Evaluation of the Mechanisms and Effectiveness of Nano-hydroxides, Wood and Dairy Manure-Derived Biochars to Remove Fluoride and Heavy Metals From Water

Anna Rose Wallace
Southern Methodist University, arwallace@mail.smu.edu

Wenjie Sun Dr
Southern Methodist University, wsun@mail.smu.edu

Chunming Su Dr
Environmental Protection Agency, su.chunming@epa.gov

Follow this and additional works at: https://scholar.smu.edu/engineering_civil_etds

Part of the Analytical Chemistry Commons, Environmental Chemistry Commons, Environmental Engineering Commons, Environmental Health and Protection Commons, Physical Chemistry Commons, and the Water Resource Management Commons

Recommended Citation
Wallace, Anna Rose; Sun, Wenjie Dr; and Su, Chunming Dr, "Evaluation of the Mechanisms and Effectiveness of Nano-hydroxides, Wood and Dairy Manure-Derived Biochars to Remove Fluoride and Heavy Metals From Water" (2019). Civil and Environmental Engineering Theses and Dissertations. 5. https://scholar.smu.edu/engineering_civil_etds/5

This Dissertation is brought to you for free and open access by the Civil Engineering and Environmental Engineering at SMU Scholar. It has been accepted for inclusion in Civil and Environmental Engineering Theses and Dissertations by an authorized administrator of SMU Scholar. For more information, please visit http://digitalrepository.smu.edu.
EVALUATION OF THE MECHANISMS AND EFFECTIVENESS OF
NANO-HYDROXIDES, WOOD AND DAIRY MANURE-DERIVED BIOCHARS
TO REMOVE FLUORIDE AND HEAVY METALS FROM WATER

Approved by:

_____________________________
Wenjie Sun, Assistant Professor, Chair

_____________________________
John H. Easton, Senior Lecturer

_____________________________
Elfi Kraka, Professor

_____________________________
Jaewook Myung, Assistant Professor

_____________________________
Andrew Quicksall, Associate Professor
EVALUATION OF THE MECHANISMS AND EFFECTIVENESS OF
NANO-HYDROXIDES, WOOD AND DAIRY MAURE-DERIVED BIOCHARS
TO REMOVE FLUORIDE AND HEAVY METALS FROM WATER

A Dissertation Presented to the Graduation Faculty of
Southern Methodist University
in
Partial Fulfillment of the Requirements
For the degree of
Doctor of Philosophy
with a
Major in Civil and Environmental Engineering
by

Anna Rose Wallace
(B.S. Environmental Science, University of Washington Tacoma, 2011)
(M.S. Environmental Engineering, Southern Methodist University, 2016)

December 21, 2019
The development of effective treatment processes for the removal contaminants, such as fluoride and heavy metals, from polluted water have been urgently needed due to serious environmental health and safety concerns. In this dissertation, a variety of materials including various (hydro)oxide nanomaterials, biochars and surface modified biochar were studied to evaluate their effectiveness and mechanism on removing fluoride or mixed heavy metals from water.

In the Chapter 2, this study investigated the adsorptive removal of fluoride from water using various (hydro)oxide nanomaterials, focusing on ferrihydrite, hydroxyapatite (HAP) and brucite, which have the potential to be used as sorbents for surface water and groundwater remediation. The Freundlich and Redlich–Peterson adsorption isotherms better described the adsorptive capacity and mechanism than the Langmuir isotherm based on higher $R^2$ values, indicating better fit of the regression predictions. Additionally, the adsorption kinetics were well described by the intra-particle diffusion model. Column studies in a fixed bed continuous flow through system were conducted to illustrate the adsorption and desorption behavior of fluoride on ferrihydrite, HAP, or
brucite. The experimental results fitted well with the Thomas model because of the $R^2$ values at least 0.885 or higher. By comparisons of the adsorption capacity and the rate constant, columns packed with ferrihydrite exhibited not only faster rates, but also higher sorption capacity than those packed with HAP or brucite. The desorption tests in deionized water showed that the adsorbed fluoride could be desorbed at a lower efficiency, ranging from 4.0% to 8.9%. The study implicated that (hydro)oxide nanomaterials of iron calcium and magnesium could be effective sorptive materials incorporated into filtration systems for the remediation of fluoride polluted water.

In Chapter 3, the exploration of cost-effective sorbent for fluoride removal from water was continued with another promising material, biochar, because of its high surface area and diverse surface functional groups. This study explored the removal of fluoride from water using a calcium hydroxide-coated dairy manure-derived biochar (Ca-DM500). The Ca-DM500 showed 3.82-8.86 times higher sorption capacity of fluoride from aqueous phases than the original manure-derived biochar (DM500). This was mainly due to strong surface complexation between fluoride and calcium hydroxide. The Freundlich and Redlich–Peterson sorption isotherms better described the experimental data than Langmuir model. Additionally, the sorption kinetics were well described by the intra-particle diffusion model, indicating combined specifically and non-specifically chemisorptive interactions occurring on the heterogeneous surface of Ca-DM500. Ca-DM500 showed high reactivity per surface area for sorption of fluoride contributing to the importance of surface complexation. Furthermore, the co-presence of anions showed the effects on reducing fluoride removal on Ca-DM-BC, following the order of $SO_4^{2-} \approx PO_4^{3-} > NO_3^-$. The Thomas model can reflect the sorption behavior of fluoride in a
continuous fixed-bed column. Column studies demonstrated that the Ca-DM500 shows strong affinity to fluoride and low desorption potential as well as stable sorption capacity through regeneration and reuse cycles. From these results, we concluded that Ca-DM500 can be applied as an efficient and reusable sorbent for removing fluoride from water.

Heavy metal is another type of pollutant often found coexisting with fluoride, and biochar is increasingly being recognized as a promising, low cost sorbent that can be used to remediate contaminated water. Therefore, in Chapter 4 this study examined the competitive removal of heavy metals ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ from water using biochars derived from douglas fir (DF-BC) and dairy manure (DM-BC) and their removal efficacy and mechanism in both static and continuous flow through systems. DF-BC and DM-BC showed the removal of mixed metal ions following the preferential order of Pb$^{2+}$ \(\gg\) Zn$^{2+}$ \(\gg\) Cd$^{2+}$. Among the various factors influencing the competitive removal, the solution pH played a decisive role in influencing the metal ion species in solution, surface charge and solubility of metal minerals, which consequently affects the electrostatic attraction/repulsion, surface complexation with functional groups and chemical precipitations of metal hydroxides and/or carbonate on biochar. Langmuir sorption isotherm better described the experimental results than the Freundlich or Redlich-Peterson models. In addition, the removal kinetics and model fitting elucidate that three steps of intraparticle diffusion might be the more representative to describe the immobilization processes of metal ions on the external surface and internal pores. Moreover, the column study showed DF-BC more consistent removal of mixed metals through regeneration and reuse, while DM-BC showed a greater pH buffering capacity.
for metal removal. In summary, both DF-BC and DM-BC prove to be an effective, reusable and stable materials for the long-term removal of mixed metals ions from water.
3.4 Appendix. ................................................................. .86

3.5 References. ............................................................. 87

4 EVALUATION OF THE IMMOBILIZATION OF CO-EXISTING
HEAVY METAL IONS FROM WATER BY DOUGLAS FIR -AND
DAIRY MANURE- DERIVED BIOCHARS: PERFORMANCE AND
REUSABILITY ................................................................. .94

4.1 Introduction ............................................................... .94

4.2 Materials and Methods. ................................................. 99

4.3 Results and Discussion .................................................. 109

4.4 References ............................................................... 155

5 SUMMARY AND FUTURE WORK ............................................. 164

5.1 Fluoride. ................................................................. 164

5.1.1 Summary .............................................................. 164

5.1.2 Future Research ...................................................... 166

5.2 Heavy Metals ............................................................ 167

5.2.1 Summary ............................................................. 167

5.2.2 Future Research ...................................................... 169
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Physiochemical Properties of Nanomaterials of (Hydro)oxides</td>
<td>17</td>
</tr>
<tr>
<td>Tested in This Study</td>
<td></td>
</tr>
<tr>
<td>2.2 Removal of Fluoride by Various Nanomaterials of (Hydro)oxides</td>
<td>24</td>
</tr>
<tr>
<td>in different salt solutions</td>
<td></td>
</tr>
<tr>
<td>2.3 Model Parameters of Freundlich, Langmuir and Redlich-Peterson</td>
<td>28</td>
</tr>
<tr>
<td>Isotherms for the Adsorption of Fluoride.</td>
<td></td>
</tr>
<tr>
<td>2.4 Thomas Model Parameters Derived from the Experimental Data in</td>
<td>33</td>
</tr>
<tr>
<td>Continuous Columns</td>
<td></td>
</tr>
<tr>
<td>2.5 Sorption and Desorption of Fluoride on Various Nanomaterials of</td>
<td>35</td>
</tr>
<tr>
<td>(Hydro)oxides in Continuous Flow Through Columns (n=2)</td>
<td></td>
</tr>
<tr>
<td>2.S1 Common Materials Used for Adsorptive Removal of Fluoride from</td>
<td>41</td>
</tr>
<tr>
<td>Water.</td>
<td></td>
</tr>
<tr>
<td>2.S2 Chemical Reagents.</td>
<td>41</td>
</tr>
<tr>
<td>2.S3 Nanomaterials.</td>
<td>42</td>
</tr>
<tr>
<td>3.1 Physiochemical Characteristics of Biochars Tested in This Study.</td>
<td>53</td>
</tr>
<tr>
<td>3.2 Model Parameters of Freundlich, Langmuir and Redlich–</td>
<td>73</td>
</tr>
<tr>
<td>Peterson Isotherms for the Adsorption of Fluoride.</td>
<td></td>
</tr>
<tr>
<td>3.3 Thomas Model Parameters Derived from the Experimental Data in</td>
<td>82</td>
</tr>
<tr>
<td>Continuous Columns</td>
<td></td>
</tr>
<tr>
<td>3.S1 Chemical Reagents.</td>
<td>86</td>
</tr>
<tr>
<td>4.1 Sorption Isotherm Models Used in This Study.</td>
<td>105</td>
</tr>
<tr>
<td>4.2 Physiochemical Characteristics of the Biochars.</td>
<td>113</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.3 Comparing Mass per Mass and Mass per SSA Basis for Removal of Mixed Metal Ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$</td>
<td>114</td>
</tr>
<tr>
<td>4.4 Sorption Isotherm Models Used in This Study</td>
<td>126</td>
</tr>
<tr>
<td>4.5 Parameters of the Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion Models for the Removal of Mixed Metal Ions at pH 5.8</td>
<td>128</td>
</tr>
<tr>
<td>4.6 Best Fit Model Parameters of Pseudo First Order (PFO), Pseudo Second Order (PSO) and Intraparticle Diffusion Model (IDM) for the Removal of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ Ions Using Biochar</td>
<td>130</td>
</tr>
<tr>
<td>4.7 Model Parameters of Freundlich, Langmuir and Redlich–Peterson Isotherms for the Sorption Cd$^{2+}$ and Zn$^{2+}$ in Single Metal System</td>
<td>135</td>
</tr>
<tr>
<td>4.8 Best Fit of Sorption Isotherm Model Parameters for Single Metal Removal Using Biochar</td>
<td>138</td>
</tr>
<tr>
<td>4.9 Best Fit of Sorption Isotherm Model Parameters for Multi-Metal Removal Using Biochar</td>
<td>139</td>
</tr>
<tr>
<td>4.10 Thomas Model Breakthrough Parameters</td>
<td>153</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 The Adsorption Isotherms of Fluoride Fit with the Freundlich,</td>
<td>27</td>
</tr>
<tr>
<td>Langmuir and Redlich-Peterson Equations.</td>
<td></td>
</tr>
<tr>
<td>2.2 The Adsorption Kinetics of Fluoride on to Ferrihydrite, HAP and</td>
<td>30</td>
</tr>
<tr>
<td>Brucite.</td>
<td></td>
</tr>
<tr>
<td>2.3 Breakthrough Curves Expressed as $C_e/C_0$ Versus Time for the</td>
<td>31</td>
</tr>
<tr>
<td>Sorption of Fluoride onto Ferrihydrite, HAP and Brucite.</td>
<td></td>
</tr>
<tr>
<td>2.4 Fitting of Experimental Data to the Thomas Equation.</td>
<td>34</td>
</tr>
<tr>
<td>2.5 X-Ray Diffraction Analysis of Mineralogy for</td>
<td>38</td>
</tr>
<tr>
<td>Ferrihydrite, HAP and Brucite.</td>
<td></td>
</tr>
<tr>
<td>2.6 Hydrodynamic Sizes Measured Using Dynamic Light</td>
<td>39</td>
</tr>
<tr>
<td>Scattering (DLS).</td>
<td></td>
</tr>
<tr>
<td>2.7 Values of pH at Point of Zero Charge ($pH_{PZC}$) for Three</td>
<td>40</td>
</tr>
<tr>
<td>Nanomaterials (Ferrihydrite, HAP and Brucite).</td>
<td></td>
</tr>
<tr>
<td>3.1 Screening Batch Test for the Removal of Fluoride onto Original</td>
<td>62</td>
</tr>
<tr>
<td>Biochars of DF-BC, DM500 and Ca-DM500.</td>
<td></td>
</tr>
<tr>
<td>3.2 XRD Analysis of Pristine DM500 and Ca-DM500.</td>
<td>63</td>
</tr>
<tr>
<td>3.3a The EDS Analysis of DM500 and Ca-DM500 Before and</td>
<td>64</td>
</tr>
<tr>
<td>After the Removal of Fluoride from Water.</td>
<td></td>
</tr>
<tr>
<td>3.3b SEM Analysis of Analysis of DM500 and Ca-DM500 Before and</td>
<td>65</td>
</tr>
<tr>
<td>After the Removal of Fluoride from Water.</td>
<td></td>
</tr>
<tr>
<td>3.4 The Measured pH at Point of Zero Charge ($pH_{PZC}$) for DF-BC,</td>
<td>67</td>
</tr>
<tr>
<td>DM500 and Ca-DM500.</td>
<td></td>
</tr>
<tr>
<td>3.5 Screening Batch Test for Effect of Initial Solution pH on the</td>
<td></td>
</tr>
</tbody>
</table>
Removal of Fluoride onto Ca-DM500. ........................................ 68

3.6 The DRIFTS Spectra of Biochars DM500 and Ca-DM500
Before and After Removal of Fluoride at Different pH Values. ........... 70

3.7 The Sorption Isotherms of Fluoride on Ca-DM500 Fit with the
Freundlich, Langmuir and Redlich-Peterson Model Equations. ............ 72

3.8 The Removal of Fluoride on Ca-DM500 over 48 hours ................. 75

3.9 The Effect of Competitive Anions (PO$_4^{3-}$, SO$_4^{2-}$, and NO$_3^-$) on the
Fluoride Removal onto Ca-DM500 Over 24 Hours. ......................... 77

3.10 Breakthrough Curves Expressed as $C_t/C_0$ versus Time for the
Sorption of Fluoride onto DM500 or Ca-DM500. ............................. 79

3.11 Fitting of Experimental Data to the Thomas Equation. ............... 81

4.1 Removal of Mixed Metal Ions of Cd$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$,
Pb$^{2+}$ and Zn$^{2+}$ on Biochars ................................................. 110

4.2 Removal of Mixed Metal Ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ on Biochars ........ 111

4.3 Effects of Solution pH on the Competitive Removal of
Mixed Metal Ions. ................................................................. 117

4.4 DRIFTS Analysis of Pristine and Metal Sorbed Biochars. .............. 120

4.5 X-ray Diffractograms of Pristine DF-BC and Metal
Loaded DF-BC. ................................................................. 122

4.6 X-ray Diffractograms of Pristine DM-BC and Metal
Loaded DM-BC. ................................................................. 123

4.7 Removal Kinetics of Mixed Metal Ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ .......... 125

4.8 Single Metal Ion Sorption Isotherms Using Metal Concentrations
Ranging from 6 to 768 mg L$^{-1}$ Over 24 Hours. .......................... 132

4.9 Single Metal Ion Sorption Isotherms Using Metal Concentrations
Ranging from 6 to 96 mg L$^{-1}$ Over 24 Hours. ............................ 134
4.10 The SEM-EDS Analysis for DF-BC on the Removal of Single Metal Ions. ................................. 141

4.11 The SEM-EDS Analysis of DM-BC on the Removal of Single Metal Ions. ................................. 142

4.12 Release of Cations from both Pristine DF-BC and DM-BC Control Columns. .............................. 146

4.13 Breakthrough Curves of Mixed Metal Ions of Cd^{2+}, Pb^{2+} and Zn^{2+}. ................................. 147

4.14 Concentration of Metals and Exchangeable Cations in the Effluent of DF-BC. ............................ 150
DEDICATION

To Daphne and Flo.

Where there is great love there will always be miracles.

~ Willa Cather
Chapter 1

GENERAL INTRODUCTION

1.1 Nano(hydro)oxides for the Removal of Fluoride from Water

Fluoride is one of the most commonly detected pollutants affecting the quality of surface water and groundwater (Miretzky et al., 2008; Kimambo et al., 2019). The World Health Organization’s (WHO) maximum contamination level (MCL) is set at 1.5 mg L\(^{-1}\) due to adverse health effects causing dental and skeletal fluorosis, neurological damage (Alhava et al., 1980; Ayoob and Gupta, 2006; Patil et al., 2018). The U.S. EPA has enforced the U.S. drinking water MCL for fluoride at 4 mg L\(^{-1}\). However, this MCL has been disputed and the secondary MCL (non-enforceable) for drinking water is established at 2 mg L\(^{-1}\) (Carton, 2006). It is estimated that 200 million people worldwide are drinking water containing fluoride above the WHO recommended levels and are suffering from fluorosis (Chuah et al., 2016).

Conventional methods, such as chemical precipitation, ion exchange, reverse osmosis and electrolysis, have been proved to be effective for removing fluoride to acceptable levels. However, these treatments are either expensive due to specific requirement for operation maintenance or lead to the generation of a large volume of toxic wastes and do not achieve concentrations below WHO MCLs. Additionally, these methods might not be available and/or affordable for some countries where
defluoridation is urgently needed. Taking the abovementioned into consideration, adsorption becomes a promising method for fluoride removal from water, showing the following advantages: high removal capacity, cost effectiveness, ease of operation, and simplicity of design and implementation (Yadav et al., 2018). Furthermore, a critical review by Biswas et al. (2017) substantiates the pressing need to find the cost-effective adsorptive materials for fluoride removal.

Adsorptive materials that have been studied include alumina, iron-based adsorbents, calcium-based adsorbents, hydroxides/metal oxides, natural materials, nanosorbents and apatite (Tomar and Kumar, 2013; Bhatnagar, 2011; Zhou et al., 2019). Of these adsorbents, alumina-based materials show a high removal capacity (reported values from 0.170 to 3259 mg F⁻⁻ kg⁻¹ sorbent (Mohapatra et al., 2009; Wang et al., 2009; Kang et al., 2018), but produce toxic aluminum residuals (e.g. Al³⁺, Al(OH)₃(aq)) that can cause neurodegenerative diseases in humans (Niquette et al., 2004, WHO, 2003; Niu, 2018).

Many materials used for defluoridation via adsorption processes do not remove fluoride below WHO and EPA MCLs. Furthermore, engineered nanomaterials for use in water treatment is a field that needs exploration (Bishoge et al., 2017; Premarathna et al., 2019). Therefore, selected engineered nanomaterials – nano-hydroxides – were investigated for fluoride removal in this study by addressing following research needs:

- Sorption efficacy and capacity of fluoride on selected nano(hydro)oxides
- Sorption mechanism of fluoride via surface interactions
- Sorption/desorption behavior of fluoride on nano(hydro)oxides in column studies
- Suitability of nano(hydro)oxides for fluoride removal
To address these research needs, the following hypotheses were framed:

- The small particle size and high surface area of nanomaterials will show an advantage for the adsorption of fluoride,
- Surface structure, morphology, charge and chemical composition will affect the adsorption capacity and mechanism of fluoride,
- The selected nanomaterials in mixed bed columns will have a benefit for the removal of fluoride below EPA and WHO MDLs.

1.2 Surface Modified Biochar for the Removal of Fluoride from Water

The exploration of cost-effective sorbent for fluoride removal from water was continued with another promising material, biochar, because of its high surface area and surface functional groups. As a carbonaceous enriched and highly porous material, biochar provides an excellent foundation for an engineered sorbent. Recently, biochar derived from biomass wastes (e.g. agricultural wastes and forest product wastes) is widely recognized as an important cost-effective adsorbent. It has been shown to remove many environmental contaminants including heavy metals and organic compounds from water and wastewater (Tan et al., 2015; Zhou et al., 2014; Li et al., 2019). However, the unique properties of biochar are significantly influenced by the feedstock and pyrolysis conditions.

To overcome the uncertainty regarding varying surface properties of biochar, surface modified biochar by the addition of various chemicals has been shown to have positive effects on enhancing the pollutant removal via sorption processes (Premarathna
et al., 2019). Biochar surfaces have been modified with different chemicals, including chitosan, aminos, methanol, and polyethylenemine, among others (Zhou et al., 2013; Yang et al., 2014; Jing et al., 2014; Ma et al., 2014; Zhou et al., 2019). A study by Chen et al. (2011) showed that magnetically modified biochar increased the removal of phosphate and organic pollutants. However, per literature review, there are few studies that evaluate biochar and, specifically, surface modified biochar for fluoride removal. Therefore, the present study investigates the removal of fluoride from water using dairy manure-derived biochar and an energy-efficient preparation of calcium hydroxide-coated biochar.

The research needs for the removal of fluoride focus specifically on the evaluation of the affinity and stability of fluoride on biochar, the effects of competition from co-existing ions, the kinetics of fluoride removal for scale up design, the application in raw wastewater, the safe disposal of fluoride-loaded biosorbents, and the desorption and regeneration/reuse studies (Mukherjee et al., 2018). Additionally, more attention is needed regarding low cost materials in economies where groundwater contamination is a major problem (Hara, 2006; Kimambo et al., 2019). Although research indicates that biomass-based adsorbents show high removal efficiency, real applications of these biosorbents in water treatment are still far from realization and more assessments are needed on the removal capabilities, sorption and desorption mechanisms, regeneration and reuse feasibility for fluoride removal (Manna et al., 2018).

For the scope of studying surface modified biochar for fluoride removal, specific research gaps were highlighted and addressed listed below:
• Sorption efficacy of fluoride on novel Ca\(^{2+}\) coated biochar in batch assays
• Sorption capacity and mechanism using sorption isotherms
• Effect of solution pH on sorption behavior
• Kinetics of fluoride removal for scale up design
• Effects of competition of co-existing ions
• Sorption-desorption and regeneration-reuse in column studies

Based on research gaps above, the following hypothesis were formulated:

• Calcium modified biochar will show an advantage for the adsorption of fluoride compared to unmodified biochar due to the strong interactions between Ca and fluoride that forms precipitation,
• Calcium-fluoride bonding could enhance the stability and minimize the leaching of adsorbed fluoride on the surface of calcium modified biochar.

1.3 Biochar for the Removal of Heavy Metals from Water

Heavy metal is another type of pollutant often found coexisting with fluoride, especially in wastewater from petroleum refineries (Schroder et al., 2003; Tian et al., 2019). Pollution from heavy metals is a serious environmental health and safety concern due to their prevalence, toxicity to aquatic organisms and persistence in the environment (Brezonik, 2002; Djukic et al., 2016). Thus, the third task of this study is devoted to evaluating the competitive removal of mixed heavy metals through the immobilization processes onto biochar. In the past decades, biochar has been widely used as a soil amendment for heavy metals remediation and many studies have shown the advantages
of its use thereof. (Seguin et al., 2018; El-Naggar et al., 2018; Ni et al., 2018; Zahedifar et al., 2018; Martins et al., 2018). Recently, biochar is increasingly being recognized as a promising, low cost sorbent that can be used to remediate heavy metal contaminated water.

Biochar’s performance on heavy metal removal is highly variable because the unique physical and chemical properties of biochar are significantly altered by the feedstock and pyrolysis conditions (Singh et al., 2017), which affect the sorption and desorption behavior, and hence the fate and transport of heavy metals in water. Researchers have embarked on understanding what parameters influence biochar as a sorbent for heavy metals. Literature review suggests that further research is needed to investigate the biochar characteristics in correlation to metal removal, because the distinct physical-chemical characteristics and molecular composition are useful in determining the sorption/desorption mechanisms and long-term effectiveness of the remediation (Ahmad et al., 2014; Jiang et al., 2016; Pathirana et al., 2019).

Recent studies have primarily focused on the heavy metal removal by biochar in a mono-metal system (Ho et al., 2017; Gazi et al., 2016; Doumer et al., 2015; Amin and Shafiq, 2019; ). However, heavy metal contamination often occurs in a mixed-metals system in the environment. Therefore, it is pressing to evaluate the effects of competitive removal of heavy metals using biochar. Despite the research indicating that biochar has an advantage as packed material for use in continuous filtration systems (Inyang et al., 2016; Xue et al., 2012), the sorption/desorption behavior as well as the regeneration and reuse of biochar for long-term remediation of metal contaminated water in a mixed metal system has not been yet well understood (Godwin et al., 2019).
To expand the research for resolving the knowledge gaps regarding heavy metal removal on biochar, the following research questions are addressed:

- At what capacity can biochar remove heavy metals from water?
- What are the driving mechanisms for surface interactions involved in the competitive removal processes?
- How reversible are the heavy metals when sorbed on the biochar?
- Can biochar be regenerated and reused in dynamic continuous flow-through columns?

Considering the research needs, the following hypotheses regarding biochar for heavy metal removal were postulated:

- Biochars made from a variety of feedstocks will have varying physicochemical properties such as:
  - surface area,
  - pH,
  - surface charge,
  - point of zero charge, and
  - surface functional groups.

- The above listed characteristics could significantly influence the removal capacity and removal mechanism as well as desorption (reversibility) for heavy metals. Examples of these mechanisms include, but are not limited to:
  - Electrostatic attraction,
  - surface (co)precipitation, and
Different heavy metals have different affinity to surface of biochar, which could affect their competitive adsorption on the surface of biochar.

1.4 References


Chapter 2

ADSORPTIVE REMOval OF FluORIDE FROM WATER USING
NANOMATERIALS OF FERRIHYDRITE, APATITE AND BRUCITE: BATCH AND
COLUMN STUDIES

This chapter has been published in the peer-reviewed journal of Environmental Engineering Science (the official journal of the Association of Environmental Engineering and Science Professors (AEESP)) as “Wallace AR, Su CM, Sun WJ. 2019. Adsorptive Removal of Fluoride from Water Using Nanomaterials of Ferrihydrite, Apatite and Brucite: Batch and Column Studies. Environmental Engineering Science. 36: 634–642” and was selected as Editor’s spotlight.

