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Removal of Chromium(VI) and Chromium(III) Ions from Aqueous Solution Using Bio-char Generated from Agricultural Waste Products

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REMOVAL OF CHROMIUM(VI) AND CHROMIUM(III) IONS FROM AQUEOUS SOLUTION USING BIO-CHAR GENERATED FROM AGRICULTURAL WASTE PRODUCTS

A Thesis

by

DIEGO FERNANDO GONZALEZ

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ABSTRACT

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Heavy metals are one of the most persistent and prevalent contaminants in the aquatic environment. Their removal of chromium from aqueous solution, especially in the hexavalent form is difficult. New technologies, techniques and/or new materials have been designed in order to effectively and efficiently remove chromium from the aqueous environment. This project focuses on the comparison of the effects of pH, time, temperature, binding capacity on biochar generated from agricultural waste produces vs an amino modified derivative of the biochar. Pineapple skins were dried, ground, sieved, and pyrolyzed to produce a biochar material. The biochar was analyzed using FTIR to help characterize the potential binding groups on the biochar. The batch studies, including pH, kinetics, isothermal, and interference; showed new precedence of binding activity that was of particular interested in comparison to previous binding trends observed previously in literature.

DEDICATION

The completion of this thesis could not have been possible without the emotional and financial support of my family. My father, Esteban Alejandro Gonzalez, my mother, Consuelo Camarillo de Gonzalez, and my brother, Cesar Alejandro Gonzalez, who inspired me to keep pushing forward even when I felt the insurmountable weight of classes, exams, and deadlines. I would also like to dedicate this thesis to my partner, Erika Martinez Trejo, her love and support of my dreams has been unending.

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CHAPTER I

BACKGROUND

Pollution of freshwater sources

Freshwater is essential to all forms of life and is perhaps one of the most precious resources on the planet for the proliferation of living things. According to the United States Geological Survey only 2.5% of the earth's total water is considered fresh water. Of the 2.5% freshwater on the earth approximately 1.2% of the freshwater is surface water, which all living things depend on for survival [1]. These percentages of fresh water and surface water are relatively stable through the water cycle; however, different factors contribute to the reduction of clean freshwater sources. These factors include the following: over consumption, climate change, and the contamination of water sources. Water contaminates include chemical contaminates such as inorganic salts, organic species, radioactive species, as well as Biological contaminates such as bacteria or viruses.

Heavy metals and their inorganic salts have been regarded as one of the more challenging types of contamination to remove from water. Heavy metals originate primarily from anthropogenic processes such as manufacturing and industrial activity. More specifically, chromium contamination of water originates from manufacturing processes such as producing chrome plating, dyes, pigments, leather tanning, and wood preservatives [2-4]. Heavy metal contaminates, such as chromium, are a major concern to the aquatic environment and in general

to both environmental and human health. Heavy metal contamination of the aqueous environment has increasingly occurred over the past few decades through global industrialization. Scholars such as Forstner and Wittman have claimed that following the industrial revolution "the efforts of removing man-made pollutants…have been unable to keep pace with the increasing amount of waste materials…" [4]. Combined with a steady growth in population there will continue to be an ever increasing demand for methods of water remediation and purification.

Within the past century, the U.S. Government has passed laws and regulatory acts in an attempt to curb and to reduce the environmental and human health effects of water pollution. These acts include the Water Act of 1912, Water Pollution Control Act of 1940. In addition, the U.S. formed the Environmental Protection Agency (EPA) in 1970, which lead to the development of the Clean Water Act of 1972, and the Safe Drinking Water Act 1974. These laws set standards for water and waste treatment. Governmental organizations such as the EPA have developed maximum contaminate levels (MCLs) for chemical pollutants present in potable water.

Heavy Metal ions and their effects

There are five traditionally known endocrine disrupting chemicals (EDCs) which are metals and one semimetal the EDCs include arsenic, cadmium, lead, mercury, and uranium [5]. More recently, manganese and zinc have been added to the list of metals that are known as EDCs [6]. In addition, many metal ions are known as carcinogenic compounds these metals include cadmium, arsenic, and chromium. The United States Environmental Protection Agency has set a

total (accounting for both Cr (III) and Cr (VI) oxidation states) chromium MCL of 100 µg/L for drinking water [7].

Chromium is found within the environment primarily in two oxidation states, which are trivalent chromium (Cr III) and hexavalent Chromium (Cr VI) [2, 8-13]. It is well known that Cr(III) is far less toxic than Cr(VI). In fact, Cr(III) is essential for natural human processes and human health. Chromium(III) is utilized in the body for the processing of sugars, proteins, fat metabolism, as well Cr(III) and plays a dietary role at low concentrations (µg/L) [2, 10, 12, 13]. On the other hand Cr(VI) has been shown to have no biological function and is in fact a carcinogen primarily affecting the lungs. Chromium, in the hexavalent oxidation state, is generally not naturally found and is generated primarily from industrial processes. The conversion of minerals into refined metals and composites has given mankind opportunities to produce different materials and devices; from chrome plated parts on automobiles to electronic equipment such as cell phones [8, 10, 12]. With the advent of these technologies and devices there has been a steady increase of chemical waste from their manufacturing, and their usage. Table 1 shows some of the metal contaminates normally found in water, their MCLs, their possible health effects from long term exposure, and their potential sources.

Contaminate	MCL or TT [mg/L]	Potential Health Effects from long term exposure	Sources of Contaminate in drinking water
Arsenic	0.01	Skin manifestations, visceral cancers, vascular disease, circulatory system, increase risk of cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes
Cadmium	0.005	Kidney damage, renal disorders, carcinogenic	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (Total)	0.1	Dermatitis, Headache, diarrhea, nausea, vomiting, carcinogenic	Discharge from steel and pulp mills; erosion of natural deposits
Copper	1.3	Gastrointestinal distress, Liver damage, Wilson disease, insomnia	Corrosion of household plumbing systems; erosion of natural deposits
Nickel	0.2	Dermatitis, nausea, chronic asthma, coughing, carcinogen	Batteries, erosion of natural deposits, steel piping, electroplating, catalyst production
Lead	0.015	Damage to fetal brain, kidney disease, circulatory system, nervous system	Corrosion of household plumbing systems; erosion of natural deposits
Mercury	0.002	Rheumatoid arthritis, kidney disease, circulatory system, nervous system	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Selenium	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines

Table 1: Heavy metal contaminates, their MCL Limits, health effects, and Sources [7].

Water Remediation Methods

With the ever-increasing amounts of pollutants in waters, there is an inherent need to invent or further develop techniques and/or methods of removing the contaminates generated from various industrial processes. A recent review, by Azimi et. al., details a vast number of methods for the remediation of metals in waters [14]. These remediation methods include the following techniques: adsorption, chemical precipitation, membrane filtration, ion exchange,

electrocoagulation, electroflotation, electrodeposition, photocatalytic, and nanotechnology. Many of these methods are not effective due to various limitations such as the production costs, production of waste byproduct, the need for pre/post water treatment, and large startup costs [14]. However, adsorption technology has shown much promise in the area of water treatment/ remediation. The method adsorption is based on the use of an absorbent, which is a material with a large surface area that can transfer pollutants between the liquid and solid phases via surface adhesion, encapsulation, or chemical binding. Chemical precipitation methods are performed by adding chemicals to waste waters to reduce metal ions to an acceptable limit for discharge. Alternatively chemical precipitation changes soluble particles into insoluble particles and forces pollutants to precipitate out of solution where they can be filtered out. Precipitation, technology often fails to remove trace level pollutants completely and requires large amounts of chemicals to be added to remove trace amounts; which in turn leads to further purification, of the newly treated water and higher operating costs [14-16]. Membrane filtration works by flowing contaminated water through semi-permeable membranes which have different size pores. Membrane technology has been used by the food and beverage industry and is commonly known as reverse osmosis [14, 16]. Ion exchange works via resins and is based on a reversible interchange of ions between solid and liquid phases. As mentioned earlier adsorption technology has shown much promise in recent years. Adsorption or sorption of Cr(III) and Cr(VI) is the focus of the present study. The sorption process occurs through one of three types of processes which include: chemisorption, physisorption, and/or ion exchange. The aforementioned types of sorption are based on the material's chemical and are determined through the thermodynamic processes between the adsorbent and adsorbent.

CHAPTER II

INTRODUCTION

Proposed Biochar Absorbent Materials

The material chosen was based on three main criteria, reduction of the overall waste from sourcing the material, low relative production cost, and the availability of the source. Based on the aforementioned criteria, several raw materials were considered which included grass clippings, corn cob, corn husks, pineapple cores, pineapple tops, and pineapple skins. All the raw materials was sourced locally and provided potential raw material candidates. Agricultural by-products were chosen as source materials based on the production and processing of biochar sorbent that can be derived from the waste biomass or the availability of the by-products. Pineapple skins were ultimately chosen, as the starting raw biomaterial, due to its moderately high waste to fruit-product ratio, due to the processed used in the production of products from pineapples. In addition, there was a relative ease of processing, and uniform production of waste from pineapple skins which also contributed to its selection as a biomaterial candidate. A limited amount of waste is produced from the production of the biochar material which can be collected and repurposed for other applications in energy production and fuels. The main objective of the present study was to successfully produced and chemically functionalize the surface of the biochar material, and measure the affinity for Cr (VI) and Cr(III) ions in solution. Other studies have successfully produced biochar and have shown the removal capacity of heavy metal ions from solution. However, many of these studies do not explore the

potential of surface modification of biochar to enhance the binding capacity and efficiency.[3, 8, 10, 17-21]. The primary objective for the nitration and subsequent amination of biochar was to increase the affinity of the biochar for chromium ions. In particular increasing the affinity of Cr(VI) to the biochar. In addition, creating a higher affinity for Cr(VI) ions indicates that creating a functionalized surface can maintain preferential binding with Cr(VI) while in the presence of interfering ions. Through successful amination of biochar materials would increase the promise of these materials functioning in high solute matrices such as sea water and among other high polluted matrices. Traditionally acids such as Nitric, Sulfuric, and Phosphoric acid have been utilized to oxidize the surface of the biochar to prepare the surface for chemical functionalization and produce what is known as Activated Carbon [22]. The problems associated with blanketed oxidation primarily is the lack of specificity or selectivity with heavily contaminated solutions or a loss in the selectivity of heavy metals compared to other ions is decreased. Subsequent to the production of the amino modified material, both the native and modified biochar was analyzed using spectroscopic techniques, which included Fourier Transform infrared spectroscopy and energy dispersive spectroscopy. The spectroscopic data indicates that the surface functionalization of the biochar that was successfully achieved. Batch studies which included the effects of pH, binding capacity, thermodynamic parameters, as well as investigating the effects of interferences were performed to provide further chemical information and material properties of the native and amino modified biochars. The subsequent results detail the material properties and outcomes from these batch studies.

CHAPTER III

MATERIALS AND METHODS

Synthesis of Native Biochar

To prepare the biochar for reaction and testing, the method listed below was followed. Pineapples, sourced locally, were washed, cut, and separated into their respective parts. The skins of the pineapples were placed in a Pyrex glass dish and left to dry in an oven at 65°C, under air, until the biomass was completely dry (approximately 1 week). Subsequent to drying the pineapple skins were ground into a fine powder the obtained powder was sieved to pass through a 125 microns sieve. The sieved powder was then placed in a ceramic crucible and heated in a tube furnace under an argon atmosphere and heated to 350°C from room temperature. Once the sample reached 350°C the sample was held at a constant temperature for 1 hour. After the sample was cooled to room temperature the Biochar was ground again with a mortar and pestle and weighed for a product yield.

