DEFLUORIDATION FROM AQUEOUS SOLUTION BY CATTLE BONE CHAR AND HYDROXYAPATITE

by

Dachuan Tang

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Civil Engineering

2019 Summer

© 2019 Dachuan Tang
All Rights Reserved
DEFLUORIDATION FROM AQUEOUS SOLUTION BY CATTLE BONE
CHAR AND HYDROXYAPATITE

by

Dachuan Tang

Approved:

Chin-Pao Huang, Ph.D.
Professor in charge of thesis on behalf of the Advisory Committee

Approved:

Sue McNeil, Ph.D.
Chair of the Department of Civil and Environmental Engineering

Approved:

Levi T. Thompson, Ph.D.
Dean of the College of Engineering

Approved:

Douglas J. Doren, Ph.D.
Interim Vice Provost for Graduate & Professional Education and Dean of the Graduate College
ACKNOWLEDGMENTS

First, I want to express my sincere appreciation to my advisor, Professor Chin-Pao Huang for his patient guidance, consistently encourage and valuable experience in research through all days in laboratory and class. I still remember the first day I came to the University of Delaware, when he told me that a person can be remembered because of his achievements rather than a rhetoric English name.

I want to thank all members in our lab: Tommy Chen, Jenn Feng, Mary Fan, JINGhua, Thomas Lin, Sean, Daniel, Michael Huang, Yuchin Kao, Cuijuan, Wanze, and Kegang for their assistance during my graduate career. Especially, thanks to Tommy Chen, who taught me how to conduct experiments; and Thomas Lin, who helped me to calculate the complex formation model. Moreover, I will keep the memories of happy lunchtimes accompanied by all lab members in my mind forever.

I would like to acknowledge the lab managers in our department: Yu-Han Yu and Michael Davidson for their patience and responsible assistance with my research.

I would like to thank all my friends in Newark: Yudi, TingTing, Dafu, Yingzhuo, Vera, Xiangming, Gabriel Shao, Jieren, Danhui, Mu Zhu, Snow and so on for their endless help and friendship during my graduate studies.

Finally, I would like to express my deepest appreciation to my parents and my family members, who supported me with love, patience and finance.
TABLE OF CONTENTS

LIST OF TABLES ................................................................. vi
LIST OF FIGURES .............................................................. vii
ABSTRACT ........................................................................... ix

Chapter

1 INTRODUCTION ............................................................... 1
2 LITERATURE REVIEW ....................................................... 3
   2.1 Overview ................................................................. 3
   2.2 Toxicity of Excess Fluoride .......................................... 3
   2.3 Fluoride Removal Methods ........................................... 4
   2.4 Hydroxyapatite ......................................................... 6
      2.4.1 Introduction ...................................................... 6
      2.4.2 Surface Charge and Zeta potential ......................... 7
      2.4.3 Electrical Properties .......................................... 8
      2.4.4 Fluoride Removal .............................................. 11
   2.5 Bone Char ............................................................... 12
      2.5.1 Introduction ...................................................... 12
      2.5.2 Fluoride Removal .............................................. 12
3 MATERIALS AND METHODS ............................................... 15
   3.1 Material ................................................................. 15
   3.2 Adsorption Experiment .............................................. 16
   3.3 Zeta Potential Measurement ....................................... 17
   3.4 Surface Characterization .......................................... 17
4 RESULTS AND DISCUSSIONS .............................................. 19
   4.1 Surface Characterizations .......................................... 19
      4.1.1 Surface Area and Pore Size ................................. 19
      4.1.2 SEM Analysis ................................................... 19
      4.1.3 FTIR Analysis .................................................. 25
      4.1.4 XRD Analysis .................................................. 27
4.1.5 XPS Analysis ................................................................. 29
4.1.6 Zeta Potential and Surface Acidity ............................. 32

4.2 Fluoride Removal Experiment ....................................... 38

4.2.1 Effect of Solution pH ................................................. 38
4.2.2 Effect of Adsorbent Dose ............................................ 41
4.2.3 Effect of Initial Fluoride Concentration ...................... 43
4.2.4 Adsorption Isotherm .................................................. 50
4.2.5 Effect of Temperature ................................................ 56
4.2.6 Adsorption Model Fitting .......................................... 59
4.2.7 Effect of Ionic Strength .............................................. 63
4.2.8 Adsorption Mechanism ............................................. 65

5 CONCLUSIONS ........................................................................... 66

REFERENCES .............................................................................. 68
LIST OF TABLES

Table 4.1: Surface area and pore size of BC and HAP ............................................. 19
Table 4.2: BC and HAP intrinsic constants................................................................. 33
Table 4.3: Langmuir isotherm parameter for BC adsorption fluoride...................... 51
Table 4.4: Langmuir isotherm parameter for HAP adsorption fluoride..................... 51
Table 4.5: Freundlich isotherm constant for BC adsorption fluoride....................... 53
Table 4.6: Freundlich isotherm constant for HAP adsorption fluoride..................... 53
Table 4.7: Thermodynamic parameters at different temperature ............................. 57
LIST OF FIGURES

Figure 4.1: SEM image of BC (a) before adsorption, (b) after adsorption at pH$_f$ = 3, (c) after adsorption at pH$_f$ = 3.0, (d) after adsorption at pH$_f$ =11 ...... 21

Figure 4.2: SEM image of HAP (a) before adsorption, (b) after adsorption at pH$_f$ = 3, (c) after adsorption at pH$_f$ = 3.0, (d) after adsorption at pH$_f$ =11 ...... 22

Figure 4.3: SEM-EDX spectrum and mapping image of BC after adsorption......... 23

Figure 4.4: SEM-EDX spectrum and mapping image of HAP after adsorption........ 24

Figure 4.5: The FTIR spectrum of (a) BC, (b) HAP before and after adsorption. ..... 26

Figure 4.6: XRD patterns of the (a) BC, (b) HAP before and after adsorption. ..... 28

Figure 4.7: XPS survey spectra of (a) BC, (b) HAP before and after adsorption. Experimental conditions: [Adsorbent]=10 g/L, pH$_f$ = 3.0, [I]$ = 10^{-2}$ M NaClO$_4$, [F$^-]$=60 mM .................................. 30

Figure 4.8: XPS Ca2p spectrum of the (a) BC and (b) HAP before and after adsorption. ................................................................. 31

Figure 4.9: (a) Zeta potential of BC, (b) Zeta potential of HAP. Experimental conditions: pH$_f$ = 2.0 to 12.0, [I] = 10$^{-1}$, 3$\times$10$^{-2}$ and 10$^{-2}$ M NaClO$_4$ ...... 34

Figure 4.10: (a) Surface potential of HAP, (b) Surface charge of HAP. Experimental conditions: pH$_r$ = 2.0 to 12.0, [I] = 10$^{-1}$, 3$\times$10$^{-2}$ and 10$^{-2}$ M NaClO$_4$. ............................................................. 35

Figure 4.11: Speciation of surface group of BC in different ionic strength. (a) [I]$ = 10^{-1}$ NaClO$_4$, (b) [I]$ = 3\times10^{-2}$ NaClO$_4$, (c) [I]$ = 10^{-2}$ NaClO$_4$. ......................... 36

Figure 4.12: Speciation surface group of HAP in different ionic strength. (a) [I]$ = 10^{-1}$ NaClO$_4$, (b) [I]$ = 3\times10^{-2}$ NaClO$_4$, (c) [I]$ = 10^{-2}$ NaClO$_4$. ................. 37

Figure 4.13: Effect of pH on fluoride removal by (a) BC, (b) HAP in different initial fluoride concentration. Experimental conditions: [Adsorbent]= 10 g/L, [I] = 10$^{-2}$ M NaClO$_4$, [F$^-]$ = 6, 8, 13, 16, 20mM ................. 39
Figure 4.1: The pH variation between before and after adsorption (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10g/L, [I] = 10^{-2} M NaClO₄, [F⁻] = 20 mM.

Figure 4.2: Effect of adsorbent dose on fluoride removal percentage and adsorption capacity. (a) BC, (b) HAP. Experimental conditions: pHᵢ = 3.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 20 mM.

Figure 4.3: Adsorption isotherm of fluoride removal by (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10 g/L pHᵢ = 3.0 to 11.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 6 to 190 mM.

Figure 4.4: Process of fitting Langmuir isotherm. (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10 g/L pHᵢ = 3.0 to 11.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 6 to 190 mM.

Figure 4.5: Fluoride adsorption in different temperature, (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 2.5 g/L pHᵢ = 3.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 6 to 80 mM.

Figure 4.6: Adsorption model fitting of BC. Experimental conditions: [Adsorbent] = 10 g/L pHᵢ = 3.0 to 10.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 2 mM.

Figure 4.7: Adsorption model fitting of HAP. Experimental conditions: [Adsorbent] = 10 g/L pHᵢ = 3.0 to 10.0, [I] = 10^{-2} M NaClO₄, [F⁻] = 2 mM.

Figure 4.8: Effect of ionic strength on fluoride removal and adsorption capacity. (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10 g/L pHᵢ = 3.0 to 11.0, [I] = 10^{-1} and 10^{-2} M NaClO₄, [F⁻] = 2 mM.

viii
ABSTRACT

Water containing fluoride beyond 1 mg/L is harmful to human health. In this study, cattle bone char (BC) and hydroxyapatite (HAP) were used in fluoride removal from water. The BC and HAP surface characteristics were investigated by BET, FTIR, XRD, XPS and SEM analysis. BET analysis shows that BC had a higher specific area (59.62 m²/g) than HAP (45.69 m²/g), and their pores size are 9.52 nm and 9.51 nm respectively. XRD analysis reveals that Ca₁₀(PO₄)₆(OH)₂ is the major constituent of BC and HAP. The effects of adsorbent dose, pH, initial fluoride concentration, temperature, and ionic strength on adsorption capacity were explored. The adsorption capacity increases with initial fluoride concentration and decreases with pH, and the maximum adsorption capacities of BC and HAP are 10.23 and 12.90 mmol/g at pH 3 respectively. The adsorption isotherms were evaluated by Freundlich and Langmuir models across fluoride concentration. Based on XRD, XPS and FTIR pattern shown, the major mechanisms of the BC and HAP for fluoride removal with increasing fluoride concentrations are surface complex formation and electrostatic interactions between adsorbent surface and fluoride, then ion exchange, and then precipitation of CaF₂
Chapter 1

INTRODUCTION

Water is a necessary natural resource, which constitutes 79% of the surface of the earth and it is important for maintaining human and other living life. Water even influences agriculture and industrial operation. However, drinkable freshwater accounts for only 0.6% of total water resource on earth. The industrial and agricultural demand for water have considerably risen with rapid population growth through the past few decades and need uncontaminated water resources to guarantee high productive efficiency [1].