2.1 Introduction

Fluoride, the 13th most abundant element in the Earth’s crust, is also one of the most widespread contaminants in surface water and groundwater (Miretzky et al., 2008). Fluoride is typically associated with many types of fluorine-bearing rocks and minerals, averaging 625 mg kg⁻¹ (Edmunds and Smedley, 2005). These fluorine-bearing rocks and minerals also supply fluoride to soil through soil forming processes such as weathering, dissolution, precipitation, and deposition, with the concentration ranging from 20 to 500 mg kg⁻¹ (Edmunds and Smedley, 2005). High concentrations of fluoride (0.1 to 10 mg L⁻¹) in surface water and groundwater were reported in western USA, Mexico, Argentina, and many countries in Asia and Africa (Edmunds and Smedley, 2013). The World Health Organization (WHO) has an allowable concentration of fluoride set at 1.5 mg L⁻¹ in drinking water. In addition, the U.S. EPA has enforced the U.S. drinking water
primary standard at 4 mg L$^{-1}$, although the secondary standard (non-enforceable) for drinking water is 2 mg L$^{-1}$ (US EPA, 2006).

Elevated fluoride concentrations in groundwater are mainly attributed to two major processes: the natural release from weathering and dissolution of fluoride-bearing rocks and geothermal processes, and anthropogenic activity from various industries manufacturing organo-fluoride compounds, semiconductors, aluminum, glass, and phosphate fertilizers (Camargo, 2003; Kabata-Pendias and Pendias, 2001; Shen et al., 2003; Sujana et al., 1998).

The presence of fluoride in drinking water has been known to be beneficial to public health (Babaeivelni and Khodadoust, 2013) and is often added to municipal drinking water to prevent dental carries. However, there are increasing concerns regarding fluoride as a commonly found water pollutant (Das et al., 2003; Vithanage and Bhattacharya, 2015). Exposure to fluoride at concentrations exceeding the allowable concentration, such as 1.5 to 2 mg L$^{-1}$, can be detrimental to humans causing dental and/or skeletal fluorosis (Gao et al., 2009). It is estimated that 200 million people worldwide are drinking water containing fluoride above the WHO recommended levels and are suffering from fluorosis (Chuah et al., 2016). Moreover, it is well documented that the antimicrobial effects of fluoride can inhibit the activity of various microbial cells and bacterial metabolisms in aquatic environment and soil (Marquis et al., 2003; Wiegand et al., 2007).

In the U.S., fluoride poses a significant threat to ecosystem health. Of concern in the local Oklahoma/Texas region is the disposal of wastewater from petroleum refineries,
as fluoride is found as a contaminant in toxic wastes from the petrochemical industry (Schroder et al., 2000). Commonly, the hazardous wastewater is disposed in land farms. However, because fluoride does not biodegrade, it accumulates in the soil and can leach out having detrimental impacts on the nearby terrestrial and aquatic ecosystems. Studies on fluoride exposures from the byproducts of petroleum refineries disclosed significant toxicological effects on sensitive keystone species such as the native Oklahoman, Cotton Rat (Kim et al., 2001; Schroder et al., 2003; Wake, 2005; Propst et al., 1999).

Petrochemical byproduct disposal and other fluoride containing industrial wastes continue to threaten the environment. Alternative or pre-treatment methods for disposal of wastewater byproducts are important to prevent toxicological impacts to sensitive ecosystems (Schroder et al., 2000).

In order to prevent the adverse effects of fluoride, many studies have examined ways to remove fluoride from water, including chemical precipitation, adsorption, ion exchange, reverse osmosis, and electrolysis (Bhatnagar et al., 2011; Dolar et al., 2011; Mohapatra et al., 2009; Viswanathan and Meenakshi, 2009). Although chemical precipitation can remove fluoride, it cannot achieve a concentration below 2 mg L⁻¹.

Additionally, it can generate a large volume of toxic solid byproducts (Mohapatra et al., 2011; Wang and Reardon, 2001). Ion exchange, reverse osmosis, electrodialysis and membrane processes can effectively remove the fluoride to an acceptable level. However, these treatments are expensive since they require frequent regeneration of resins, or prevention of the membrane fouling and scaling (Pervov et al., 2000; Shen and Schäfer, 2014; Viswanathan and Meenakshi, 2008). Adsorption is a more attractive method for the removal of fluoride in terms of cost, simplicity of design, ease of
operation, convenience and availability of materials (Bhatnagar et al., 2011; Loganathan et al., 2013). Therefore, adsorption becomes the most promising technique for fluoride removal through infiltration systems that prevent the release of fluoride to receiving water bodies.

The selection of suitable and efficient sorbents is still problematic for fluoride removal in various infiltration systems. Sorbents such as granular activated carbon (GAC), aluminum hydroxides, gibbsite and hydrous ferric oxides, and other (hydro)oxides have been used to remove fluoride from water. Wang (2009) reported that GAC does not effectively remove fluoride, however, metal oxides modified GAC (e.g., MnO₂ coated GAC) demonstrated better removal efficiency that fits well with Freundlich isotherm model. Additionally, various (hydro)oxides showed promising potentials for effective removal of fluoride, as summarized in Table 2.S1 (Appendix at page 41). Moreover, (hydroxyl)apatite has been illustrated to be favorable sorbents for the removal of fluoride from aqueous solutions (Goa et al., 2009; Hammari et al., 2004). The findings elucidate that increasing surface area could potentially enhance removal capacity. Thus, nanoscale (hydro)oxides were selected to evaluate fluoride removal from water due to their physiochemical properties and high surface area as well as natural presence in natural environment. The objectives of this study were to investigate the adsorption capacity of these nanomaterials for fluoride removal from water in both batch and fixed bed continuous flow through column systems.
2.2 Materials and Methods

2.2.1 Chemical reagents

All chemicals used in this study were reagent grade of 99 % purity or better. Chemicals were purchased from Fischer Scientific, Thermo Scientific or Sigma-Aldrich. A complete list of chemicals including ID/CAS number is provided in Table 2.S2 (Appendix at page 41).

2.2.2 Selected Nanomaterials

Eleven (hydro)oxides nanomaterials were selected and used as adsorptive materials in this study, including hematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), ferrihydrite (Fe(OH)$_3$), goethite (FeOOH), hematite-alpha (α-Fe$_2$O$_3$), hydroxyapatite (HAP, (Ca$_5$(PO$_4$)$_3$OH), brucite (Mg(OH)$_2$), and four different nano-sized titanium dioxides (TiO$_2$). Nanomaterials purchased from Nano-Amor Inc (Houston, TX) include Fe$_2$O$_3$, Fe$_3$O$_4$, α-Fe$_2$O$_3$, Ca$_5$(PO$_4$)$_3$OH, Mg(OH)$_2$, TiO$_2$-A (anatase), TiO$_2$-B (rutile), and TiO$_2$-C (rutile). TiO$_2$-D (anatase) was purchased from Sigma-Aldrich (St. Louis, MO). In addition, two nanoscale iron hydroxides, ferrihydrite (Fe(OH)$_3$) and goethite (FeOOH) were synthesized in this study. A complete list of nanomaterials including ID/CAS number is provided in the Table 2.S3 (Appendix at page 42).

The synthesis and characterization of ferrihydrite procedure was reported by Su and Suarez (1995), in which 200 mL of 1.5 M ferric chloride (FeCl$_3$) was added to 450 mL solution of 2 M NaOH at a rate of 50 mL min$^{-1}$. The synthesis of goethite followed a procedure reported by Cornell and Schwertmann (1991), in which 200 mL of 0.1 M ferric nitrate (Fe(NO$_3$)$_3$) was added to 450 mL solution of 5 M KOH at a rate of 50 mL min$^{-1}$. 
The pH of the solution was adjusted to between 7 and 8 to ensure complete precipitation of formed ferrihydrite or goethite. The precipitate was rinsed with deionized water until the supernatant conductivity reached the range of 14 to 24 µS cm\(^{-1}\). The precipitate was then collected and dried at 70 °C for 60 hours and gently ground to pass through a 53 µm sieve. The characteristics of these nanomaterials are summarized in Table 2.1 (and Figure 2.S1., Appendix at page 38).

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>Particle size (nm)</th>
<th>Specific surface area (^b) (m(^2) g(^{-1}))</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite ((\text{Ca}_5\text{PO}_4)_3\text{OH})^a)</td>
<td>200</td>
<td>17.3±0.34</td>
<td>97</td>
</tr>
<tr>
<td>Magnesium Hydroxide ((\text{Mg(OH)}_2)^a)</td>
<td>15</td>
<td>104.9±16.3(^1)</td>
<td>99</td>
</tr>
<tr>
<td>Ferrihydrite (\text{Fe(OH)}_3^a)</td>
<td>&lt;53000</td>
<td>241.5±0.62</td>
<td>Synthesized in this study</td>
</tr>
<tr>
<td>Hematite (\text{Fe}_2\text{O}_3)</td>
<td>20-50</td>
<td>25.3±0.13</td>
<td>98</td>
</tr>
<tr>
<td>Magnetite (\text{Fe}_3\text{O}_4)</td>
<td>20-30</td>
<td>38.2±0.19</td>
<td>98</td>
</tr>
<tr>
<td>Hematite alpha ((\text{Fe}_2\text{O}_3-\text{alpha}))</td>
<td>20-50</td>
<td>19.7±0.02</td>
<td>98</td>
</tr>
<tr>
<td>Goethite</td>
<td>200</td>
<td>21.6±1.20</td>
<td>Synthesized in this study</td>
</tr>
<tr>
<td>(\text{TiO}_2 ) &quot;D&quot;</td>
<td>50</td>
<td>38.9±0.50</td>
<td>99</td>
</tr>
<tr>
<td>(\text{TiO}_2 ) &quot;C&quot;</td>
<td>30-40</td>
<td>25.5±0.60</td>
<td>99</td>
</tr>
<tr>
<td>(\text{TiO}_2 ) &quot;B&quot;</td>
<td>10x40</td>
<td>151.9±23.6</td>
<td>99</td>
</tr>
<tr>
<td>(\text{TiO}_2 ) &quot;A&quot;</td>
<td>10</td>
<td>273.1±34.3</td>
<td>99</td>
</tr>
</tbody>
</table>

\(^{a}\) Materials selected for further study.

\(^{b}\) BET surface area, n = 2.
2.2.3 Batch experiments

Batch experiments were carried out to investigate the adsorption behavior of fluoride onto various nanomaterials. In this study, 100 mg of each sorbent was added to a 50 mL polypropylene tube mixed with 20 mL of 5 mg L\(^{-1}\) sodium fluoride (NaF) solution, in the presence of either 1.0 mM sodium chloride (NaCl), or 0.33 mM magnesium chloride (MgCl\(_2\)). These electrolytes were used to evaluate the effect of different cations at the same ionic strength on the adsorption of fluoride. The tubes were incubated for 48 hours on an agitator shaker at a constant speed (200 rpm) at ambient room temperature. Each batch experiment was conducted in duplicates and the results are presented as averaged value with standard deviation calculated.

Of the eleven (hydro)oxide nanomaterials tested, ferrihydrite, HAP and brucite, were the three nanomaterials that showed the higher adsorption capacity of fluoride. Thus, they were selected to examine the adsorption isotherms and kinetics for fluoride based on the sorption capacity measured in previous batch experiments. For the adsorption isotherm experiments, 100 mg of nanomaterials were added into a 50 mL polypropylene tube with 20 mL of NaF at a concentration ranging from 2.5 to 240 mg L\(^{-1}\) for ferrihydrite, or 0.4 to 47 mg L\(^{-1}\) for HAP and brucite, respectively. Because ferrihydrite removed 100% of the fluoride when the concentrations were below 2.5 mg L\(^{-1}\), these values were not included in the isotherm experiments. Additionally, the concentration of fluoride was up to 240 mg L\(^{-1}\) for the ferrihydrite isotherm to obtain more data for a better fitting model. The adjusted pH was measured at 6.8, 7.0, and 9.8 for ferrihydrite, HAP and brucite, respectively, using 1 M HCl or NaOH. For isotherm tests, ferrihydrite and HAP were evaluated at near neutral, however brucite, begins
dissolving at a pH below 9, thus the pH was controlled at 9.8. In this study, 1 mM NaCl was used to maintain ionic strength. The tubes were incubated for 48 hours on an agitator shaker at a constant speed (200 rpm) at ambient room temperature. The samples were centrifuged at 3,500 rpm for 30 minutes and the supernatants were stored at 4 °C until fluoride analysis. For the adsorption kinetics experiment, the same setup as the isotherm experiment was used, except the concentration of F⁻ was 5 mg L⁻¹. The tubes were removed one by one from the shaker after 0, 2, 4, 24, and 48 hours. The supernatant was immediately collected and then filtered through a 0.22 µm membrane filter made from mixed cellulose esters (MCE), which was purchased from Sigma-Aldrich (catalog # GSWPO2500) prior to fluoride analysis. Quality control tests were performed using NaF in DI water as well as NaF with 1 mM NaCl, which demonstrated that there was no retention of fluoride on the filters.

2.2.4 Adsorption models

The mass of fluoride adsorbed on the adsorbent was calculated based on Equation 2.1:

$$q = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (2.1)

where $q$ is the fluoride adsorbed on the adsorbent (mg g⁻¹), $C_0$ is the initial concentration of fluoride (mg L⁻¹), $C_e$ is the equilibrium concentration of fluoride (mg L⁻¹), $V$ is the liquid volume (L), and $m$ is the mass of adsorbent (g).

The experimental data was analyzed using adsorption isotherm models, which include Langmuir, Freundlich and Redlich–Peterson isotherms. Langmuir isotherm
assumes monolayer coverage of adsorbate on a structurally homogenous adsorbent surface. The Langmuir isotherm is given as Equation 2.2:

\[
q = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{2.2}
\]

where \(K_L\) is the Langmuir adsorption constant (L mg\(^{-1}\)), \(q_{max}\) is the maximum capacity of the adsorbent (mg g\(^{-1}\)), and \(C_e\) is the equilibrium concentration of fluoride (mg L\(^{-1}\)).

Freundlich isotherm model describes the multilayer adsorption of adsorbate on a heterogeneous surface of the adsorbent. The Freundlich isotherm is presented as Equation 2.3:

\[
q = K_F C_e^{\frac{1}{n}} \tag{2.3}
\]

where \(K_F\) is the Freundlich affinity coefficient ((mg g\(^{-1}\) (mg L\(^{-1}\))\(^{-1/n}\)), \(C_e\) is the equilibrium concentration of fluoride (mg L\(^{-1}\)), and \(n\) is an empirical parameter constant.

The Redlich–Peterson isotherm is a hybrid form of both Freundlich and Langmuir isotherms, approaching the Freundlich equation at high concentrations while fitting in the Langmuir equation at low concentrations. The Redlich–Peterson isotherm includes three empirical parameters, and therefore, can describe the adsorption on either homogenous or heterogeneous surface. This isotherm is illustrated as Equation 2.4:

\[
q = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \tag{2.4}
\]

where \(K_R\) is the Redlich–Peterson isotherm constant (L mg\(^{-1}\)), \(\alpha_R\) is a constant (L mg\(^{-1}\))\(^\beta\) and \(\beta\) is the exponent with a value between 0 and 1.
2.2.5 Column adsorption experiments

Ferrihydrite, HAP, or brucite was used as individual adsorbent in continuous flow columns to investigate the adsorption and desorption mechanisms of fluoride and to illustrate the adsorption capacities in both batch and column systems. Glass columns (cross sectional area as 4.91 cm$^2$ and height as 30 cm) were used as fixed bed (30 cm of the bed depth) up-flow reactors and packed with 1 g of adsorptive nanomaterial and 92 g of acid washed quartz sand (particle size: 0.25-0.29 mm, Sigma-Aldrich). The packed materials were pre-mixed to create a homogeneous mixture. The pore volume was measured at 24, 22 and 21 mL for columns filled with ferrihydrite, HAP or brucite, respectively. During the operation of each column, the influent containing 35 mg L$^{-1}$ fluoride and 10 mM NaCl was pumped through the packed columns in an up-flow mode with a peristaltic pump at a flow rate of 1.0 mL min$^{-1}$ at an ambient room temperature. The adsorption capacity at the point of breakthrough ($q_B$) is defined as the mass of fluoride ions adsorbed on the nanomaterials when the effluent concentration of fluoride reaches 5% or lower of the initial influent concentration of 35 mg L$^{-1}$. The adsorption capacity at the point of exhaustion ($q_E$) is defined as the mass of fluoride ions adsorbed on the nanomaterials when the effluent concentration of fluoride reaches 95% or higher of the influent concentration. After the fluoride exhausted from the column, desorption experiments were performed by passing DI water as the desorption solution through the exhausted columns. The effluent was collected every 7 minutes for ferrihydrite, HAP or brucite and every 9 minutes for quartz in the collection vessels on the fraction collector, and the pH was measured immediately. A 10 mL sample of the effluent was collected and filtered with 0.22 µm membrane filter and stored at 4 °C until fluoride analysis.
2.2.6 Analytical methods

The fluoride concentration of the solutions was measured using a Waters Quanta 4000 capillary ion analyzer. The procedure is briefly summarized as follows: 0.5 ml solution was injected into a 60 cm × 75 µm silica capillary column filled with a buffered electrolyte solution containing an UV-absorbing anion salt (4.6 mM sodium chromate) and an electro-osmotic flow modifier (0.46 mM OFM) with a pH at 8. The sample was introduced at the cathode end of the capillary and the anions were separated in the electric field and then were detected indirectly from the absorption of chromate using an Hg UV lamp set at 254 nm. The instrument was operated with a voltage of 20 kV and a current of 18 to 20 µA at 25 °C. The injection mode was hydrostatic with a flow of 10 cm every 30 seconds. The duration was performed at a run time of 3.5 minutes.

The measurement of specific surface area was performed using a Quantachrome NOVA 2000e Surface Area and Pore Size Analyzer (BET). For each analysis, 0.1 g of dry sample was placed in a bulb cell under the parameters (e.g., temperature, duration) described in the manual instruction.

The values of pH at point of zero charge (pH$_{PZC}$) for three nanomaterials (ferrihydrite, HAp and brucite) were determined using a modified method described in a previous study (Tan et al., 2008). Briefly, 50 mL of 0.1 M KCl solution was added in different 60 mL polypropylene centrifuge tubes. The initial pH of the mixture solution was adjusted to the range of 3-11 for ferrihydrite and HAp, and 9-12 for brucite using either 1.0 M HCl or 1.0 M NaOH solution. Nitrogen gas was bubbled during the pH adjustment to prevent dissolution of atmospheric CO$_2$. 0.5 g of dry nanomaterial sample was added into each tube, and each tube was vigorously agitated in a shaker for 24 hr at
ambient room temperature. After that, the suspensions were settled down and the final pH was measured immediately. The differences between final and initial pH values (ΔpH) were calculated and plotted against the initial pH values. Therefore, the initial pH at which ΔpH is zero is the pH\textsubscript{PZC}.

2.3 Results and Discussion

2.3.1 Removal of fluoride using various nanomaterials

The purpose of selecting the eleven (hydro)oxide nanomaterials was to screen potential effective materials for fluoride removal. To accomplish this screening, batch tests were run on eleven nanomaterials to evaluate their adsorption capacity. Tests were run using both NaCl and MgCl\textsubscript{2} as background electrolyte. As summarized in Table 2.2, using NaCl or MgCl\textsubscript{2} solutions to maintain constant ionic strength (I\textsubscript{NaCl} = 1.12 x 10\textsuperscript{-3} M and I\textsubscript{MgCl2} = 1.11 x 10\textsuperscript{-3} M) showed no significant difference in the adsorption of fluoride when comparing the same nanomaterials.

Among the eleven (hydro)oxide nanomaterials, ferrihydrite, HAP and brucite demonstrated the 2-5 times higher adsorption capacity than other nanomaterials for fluoride removal from aqueous solutions, 0.99 (±0.00), 0.92 (±0.01) and 0.59 (±0.01) mg F g\textsuperscript{-1} dry material respectively in NaCl solution, , and 0.93 (±0.00), 0.40 (±0.14) and 0.52 (±0.02) mg F g\textsuperscript{-1} dry material respectively in MgCl\textsubscript{2} solution. For ferrihydrite and brucite, there was no observed difference for fluoride sorption capacity in NaCl or MgCl\textsubscript{2} solution. By comparison, HAP showed less sorption capacity in MgCl\textsubscript{2} solution than in NaCl solution, which may be attributed to the precipitation of Mg\textsuperscript{2+} on the HAP surface.
blocking the sorption sites (Farzadi et al., 2014). Therefore, NaCl solution was used for the rest of the experiments.

Table 2.2. Removal of fluoride by various nanomaterials of (hydro)oxides in different salt solutions

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>NaCl (1mM)</th>
<th>MgCl₂ (1mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg F g⁻¹ dry material</td>
<td>pH</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>0.99±0.00</td>
<td>3.1</td>
</tr>
<tr>
<td>HAP</td>
<td>0.92±0.01</td>
<td>9.8</td>
</tr>
<tr>
<td>Brucite</td>
<td>0.59±0.01</td>
<td>9.4</td>
</tr>
<tr>
<td>TiO₂-A</td>
<td>0.04±0.03</td>
<td>7.3</td>
</tr>
<tr>
<td>TiO₂-B</td>
<td>0.00±0.01</td>
<td>7.3</td>
</tr>
<tr>
<td>TiO₂-C</td>
<td>0.12±0.04</td>
<td>6.1</td>
</tr>
<tr>
<td>TiO₂-D</td>
<td>0.00±0.00</td>
<td>6.5</td>
</tr>
<tr>
<td>Hematite-alpha</td>
<td>0.10±0.01</td>
<td>5.6</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.03±0.02</td>
<td>8.0</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.00±0.04</td>
<td>8.1</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.12±0.03</td>
<td>5.5</td>
</tr>
</tbody>
</table>

2.3.1.1 Specific Surface Area

Specific surface area (SSA) was compared with removal capacity. It was found that there was a negative relationship between the removal capacity of fluoride and specific surface area of selected nanomaterials. Sorption capacity of F⁻ vs. specific surface area was 0.0075 ± 0.00012, 0.310 ± 0.034, and 0.037 ± 0.0001 mg/m² at 48 hrs equilibrium time for ferrihydrite (SSA, 241.5 m²/g), HAP (17.3 m²/g), and brucite (104.9 m²/g), respectively. Interestingly, HAP, having the lowest specific surface area, demonstrated the second highest removal of fluoride (Table 2.2).
2.3.1.2 Removal Mechanisms

The removal of fluoride using ferrihydrite was conducted at pH of 6.8, which is slightly lower that the measured pH_{PZC} of 7.7 indicating the positive surface charge (Figure 2.S3., Appendix at Page 40). Thus, the removal of fluoride using ferrihydrite is mainly due to electrostatic attraction on the surface of ferrihydrite (Huang et al., 2011). It has been shown that both physical adsorption from electrostatic interaction and chemical adsorption from ion exchange can be the driving forces for the removal mechanism of fluoride using HAP (Wang et al., 2011; Sandaram et al., 2009; Zhang et al., 2012). In this case, the formation of fluorite (CaF_2) was determined as the primary removal mechanism, based on 1) thermodynamic modeling of the system (MINTEQ 3.1 Software) showing supersaturation of CaF_2, and, 2) batch experiments conducted at a pH of 7 leading to the slight dissolution of HAP (solubility = 6.8 mg/dm^3), releasing Ca^{2+} and precipitating CaF_2 (Uskoković, 2015). Thus, the removal of fluoride using HAP is attributed to the strong chemical bond of fluoride with the structural calcium of HAP. As for the removal of fluoride using brucite, one mechanism could be electrostatic attraction, since the pH of adsorption at 9.8 was lower than the measured pH_{PZC} of 10.1, suggesting a positively charged surface.

Although the measured pH_{PZC} is close to the pH of adsorption (only 0.3 pH units apart), electrostatic attraction is still considered to be the main adsorption mechanism, because the solubility of MgF_2 (K_{sp} = 2.6 \times 10^{-4}) is much less than CaF_2 (K_{sp} = 3.9 \times 10^{-11}), indicating weaker binding of F^- with Mg^{2+} than F^- with Ca^{2+}. Thus, the system is more likely to remove the fluoride anion due to electrostatic attractions with Mg^{2+} than surface precipitation of MgF_2. Because MgF_2 does occur naturally, it could be argued
that direct bonding between Mg$^{2+}$ and F$^{-}$ to form MgF$_2$ may be occurring. However, the simulation using desorption chemistry modeling (MINTEQ 3.1 software) shows that the solution is unsaturated with respect to MgF$_2$, further supporting electrostatic interactions as the primary mechanism.

2.3.1.3 Adsorption Isotherms

Batch experiments of the adsorption isotherms were performed to evaluate the affinity of fluoride removal to three nanomaterials, including ferrihydrite, HAP and brucite. As shown in Figure 2.1, the experimental data were fitted to the Langmuir, Freundlich and Redlich–Peterson isotherm equations. The isotherm parameters and $R^2$ values for each model are summarized in Table 2.3.
Figure 2.1. The adsorption isotherms of fluoride fit with the Freundlich, Langmuir, and Redlich–Peterson equations. The experiment was operated at pH of 6.8, 7.0, and 9.8 for ferrihydrite, HAP and brucite, respectively, in 1 mM NaCl solution at ambient room temperature. Fitting lines were extrapolated with linear integration. Error bars are calculated from standard deviation (n = 2).
Table 2.3. Model parameters of Freundlich, Langmuir and Redlich–Peterson isotherms for the adsorption of fluoride

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Redlich–Peterson</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_F$</td>
<td>$n$</td>
<td>$R^2$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>Nano-Ferrihydrite</td>
<td>0.43</td>
<td>0.38</td>
<td>0.987</td>
<td>0.04</td>
</tr>
<tr>
<td>Nano-HAP</td>
<td>1.56</td>
<td>0.43</td>
<td>0.995</td>
<td>0.14</td>
</tr>
<tr>
<td>Nano-Brucite</td>
<td>0.70</td>
<td>0.44</td>
<td>0.937</td>
<td>0.10</td>
</tr>
<tr>
<td>Hydrous ferric oxide (HFO)</td>
<td>2.69</td>
<td>1.63</td>
<td>0.800</td>
<td></td>
</tr>
<tr>
<td>Nano-HFO</td>
<td>5.06</td>
<td>1.81</td>
<td>0.940</td>
<td>0.06</td>
</tr>
<tr>
<td>Nano-HAP</td>
<td>2.53</td>
<td>2.18</td>
<td>0.981</td>
<td>0.07</td>
</tr>
<tr>
<td>HAP</td>
<td>0.72</td>
<td>1.31</td>
<td>0.992</td>
<td>0.05</td>
</tr>
<tr>
<td>Nano-HAP</td>
<td>1.76</td>
<td>2.97</td>
<td>0.954</td>
<td>1.32</td>
</tr>
<tr>
<td>Nano-HAP</td>
<td>0.55</td>
<td>3.14</td>
<td>0.897</td>
<td>0.53</td>
</tr>
<tr>
<td>Mg/Fe hydroxide</td>
<td></td>
<td></td>
<td>0.52</td>
<td>50.91</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.02</td>
<td>1.00</td>
<td>1.000</td>
<td></td>
</tr>
</tbody>
</table>
The $R^2$ values indicate that Freundlich and Redlich–Peterson isotherms can best represent the adsorption of fluoride on each nanomaterial. Thus, the best fit of both Freundlich and Redlich–Peterson isotherms strongly indicates the adsorption of fluoride on the heterogenous surfaces of the nanomaterials. The $\beta$ values, ranging from 0.59, 0.63 and 0.39 for ferrihydrite, HAP and brucite, respectively, are lower than the unity indicating that the fluoride has not reached maximum coverage on the nanomaterials. This result showed that the multiple active sites on the heterogenous surfaces of nanomaterials express different affinities for the removal of fluoride. Previous studies reported similar findings on the adsorption isotherms of fluoride by different materials. The comparison on the model parameters of Freundlich and Langmuir isotherms as well as Redlich–Peterson isotherm are given in Table 2.3.