Amino Modification of Biochar

Chemical modification of biochar was performed to determine if modification of the surface groups would enhance or change the sorption properties of the Biochar. The amino modified biochar was performed using a method similar to Yang et. al., 2014 [23]. In brief the method of modification is described as follows. In a 250ml-round bottom flask, 100ml of a 50:50 mixture of HNO_3/H_2SO_4 acids and magnetic stir bar were added. The flask was placed on an ice-water bath to cool the mixture to between 0 and 4°C. To the cooled mixture of acids, 6.0

grams of previously synthesized biochar was added and the mixture was stirred for 2 hours. This process should have resulted in the nitration of the surface groups on the biochar. After nitration, the reaction was cooled to room temperature and the product was separated using vacuum filtration with a fritted glass funnel and washed with several portions of water and isopropanol. The isolated powder was dried overnight at 50□ to remove residual moisture. The nitrated biochar was then placed into a clean three-neck round bottom flask with a magnetic stir bar and 50mL of deionized water was added, which was followed by the addition of 20mL of 15 M ammonium hydroxide. The reaction was homogenized by stirring for 15 minutes. Subsequent to homogenization 28g of $Na_2S_2O_4$ was added to the mixture and stirred for an additional 24 hours. Once the reaction time was reached a 120mL aliquot of 2.9 M glacial acetic acid was added to the flask followed by a 5 hour reflux at 100□. The sample was then cooled to room temperature and the product was collected through vacuum filtration. The amino modified biochar was then dried overnight at 50□.

FTIR-ATR Analysis

FTIR spectra were collected using a Perkin Elmer Frontier FTIR equipped with a UTAR (Universal Total Attenuated Reflection) attachment. The FTIR spectrum were collected from 600 cm^{-1} to 4000 cm^{-1} with a resolution of 4.0 cm^{-1}.

SEM/EDS Analysis

SEM data were collected using a Zeiss LS10 EVO SEM microscope equipped with an EDAX EDS detector. The SEM were collected using a working voltage of 20kV, an operating current of 2.5A. As well the working distances of the SEM ranged from 6.0 mm to 4.5mm for the low and high magnification micrographs, respectively. The EDS data were collected using an operating voltage of 20kV at a working distance of 8.0, the optimum working distance

determined from the SEM-EDS setup. Furthermore, the samples were sputter coated using an Au-Pd target to enhance sample conductivity to improve the image quality.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) Analysis

All samples obtained from the aqueous reactions, which included pH, time dependency, thermodynamics, and binding interference studies were analyzed using a Perkin Elmer Optima 8300 DV ICP-OES. Table 2 details the instrumentation parameters used during sample analysis.

Parameter	Setting
λ	267.16 nm
RF power	1500 W
Nebulizer	Gemcone (low flow)
Plasma Flow	15 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.55 L/min
Sample Flow	1.50 mL/min
Injector	2.0 mm Alumina
Spray Chamber	Cyclonic
Integration Time	20 seconds
Replicates	3

Table 2: ICP-OES operating parameters for the determination of Cr in solution.

Optimal pH Determination

The effect of pH on the binding for both Cr(III) and Cr(VI) to the native and amino modified Biochars were tested from pH 2 to pH 5. Solution containing 300 ppb of either Cr(III) or Cr(VI) were pH adjusted using dilute nitric acid or sodium hydroxide solutions. In the reactions 4.0 mL aliquots of the pH adjusted Cr solutions were added to clean 5 mL test tube, which contained 10 mg of the Biochar material. Control samples consisted of either the pH adjusted Cr(III) or Cr(VI) ions at a concentration of 300 ppb. The control samples were prepared and treated similarly to the reaction samples. For statistical purposes, the controls and samples reactions were replicated in triplicate. The reaction samples and control solutions were capped placed on a bench rocker and equilibrated for an hour at room temperature. Subsequent to equilibration, the samples and the controls were centrifuged for 5 minutes at 3,600 rpm and the supernatants were decanted and saved for analysis using ICP-OES.

Time dependency studies

Studies were performed at different time intervals and temperatures to determine the amount of time required for the binding to occur and to determine the stability of the Cr(III) and Cr(VI) ions to the native an amino modified biochar materials. The reactions were performed using a 30 ppm solution of either Cr(III) or Cr(VI) as well as at the optimum binding pH as determined from the pH study. The pH of the Cr(III) and Cr(VI) solution were adjusted to the optimum binding solution using either dilute nitric acid or sodium hydroxide. 4.0 mL aliquots of either pH adjusted Cr(III) or Cr(VI) solutions were extracted and added to clean 5.0 mL tubes, which containing 10 mg of either the native or amino modified biochar material. Furthermore, control samples, which contained only the pH adjusted Cr solutions, were treated similarly to the samples. For statistical quality control/quality assurance purposes, the study was performed in

triplicate. The samples and controls were placed on bench rockers and equilibrated at temperatures of 4°C, 25°C, and 45°C and equilibrated on rockers for the following time intervals: 5,10,15,30,60,90, 120 min. Subsequent to equilibration, the samples and controls were centrifuged at 3,600 rpm for 5 minutes and the supernatants were decanted and saved for analysis using ICP-OES.

Thermodynamic studies

Isotherm studies were performed to obtain the thermodynamic properties of Cr(III) and Cr(VI) binding to the native and amino modified biochar materials. 10 mg of native biochar was added to a 5 mL test tube and a 4.0 mL aliquot of either Cr(III) at pH 4 or Cr(VI) at pH 2 was added. The concentration of the chromium ions were varied to the following concentrations: 0.3, 3.0, 30.0, 90.0 300, and 1000 ppm. Furthermore, control samples, which consisted of either the pH adjusted Cr(VI) or pH adjusted Cr(III) ions and no biochar, were prepared in triplicated at each of the afore mentioned concentrations. The samples and controls were capped, placed on a bench rocker and equilibrated for 1 hour. Subsequent to equilibration the samples and controls were centrifuged at 3,500 rpm for 5 minutes, the supernatants were decanted and saved for analysis using ICP-OES. In addition, these reactions were performed at three temperatures, which were 4.0 ˚C, 21˚C and 45˚C, to determine the thermodynamic variables of the binding process. The same process was performed for the amino modified biochar for comparative purposes of properties of both biochar materials.

Binding Interference studies

The effects of the presence of secondary ions on the binding of Cr(III) to the native and modified biochar was determined by spiking 0.3 ppm, 3 ppm, 30 ppm, 300 ppm, and 3000 ppm solutions of Na^+, K^+, Ca^{2+}, or Mg^{2+} with a Cr(III) concentration of 0.3 ppm. These solutions

were then pH adjusted to optimum binding pH. 4 mL aliquots were placed into 5 mL test tubes containing 10 mg of native or modified biochar. In addition, 4 mL aliquots were also poured into test tubes without biochar to server as controls. Test tubes were capped and equilibrated for 1 h at room temperature. After the 1 h equilibration the test tubes were centrifuged for 5 min at 3,500 rpm, the supernatants were decanted and saved for ICP-OES analysis. The reaction procedure was also repeated with solutions that contained a combination of Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} each at the afore mentioned concentrations. The effects of the presence of interference by the presence of secondary ions on the binding of Cr(VI) to the native and modified biochar was determined using anionic species. 0.300 ppm Cr(VI) solutions were spiked with 0.3 ppm, 3 ppm, 30 ppm, 300 ppm, and 3000 ppm solutions of Cl^{-}, NO_3^{2-}, SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}, or CO_3^{2-} ions. These solutions were pH adjusted to the optimum binding pH and 4 mL aliquots were added to 5 mL test tubes which contained 10 mg of either the native or amino modified biochar. In addition, 4 mL aliquots were also added to empty test tubes to, which served as reaction controls. The test tubes were capped and equilibrated on a rocker for 1 h. After the 1 h equilibration the test tubes were centrifuged for 5 min at 3,500 rpm and the supernatants were decanted and saved for analysis using ICP-OES. This procedure was repeated with solutions that contained combined Cl^{-}, NO_3^{2-}, SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}, and CO_3^{2-} to observe the effects of combined anion interferences on the binding of Cr(VI). All reaction samples and controls were performed in triplicate for statistical as well as quality assurance and quality control purposes.

CHAPTER IV

RESULTS

FTIR-ATR Analysis

Following the production of biochar and chemical modification to generate amino surface modified biochar, Fourier Transform Infrared Spectroscopy (FTIR) with an Attenuated Total Reflectance (ATR) attachment was utilized to characterize the chemical modification of the biochar materials. Figures 1 and 2 show FTIR spectra collected on the native and chemically modified biochar, respectively. The functional groups on the materials show different stretches in the FTIR spectrum. The stretches of interest observed in the native biochar were as follows: 760 C-H (Bending), 1110 C-O (Stretch), 1370 N-O (Stretch), 1435 O-H (Bending), 1575 C=C/N-O (Bending), 1980 C-H (Bending), 2165 CN, and 2930 C-H (Stretch). The observed stretches observed in the FTIR of the amino modified biochar are as follows: 1040 C-N (Stretch), 1180 C-O (Stretch), 1370 S=O (Stretch), 1430 O-H (Bending), and 1590 C=C/N-H (Bending). The visual differences in 1000-1100 cm^{-1} and the 1500-1600 cm^{-1} show that the functional groups observed are different in intensity and peak shape indicating that the intended modification achieved was achieved [23, 24].

