal, and B/B achieved an average of 85% removal. The results for S/S and P/P are very similar to previous experiments carried out on commercial BSFs in the USF Botanical Gardens, where 36% average removal of UV$_{254}$ was reported (Lynn, Wanjugi et al. 2013). P/P and S/S did not have
significant differences in removal overall (p>0.05). There are no drinking water guidelines for UV$_{254}$, but it is a reliable surrogate measurement for the amount of organic matter in water because many organic compounds found in water absorb UV light (Rice, Baird et al. 2017). The removal of organic matter is especially important if chlorine disinfection is applied to the BSF effluent. Organic matter has been reported to generate harmful disinfection by-products when chlorinated, and increases the chlorine demand (WHO 2017).

The filtration rates of S/S, P/P, and B/B were highly variable throughout the experiment, ranging from 0.11 m/hr – 0.20 m/hr in S/S, 0.15 m/hr – 0.45 m/hr in P/P, and 0.09 m/hr to 0.23 m/hr in B/B. However, P/P had a significantly higher filtration rate than S/S overall (p <0.05). These results agree with experiments performed by others (Ghebremichael, Wasala et al. 2012, Zhao 2017). Pumice may have better hydraulic performance because its porosity (0.52) is greater than that of sand (0.36). Typically, BSFs experience a decline in filtration rate as they ripen and the biolayer grows (Ngai, Baker et al. 2014). So far, these filters have not experienced that decrease in filtration rate but they are expected to as they are operated longer.

Log$_{10}$ removal of *E. coli* for each filter ranged between 1.83 and 2.69, as shown in Figure 4.5. Statistical analysis concluded that there was no significant difference between any of the filters (p>0.05). However, P/P displayed the lowest removal of *E. coli*, while S/CS displayed the greatest. Metal oxide coatings have been used successfully to remove bacteria (Chen, Truesdail et al. 1998, Lukasik, Cheng et al. 1999, Lee, Park et al. 2010). In laboratory-scale batch experiments, Lukasik et al. (1999) reported 3.5 log$_{10}$ removal of *E. coli* in various buffers using aluminum oxide coated sand. It is expected that B/B performed similarly to S/S because it is 80% sand by volume. Bacteria are removed in BSFs through predation in the biolayer, natural death, and trapping (CAWST
It is hypothesized that the filters containing sand had better performance due to increased trapping as sand has a lower porosity than pumice.

4.2.2 Coated Sand and Pumice BSFs

The coated sand and pumice BSFs, S/CS and P/CP, respectively, were tested for the same parameters as their uncoated counterparts to see if they can achieve the same hydraulic and water quality. It is important to note that S/CS was damaged and out of commission on days 29-38. S/S had an average of 0.91 NTU product water turbidity while S/CS had an average of 0.89 NTU product water turbidity. The difference in performance between S/S and S/CS with regard to turbidity was not statistically significant (p>0.05). P/P and P/CP, on the other hand, did have significant differences in performance (p<0.05). P/CP had an average of 79% turbidity removal while P/P had an average of 88% removal. Higher product water turbidity may have been due to flushing of fine aluminum oxide particles from the media due to the in-situ coating method discussed in Section 4.2.3.

S/CS and P/CP both consistently exhibited approximately twice as much removal of UV254 as S/S and P/P (see Figure 4.4). It is likely that the aluminum oxide coating helps to adsorb organic matter. This result was expected, as metal oxide coatings have been shown to remove organic matter from water (Johannsen, Cederkvist et al. 2016). S/CS and P/CP achieved similar performances, removing 61% and 62% of UV254, respectively.

As stated previously, the Bucket-BSFs had highly variable filtration rates (see Figure 4.4), with S/CS ranging from 0.06-0.12 m/hr and P/CP ranging from 0.16-0.31 m/hr. S/CS had a significantly slower flow rate than S/S (p<0.05) while there was not a significant difference between the flow rates of P/CP and P/P (p>0.05).
Table 4.1 Average Effluent Water Quality for All Filters

<table>
<thead>
<tr>
<th>Filter</th>
<th>Turbidity (NTU)</th>
<th>UV (_{254}) (cm(^{-1}))</th>
<th>Flow Rate (mL/min)</th>
<th>(E.\ coli) Log(_{10}) Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/S</td>
<td>0.91 ± 0.28 (^A)</td>
<td>0.09 ± 0.02 (^A)</td>
<td>144 ± 47 (^A)</td>
<td>2.44 (^A)</td>
</tr>
<tr>
<td>P/P</td>
<td>0.89 ± 0.32 (^A)</td>
<td>0.09 ± 0.02 (^A)</td>
<td>279 ± 103 (^B)</td>
<td>1.83 (^A)</td>
</tr>
<tr>
<td>B/B</td>
<td>0.73 ± 0.30 (^A)</td>
<td>0.02 ± 0.02 (^A)</td>
<td>152 ± 36 (^A)</td>
<td>2.63 (^A)</td>
</tr>
<tr>
<td>S/CS</td>
<td>0.89 ± 0.36 (^A)</td>
<td>0.05 ± 0.01 (^C)</td>
<td>83 ± 16 (^C)</td>
<td>2.69 (^A)</td>
</tr>
<tr>
<td>P/CP</td>
<td>1.51 ± 0.99 (^B)</td>
<td>0.05 ± 0.01 (^C)</td>
<td>268 ± 65 (^B)</td>
<td>2.51 (^A)</td>
</tr>
</tbody>
</table>