The batch adsorptions for fluoride as a function of time on ferrihydrite, HAP and brucite, are presented in Figure 2.2. Since the adsorption started immediately and reached the maximum equilibrium quickly, not enough experimental data were available to be processed and fitted in common kinetics models (e.g., pseudo-first-order model and pseudo-second-order model). However, the experimental adsorption data were well described by the three-step intra-particle diffusion model (Sun and Yang, 2003; Noroozi et al., 2007). The first step reflects the instantaneous external surface adsorption stage; the second step represents the gradual adsorption stage, which takes place very fast. The third step reaches the final equilibrium stage, where the intra-particle diffusion slows due to the extremely low solute concentration in solution.
Figure 2.2. The adsorption kinetics of fluoride onto ferrihydrite, HAP, or brucite. The experiment was operated at pH of 6.8, 7.0, and 9.8 for ferrihydrite, HAP and brucite, respectively, in 1 mM NaCl solution. Error bars are calculated from standard deviation (n = 2).

2.3.2 Continuous column experiment

In this study, the continuous flow columns were operated to investigate the adsorption and desorption of fluoride on ferrihydrite, HAP, brucite. The column filled with pure quartz sand without addition of nanomaterial was included as a control treatment. The breakthrough curves for the columns are given in Figure 2.3. In the control columns with pure quartz sand, fluoride adsorption was not observed in an appreciable amount over the operation time of 200 minutes. By comparison, treatment columns filled with nanomaterials demonstrated better adsorption, but showed different
breakthrough points occurring at 60, 20 and 7 minutes for ferrihydrite, HAP, and brucite, respectively. The results confirm that the presence of nanomaterials played the most important role in adsorbing fluoride from the aqueous phase. Furthermore, ferrihydrite demonstrated better adsorption capacity for the fluoride than brucite and HAP in the column study.

Figure 2.3. Breakthrough curves expressed as $Ce/C_0$ versus time for the sorption of fluoride onto ferrihydrite, HAP, or brucite, mixed with quartz sand medium in a continuous flow column. Control columns are filled with quartz sand. The initial fluoride concentration was 35 mg L$^{-1}$ in 10 mM NaCl solution. Error bars are calculated from standard deviation ($n = 2$).

During the operation, the influent containing fluoride ions flows through the fixed bed of adsorbents and forms a mass transfer zone, where the fresh solution is in contact
with unsaturated adsorbents. This zone moves through the column and reaches the exhaustion point. The height of the mass transfer zone \( h_Z \) can be calculated using Equation 5:

\[
h_Z = \frac{H (V_E-V_B)}{V_E-(1-f)(V_E-V_B)} \quad (2.5)
\]

where \( H \) is the bed depth (cm), \( f \) is the parameter indicating the symmetry of the breakthrough curve, or the fraction of adsorbents present in the column that is still capable of adsorbing fluoride ions. The \( f \) can be defined as Equation 6:

\[
f = \int_0^1 (1 - \frac{c}{c_0}) \, d\left(\frac{V-V_B}{V_E-V_B}\right) = \int_{V_B}^{V_E} \frac{(c_0-c)}{c_0(V_E-V_B)} \, dV \quad (2.6)
\]

where \( V \) is the effluent volume (L).

The parameters given by Equations 2.5 and 2.6 were calculated from the experimental data and summarized in Table 2.4. Because the adsorption is not at steady state while the influent is still passing through the column, it is difficult to describe the dynamic behavior of fluoride in a fixed bed under the defined operating conditions. Several simple mathematical models have been developed to describe and possibly predict the dynamic behavior in fixed bed column (Aksu and Gonen 2004). Among these models, the Thomas model is commonly used for continuous flow conditions (Thomas 1944), which is given in Equation 2.7:

\[
\frac{c_e}{c_0} = \frac{1}{(1+\exp\left(\frac{q_T}{\Theta} - \frac{m-c_0\theta}{\Theta}\right))} \quad (2.7)
\]

where \( C_0 \) and \( C_e \) are the fluoride concentrations in the influent and effluent (mg L\(^{-1}\)), respectively, \( k_T \) is the rate constant (Lmg\(^{-1}\) h\(^{-1}\)), \( \Theta \) is the flow rate L h\(^{-1}\), \( q_T \) is the total
sorption capacity (mg g⁻¹), V is the throughput volume (L), and m is the mass of adsorbent.

### Table 2.4. Thomas model parameters derived from the experimental data in continuous columns

<table>
<thead>
<tr>
<th></th>
<th>Ferrihydrite</th>
<th>HAP</th>
<th>Brucite</th>
</tr>
</thead>
<tbody>
<tr>
<td>qₑ (mg g⁻¹)</td>
<td>2.28</td>
<td>0.89</td>
<td>0.48</td>
</tr>
<tr>
<td>qₑ (mg g⁻¹)</td>
<td>3.32</td>
<td>1.58</td>
<td>1.22</td>
</tr>
<tr>
<td>F</td>
<td>0.46</td>
<td>0.31</td>
<td>0.29</td>
</tr>
<tr>
<td>hz (cm)</td>
<td>22.1</td>
<td>24.4</td>
<td>23.3</td>
</tr>
<tr>
<td><strong>Thomas Model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kₜ (L mg⁻¹ h⁻¹)</td>
<td>0.18</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>qₜ (mg g⁻¹)</td>
<td>3.48</td>
<td>1.01</td>
<td>1.02</td>
</tr>
<tr>
<td>R²</td>
<td>0.957</td>
<td>0.909</td>
<td>0.885</td>
</tr>
</tbody>
</table>

As shown in Figure 2.4, the experimental data were fitted reasonably well to the Thomas model and the calculated parameters are summarized in Table 4. The total adsorption capacity qₜ calculated was close to the qₑ calculated above up to saturation point. The agreement of qₜ and qₑ verifies the applicability of the Thomas model to describe the adsorption of fluoride in the continuous up-flow column system. By comparison of the total adsorption capacity and the rate constant kₜ, columns filled with ferrihydrite not only demonstrated faster rates, they also showed a higher sorption capacity than brucite and HAP.
Moreover, the results showed that the sorption capacities from column study are lower than the corresponding sorption capacities calculated using the Redlich–Peterson model from batch experiment. The observed differences between the sorption capacity in the continuous flow column and batch systems have been reported by previous studies (Gupta et al., 2001; Tor et al., 2009). The discrepancies might be attributed to the shorter time of reaction in the column test (< 3 h) than in the batch test (48 h).

When the adsorbents were saturated with fluoride, the desorption process was carried out to examine the stability of fluoride adsorbed on the packed materials in the

**Figure 2.4.** Fitting of experimental data to the Thomas equation. Error bars are calculated from standard deviation (n = 2).
continuous flow columns. The exhausted fixed bed columns were washed by passing DI water through the bed at a flow rate of 1 mL min\(^{-1}\) until no fluoride could be desorbed. The duration for desorption was 99, 64, 62, and 87 minutes for quartz, ferrihydrite, HAP and brucite, respectively. The mass of desorption was calculated in the way identical to calculation of the mass adsorbed in the columns. Due to possible fluoride solution left in the pores of columns when the influent was changed to DI water, the desorption mass in the column packed with nanomaterials and quartz was corrected by subtracting the desorption mass from the control columns composing of quartz alone. The calculated column desorption parameters are listed in Table 2.5. It is concluded that the adsorbed fluoride could be desorbed, however, the desorption efficiency was not very high, ranging from 4.0% to 8.9%.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sorption Phase</th>
<th>Desorption Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorbed F (mg F g(^{-1}) material)</td>
<td>F Removal efficiency (%)</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.01±0.00</td>
<td>8.21±1.59</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>3.33±0.01</td>
<td>65.1±0.23</td>
</tr>
<tr>
<td>HAP</td>
<td>1.58±0.02</td>
<td>36.7±0.54</td>
</tr>
<tr>
<td>Brucite</td>
<td>1.33±0.17</td>
<td>29.3±3.68</td>
</tr>
</tbody>
</table>
2.3.3 Conclusions

In this study, eleven (hydro)oxide nanomaterials were evaluated for their effectiveness on the adsorption of fluoride. Three out of the eleven (hydro)oxide nanomaterials, ferrihydrite, HAP, and brucite were closely examined for physiochemical characterization, adsorption capacity and kinetics in batch tests. Adsorption-desorption behavior in was also evaluated in continuous flow column experiments. These three nanomaterials showed the potential to be used as effective sorptive materials for remediating fluoride polluted water. The main conclusions are summarized as follows:

(i) Among eleven (hydro)oxide nanomaterials tested in this study, ferrihydrite, HAP, and brucite showed the higher affinity for fluoride adsorption from aqueous phases.

(ii) The adsorption of fluoride on these nanomaterials in batch experiments are best represented by the Redlich–Peterson and Freundlich isotherms.

(iii) The adsorption kinetics were well described by the intra-particle diffusion model.

(iv) Higher fluoride sorption capacity was obtained in batch systems than that in continuous column systems, which might be due to 1) the longer reaction time (48 h) in the batch test than that in the column test (< 3 h), and 2) preferential flow paths in the column media inhibiting the exposure to all available sorption sites.

(v) The Thomas model can be used for describing the sorption behavior of fluoride removal in a fixed bed continuous flow column.

(vi) The desorption study showed that the adsorbed fluoride could be desorbed, however, the desorption efficiency was low, in the range of 4 to 9%. Low desorption is attributed to strong binding of fluoride on sorbent(s).
Future work is needed to better understand fluoride removal on a pilot scale level using the nanomaterials ferrihydrite, HAP and brucite, especially pertaining to petroleum and industrial waste remediation. Additionally, further studies examining the the regeneration capacity of each nanomaterial for practical application and re-use should be conducted.

2.4 Appendix

2.4.1 Acknowledgements

This research was partially funded by the U.S. Environmental Protection Agency (U.S. EPA). Anna Rose Wallace is a Student Trainee (Engineering) under the U.S. EPA Pathways Internship Program and produced this manuscript while conducting research as part of her Master of Science degree program at Southern Methodist University. We appreciate Lynda Callaway, Kristie Rue, and Gary Brooks for laboratory assistance.

2.4.2 Disclaimer

Although the U.S. EPA partially funded this research and U.S. EPA employees contributed to this article; the views, interpretations, and conclusions expressed in the article are solely those of the authors and do not necessarily reflect or represent the U.S. EPA’s views or policies. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. EPA or the U.S. Government.
2.4.3 Supplemental Information

Figure 2.S1. The X-ray diffraction analysis of mineralogy for ferrihydrite, HAP, or brucite.

The X-ray diffraction analysis of mineralogy for nanomaterials three nanomaterials (ferrihydrite, Hap and brucite) before and after adsorption with fluoride was performed following a procedure described by Galletti et al. (2016). Briefly, 20 mg of sample was taken to fill up a cavity (7 mm diameter) on an elemental silicon slide sample holder, and then pressed to form a smooth surface using a stainless-steel spatula. The samples were scanned with a Rigaku Miniflex X-ray diffractometer at a scan rate of ...
0.5° 2θ min⁻¹ and a sampling width of 0.02° 2θ (Fe Kα radiation, λ = 1.9373 Å; operated at 30 keV and 15 mA).

Figure 2. S2. Hydrodynamic sizes measured using dynamic light scattering (DLS) for nanomaterials, ferrihydrite, HAP, and brucite.

Nanomaterials were suspended at a ratio of 0.5 g in 50 mL (10 g L⁻¹) of 1 mM NaCl and sonicated for 10 minutes at 25 °C prior to analysis. The hydrodynamic size was 821.16 ± 10.42 nm, 1.54 x 10⁴ ± 2.10 x 10⁴ nm, and 1.97 x 10⁵ ± 6.92 x 10⁴ nm for ferrihydrite, HAP, and brucite, respectively. These results showed that the nanomaterials aggregated quickly when added to 1 mM NaCl solution.
Figure 2.S3. Values of pH at point of zero charge (pH_{PZC}) for three nanomaterials (ferrihydrite, HAP, and brucite).
### Table 2.S1. Common Materials Used for Adsorptive Removal of Fluoride from Water

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>Langmuir Adsorption Capacity</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite, Al(OH)$_3$ or alumina (Al$_2$O$_3$)</td>
<td>5 and 7.5</td>
<td>41.988 mg/g</td>
<td>Farrah et al., 1987</td>
</tr>
<tr>
<td>Metallurgical grade alumina (α-Al$_2$O$_3$)</td>
<td>9</td>
<td>1.56 mg/g</td>
<td>Valdivieso et al. 2006</td>
</tr>
<tr>
<td>Alum (Al$_2$(SO$_4$)$_3$)</td>
<td>6.5</td>
<td>40.68 mg/g</td>
<td>Tripathy et al., 2006</td>
</tr>
<tr>
<td>Alum impregnated alumina (Al$_2$O$_3$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated quick lime (CaO)</td>
<td>&gt;12</td>
<td>16.67 mg/g</td>
<td>Islam and Patel, 2007</td>
</tr>
<tr>
<td>Schwertmannite (Fe$_8$O$_6$(OH)$_6$(SO$_4$)$_2$·nH$_2$O)</td>
<td>3.7</td>
<td>50.2–55.3 mg/g</td>
<td>Eskandarpour et al., 2008</td>
</tr>
<tr>
<td>Granular ferric hydroxide (Fe(OH)$_3$)</td>
<td>6.0–7.0</td>
<td>7.0 mg/g</td>
<td>Choi et al., 2009</td>
</tr>
<tr>
<td>Geothite (Fe(OH))</td>
<td>6-8</td>
<td>59 mg/g</td>
<td>Mohapatra et al., 2010</td>
</tr>
<tr>
<td>Bone char (Bovine)</td>
<td>n/a</td>
<td>0.75 mg/g</td>
<td>Kaseva, 2006</td>
</tr>
<tr>
<td>Graphite (C)</td>
<td>7</td>
<td>3.13 mg/g</td>
<td>Karthikeyan and Elango, 2007</td>
</tr>
</tbody>
</table>

*not available

### Table 2.S2. Chemical Reagents

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Grade</th>
<th>Purity</th>
<th>Manufacturer</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>Reagent</td>
<td>99.7 %</td>
<td>Fisher Scientific</td>
<td>7647-14-5</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl</td>
<td>Aqueous</td>
<td>Trace Metal Grade</td>
<td>Sigma-Aldrich</td>
<td>7647-01-0</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Reagent</td>
<td>99.4 %</td>
<td>Fisher Scientific</td>
<td>1310-732</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>FeCl$_3$</td>
<td>Reagent</td>
<td>99.5 %</td>
<td>Sigma-Aldrich</td>
<td>10025-77-1</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>NaF</td>
<td>Aqueous</td>
<td>n/a</td>
<td>Thermo Scientific</td>
<td>7681-49-4</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>NaF</td>
<td>Reagent</td>
<td>99.9 %</td>
<td>Sigma-Aldrich</td>
<td>7681-49-4</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>MgCl$_2$</td>
<td>Reagent</td>
<td>100.1 %</td>
<td>Sigma-Aldrich</td>
<td>7786-30-3</td>
</tr>
</tbody>
</table>

*not available
<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Purity (%)</th>
<th>Manufacturer</th>
<th>Manufacturer description</th>
<th>ID/ CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>98</td>
<td>Nano-Amor Inc.</td>
<td>20-50 nm, 30 m$^2$/g</td>
<td>2540MY/1309-37-1</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>98</td>
<td>Nano-Amor Inc.</td>
<td>20-30 nm, 60 m$^2$/g</td>
<td>2650MY/1317-61-9</td>
</tr>
<tr>
<td>Hematite alpha</td>
<td>Fe$_2$O$_3$-α</td>
<td>98</td>
<td>Nano-Amor Inc.</td>
<td>20-50 nm, 50 m$^2$/g</td>
<td>2520MY/1309-37-1</td>
</tr>
<tr>
<td>Goethite</td>
<td>α-FeO(OH)</td>
<td>n/a*</td>
<td>This study</td>
<td>Synthesized, 1996</td>
<td>n/a*</td>
</tr>
<tr>
<td>Amorphous Ferrihydrite</td>
<td>Fe(OH)$_3$</td>
<td>n/a*</td>
<td>This study</td>
<td>Synthesized, 1996 and 2016</td>
<td>n/a*</td>
</tr>
<tr>
<td>Titanium dioxide &quot;E&quot;</td>
<td>TiO$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>50 nm, 160 m$^2$/g anatase</td>
<td>5485MR/13463-67-7</td>
</tr>
<tr>
<td>Titanium dioxide &quot;D&quot;</td>
<td>TiO$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>30-40 nm, 30 m$^2$/g rutile</td>
<td>5485HT/13463-67-7</td>
</tr>
<tr>
<td>Titanium dioxide &quot;C&quot;</td>
<td>TiO$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>10x40 nm, 150 m$^2$/g rutile</td>
<td>5480MR/13463-67-7</td>
</tr>
<tr>
<td>Titanium dioxide &quot;B&quot;</td>
<td>TiO$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>10 nm, 120 m$^2$/g anatase</td>
<td>5425HT/13463-67-7</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Ca$_5$(PO$_4$)$_3$ (OH)</td>
<td>97</td>
<td>Sigma-Aldrich</td>
<td>200 nm calcium phosphate tribasic</td>
<td>100263394/12167-74-7</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>15 nm, 80 m$^2$/g</td>
<td>3320HT/1309-42-8</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>SiO$_2$</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>10 nm, 640 m$^2$/g</td>
<td>4850MR/7631-86-9</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>99</td>
<td>Nano-Amor Inc.</td>
<td>20 nm</td>
<td>5830CD/1314-13-2</td>
</tr>
</tbody>
</table>

*not available
2.5 References


Chapter 3

REMOVAL OF FLUORIDE FROM WATER USING A CALCIUM HYDROXIDE-COATED DAIRY MANURE-DERIVED BIOCHAR

3.1 Introduction

3.1.1 Fluoride Leaching

As the 13th most abundant element in the Earth’s crust ($625 \text{ mg kg}^{-1}$), fluoride is commonly found in almost all groundwater ranging from low concentrations ($<0.5 \text{ mg L}^{-1}$) up to 10 mg L$^{-1}$ and sometimes greater than 330 mg L$^{-1}$ (Amini et al., 2008; Msonda et al., 2007; Rasool et al., 2018; Kimambo et al., 2019). Fluoride leaches into surface water and groundwater from fluorine-bearing rocks and minerals due to natural weathering and hydrogeochemical interactions. Aside from natural weathering, fluoride can contaminate water bodies through a variety of anthropogenic sources, including waste streams from coal powered plants, mining, industrial accidents fertilizer production and application, irrigation, and petroleum refineries (Wang et al., 2016; Thole, 2013; Vithangage et al., 2015; Kundu et al., 2009; Mohapatra et al., 2009; Reddy, 2014; Schroder et al., 2000).

3.1.2 Fluoride Health Effects

Fluoride is often added into drinking water supplies at low concentrations (e.g., 0.5 to 1 mg L$^{-1}$) to promote the development of strong bones and prevent dental cavities (Rao and Karthikeyan, 2011; Touyz and Nassani, 2019).
However, fluoride can cause serious diseases at concentrations of 5 to 10 mg L\(^{-1}\), such as dental fluorosis, ossification of joints, neurological damage and in rare cases death (Thole 2013; Wang et al., 2004; Irigoyen-Camacho et al., 2016; Chouhan, 2010; WHO, 2008; Patil et al., 2018) and even manifest these diseases via prolonged exposure at low levels of 1-2 mg L\(^{-1}\) (Reardon and Wang, 2000). Dental fluorosis is a concern in developing children, since those under 6 years of age are especially vulnerable (Chen et al., 2017; Mascarenhas, 2000). Therefore, the World Health Organization (WHO) has set the fluoride drinking water level at 1.5 mg L\(^{-1}\). The U.S. Environmental Protection Agency (EPA) has also set an enforceable level at 4 mg L\(^{-1}\) with the recommended limit at 2 mg L\(^{-1}\).

Exposure to fluoride contaminated water effects approximately 200 million people worldwide. Fluoride levels in drinking water in countries such as India, Turkey, Sri Lanka, Pakistan and China have been reported in the range of 1.01 to 24.7 mg L\(^{-1}\) (Narsimha and Sudarshan, 2017; Amini et al., 2008; Shah and Danishwar, 2003; Maheshwari, 2006). For example, as much as 95% of available drinking water in Northern Rajasthan, India is unsafe for consumption due to fluoride contamination (Suthar et al., 2008; Choubisa, 2018). Fluoride is also found in the western United States at levels ranging from 2 to 15 mg L\(^{-1}\) (Reardon and Wang, 2000). Thus, it is imperative to develop suitable treatment processes for resolving this water quality crisis in countries and regions that rely heavily on fluoride-polluted water bodies as their main drinking water sources (WHO, 2008).
3.1.3 Treatment Technologies

Treatment technologies, such as coagulation, sorption, ion exchange, reverse osmosis, and electrolysis, have been extensively evaluated (Behbahani et al., 2011; Gong et al., 2012; Chubar et al., 2011; Richards et al., 2011; Zhou et al., 2014; Bhatnagar et al., 2011). Among these methods, sorption is considered the most promising to remove fluoride because it is cost effective, simplistic, convenient to operate, and most importantly, sorptive materials such as alumina, iron oxides and apatite are readily available (Bhatnagar et al., 2011; Loganathan et al., 2013). Porous carbons, such as activated carbon and carbon nanotubes, are commonly used sorbents for sorptive removal of fluoride because of large surface area and continuous porosity (Tchomgui-Kamga et al., 2010). However, Wang (2009) reported that GAC does not effectively remove fluoride and high associated costs of these carbon materials restrict the widespread use.

Biochar was selected for continued exploration of adsorption materials. As a carbonaceous enriched and highly porous material, biochar has recently received much attention for its adsorptive properties and as an excellent foundation for engineered sorbents. Biochar can be made by pyrolyzing a variety of biomass under oxygen-limited conditions such as rice hulls, cornhusks, walnut shells, wood, grass, poultry litter and dairy manure. Biochar’s physiochemical properties are highly variable based on parameters such as types of feedstock, pretreatments of feedstock, pyrolysis conditions (e.g., temperature, oxygen level), and post-treatment of biochar (Ok et al., 2015; Oh and Seo, 2016). High surface area and favorable pore architecture characteristics enable biochars with high efficiency in the retention of contaminants, including metal(loid)s and organic pollutants in aqueous and soil systems (Mohan et al., 2014; Ahmed et al., 2016).
However, the use of biochar composites in environmental engineering is still in its infancy and few studies have evaluated the biochar and/or surface modified biochar for the removal of fluoride from water (Pramarathna et al., 2019). Mohan et al. (2012, 2014) found that biochars made from pine bark, pine wood or corn stover showed varying sorption capacity on the removal of fluoride. By comparison, surface modified biochars, such as magnetic corn stover biochar, aluminum hydroxide coated mushroom compost biochar or bone derived and magnetic biochar, yielded higher sorption capacity compared with unmodified biochars (Mohan et al., 2014; Chen et al., 2016; Zhou et al., 2019). Despite the promising effectiveness on fluoride removal, these sorbents have some significant drawbacks due to expensive modification methods and pH adjustments.

3.1.4 Treatments Using Calcium

Calcium salts, such as calcium hydroxide, calcium phosphate and quick lime (CaO), are known to enhance fluoride removal from water due to the strong binding of calcium and fluorine (Jadhav et al., 2014; Larsen et al., 1993; Islam and Patel, 2007). However, pure calcium (hydro)oxides display some significant limitations in practice. For example, the treatment using quick lime only works for high fluoride polluted waters (10 mg L\(^{-1}\) or higher) and cannot reduce fluoride concentration below the WHO permissible limit for drinking water (< 1.5 mg L\(^{-1}\)) (Islam and Patel, 2007). Additionally, the use of calcium hydroxide and liming agents increased the pH of the water, which requires post-treatment for neutralization. Biochar has the buffering capacity to maintain pH near a neutral range and the presence of calcium on the biochar surface can enhance the sorption of fluoride via strong precipitation of CaF\(_2\). Additionally, interstitial binding interactions with the unique chemical properties of biochar aid in fluoride removal. Thus,
using calcium hydro(oxides) to coat biochar presents a promising material to overcome the limitations on the removal of fluoride.

3.1.5 Purpose of Study

The purpose of this study was to evaluate the effectiveness and mechanism of calcium hydroxide coated dairy manure derived biochar (Ca-DM500) for the removal of fluoride from water. Batch experiments were performed to assess the removal capacity and kinetics of fluoride on biochar and calcium hydroxide coated biochar. In addition, surface interactions were characterized using solid phase analysis to determine the sorption mechanism. Furthermore, a column study was conducted to evaluate the sorption-desorption dynamics of fluoride onto Ca-DM500 in continuous fixed-bed system and the stability of regeneration-reuse of Ca-DM500 on the fluoride removal efficiency.