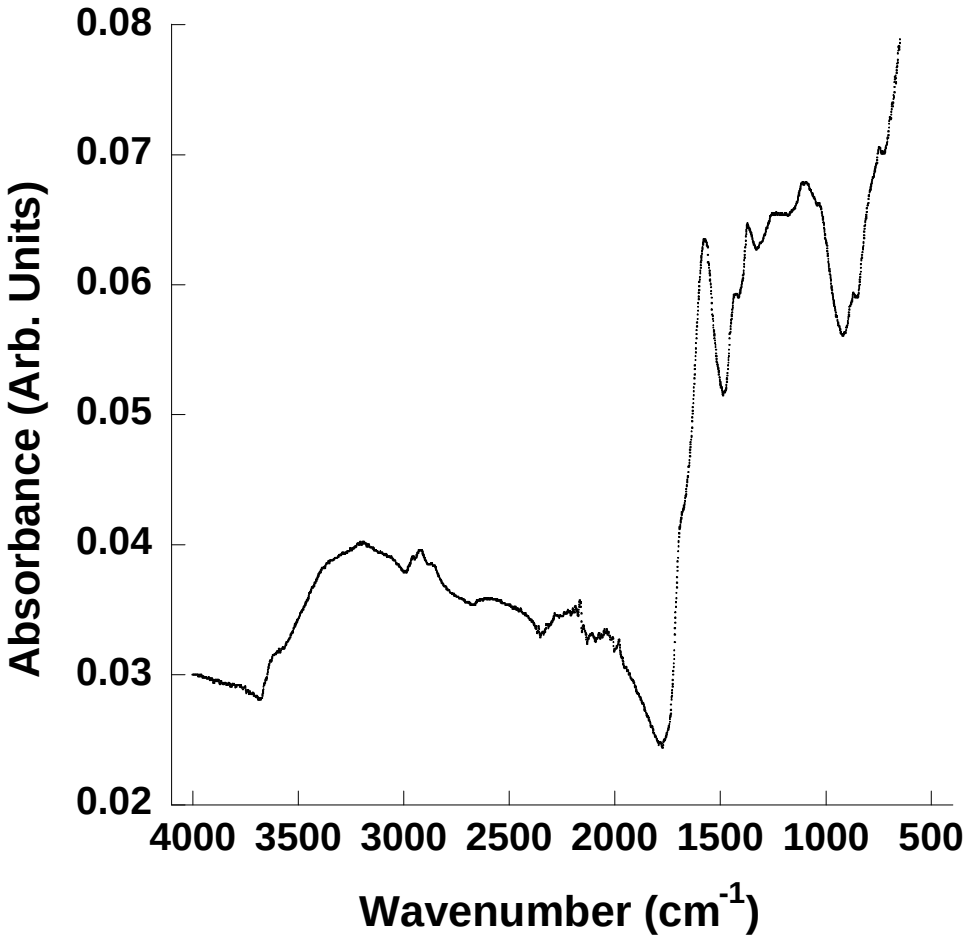

Figure 1: FTIR-ATR of Native Biochar

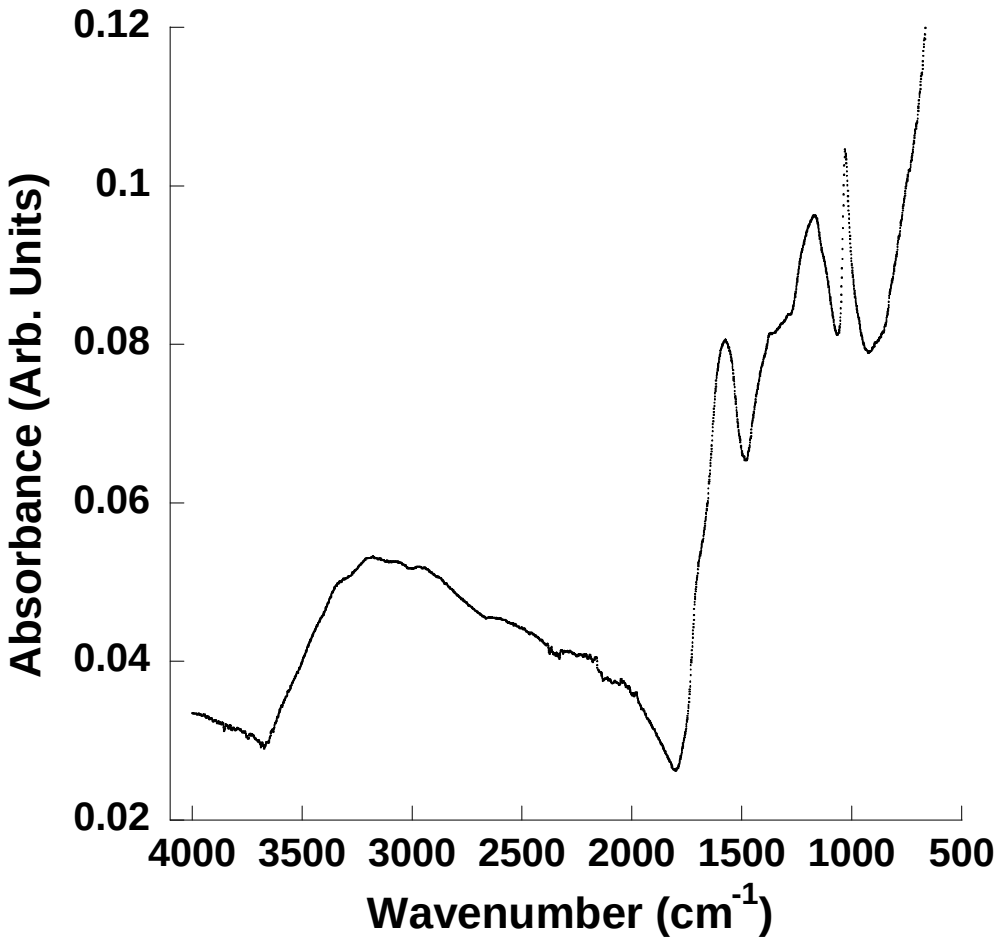

Figure 2: FTIR-ATR of Amino Modified Biochar

SEM Imaging and Analysis

SEM Imaging was also performed to investigate the morphology of the produced biochar materials. The morphology shown in the SEM images indicates that the pineapple skin, used to produce the biochar materials, maintains its cellular structure as can be seen in Figures 3, 4, and 5. These porous tubular structures may play a role in increased surface area binding and porosity.

The SEM also indicates that the Biochar material lacks in crystallinity and has an amorphous structure such as is observed with activated carbon or carbon black materials [25-27].