Fluoride is a common chemical element. The fluoride concentration in drinking water is one important standard to evaluate water quality. Excessive fluoride in drinkable water poses a threat to humans and animals. Fluoride-rich water has been a worldwide issue and threatens the health of 200 million people from over 25 countries.

Some global methods to remove fluoride from water have been discussed, such as adsorption, membrane-based defluoridation and precipitation-coagulation which are widely apply to remediate sewage [2]. Generally, most of the fluoride removal methods are related to coagulation and adsorption.

Bone char (BC) is a mixed component adsorbent, which is manufactured from the pyrolysis of animals’ bone. Compared to plant biochar, BC consists of 10% carbon and 90% calcium phosphate [3]. BC has been widely used as an adsorbate in environmental improvement due to availability, low cost and high adsorption capacity. Hydroxyapatite (HAP), Ca_{10}(PO_{4})_{6}(OH)_{2}, which is known as phosphate mineral, is
abundant on Earth [4]. Moreover, phosphate also founded in rock and sandstone. According to other studies described, HAP is the major constituent of bone char [5].

The objective of this research is to determine the efficiency of BC and HAP for fluoride removal. Surface characteristics, such as specific surface area, pore size intrinsic constant and surface site were revealed in this study. In addition, some potential factors that could affect adsorption ability were also investigated. Finally, the adsorption mechanisms of fluoride removal by BC and HAP were also explored through the surface characteristic analysis.
Chapter 2
LITERATURE REVIEW

2.1 Overview

Fluoride is an irritating yellow-green gas, which cannot exist in nature freely and always has been in compound form. Fluoride contamination presented in water results from industrial and geological sources. Some of the fluoride-containing mineral, such as granite, biotites topaz and fluorite were washed by water flow lead to release fluoride into ground [6].

Fluoride can be utilized for semiconductor, ceramic manufacturing, aluminum industrial, even our daily toothpaste. As a result of using so much fluoride, there is a large amount of fluoride inflow to the underground due to the industrial discharging wastewater [7]. Water fluorine pollution occurs in many countries. The United States government has reported the data about median percentage and interquartile range of the population. The median percentage popularity of fluoride pollution has increased by 8% from 1992 to 2008. In addition, interquartile ranges also increase by 5% in that period. Since the total population is constantly growing, fluoridation pollution increases year by year [8].

2.2 Toxicity of Excess Fluoride

Excessive fluoride in drinking water has been known as a pathogenic cause [6]. The World Health Organization (WHO) declares the human daily essential fluoride consumption is from 0.5 to 1.5 mg. When the drinking water fluoride concentration is below 0.5 mg/L, humans suffer from dental disease and mineralization deficiency. In
contrast, taking excess amounts of fluoride also brings some serious problems to bodily health [9]. According to WHO report, humans will suffer from dental fluorosis once the fluoride in drinking water is over 1.5 mg/L. Once fluoride in drinking water is over 4 mg/L, it could cause permanent bone deformation and skeletal fluorosis [10].

2.3 Fluoride Removal Methods

Fluoride removal from water has been investigated in many studies [11]. Adsorption, membrane techniques and precipitation-coagulation are the three main approaches that have been employed for different pollution conditions. Moreover, choosing the most compatible technique could make the defluoridation procedure more efficient.

Adsorption

Adsorption is a general and reliable method to treat impurity water due to low cost and convenient design [2]. Two main adsorption mechanism illustrate how the fluoride is absorbed on the adsorbent. First, fluoride moves to the adsorbent surface directly which relies on structure of the adsorbent. Second, fluoride reacts with the component on the adsorbet, this was seen as the chemisorption because of chemical reaction involved [12].

Clay is reported to be an effective adsorbent for fluoride removal. some studies [13] show the modified composite clay could adsorb fluoride from water. The maximum adsorption density is 303.54 mg/g, it is an immense improvement to natural clay. However, applying modified clay in fluoride removal could bring side effects to the aqueous body. Also, the cost of modified clay is several times than natural clay. If the finance is limited, using modified clay is not regarded as an ideal method to remove fluoride.
Biochar as a carbon-rich product made from pyrolysis plants and animals, is generally employed for soil conditioning modification and water remediation. Because of the relatively convenient manufacturing process and availability of waste bone and plant, biochar is cheaper than other adsorbent and can be utilized for massive field pollution. Some studies reported that biochar could remove solvent, dye, miscellaneous and other organic substance. In addition, biochar also could remove metal ions, but the efficiency is limited.[12].

Many studies have examined to get a new adsorbent by combining traditional adsorbent with other chemical component. For example, coating aluminum hydroxide on rice husk could obtain excellent fluoride removal efficiency (9-10 mg/g) [14]. Moreover, comparing to single zirconium and calcium compound, zirconium-loaded orange waste gel [15], calcium-based material [16] and zirconium-impregnated collagen fiber [17], and another hybrid materials have better performance in fluoride removal.

**Membrane Technique**

Reverse osmosis (RO) membrane is a new technique to treat water pollution in recent years. RO as a physical method, selects ions based on particle size and liquid pressure. Contaminants are removed by increasing pressure on disposed water through semi-permeable membrane. This technique differs from other conventional methods, no secondary pollution added and low-cost make RO popular in water treatment, even fluoride removal efficiency is up to 98%. However, Membrane fouling was represent after operating many times so that total running cost increase.[1].

The electrolytic defluoridation technique is consist of two electrodes submerged in wastewater, dissolution reaction happens when the directly current pass through electrodes. Behbahani et al. [18] reported that fluoride removal efficiency by
electrocoagulation could achieve 94.5% in pH of 7, adsorption capacity is about 25 mg/g. Furthermore, pH value, initial concentration of fluoride, current density and reaction time effect to the fluoride removal efficiency. The electrodialysis differs from RO process, no fluoride remains on the electrodes surface after fluoride removed. Cui et al. [19] studied controlled anions exchange by modified electrode reactor with polyaniline. According to batch test and flow experiment, polyaniline modified electrode reactor has better removal capability (20mg/g) than unmodified electrode (5mg/g) to fluoride removal. However, constant charging electrode results in the electrolytic defluoridation is more expensive than other methods. Besides, pH correction by chemical products brings side-effect to water.

**Precipitation-Coagulation**

The aim of precipitation-coagulation is assembled colloid particle to an insoluble massive cluster to immobilize contaminants. Coagulation is always accompanied by a chemical reaction. Lime and aluminum compound are two general coagulants to fluoride removal, which are used to promote precipitation and cause coagulation respectively. At alkalinity conditions, Al(OH)₃ could react with free fluoride and form AlF₃, which is insoluble in water. So that the free fluoride in water has been restricted by AlF₃. However, how to deal with the residual aluminum complex also needs to be taken into consideration [1].

### 2.4 Hydroxyapatite

**2.4.1 Introduction**

Hydroxyapatite (HAP) is a calcium phosphate-based mineral, bone and tooth are present in HAP, thus it is the main component in the human and animal body [20]. HAP,
Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ belongs to apatite family, some studies reported it has many functions, because anionic and cationic features coexist on HAP structure [21]. Fihri et al. [22] reported HAP could be obtained from several methods, such as dry and wet method, coprecipitation, hydrolysis and hydrothermal methods. For instance, HAP hydrolysis at high temperature (around 1050°C) can be expressed by the following equations:

$$2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$$ (2-1)

or $$3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$$ (2-2)

Further, the final product quality is also determined by different temperature and weight of the raw material. The percentage of free CaO increases with increasing temperature. Comparing to synthetic HAP, natural HAP has a higher Ca/P ratio, and contains more carbonate groups. At temperature over 700 °C, crystallite become intensive and surface area declines, which leads to total adsorption capacity decrease [23].

2.4.2 Surface Charge and Zeta potential

Surface charge as a fundamental parameter often be discussed in adsorption by electrostatic interaction. Rocha et al. reports that the positive charge on adsorbate could be attracted by negative ion on adsorbent [24]. Zeta potential is related to surface charge, which could be determined by measuring suspended material in the voltage field [25]. Further, zeta potential is influenced by solution pH. The pH when zeta potential becomes zero is pH$_{zpc}$. In general, if the solution pH is above the pH$_{zpc}$, the material surface has more negative charge. By contrast, when the pH is below pH$_{zpc}$, that indicates the material surface surrounded by positive charge. Mourabet et al. [26] reported the pH effect fluoride removal by electrostatic interaction. Comparing to the
pH > pH_{zpc}, HAP for fluoride removal is more effective at pH < pH_{zpc}. In contrast, HAP surface contains more negative charges at high pH condition that could weaken electrostatic force between adsorbate and adsorbent and leads to total adsorption capacity decreased.