3.2 Materials and Methods

3.2.1 Chemical Reagents

All chemicals used in this study were reagent grade of 99% purity or better. Chemicals were purchased from Fischer Scientific, Thermo Scientific or Sigma-Aldrich. A complete list of chemicals including ID/CAS number is provided in Table 3.S1 (Appendix at page 86).

3.2.2 Original Biochars and Surface Modified Biochar

Two types of original biochars were used in this study, which were made from unique feedstock under different pyrolysis conditions. The douglas fir ultra-dry biochar
(DF-BC, hereafter) was purchased from Black Owl Biochar (Biochar Supreme, LLC., Bellevue, WA), which was generated from gasification of timber industrial waste wood in an air-fed updraft gasifier at 900-1000 °C with a residence time of about 1-10 seconds, ground and sieved to a particle size of 0.1-0.6 mm and stored in closed vessels until usage (Karunanayake et al., 2018).

The dairy manure-derived biochar (DM500, hereafter) was obtained from Professor Sergio Capareda at Texas A&M University (College Station, TX), which was produced from a fluid bed gasification of dairy manure in a gasifier at 500 °C, and milled, sieved through a 2 mm sieve and stored in closed vessels until usage (Nam et al., 2016). The preparation of calcium hydroxide coated DM500 (Ca-DM500, hereafter) was carried out using a modified method that was used to coat iron onto biochar and activated carbon under ambient conditions (Kan and Huling, 2009; Samsuri et al., 2013). Briefly, the Ca-DM500 was prepared by gently stirring 400 mL of 2 M CaCl₂ solution and 20 g of DM500 for 1 d at 20 °C. After that, the DM500 coated with calcium was placed to an oven for drying at 105 °C for 12 h. The physicochemical characteristics of the biochars are presented in Table 3.1.
Table 3.1. Physiochemical characteristics of biochars tested in this study

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size (mm)</th>
<th>SSA (m²/g)</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF-BC</td>
<td>≤ 2.0</td>
<td>493.6 ± 2.6</td>
<td>10</td>
</tr>
<tr>
<td>DM500</td>
<td>≤ 0.53</td>
<td>4.0 ± 0.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Ca-DM500</td>
<td>≤ 0.53</td>
<td>2.6 ± 0.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Alumina (standard)</td>
<td>2.0 (pellet)</td>
<td>99.62</td>
<td>3.1</td>
</tr>
</tbody>
</table>

3.2.3 Characterization of DM500 and Ca-DM500

The measurement of specific surface area for DM500 and Ca-DM500 was performed using a Quantachrome NOVA 2000e Surface Area and Pore Size Analyzer (BET). For each analysis, 0.5 g dry sample were placed in a bulb cell under the parameters described in the manual instruction.

The X-ray diffraction (XRD) analysis of DM500 and Ca-DM500 was performed on a Rigaku Miniflex X-ray diffractometer (Ultima IV, Riigaku, Japan) following the procedure described in Galletti et al. (2016). Approximately 20 mg sample was taken to fill up a cavity (7 mm diameter) on an elemental silicon slide sample holder. The sample cavity was pressed to form a smooth surface using a stainless-steel spatula. The samples were scanned at a rate of 0.5° 2θ min⁻¹ and a sampling width of 0.02° 2θ (Fe Kα radiation, λ = 1.9373 Å; operated at 30 keV and 15 mA).

The surface morphology and elemental compositions of DM500 and Ca-DM500 before and after the sorption of fluoride were captured by a Leo-Zeiss 1450VPSE.
scanning electron microscope (SEM, Carl Zeiss Microscopy, USA) equipped with an EDAX Genesis 4000 XMS SYSTEM 60 energy-dispersive spectrometer (EDS).

In addition, the surface functional groups of DM500 and Ca-DM500 before and after the removal of fluoride were examined with a Bruker Vertex 70 Fourier-transform infrared spectroscopy (FTIR) using the diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) method. A dry sample was ground to a fine powder in a mortar and pestle. Approximately 20 mg powdered sample was mixed with 45 g potassium bromide (KBr) and then transferred to a small vessel and placed in the instrument. A KBr background (potassium bromide (KBr)) and a control (calcite, CaCO₃) were analyzed prior to sample analysis. Each sample was scanned 1200 times to minimize sample noise with measured wavenumbers in the range from 600 to 4000 cm⁻¹. The samples were analyzed five times and the average was reported as the result. The instrument was purged with CO₂-free air from a CO₂ adsorbent for 30 minutes between each analysis.

The values of pH at point of zero charge (pHₚₑ заявил) for DM500 and Ca-DM500 were determined using a modified method described by (Tan et al., 2008). Briefly, 50 mL of 0.1 M KCl solution was added in different 60 mL polypropylene centrifuge tubes. The initial pH of the mixture solution was adjusted to the range of 4-11 using either 1.0 M HCl or 1.0 M NaOH solution. Nitrogen gas was bubbled during the pH adjustment to prevent dissolution of atmospheric CO₂. A dry sample (0.5 g) was added into each tube, and each tube was vigorously agitated in a shaker for 24 hr at ambient room temperature. After that, the suspensions were settled down and the final pH was measured immediately. The differences between final and initial pH values (ΔpH) were calculated
and plotted against the initial pH values. Therefore, the initial pH at which ΔpH is zero is the pH_{PZC}.

### 3.2.4 Batch Experiments

Batch experiments were carried out to investigate the removal behavior of fluoride onto various original biochars, DF-BC and DM500, and calcium hydroxide coated biochar, Ca-DM500. In this study, 100 mg of biochar sample was added to a 50 mL polypropylene tube mixed with 30 mL of 5 or 225 mg L^{-1} sodium fluoride (NaF) in the presence of 10 mM sodium chloride (NaCl). The pH was not adjusted and allowed to free drift to equilibrium. The tubes were incubated for 24 hours on an agitator shaker at a constant speed (200 rpm) at ambient room temperature. Prior to fluoride analysis, liquid samples were filtered through a 0.22 µm mixed cellulose esters (MCE) membrane filters (Sigma-Aldrich, catalog # GSWPO2500). Each batch experiment was conducted in duplicates and the results are presented as averaged value with standard deviation calculated.

Based on our preliminary results, the Ca-DM500 showed the higher removal capacity of fluoride than original DF-BC and DM500 from water. Therefore, Ca-DM500 was further examined for the fluoride sorption isotherm and kinetics. For the sorption isotherm experiment, 30 mL of fluoride solution (5 mg L^{-1} F^{-} with 10 mM NaCl) was added into 50 mL polypropylene tubes with increasing dosages of Ca-DM500 at 50, 100, 500, 750, 1000, 1500 and 2000 mg, which were incubated for 48 hours on an agitator shaker (200 rpms) at ambient room temperature (25 ºC). The pH was not adjusted and achieved a consistent pH at 5.7 ± 0.27. In this study, 10 mM NaCl was used to maintain ionic strength. After incubation, the samples were filtered through a 0.22 µm membrane.
filter prior to fluoride analysis. For the removal kinetics experiment, 1500 mg Ca-DM500 was weighed into a 50 mL polypropylene tube with 45 mL of NaF at a concentration of 5 mg L\(^{-1}\) in 10 mM NaCl. The tubes were incubated under static conditions at ambient room temperature (25 °C) and the pH was not adjusted and was stable at 5.8±0.16. One mL of supernatant was sampled at 5, 10, 20, 60, 240, 720, 1440 and 2880 minutes and then filtered through a 0.22 µm membrane filter prior to fluoride analysis. Quality control tests were performed using NaF in DI water as well as NaF with 10 mM NaCl, which demonstrated that there was no retention of fluoride on the filters.

To evaluate the stability of fluoride sorbed on Ca-DM500, the desorption kinetics experiment was conducted using the Ca-DM500 samples recovered from the removal kinetics experiment. The Ca-DM500 samples were centrifuged and decanted, and then air-dried for 10 days at ambient room temperature (25 °C). Then, 45 mL of 10 mM NaCl was mixed with Ca-DM500 and the supernatant was sampled at 5, 10, 20, 60, 240, 720, 1440 and 2880 minutes and filtered through a 0.22 µm membrane filter prior to fluoride analysis.

To understand the competitive effects of co-existing anions on the sorption of fluoride on Ca-DM500, batch experiments were conducted as described above, except using 500 mg of Ca-DM500. Three stock solutions were used containing either 1.0 mg L\(^{-1}\) sodium phosphate (Na\(\text{H}_{2}\text{PO}_{4}\cdot\text{H}_{2}\text{O})\), 1.0 mg L\(^{-1}\) sodium sulfate (Na\(_{2}\text{SO}_{4}\cdot10\text{H}_{2}\text{O}\)), or 4.0 mg L\(^{-1}\) sodium nitrate (Na\(\text{NO}_{3}\)) with 5 mg L\(^{-1}\) NaF and 10 mM NaCl. The pH was not adjusted and was stable at 8.0 ± 0.5 for all samples. The supernatant was sampled
after 48 hours and then filtered through a 0.22 µm membrane filter prior to fluoride analysis.

3.2.5 Sorption models

The mass of fluoride adsorbed on the adsorbent was calculated based on Equation 3.1:

\[ q = \frac{(C_0 - C_e) V}{m} \]  

(3.1)

where \( q \) is the fluoride adsorbed on the adsorbent (mg g\(^{-1}\)), \( C_0 \) is the initial concentration of fluoride (mg L\(^{-1}\)), \( C_e \) is the equilibrium concentration of fluoride (mg L\(^{-1}\)), \( V \) is the liquid volume (L), and \( m \) is the mass of adsorbent (g).

The experimental data was analyzed using sorption isotherm models, which include Langmuir, Freundlich and Redlich–Peterson isotherms. Langmuir isotherm assumes monolayer coverage of adsorbate on a structurally homogenous adsorbent surface. The Langmuir isotherm is given as Equation 3.2:

\[ q = q_{\text{max}} \frac{K_L C_e}{1 + K_L C_e} \]  

(3.2)

where \( K_L \) is the Langmuir sorption constant (L mg\(^{-1}\)), \( q_{\text{max}} \) is the maximum capacity of the adsorbent (mg g\(^{-1}\)), and \( C_e \) is the equilibrium concentration of fluoride (mg L\(^{-1}\)).

Freundlich isotherm model describes the multilayer sorption of sorbate on a heterogeneous surface of the adsorbent. The Freundlich isotherm is presented as Equation 3.3:

\[ q = K_F C_e^{1/n} \]  

(3.3)
where $K_F$ is the Freundlich affinity coefficient ($\text{mg g}^{-1} \cdot \text{mg L}^{-1} \cdot \text{L}^{1/n}$), $C_e$ is the equilibrium concentration of fluoride (mg L$^{-1}$), and $n$ is an empirical parameter constant.

The Redlich–Peterson isotherm is a hybrid form of both Freundlich and Langmuir isotherms, approaching the Freundlich Equation at high concentrations while fitting in the Langmuir Equation at low concentrations. The Redlich–Peterson isotherm includes three empirical parameters, and therefore, can describe the sorption on either homogenous or heterogeneous surface. This isotherm is illustrated as Equation 3.4:

$$q = \frac{K_R C_e}{1 + \alpha_R C_e^\beta}$$  \hspace{1cm} (3.4)

where $K_R$ is the Redlich–Peterson isotherm constant (L mg$^{-1}$), $\alpha_R$ is a constant (L mg$^{-1}$)$^\beta$ and $\beta$ is the exponent with a value between 0 and 1.

3.2.6 Column Study of Fluoride Removal

DM500 and Ca-DM500 were used as individual adsorbents in continuous fixed-bed columns to investigate the sorption and desorption mechanisms of fluoride from water and to illustrate the sorption capacities and stability through the regeneration-reuse processes. Glass columns (cross sectional area as 4.91 cm$^2$ and height as 30 cm) were used as fixed bed (30 cm of the bed depth) up-flow reactors and packed with 4.5 g of adsorbents and 80 g of acid washed quartz sand (particle size: 0.25-0.29 mm, Sigma-Aldrich). The packed materials were pre-mixed to create a homogeneous mixture. In addition, a quartz sand column was operated as control. The pore volume was measured at 20.9 mL, 22.4 mL and 28.9 mL for columns filled with DM500, Ca-DM500 and quartz sand, respectively. During the operation of each column, the influent containing 10 mg L$^{-1}$ fluoride in 10 mM NaCl was pumped through the packed columns in an up-flow
mode with a peristaltic pump at a flow rate of 1.0 mL min\(^{-1}\) at an ambient room temperature. The sorption capacity at the point of breakthrough \((q_B)\) is defined as the mass of fluoride ions sorbed on the nanomaterials when the effluent concentration of fluoride reaches 5\% or lower of the initial influent concentration of 10 mg L\(^{-1}\). The sorption capacity at the point of exhaustion \((q_E)\) is defined as the mass of fluoride ions adsorbed on the nanomaterials when the effluent concentration of fluoride reaches 95\% or higher of the influent concentration. After the fluoride exhausted from the column, the column was left standing to allow most of the pore water to drain by gravity overnight up to 24 hours, and then sparged with N\(_2\) gas for 5 minutes at 20 psi to ensure all pore liquid was removed from the column.

Desired pore volumes of 10 mM NaCl were run through the column for desorption through the exhausted columns until no fluoride was detected or no further decrease of fluoride concentration was detected in the effluent. The effluent was collected every 10 minutes in the collection vessels on the fraction collector for DM500 and Ca-DM500 columns, and the pH was measured immediately. A 10 mL sample of the effluent was collected and filtered with 0.22 \(\mu\)m membrane filter and measured immediately using a fluoride ion selective electrode.

Once the desorption experiment was completed, the column was regenerated by dewatering as described above and soaking and rinsing with 0.1 M NaOH and 10 mM NaCl to remove all the sorbed fluoride and then being air-dried under N\(_2\) gas. The regenerated columns were operated with sorption-desorption cycle two more times to evaluate the effectiveness of regenerated DM500 and Ca-DM500 on the adsorptive removal of fluoride from water.
The Thomas model (Equation 3.5) is commonly used to evaluate the sorption behavior in a continuous fixed-bed column (Thomas 1944).

\[
\ln \left( \frac{C_0}{C_e} - 1 \right) = \frac{k_T q_T M}{Q} - k_T C_0 t
\]  

(3.5)

Where \( k_T \) = Thomas rate constant (mL/min mg), \( q_T \) = equilibrium F\(^-\) uptake per g of biochar (mg g\(^{-1}\)), \( C_0 \) = influent F\(^-\) concentration (mg L\(^{-1}\)), \( C_e \) = effluent F\(^-\) concentration at time \( t \) (mg L\(^{-1}\)), \( M \) = mass of biochar (g), \( Q \) = filtration velocity (mL/min), and \( t \) = time of influent passed through the column. The parameters \( k_T \) and \( q_T \) are calculated from the plot of \( \ln[(C_0/C_e) - 1] \) vs. time \( t \).

### 3.2.7 Analytical Methods

The concentration of fluoride in aqueous solution was determined using the Orion ion selective electrode (Thermo Scientific) as described in the manual instruction. The fluoride electrode was calibrated for concentrations of 0.1, 1, 10 mg L\(^{-1}\) fluoride solution using the total ionic strength adjustment buffer (TISAB). The accuracy of fluoride ion selective electrode was verified using a Waters Quanta 4000 capillary ion analyzer as previously reported by Wallace (Wallace et al., 2019).

### 3.3 Results and Discussion

#### 3.3.1 Screening experiments for the removal of fluoride

Batch experiments were conducted to examine two original biochars, douglas fir derived biochar (DF-BC) and dairy manure derived biochar (DM500), and one calcium hydroxide coated biochar (Ca-DM500) for their potential effectiveness on the removal of
fluoride from water under uncontrolled pH conditions. As presented in Figure 3.1, the original biochars of DF-BC and DM500 showed very low removal capacity in the range of 0.05-1.2 and 0.11-0.43 mg F/g on average at the fluoride concentrations of 5 and 225 mg L\(^{-1}\), respectively. By comparison, Ca-DM500 significantly increased the removal capacity of fluoride by 3.82 and 8.86 times to 0.41 and 3.81 mg F/g on average at the fluoride concentrations of 5 and 225 mg L\(^{-1}\), respectively. Although the DF-BC has the larger specific surface area of 493.6 m\(^2\)/g than those of DM500 (4.0 m\(^2\)/g) and Ca-DM500 (2.6 m\(^2\)/g), it has the lowest removal capacity. Therefore, the surface area is not the key factor controlling the removal of fluoride.
Figure 3.1. Screening batch test for the removal of fluoride onto original biochars of DF-BC, DM500 and Ca-DM500. Experiment was run in duplicate using 30 mL of 5 and 225 mg L$^{-1}$ fluoride with 10 mM NaCl. The mass of biochar was 100 mg biochar and the samples were incubated for 24 hours at room temperature (25° C).

3.3.2 X-Ray Diffraction and Scanning Electron Microscopy

The main mechanism of enhanced removal is most likely attributed to the presence of Ca$^{2+}$, which has been well known to have a strong affinity with fluoride ions and can be precipitated/immobilized as CaF$_2$ (Islam and Patel, 2007; Camacho et al., 2010; Zhang et al., 2011). As shown in Figure 3.2, the XRD patterns showed that both DM500 and Ca-DM500 contain the diffraction peaks at 2θ of 26, 50 (for SiO$_2$), 33, 46 (for calcium hydroxide (Ca(OH)$_2$), and 54, 64 (for CaO). Especially, the major peak at 2θ of 33 indicated the Ca(OH)$_2$ was predominant on the surface of Ca-DM500 compared
with that on the surface of original DM500, which would play a significant role in the enhanced removal of fluoride via surface complexation of CaF₂.

The EDS analysis of Ca-DM500 revealed strong peaks for Ca compared with the DM500, ensuring the presence of abundant calcium on the surface of Ca-DM500 and the formation of strong precipitation of CaF₂ (Figure 3.3a). Moreover, the SEM images (Figure 3.3b) of DM500 and Ca-DM500 displayed that the surface of Ca-DM500 had calcium aggregates deposited while the DM500 showed mostly the irregular pores with different sizes and little aggregates.

Figure 3.2. XRD analysis of Pristine DM500 and Ca-DM500.
Figure 3.3a. The EDS analysis of DM500 and Ca-DM500 before and after the removal of fluoride from water. Legends: A, original DM500; B, original Ca-DM500; C, Ca-DM500 after the removal of fluoride at 5 ppm; and D, Ca-DM500 after the removal of fluoride at 10 ppm.
Figure 3.3b. The SEM analysis of DM500 and Ca-DM500 before and after the removal of fluoride from water. Legends: A, original DM500; B, original Ca-DM500; C, Ca-DM500 after the removal of fluoride at 5 mg L\(^{-1}\); and D, Ca-DM500 after the removal of fluoride at 10 mg L\(^{-1}\).
3.3.3 pH Effects

Another possible removal mechanism is the electrostatic attraction of opposite surface charges and fluoride anions. The measured pH for the point of zero charge (pH\textsubscript{PZC}) was 10.0, 9.5 and 8.8 for DF-BC, DM500 and Ca-DM500, respectively (Figure 3.4). During the batch removal, the change of solution pH showed different patterns between the three biochars. The solution pH increased to 9.5-9.9 for DF-BC and DM500 from the initial solution pH of 5.8.

Therefore, the surface charges were most likely neutral or slightly negative for DF-BC and DM500 since the solution pH was close or higher than their measured pH\textsubscript{PZC}, causing electrostatic repulsion and lowering removal of fluoride anions. On the other hand, the solution pH for Ca-DM500 stabilized to 7.2, which was lower than its pH\textsubscript{PZC} of 8.8, leading to positive surface charges and enhanced electrostatic attraction of fluoride anions. Thus, the surface coating of Ca strengthens the pH buffering capacity and the removal capacity of fluoride onto Ca-DM500.
Figure 3.4. The measured pH at point of zero charge (pH\textsubscript{PZC}) for DF-BC, DM500, and Ca-DM500 at 10.0, 9.5 and 8.8, respectively.

To further understand the effect of initial solution pH on the removal of fluoride onto Ca-DM500, batch removal was performed at three initial solution pH values of 2.5, 5.8 and 8.4 (Figure 3.5). The Ca-DM500 showed the highest fluoride removal capacity of 0.23 mg F g\textsuperscript{-1} at pH 5.8, which is similar to those reported studies on fluoride removal, such as pH 5.1-6.2 for orange peel or water treatment sludge derived biochars (Oh et al., 2012), pH 5.8 for biomass carbon (Sinha et al., 2003), pH 6.0 for montmorillonite (Tor, 2006), and pH 5.5 for manganese-dioxide-coated activated alumina (Tripathy and Raichur, 2008).
Figure 3.5. Screening batch test for effect of initial solution pH on the removal of fluoride onto Ca-DM500. Experiment was run in duplicate using 30 mL 5 mg L$^{-1}$ fluoride with 10 mM NaCl. The mass of biochar was 500 mg and the samples were incubated for 24 hours at room temperature (25° C). The initial solution pH was adjusted to 2.5, 5.8 and 8.4 using 0.5 M HCl and NaOH.

The removal capacity decreased to 0.08 mg F g$^{-1}$ when pH increased to 8.4, which is due to a shift of surface charges to neutral or negative on Ca-DM500 with increased pH, causing repulsion of the negatively charged fluoride anions. Additionally, the increased OH$^-$ anions at higher pH value competed with fluoride anions for removal. Removal of fluoride is favored at low pH than at a high pH because of the presence of more hydroxylated sites for ligand exchange with fluoride. These findings are consistent with observation from other studies of fluoride removal on
various biochars (Oh et al., 2012; Mohan et al., 2014; Goswami and Kumar, 2018) and
other sorbents (Sinha et al., 2003; Tripathy and Raichur, 2008).

On the other hand, the removal capacity also declined to 0.18 mg F g\(^{-1}\) when
solution pH decreased to 2.5. As shown in Figure 3.4, the reduced pH should increase
the surface positive charges on Ca-DM500, enhancing removal of the negatively
charged fluoride anions. However, weakly ionized hydrofluoric acid forms under acid
conditions with higher H\(^+\) concentration and relatively decreases the removal of fluoride
on the surface. In addition, the lower removal of fluoride can be attributed to the
exchange with OH\(^-\) combined with calcium and other metal ions such as iron and
aluminum or other functional groups on the surface of Ca-DM500 (Oh et al., 2012).

3.3.4 Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS)

The DRIFTS spectra of Ca-DM500 before and after removal of fluoride (Figure
3.6) did not show significant changes on surface peaks, which might be due to the
adsorbed fluoride below the detection limit. The major peaks observed in the biochar
that might influence fluoride removal at different solution pH were aromatic C=C
stretches (1645 cm\(^{-1}\)) (Uchimiya et al., 2013), C-O stretching and C-O deformation
(1060 cm\(^{-1}\)) (Reza et al., 2014), and carboxylate (COO\(^-\)) deviational vibration and
symmetric stretching (785 cm\(^{-1}\)) (Jiang et al., 2012), as well as symmetric and
asymmetric stretching of O-H (3000-3700 cm\(^{-1}\)) (Reza et al., 2014; Uchimiya et al.,
2013).
Figure 3.6. The DRIFTS spectra of biochars DM500 and Ca-DM500 before and after removal of fluoride at different pH values.
3.3.5 Sorption isotherm

Batch sorption experiments were carried out to assess the affinity of fluoride onto Ca-DM500. The sorption data were fitted to Langmuir, Freundlich and Redlich-Peterson isotherm Equations (Figure 3.7). The $R^2$ values (0.986-0.994) show satisfactory fit to all three models, especially Freundlich and Redlich–Peterson isotherms (Table 3.2). The best fit to both Freundlich and Redlich–Peterson isotherms strongly indicates the sorption of fluoride on the heterogenous surfaces of Ca-DM500 and the multilayer coverage of fluoride. The $\beta$ value (0.37) of Redlich-Peterson model was lower than the unity, suggesting that the fluoride had not reached maximum coverage onto Ca-DM500. Thus, the multiple active sites on the heterogenous surface of Ca-DM500 demonstrate different affinities for the sorption of fluoride, which is consistent with previous studies on the sorption isotherms of fluoride by different materials (Mohan et al., 2012; Goswani and Kumar, 2018; Wallace et al., 2019).
Figure 3.7. The adsorption isotherms of fluoride on Ca-DM500 fit with the Freundlich, Langmuir and Redlich-Peterson model Equations. The experiment was operated at pH of 6.8 in 10 mM NaCl solution.
Table 3.2. Model parameters of Freundlich, Langmuir and Redlich–Peterson isotherms for the adsorption of fluoride

| Material                   | Freundlich | | | | Langmuir | | | | | | Redlich–Peterson | | | | | | Reference |
|----------------------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|
|                            | $K_F$      | $n$       | $R^2$     | $K_L$     | $q_{max}$ | $R^2$     | $K_R$     | $\alpha_R$| $\beta$   | $R^2$     |           |           |           |           |           |           |
| Ca-DM500                   | 0.13       | 1.29      | 0.994     | 0.20      | 0.82 (0.32)| 0.986     | 0.33      | 1.50      | 0.37      | 0.992     | This study |
| Pine wood BC               | 2.28       | 3.14      | 0.803     | 0.36      | 7.66 (2.81)| 0.956     | 1.90      | 0.11      | 1.24      | 0.974     | Mohan et al., 2012 |
| Pine bark BC               | 1.18       | 1.95      | 0.944     | 0.08      | 9.77 (5.20)| 0.921     | 15.66     | 12.39     | 0.50      | 0.944     | Mohan et al., 2012 |
| Corn stove BC              | 1.86       | 3.33      | 0.893     | 0.29      | 6.42 (n/a)| 0.981     | 1.79      | 0.26      | 1.02      | 0.981     | Mohan et al., 2014 |
| Magnetic corn stove BC     | 1.37       | 3.85      | 0.881     | 0.35      | 4.11 (1.14)| 0.992     | 1.31      | 0.28      | 1.03      | 0.993     | Mohan et al., 2014 |
| Biomass activated carbon   | 0.53       | 0.99      | 0.990     | 0.81      | 1.57 (0.002)| 0.980     | n/a       | n/a       | n/a       | n/a       | Pongener et al., 2018 |
| Nanoscale rice-hull BC     | 12.6       | 0.91      | 0.995     | 0.06      | 21.7 (n/a)| 0.991     | n/a       | n/a       | n/a       | n/a       | Goswani and Kumar 2018 |
| Nano-Ferrihydrite          | 0.43       | 0.38      | 0.987     | 0.04      | 3.77 (0.02)| 0.894     | 1.67      | 4.46      | 0.59      | 0.995     | Wallace et al., 2019 |
| Nano-HAP                   | 1.56       | 0.43      | 0.995     | 0.14      | 9.20 (0.53)| 0.935     | 3.81      | 2.02      | 0.63      | 0.993     | Wallace et al., 2019 |
| Nano-Brucite               | 0.70       | 0.44      | 0.937     | 0.10      | 5.10 (0.05)| 0.914     | 1.42      | 2.71      | 0.39      | 0.976     | Wallace et al., 2019 |
| HAP                        | 0.72       | 1.31      | 0.992     | 0.05      | 12.42 (n/a)| 0.994     | n/a       | n/a       | n/a       | n/a       | Melidis, 2015 |
| Quartz                     | 0.02       | 1.00      | 1.000     | n/a       | n/a       | n/a       | n/a       | n/a       | n/a       | n/a       | Fan et al., 2003 |

n/a means that data are not available from literature
The Langmuir isotherm can be expressed using the dimensionless separation factor, $R_L$, which is defined by Equation 3.6 (Hall et al., 1966).

$$R_L = \frac{1}{1 + bC_0} \quad (3.6)$$

Where $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible. In this study, the $R_L$ value derived from the Langmuir isotherm data was 0.43, indicating a favorable removal of fluoride onto Ca-DM500. The maximum adsorption capacity ($q_{max}$) calculated from the Langmuir model is 0.82 mg F g$^{-1}$ Ca-DM500. Although the Langmuir $q_{max}$ value was lower than those reported in Table 3.2, Ca-DM500 showed high reactivity per surface area for adsorption of fluoride contributing to the importance of surface adsorption capacity.