Note: Different letters indicate that values are significantly different (p<0.05) and vice versa.

Figure 4.2 Turbidity (NTU) in Influent and Effluent of S/S, S/CS, P/P, P/CP, and B/B
Figure 4.3 UV$_{254}$ in Influent and Effluent of S/S, S/CS, P/P, P/CP, and B/B

Figure 4.4 Filtration Rate of S/S, S/CS, P/P, P/CP, B/B
4.2.3 In-Situ Coating Method

The aluminum oxide coating method used to coat the full-scale filters was analyzed for its effectiveness. As discussed in Section 4.2.2, the flow rate S/CS was significantly slower than S/S while there was not a significant difference in the flow rates of P/P and P/CP. This alludes to the coating method having a different effect on pumice and sand. Aluminum Oxide gel (Al(OH)₃ gel) formed on both filters, but seemed to penetrate less through P/CP than S/CS. This gel formed because the media was not able to dry completely in the given time (24 hours) under the field conditions. Zhao (2017) experienced the same phenomena when attempting to re-coat spent aluminum oxide coated pumice in-situ. Another observation by Zhao (2017) was that the pH of the filters sharply increased after re-coating and then dropped to as low as 4. A similar spike in pH was observed in this study, as shown in Figure 4.7. The influent water was 7.2, on average while the average pH of S/CS and P/CP was 8.28 and 8.25, respectively. Over time, however, the pH in
both filters has declined and was similar to the influent and the uncoated filters at approximately Day 21.

Figure 4.6 shows fluoride concentrations for all filters as they were operated. On days 6 and 7 all filters showed removal of fluoride. This contradicts existing studies that reported no significant removal of fluoride in BSFs (Murphy, McBean et al. 2010). There may have been some material in the BSFs adsorbing fluoride soon after start-up, but the removal soon ended in S/S, P/P, and B/B (p>0.05). S/CS and P/CP, however, continued to show significant removal of fluoride (p<0.05) throughout the experiment. The effluents of S/CS and P/CP began having fluoride concentrations above the WHO limit on days 10 and 31, respectively. As expected from the results of the batch adsorption experiments, the coated pumice had better fluoride removal than coated sand. Not only was the coating method more effective on the pumice, it was longer lasting.

Figure 4.6 shows average aluminum concentrations in the influent and effluent of the two coated filters over the course of the experiment, excluding days where S/CS was damaged. It is evident that P/CP was releasing more aluminum than S/CS, which is supported by the pH data as well as the turbidity data. It is hypothesized that the larger pore size of pumice made it easier for the aluminum gel to leave the filter. P/CP exceeded the WHO limit for aluminum consumption (<0.2 mg/L) during days 10 and 16 but decreased to below the limit by Day 23 (WHO 2017). S/CS was above the WHO limit on Day 10, but fell below the limit by Day 168.
Figure 4.6 Fluoride Concentration in Influent and Effluent of S/S, P/P, B/B, S/CS, and P/CP

Figure 4.7 pH of Influent and Effluent of S/S, P/P, S/CS, and P/CP
4.2.4 Filter Performance by Stage

Turbidity and UV$_{254}$ were measured in the pre-filters (first bucket) of each filter once per week and data for each of the filters averaged over the per week measurements is shown in Figures 4.9 and 4.10. As the Bucket-BSF design has two stages, it is important to understand the role of each stage so the best combination of media can be found. Figure 4.9 shows the percent turbidity removal efficiency by filter stage for each filter. P/CP had higher turbidity in the effluent from the second stage than the first stage, showing that the Al(OH)$_3$ gel was likely leaching. This is also supported by the pH and aluminum data (Section 4.2.3). 91%-94% of the turbidity removal for each filter occurred in the pre-filter, showing one of the main benefits of two-stage systems.