2.4.3 Electrical Properties

**Surface Potential \( \Psi_o \)**

Boltzmann distribution is used to discuss intrinsic ionization and complexation constants of oxide surface [27]. It could be expressed by the following equation:

\[
\frac{n_i}{n_{i\infty}} = \exp\left(\frac{-z_i e \psi}{k_B T}\right)
\]

(2-3)

Where \( \psi \) is layer potential, \( k \) is Boltzmann constant, and \( T \) is the absolute temperature. \( n_i \) and \( n_{i\infty} \) are the number of ions (i) per unit volume near the surface and bulk solution respectively. For the boundary condition, depending on Debye-Huckel equation:

\[
\psi = \psi_0 \exp\left(\frac{-x}{\kappa^{-1}}\right)
\]

(2-4)

The \( x \) is the distance, \( \kappa^{-1} \) is “thickness of double layer”. Assume \( \Psi_o < 25 \text{mV} \), \( x = \kappa^{-1} \), The above-equation could be reformulated by following equation:

\[
\psi = \psi_0 e^{-1}
\]

(2-5)

At 25°C

\[
\kappa^{-1} = \frac{4.31 \times 10^{-10}}{\sqrt{T}}
\]

(2-6)

The \( I \) is the solution concentration (mol/L).
Surface Charge Density $\sigma^*$

The counterions on the particles produce the surface charges neutralized near the surface. According to Poisson equation and Gouy-Chapman model [28]:

$$\sigma_0 = \int_0^\infty -\rho\, dx$$

$$\sigma_0 = -\varepsilon \left( \frac{d\psi}{dx} \right)_0$$

$$\sigma_0 = \frac{\varepsilon k_B T}{ze} 2\kappa \sinh \left( \frac{ze \psi_0}{2 k_B T} \right)$$

$$\sigma_0 = 0.1174 c^{1/2} \sinh \left( \frac{zF \psi_0}{2RT} \right) \quad \text{(C m}^2, 25^\circ\text{C)} \quad (2-7)$$

Where $C$ and $Z$ are concentration and charge of the supporting electrolyte counterion in diffuse layer respectively. $F$ is Faraday constant, $R$ and $T$ are gas constant and absolute temperature respectively.

Intrinsic Acidity Constant

For particle in aqueous phase, the amphoteric equilibrium reaction and intrinsic constant could be expressed by following equations:

$$SOH_2^+ = SOH + H^+ \quad K_{a1}^{int} \quad (2-8)$$

$$SOH = SO^- + H^+ \quad K_{a2}^{int} \quad (2-9)$$

$$K_{a1}^{int} = \frac{[SOH][H^+]}{[SOH_2^+]} \quad (2-10)$$

$$K_{a2}^{int} = \frac{[SO^-][H^+]}{[SOH]} \quad (2-11)$$

$$S_T = \{SOH_2^+\} + \{SO^-\} + \{SOH\} \quad (2-12)$$
Where the S means particle surface, \{SOH_2^+\}, \{SOH\} and \{SO^-\} indicate positive, neutral and negative hydroxy complex group on the surface respectively. \(S_T\) indicates total surface sites sum of all groups. According to Huang and Stumm [28] reported that the acidity constant following the Boltzman distribution equations:

At positive surface and negative surface:

\[
\{H^+\} = [H^+] \exp \frac{F\psi_0}{RT} \tag{2-13}
\]

\[
\{H^+\} = [H^+] \exp \frac{-F\psi_0}{RT} \tag{2-14}
\]

Where \([H^+]\) is proton concentration. \(\{H^+\}\) is proton concentration on surface. R is the universal gas constant (8.314J/mol K\(^{-1}\)). T is absolute temperature (K), F is Faraday constant (96485C/mol). Replaced \([H^+]\) by intrinsic constant \(K_{\text{int}}^1\):

when \(pH < p\text{H}_{\text{ZPC}},\)

\[
S_T = \{\text{SOH}_2^+\} + \{\text{SOH}\} \tag{2-15}
\]

When \(pH > p\text{H}_{\text{ZPC}}\)

\[
S_T = \{\text{SO}^-\} + \{\text{SOH}\} \tag{2-16}
\]

By rearranging Equations (2-10) and (2-13), obtains follow equation:

\[
\frac{1}{[H^+]} = \frac{S_T}{K_{a1}^{\text{int}}} \frac{1}{\sigma^+} - \frac{1}{K_{a1}^{\text{int}}} \tag{2-17}
\]

By rearranging Equations (2-11) and (2-14), obtains follow equation:

\[
\{H^+\} = \frac{S_T}{K_{a2}^{\text{int}}} \frac{1}{\sigma^-} - K_{a2}^{\text{int}} \tag{2-18}
\]

Further, plotting \(1/\sigma\) as x axis, \(1/[H^+]\) or \(\{H^+\}\) as y axis. The intrinsic constant. \(K_{a1}^{\text{int}}\) and \(K_{a2}^{\text{int}}\) could be figured out from intercept, and the \(S_T\) could be calculated.
2.4.4 Fluoride Removal

Several researchers studied HAP to remove fluoride from water. Sairam et al. [29] found HAP exhibited relatively high capacity for fluoride-exchange and specific reaction for fluoride ion, and try to fit fluoride sorption model by Freundlich and Langmuir isotherms. Some thermodynamic parameters help to understand the adsorption related to pseudo-second order and pore diffusion models. He reported that the reaction mechanisms are adsorption and ion-exchange and given by following equation:

\[ \text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{(OH)}_2 + 2 \text{F}^- \rightarrow \text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{(F)}_2 + 2 \text{OH}^- \]  \hspace{1cm} (2-19)

Liang et al. reported the fluoride removal by glass transferred hydroxyapatite. This adsorption reaction needs 12 hours to get equilibrium; and the maximum adsorption capacity is around 86.7% to 96.6% at pH value of 6.72 within adsorbent dose from 5 to 10 g/L [30].

Mourabet et al. investigated that HAP for fluoride adsorption capacity is related to some factors, such as solution pH, the concentration of fluoride, adsorbent dose and temperature. Adsorbent dose increasing and pH decreasing are beneficial for fluoride removal. Moreover, 39.02°C is the optimal temperature for fluoride removal by HAP. Whether the reaction belongs to endothermic or exothermic and temperature influence can be investigated by determining thermodynamic parameters, such as enthalpy (\( \Delta H^\circ \)), entropy (\( \Delta S^\circ \)) and Gibbs free energy (\( \Delta G^\circ \)) [26].

Wang et al. shows the low molecular weight organic acids (LMWOAs) could boost the fluoride onto HAP by producing positive charge and protonated on HAP surface for enhance electrostatic interaction. The defluoridation capacity is decreasing with the increasing pH and increasing adsorbent dose [31]. The adsorption was
endothermic and spontaneous. Besides, Liang et al. modified the HAP by sulfate. The sulfate-dropped HAP shows high adsorption density to fluoride. Moreover, the ratio of S to P is 1:6, could guarantee defluoridation efficiency and relatively lower cost [32].

2.5 Bone Char

2.5.1 Introduction

Bone char (BC) is carbon-rich material, which is carbonized at pyrolysis process to remove organics from plant and animal bones. BC consists of calcium phosphates and carbonates containing about 76 wt% of HAP. BC and HAP have some similar chemical and physical properties [33]. Medellin et al. analyzed cattle BC by scanning electron microscope (SEM), and the result shows that the BC porous structure and surface are irregular. The P, Ca, C, O, Si, Na, and Al can be found on BC surface through X-ray microanalysis probe. Further, the weight percentages of HAP, carbon and calcite (CaCO₃) are 76%, 11% and 9% respectively [34].

Based on some studies, different animal bones show various properties after carbonization, for instance, BC made from fish and cow are differ in phosphorous content. And their surface acidities also differ to each other. Cow BC contains more positive charge on the surface [35].

2.5.2 Fluoride Removal

Several projects about BC and modified BC for fluoride removal have been published over the years. Medellin et al. reports that OH⁻ and PO₄³⁻ ions on BC as the ionic species can react with fluoride ions. Furthermore, the adsorption capacity of BC for fluoride removal is reduced with solution pH. Fluoride ions can be attracted by BC since BC surface shows positive charge while pH value below pH_{zpc}. Moreover,
competing anions in solution influence fluoride removal. NO$_2^-$, NO$_3^-$ and SO$_4^{2-}$ were adsorbed by BC, this leads to decline of active adsorption sites on the adsorbent. In addition, competition between F$^-$ and Cl$^-$ to replace hydroxy on BC also reduces adsorption capacity [36].

Brunson and Sabatini investigated fish BC for fluoride removal through batch test, specific surface area and chemical composition measurement. The optimum charring temperature to BC is 500 °C. Organic matter within BC cannot be removed thoroughly when the burning temperature below 500 °C. In contrast, some hydroxyapatite structure decays at temperature over 500 °C. Furthermore, Langmuir and Freundlich isotherm models are used to fit the data and relative parameters obtained. Evaluating $R^2$ of two model, the Langmuir isotherm is more appropriate for that adsorption study [35].

Zúñiga-muro et al. investigated fluoride removal research by modified BC with cerium species. As the result shows BC modified by Ce$^{4+}$ has advanced adsorption property than Ce$^{3+}$. The maximum cerium-loaded BC adsorption density is 13.6 mg/g at pH 7 with 30 °C, which is higher than conventional unmodified BC shown [37]. Moreover, the thermal regeneration, as one of environmentally and economics process was used to disposal exhausted BC. Relevant reaction shows in the following equation:

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2 + 2\text{OH}^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6 + 2\text{HF} \uparrow + \text{O}_2 \uparrow \quad (2-20)$$

After regeneration, the BC maximum adsorption capacity can be attained to 2.37 mg/g, which is half of original BC [24].

Dahi et al. reported that BC adsorption capacity vary slightly from black and white color, and black one has better defluoridation capacity [38]. Since the black BC
has been pyrolyzed completely and less organic component is benefited to adsorb fluoride. Ismail et al. found that dicalcium phosphate anhydrate (Ca$_2$HPO$_4$), Tricalcium phosphate (Ca$_3$(PO$_4$)$_3$) and Dicalcium phosphate dehydrate (Ca$_2$HPO$_4$•2H$_2$O) help fluoride combining with Ca$^{2+}$ and release phosphate [39].