### 3.3.6 Removal and desorption kinetics

The kinetics of fluoride removal on Ca-DM500 at an initial concentration of 5 mg L$^{-1}$ and Ca-DM500 dosage of 0.33 g mL$^{-1}$ showed that the removal capacity increased immediately and reached the removal efficiency of 75% with contact time up to 5 minutes. Removal continued increasing after 5 minutes, but at a much slower rate (Figure 3.8). Since the removal started immediately and reached the maximum equilibrium quickly, not enough experimental data were available to be processed and fitted in common kinetics models (e.g. Pseudo-first-order model and Pseudo-second-order model).

However, the experimental removal data are well described by the three-step intra-particle diffusion model (Sun and Yang, 2003; Noroozi et al., 2007), which is like a previous study of fluoride removal on nano-sized hydroxides, such as ferrihydrite.
hydroxyapatite, and brucite (Wallace et al., 2019). The first step represents the instantaneous external surface removal, in this case, via surface precipitation as CaF₂; the second step reflects fast-pace gradual removal, and the final equilibrium stage of intra-particle diffusion takes place very slowly due to the extremely low solute concentration in solution. As for the desorption phase, the results showed that fluoride was not detectable in solution when the biochar was incubated in 10 mM NaCl over 48 hours (data not shown). The results strongly indicate the stable immobilization of the adsorbed fluoride on the surface of Ca-DM500 with very low leaching potential to water.

**Figure 3.8.** The removal of fluoride on Ca-DM500 over 48 hours (Ca-DM500 dose 1.5 g in 45 mL of initial fluoride concentration at 5 mg L⁻¹ in 10 mM NaCl). The solution was incubated under static conditions at 25 °C with pH controlled at 8.0 ± 0.5.
3.3.7 Effect of co-existing anions

Anions such as sulfate, nitrate, and phosphate are usually present in fluoride-contaminated water and competes with fluoride for active removal sites. Figure 3.9 shows the interfering effect of co-existing anions, PO$_4^{3-}$, SO$_4^{2-}$, and NO$_3^-$, on the removal of fluoride onto Ca-DM500 from water. As previously reported by Mohan et al. (2012), the influence of ionic interactions can be interpreted by using the ratio of removal capacity of fluoride in the presence ($Q^\text{mix}$) and absence ($Q^0$) of complementary anions in solution. When $Q^\text{mix}/Q^0$ is higher than 1, the presence of complementary anions enhances the removal of fluoride; when $Q^\text{mix}/Q^0$ is equal to 1, there is no net impact; and when $Q^\text{mix}/Q^0$ is smaller than 1, the presence of complementary anions decreases the removal of fluoride.

In this study, the values of $Q^\text{mix}/Q^0$ were 0.47, 0.44 and 0.75 for PO$_4^{3-}$, SO$_4^{2-}$, and NO$_3^-$, respectively, indicating that the three anions suppressed the removal of fluoride onto Ca-DM500. The reduction of fluoride removal efficiency was observed in the order of SO$_4^{2-} \approx$ PO$_4^{3-} >$ NO$_3^-$, which is consistent with that reported by others (Dey et al., 2004; Kumar et al., 2009; Nur et al., 2014). Previous studies showed that PO$_4^{3-}$ and SO$_4^{2-}$ can form strong specific inner-sphere complexation through chemical bond with calcium oxides and hydroxides, which out-compete specifically adsorbed fluoride. However, NO$_3^-$ only weakly adsorbed via outer-sphere and non-specific complexation, lowering the removal competition with fluoride.
Figure 3.9. The effect of competitive anions (PO\(_4^{3-}\), SO\(_4^{2-}\), and NO\(_3^{-}\)) on the fluoride removal onto Ca-DM500 over 24 hours (Ca-DM500 dose 0.5 g in 30 mL of initial fluoride concentration at 5 mg L\(^{-1}\) in 10 mM NaCl). The concentration of PO\(_4^{3-}\), SO\(_4^{2-}\), and NO\(_3^{-}\) was 1.0, 1.0, and 4.0 mg L\(^{-1}\), respectively. The solution was incubated under static conditions at 25 °C with pH controlled at 8.0 ± 0.5.

3.3.8 Continuous fixed-bed column experiments

In this study, the continuous flow through fixed-bed columns were operated to investigate the removal and desorption of fluoride on DM500 and Ca-DM500 and explore their stability for the removal of fluoride after two cycles of regenerations and reuse. The column filled with pure quartz sand was included as a control treatment without addition of DM500 and Ca-DM500. In control columns with pure quartz sand, negligible removal of fluoride (Figure S2.12) was observed through the operation of 150
minutes (equal to 5 pore volumes). Removal of fluoride ions by DM500 and Ca-DM500 is presented in the form of breakthrough curves for these columns through three cycles of removal-desorption and regeneration-reuse (Figure 3.10).

The results illustrated that the presence of DM500 and Ca-DM500 significantly enhanced the removal of fluoride from aqueous solution, although each biochar displayed different removal behaviors of breakthrough in the column study. The fluoride breakthrough occurred faster, and the breakthrough curve was steeper in the columns filled with DM500 than in the columns filled with Ca-DM500. The exhaustion time to reach the plateau of $C_e/C_0$ was much shorter for the columns filled with DM500 occurring 40 minutes than for the columns filled with Ca-DM500 at 80 minutes. The results suggest that surface coating with Ca on DM500 extends the removal breakthrough pattern and enhances the removal capacity of the biochar to remove fluoride ions.
Figure 3.10. Breakthrough curves expressed as $C_e/C_0$ versus time for the sorption of fluoride onto DM500 or Ca-DM500, mixed with quartz sand medium in a continuous fixed-bed column. The initial fluoride concentration was 10 mg L$^{-1}$ in 10 mM NaCl solution. Error bars are calculated from standard deviation ($n = 2$).
During the fixed-bed column operation, the influent containing fluoride ions passes through the column, attaches to the unsaturated adsorbents and reaches the exhaustion point. Because the removal is not at steady state while the influent is still flowing through the column, it is difficult to describe the dynamic behavior of fluoride in a fixed-bed under the defined operating conditions. However, the Thomas model is often used to describe the dynamic behavior of a fixed-bed column. A seen in Figure 3.11, the Thomas model fitted reasonably well to the experimental data by the high $R^2$ values (0.930-0.993), and the calculated parameters are summarized in Table 3.3.
Figure 3.11. Fitting of experimental data to the Thomas Eqn. Error bars are calculated from standard deviation (n = 2).
Table 3.3. Thomas model parameters derived from the experimental data in continuous columns

<table>
<thead>
<tr>
<th></th>
<th>Cycle #1</th>
<th>Cycle #2</th>
<th>Cycle #3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DM500</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_T$ (L mg$^{-1}$ h$^{-1}$)</td>
<td>0.011</td>
<td>0.015</td>
<td>0.011</td>
</tr>
<tr>
<td>$q_T$ (mg g$^{-1}$)</td>
<td>0.02</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.965</td>
<td>0.930</td>
<td>0.970</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ca-DM500</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_T$ (L mg$^{-1}$ h$^{-1}$)</td>
<td>0.011</td>
<td>0.013</td>
<td>0.016</td>
</tr>
<tr>
<td>$q_T$ (mg g$^{-1}$)</td>
<td>0.11</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.986</td>
<td>0.993</td>
<td>0.952</td>
</tr>
</tbody>
</table>

Based on the Thomas model calculated sorption capacity $q_T$ and the rate constant $k_T$, columns filled with Ca-DM500 demonstrated similar rates but showed a higher sorption capacity than DM500. Moreover, the results showed that the Ca-DM500 sorption capacity of fluoride ions from column study are lower than the corresponding sorption capacity calculated using the Langmuir model from batch isotherm experiment. Although higher fluoride concentration is expected to produce higher fluoride sorption, inlet concentration of fluoride ion in the column study was maintained at 8.6 ± 0.25 mg L$^{-1}$, which is close to initial fluoride concentration of 10 mg L$^{-1}$ used in batch study. Therefore, sorption equilibrium would not cause the lower adsorption capacity obtained in the Thomas models than that derived from the Langmuir adsorption maximum. The differences of obtained sorption capacity between continuous fixed-bed columns and batch systems have been reported by previous studies (Tor et al., 2009; Wallace et al., 2019). The discrepancies might be attributed to the longer time of reaction (48 h) in the batch test than in the column test (< 1.5 h).
After the fixed-bed columns were saturated with fluoride, the stability of adsorbed fluoride on the packed materials (DM500 or Ca-DM500) was examined through a desorption process, in which 10 mM NaCl passed through the exhausted columns at a flow rate of 1 mL/min until no fluoride was detected in the effluent. Due to possible fluoride solution left in the pores of columns when the influent was changed to 10 mM NaCl, the desorption mass in the column packed with DM500 or Ca-DM500 and quartz was corrected by subtracting the desorption mass from the control columns composed of quartz alone. The calculated column desorption efficiency was 10 and 5% for DM500 and Ca-DM500, respectively, indicating that the sorbed fluoride could be desorbed, but at low level, especially for Ca-DM500. These results show that the coating of Ca on surface of DM500 enhances the stability of adsorbed fluoride.

NaOH (0.1 M) has been reported to be the most suitable reagent to desorb fluoride from adsorbent materials e.g. Hydrous Ferric Oxide (HFO) compared with 0.1 M anions Cl\(^-\) and SO\(_4^{2-}\) (Dey et al., 2004; Nur et al., 2014). Thus, after desorption, the remaining sorbed fluoride was desorbed using 0.1 M NaOH to regenerate the surface-active sorption sites of packed DM500 or Ca-DM500 in the columns. As shown in Figure 3.10, the time for breakthrough for regenerated DM500 or Ca-DM500 was like that in the column with virgin DM500 or Ca-DM500. In addition, the Thomas model derived fluoride sorption capacity and the rate constant were very close after the first and second cycles of regeneration-reuse (Table 3). The results demonstrated that Ca-DM500 could be regenerated by leaching the adsorbed fluoride and maintain strong removal capacity with repeated reuse. In contrast, previous studies using HFO found that the removal capacity of regenerated HFO continuously decreased by 50% when HFO was
reused by through 3 cycles of sorption/desorption (Nur et al., 2014). The reduction in removal capacity may be due to surface modification by exposure to high concentration of NaOH. However, Ca-DM500 maintained its removal capacity over all three regeneration cycles. Thus, Ca-DM500 proves to be an effective and stable sorbent for the long-term removal of fluoride from water.

3.3.9 Conclusion

In this study, the removal of fluoride from water was investigated using a calcium hydroxide-coated dairy manure-derived biochar. The Ca-DM500 was closely examined for physiochemical characterization, adsorption capacity and kinetics in batch tests, and adsorption-desorption and regeneration-resue behavior in continuous fixed-bed column experiments. The Ca-DM500 showed the potential to be an effective and reusable sorptive material for remediating fluoride polluted water. The main conclusions are summarized as follows:

(i) The Ca-DM500 showed the 3.82 to 8.86 times higher removal capacity of fluoride than original DM500 from water, which was mainly due to in strong removal complexation between fluoride and calcium hydroxide.

(ii) The Freundlich and Redlich–Peterson sorption isotherms better described the experimental data than the Langmuir model.

(iii) The sorption kinetics were well described by the three step intra-particle diffusion model, indicating combined specifically and non-specifically chemisorptive interactions occurred on heterogeneous surface of Ca-DM500.

(iv) Furthermore, the coexistence of anions reduced fluoride removal on Ca-DM500, following the order of $SO_4^{2-} \simeq PO_4^{3-} > NO_3^-$. 

84
(v) The Thomas model well describes the sorption behavior of fluoride in a continuous fixed-bed column.

(vi) Column studies demonstrated that the Ca-DM500 has a strong affinity to fluoride and low desorption potential as well as stable sorption capacity through regeneration and reuse cycles.

Acknowledgements

This research was partially funded by the U.S. Environmental Protection Agency (U.S. EPA). Anna Rose Wallace is a Student Trainee (Engineering) under the U.S. EPA Pathways Internship Program and produced this manuscript while conducting research as part of her Doctor of Philosophy degree program at Southern Methodist University.

Disclaimer

Although the U.S. EPA partially funded this research and U.S. EPA employees contributed to this article; the views, interpretations, and conclusions expressed in the article are solely those of the authors and do not necessarily reflect or represent the U.S. EPA’s views or policies. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. EPA or the U.S. Government.
3.4 Appendix

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Grade</th>
<th>Purity</th>
<th>Manufacturer</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl</td>
<td>Aqueous</td>
<td>Trace Metal Grade</td>
<td>Sigma-Aldrich</td>
<td>7647-01-0</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>KCl</td>
<td>Reagent</td>
<td>99.0 %</td>
<td>Mallinckrodt</td>
<td>7447-40-7</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Phosphate</td>
<td>NaH₂PO₄</td>
<td>Reagent</td>
<td>98.5 %</td>
<td>Sigma-Aldrich</td>
<td>10049-21-5</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>Na₂SO₄</td>
<td>Reagent</td>
<td>99.0 %</td>
<td>J.T. Baker</td>
<td>7767-82-3</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>NaNO₃</td>
<td>Reagent</td>
<td>99.0 %</td>
<td>Fisher Scientific</td>
<td>7631-99-4</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Reagent</td>
<td>99.4 %</td>
<td>Fisher Scientific</td>
<td>1310-732</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>Reagent</td>
<td>99.7 %</td>
<td>Fisher Scientific</td>
<td>7647-14-5</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>NaF</td>
<td>Reagent</td>
<td>99.9 %</td>
<td>Sigma-Aldrich</td>
<td>7681-49-4</td>
</tr>
<tr>
<td>TISAB (II) with CDTA</td>
<td>n/a</td>
<td>Aqueous</td>
<td>n/a</td>
<td>Orion</td>
<td>940909</td>
</tr>
<tr>
<td>Fluoride Standard (100 mg L⁻¹)</td>
<td>F⁻</td>
<td>Aqueous</td>
<td>100 ± 0.5</td>
<td>Orion</td>
<td>940907</td>
</tr>
<tr>
<td>Fluoride Standard (0.1 M)</td>
<td>F⁻</td>
<td>Aqueous</td>
<td>0.1 ± 0.0005</td>
<td>Orion</td>
<td>940906</td>
</tr>
</tbody>
</table>

* not available
3.5 References


88


Samsuri, A. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (2013). Adsorption of As (III) and As (V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. Journal of Environmental Chemical Engineering, 1(4), 981-988.


Sun, Q., and Yang, L. (2003). The adsorption of basic dyes from aqueous solution on modified peat–resin particle, Water Res. 37, 1535-1544


Chapter 4

EVALUATION OF THE IMMOBILIZATION OF CO-EXISTING HEAVY METAL IONS FROM WATER BY DOUGLAS FIR- AND DAIRY MANURE-DERIVED BIOCHARS: PERFORMANCE AND REUSABILITY

4.1 Introduction

Increasing pollution associated with heavy metals causes serious environmental health and safety concerns due to their toxicity and persistence in the environment (Berzonik, 2002; Djukic et al., 2016). Unlike organic contaminants, heavy metals are non-biodegradable and can persist for many years in the environment. Although some heavy metals are nutritionally essential at trace levels, most of them can become toxic or carcinogenic to all forms of life when their concentrations exceed certain tolerance levels (Goyer et al., 2004). For example, cadmium (Cd) is a known carcinogen that causes kidney damage, and lead (Pb) can retard physical and mental development in children as well as cause kidney problems and high blood pressure in adults (U.S. EPA, 2018). By comparison, zinc (Zn), an essential trace element for regulating the immune system in humans, has significant ecotoxicological impacts (Salgueiro et al., 2000; de Vries et al., 2007; Nandi et al., 2012; Fäth et al., 2018). Studies have reported that Zn at concentrations above 120 µg L\(^{-1}\) causes acute and chronic toxic effects to aquatic life (U.S. EPA, 2019), affecting life cycle completion and embryonic development
in fish and other organisms (Sfakianakis et al., 2015; Langston, 2018).

Cd, Pb and Zn as well as other heavy metals have been included in the list of 126 priority pollutants regulated by the U.S. EPA’s Clean Water Act (CWA), which provides the standard for the national pollutant discharge elimination systems (NPDES) (U.S.EPA, 2010). Because of the human health risks regarding heavy metals in drinking water, the U.S. EPA has set maximum contamination levels (MCLs) for heavy metals in drinking water including cadmium (0.005 mg L\(^{-1}\)), copper (1.0 mg L\(^{-1}\)), lead (0.015 mg L\(^{-1}\)) and zinc (5.0 mg L\(^{-1}\)) (U.S. EPA, 2018).

Heavy metal contaminated water over MCLs has been found worldwide. Continuous release of heavy metal into lakes, such as Lake Pontchartrain Basin in Louisiana, U.S. and Taihu Lake in China, leads to severe concerns on the bioaccumulation of heavy metals and consequent risks to aquatic organisms (Rajeshkumar et al., 2018; Zhang et al., 2016;). The concentrations of Cd\(^{2+}\) and Pb\(^{2+}\) in the Ajay River as a drinking water source in India are found over 0.053 and 0.030 mg L\(^{-1}\) respectively, posing a high health risk to adults and children (Singh and Kumar, 2017). Additionally, the Bangshi River near Bangladesh poses significant public health concerns due to elevated levels of arsenic (As), chromium (Cr), Cu and Pb (Saha et al., 2017). Moreover, plant crops irrigated with reclaimed wastewater can uptake and accumulate high levels of heavy metal, causing severe problems related to sustainable agricultural production and food safety via consumption of polluted crops (Ahmad et al., 2019).

Heavy metals including Cd, Zn and copper (Cu) are prevalent in various industries, such as mining, aluminum smelting, electronic and battery manufacturing,
petroleum refining, and fertilizer production (Schroder et al., 2003; Du et al., 2015; Ismail et al., 2016; Cowden and Aherene, 2019). These industrial processes are responsible as point sources for the discharge of heavy metals into environment through wastewater disposal, the major cause of water and soil contamination. Additionally, heavy metals can be released into receiving water bodies via non-point sources, such as automobiles, bridges, atmospheric deposition, industrial areas, soil erosion, corroding metal surfaces, and combustion processes (Brown, 2006; Rahman et al., 2019).

To comply with the MCLs and improve environmental health and safety, the removal of heavy metals from water has become a critical issue. Common treatment methods, such as coagulation and flocculation, chemical precipitation, ion exchange, reverse osmosis, membrane separation and filtration processes, electrochemical techniques and sorption, have been applied to remove heavy metal ions from water (Guntailake, 2015; Mohsen-Nia et al., 2007; Erdem et al., 2004; Sikdar and Kundu, 2018)

However, many of abovementioned methods have proved to be expensive, because they either require specialized chemicals/reagents and apparatus or co-produce a large quantity of metal containing hazardous wastes (Fu and Wang, 2011; Gupta et al., 2015; Crini et al., 2019; Bolisetty et al., 2019).

Considering the above drawbacks, sorption is widely regarded as a promising treatment for the large volume of heavy metal polluted water by immobilizing them onto cost-effective materials. In addition, sorptive materials have an advantage because of their broad applications into groundwater remediation and green infrastructure (GI) (Xue et al., 2012; Inyang et al., 2016). Currently, a large variety of carbonaceous materials, such as activated carbon (AC), are commonly used in the removal processes of heavy
metals from water, which are attributed to high surface area and large micropore and mesopore volumes. However, the depletion of coal-based products is causing a commercial resource crisis for AC generation due to the current environmental climate, leading to the urgency of alternative materials (Chen, 2015).

Recently, biochar has been increasingly recognized as a promising and low-cost sorbent that can be used to remediate heavy metal contaminated water. Biochar is produced as a carbon-rich byproduct by pyrolyzing organic matter in an oxygen-depleted environment. Natural organic wastes such as forest and plant wastes, animal manures and organic fraction of municipal solid wastes are widely available in large quantities, providing great potential as low-cost materials. Most importantly, the production of waste-derived biochar also creates positive impacts on sustainable waste management and environmental protection. Compared with AC, biochars have similar properties of a large specific surface area and a high degree of porosity but present better advantages due to the presence of a great variety of surface functional groups. Therefore, biochar could be an ideal alternative for AC as cost-effective sorbent.

Surface properties of biochar, especially functional groups, play decisive roles in influencing the removal behavior of heavy metals from water and the subsequent stability on the surface of biochar. However, the physical and chemical surface characteristics of biochar are highly variable depending on the feedstock type, pyrolysis temperature and various pre- and post-feedstock treatments (Singh et al., 2017). These parameters are useful in determining the removal mechanisms and long-term effectiveness of biochar as a remedial material for heavy metal contaminated water (Ahmad et al., 2014; Jiang et al., 2016).
Researchers have embarked on understanding the effects of these parameters controlling the efficiency and retention ability of biochar as a sorbent for heavy metal removal from water. A review by Ahmad et al. (2014) compared the effects of pyrolysis temperature on the surface properties of biochar. Overall, they found that biochar contains less H and O functional groups and shows lower ion exchange capacity when produced at high temperatures (600-900 ºC). Conversely, biochars made at low pyrolysis temperatures (350-600 ºC) contains more H and O functional groups and shows favorable Pb\(^{2+}\) removal (Ahmad et al., 2014). For example, a study by Uchimiya et al. (2010) measured 4.00 % (H) and 18.30 % (O) when biochar was pyrolyzed at 350 ºC, however, these elemental components dropped to 1.42 % (H) and 7.4 % (O) when the pyrolysis temperature increased to 700 ºC. Furthermore, biochar shows varied organic aliphatic and cellulose structures and contains more C-H and C=C groups when made at low temperatures (250-400 ºC) (Godwin et al., 2019).

Most studies have primarily focused on the removal of mono-metal system by various types of biochar. Doumer et al. (2015) examined the removal of Cd, Cu, Pb and Zn in mono-metal system and found that biochar could achieve 95% removal or better for each metal. However, the co-existence of multiple heavy metals is more realistic in the contaminated environment, anticipating some levels of competitive removal. Gazi et al. (2016) showed that magnetically modified palm seed biochar removed nickel up to 28 mg/g at pH 3, but was inhibited by competing ions of copper, manganese and Rhodamine B dye. Thus, it is imperative to expand the understanding of competitive removal of heavy metals and underlying mechanism for the removal preference by biochar in multi-metal systems (Godwin et al., 2019).
Competitive immobilization/release behavior and underlying mechanism for heavy metal removal by biochar are not yet well understood regarding the remediation of heavy metal contaminated water. In addition, uncovering the capacity and reusability of biochar will create a pathway for biochar to be utilized as a promising replacement for conventional materials such as AC. For example, a recent study by Li, et al (2019) used a novel microwave-mediated method for extracting heavy metals from biosolids, and this method has potential use for reclaiming heavy metals removed by biochar. The main objectives of this study are to evaluate the immobilization/release performance of biochar as a sustainable material for competitive removal of co-existing heavy metal ions from water and to elucidate the underlying mechanism for regeneration/reusability of biochar.

4.2 Materials and Methods

4.2.1 Chemical reagents

All chemicals used in this study were reagent grade of 99% purity or better. Chemicals were purchased from Fischer Scientific, Thermo Scientific or Sigma-Aldrich.

4.2.2 Selected biochar

Six biochars made from different feedstock under various pyrolysis conditions were used in this study. Three douglas fir derived biochars include douglas fir ultra-dry (DF-BC), douglas fir with compost tea (Tea-DF-BC), and douglas fir with organics (Org-DF-BC). All three douglas fir derived biochars were purchased from Black Owl Biochar (Biochar Supreme, LLC., Bellevue, WA), which were generated from gasification in an air-fed updraft gasifier at 900-1000 °C with a residence time of about 1-10 seconds,
ground and sieved to a particle size of < 2.0 mm and stored in closed vessels until usage (Karunanayake et al., 2018). The other three biochars were pyrolyzed from dairy manure, including DM500, DM-BC and DM-BC-CV. DM500 was obtained from Professor Sergio Capareda at Texas A&M University (College Station, TX), which was produced from a fluid bed gasification of dairy manure in a gasifier at 500 °C, and milled, sieved through a 2 mm sieve and stored in closed vessels until usage (Nam et al., 2016). The DM-BC-CV was produced by Coaltec Energy USA, Inc. located in Carterville, Illinois. The raw dairy manure was gasified at ~1100 °C following a process undisclosed by the manufacturer. The DM-BC was supplied by collaborators from an industrial vendor, who did not disclose the specific pyrolysis conditions for the DM-BC. Both DM-BC-CV and DM-BC samples were sieved through a 2 mm sieve and stored in closed vessels until usage.

4.2.3 Characterization of douglas fir and dairy manure derived biochars

The pH of each biochar was measured using the method described in our previous study (Wallace et al., 2019). Briefly, 2.5 g of biochar was weighed in a 50 mL polypropylene tube with 25 mL of DI water or 10 mM NaCl. The sample was shaken at 200 rpms for 1 hour, removed from the shaker and let stand for 30 min and the pH was measured.