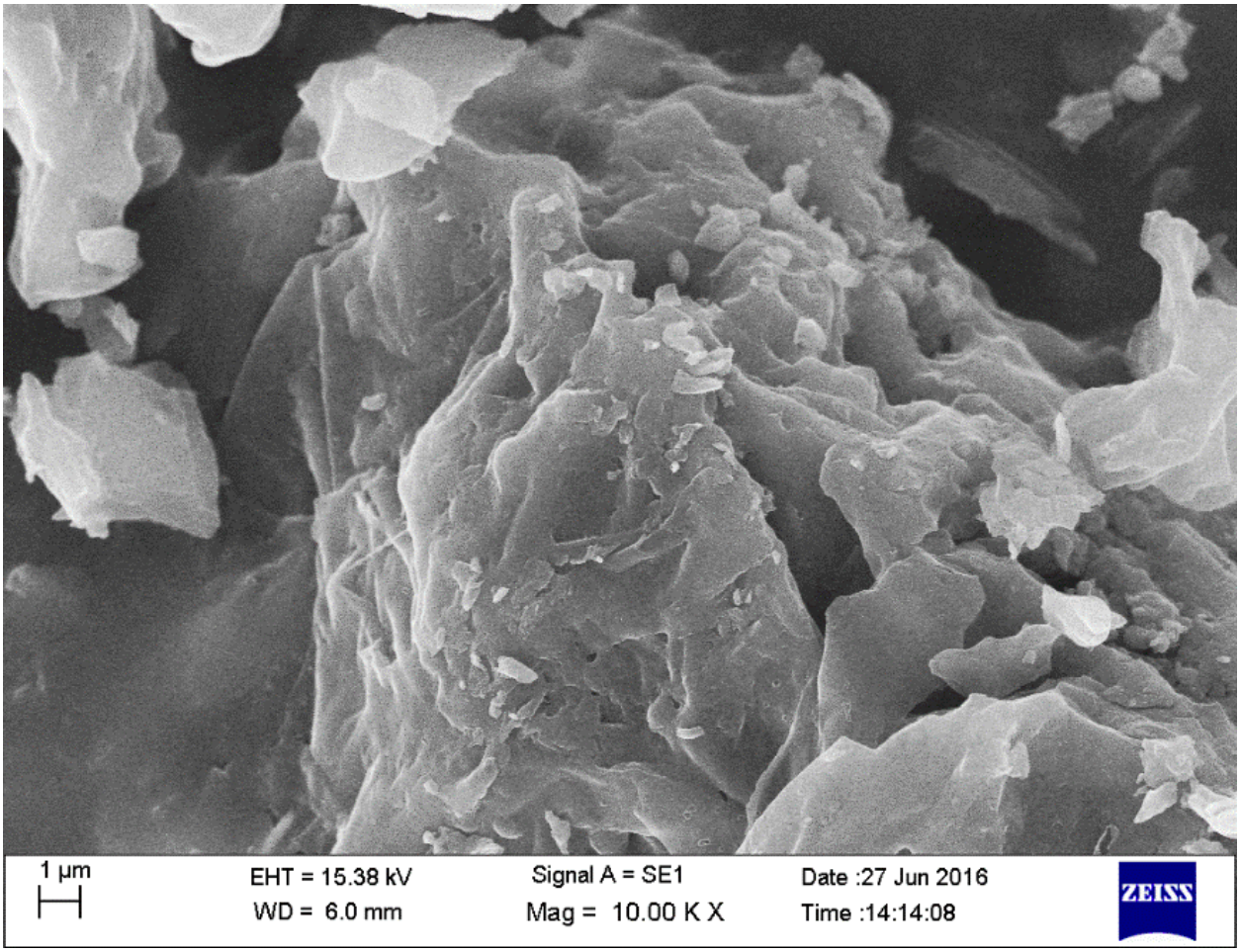

Figure 3: SEM Imaging of Native Biochar

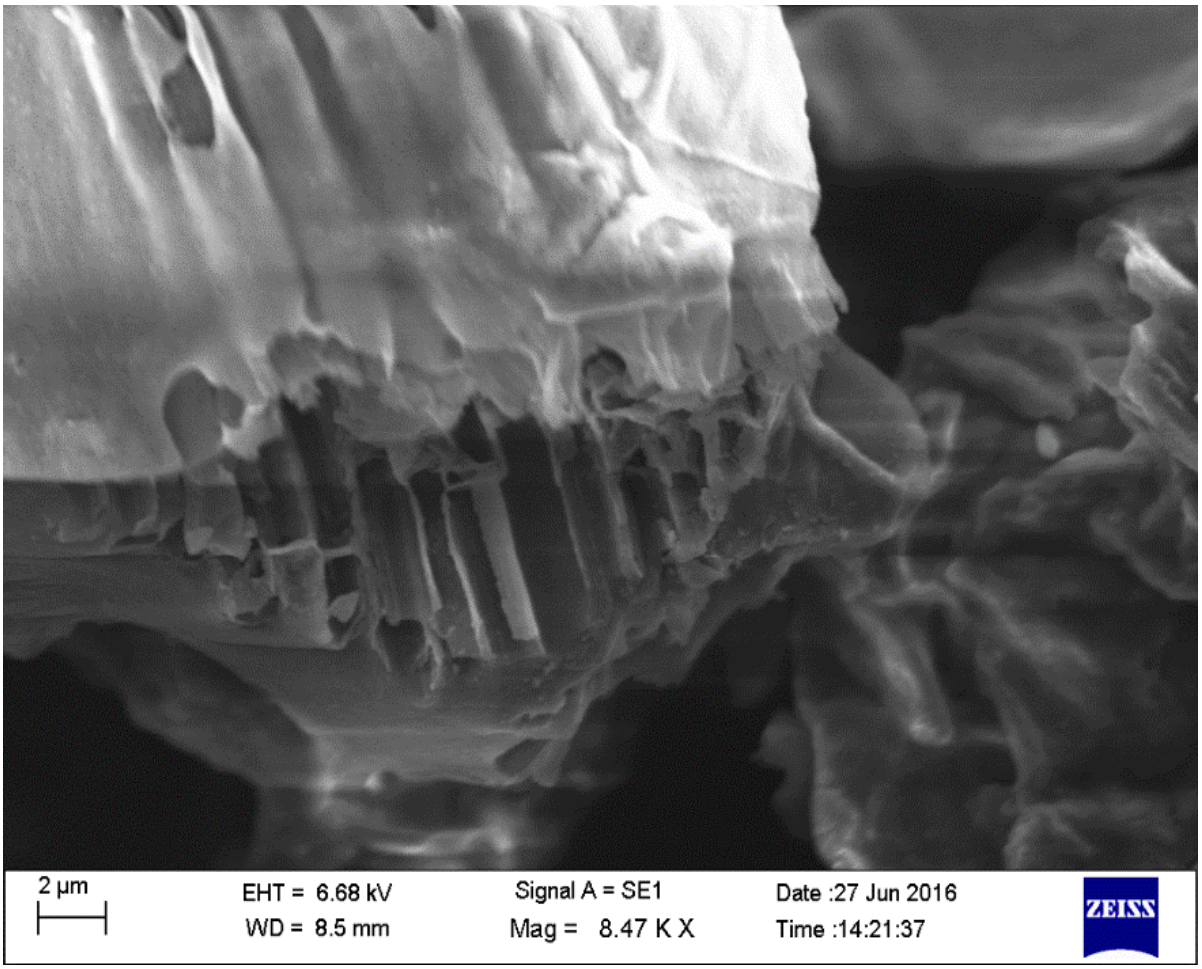

Figure 4: SEM Imaging of Amino Modified Biochar

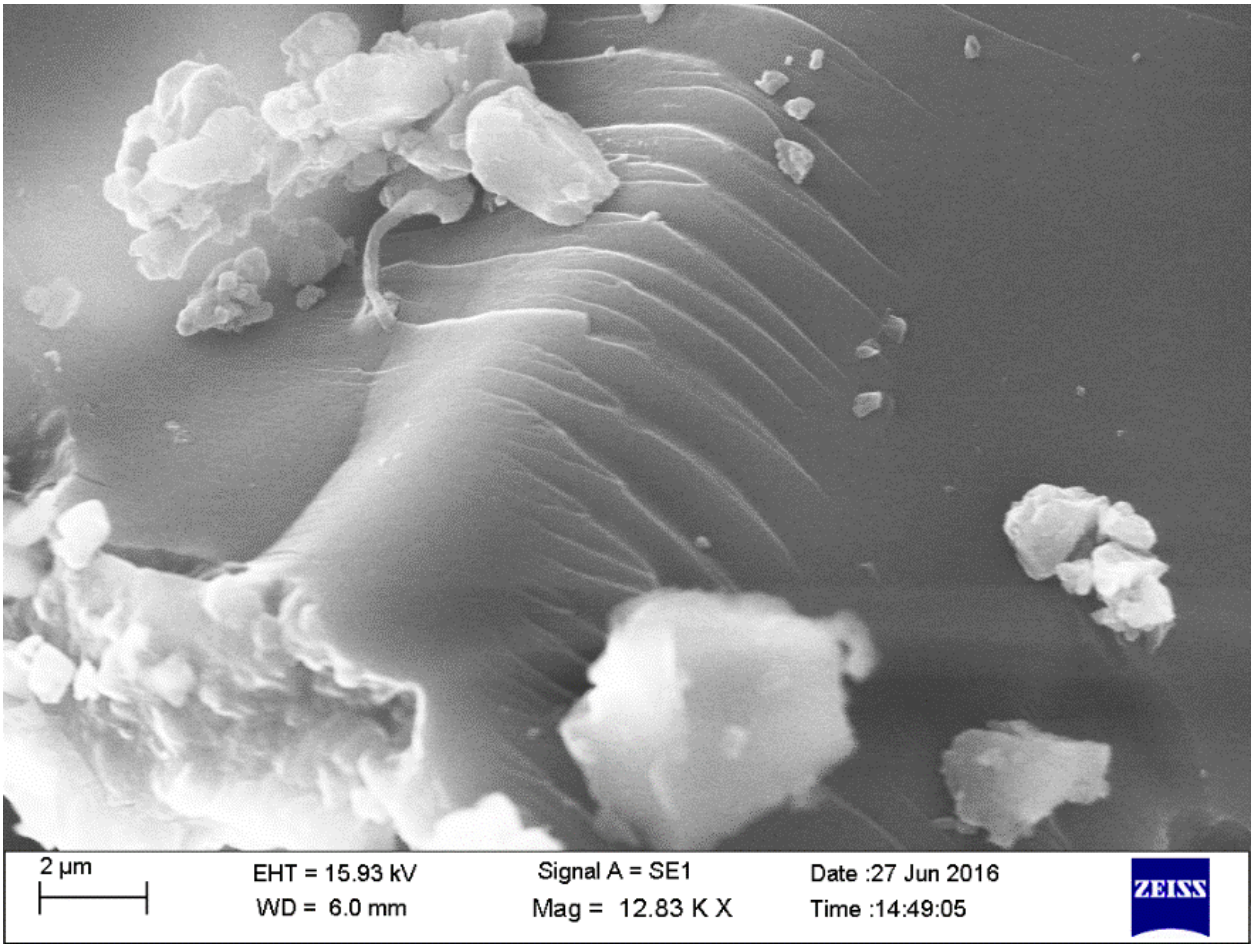

Figure 5: SEM Imaging of Amino Modified Biochar

EDS Mapping and Analysis of Reacted Biochar

In addition, to the SEM imaging, elemental mapping of the biochar materials was performed using energy-dispersive x-ray spectroscopy (EDS). Figures 6-9 show the SEM image along with elemental maps of sulfur, oxygen, nitrogen, carbon, and chromium for the native and amino modified biochar materials after being equilibrated with 100 ppm Cr(VI) and Cr(III) solutions at pH of 2 and 4, respectively. These characterizations of the native, amino modified, and the reacted samples were performed to observe and elucidate the possible functional groups

involved in chromium binding. As can be seen in Figure 6 and 7 the Cr(VI) and Cr(III) appears to be distributed throughout the entire biochar sample. The homogenous distribution of the chromium indicates that there is no functional specifically responsible for the binding of the Cr(VI) and Cr(III) to the native and chemically modified biochar. However, as can be seen in Figure 8 and 9 the signal in the chromium maps appear where there is also a higher apparent concentration of signal observed in the map for nitrogen. The correlation may be an indication of an increase in the binding of the Cr(VI) and Cr(III) occurs at nitrogen species on the surface of the amino modified biochar. From the combination of the FTIR analysis, which indicated the presence of the amino functional groups, it may be that the binding is occurring through an amino group added through the chemical modification.

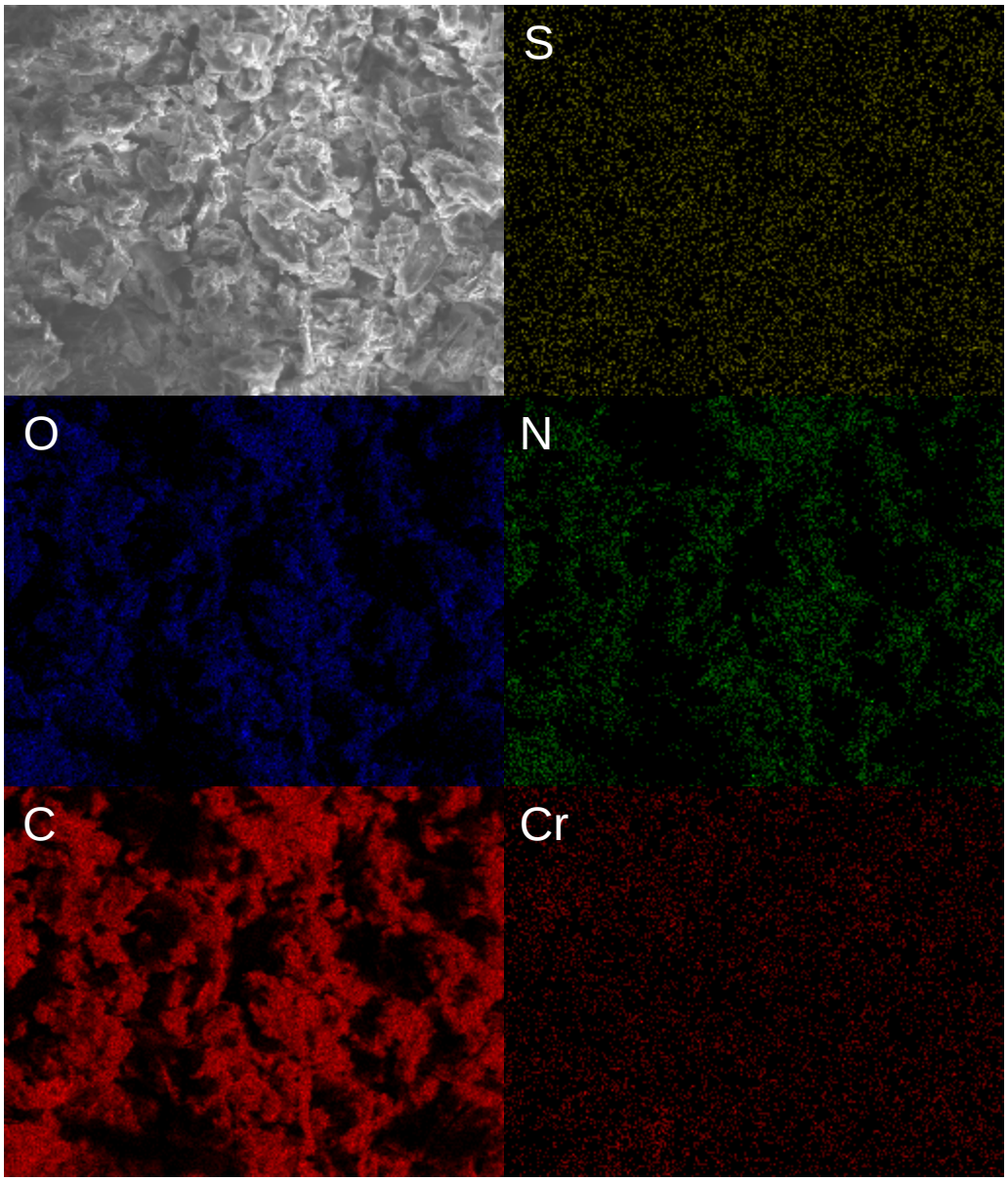

Figure 6: EDS Mapping of Native Biochar After Reaction with 100ppm Cr(VI) (pH 2)