According Liang et al. reported that adsorption mechanism is different in fluoride concentration [30]. At low fluoride concentration, follow reactions occur:

\[
\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2 + F^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_{6}(\text{F,OH}) + \text{OH}^- \quad (2-21)
\]

\[
\text{Ca}_{10}(\text{PO}_4)_{6}(\text{F,OH}) + F^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_{6}F_2 + \text{OH}^- \quad (2-22)
\]

At high fluoride concentration:

\[
\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2 + 20F^- \rightarrow 10\text{CaF}_2 \downarrow + 6\text{PO}_4^{3-} + 2\text{OH}^- \quad (2-23)
\]

At low fluoride concentrations, chemisorption, such as ion exchange can seem as main mechanism of adsorption fluoride. Further, at high fluoride concentration, the formation of CaF$_2$ precipitation causes the fluoride concentration decreased in aqueous.
Chapter 3
MATERIALS AND METHODS

3.1 Material

BC

The granular BC is commercially produced from old cattle in Brazil. It contains both carbon surface area and hydroxyapatite lattice surface area which is different from activated carbon. Before adsorption experiments, Sieved BC to 20-60 mesh and washed BC with 0.1 mM HCl and 0.1 mM NaOH for 24 hours respectively to remove some soluble constituents, such as Al₂O₃ and CaO [40]. Then, rinsing washed BC in DI (deionized water) for one week to remove remaining acid and base impurities on the BC surface. This step could control the pH value of BC trend to 7. Finally, the rinsed BC was dried in room temperature overnight, and is stored in a desiccator.

HAP

The HAP, Ca₁₀(PO₄)₆(OH)₂ was made by Alfa Aesar Scientific Co., which contains 34-40% calcium.

Chemicals

Sodium hydroxide (NaOH) and perchloric acid (HClO₄) purchased from Fisher Scientific Co., were used to adjust the pH of the solution. Sodium perchlorate (NaClO₄) purchased from Acros Co., was used to control ionic strength in fluoride solution. Sodium carbonate (Na₂CO₃) purchased from Fisher Scientific Co., was used to measure fluoride concentrations by IC. Sodium fluoride (NaF) purchased from Fisher Scientific
Co., was used to stabilize fluoride concentration. All water used among the whole experimental procedure was de-ionized water.

3.2 Adsorption Experiment

A series of different fluoride solution were prepared by NaF (from 6 mmol/L to 100 mmol/L). Then the appropriate amount of NaClO₄ (10⁻¹, 10⁻² M) was dissolved to control the ionic strength of fluoride solution. Each fluoride solution was separated into 9 centrifuge tubes at 40mL. All the centrifuge tubes had been washed by DI water, and dried in room temperature overnight. To control the final pH values, ranging from 3 to 11, the pH of solution was adjusted by adding HClO₄ and NaOH. after adsorption on time, the final pH was recorded. Then, 0.4 g adsorbent was added (Bone char and HAP) into centrifuge tubes, shaking for 24 hours and record the final pH. Finally, sampling with Nylon syringe filter (0.45μm, dia. 25mm), diluted all fluoride concentration of samples below 1 mM for measuring final fluoride concentration by Ion Chromatography (IC).

For the temperature variation experiment, 0.1g BC or HAP was added in 40 mL of different fluoride solutions. Titrated HClO₄ into solution for control final pH to 3, then put sample into different temperatures (5, 30, 40°C) in the greenhouse. Finally, fluoride concentrations were determined with the same method. The adsorption capacity Γ (mmol/g) was calculated as follows:

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

(3-1)

Where:  
C₀ (mmol/L): the initial fluoride concentration.  
Cₑ (mmol/L): equilibrium fluoride concentration.  
V (ml): the volume of total solution.
m (g): the mass of adsorbent.

### 3.3 Zeta Potential Measurement

To determine zeta potential of BC and HAP, grinding washed BC and HAP into powder particle. Divided the powder into three different NaClO₄ solutions of (1×10⁻¹, 3×10⁻², 1×10⁻² M) respectively. Separate each solution into 9 and titrating pH with HClO₄ and NaOH manually. Afterwards, the centrifuge tubes must shake overnight to get equilibrated. Sampled BC solution into quartz cell which has been washed by ethanol for analysis. The Zetasizer Nono ZS (made from Malvern Co) were used to measure zeta potential.

### 3.4 Surface Characterization

The surface area and pore size analysis were based on Brunauer–Emmett–Teller (BET), measured by Micromertics ASAP200. Before measurement, all sample were evacuated 10⁻⁶ Torr pressure for 2 days to remove the inner water and moisture.

Scanning Electron Microscopy (SEM) was applied for the surface pattern and pore distribution of BC and HAP. Before analysis, BC and HAP were pretreated with gold coated for 90 seconds to remove charge on the surface. Then, scan the surface morphology and structure through SEM equipment (Carl Zeiss Co., Auriga 60).

The Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the function group of the BC and HAP surface. The wavenumber range was from 500 to 4000 cm⁻¹.

X-ray Diffraction (XRD) was used to determine the structure of BC and HAP before and after adsorption. The scanning degree is from 10° to 80° at the increment of 0.05.
X-ray Photoelectron Spectroscopy (XPS) analysis served to prove whether fluoride intake by BC and HAP after adsorption experiment.
Chapter 4

RESULTS AND DISCUSSIONS

4.1 Surface Characterizations

4.1.1 Surface Area and Pore Size

The surface area and pore size of BC and HAP are shown in Table 4.1. Those values are very close to the general surface area in other studies [24]. As the table shows, BC has a larger surface area pore size and higher pore volume than HAP. The carbon content causes of BC to have a larger surface area.

Table 4.1: Surface area and pore size of BC and HAP

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
<th>Average Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>59.62</td>
<td>0.14</td>
<td>9.52</td>
</tr>
<tr>
<td>HAP</td>
<td>45.69</td>
<td>0.11</td>
<td>9.51</td>
</tr>
</tbody>
</table>

4.1.2 SEM Analysis

Morphological analysis by Scanning Electron Microscope (SEM) offers important structure and pore information. SEM images of BC show in Figure 4.1. For Figure 4.1 (a), the original BC surface is disorganized and tough, and shows a lot of macropores. Figures 4.1 (b) and (c) show BC after adsorption with pHf 3 at initial
fluoride concentration 20 mM. There is a closely packed distribution of spheres that, in some cases, cover the pores on the surface. Figure 4.1 (d) shows BC after adsorption with pH$_f$ 11 at initial fluoride concentration 20mM that is different from image of BC in pH$_f$ 3, because the surface is smoother, and does not have many spheres in the pattern. After comparing the final adsorption capacity, BC in pH$_f$ 3 is much higher than BC in pH$_f$ 11. Some component formed in the adsorption procedure results in a greater intake of fluoride onto BC.

Figure 4.2 shows SEM images of HAP surface. Figure 4.2 (a) shows HAP before adsorption. It seems like irregular particles detached. Figures 4.2 (b) and (c) demonstrate the SEM image of HAP with high adsorption capacity. Some irregular detached particles combine to form a larger particle. Micropores on HAP have been covered. Moreover, Figure 4.2 (d) shows the pattern of HAP after adsorption with pH$_f$ 11, which is very similar to Figure 4.2 (a). HAP does not show good performance for fluoride removal at condition. Thus, the difference between HAP pattern before and after adsorption might be related to fluoride removal.

Figure 4.3 shows SEM-EDS analysis result of BC after adsorption. There are still many spheres distributed on the BC surface. The EDX spectrum reveals the constituent of BC by weight percentage. O and C as the central elements, their weight percentage are up to 40.5% and 13.2% respectively. Ca, F and N are also displayed, and their weight percentages are 2.2%, 1.6%, 1.2% respectively. Some mental elements also show on the spectrum, such as Pd, Au, Fe. Comparing the mapping images of the specific portion to SEM image; the F, Ca and O distributions are very similar to the sphere particle distribution. This result indicates the sphere particle on HAP surface might consistent of F, Ca and O.
HAP after adsorption SEM-EDS results are shown in Figure 4.4. The amount of O and C is also higher than other elements. But Ca, P, and Cl EDS mapping agree more with the surface imaging in the case of HAP than in the case of BC. Especially for Ca, which is 3 times higher than Ca on BC. Also, there is not much metal elements found on HAP.

Figure 4.1: SEM image of BC (a) before adsorption, (b) after adsorption $\text{pH}_f = 3$, (c) after adsorption $\text{pH}_f = 3$, (d) after adsorption at $\text{pH}_f = 11$
Figure 4.2: SEM image of HAP (a) before adsorption, (b) after adsorption at $\text{pH}_f = 3$, (c) after adsorption at $\text{pH}_f = 3$, (d) after adsorption at $\text{pH}_f = 11$
Figure 4.3: SEM-EDX spectrum and mapping image of BC after adsorption.
Figure 4.4: SEM-EDX spectrum and mapping image of HAP after adsorption
4.1.3 FTIR Analysis

In general, FTIR spectrums represent hydroxyl, phosphate and carbonate ions on the material [41]. The FTIR spectrum of BC is shown in Figure 4.5 (a), which explains the reaction and surface change of BC before and after adsorption. In this figure, bands emerging at range 550-600, 1016 and 2015 cm⁻¹ indicate PO₄³⁻ presence. Comparing the peak of BC before adsorption, Some of the BC after adsorption peaks are weaker and disappear after adsorption, especially in peak of PO₄³⁻. This fact represents that adsorption process remove PO₄³⁻ from adsorbent surface [42]. Moreover, band 1415 cm⁻¹ arise from lattice carbonate vibrations and fade after adsorption, which indicates partial CO₃²⁻ replaced by PO₄³⁻. According to Joschek et al. reports that the band shown in 3420 cm⁻¹ is the evidence of BC containing water. Further, the lost intensity of OH at 630 cm⁻¹ band after adsorption suggests that hydroxy has been replaced by F⁻ and forming fluorapatite. The adherent water on BC could been represented by peak 3739 cm⁻¹ [43].