The measurement of specific surface area for each biochar was performed using a Quantachrome NOVA 2000e Surface Area and Pore Size Analyzer (BET). For each analysis, 0.5 g dry sample were placed in a bulb cell under the parameters described in the manual instruction.
The X-ray diffraction (XRD) analysis of each biochar was performed on a Rigaku Miniflex X-ray diffractometer (Ultima IV, Rigaku, Japan) following the procedure described by Galletti et al. (2016). Approximately 20 mg sample was taken to fill up a cavity (7 mm diameter) on an elemental silicon slide sample holder. The sample cavity was pressed to form a smooth surface using a stainless-steel spatula. The samples were scanned at a rate of 0.5° 2θ min\(^{-1}\) and a sampling width of 0.02° 2θ (Fe K\(\alpha\) radiation, \(\lambda = 1.9373\) Å; operated at 30 keV and 15 mA).

The surface morphology and elemental compositions of each biochar before and after the adsorption of metals were captured by a Leo-Zeiss 1450VPSE scanning electron microscope (SEM, Carl Zeiss Microscopy, USA) equipped with an EDAX Genesis 4000 XMS SYSTEM 60 energy-dispersive spectrometer (EDS).

In addition, the surface functional groups of each biochar before and after the adsorption of metals were examined with a Bruker Vertex 70 Fourier-transform infrared spectroscopy (FTIR) using the diffuse reflectance infrared Fourier -transform spectroscopy (DRIFTS) method. A dry sample was ground to a fine powder in a mortar and pestle. Approximately 20 mg powdered sample was mixed with 45 g potassium bromide (KBr) and then transferred to a small vessel and placed in the instrument. A KBr background (potassium bromide (KBr)) and a control (calcite, CaCO\(_3\)) were analyzed prior to sample analysis. Each sample was scanned 1200 times to minimize sample noise with measured wavenumbers in the range from 600 to 4000 cm\(^{-1}\). The samples were analyzed five times and the average was reported as the result. The instrument was purged with CO\(_2\) -free air from a CO\(_2\) adsorbent for 30 minutes between each analysis.
The values of pH at point of zero charge ($\text{pH}_{\text{PZC}}$) for each biochar was determined using a modified method described by Tan et al. (2008). Briefly, 50 mL of 0.1 M KCl solution was added in different 60 mL polypropylene centrifuge tubes. The initial pH of the mixture solution was adjusted to the range of 4-11 using either 1.0 M HCl or 1.0 M NaOH solution. Nitrogen gas was bubbled during the pH adjustment to prevent dissolution of atmospheric CO$_2$. A dry sample (0.5 g) was added into each tube, and each tube was vigorously agitated in a shaker for 24 hr at ambient room temperature. After that, the suspensions were settled down and the final pH was measured immediately. The differences between final and initial pH values ($\Delta$ pH) were calculated and plotted against the initial pH ($\text{ipH}$) values. Therefore, the ipH at which $\Delta$ pH is zero is the pH$_{\text{PZC}}$.

### 4.2.4 Batch Experiments

Batch experiments were carried out to investigate the competitive immobilization/release behavior of mixed metals onto three douglas fir derived biochars and three dairy manure derived biochars. In this study, mixed metals in both forms of chloride and nitrate salts were used to evaluate the effect of different anions at the same ionic strength on the competitive removal of mixed metal ions. Briefly, 100 mg of biochar sample was added to a 50 mL polypropylene tube mixed with 30 mL of each metal (1.0 mM) in the chloride salt forms: cadmium chloride (CdCl$_2$), cobalt chloride (CoCl$_2$), copper chloride (CuCl$_2$), nickel chloride, (NiCl$_2$), zinc chloride (ZnCl$_2$), and lead nitrate (Pb(NO$_3$)$_2$) (substituted due to the insolubility of lead chloride); or nitrate salts forms: cadmium nitrate (Cd(NO$_3$)$_2$), cobalt nitrate (Co(NO$_3$)$_2$), copper nitrate (Cu(NO$_3$)$_2$), nickelous nitrate (Ni(NO$_3$)$_2$), lead nitrate (Pb(NO$_3$)$_2$), and zinc nitrate (Zn(NO$_3$)$_2$).
During the experimental operation, the solution pH was not adjusted and allowed to free drift to the equilibrium. The tubes were incubated for 24 hours on an agitator shaker at a constant speed (200 rpm) at ambient room temperature. Prior to metals analysis, liquid samples were filtered through a 0.22 µm mixed cellulose esters (MCE) membrane filters (Sigma-Aldrich, catalog # GSWPO2500). Samples were fixed with 0.30 mL of 70% nitric acid, diluted 10 times and stored at 4 ºC to await metals analysis. Each batch experiment was conducted in duplicates and the results are presented as averaged value with standard deviation calculated. Subsequently, batch experiments containing only three selected mixed metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ were conducted in both chloride and nitrate systems as described above.

For the sorption isotherm experiments, 30 mL of each individual metal ion (Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$) solution at concentrations of 6, 12, 24, 48 and 96 mg L$^{-1}$ were added to 50 mL polypropylene tubes with 100 mg DF-BC or DM-BC. Samples were incubated for 24 hours on an agitator shaker (200 rpms) at ambient room temperature (25 ºC). The pH was adjusted to 7.00 ± 0.25 at time zero and was adjusted back to 7.00 ± 0.25 at 24 hours if the pH drifted over the duration of the experiment. In this study, 10 mM NaCl was used as electrolytes to maintain solution ionic strength. After incubation, the liquid samples were prepared and stored as described above for metal analysis.

For the sorption kinetics experiment, 100 mg DF-BC or DM-BC was weighed into a 50 mL polypropylene tube with 30 mL of mixed metal ions of Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ (1.0 mM) in chloride or nitrate forms in 10 mM NaCl. The tubes were incubated under static conditions at ambient room temperature (25 ºC) and the pH was not adjusted and become stable at 5.8 ± 0.16. Liquid samples were collected at time intervals of 2, 4, 6,
10, 24, 48, 96 and 168 hours and were prepared and stored as described above for metal analysis.

To understand the effects of pH on the metal sorption using DF-BC and DM-BC7, batch experiments were conducted as described above in a chloride system with Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ ions (1.0 mM). The pH was adjusted using 1 M HCl or NaOH from 3 to 11 with the increment of one unit. Liquid samples were prepared and stored as described above for metal analysis.

4.2.5 Sorption isotherm models

Table 4.1 presents the sorption models and parameters used to understand the surface interactions of metals onto DF-BC and DM-BC.
### Table 4.1. Sorption isotherm models used in this study

<table>
<thead>
<tr>
<th>Equation</th>
<th>Linear Equation</th>
<th>Model</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q = q_{max} \frac{K_L C_e}{1 + K_L C_e} )</td>
<td>( C_e = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e )</td>
<td>Langmuir</td>
<td>( C_e = ) Concentration at equilibrium (mg L(^{-1})) ( q = ) mass sorbate removed (mg g(^{-1})) ( q_{max} = ) adsorption capacity (mg g(^{-1})) ( K_L = ) Langmuir adsorption constant (L mg(^{-1}))</td>
</tr>
<tr>
<td>( q = K_F C_e^{\frac{1}{n}} )</td>
<td>( \log(q) = \log(K_F) + \frac{1}{n} \log(C_e) )</td>
<td>Freundlich</td>
<td>( C_e = ) Concentration at equilibrium (mg L(^{-1})) ( q = ) mass sorbate removed (mg g(^{-1})) ( n = ) adsorption intensity ( K_F = ) affinity intensity (mg g(^{-1}))</td>
</tr>
<tr>
<td>( q = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} )</td>
<td>( \ln \left( \frac{K_R C_e}{q} \right) - 1 = \ln(\alpha_R) + \beta \ln(C_e) )</td>
<td>Redlich-Peterson</td>
<td>( C_e = ) Concentration at equilibrium (mg L(^{-1})) ( q = ) mass sorbate removed (mg g(^{-1})) ( \alpha_R = ) empirical constant (L mg(^{-1})) ( \beta = ) exponent between 0 and 1 ( K_R = ) model isotherm constant</td>
</tr>
</tbody>
</table>
4.2.6 Removal of mixed metal ions of Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ in column study

DF-BC and DM-BC were used as individual sorbent in continuous fixed-bed columns to investigate the immobilization/release behavior of mixed metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ in a chloride system, and to illustrate the removal capacities and stability through the regeneration-reuse processes. Glass columns (cross sectional area as 4.91 cm$^2$ and height as 30 cm) were used as fixed bed (30 cm of the bed depth) up-flow reactors and packed with 5.3 g of DF-BC or 42.5 g of DM-BC.

In addition, control columns were operated with only 10 mM NaCl without addition of metals for both DF-BC and DM-BC. The pore volume was measured at 42.4 mL and 22.6 mL for DF-BC and DM-BC respectively in the metal columns, and 42.9 mL and 26.9 mL for DF-BC and DM-BC respectively in the control columns. During the operation of each column, the influent containing mixed metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ at 1.0 mM each with 10 mM NaCl was pumped through the packed columns in an up-flow mode with a peristaltic pump at a flow rate of 1.0 mL min$^{-1}$ at an ambient room temperature.

The removal capacity at the point of breakthrough ($q_B$) is defined as the effluent concentration of the metals reaches 10% or lower of the initial influent concentration of 1.0 mM. The removal capacity at the point of exhaustion ($q_E$) is defined as the effluent concentration of metal ions reaches 90% or higher of the influent concentration. After the metal concentration exhausted from the column, the column was left standing to allow most of the pore water to drain by gravity overnight up to 24 hours, and then sparged with N$_2$ gas for 5 minutes at 20 psi to ensure all residual pore water removed from the column.
Desired pore volumes of 10 mM NaCl were run through the column for the desorption through the exhausted columns until no metal ions were detected or no further decrease of metal concentration was detected in the effluent. The effluent was collected every 22 minutes and 42 minutes in the collection vessels on the fraction collector for DF-BC and DM-BC respectively, and the pH was measured immediately. Liquid samples were prepared and stored as described above for metal analysis.

Once the desorption experiment was completed, the column was regenerated by dewatering as described above and soaked with 2.0 M HCl and rinsed with 10 mM NaCl to remove all the sorbed metals and then air-dried under N₂ gas. The regenerated columns were operated with two more cycles of adsorption-desorption cycle to evaluate the effectiveness of regenerated DF-BC and DM-BC on the competitive removal of mixed metal ions of Cd²⁺, Pb²⁺ and Zn²⁺ from water.

The Thomas model (Equation 4.1) is commonly used to evaluate the removal behavior in a continuous fixed-bed column (Thomas 1944).

\[
\ln \left( \frac{C_0}{C_e} - 1 \right) = k_T q_T \frac{M}{Q} - k_T C_0 t \quad (4.1)
\]

Where \( k_T \) = Thomas rate constant (mL/min mg), \( q_T \) = equilibrium F⁻ uptake per g of biochar (mg/g), \( C_0 \) = influent F⁻ concentration (mg L⁻¹), \( C_e \) = effluent F⁻ concentration at time \( t \) (mg L⁻¹), \( M \) = mass of biochar (g), \( Q \) = filtration velocity (mL/min), and \( t \) = time of influent passed through the column. The parameters \( k_T \) and \( q_T \) are calculated from the plot of \( \ln[\left( C_0/C_e \right) - 1] \) vs. time (t).
4.2.7 Analytical Methods

Metals analysis was conducted using a Perkin-Elmer Optima 8300 DV inductively coupled plasma optical emission spectrometry (ICP-OES), and the instrumental conditions were described as follows. The temperature of the spray chamber is maintained at 30 °C. The gases used for instrumental operation are nitrogen and argon (UHP) set at 80 and 100 psi, respectively, and compressed air as sheer gas set at 100 psi. A water circulator was used to cool the instrument. Polyvinyl chloride (PVC) tubing and suitable for aqueous acidic solutions were used for sample transport within the instrument. Plasma, auxiliary, and nebulizer gas flows were set at 15, 0.2, 0.65 L min\(^{-1}\), respectively. RF power was set at 1500 watts. Exhaust rate from the instrument was 660 CFM. In this study, quality control tests using metal stock solution(s) demonstrated that there was no retention of metals on the 0.22 µm membrane filter.

The standard operating procedure (SOP) for ICP-OES analysis used is NRMRL-GWERD-09-0 and was adapted from the EPA method 200.7. Standard operating procedures are described as follows. Briefly, 8 mL of the aqueous samples are nebulized into the spray chamber of the ICP. A stream of argon carries the sample aerosol into a plasma (~6000 °K) where sample particles are atomized, ionized and excited. The optical emission of each element is detected by a segmented-array charge coupled device detector (CCD). The elemental concentrations in the samples are obtained by comparing the signals with that of the standards. Error between duplicate samples was 5%. A 2% nitric acid rinse was run between each sample to avoid cross contamination of samples.
4.3 Results and Discussion

4.3.1 Batch removal of mixed heavy metal ions

4.3.1.1 Screening of mixed metal ions removal on biochars

Batch tests were conducted to investigate the competitive removal of six mixed metal ions (Cd$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$) on three douglas fir derived biochars and three dairy manure derived biochars in a chloride (10 mM NaCl) or nitrate (10 mM NaNO$_3$) system. As presented in Figure 4.1, all six biochars showed similar patterns to remove six metal ions in the order of Pb$^{2+}$ > Cu$^{2+}$ > Zn$^{2+}$ ≈ Cd$^{2+}$ > Ni$^{2+}$ ≈ Co$^{2+}$, but at varying removal capacity.

Among these heavy metal ions, Cu$^{2+}$ and Pb$^{2+}$ ions demonstrated much higher preferential removal over other metal ions from water. In addition, no significant difference was observed for the removal of heavy metal ions by biochar in either nitrate or chloride system, except for Org-DF-BC and DF-BC. DF-BC displayed the higher removal in nitrate system than that in chloride system, while Org-DF-BC released the heavy metal ions of Zn$^{2+}$, Cd$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ to solution. Furthermore, three douglas fir derived biochars showed similar removal efficiency, but three dairy manure derived biochars displayed different removal effectiveness, in which DM-BC and DM-BC-CV achieved a higher removal capacity. This inconsistent performance of dairy manure derived biochars may be attributed to the distinct sources of dairy manure.
Figure 4.1. Removal of mixed metal ions of Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, Pb\textsuperscript{2+} and Zn\textsuperscript{2+} (each at 1.0 mM) after 24 hours in a chloride (10 mM NaCl) or nitrate (10 mM NaNO\textsubscript{3}) system. The pH was stable at 5.8 ± 0.2. A 100% removal would be equivalent to the amount of sorption of 33.6 mg kg\textsuperscript{-1} for Cd\textsuperscript{2+}, 17.68 mg kg\textsuperscript{-1} for Co\textsuperscript{2+}, 19.06 mg kg\textsuperscript{-1} for Cu\textsuperscript{2+}, 20.61 mg kg\textsuperscript{-1} for Ni\textsuperscript{2+}, 62.16 mg kg\textsuperscript{-1} for Pb\textsuperscript{2+}, and 19.61 mg kg\textsuperscript{-1} for Zn\textsuperscript{2+}.

Taken all into consideration, biochars DF-BC and DM-BC were used to further examine the immobilization of mixed three metal ions of Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Zn\textsuperscript{2+} for the rest of this study, since Pb\textsuperscript{3+}, Zn\textsuperscript{2+} and Cd\textsuperscript{2+} represent the high, intermediate and low affinity onto six biochars. In addition, metal ions of Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Zn\textsuperscript{2+} are in the top five most commonly found metals in contaminated groundwater and soil (Liu et al., 2018; Evanko and Dzombak, 1997;), which are known to pose significant risks to public health and ecological safety (U.S. EPA, 2018; U.S. EPA, 2019).
Similar phenomena were observed for the removal of mixed three metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) from water by both DF-BC and DM-BC. Results confirmed the competitive metal removal in the order of Pb\(^{2+}\) >> Zn\(^{2+}\) > Cd\(^{2+}\) in both chloride and nitrate systems (Figure 4.2). Compared with DF-BC, DM-BC achieved similar removal percentage for Pb\(^{2+}\), but much higher removal efficiency for Zn\(^{2+}\) and Cd\(^{2+}\).

**Figure 4.2.** Removal of mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) (each at 1.0 mM) after 24 hours in a chloride (10 mM NaCl) or nitrate (10 mM NaNO\(_3\)) system. The pH was stable at 5.8 ± 0.2. A 100% removal would be equivalent to the amount of sorption of 33.6 mg kg\(^{-1}\) for Cd\(^{2+}\), 62.16 mg kg\(^{-1}\) for Pb\(^{2+}\), and 19.61 mg kg\(^{-1}\) for Zn\(^{2+}\).
The observed preferential removal of Pb\(^{2+}\) ions over Zn\(^{2+}\) and Cd\(^{2+}\) ions on the biochars in this study is consistent with previous studies using biochar and other sorbents (Ding et al., 2016; Pagnanelli et al., 2003; Reddad et al., 2002; Park et al., 2016). The selective removal is attributable to the physicochemical properties of Pb\(^{2+}\) ions, such as a smaller hydrated radius, a higher electronegativity and a lower higher hydrolysis constant (pKH). Especially, the higher pKH (7.71) of Pb\(^{2+}\) ion than that of Zn\(^{2+}\) ion (10.1) and Cd\(^{2+}\) ion (9.0) lowers the degree of solvation of Pb\(^{2+}\) ion, allowing Pb\(^{2+}\) ion to better approach to the sorbent surface (Park et al., 2016). In addition, Pb\(^{2+}\) ion has a greater affinity for organic functional groups such as carboxylic and phenolic groups because Pb\(^{2+}\) ion as a hard Lewis base (2.33) is more electronegative than Zn\(^{2+}\) ion (1.65) and Cd\(^{2+}\) ion (1.69) as a soft Lewis base (Park et al., 2016). Therefore, Pb\(^{2+}\) ion is more favorably removed through inner sphere sorption and surface complexation than Cd\(^{2+}\) and Zn\(^{2+}\) on biochars.

4.3.1.2 Factors controlling the immobilization of heavy metal ions on biochar

The surface characteristics of biochar and the solution chemistry play the decisive roles in the influencing the competitive removal of these metal ions from aqueous solutions.

**Surface area**

Surface area is an important factor in affecting the removal capacity of metal ions onto biochar, as higher surface area creates more available binding sites on the surface of biochar. The physiochemical characteristics including specific surface area (SSA),
particle size, pH, and point of zero charge ($\text{pH}_{\text{PZC}}$) were determined for two biochars and summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Biochar sample</th>
<th>DF-BC</th>
<th>DM-BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA ($\text{m}^2 \text{ g}^{-1}$)</td>
<td>$493.6 \pm 2.6$</td>
<td>$158.6 \pm 2.7$</td>
</tr>
<tr>
<td>Size (mm)</td>
<td>$\leq 2$</td>
<td>$\leq 2$</td>
</tr>
<tr>
<td>pH (DI water)</td>
<td>$9.6 \pm 0.03$</td>
<td>$10.4 \pm 0.14$</td>
</tr>
<tr>
<td>pH (10 mM NaCl)</td>
<td>$9.5 \pm 0.11$</td>
<td>$9.9 \pm 0.0$</td>
</tr>
<tr>
<td>pH$_{\text{PZC}}$</td>
<td>10</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Both DF-BC and DM-BC had a surface area greater than 100 $\text{m}^2 \text{ g}^{-1}$, but the value of DF-BC is 3 times higher than that of DM-BC. Therefore, it is expected that DF-BC should demonstrate much higher removal efficiency of metal ions than DM-BC. However, the opposite result was observed that DM-BC had higher removal capacity on a basis of surface area for $\text{Cd}^{2+}$, $\text{Pb}^{2+}$ and $\text{Zn}^{2+}$ ions in a mixed metal system (Tables 4.3), suggesting that surface area is not the primary factor controlling the removal of mixed metal ions. Thus, it is imperative to examine other factors influencing the removal of three mixed metal ions by these two biochars.
**Table 4.3.** Comparing mass per mass and mass per SSA basis for removal of mixed metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ (each at 1.0 mM) after 24 hours in a chloride (10 mM NaCl) or nitrate (10 mM NaNO$_3$) system$^\text{v}$.

<table>
<thead>
<tr>
<th>Metals</th>
<th>DF-BC Removal</th>
<th>DM-BC Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg g$^{-1}$</td>
<td>(mg m$^{-2}$)</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>0.4</td>
<td>0.001</td>
</tr>
<tr>
<td>Cd(NO$_3$)$_2$</td>
<td>2.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Pb(NO$_3$)$_2$*</td>
<td>36.8</td>
<td>0.11</td>
</tr>
<tr>
<td>Pb (NO$_3$)$_2$</td>
<td>39.1</td>
<td>0.11</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>0.2</td>
<td>0.001</td>
</tr>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>1.3</td>
<td>0.001</td>
</tr>
</tbody>
</table>

$^*$: Pb(NO$_3$)$_2$ was used due to insolubility of PbCl$_2$

$^\text{v}$: The pH was stable at 5.8 ± 0.2.

**Influences of solution pH**

Solution pH is another factor in significantly controlling the immobilization of metal ions on biochar, since the solution pH could remarkably alter the surface charge of biochar, the species of metal ions and the precipitation of metal hydroxides. To understand these effects on the competitive removal of mixed metal ions from water, batch experiments were performed with the solution pH adjusted in the range of 3 to 10 at 1-unit increment. Figure 4.3 clearly demonstrated that the metal removal efficacy by both DF-BC and DM-BC increased with the increasing pH up to 10 regardless of chloride or nitrate system, except for Zn$^{2+}$ ion removal. The removal of metal ions followed the preferential order of Pb$^{2+}$ >> Zn$^{2+}$ > Cd$^{2+}$, which is consistent with previous observations and literature reports (Park et al., 2016; Xu et al., 2013).

The increased solution pH can decrease the cation H$^+$ concentration on the surface, alleviating the competition for the surface sorption sites and electrostatic
repulsion for positively charged metal ions on biochar. It has been reported that cation 
H$^+$ competes with the divalent metal cations and further prevents their sorption (Chen et 
al., 2015). Additionally, as the solution pH increased, the surface charges changed. It 
has been reported that the pH$_{PZC}$ can range from 2 to 10 for both douglas fir and dairy 
manure derived biochars, depending on the pyrolysis conditions (Karunanayake et al., 
2017; Dewage et al., 2018; Suliman et al., 2016; Gogri, 2017).

In this study, the pH$_{PZC}$ values for DF-BC and DM-BC were determined at 10 and 
10.5, respectively. At a solution pH much below the pH$_{PZC}$, the surface of the biochar is 
positively charged, and the metal cations are repelled. While the solution pH increased 
up to 10, surface charges of biochar changed from mostly positive to near neutral, 
alleviating the repulsion and enhancing the sorption of metal cations.

Moreover, previous studies showed that the solution pH could dramatically affect 
the species of metal ions and solubility of metal hydroxides but vary by different metal 
hydroxides (Pagnanelli et al., 2000; Sheng et al., 2004). Therefore, the mechanism and 
controlling factors varied and influenced each metal removal differently in the mixed 
system (Figure 4.3). As for the removal behavior of Pb$^{2+}$ ion, there was no significant 
difference for DF-BC and DM-BC in both chloride and nitrate systems. When the 
solution pH was below 7, the removal efficiency of Pb$^{2+}$ ion increased up to 100% with 
the increase of pH, and then became consistent with the continuous increase of pH. The 
Pb ions occur dominantly as positively charged Pb$^{2+}$ and/or Pb(OH)$^+$ when the solution 
pH is lower than 5, but the Pb(OH)$_2$ precipitate increases with increasing pH and 
becomes prevalent in a pH range of 6-10 (Sočo and Kalembkiewicz, 2016; Sheng et al., 
2004; Lodeiro et al., 2006).
In this case, the removal of Pb\(^{2+}\) ion is most likely due to surface sorption onto biochar at pH below 7, since increased pH decreases H\(^+\) concentration and the repulsion to positively charged metal cations. When the solution pH continues to increase above 7, the Pb\(^{2+}\) ions start to precipitate as Pb(OH)\(_2\).

By comparison, the removal of Zn\(^{2+}\) ion occurred when the solution pH was 6 and higher in both chloride and nitrate systems but behaved differently for DF-BC and DM-BC. The removal efficiency of Zn\(^{2+}\) on DF-BC reached maximum of 100% at pH 8.5 and stayed consistent thereafter. However, the removal of Zn\(^{2+}\) by DM-BC achieved maximum of 70% around pH 7.5, but dramatically decreased to zero with the increase of pH. The enhanced removal efficacy relied on the combined effects: increase of solution pH from 6 to 8 decreased H\(^+\) concentration and subsequent surface positive charges that minimize the electrostatic repulsion and promoted the formation of Zn(OH)\(_2\) precipitate on biochar. Zn ions present predominantly as Zn\(^{2+}\) and Zn(OH)\(^+\) when the solution pH is lower than 5, but the Zn(OH)\(_2\) precipitates start and increase with pH up to 7 (Bénézeth et al., 2002).

However, the continuous increase of pH decreases the formation of Zn(OH)\(_2\) precipitates but increase the redissolution of Zn ions in form the soluble complex Zn(OH)\(_3\)\(^-\) (Bénézeth et al., 2002). Interestingly, the re-dissolution of Zn(OH)\(_2\) precipitate did not happen with DF-BC, which might be due to the strong interactions between Zn\(^{2+}\) ions and surface functional groups. In the case of Cd\(^{2+}\) ions the removal showed similar pattern as Zn\(^{2+}\) ions on DF-BC in both chloride and nitrate system, except that the maximum removal occurred at pH 10.
As for DM-BC, no removal of Cd\(^{2+}\) ions were observed in the chloride system, while the removal of Cd\(^{2+}\) ions started at pH 8 and reached plateau at pH 10 in the nitrate system. The Cd ions exist primarily as positively charged Cd\(^{2+}\) and/or Cd(OH\(^{+}\) when the solution pH is lower than 6.5, but the Cd(OH\(_2\)) becomes dominant with pH increasing from 7 to 10 (Smičiklas et al., 2000; Sočo et al., 2016; Lodeiro et al., 2006). In summary, the immobilization of metal ions on biochar was a result of combined mechanisms of surface sorption and precipitation.

![Figure 4.3](image-url)

Figure 4.3. Effects of solution pH on the competitive removal of mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\) (1.0 mM each) in a chloride (10 mM NaCl) or nitrate (10 mM NaNO\(_3\)) system. The solution pH was adjusted from 3 to 10 at 1-unit increment.
4.3.2  Effect of surface functional groups

4.3.2.1 DRIFTS

As indicated by DRIFTS analysis (Figure 4.4), the functional groups on the surface of DF-BC and DM-BC include carboxylate (-COO\(^-\), 1590-1520 cm\(^{-1}\)), aldehydes (-COH, 1260 cm\(^{-1}\)), carbonate/calcite (CO\(_3^{2-}\), 1430 cm\(^{-1}\)), phenolic (-OH, 1390-1310 cm\(^{-1}\)), aliphatic (-CH\(_3\), -CH\(_2\), 2990-2840 cm\(^{-1}\)), and clay minerals (v(Si-O, 1030 cm\(^{-1}\)). Specifically, the DF-BC shows strong presence of CO\(_3^{2-}\), -COO\(^-\), -OH, -COH, -CH\(_3\) and -C(H\(_2\)), whereas, the DM-BC contains primarily -OH and v(Si-O). These functional groups are commonly found on the surface of biochar (Azargohar et al., 2014; Sing et al., 2017; Filley et al., 2008).