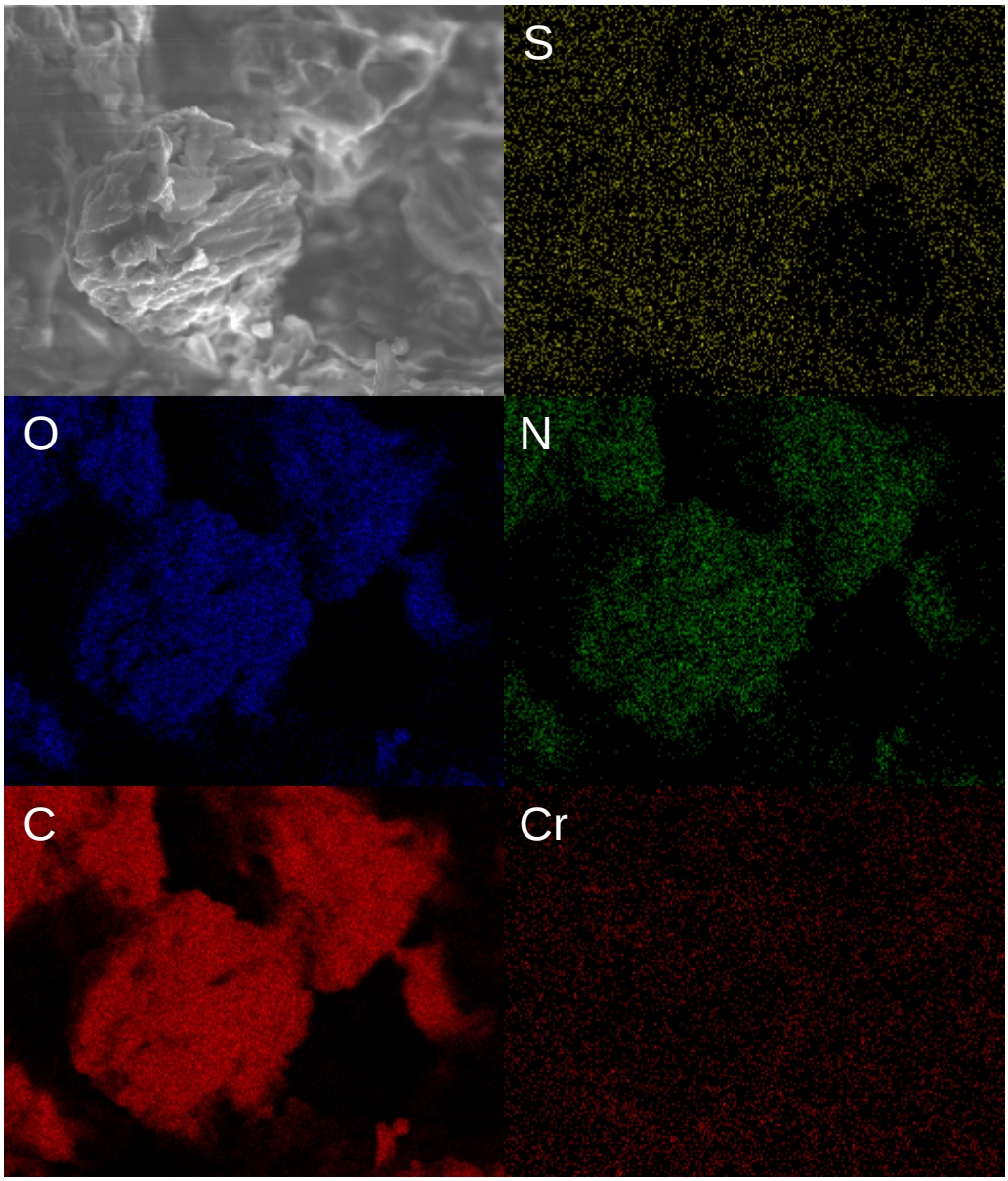

Figure 7: EDS Mapping of Native Biochar After Reaction with 100ppm Cr(III) (pH 4)

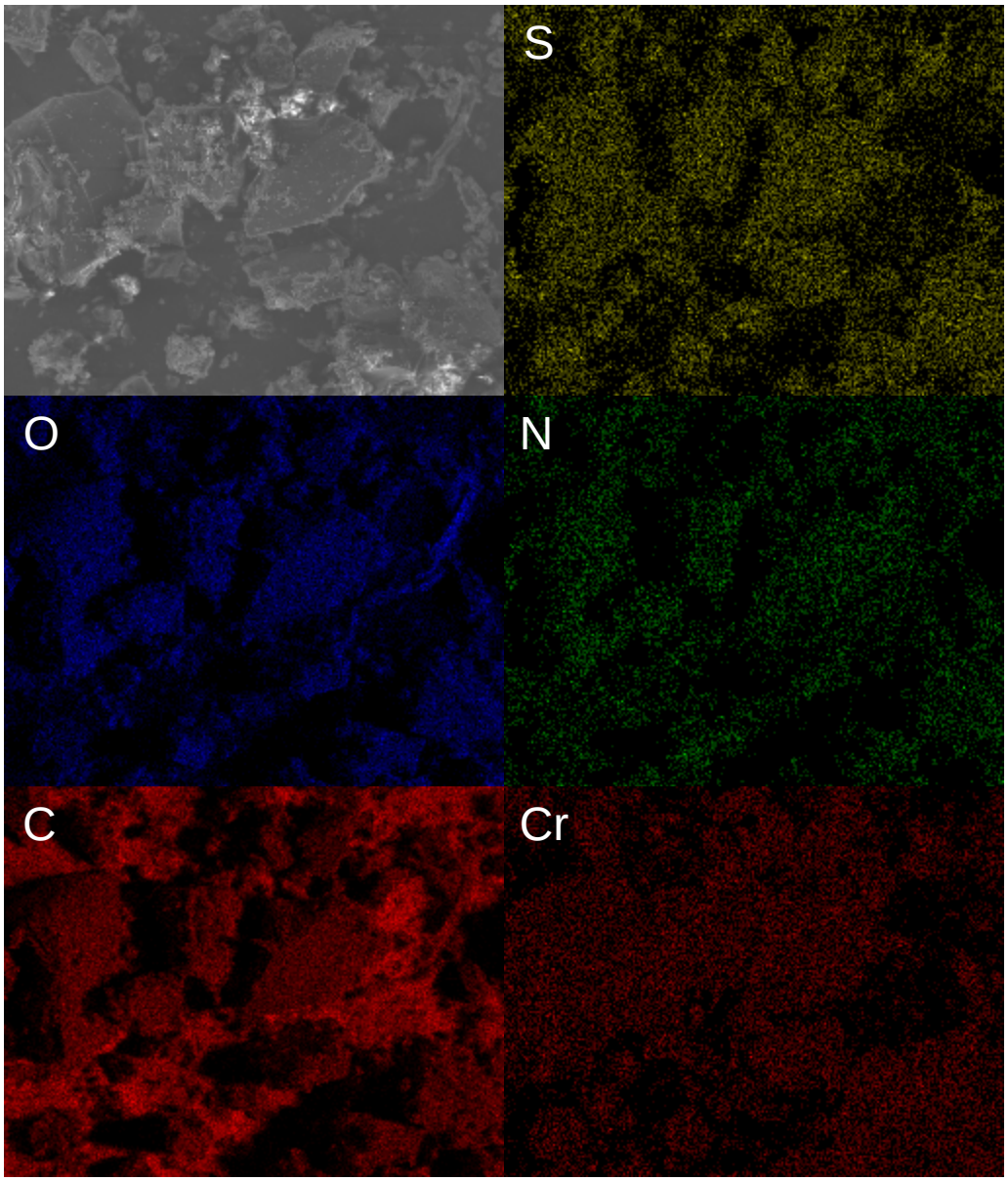

Figure 8: EDS Mapping of Amino Modified Biochar After Reaction with 100ppm Cr(VI) (pH 2)

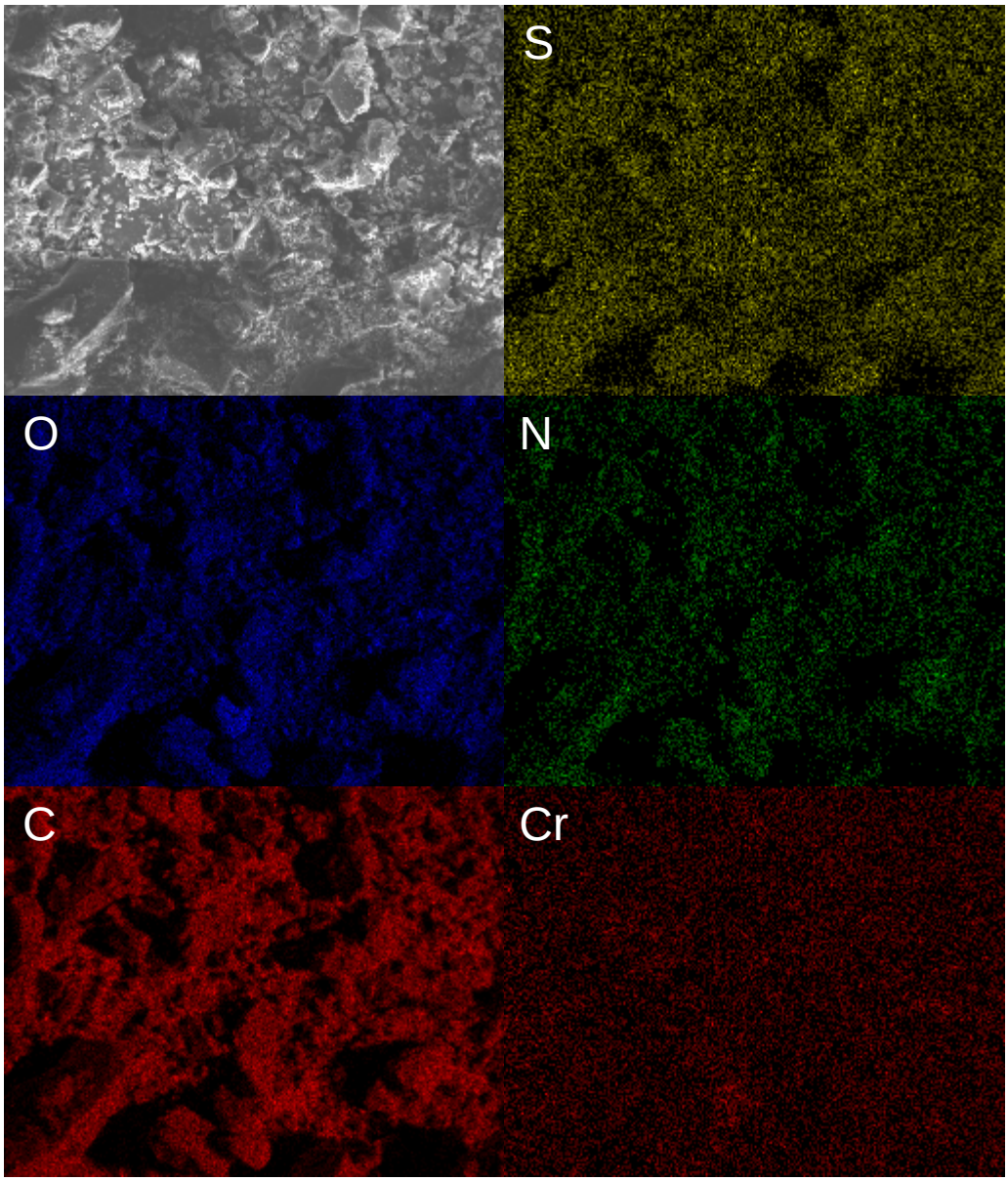

Figure 9: EDS Mapping of Amino Modified Biochar After Reaction with 100ppm Cr(III) (pH 4)

Optimum pH Binding Studies

The results from the pH studies performed in the present study showed a change in the Cr binding trend changing pH directly affected the binding of the both Cr species. Previous studies biochar materials exhibit similar binding behavior, which shows Cr(VI) optimally binds at the lower pHs (pH ≤ 2.0) [8, 10, 13, 19-21, 28]. The higher binding at lower pH generally is explained through surface charge. At low pHs most organic functional groups on the surface are protonated or positively charged, which attracts the chromate anion from solution and facilitates the binding. As the pH is increased the surface charge changes and the surface will initially become a zero changed surface, at the point of zero charge (PZC). Once the pH is increased above the PZC then the surface becomes negatively charged and in effect repulses the chromate and eliminates the binding [29]. These surface charge effects are observed in the binding of metals to minerals, metal oxides nanoparticles, biomass, biochar, as well as activated carbon [11-13, 29, 30]. The high binding at low pH was observed in the present study with native biochar, as can be seen in Figure 10. At pH 2 the observed binding was approximately 40% and decreased to less than 10% at pH 3 and above. However, as shown in Figure 11, after the amino modification of the biochar a different trend is observed. The optimal binding for Cr(VI) shifts up in pH to be at pH 3 and remains relatively independent thereafter. Even at pH 2 the binding of Cr(VI) was observed to approximately double from 40% at pH 2 (native biochar) to 80% binding for the amino modified biochar. The data indicates a change in the binding mechanism for the Cr(VI) to the amino modified biochar. This change in the pH dependence in the binding is very interesting as the biochar becomes able to remove Cr(VI) at more environmentally relevant pHs and potentially increases the effectiveness of using biochar in real world applications for Cr(VI) remediation. In addition, the data indicate that the chromium binding to the amino modified

biochar is not electrostatically controlled. The effects of the amino binding behavior are also noticed throughout the subsequent studies and trends.