Figure 4.5 (b) shows the FTIR spectrum of HAP. The band represented in this figure is very similar to the figure of BC. The band 1427 cm⁻¹ indicates carbonate groups. The intensity bands occur on 560, 1018 and 2100 cm⁻¹ are represented PO₄³⁻. And the peaks of those bands are shorter after adsorption, which indicates the amount of PO₄³⁻ on HAP decreased. The intensity of 962 cm⁻¹ and 3575 cm⁻¹ originated by OH group means HAP lost intensity after adsorption procedure due to ion exchange during HAP crystallization [44].

Through analyzing variation of the peaks between before and after adsorption, the result is corresponding to reactions shown in equations (2-19), (2-20) and (2-21). The chemisorption such as ion exchange might be the main mechanism of fluoride removal by BC and HAP since fluoride concentration ranges from 6 to 60 mM.
Figure 4.5: FTIR spectrum of (a) BC, (b) HAP before and after adsorption. Experimental conditions: [Adsorbent]=10 g/L, pH$_f$ = 3.0, [I] = 10$^{-2}$ M NaClO$_4$, [F$^{-}$] = 20 mM
4.1.4 XRD Analysis

The BC and HAP surface crystal structures are revealed by XRD patterns [45]. Figure 4.6 illustrates the difference in XRD patterns between before and after adsorption. For Figure 4.6 (a) the before BC pattern, the crystalline peaks show in 2θ = 26°, 31°, 39°, 46°, 49°, correspond to the plane (0 0 2), (2 2 1), (-3 8 0), (2 4 2), (-1 6 3), indicate the main component of BC is Ca₅(PO₄)₃OH. For BC after adsorption at initial fluoride concentration 2, 8 and 20 mM, the peak distribution is very similar to BC before adsorption, which suggests that Ca₅(PO₄)₃OH is still a high proportion of BC. Moreover, the peak at 2θ = 28° corresponding to CaF₂ is increasingly clear with initial fluoride concentration increasing. Moreover, the peaks at initial fluoride concentration 60 mM are very different with peaks at lower fluoride intake BC. Two distinct peaks at 2θ = 28° and 47° reflect CaF₂ replaced Ca₅(PO₄)₃OH, and CaF₂ becomes the main component on BC. This result represents that CaF₂ was formed on BC surface at the high concentration of fluoride. Ismail et al. also has similar consequence in his report [39].

Figure 4.6 (b) is the XRD pattern change of HAP. For HAP before adsorption, peaks shown in 2θ = 26°, 31°, 39°, 46°, 49°, are matched thoroughly with Ca₅(PO₄)₃OH pattern, resulting in a single Ca₅(PO₄)₃OH crystalline phase. The HAP patterns at initial fluoride concentration 2, 8, 20 mM are identical to each other. While, the peak shown in 2θ = 28° corresponds to CaF₂ and it rises with fluoride concentration increasing. At initial fluoride 60 mM, this peak totally dominates on HAP, which means the CaF₂ become the main component of HAP. Thus, high concentration of fluoride removal is related to CaF₂ precipitation formation on HAP.
Figure 4.6: The XRD patterns of the (a) BC and (b) HAP before and after adsorption.
Experimental conditions: [Adsorbent]=10 g/L, pH$_f$ = 3.0, [I] = 10$^{-2}$ M NaClO$_4$. [F$^-$] = 2, 8, 20, 60 mM
4.1.5 XPS analysis

XPS is a surface sensitive technique was used to investigate the BC and HAP surface elements, which also offers stochiometric information. Figure 4.7 shows the different XPS spectrum of BC and HAP before and after adsorption. Each peak responds to a certain element. There is a distinct change in the spectrum at the peak of fluoride (F1s) appearing at binding energy 700 eV after adsorption. Further, according to Figure 4.8, the energy value of Ca2p shifts from 347.6 eV to 348.3 eV after adsorption. Another study reveals that, the binding energy 347.6 eV and 348.3 eV indicate Ca on the material surface as Ca_{10}(PO_4)_6(OH)_2 and CaF_2 respectively [46]. Thus, it proves that the Ca_{10}(PO_4)_6(OH)_2 on BC and HAP surface transform into CaF_2 while fluoride has been removed. This reaction represents the core mechanism of BC and HAP for high concentration of fluoride removal is CaF_2 precipitation.
Figure 4.7: XPS survey spectra of (a) BC, (b) HAP before and after adsorption. Experimental conditions: [Adsorbent]=10 g/L, pH_r = 3.0, [I] = 10^{-2} M NaClO_4, [F^-] = 60 mM
Figure 4.8: XPS Ca2p spectrum of the (a) BC and (b) HAP before and after adsorption.
4.1.6 Zeta Potential and Surface Acidity

Depending on the theory and formulas mentioned in Chapter 2.4.3, the surface acidity and intrinsic constant can be determined by calculation [47]. Figure 4.9 is the zeta potential of BC and HAP in different ion strength. As shown in the figure, zeta potential is strongly dependent on pH, and the pH_{zpc} of BC and HAP is 3.5 and 10 respectively. According to Gouy-Chapman theory, the surface potential could be obtained by the following equations [48]:

\[ \ln \tanh \left( \frac{2e\Psi_x}{4k_BT} \right) = \ln \tanh \left( \frac{2e\Psi_o}{4k_BT} \right) - Kx \]  \hspace{1cm} (4-1)

Or

\[ \tanh(9.74\Psi_x) = \tanh(9.74\Psi_o) \exp(-3.28 \times 10^9 \times I^{1/2}) \]

\[ \ln [\tanh(9.74\Psi_x)] = \ln [\tanh(9.74\Psi_o)] - 3.28 \times 10^9 \times I^{1/2} \]  \hspace{1cm} (4-2)

where \( \Psi_x \) and \( \Psi_o \) are the potential (V) at position \( x \) (m) and at surface. \( I \) is ionic strength (10^{-1}, 3\times 10^{-2}, 10^{-2} M NaClO_4), K is the thickness of the electric double layer. By plotting \( I^{1/2} \) as a function of \( \ln [\tanh(9.74\Psi_x)] \), \( \Psi_o \) can be determined.

In addition, relationship of surface charge density (\( \sigma_0 \)) with \( \Psi_o \) can be linearized as:

\[ \sigma_0 = 0.1174 I^{1/2} \sinh \left( \frac{2F\Psi_0}{2RT} \right) \]  \hspace{1cm} (4-3)

The calculation result shown in Figure 4.10.

Based on Boltzman distribution approximation, correcting surface bound proton (\( \{H\} \)) by bulk pH value (\( [H]\)). SOH^{2+}, SOH and SO^{-} are corresponding to positive, neutral and negative surface hydroxy group respectively. When the pH < pK_{a1}^{int}, \( \{SOH^{2+}\} \) dominates and more positive charge shows on the surface. When the pH < pK_{a1}^{int} < pH < pK_{a2}^{int}, \( \{SOH\} \) dominates and material surface shows neutral. When the pH >
p$K_{a2}$, \{SO\’\} dominates and more negative charges show on the surface. The surface charge density and surface acidity constants can be determined by the following equations:

\[
\frac{1}{(H^+)} = \frac{s_T}{K_{a1}^{\text{int}}} \left( \frac{1}{\text{SOH}_2^2} \right) - \frac{1}{K_{a1}^{\text{int}}} \tag{4-5}
\]

\[
\{H^+\} = \frac{s_T}{K_{a2}^{\text{int}}} \left( \frac{1}{\text{SO}^-} \right) - K_{a2}^{\text{int}} \tag{4-6}
\]

Based on Equation (4-5) and (4-6), intrinsic constants $K_{a1}^{\text{int}}$ and $K_{a2}^{\text{int}}$ and total number of surface sites, $S_T$ was calculated. The result are shown in Table 4.2

Furthermore, the intrinsic constant $K_{a1}^{\text{int}}$ and $K_{a2}^{\text{int}}$ could help to access speciation of BC and HAP in different ionic strength, and the results are shown in Figure 4.11 and Figure 4.12.

Table 4.2: BC and HAP intrinsic constants

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pKint</th>
<th>10^{-1} M</th>
<th>3 \times 10^{-2} M</th>
<th>10^{-2} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>$K_{a1}^{\text{int}}$</td>
<td>3.1</td>
<td>3.6</td>
<td>3.1</td>
</tr>
<tr>
<td>BC</td>
<td>$K_{a2}^{\text{int}}$</td>
<td>4.5</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>HAP</td>
<td>$K_{a1}^{\text{int}}$</td>
<td>7.8</td>
<td>9.3</td>
<td>8.9</td>
</tr>
<tr>
<td>HAP</td>
<td>$K_{a2}^{\text{int}}$</td>
<td>10.3</td>
<td>10.7</td>
<td>10.3</td>
</tr>
</tbody>
</table>
Figure 4.9: (a) Zeta potential of BC, (b) Zeta potential of HAP. Experimental conditions: pH$_f$ = 2.0 to 12.0, [I] = 10$^{-1}$, 3x10$^{-2}$ and 10$^{-2}$ M NaClO$_4$
Figure 4.10: (a) Surface potential of HAP, (b) Surface charge of HAP. Experimental conditions: pHf = 2.0 to 12.0, [I] = 10^{-1}, 3 \times 10^{-2} and 10^{-2} M NaClO_4
Figure 4.11: Speciation surface group of BC in different ionic strength. (a) $[I] = 10^{-1}$ NaClO$_4$, (b) $[I] = 3 \times 10^{-2}$ NaClO$_4$, (c) $[I] = 10^{-2}$ NaClO$_4$. 
Figure 4.12: Speciation surface group of HAP in different ionic strength. (a) \([I] = 10^{-1}\) NaClO₄, (b) \([I] = 3 \times 10^{-2}\) NaClO₄, (c) \([I] = 10^{-2}\) NaClO₄.
4.2 Fluoride Removal Experiment

4.2.1 Effect of Solution pH

As Figure 4.13 (a) shows, fluoride removal by BC was strongly affected by solution pH. The adsorption capacity decreases from 2.0 mmol/g at pH 3 to 0.11 mmol/g at pH 11. This result is very similar to Castillo’s study illustrated in his report [36]. Further, with the initial fluoride concentration increasing, the variations trend of capacity is more pronounced. It might be that not a single adsorption mechanism can illustrate fluoride intake by BC.