As discussed in Sections 4.2.1 and 4.2.2 S/CS and P/CP displayed much better UV$_{254}$ removal than S/S and P/P, and B/B had the overall best removal. Figure 8 shows the percent UV$_{254}$ reduction within each of the filter stages. Of the overall UV$_{254}$ removal in B/B, 95% occurred in
the pre-filter, showing the high capacity for biochar to remove organic matter. On the other hand, 59% of UV$_{254}$ removal in S/CS occurred in the secondary filter, and 49% of the overall removal for P/CP occurred in the secondary filter. This difference indicates that the coating method was less effective for pumice than it was for sand, as aluminum oxide aids in the adsorption of organic matter. Overall, the sand and pumice pre-filters had similar performance regarding turbidity and UV$_{254}$.

**Figure 4.9** Percent Turbidity Reduction by Filter Stage

**Figure 4.10** Percent UV$_{254}$ Reduction by Filter Stage
Chapter 5: Conclusions and Recommendations

This research involved the design and start-up of a new BSF design using different filter media along with aluminum oxide coated media. The first objective of this research was to compare the hydraulic and water quality performance of the sand, pumice, and biochar BSFs that contained uncoated media. The uncoated pumice filter (P/P) showed the most desirable hydraulic characteristics, consistently displaying the highest filtration rate (0.27 m/hr). The CAWST recommends a filtration rate between 0.14 m/hr and 0.56 m/hr for BSFs to be acceptable to users. S/S and B/B had similar average filtration rates of 0.14 m/hr and 0.15 m/hr, respectively. While all of these rates are within the desired range, as the filters are operated over a longer period of time, filtration rates are expected to decrease as the schmutzdecke grows. While the biochar filter did not have the best filtration rate, it achieved the highest turbidity and UV$_{254}$ removal of all filters, including S/CS and P/CP. The structure of the biochar may be accountable for this phenomena.

The second objective of this experiment was to compare the performance of the coated and uncoated filters. P/CP had a significantly higher filtration rate than S/CS. It is hypothesized that more of the aluminum oxide gel formed during the in-situ coating was able to slough from the pumice than sand due to its higher porosity. The coating did not have a significant effect on the filtration rate of P/CP, but it significantly decreased the filtration rate of S/CS. S/CS performed similarly to S/S and the other uncoated filters with respect to turbidity removal. P/CP showed higher effluent turbidity than the other filters, likely due to the leeching of aluminum oxide gel.
P/CP and S/CS both had significantly higher removal of UV$_{254}$ than their uncoated counterparts. S/S, P/P, and B/B did not show significant removal of fluoride. S/CS had an average effluent fluoride concentration of 1.3 mg/L, which is below the WHO limit of 1.5 mg/L. P/CP showed even better performance with an average effluent fluoride concentration of 0.5 mg/L. This result shows that the in-situ coating method was more effective with respect to fluoride removal on the pumice than the sand.

To assess the in-situ coating method, aluminum measurements were taken once a week. Effluent aluminum concentrations showed that P/CP was leeching more aluminum than S/CS. In the first week of operation, P/CP exceeded the WHO limit of 0.2 mg/L, but fell below the limit in the second week. Both S/CP and P/CP displayed higher pH levels than the influent water. This is a sign that the aluminum in the filter is adsorbing fluoride and may be releasing hydroxyl groups. The pH of both coated filters has shown a decrease over time, which may signal that aluminum is leaving the filters.

Results of the testing on the individual stages of each filter showed that the majority of the turbidity removal occurred in the first stage, or pre-filter. By removing the turbidity, the pre-filter is likely increasing the longevity of the secondary filter as well as increasing the performance of the coated media. P/CP and showed higher turbidity in the effluent than the influent.

My recommendations for the future of this research include continuing to operate the BSFs in order to assess their long-term performance and investigating the in-situ coating method further. It is vital to know how the new BSF design operates over extended periods of time to understand if it is feasible for household use. It will also be important to know the effect of increasing the charge volume from 6 L to 12 L. Throughout the experiment the charge volume was equal to approximately one pore volume of one bucket, however, BSFs are typically operated with a charge
volume equal to the pore volume of the entire filter. We will likely observe a significant decrease in performance with this change but it will inform potential future design changes. The in-situ coating method caused the precipitation of aluminum oxide gel in the filters, but it is unclear how the aluminum is stratified, if at all, throughout the filters. A noticeable layer of aluminum oxide gel formed on the surface of the coated sand filter, and even more so on the coated pumice filter. Measuring the depth and concentration of aluminum in this layer may provide more information about the mechanism of fluoride removal in these filters. It is apparent from the data that there was more aluminum leeching from the pumice filter than the sand filter, yet the pumice filter has consistently achieved better fluoride removal. This may be due to the complex, porous structure of the pumice allowing the coating of more aluminum oxide per gram of pumice than sand. Future studies will involve coating a biochar filter ex-situ as coated biochar achieved the best removal of fluoride in the batch studies so we can expect positive results.
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