The binding of Cr(III) the trend for both the native and amino modified biochar is consistent with what has been observed in the literature for similar systems [12, 31]. Figure 10 and 11 shown the binding of Cr(III) to the native and amino modified biochars respectively. Generally, Cr(III) binds low at low pH and increase with increasing pH, due to electrostatic attraction and subsequent binding to the biochar. Generally, at low pH a biochar will have all the oxygen groups protonated, which generally gives a positive surface charge to the biochar repelling cations in solution from binding [31]. Once the pH is increased above the PZC (point of zero charge) the surface generally takes on a negative charge. A negatively charges surface will electrostatically attract the cations from solution which facilitates binding.

The optimum binding of Cr(VI) and Cr(III) to the native biochar was taken to be at pH 2 and pH 4, respectively. Furthermore, the optimum binding of Cr(VI) and Cr(III) using amino modified biochar was also taken to be at pH 2 and pH 4. The Cr(VI) binding at pH 2 for the amino modified biochar approximately double the amount binding was observed. All the subsequent reactions for the native and amino modified biochar were performed at pH 2 and pH 4 for comparisons between the Cr(VI) and Cr(III) binding, respectively.

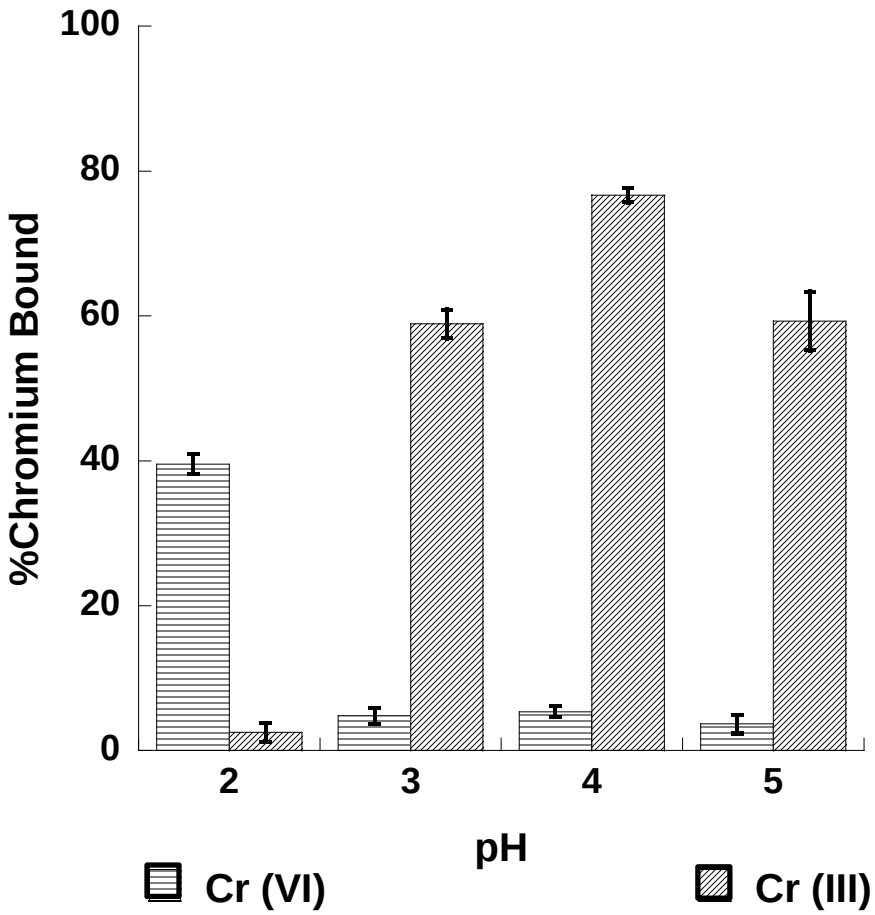

Figure 10: Optimum pH Binding using Native Biochar

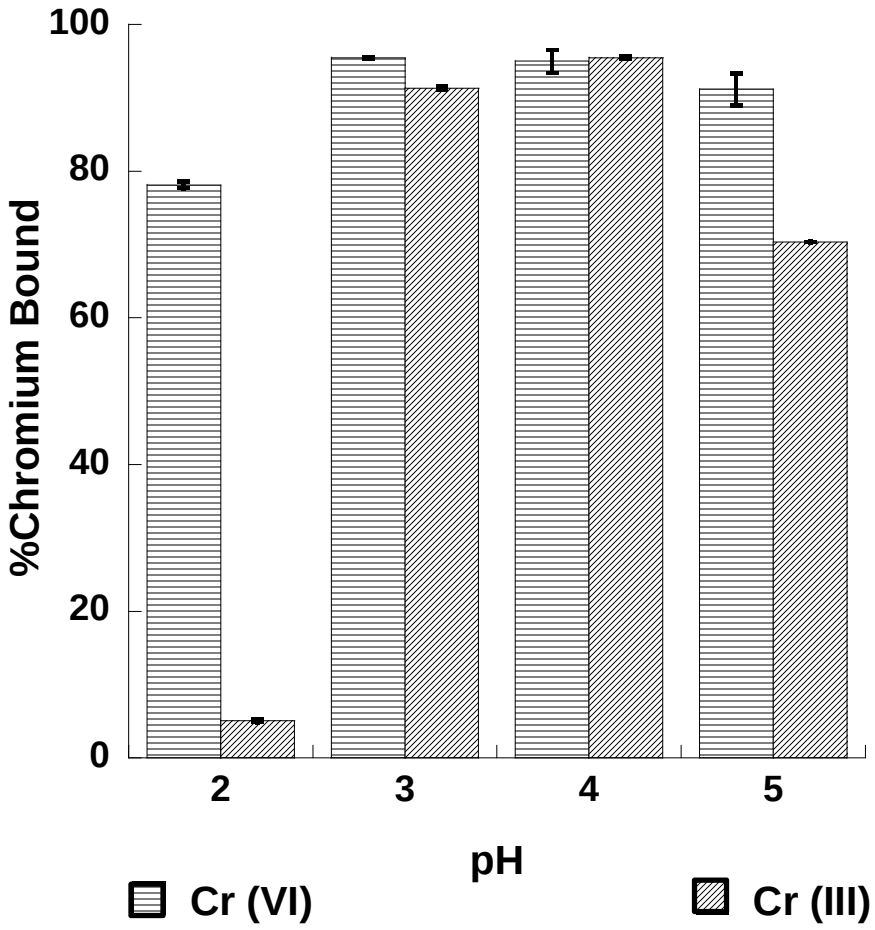

Figure 11: Optimum pH binding using Amino Modified Biochar

Time Dependency Studies

Time dependency studies were performed to obtain kinetic data, to better understand the binding process for both the native and modified biochar material. The reactions were performed at three different temperatures, which allows the generation of Arrhenius plots, which are shown below. From the Arrhenius plots the activation energy of their respective binding reactions can be determined, which is indicative of the type of reaction occurring during the binding process. Figures 12 and 13 show the Arrhenius plots derived from the kinetics data for the binding of

Cr(VI) and Cr(III) to the native and amino modified biochars, respectively. The kinetics data for the binding of the Cr(VI) and Cr(III) to the native and amino modified biochar are presented in Table 3 and 4. In addition, Tables 3 and 4 show the calculated activation energies determined from the Arrhenius plots. For the native biochar material, the reaction with either Cr(VI) or Cr(III) had activation energies of 18.4 kJ/mol and 11.4 kJ/mol respectively. Whereas the chromium binding to the amino modified biochar material, the Cr(VI) and Cr(III) had activation energies of 18.4 kJ/mol and 21.2 kJ/mol, respectively. The activation energy for the Cr(VI) binding to either the native or amino modified biochar was not affected, indicating binding to both types of materials was consistently through chemisorption, which has been observed to occur in energy ranges between 8.4 and 83.7 kJ/mol [32]. The binding of the Cr(III) to native and amino modified biochar also occurs through chemisorption. However, the activation energy for the binding approximately doubles in magnitude between the native and amino modified biochars. The increase in the activation energy of binding indicates there are two different types of chemisorption occurring, which are non-activated and activated. The low activation for the native biochar at 11.4 kJ/mol, is close to the transition between physisorption and chemisorption, as well as that observed for ion-exchange.