Figure 4.13 (b) shows fluoride removal by HAP at different pH. For initial fluoride concentration at 6 and 8 mM, there is no difference in adsorption capacity from pH 3 to 7.5. Meanwhile, Figure 4.12 (c) shows positive surface charge decrease through pH from 5 to 10. When the initial fluoride concentrations are 13, 16 and 20 mM, the adsorption capacity declined within pH 4.5 to 11. Same result has been reported by Ruan et al. [49]. Therefore, the mechanism of fluoride removal by HAP is also different in distinct fluoride concentration. In conclusion, the optimum pH for BC and HAP to remove fluoride is 3 or 4. The maximum adsorption capacity is 2.0 mmol/g when the initial F\textsuperscript{-} concentration is 20 mM.

Figure 4.14 shows the pH variation before and after adsorption. For BC and HAP, comparing to before adsorption, the final pH increases when the initial pH ranges from 1 to 10, no pH changes occur during initial pH 10 and 11. This result indicates the hydroxyl on adsorbent was replaced by fluoride in solution, thus the final solution pH increase.
Figure 4.13: Effect of pH on fluoride removal by (a) BC, (b) HAP in different initial fluoride concentration. Experimental conditions: [Adsorbent]=10 g/L, [I] = $10^{-2}$ M NaClO$_4$, [F$^-$] = 6, 8, 13, 16, 20 mM
Figure 4.14: pH variation between before and after adsorption (a) BC (b) HAP. Experimental conditions: [Adsorbent] = 10g/L, [I] = 10^{-2} M NaClO_4, [F^-] = 20 mM
4.2.2 Effect of Adsorbent Dose

Figure 4.15 shows the adsorption capacity is affected by adsorbent dosage. The initial fluoride concentration is 20 mM, the adsorbent dose is from 1 g/L to 10 g/L. As Figure 4.15 (a) shows the BC adsorption capacity increases from adsorbent dose range from 1 g/L to 2 g/L, then it drastically decreases 2 g/L to 10 g/L. The defluoridation capacity increase generates extra adsorption sites, enhancing attractive force between BC and fluoride in solution. While the adsorption capacity decreasing from 2 to 10 g/L might be caused by overlap within BC particles. The interface between BC and fluoride is diminished. Further, BC surface is heterogeneous, all adsorption sites are easier to expose to absorbate and faster to be saturated. Meanwhile, the total percentage of fluoride removal raised and did not reach 100%. It indicates BC adsorption sites are unsaturated, and the growth rate slows down.

Figure 4.15 (b) shows the HAP dose effect on adsorption. The adsorption capacity decreases with HAP dose increase. HAP surface is not homogeneous, the interface between adsorbate and adsorbent is reduced due to overlap. The reduction in capacity results from decrease in the amount of adsorption at the site. From 7.5 to 10 g/L, fluoride removal percentage is about 100%, which implies the adsorption site of HAP has reached saturation, adding extra adsorbent cannot influence total capacity. Thus, adding an appropriate adsorbent quantity improves adsorption efficiency rather than excess quantity.
Figure 4.15: Effect of adsorbent dose on fluoride removal percentage and adsorption capacity. (a) BC, (b) HAP. Experimental conditions: pH$_f$ = 3.0, [I] = $10^{-2}$ M NaClO$_4$, [F$^-$] = 20 mM
4.2.3 Effect of Initial Fluoride Concentration

Figure 4.16 demonstrates the relationship between initial fluoride concentration and adsorption capacity. As the Figure 4.16 (a) shows the adsorption capacity of BC increases from initial fluoride concentrations 6 mM to 160 mM. At pH 3, the maximum adsorption capacity is 9.8 mmol/g.

Figure 4.16 (b) shows HAP adsorption capacity increases with initial fluoride concentration. The maximum adsorption capacity is 12.5 mmol/g at pH 3 when the initial fluoride concentration is 190 mM. Both adsorption capacity of BC and HAP rises faster in lower fluoride concentration and then slows down. Finally, adsorption gets to equilibrium and the isotherm tends to steady at high fluoride concentration.

A study conducted by Liang et al. mentioned that fluoride could precipitate upon reaction with calcium in BC and HAP to form CaF$_2$, which could be an alternative explanation of fluoride removal [30]. In fact, coagulation-precipitation is a conventional method for removing fluoride. In this study, forming CaF$_2$ is investigated as one of the driving forces of fluoride removal. Katagiri et al.[50] illustrates the chemical behavior of fluoride and fluoride-containing species is given by following equations:

\[
[F^-]_T = 2[H_2F_2] + 2[HF_2^-] + [HF] + [F^-] \tag{4-7}
\]

\[
K_{H_2F_2} = \frac{[H_2F_2]}{[HF]^2} = 10^{0.431} \tag{4-8}
\]

\[
K_{HF_2^-} = \frac{[HF][F^-]}{[HF_2^-]} = 10^{-0.598} \tag{4-9}
\]

\[
K_{HF} = \frac{[H^+][F^-]}{[HF]} = 10^{-3.165} \tag{4-10}
\]

Where the $[F^-]_T$ is total fluoride-containing species. Depending on the above equations, the ratio of fluoride-containing species with pH change was calculated. The result is shown in Figure 4.17.
Further, the relationship of CaF$_2$ and Ca$^{2+}$ in fluoride environment is given by following equations [51]:

\[ \text{CaF}_2(S) = Ca^{2+} + 2F^- \quad (4-11) \]

\[ K_{SP} = [Ca^{2+}][F^-]^2 = 10^{-13.35} \quad (4-12) \]

For Ca$_5$(PO$_4$)$_3$OH solubility in solution:

\[ \text{Ca}_5(\text{PO}_4)_3\text{OH} = 5Ca^{2+} + 3PO_4^{3-} + OH^- \quad (4-13) \]

\[ K_{SP} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] = 10^{-57.3} \quad (4-14) \]

In addition, the relationship between phosphate and calcium could be express as:

\[ \frac{[Ca^{2+}]}{[P]_T} = \frac{5}{3} \quad (4-15) \]

The corresponding mass balance are expressed as follows:

\[ [P]_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [P^{3-}] \quad (4-16) \]

\[ [H_3PO_4] = \frac{[H^+]^3}{K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}[H^+] + K_{a1}[H^+]^2 + [H^+]^3} \quad (4-17) \]

\[ [H_2PO_4^-] = \frac{K_{a1}[H^+]^2}{K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}[H^+] + K_{a1}[H^+]^2 + [H^+]^3} \quad (4-18) \]

\[ [HPO_4^{2-}] = \frac{K_{a1}K_{a2}[H^+]}{K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}[H^+] + K_{a1}[H^+]^2 + [H^+]^3} \quad (4-19) \]

According to Liu et al. reported that in the phosphate system, equilibrium constants of $K_{a1}$, $K_{a2}$ and $K_{a3}$ are 10$^{-2.2}$, 10$^{-7.2}$ and 10$^{-12.3}$ respectively [52].

Based on above-mentioned equations, the relationship of Ca$^{2+}$ concentration required for precipitation versus pH is displayed in Figure 4.18. Precipitation will occur in cases above the lane shown in figure, when Ca$^{2+}$ concentration is higher than
solubility limit, in cases below the line, no precipitation will form since Ca\textsuperscript{2+} present is soluble.

CaF\textsubscript{2} precipitation formed on BC and HAP surface could be described as following equation:

\[ Ca_{10}(PO_4)_6(OH)_2(s) + 20F^- = 10CaF_2(s) + 6PO_4^{3-} + 2OH^- \]  \hspace{1cm} (4-20)

The solubility constant (pK\textsubscript{sp}) of above-equation could be obtained from the following equations:

\[ Ca_{10}(PO_4)_6(OH)_2 = 10Ca^{2+} + 6PO_4^{3-} + 2OH^- \quad pK_{sp}^1 = 114.66 \]  \hspace{1cm} (4-21)

\[ Ca^{2+} + 2F^- = CaF_2(s) \quad pK_{sp}^2 = 10.3 \]  \hspace{1cm} (4-22)

\[ pK_{sp}^3 = pK_{sp}^1 + 10pK_{sp}^2 \]  \hspace{1cm} (4-23)

From Equation (4-23), the total pK\textsubscript{sp} of HAP in high fluoride concentration (4-20) is 217.66 [53]. Moreover, depending on Equation (4-28), the negative final $\Delta G^0$ value means this reaction is spontaneous.

In this study, the maximum initial fluoride concentration is 190 mmol/g; while the minimum initial fluoride concentration employed is 6 mmol/g. Figure 4.19 reflects the influence of pH on the equilibrium of calcium dissolution and precipitation with and without fluoride. Based on the Figure 4.19, the boundary of dissolution and precipitation moves down with increasing fluoride concentration, indicating that lower concentration of Ca\textsuperscript{2+} will be required for the precipitation of fluoride. This circumstance symbolizes higher fluoride concentration enhanced CaF\textsubscript{2} precipitation reaction; consequently, this improves the adsorption capacity for the same amount of Ca\textsuperscript{2+} employed. So,
precipitation is regarded as the primary mechanism of high concentration fluoride removal in this study.
Figure 4.16: Adsorption isotherm of fluoride removal by (a) BC, (b) HAP.
Experimental conditions: [Adsorbent] = 10g/L pH<sub>f</sub> = 3.0 to 11.0, [I] = 10^{-2} M NaClO<sub>4</sub>, [F<sup>-</sup>] = 6 to 190 mM
Figure 4.17: The ratio of fluoride-containing species in different pH. $[F_\text{r}]=0.1\text{M}$
Figure 4.18: Effect of pH on equilibrium of $[\text{Ca}^{2+}]$ dissolution/precipitation.