Several studies reported that oxygen containing functional groups on the surface of biochars increase the interactions with metal cations like Pb\(^{2+}\) and Zn\(^{2+}\) and can directly or indirectly affect the adsorption mechanisms such as electrostatic interaction, surface complexation, ion exchange, physical adsorption and precipitation, aiding in metal removal from aqueous solutions (Yang et al., 2019; Ricordel et al., 2001; Ho, 2003; Bhattacharyya and Sharma, 2004; Mohan et al., 2007). Mohan et al. (2007) reported that functional groups (C=O, C-O, -OH) on partially aromatized oak biochars provided negatively charged surfaces, contributing to metal removal.

Additionally, it has been suggested that oxygen containing functional groups (e.g. -COOH, -OH, -COH) can sorb metals such as Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) through the surface complexation (El-Hendawy, 2009). Moreover, the dissociation of carboxylic groups (-
COOH) can facilitate and/or increase Pb\(^{2+}\) or Cd\(^{2+}\) deposition on biochar surface (El-Hendawy, 2009).

Surface mineral functional groups on both biochar, such as calcite and clay, could also influence the removal of metal ions from aqueous solution (Gu et al., 2019; Uddin, 2017; Vhahangwele et al., 2015). Due to the higher affinity of Pb\(^{2+}\) ions over Ca\(^{2+}\) ions, Pb\(^{2+}\) ions can replace the Ca\(^{2+}\) ions from the calcite and form a surface binding with CO\(_3^{2-}\) and enhance the removal of Pb\(^{2+}\) (Yuan et al., 2018; Golditsas et al., 2003). Additionally, the functional group SiOH on clay minerals was found to be a sorption site for Cd\(^{2+}\) removal (Rao and Kashifuddin, 2016), when the clay was heat treated between 300 and 600 °C due to the dissociation of surface hydroxyl groups (Waseem et al., 2011).

It has been reported that precipitation of Pb-containing minerals existed in the form of cerussite and hydrocerussite on dairy manure and anaerobically digested sugarcane bagasse derived bicochars (Inayng et al., 2011; Cao et al., 2009), which highly depended on both high pH and surface functional groups. As the pH increased, cerussite precipitates formed to pH 8.5, and then hydrocerussite precipitates occurred with increase of pH from 8.5 to 10 (Davis et al., 2018). The peak shifts in the biochar at equilibrium compared to the pristine DF-BC and DM-BC indicate that the functional groups OH, CO\(_3^{2-}\) and v(Si-O), may be playing a role in metal removal.
Figure 4.4. DRIFTS analysis of pristine and metal sorbed biochars. DF-BC with removal of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) ions at 14.5, 29.3, 14.0 mg/g respectively, and DM-BC with removal of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) ions at 12.4, 28.9, 11.4 mg/g respectively. Samples incubated at room temperature over 24 ours at pH 7.
4.3.2.2 XRD

Furthermore, XRD analysis was performed to examine the mineralogical composition on both DF-BC and DM-BC (Figures 4.5 and 4.6). The XRD pattern shows that pristine DF-BC is amorphous without any distinct crystallinity. Once metal ions were immobilized on DF-BC, Cd and Pb dominantly exist as carbonate forms such as otavite (CdCO$_3$) and hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$). XRD analysis displays the distinct quartz, calcite and graphite patterns on pristine DM-BC. Although XRD data do not indicate the formation of crystallized phases of zinc, such as wuelfingite (Zn(OH)$_2$) and smithsonite (ZnCO$_3$), due to the low surface load of Zn (~1.4 wt %), the formation of their amorphous counterparts could not be excluded (Qian et al., 2016). By comparison, the metal retained on DM-BC predominantly formed carbonate minerals, including otavite (CdCO$_3$), cerussite (PbCO$_3$), hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$), and smithsonite (ZnCO$_3$).
Figure 4.5. X-ray diffractograms of pristine DF-BC and metal loaded DF-BC. Single metal ion of Cd$^{2+}$, Pb$^{2+}$ or Zn$^{2+}$ at initial concentration of 96 mg L$^{-1}$ was sorbed onto 100 mg of DF-BC in 10 mM NaCl. The pH was controlled at 7. Metal sorption capacity was 14.5 ± 0.1, 29.3 ± 0.2 and 14.0 ± 0.2 mg/g for Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ ions respectively.
Figure 4.6. X-ray diffractograms of pristine DM-BC and metal loaded DM-BC. Single metal ion of Cd\textsuperscript{2+}, Pb\textsuperscript{2+} or Zn\textsuperscript{2+} at initial concentration of 96 mg L\textsuperscript{-1} was sorbed onto 100 mg of DM-BC7 in 10 mM NaCl. The pH was controlled at 7. Metal sorption capacity was 12.4 ± 0.03, 28.9 ± 0.1 and 11.4 ± 0.7 mg/g for Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Zn\textsuperscript{2+} ions respectively.
These mineralogical characterizations provide consistent evidences as indicated from DRIFTS that surface complexation and/or precipitation of metal carbonate and/or hydroxides play important role in controlling the removal of metal ions from aqueous solution by biochar.

4.3.3 Removal kinetics

Figure 4.7 shows the removal kinetics of mixed metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ by DF-BC and DM-BC in both chloride and nitrate systems. The solution pH buffered naturally and was stable at 5.8 for the duration of the experiment. The results showed that there was no removal difference observed between chloride and nitrate system. DF-BC only removed Pb$^{2+}$ ions efficiently in both chloride and nitrate system, respectively, in which the removal capacity increased dramatically within 2 hours to reach 36.7 and 36.4 mg Pb$^{2+}$/g biochar (~60% in removal percentage), and continued to increase to 52.9 and 53.9 mg Pb$^{2+}$/g biochar (84-86%) at 24 hours, achieving the maximum removal capacity at 58.8 and 57.1 mg Pb$^{2+}$/g biochar (93%) at 168 hours.

In contrast, negligible removal of Cd$^{2+}$ and Zn$^{2+}$ ions by DF-BC was observed. These results are consistent with previous discussion on the effect of solution pH, in which solution pH below 6 remarkably prevent the removal of Cd$^{2+}$ and Zn$^{2+}$ ions by biochar. On the other hand, DM-BC demonstrated much better removal capacity for the mixed metal ions, especially for Cd$^{2+}$ and Zn$^{2+}$ ions. The removal of Pb ions increased quickly and achieved the removal capacity at 59.5 and 55.7 mg Pb$^{2+}$/g biochar (>95%) at 24 hours, and slowly increased to maximum removal capacity at 62.0 mg Pb$^{2+}$/g biochar (99.5%) at 168 hours. DM-BC demonstrated a gradually increased removal of Cd$^{2+}$ and
Zn$^{2+}$ ions, reaching the highest removal capacity at 8.7 mg/g biochar (26%) and 9.9 mg/g biochar (50%) at 168 hours.

Figure 4.7. Removal kinetics of mixed metal ions of Cd$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$ (1.0 mM each) at pH 5.8 in chloride (10 mM NaCl) or nitrate (10 mM NaNO$_3$) systems.

The experimental data were fitted with commonly used removal kinetic models including pseudo first order (PFO, Equation 4.2) model (Lagergren, 1898), pseudo second order (PSO, Equation 4.3) model (Ho and McKay, 1999), and intraparticle
diffusion model (IDM, Equation 4.4), and the model parameters are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Plot</th>
<th>Model</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_t = q_e (1 - e^{-k_1 t}) ) ( (4.2) )</td>
<td>( \log(q_e - q_t) ) vs. ( t )</td>
<td>Pseudo First Order</td>
<td>( q_t = ) metal sorbed at time ( (t) ) ( q_e = ) metal sorbed at equilibrium ( k_1 = ) slope ( (h^{-1}) )</td>
</tr>
<tr>
<td>( q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} ) ( (4.3) )</td>
<td>( t ) vs. ( q_t )</td>
<td>Pseudo Second Order</td>
<td>( q_e = ) metal sorbed at equilibrium ( k_2 = ) slope ( 2/y)-int ( (g/mg \text{ h}) ) ( q_t = ) metal sorbed at time ( (t) )</td>
</tr>
<tr>
<td>( q_t = k_i t^{1/2} ) ( (4.4) )</td>
<td>( q_t ) vs. ( t^{1/2} )</td>
<td>Intraparticle Diffusion</td>
<td>( t = ) time ( (hours) ) ( k_i = ) slope ( (g/mg \text{ h}^{1/2}) )</td>
</tr>
</tbody>
</table>

In summary, the PSO model best describe the removal kinetics of mixed metal ions of \( \text{Cd}^{2+} \), \( \text{Pb}^{2+} \) and \( \text{Zn}^{2+} \) onto both DF-BC and DM-BC, indicating that chemisorption is the rate limiting mechanism for the retention of \( \text{Cd}^{2+} \), \( \text{Pb}^{2+} \) and \( \text{Zn}^{2+} \) ions on both biochars (Inyang et al., 2016; Momčilović et al., 2011). Although PFO model for DM-BC when removing \( \text{Cd}^{2+} \) and \( \text{Zn}^{2+} \) ions showed the \( R^2 \) values above 0.85, these values were not considered a reliable prediction due the high uncertainty reflected in the standard deviation.
The IDM integration by plotting $q_t$ vs $t^{0.5}$ showed multilinear removal behaviors, which describe the three steps for the removal of metal ions by biochars. The first step reflects the instantaneous retention of metal ions on external surface of biochar and the second step represents the gradual retention of metal ions on biochar, which both take place very fast (Wu et al., 2001; Cheung et al., 2007). These two steps could not be distinguished due to the fast removal in this study. The third step reaches the final equilibrium stage, where the intra-particle diffusion slows due to the low metal ions concentration in solution.

Two different rate constants, $k_{i1}$ (first and second steps) and $k_{i2}$ (third step) were calculated with $R^2$ values in the range of 0.858-0.979 for DF-BC (Pb$^{2+}$ ions removal only) and 0.858-0.979 for DM-BC (Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ ions removal), which are like the findings reported by Galnaz et al. (2005) and Kusveran et al. (2012). Model parameters for PFO, PSO and IDM are found in Table 4.5.
Table 4.5. Parameters of the Pseudo First Order, Pseudo Second Order and Intraparticle Diffusion models for the Removal of Mixed Metal Ions at pH 5.8

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Metal</th>
<th>Pseudo First Order</th>
<th>Pseudo Second Order</th>
<th>Intraparticle Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (h$^{-1}$)</td>
<td>$q_{(\text{calc})}$ (mg g$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF-BC</td>
<td>Cd$^{2+}$ (Cl$^-$)</td>
<td>-5.3E$^{-3}$ ± 7.6E$^{-3}$</td>
<td>-0.068</td>
<td>-0.349</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$ (NO$_3^-$)</td>
<td>6.4E$^{-3}$ ± 9.3E$^{-3}$</td>
<td>-0.789</td>
<td>-0.118</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$ (Cl$^-$)</td>
<td>1.5E$^{-3}$ ± 3.4E$^{-3}$</td>
<td>2.72</td>
<td>0.775</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$ (NO$_3^-$)</td>
<td>0.03 ± 0.01</td>
<td>3.01</td>
<td>0.717</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$ (Cl$^-$)</td>
<td>-1.5E$^{-3}$ ± 0.01</td>
<td>-1.58</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$ (NO$_3^-$)</td>
<td>2.2E$^{-3}$ ± 1.1E$^{-3}$</td>
<td>-1.20</td>
<td>-0.237</td>
</tr>
<tr>
<td>DM-BC</td>
<td>Cd$^{2+}$ (Cl$^-$)</td>
<td>0.02 ± 1.8E$^{-3}$</td>
<td>1.47</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$ (NO$_3^-$)</td>
<td>0.03 ± 5.0E$^{-3}$</td>
<td>1.26</td>
<td>0.856</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$ (Cl$^-$)</td>
<td>0.03 ± 1.1E$^{-3}$</td>
<td>2.97</td>
<td>0.660</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$ (NO$_3^-$)</td>
<td>0.03 ± 8.0E$^{-3}$</td>
<td>3.01</td>
<td>0.717</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$ (Cl$^-$)</td>
<td>0.01 ± 1.0E$^{-3}$</td>
<td>1.89</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$ (NO$_3^-$)</td>
<td>0.01 ± 1.7E$^{-3}$</td>
<td>1.89</td>
<td>0.847</td>
</tr>
</tbody>
</table>
Through the literature review, the DF-BC and DM-BC showed similar, and in some cases the better, kinetic model fit, and removal performance compared with other biochars (Table 4.6). The results further support that both DF-BC and DM-BC have the promising potential to efficiently remove heavy metal ions in multi metal systems from water. However, most literatures based on the single metal system, since very few studies used the PFO and PSO models in mixed metal systems. Therefore, it is pressing to bring the attention that future research needs focus on studying the removal kinetics in mixed metal systems.
<table>
<thead>
<tr>
<th>Biomass type (temperature [°C])</th>
<th>Metal</th>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>$R^2$</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Straw (600)</td>
<td>Cd$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (min$^{-1}$) = 0.027</td>
<td>$q_{e1}$ (mg g$^{-1}$) = 25.87</td>
<td>0.969</td>
<td>4-6</td>
<td>Zhou et al., 2018</td>
</tr>
<tr>
<td>Modified Corn Straw (600)</td>
<td>Cd$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$) = 2.04E$^{-3}$</td>
<td>$q_{e2}$ (mg g$^{-1}$) = 26.32</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corn Straw (600)</td>
<td>Cd$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (min$^{-1}$) = 0.019</td>
<td>$q_{e1}$ (mg g$^{-1}$) = 94.06</td>
<td>0.968</td>
<td>4-6</td>
<td></td>
</tr>
<tr>
<td>Activated Sludge (80)</td>
<td>Cd$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$) = 3.47E$^{-4}$</td>
<td>$q_{e2}$ (mg g$^{-1}$) = 100.0</td>
<td>0.998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Hyacinths (450)</td>
<td>Pb$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (min$^{-1}$) = 0.062</td>
<td>$q_{e1}$ (mmol g$^{-1}$) = 0.167</td>
<td>0.987</td>
<td>6</td>
<td>Kusvuran et al., 2012</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (min$^{-1}$) = 0.762</td>
<td>$q_{e2}$ (mmol g$^{-1}$) = 0.167</td>
<td>0.993</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>IDM</td>
<td>$k_{i1}$ (mmol g min$^{-1}$) = 28.7E$^{-3}$</td>
<td>$k_{i2}$ (mmol g min$^{-1}$) = 2.3E$^{-3}$</td>
<td>0.989 ($k_{i1}$), 0.992 ($k_{i2}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Hyacinths (450)</td>
<td>Zn$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (h$^{-1}$) = 0.130</td>
<td>$q_{e1}$ (mmol g$^{-1}$) = 0.155</td>
<td>0.960</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Hardwood (450)</td>
<td>Zn$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (g mg$^{-1}$ h$^{-1}$) = 0.066</td>
<td>$q_{e2}$ (mmol g$^{-1}$) = 0.155</td>
<td>0.996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut Shell (500)</td>
<td>Pb$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (h$^{-1}$) = 0.141</td>
<td>$q_{e1}$ (mmol g$^{-1}$) = 2.63</td>
<td>0.921</td>
<td>5</td>
<td>Chen et al., 2011</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (g mg$^{-1}$ h$^{-1}$) = 0.099</td>
<td>$q_{e2}$ (mmol g$^{-1}$) = 3.14</td>
<td>0.988</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canna indica (500)</td>
<td>Cd$^{2+}$</td>
<td>PFO</td>
<td>$k_1$ (h$^{-1}$) = 27.6</td>
<td>$q_{e1}$ (mg g$^{-1}$) = 98.09</td>
<td>0.994</td>
<td>5</td>
<td>Wang et al, 2015</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>PSO</td>
<td>$k_2$ (g mg$^{-1}$ h$^{-1}$) = 1.57</td>
<td>$q_{e2}$ (mg g$^{-1}$) = 98.52</td>
<td>0.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>IDM</td>
<td>$k_{i1}$ (g/mg hr$^{0.5}$) = 5.09</td>
<td>/</td>
<td>0.884</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.4 Sorption isotherms

In this study, batch experiments were conducted to illustrate the sorption isotherm for each individual metal ion on DF-BC and DM-BC, respectively. The experimental data were modeled to fit in the Langmuir, Freundlich, and Redlich-Peterson isotherm equations, except for the removal of Pb$^{2+}$ ions because of 100% removal observed for the tested concentrations, representing the environmental relevant range of 6 to 96 mg L$^{-1}$ and higher concentrations (192 and 768 mg L$^{-1}$). Figure 4.8 shows the Langmuir, Freundlich, and Redlich-Peterson isotherm model fitting for Cd$^{2+}$ and Zn$^{2+}$ ions (6 to 768 mg L$^{-1}$) using DF-BC and DM-BC. As for the sorption of Cd$^{2+}$ and Zn$^{2+}$ ions on DF-BC, the $R^2$ values show the best fit to Langmuir isotherm (0.921) for Cd$^{2+}$ ions and Freundlich isotherm (0.994) for Zn$^{2+}$ ions.

These isotherms indicate that the sorption of Cd$^{2+}$ ions occurs as monolayer coverage on a structurally homogenous surface of DF-BC, while the sorption of Zn$^{2+}$ ions is multilayered on a structurally heterogeneous surface of DF-BC. On the other hand, as for the sorption of Cd$^{2+}$ and Zn$^{2+}$ ions on DM-BC, the $R^2$ values reflect the best fit to Redlich-Peterson isotherm (0.992) for Cd$^{2+}$ ions and Langmuir isotherm (0.939) for Zn$^{2+}$ ions. The $\beta$ value (0.7) of Redlich-Peterson model was lower than the unity, suggesting that the Cd$^{2+}$ ions had not reached maximum coverage onto both homogenous and heterogeneous surface of DM-BC. Whereas, the Langmuir isotherm suggests that sorption of Zn$^{2+}$ ions forms monolayer on a homogenous surface of DM-BC. These differences might be due to the multiple removal mechanism of metals ions on biochar as discussed in previous section, including physical sorption, electrostatic attraction, surface complexation and precipitation.
Figure 4.8. Single metal ion sorption isotherms using metal concentrations ranging from 6 to 768 mg L\(^{-1}\) over 24 hours. The solution pH was controlled at 7.
Furthermore, the experimental data were also examined for isotherm model parameters only at environmentally relevant concentrations in the range of 6 to 96 mg L\(^{-1}\) (Figure 4.9 and Table 4.7). No significant difference was observed between the high concentration, and environmentally relevant isotherms, suggesting the concentration of metal ions are not an influencing factor in this study. Regarding the sorption of Cd\(^{2+}\) and Zn\(^{2+}\) ions on DF-BC, the best-described isotherm is the Langmuir isotherm model for Cd\(^{2+}\) ions, while the sorption of Zn\(^{2+}\) ions fits equally well to all three isotherm models. By comparison, the Redlich-Peterson model best represents the sorption isotherm of Cd\(^{2+}\) ions on DM-BC, whereas, the sorption of Zn\(^{2+}\) ions best fits in Langmuir isotherm, but with \(R^2\) value only 0.84. Thus, the multiple active sites on the heterogeneous surface of DF-BC and DM-BC demonstrate different affinities for the sorption of Cd\(^{2+}\) and Zn\(^{2+}\) ions.
Figure 4.9. Single metal ion sorption isotherms using metal concentrations ranging from 6 to 96 mg L$^{-1}$ over 24 hours. The solution pH was controlled at 7.
Table 4.7. Model parameters of Freundlich, Langmuir and Redlich–Peterson isotherms for the sorption Cd$^{2+}$ and Zn$^{2+}$ in single metal system

<table>
<thead>
<tr>
<th>Material</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Redlich–Peterson</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_F$</td>
<td>$n$</td>
<td>$R^2$</td>
<td>$K_L$</td>
</tr>
<tr>
<td></td>
<td>[(mg g$^{-1}$) (mg L$^{-1}$)$^{1/n}$]</td>
<td>(L mg$^{-1}$)</td>
<td>(mg g$^{-1}$)</td>
<td>(L mg$^{-1}$)</td>
</tr>
<tr>
<td>DF-BC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>2.0 ± 0.2</td>
<td>2.0 ± 0.2</td>
<td>0.856</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.0 ± 0.1</td>
<td>1.9 ± 0.1</td>
<td>0.994</td>
<td>0.17 ± 0.0</td>
</tr>
<tr>
<td>DM-BC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>1.8 ± 0.3</td>
<td>2.2 ± 0.1</td>
<td>0.977</td>
<td>0.03 ± 0.0</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>5.1 ± 0.2</td>
<td>2.9 ± 0.2</td>
<td>0.924</td>
<td>0.17 ± 0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF-BC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>1.8 ± 0.3</td>
<td>1.8 ± 0.2</td>
<td>0.871</td>
<td>0.1 ± 0.02</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.0 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>0.995</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>DM-BC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>1.5 ± 0.4</td>
<td>1.7 ± 0.3</td>
<td>0.831</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.1 ± 0.2</td>
<td>1.7 ± 0.3</td>
<td>0.771</td>
<td>0.07 ± 0.03</td>
</tr>
</tbody>
</table>

(Concentrations in the range of 6 to 768 mg L$^{-1}$)

(Concentrations in the range of 6 to 96 mg L$^{-1}$)
The sorption isotherms from this study were compared to those from literatures including both single metal system (Table 4.8) and mixed metals system (Table 4.9). No consistent conclusions achieved for the best fitting of isotherm models and calculated removal capacity for Cd\(^{2+}\), Zn\(^{2+}\) and Pb\(^{2+}\) ions, which is mainly due to the unique physicochemical characteristics of biochar made from various feedstock under different pyrolysis conditions. Koldynska et al. (2012) found that overall the Langmuir isotherm fitted the best for the sorption of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) ions on pig manure and dairy manure derived biochars, suggesting monolayer sorption on a finite number of identical sites.

However, the Freundlich isotherm showed the best fits for the sorption of Pb\(^{2+}\) ions by biochar made from peanut hull and medicine residue (Wang et al., 2015), Rice husk (Lui and Zhang, 2009) and Oak Wood (Mohan et al., 2007), indicating heterogenous sorption affinity. Whereas, the Langmuir isotherm well described the sorption of Pb\(^{2+}\) ions on biochar made from pinewood (Lui and Zhang, 2009) and pine bark (Mohan et al., 2007). In addition, Cui et al. (2016) showed that the Langmuir model described the removal of Cd\(^{2+}\) ions by C. indica derived biochar, in which the sorption mechanism was attributed to precipitation, ion exchange, complexation with functional groups and coordination with π electrons.

Finally, the removal of Zn\(^{2+}\) ions using corn straw and hardwood derived biochars demonstrated the best fit for the Langmuir isotherm (Chen et al., 2011), which is consistent with our results for the isotherms of individual metal ion of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) (6 to 96 mg L\(^{-1}\)). Moreover, DF-BC and DM-BC showed similar or higher model calculated sorption capacity (\(q_{\text{max}}\)) than those from many of the reported biochars,
including corn straw, rice husk, and pine wood. Similar phenomena were observed for the removal of mixed metal ions, although much less studies are available in the literature, which guarantees further research in this area.
<table>
<thead>
<tr>
<th>Biochar type (temperature [°C])</th>
<th>Metal</th>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>$R^2$</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canna indica (600)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 140</td>
<td>$K_L$ (1 mg$^{-1}$) = 1.03</td>
<td>0.876</td>
<td>5</td>
<td>Lui and Zhang, 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 3.89</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.36</td>
<td>0.98</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lui and Zhang, 2009</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 11.0</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.232</td>
<td>0.998</td>
<td>5</td>
<td>Chen et al., 2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut Hull (400)</td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 49.9</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.59</td>
<td>0.912</td>
<td>5</td>
<td>Wang et al., 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medicine Residue (400)</td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 82.5</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.58</td>
<td>0.932</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canna indica (600)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 58.1</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.006</td>
<td>0.970</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine Bark (400/450)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 0.34</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.0002</td>
<td>0.743</td>
<td>5</td>
<td>Mohan et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 3.0</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.226</td>
<td>0.963</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oak Wood (400/450)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 0.37</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.037</td>
<td>0.575</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg g$^{-1}$) = 2.62</td>
<td>$K_L$ (1 mg$^{-1}$) = 0.163</td>
<td>0.908</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Cd$^{2+}$ = Cadmium, Pb$^{2+}$ = Lead, Zn$^{2+}$ = Zinc, Lui and Zhang, 2009; Mohan et al., 2007; Lui and Zhang, 2009; Cui et al., 2016; Koldynska et al., 2012; Wang et al., 2015; Chen et al., 2011; Wang et al., 2015; Cui et al., 2016.
Table 4.9. Best fit of sorption isotherm model parameters for multi-metals removal using biochar

<table>
<thead>
<tr>
<th>Biochar type (temperature [ºC])</th>
<th>Metal</th>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>$R^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sesame Straw (700)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 5</td>
<td>$K_F$ (mg g$^{-1}$) = 1.2</td>
<td>0.978</td>
<td>Park et al., 2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.232$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 88</td>
<td>$K_F$ (mg g$^{-1}$) = 0.29</td>
<td>0.988</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.684$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 7</td>
<td>$K_F$ (mg g$^{-1}$) = 1.4</td>
<td>0.986</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.279$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 21</td>
<td>$K_F$ (mg g$^{-1}$) = 1.8</td>
<td>0.992</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.495$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 40</td>
<td>$K_F$ (mg g$^{-1}$) = 2.4</td>
<td>0.956</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.5137$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dairy Manure (350)</td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mmol kg$^{-1}$) = 789</td>
<td>$K_F$ (mmol kg$^{-1}$) = 704</td>
<td>0.97</td>
<td>Xu et al., 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$n = 2.48$</td>
<td>$K_L$ (mmol kg$^{-1}$) = 4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mmol kg$^{-1}$) = 297</td>
<td>$K_F$ (mmol kg$^{-1}$) = 203</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$n = 4.09$</td>
<td>$K_L$ (mmol kg$^{-1}$) = 3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>Langmuir</td>
<td>/</td>
<td>/</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>/</td>
<td>/</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice Husk (350)</td>
<td>Pb$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mmol kg$^{-1}$) = 79.9</td>
<td>$K_F$ (mmol kg$^{-1}$) = 14</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mmol kg$^{-1}$) = 27.4</td>
<td>$K_F$ (mmol kg$^{-1}$) = 14</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>Langmuir</td>
<td>/</td>
<td>/</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>/</td>
<td>/</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chicken Bone (600)</td>
<td>Cd$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 53</td>
<td>$K_F$ (mg g$^{-1}$) = 4.39</td>
<td>0.957</td>
<td>Park et al., 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.442$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.039</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 107.5</td>
<td>$K_F$ (mg g$^{-1}$) = 7.87</td>
<td>0.984</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.548$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.069</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$) = 43.9</td>
<td>$K_F$ (mg g$^{-1}$) = 3.82</td>
<td>0.956</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freundlich</td>
<td>$1/n = 0.399$</td>
<td>$K_L$ (mg g$^{-1}$) = 0.026</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

139
4.3.5 SEM-EDS

Figures 4.10 and 4.11 provide the SEM-EDS analysis for the sorption of single metal ion of Cd$^{2+}$, Pb$^{2+}$ or Zn$^{2+}$ on DF-BC and DM-BC respectively from the sorption isotherm experiments (768 mg L$^{-1}$). The SEM images showed that DF-BC has a highly porous and long fiber like surface, which made from the structured cellulose fibers of the douglas fir wood, while DM-BC does not have uniform porous surface. The highly porous surface of DF-BC provides the higher potential for surface sorption and complexation. As shown on the SEM, each metal was immobilized on the surface of DF-BC through both surface sorption/complexation and precipitation in the form of aggregates. Similar patterns could apply for the DM-BC, although the surface sorption/complexation is not clearly shown in the SEM image. In addition, all the intense EDS peaks strongly verify the presence of metal bonded on the surface of biochar.
Figure 4.10. The SEM-EDS analysis for DF-BC on the removal of single metal ions of Cd$^{2+}$ (panel A and B), Pb$^{2+}$ (panel C and D) or Zn$^{2+}$ (panel E and F) at 768 mg L$^{-1}$ in sorption isotherm experiments.
Figure 4.11. The SEM-EDS analysis of DM-BC on the removal of single metal ion of Cd$^{2+}$ (panel A and B), Pb$^{2+}$ (panel C and D) or Zn$^{2+}$ (panel E and F) at 768 mg L$^{-1}$ in sorption isotherm experiments.
4.3.6 Columns

In addition to the batch experiments and solid phase analyses, column studies were carried out to explore the competitive removal and immobilization stability of mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) on DF-BC and DM-BC in a continuous flow through system over three cycles of regeneration and reuse.