Sample	Temp (°C)	Equation	R^2	E_a (kJ/mol)
Cr(VI)	4	0.0114x + 0.580	0.99	
Native	25	0.0150x + 0.880	0.99	18.4
Biochar	58	0.0353x + 1.196	0.99	
Cr(III)	4	0.0033x + 0.016	0.98	
Native	25	0.0047x + 0.562	0.98	11.4
Biochar	45	0.0063x + 0.227	0.96	

Table 3: Reaction Rates for the Sorption of Cr(VI) and Cr(III) with Native Biochar

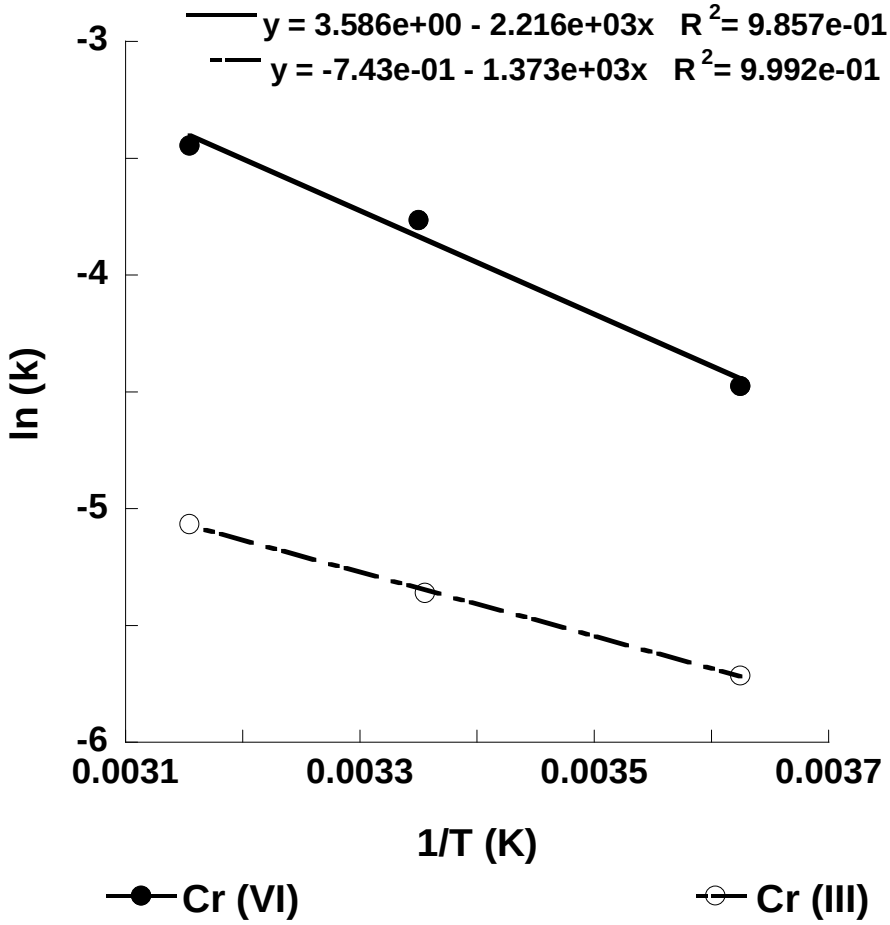

Figure 12: Arrhenius Plot using Native Biochar

Sample	Temp (°C)	Equation	R^2	E_a (kJ/mol)
Cr(VI) amino modified Biochar	4	0.1622x + 19.50	0.99	18.4
	25	0.0956x + 13.67	0.96	
	40	0.2688x + 18.91	0.98	
Cr(III) amino modified Biochar	4	0.0593x + 20.03	0.99	21.2
	25	0.1311x + 22.38	0.99	
	40	0.1957x + 24.78	0.93	

Table 4: Reaction Rates for the Sorption of Cr(VI) and Cr(III) with Amino Modified Biochar

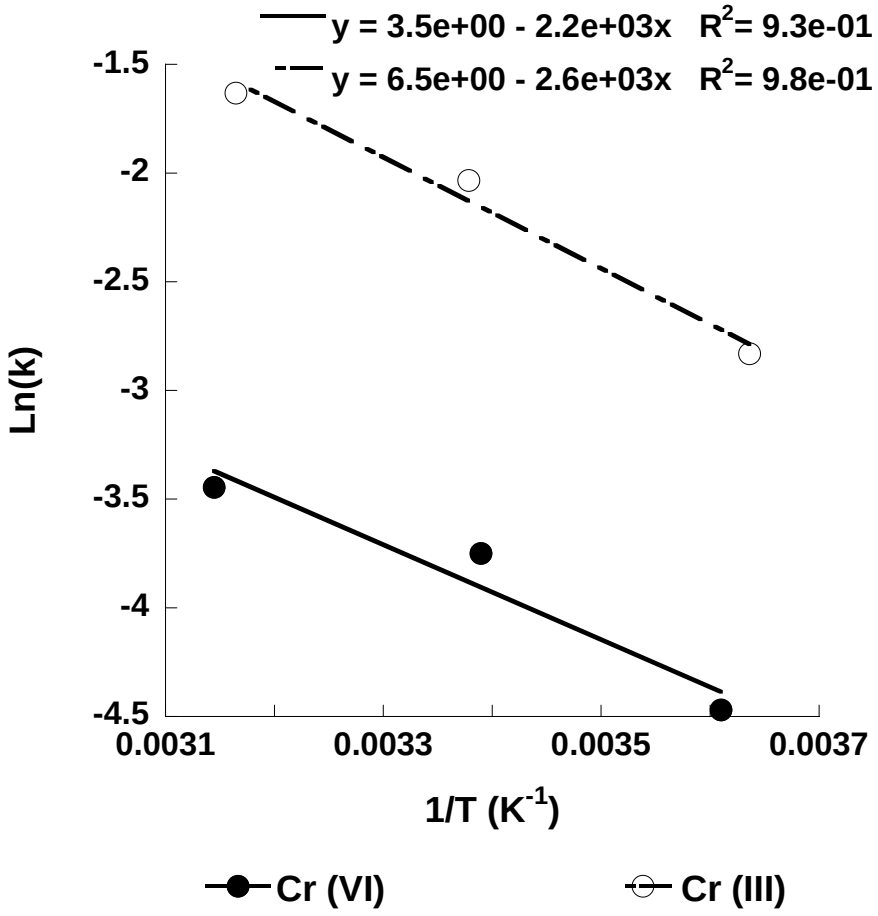

Figure 13: Arrhenius Plot using Amino Modified Biochar

Adsorption Thermodynamics of Biochar Materials

The general Gibbs free energy formula is, as shown in equation 1 below, which can be used as a base equation to derive different relationships for Gibbs free energy:

$$\Delta G = \Delta H - T\Delta$$

Where ΔG is the Gibbs free energy of reaction, ΔH is the enthalpy of the reaction, ΔS is the entropy of reaction, and T is the reaction temperature given in Kelvin.

ΔG can also be related to the equilibrium constant for a reaction. Sorption or adsorption reactions are similar to precipitation reactions which have an equilibrium constant, or a constant between the liquid and solid phases which can be described as k_d. In equation 2 below the relationship between the adsorption constant and ΔG is presented.

$$\Delta G = -RTln(k_d)$$

Where R is the gas constant 8.314 x 10^{-3} kJ mol^{-1} K^{-1}, T is the temperature at which the study was performed in degrees Kelvin, and where k_d is the distribution coefficient.

By combining equation 1 and equation 2 a third equation is developed which relates the adsorption to the enthalpy and entropy as is shown in equation 3 below:

$$\ln(k_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Therefore a plot of the natural log of the distribution coefficient ln(k_d) with 1/T (in Kelvin) on the X-axis generates a liner plot. The slope of the plot is the – ΔH/R thus the enthalpy of reaction can be determined by multiplying the slope by –R. The entropy of the adsorption process is determined by multiplying the intercept of the line by the gas constant (R).

Figures 14 and 15 show the results of the thermodynamic experiments for the binding of Cr(VI) and Cr(III) to the native and amino modified biochar materials. The data was generated through isotherm studies. In addition, the binding capacity for Cr(VI) and Cr(III) binding to the native and amino modified biochar materials was also determined. The isotherm studies were performed at temperatures of 4°C, 25°C, and 45°C and were found to be best fitted by the Langmuir isotherm model. Table 5 and Table 6 show the calculated thermodynamic parameters for the binding of Cr(VI) and Cr(III) to the native and amino modified biochar, which were ΔG,

ΔH, and ΔS biochar. From the thermodynamic data the Cr(VI) binding to the native biochar was found to be spontaneous throughout at all three temperatures. In addition, the ΔG was found to increase with increasing temperature indicating the binding is an endothermic reaction. The endothermic nature of the reaction is further supported by the positive value of 15.07 kJ/mol for ΔH and the positive value of 63.74 J/mol for the ΔS of the reaction between Cr(VI) and the biochar material. However, the binding of the Cr(VI) to the amino modified biochar the ΔG for the binding is observed to increase with decreasing temperature indicating a exothermic reaction is occurring. The ΔG for the Cr(VI) binding with the native biochar was observed to become larger with increasing temperature indicating an endothermic reaction was occurring for the binding process. Although the reaction is spontaneous at the three temperature tested the ΔG does become less negative as the temperature is decreasing. The sign on the ΔH has also changed to become positive and the observed ΔH was 15.07 kJ/mol, which is further evidence that the reaction has become endothermic in nature. Finally, the ΔS has also changed signs and has become a 63.74 J/mol. The amino modification has changed the thermodynamics of binding for Cr(VI) to the amino modified biochar compared to the binding to the native biochar.

The calculated ΔG of sorption of Cr(III) to the native biochar were all determined to be positive and were also found to increase with increasing temperature indicating the reaction is both non-spontaneous and exothermic in nature. The exothermic nature of the reaction is further supported by the calculated ΔH of -9.98 kJ/mol, which is indicative of an exothermic reaction. The calculated ΔS of -48.6 J/mol indicates the reaction is a non-spontaneous reaction, for the binding of Cr(III) to the native biochar. The thermodynamics of the binding of the Cr(III) to the amino modified biochar followed the same trend as the native biochar. From the ΔG values the reaction is endothermic in nature; however at low temperature the reaction is spontaneous. The

ΔH of binding was found to be -51.52 kJ/mol indicting an exothermic reaction is occurring during the binding. Also the ΔS for the sorption was found to be negative -172.12 J/mol indicating a non-spontaneous reaction is occurring for the sorption.

The values determined for ΔH and ΔS of both Cr(VI) and Cr(III) binding to amino modified biochar and consistent with the statement that the Cr(VI) the process is exothermic and the Cr(III) process is exothermic. The binding of Cr(VI) to many different materials including activated carbons and mineral surfaces has been shown to be an exothermic reaction in the literature [11, 12, 33]. Similarly the binding of Cr(III) to activated carbons and different metal oxides and mineral surfaces has also been shown to be exothermic in nature [11, 12, 33]. In addition, the change in the Cr(VI) from an endothermic reaction to an exothermic reaction may be due to a reaction between the lone pair of electrons on the amino groups on the amino modified. The presence of the lone pair of electrons may induce a reduction reaction for the Cr(VI) bound to the amino modified biochar. The reduction of Cr(VI) to Cr(III) during the binding process has been observed to occur in multiple binding systems involving biomass [30, 34, 35]. In addition, in the presence of sulfur groups and amino groups such as found in L-Cysteine Cr(VI) has successfully been reduced by 1 electron transfers to Cr(III) [36]. Both Sulfur and amino groups are present in the biochar and in much higher concentrations in the amino modified biochar. The mechanism for the binding may be involving a reduction of the Cr(VI) to Cr(III), which would change the thermodynamics of the process from endothermic to exothermic.