Figure 4.19: Effect of pH on equilibrium of $[\text{Ca}^{2+}]$ dissolution/precipitation with fluoride existence.
4.2.4 Adsorption Isotherm

**Langmuir isotherm**

The Langmuir isotherm is used to depict monolayer adsorption, which can be expressed by the following equation: [55]

\[
\frac{1}{\Gamma} = \frac{1}{\Gamma_{\text{max}}K_L} \cdot \frac{1}{C_F} + \frac{1}{\Gamma_{\text{max}}} \tag{4-24}
\]

Where the \(\Gamma\) (mmol/g) is the amount of adsorbate on adsorbent. \(C_F\) (mmol/L) is the concentration of adsorbate remaining in the solution. \(\Gamma_{\text{max}}\) is the maximum adsorption capacity (mmol/g), and \(K_L\) (L/mmol) is Langmuir constant, which is defined as the affinity between adsorbate and adsorbent [55]. Langmuir isotherm could be formulated as:

\[
\frac{C_F}{\Gamma} = \frac{1}{\Gamma_{\text{max}}K_L} + \frac{C_F}{\Gamma_{\text{max}}} \tag{4-25}
\]

Based on the experimental data, plotting \(C_F/\Gamma\) as function of \(C_F\), the slope is \(1/\Gamma_{\text{max}}\); the intercept is \(1/(\Gamma_{\text{max}}K_L)\). For example, the data of BC and HAP adsorption isotherm at final pH 3 was calculated, Figures 4.20 (a) and (b) show the fitting result of Langmuir isotherm. After acquiring the slope and intercept, \(\Gamma_{\text{max}}\) and \(K_L\) could be obtained easily. For BC, \(\Gamma_{\text{max}}\) is 10.2 mmol/g, \(K_L\) is 0.27 L/mmol. For HAP, \(\Gamma_{\text{max}}\) and \(K_L\) are 12.9 mmol/g and 0.32 L/mmol respectively. Likewise, \(\Gamma_{\text{max}}\) and \(K_L\) of adsorption isotherm of BC and HAP in different final pH could be obtained. The results are shown in Figure 4.21 (a), (b). \(\Gamma_{\text{max}}\) of BC and HAP decrease with pH rise; the highest adsorption capacity of BC and HAP are represented at pH 3, the capacity decrease is very slow when the final pH is between 3 to 5, then it declines intensively from pH 6 to 8. Finally, capacity tends to be stable at the final pH from 8 to 11. The change of \(K_L\) in this adsorption reaction is irregular. For the final pH from 3 to 8, the \(K_L\) is decreasing with pH rise.
However, the $K_L$ have a sudden increase at pH 7 to 8, and then decrease with pH increasing. Finally, all of BC and HAP Langmuir isotherm parameters are shown in Table 4.3 and 4.4. The higher $R^2$ value is means higher dependence.

Table 4.3: Langmuir isotherm parameter for BC adsorption fluoride.

<table>
<thead>
<tr>
<th>pH$_f$</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{max}}$ (mmol/g)</td>
<td>10.235</td>
<td>9.259</td>
<td>10.267</td>
<td>6.035</td>
<td>3.114</td>
<td>0.548</td>
<td>0.377</td>
<td>0.439</td>
<td>0.032</td>
</tr>
<tr>
<td>$K_L$ (L/mmol)</td>
<td>0.279</td>
<td>0.252</td>
<td>0.055</td>
<td>0.037</td>
<td>0.070</td>
<td>0.400</td>
<td>0.328</td>
<td>0.113</td>
<td>0.235</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.994</td>
<td>0.995</td>
<td>0.987</td>
<td>0.932</td>
<td>0.991</td>
<td>0.974</td>
<td>0.916</td>
<td>0.700</td>
<td>0.836</td>
</tr>
</tbody>
</table>

Table 4.4: Langmuir isotherm parameter for HAP adsorption fluoride.

<table>
<thead>
<tr>
<th>pH$_f$</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{max}}$ (mmol/g)</td>
<td>12.903</td>
<td>12.376</td>
<td>12.136</td>
<td>10.384</td>
<td>3.617</td>
<td>1.008</td>
<td>0.840</td>
<td>0.858</td>
<td>0.802</td>
</tr>
<tr>
<td>$K_L$ (L/mmol)</td>
<td>0.328</td>
<td>0.266</td>
<td>0.058</td>
<td>0.065</td>
<td>0.048</td>
<td>0.134</td>
<td>0.124</td>
<td>0.108</td>
<td>0.078</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.978</td>
<td>0.994</td>
<td>0.898</td>
<td>0.972</td>
<td>0.583</td>
<td>0.981</td>
<td>0.957</td>
<td>0.988</td>
<td>0.929</td>
</tr>
</tbody>
</table>
**Freundlich isotherm**

The Freundlich isotherm is an empirical model, which could be used to predict increasing adsorbate adsorbed on the heterogeneous surface when the concentration of solution is increasing [54]. The Freundlich isotherm is described by the following equations:

\[
\Gamma = K_F \cdot C_F^{1/n}
\]

(4-26)

Or

\[
Ln\Gamma = \frac{1}{n} Ln\ C_F + Ln\ K_F
\]

(4-27)

Where the \(\Gamma\) (mmol/g) is the amount of adsorbate capacity. \(C_F\) (mmol/L) is the concentration of adsorbate remaining in solution. \(1/n\) is the Freundlich exponent related to the relevant distribution of energy sites on the surface. The constant value \(K_F\) is related to adsorption capacity. Plotting \(Ln\Gamma\) versus \(Ln\ C_F\), \(1/n\) and \(LnK_F\), are represented as slope and intercept respectively. Further, \(K_F\) and \(n\) could be calculated. The related parameters are represented in Table 4.5 and Table 4.6. the \(1/n\) between 0.1 and 1 indicates the favorable condition of sorption. Further, the \(1/n = 0.501\) implies 50.1% of active sites involved in fluoride removal at the same energy level [56].

According to \(R^2\) in Table 4.3, 4.4, 4.5 and 4.6 shown, it is hard to define exactly which adsorption isotherm is better to BC and HAP for fluoride removal, due to ion exchange and precipitation formation as the major adsorption mechanisms. However, depending on the definition of Langmuir and Freundlich isotherm, Freundlich isotherm indicates decaying on adsorption site energy and the adsorbent surface is heterogeneous.
In conclusion, Freundlich isotherm is more reasonable than Langmuir isotherm to describe fluoride removal at concentration from 6 to 120 mM in this study.

Table 4.5: Freundlich isotherm constant for BC adsorption fluoride.

<table>
<thead>
<tr>
<th>pHf</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_F</td>
<td>1.923</td>
<td>1.724</td>
<td>0.527</td>
<td>0.275</td>
<td>0.242</td>
<td>0.187</td>
<td>0.092</td>
<td>0.124</td>
<td>0.021</td>
</tr>
<tr>
<td>1/n</td>
<td>0.501</td>
<td>0.455</td>
<td>0.719</td>
<td>0.744</td>
<td>0.660</td>
<td>0.424</td>
<td>0.485</td>
<td>0.302</td>
<td>0.656</td>
</tr>
<tr>
<td>R²</td>
<td>0.913</td>
<td>0.944</td>
<td>0.952</td>
<td>0.986</td>
<td>0.943</td>
<td>0.768</td>
<td>0.984</td>
<td>0.995</td>
<td>0.983</td>
</tr>
</tbody>
</table>

Table 4.6: Freundlich isotherm constant for HAP adsorption fluoride.

<table>
<thead>
<tr>
<th>pHf</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_F</td>
<td>2.634</td>
<td>2.247</td>
<td>0.893</td>
<td>0.619</td>
<td>0.377</td>
<td>0.217</td>
<td>0.150</td>
<td>0.126</td>
<td>0.094</td>
</tr>
<tr>
<td>1/n</td>
<td>0.374</td>
<td>0.463</td>
<td>0.581</td>
<td>0.584</td>
<td>0.473</td>
<td>0.396</td>
<td>0.473</td>
<td>0.531</td>
<td>0.559</td>
</tr>
<tr>
<td>R²</td>
<td>0.474</td>
<td>0.879</td>
<td>0.944</td>
<td>0.934</td>
<td>0.859</td>
<td>0.963</td>
<td>0.978</td>
<td>0.994</td>
<td>0.989</td>
</tr>
</tbody>
</table>
Figure 4.20: Process of fitting Langmuir isotherm. (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10g/L pH$_f$ = 3.0, [I] = 10$^{-2}$ M NaClO$_4$, [F$^-$] = 6 to 190 mM
Figure 4.21: (a) BC and HAP Langmuir isotherm $\Gamma_{max}$ (mmol/g). (b) $K_L$ (L/mol)

Experimental conditions: [Adsorbent] = 10g/L $pH_f$ = 3.0 to 11.0, $[I] = 10^{-2}$
M NaClO$_4$, $[F^-] = 6$ to 190 mM
4.2.5 Effect of Temperature

The effect of reaction temperature of fluoride adsorption was obtained by this adsorption experiment at different temperature (5, 20, 30, 40°C). Figure 4.22 shows BC and HAP adsorption capacity variation with temperature. For BC, the adsorption capacity increases slightly with temperature increases and the maximum capacity occurs at 40 °C. In contrast, for HAP, the figure shows that the adsorption capacity is independent to temperature, there is no obvious adsorption capacity difference between four temperature conditions. Therefore, when comparing to BC, the temperature effect on HAP for fluoride removal is limited.

Langmuir isotherm was used to fit the experiment data at various temperatures to determine adsorption free energy [56]. The thermodynamic parameters related to the adsorption procedure are shown in following equations:

\[
\Delta G^o = -2.303RT \log K_L
\]

\[
\log K_L = - \frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R}
\]

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]

Where the \( \Delta G^o \) is Gibbs free energy, \( \Delta H^o \) is enthalpy and \( \Delta S^o \) is entropy. \( K_L \) is the adsorption equilibrium constant. \( R \) is universal gas constant (8.314 J/mol K\(^{-1}\)). \( T \) (K) is the absolute temperature. Plotting \( \log K_L \) versus \( 1/T \), the \( \Delta H^o \) and \( \Delta S^o \) can be determined from the slope and intercept.