4.3.6.1 Biochar control columns

In order to understand the background concentration of metals and other elements from the biochar in a continuous flow through system, control columns filled with pristine DF-BC or DM-BC were operated by flushing with 10.0 mM NaCl over a period of 315 minutes (equal to 7 or 12 pore volumes). In both control columns, no metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) were detected in the effluent during the entire period, nor were detected from the acid wash (2 M HCl) in either biochars. On the other hand, the release of Al\(^{3+}\), Mg\(^{2+}\) and Na\(^{+}\) cations was considerably lower from DF-BC columns than those from DM-BC columns, whereas the release of Ca\(^{2+}\), K\(^{+}\) and Si\(^{4+}\) cations was higher from DF-BC columns than those from DM-BC columns (Figure 4.12).

The release of background cations from DF-BC control columns showed an overall decrease in concentration for Al\(^{3+}\), K\(^{+}\) and Si\(^{4+}\) cations, but concentration remained steady for Na\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\) cations over 315 minutes. By comparison, the release of background cations from DM-BC control columns showed an overall decrease in concentration for Al\(^{3+}\), Na\(^{+}\), Mg\(^{2+}\) and Ca\(^{2+}\) cations, while overall K\(^{+}\) and Si\(^{4+}\) cation concentration remained steady over 315 minutes.
These different patterns are attributed to the selected feedstock pyrolyzed to produce the biochar, since dairy manures commonly contain higher content of minerals than wood biochars, either from feed ingested by the cows or external environments (e.g., barnyard, field or other areas) where the manure is collected (Zhao et al., 2013). The results are consistent with the findings from the solid phase mineralogical characterization, which showed that the variances of mineral composition can influence the surface characteristics and interactions (e.g., complexation, cation exchange) with metal ions on biochar. Biochars have been reported to have high cation exchange capacity (CEC), but vary significantly from 41.9 to 2000 mmol_c/kg (Singh et al., 2017). For instance, wood derived biochars have a CEC ranging from 102 to 690 mmol_c/kg (Mukherjee et al., 2011), while the CECs of dairy manure derived biochar are in the range of 200 to 1490 mmol_c/kg (Sarkhot et al., 2013; Zhao et al., 2013).
Figure 4.12. Release of cations from both pristine DF-BC and DM-BC control columns when flushed with 10 mM NaCl over 315 minutes. The solution pH was allowed to free drift and was stable at 9.6 (±0.09) and 10.5 (±0.08) for the duration of the column with DF-BC and DM-BC, respectively.
4.3.6.2 Competitive removal of mixed metal ions in columns

The competitive removal of mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) on DF-BC and DM-BC is presented in the form of breakthrough curves for these columns over three cycles of immobilization-desorption and regeneration-reuse (Figure 4.13). The results illustrated that both DF-BC and DM-BC effectively retained the mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\), although each biochar displayed different removal behaviors of different metal ions in the column study.
Figure 4.13. Breakthrough curves of mixed metal ions Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ (each at 1 mM) with 10 mM NaCl from DF-BC and DM-BC columns.
Surprisingly, no breakthrough of three metal ions was observed for the DM-BC columns over the three cycles of regeneration and reuse, suggesting all three metal ions were immobilized on the DM-BC inside the columns. The primary causes of the complete removal of metal ions were attributed to the precipitation of metal hydroxides and/or surface complexation with mineral components such as CO$_3^{2-}$ and SiO$_3^{2-}$, since the effluent pH were 10.6, 8.2, and 7.7 at each of three cycles, respectively. As discussed previously, when the solution pH is higher than 7-8, all three metal ions will predominantly form metal hydroxides and/or carbonates and immobilize on the surface of DM-BC. Therefore, no further model analysis was performed for the DM-BC column study.

On the other hand, the metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ from DF-BC columns did show breakthrough behaviors during the cycle #1, the breakthrough points for Cd$^{2+}$ and Zn$^{2+}$ ions from the DF-BC columns occurred at 140 and 180 minutes respectively, reaching the exhaustion points (the plateau of $C_e/C_0$) at 225 and 315 minutes respectively, while Pb$^{2+}$ ions did not break through at all during the operation, suggesting the preferred removal of Pb$^{2+}$ ions over Cd$^{2+}$ and Zn$^{2+}$ ions. This observation is consistent with the findings from batch studies for the preferential removal in the order of Pb$^{2+} >>$ Zn$^{2+} >$ Cd$^{2+}$, which results from the combination of multiple immobilization mechanism simultaneously or in succession as discussed before, including physical sorption, cation exchange, surface complexation and precipitation.

Due to the release of high alkalinity from DF-BC, the effluent pH first increased to 9.59 ($\pm$0.04) and then dropped to 6.19 ($\pm$0.05) over 315-minute operation. As discussed previously, the solution pH higher than 5.5 favors the immobilization of Pb$^{2+}$ ions on DF-BC via precipitation as metal hydroxides, and/or surface complexation with mineral functional groups.
such as $\text{CO}_3^{2-}$ and $\text{SiO}_3^{2-}$, although other removal pathways like cation exchange could happen simultaneously, especially when the solution pH decreased.

The removal of $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ ions demonstrated different behaviors, since $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ ions precipitate as hydroxides only when the solution pH is higher than 6-8 ($\text{Cd}^{2+}$) and 7 ($\text{Zn}^{2+}$). The breakthrough of $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ ions clearly coincided the solution pH change. When the solution pH increased to 9.59 ($\pm$0.04), the removal of $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ ions showed precipitation, like the removal mechanism of $\text{Pb}^{2+}$ ions. However, when the solution pH decreased to below 8 or 7, cation exchange and electrostatic attraction are suggested as the major removal mechanisms for $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$. Thus, the release of exchangeable cations at the pH below 8-7 (e.g., $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$ and $\text{Na}^+$), especially $\text{K}^+$ and $\text{Ca}^{2+}$ ions, is attributed to exchange with $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ on binding sites of DF-BC.

However, the cation exchanges form weaker binding with metal ions than chemical binding, leading to partial breakthrough of the metal ions passing through the columns. The cation exchanges of metal ions with common cations of $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$ and $\text{Na}^+$ vary significantly and consequently influence the removal of different metal ions. For example, higher concentration of $\text{Ca}^{2+}$ in the effluent was observed for the removal of metals from columns than that from control column (Figure 4.14 and 4.12), indicating that the exchangeable $\text{Ca}^{2+}$ can be replaced by metal ions on DF-BC. Previous studies have shown that the removal of $\text{Cd}^{2+}$ can be significantly influenced by the concentration of $\text{Ca}^{2+}$ in solution due to competition between $\text{Ca}^{2+}$ and $\text{Cd}^{2+}$ to occupy the active sites released by dissociation of $\text{Ca}^{2+}$ from the sorbate matrix (Chen et al., 2015). Furthermore, the decrease of soluble $\text{Ca}^{2+}$ in the column suggested less available $\text{Ca}^{2+}$ exchangeable sites on DF-BC, which caused the more soluble metal ions to break through the columns.
Figure 4.14. Concentration of metals and exchangeable cations in the effluent of DF-BC column over three cycles, in which each cycle was operated for 315 minutes.

After the duration of cycle #1, the DF-BC in column was soaked with 2 M HCl overnight and then rinsed with 10.0 mM NaCl continuously for at least 3 pore volumes of the columns, which released the immobilized metals on DF-BC and regenerated the surface-active sites of DF-BC. HCl (2 M) has been reported to be the effective reagent to desorb metals from carbonaceous sorbent materials including activated carbon (Rao et al., 2009; Anirudhan and Sreekumari, 2011) and biochar (Vilvanathan and Shanthakumar, 2018; Kołodyńska et al., 2017). During the operation of cycle #2, all three metal ions broke through at 15 minutes. Cd$^{2+}$ and Zn$^{2+}$ ions followed a nearly identical breakthrough curve, reaching the exhaustion points at 90 minutes. However, Pb$^{2+}$ ions only achieved the 85% of exhaustion after 315 minutes.
The different pattern between cycles #1 and #2 was due to the lower solution pH in the range of 2.5-2.9 during cycle #2, caused by the unexpected residual HCl from the incomplete rinse of HCl used for the regeneration of DF-BC filled in the columns after cycle #1. The surface charges were predominantly positive at pH 2.9, leading to electrostatic repulsion of the positively charged metal ions away from the DF-BC surface. Additionally, the acidic conditions also disfavored the formation of metal precipitates (e.g., carbonates and/or hydroxides) on the DF-BC surface.

After the operation of cycle #2, second regeneration of DF-BC was performed using 2 M HCl and rinsed with 10.0 mM NaCl thoroughly to avoid residual HCl. Similar removal patterns for three metal ions were observed during the cycle #3 as cycle #1, although the primary mechanism driving removal may have slightly changed, considering the lower effluent pH (from beginning of 8.41 (±0.09) to the end of 6.26 (±0.03)) and lower cation exchange capacity due to continuous wash out of alkalinity and exchangeable cations, but increased surface binding sites for metal ions of Cd$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$. Cd$^{2+}$ and Zn$^{2+}$ ions broke through after 170 and 160 minutes, reaching the exhaustion at 225 and 315 minutes, respectively. Like cycle #1, all Pb$^{2+}$ ions were retained on DF-BC during the duration of 315 minutes.

The results proved that the acid regenerated and then reused DF-BC could maintain the removal efficacy of mixed metal ions. Li et al. (2014) reported that the surface modification of wheat straw-derived biochar using 1 M and 6 M HCl increased the heterogeneity of the pores compared to the unmodified biochar, which enhanced the removal of nitrate and phosphate from water. In addition, treatment with strong acids can introduce amine, and carboxylic acid functional groups on the carbonized surface, increasing metal sorption capacity through cation exchange and surface complexation (Rajapaksha et al., 2016). Previous studies showed that the
increased presence of oxygen-containing functionalities and groups such as amide, imide, lactame, pyrrolic, and pyridinic groups provide binding sites that increase the affinity for metal sorption, especially metal cations such as Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) (Zhou et al., 2013; Buttry et al., 1999; Shafeeyan et al., 2010). Thus, the regeneration treatment that employed with 2 M HCl, not only stripped the immobilized metals from the biochar but acted as a surface modifying agent that increased the active metal binding sites through the regeneration and reuse cycles.

During the operation of continuous flow through fixed-bed columns, the influent containing metal ions passes through the column. The metal ions are retained by the unsaturated sorbents through multiple mechanisms as mentioned before (e.g., physical sorption, electrostatic attraction, surface complexation and/or precipitation) and reach the exhaustion point. Because the immobilization of metal ions is not at steady state while the influent is still passing through the column, it is difficult to describe the dynamic behavior of the metal ions in a fixed-bed column under the defined operating conditions.

Several simple mathematical models have been developed to describe and possibly predict the dynamic behavior in a fixed bed column. The Thomas model is commonly used for continuous flow conditions (Thomas 1944) and has been adapted to model throughput volume where throughput volume is defined as the fractional volume of solution that has passed through the column and is collected at a specified time interval (Sivaiah et al., 2004). The experimental data over three regeneration and reuse cycles fitted reasonably well to the Thomas model with \(R^2\) values of 0.951 or better, and the calculated parameters are summarized in Table 4.10. Because Pb\(^{2+}\) ions showed complete removal by DF-BC in cycles #1 and #3, only experimental data from cycle #2 is available for the model prediction of Pb\(^{2+}\) removal.
Table 4.10. Thomas Model Breakthrough Parameters

<table>
<thead>
<tr>
<th></th>
<th>$k_T$ (mL/min mg)</th>
<th>$q_T$ (mg/g)</th>
<th>Reduced Chi-Sqr</th>
<th>Adj. $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DF-BC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cd$^{2+}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle 1</td>
<td>0.048 ± 0.029</td>
<td>3.89 ± 0.20</td>
<td>0.011</td>
<td>0.963</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>0.038 ± 0.004</td>
<td>0.713 ± 0.035</td>
<td>0.0017</td>
<td>0.972</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>0.196 ± 19337.2</td>
<td>4.19 ± 1572.70</td>
<td>0.0095</td>
<td>0.967</td>
</tr>
<tr>
<td><strong>Pb$^{2+}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle 1</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>0.004 ± 0.0005</td>
<td>5.61 ± 0.33</td>
<td>0.0045</td>
<td>0.951</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td><strong>Zn$^{2+}$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle 1</td>
<td>0.040 ± 0.0024</td>
<td>3.34 ± 0.040</td>
<td>0.000030</td>
<td>0.999</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>0.062 ± 0.008</td>
<td>0.396 ± 0.025</td>
<td>0.0025</td>
<td>0.953</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>0.0703 ± 0.04</td>
<td>2.79 ± 0.22</td>
<td>0.00068</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Considering the low pH of 2.9 in cycle #2, the Thomas model calculated parameters for the removal of Cd$^{2+}$ and Zn$^{2+}$ ions are compared only between cycles #1 and #3. Based on the Thomas model calculated removal capacity $q_T$ and the rate constant $k_T$, these values were observed at similar magnitude after regeneration-reuse (Table 4.10). The results demonstrated that DF-BC could be regenerated by leaching the immobilized metals and maintain strong retention capacity with repeated reuse, although it must be acknowledged that limited experimental data points from the breakthrough points to saturation points might not provide accurate model prediction. Even so, DF-BC proves to be an effective and stable materials for the long-term removal of mixed metals ions from water.

4.3.7 Conclusions

In this study, the removal of mixed metal ions from water was investigated using douglas fir derived biochar and dairy manure derived biochar and their removal efficiency and
mechanism in both static and continuous flow through systems. The DF-BC and DM-BC were closely examined for physiochemical characterization, surface interaction mechanisms, removal capacity and kinetics in batch tests, and regeneration-resue behavior in continuous fixed-bed column experiments. DF-BC and DM-BC showed the potential to be an effective and reusable material for the long-term remediation of synthetic mixed metal polluted water. The main conclusions are summarized as follows:

(i) DF-BC and DM-BC showed the competitive removal of mixed metal ions following the preferential order of \( \text{Pb}^{2+} \gg \text{Zn}^{2+} > \text{Cd}^{2+} \). The preferential removal of \( \text{Pb}^{2+} \) ions over \( \text{Cd}^{2+} \) and \( \text{Zn}^{2+} \) ions is attributed mainly to physicochemical properties of \( \text{Pb}^{2+} \) ions, such as a smaller hydrated radius, a higher electronegativity and a lower hydrolysis constant (pKH).

(ii) The removal sequence of metal ions depends on the special properties of metal ions and their unique interactions with biochar under specific solution conditions. Among the various factors influencing the removal, the solution pH plays a decisive role in influencing the metal ion species in solution, and the surface charge and solubility of metal minerals. Consequently, the pH affects the electrostatic attraction/repulsion, surface complexation with oxygen-containing functional groups (e.g., -OH, \( \text{CO}_3^{2-} \) and v(Si-O)) and chemical precipitations of metal carbonate and hydroxides on biochar. These interactions and precipitation reactions were observed using DRIFTS, SEM/EDS, and XRD analysis.

(iii) The removal kinetics and model fitting elucidate that the three steps of intraparticle diffusion might more representative for describing the immobilization processes of metal
ions on the external surface and internal pores, although pseudo second order model best fit the experimental data.

(iv) Both DF-BC and DM-BC effectively retained the mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\), although each biochar displayed different removal behaviors for different metal ions in the column study. DF-BC showed that the breakthrough curves of Cd\(^{2+}\) and Zn\(^{2+}\) fit well with the Thomas model, while Pb\(^{2+}\) ions were completely removed. The removal was attributed to the combined effects of solution pH, cation exchange, surface complexations and precipitations over the three cycles. DM-BC showed complete removal of Cd\(^{2+}\) Pb\(^{2+}\) and Zn\(^{2+}\) via the precipitation of metal hydroxides and/or surface complexation with mineral components such as CO\(_3^{2-}\) and SiO\(_3^{2-}\) across the three regeneration cycles due to high solution pH from the alkalinity released by the biochar.

4.4 References


Chapter 5

SUMMARY AND FUTURE WORK

5.1 Fluoride Removal

5.1.1 Summary

Through batch experiments and column studies, the nanomaterials of ferrihydrite, hydroxyapatite (HAP) and brucite showed a strong affinity and effectiveness for the removal of fluoride from water. However, these nanomaterials demonstrated different removal mechanism: the adsorption of fluoride to ferrihydrite and brucite is mainly due to electrostatic attraction on the surface, while the removal of fluoride using HAP is attributed to combined effects of electrostatic attraction, ion exchange and precipitates (CaF$_2$). The adsorption of fluoride on these nano-sized hydroxides best fit the Freundlich and Redlich-Peterson models compared to the Langmuir, suggesting the multiple active sites on the heterogenous surfaces of nanomaterials express different affinities for the removal of fluoride.

In addition, the adsorption kinetics were well described by intra-particle diffusion, indicating the stepwise adsorption behavior on nano hydroxides that are controlled by various factors. The adsorption and desorption of fluoride on these (hydro)oxide nanomaterials in continuous up-flow columns showed that the
nanomaterials exhibited removal (q_T) of 3.48, 1.01 and 1.02 mg F g\(^{-1}\) for ferrihydrite, HAP and brucite respectively with relatively low desorption. These results show promise for ferrihydrite, HAP and brucite as effective sorptive materials incorporated into filtration systems for the remediation of fluoride-polluted water.

In addition, a calcium hydroxide-coated dairy manure-derived biochar (Ca-DM500) also showed promise as a remedial material for the removal of fluoride from water. The removal of fluoride on Ca-DM-BC was primarily attributed to the strong adsorption complexation between fluoride and calcium hydroxide, which was coated on the surface of dairy manure derived biochar using environmentally friendly procedures.

The adsorption best fit the Freundlich and Redlich-Peterson models compared to the Langmuir. The kinetics were well described by intra-particle diffusion indicating combined specifically and non-specifically chemisorptive interactions occurring on the heterogeneous surface of Ca-DM-BC. Most importantly, Ca-DM-BC showed high reactivity per surface area for sorption of fluoride contributing to the importance of surface complexation. Moreover, the coexistence of anions (SO\(_4^{2-}\), PO\(_4^{3-}\) and NO\(_3^{-}\)) showed different level of reduction on the fluoride removal by Ca-DM-BC.

The column studies and the Thomas model prediction strongly demonstrated that the Ca-DM-BC could be regenerated and reused with slight decrease in removal efficiency over three tested cycles, which presents the great as an efficient and reusable sorbent for remediation of fluoride contaminated water.

Taking the above into consideration, both nanomaterials and biochar-based materials showed advantages and disadvantages for the removal of fluoride from water.
The nanomaterials showed strong affinity for the removal of fluoride. For instance, ferrihydrite had the highest $q_T$ and longest time to breakthrough, making it one of the most promising material for exploring scale up design. However, the synthesis and production of large quantity of ferrihydrite could prove costly.

On the other hand, Ca-DM-BC could prove a cheaper and more accessible material than nano-hydro(oxides), considering biochar made from large variety of biomass including forest and manure wastes. In addition, increasing dosage of biochar in the packed materials in fixed bed columns may improve the removal capacity as indicated in batch studies, which prove the feasibility and suitability of Ca-DM-BC for broad applications. However, the batch test also showed the co-presence of anions cause the competitive reduction of fluoride removal by Ca-DM-BC at different levels depending on anion species, which might limit the treatment efficiency.

5.1.2 Future Research Works

For future research on fluoride removal, exploring cost-effectiveness of material design and synthesis, regeneration-reuse capabilities, and competitive ions of nano-ferrihydrite and biochar-based materials would be paramount. Bench scale tests using environmentally contaminated water rather than synthetic fluoride solution are also necessary for better understanding the sorptive material in an environmentally relevant setting. Finally, future work is needed to better understand fluoride removal on a pilot scale level using the nanomaterials and biochar based materials, especially pertaining to petroleum and industrial waste remediation before broad application in real contaminated sites.
5.2 Heavy Metal Removal by Biochar

5.2.1 Summary

Batch experiments showed that three Douglas fir derived biochars (Tea-DF-BC, Org-DF-BC, DF-BC) and three dairy manure derived biochars (DM-BC-CV, DM500 and DM-BC) displayed different levels of removal efficiency for mixed metal ions of Cd\(^{2+}\), Co\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) ions from water. When the two selected biochars, DF-BC and DM-BC were evaluated with the focus metals Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) at (environmentally relevant concentration 6-96 mg L\(^{-1}\)), results showed removal following the preferential order of Pb\(^{2+}\) >> Zn\(^{2+}\) > Cd\(^{2+}\).

As expected, different biochars have unique physicochemical characteristics, controlling the competitive removal of mixed metal ions from water. In addition, the solution pH plays a decisive role in influencing the metal ion species in solution, surface charge and solubility of metal minerals, which consequently affect the surface sorption, surface complexation with functional groups and chemical precipitations of metal ions on the surface of biochar. The variable fitting of sorption isotherms for the removal of metal ions on DF-BC and DM-BC indicated the different mechanism on the surface interactions (e.g. monolayer vs. multiple layers, homogenous vs. heterogeneous sites, physical sorption, ion exchange and/or precipitations) between the metal ions and surface functional groups of biochar.

In summary, the sorption isotherm modeling and solid phase analysis (e.g. DRIFTS, XRD, and SEM-EDS) verified multiple driving mechanisms for the competitive removal of mixed metal ions of Cd\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) on DF-BC and DM-BC. These mechanisms included the physical sorption of metal ions on the porous surface of
biochar, the electrostatic attractions between positively charged metal ions and negatively charged surface functional groups (e.g., -COO\(^-\), CO\(_3\)\(^{2-}\)), and the formation of chemically bonded precipitates (e.g. metal carbonate and hydroxides).

In addition, the removal kinetics and model fitting elucidate that the three steps of intraparticle diffusion might be more representative for describing the immobilization processes of metal ions on the external surface and internal pores, although pseudo second order model best fits the experimental data.

In the DF-BC column studies, Pb\(^{2+}\) ions continued to show preferential removal over Cd\(^{2+}\) and Zn\(^{2+}\) ions, which is mainly attributed to the physiochemical properties of Pb\(^{2+}\) ions such as a smaller hydrated radius, a higher electronegativity and a lower hydrolysis constant (pKH). The Thomas model fit well to the DF-BC data for the removal Cd\(^{2+}\) and Zn\(^{2+}\) ions in a continuous up flow column. The competitive removal of mixed metal ions using DF-BC is attributed to solution pH, cation exchange, surface complexation and precipitation. On the other hand, DM-BC showed complete removal of all three metal ions over the three regeneration cycles. The alkalinity released by the DM-BC played a decisive role in column removal influencing metal ion species in solution and driving the removal mechanisms: cation exchange, surface complexation, and chemical precipitation.

Overall, DF-BC and DM-BC showed the potential to be an effective and reusable materials for the long-term remediation of mixed metal polluted water and could prove to be a competitive replacement when compared with other biochars and conventional materials such as zeolites and activated carbon.

168
5.2.2 Future Research Works

Although the six biochars tested in this study showed great potential for removing heavy metal ions from water, the type and number of biochars still only represent a small group biochars with distinct physicochemical properties. In addition, batch experiments demonstrated that the removal of mixed metal ions on two types of biochars (douglas fir derived biochars and dairy manure derived biochars) varied on different competition mechanism and controlling factors, strongly indicating additional works need to be explored for a large variety of biochars.

Moreover, the column studies demonstrated the feasibility and suitability of biochar as a cost-effective material for the remediation of heavy metal contaminated water, since the biochar presented the stable removal efficiency over regeneration and reuse processes. However, additional studies are necessary to explore the effects of co-existence of ions on the competitive removal of metal ions, the mechanistic impacts of cation exchange on the removal of metal ions, the alternative environmentally sustainable methods (e.g., lower concentration of HCl, organic acid) for effective regeneration and reuse of biochar. Furthermore, future works will evaluate the leaching potential of pollutants from biochar (e.g., high concentrations of phosphates and nitrates and develop the strategy to mitigate these negative impacts, which provides the valuable information for the best management practice in field study.