Table 4.7 shows relevant thermodynamic parameters of BC and HAP for fluoride adsorption after calculation. Both of the \( \Delta G^o \) values of BC and HAP are negative, which indicates the fluoride adsorption onto BC and HAP is spontaneous. Further, \( \Delta G^o \) values increase with temperature increase; this result proves the
adsorption reaction had a deeper affinity to a higher temperature. The positive values of \( \Delta H^o \) suggests BC and HAP adsorption are endothermic [7]. The positive values of \( \Delta S^o \) indicate randomness increased after the adsorption [31].

From the studies on the effect of thermodynamic factors that affect adsorption (temperature and 4.2.3 initial fluoride concentration), it was found that increasing temperature and F\(^-\) concentrations will improve adsorption rate. If there is need to accelerate adsorption reaction, increasing temperature could be a feasible method.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( \Delta G )(kJ/mol)</th>
<th>( K_L ) (L/mmol)</th>
<th>( \Delta H^o )(kJ/mol)</th>
<th>( \Delta S^o )(J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bone</td>
<td>278</td>
<td>-13.012</td>
<td>0.278</td>
<td></td>
</tr>
<tr>
<td>char</td>
<td>293</td>
<td>-16.991</td>
<td>1.069</td>
<td>26.199</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-17.404</td>
<td>1.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-17.975</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>HAP</td>
<td>278</td>
<td>-14.191</td>
<td>0.464</td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>-14.918</td>
<td>0.456</td>
<td>8.606</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-16.109</td>
<td>0.598</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-17.009</td>
<td>0.689</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.22: Fluoride adsorption at different temperature, (a) BC, (b) HAP.
Experimental conditions: [Adsorbent] = 2.5 g/L pH$_f$ = 3.0, [I] = 10$^{-2}$ M NaClO$_4$, [F$^-$] = 6 to 80 mM
4.2.6 Adsorption Model Fitting

Many concepts have been used to describe fluoride ions adsorption on BC and HAP surface, including adsorption hydrolysis model, the Gouy-Chapman-Stern-Grahame model and ion exchange model [57]. In this study, at low fluoride condition (2 mM), complex formation model is seen as the main mechanism of fluoride removal [58].

For BC, Figure 4.23 (a) shows speciation surface group of BC from pH 3 to pH 10, SOH₂⁺, SOH and SO⁻ distribution. In this experimental pH condition, SO⁻ is the primary surface hydroxyl group. The complex formation is expressed in the following equation:

$$3 < \text{pH} < 10$$

$$SO^- + F^- + H^+ = SOH - F \quad K_{s1} = 10^{12}$$

(4-31)

Where $K_{s1}$ is the stability constant. This equation illustrates the complex SOH formation with H⁺ releasing at pH < 10, which is corresponding to Figure 4.23 (c) shows the final pH of adsorption is higher than the control group. Figure 4.24 (b) shows the calculation of SOH-F complex and experimental result, tendency of two line is further prove such complex helps fluoride intake.

For HAP, Figure 4.24 shows the adsorption model fitting of HAP results. Figure 4.24 (a) presents that SOH₂⁺ and SOH are the main species on HAP surface from pH 3 to pH 11. Based upon the results shown in Figure 4.24 (b), and the total adsorbed fluoride is steady from pH 3 to 7 and decreasing from pH 7 to 11. As Hao et al. reported in his study [59], the adsorption model could be represented by follow equations:

$$3 < \text{pH} < 8$$

$$SOH_2^+ + F^- = SOH_2 - F \quad K_{s1} = 10^{5.4}$$

(4-32)

pH > 8
\[ SOH + F^- = SOH - F \quad K_{s2} = 10^{3.6} \] (4-33)

When pH < 8, abundant SOH$_2^+$ indicates positive charge on HAP surface attract negative ion fluoride through electrostatic interaction. At pH > 8, fluoride removal is attributed to SOH-F formation. Figure 4.25 (c) shows that pH variation of control and experimental are close to each other, which indicates no H$^+$ and OH$^-$ release or intake during adsorption procedure. It is evidence that fitting models described by Equation (4-32) and (4-33) are reasonable.
Figure 4.23: Adsorption model fitting of BC. Experimental conditions: [Adsorbent] = 10 g/L, pH<sub>f</sub> = 3.0 to 10.0, [I] = 10<sup>-2</sup> M NaClO<sub>4</sub>, [F<sup>-</sup>] = 2 mM
Figure 4.2: Adsorption model fitting of HAP. Experimental conditions: [Adsorbent] = 10 g/L pH \( f \) = 3.0 to 10.0, [I] = 10\(^{-2}\) M NaClO\(_4\), [F\(^-\)] = 2 mM
4.2.7 Effect of Ionic Strength

In order to investigate the effect of ionic strength in fluoride removal with BC and HAP, NaClO$_4$ was used to control the ionic strength in the fluoride solution. The initial fluoride concentration was 2 mmol/L at pH 3 to 10. Figure 4.25 shows the result of adsorption capacity of BC and HAP. For BC, there is not much difference of adsorption capacity between $10^{-1}$ and $10^{-2}$ M NaClO$_4$. Applying the calculation method for $K_{s1}$ to BC as represented in Equation (4-30), the $K_{s1}$ of BC at $10^{-1}$ M NaClO$_4$ is $10^{12.4}$, which is equal to $K_{s1}$ at $10^{-2}$ M NaClO$_4$. Therefore, NaClO$_4$ could not influence fluoride removal by BC at 2 mM fluoride concentration.

Figure 4.25 (b) represents the effect of NaClO$_4$ for HAP to adsorb fluoride. There is no noticeable adsorption capacity difference between $10^{-1}$ and $10^{-2}$ NaClO$_4$. The HAP surface shows positive and neutral site from pH 3 to pH 10 on Figure 4.10 (c). Likewise, in Equation (4-32) and (4-33) the adsorption model was calculated. $K_{s1}$ and $K_{s2}$ of $10^{-1}$ NaClO$_4$ is 5.5 and 3.2 respectively, which is very close to K values of $10^{-2}$ NaClO$_4$. So that NaClO$_4$ cannot change the adsorption capacity of HAP to fluoride.

In utilizing NaClO$_4$ to study the effect of ionic strength on the adsorption capacity, this research shows that ionic strength in the solution does not significantly impact the adsorption capacity of BC and HAP.
Figure 4.25: Effect of ionic strength on fluoride removal and adsorption capacity. (a) BC, (b) HAP. Experimental conditions: [Adsorbent] = 10 g/L pH\(_f\) = 3.0 to 11.0, [I] = 10\(^{-1}\) and 10\(^{-2}\) M NaClO\(_4\) [F\(^-\)] = 2 mM
4.2.8 Adsorption Mechanism

The adsorption mechanism of BC and HAP is dependent on the initial fluoride concentration ($C_o$). For both adsorbents, three adsorption mechanisms become dominant at different fluoride concentrations. For BC, when the initial fluoride concentration is 2 mM, the adsorption mechanism is a complex formation on the surface-active site of BC with fluoride protons present in solution (Figure 4.23). At $C_o$ from 6 to 60 mM, ion exchanges lead to fluoride removal. This is evidenced by the fading of the OH$^-$ band on BC FTIR pattern (Figure 4.5), which indicate the hydroxy bonds replaced by F$^-$. Furthermore, variation between initial solution pH$_i$ and final pH$_f$ reflects hydroxy leaking into the solution due to ion exchange reaction. At $C_o$ over 60 mM, fluoride removal by BC is not only attributed to ion exchange but also precipitation of CaF$_2$ (Equation 2-23). This conclusion is reflected in XRD and XPS patterns (Figure 4.6 and Figure 4.7), and very close to what Liang et al. reported [30].

For HAP at 2 mM $C_o$, electrostatic interactions between positive HAP surface and negative fluoride result in the adsorption of fluoride on HAP. At higher concentrations fluoride adsorption on HAP follows similar mechanisms to that of BC. At $C_o$ from 6 to 60 mM, FTIR pattern (Figure 4.5) proves ion exchange between -OH on HAP surface and aquatic F$^-$ as the main mechanism of adsorption. And for $C_o$ over 60 mM, XRD and XPS patterns (Figure 4.6 and Figure 4.7) show the CaF$_2$ formation, which indicates fluoride removal by precipitation.
Chapter 5
CONCLUSIONS

Based on the findings from this study, both BC and HAP show high adsorption capacity to remove fluoride from water. The specific surface area of BC and HAP are 49.62 and 45.69 m²/g respectively. Also, the total pore volume and average pore size of BC and HAP are very close. SEM and SEM-EDX represent BC and HAP surface structure and element ingredients. The pH_{zpc} of BC and HAP are 3.5 and 10 respectively at 10⁻² NaClO₄.

For this adsorption experiment, the maximum of adsorption capacity of BC and HAP is 10.23 and 12.90 mmol/g respectively, which is about 10 times higher than another active carbon [58]. Further, several factors affecting adsorption capacity have been discussed in this study. For BC, the adsorption capacity increases with increases in reaction temperature. But the temperature cannot affect fluoride removal by HAP. Both of BC and HAP has better performance in low pH condition and high initial fluoride concentration. The best adsorbent doses for BC and HAP are 2 g/L and 1 g/L respectively. Moreover, it was found that variation of ionic strength of the solution by changing NaClO₄ does not affect fluoride removal efficiency.

The XRD, XPS and FTIR analysis results prove that both BC and HAP adsorption mechanism change with the initial fluoride concentration. The dominant mechanism for BC from low to high initial F⁻ concentration are complex formation, ion exchange and CaF₂ precipitation. The dominant mechanism for HAP from low to high
initial $F^-$ concentration are electrostatic interactions, ion exchange and CaF$_2$ precipitation.

The adsorption data agrees with the Langmuir and Freundlich isotherm models. Negative values of $\Delta G$ and positive $\Delta H$ indicate this adsorption reaction is spontaneous and endothermic.
REFERENCES