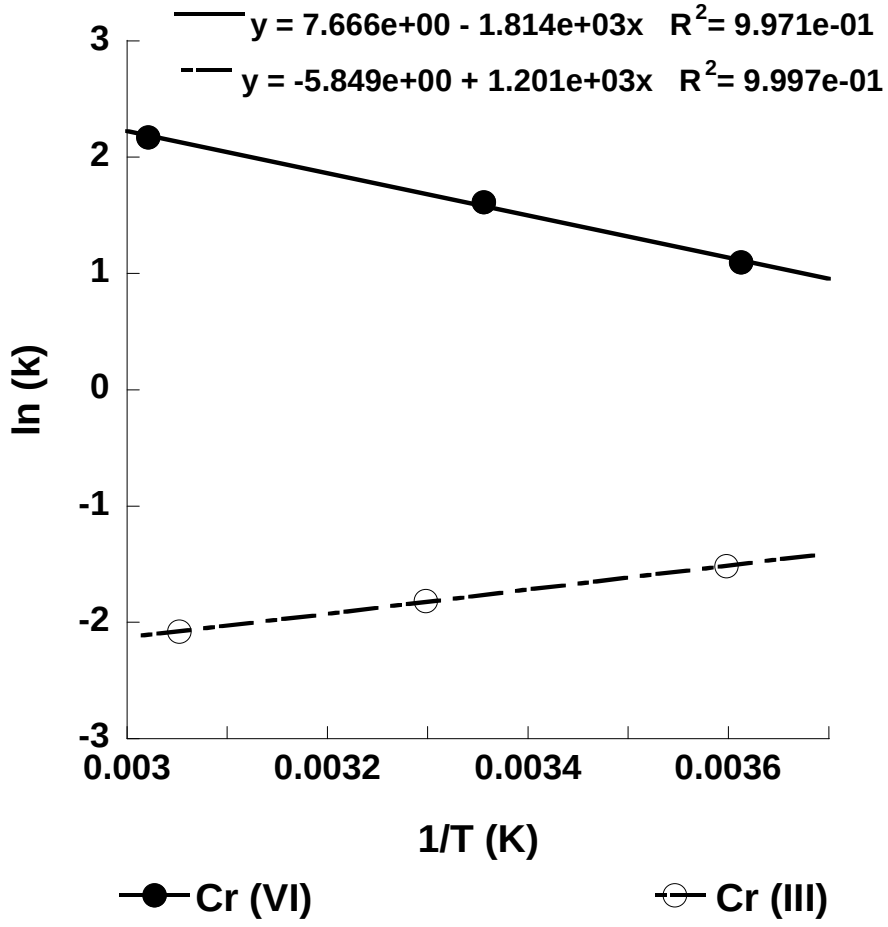

Figure 14: Thermodynamics Plot using Native Biochar

Sample	Temp (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
Cr(VI) Native Biochar	4	-2.52	15.07	63.74
	25	-4.00		
	58	-5.97		
Cr(III) Native Biochar	4	3.50	-9.98	-48.6
	25	4.49		
	45	5.49		

Table 5: Thermodynamic Properties of Native Biochar

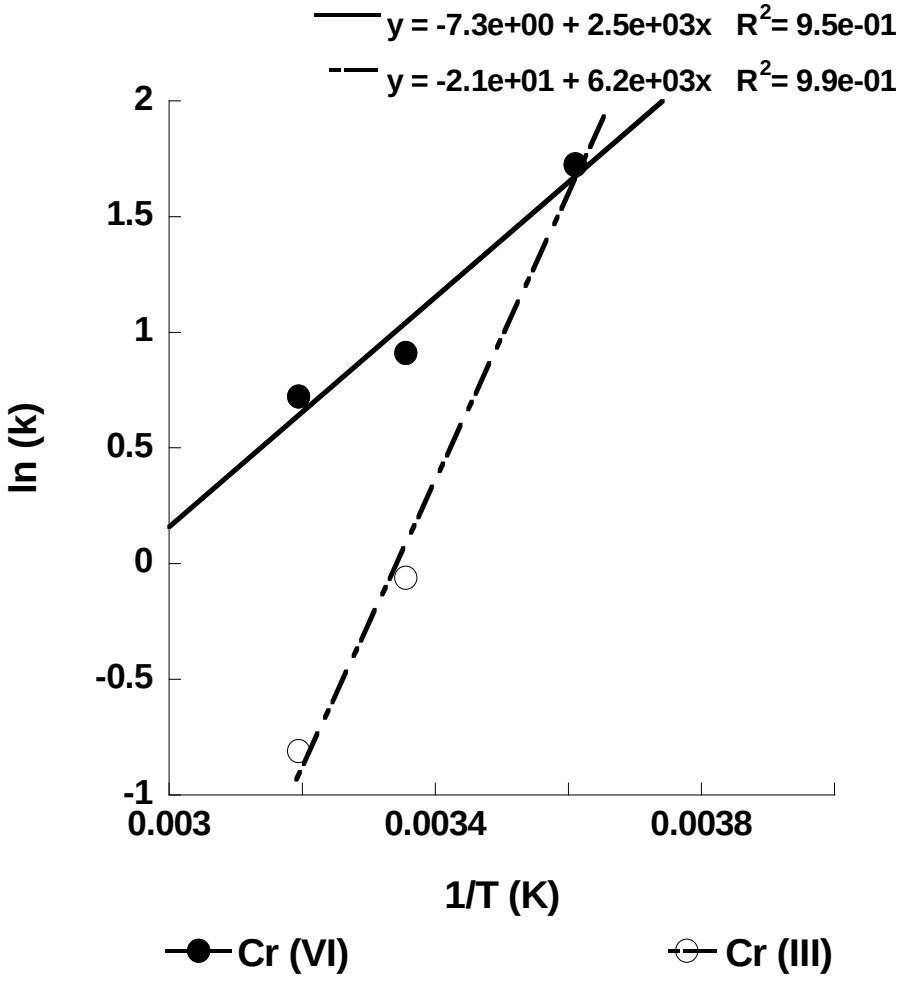

Figure 15: Thermodynamics Plot using Amino Modified Biochar

Sample	Temp (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
Cr(VI) Amino modified Biochar	4	-3.97	-20.63	-60.56
	25	-2.26		
	40	-1.88		
Cr(III) Amino modified Biochar	4	-3.98	-51.52	-172.12
	25	0.15		
	40	2.11		

Table 6: Thermodynamic Properties of Amino Modified Biochar

Binding Capacity of Native Biochar

The binding capacities for the Cr(VI) and Cr(III) adsorption to the native biochar and the amino modified biochar was determined using isotherm binding studies. The Langmuir equation in linear form is given in equation 4 below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m C_e}$$

Langmuir isotherm equation (Capacity)

Where, q_e is defined as the binding at a given concentration (mg/g), q_m is the maximum binding for a given sorbent (mg/g), C_e is the equilibrium constant (ppm), and K_a is a constant based on the ionic strength, pH, temperature, and among other factors. Form the binding data it was determined that the Langmuir equation best fitted the experimental data.

The determined capacities were calculated on the data from three different temperatures hot, room temperature, and cold. The results of the binding capacities are presented in Table 7 for the native biochar and Table 8 for the amino modified biochar. For the native biochar the binding was lowest at the low temperature and the maximum binding capacity for Cr(VI) was under the hot conditions at 58°C with a capacity of 5.06 mg/g chromium per gram of adsorbent material. Whereas the maximum binding capacity for Cr(III) binding to the native biochar was observed under the cold conditions with a capacity of 4.61 mg/g. As the temperature increased the binding capacity was observed to decrease. The difference in binding capacity trend between the Cr(VI) and Cr(III) ions coincides with the thermodynamic data. The binding process for Cr(VI) to the native biochar is endothermic in nature whereas the binding of the Cr(III) to the native biochar is exothermic in nature.

Sample	Temp (°C)	Capacity (mg/g)
Cr(VI) Native Biochar	4	3.45
	25	4.11
	58	5.06
Cr(III) Native Biochar	4	4.61
	25	4.49
	45	1.32

Table 7: Binding Capacity of Native Biochar at Different Temperatures

Capacitance of Amino Modified Biochar

The binding capacity of Cr(VI) and Cr(III) to the amino modified biochar was also determined from the intercepts of the Langmuir isotherms. As with the native biochar the binding was followed at three different temperature conditions hot, room temperature, and cold.

These results are based off the use of the amino modified biochar with their respective ion and temperature conditions. For the Amino-modified Biochar the maximum capacitance for Cr(VI) was under hot conditions at 45°C with a capacity of 344.83 mg/g. The binding capacity was noted to increase with increasing temperature. The maximum capacitance for Cr(III) occurred under the hot conditions with a capacity of 34.36 mg/g. Again the binding was observed to increase with increasing temperature similar to the Cr(VI) binding. This difference in binding capacity with the respective Cr(VI) and Cr(III) ions confirms the change in the reaction process. Both the Cr(VI) and Cr(III) have large increases with the amination of the biochar. The Cr(VI) and Cr(III) observed binding capacities no longer follow a pure adsorption process as indicated by the thermodynamics of the reactions. The process for binding has changed for both the Cr(VI) and Cr(III) it is no longer a simple sorption reaction as is observed with the native biochar. The binding has become a complex formation reaction for both the Cr(VI) and Cr(III), where the thermodynamics are now a combined processes for the sorption and the formation of the complex between the amino modified biochar and the Cr(VI) and Cr(III) ions. As mentioned earlier Cr(VI) can be reduced in the presence of sulfur and amino groups to form Cr(III) complexes. It is believed that there large increase in the binding on the amino modified biochar and change in the thermodynamics is a function of the reduction of Cr(VI) to Cr(III). This binding process changes the binding kinetics and the thermodynamics. The Cr(III) binding changes from the "pure" adsorption process into a facilitated binding process in the presence of the amino groups on the surface of the amino modified biochar. The facilitated sorption is involving both the traditional sorption process but also a complex formation. More than likely the complex formation is the driving force behind the large sorption values observed in the amino modified biochar. Thus the true thermodynamics of the binding process are not

measurable through the thermodynamics determined for the sorption and the binding capacities do not reflect the ΔG and ΔH observed for sorption.

Sample	Temp (°C)	Capacity (mg/g)
Cr(VI) Amino modified Biochar	4	53.76
	25	112.36
	45	344.83
Cr(III) Amino modified Biochar	4	21.32
	25	26.95
	43	34.36

Table 8: Binding Capacitance of Amino Modified Biochar at Different Temperatures

Binding Interference Studies

The previous studies were performed under ideal conditions and all solutions were prepared with the respective Cr ion using 18MΩ water to provide a clear picture of the binding process. However, this is an unrealistic situation for environmental solutions and natural aquatic systems are very complex containing multiple ions. To account for the presence of multiple ions the interference studies were performed with the specific intention to observe and determine the binding effects of similarly charged ions on the binding of Cr(VI) and Cr(III). Common anions found in aquatic systems include Cl^-, NO^{3-}, SO_4^{2-} (or HSO^{4-}), PO_4^{3-} (or some protonated form of the phosphate anion), CO_3^{2-} (or bicarbonate), and SiO_4^{2-} (or $HSiO^{4-}$), the forms are pH dependent and these anions were tested for interference with Cr(VI) binding to the native and amino modified biochar. Anions were used to test the Cr(VI) binding interferences to the native an

amino modified biochar materials due to the fact that Cr(VI) is an anion in solution. Whereas cations were tested for their interferences with the Cr(III) ions as Cr(III) forms a cation in solution. The common hard cations Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} found in most natural fresh water aquatic systems were used to test the binding interference of Cr(III). In addition, the interference studies were performed in individual interference studies as well as combined interference studies which was performed using all the anions in one solution for Cr(VI) and all the cations in one solution for Cr(III). The results give a understanding possible antagonist or synergistic effects for the chromium binding within a more naturally found aqueous matrix. In addition, all reactions were performed at their optimum binding pH as was determined from the pH binding study. For the native biochar, the anions solutions, were all pH adjusted to pH 2, all of the anions had a slight antagonistic effect with the overall binding of Cr(VI), compared to the binding of the Cr(VI) without the anions present. The binding observed in the absence of any of the anions was approximately 40% binding, which decreased in the interference studies to between 30 to 38% binding as can be seen in Figures 16 and 17. The amino modified biochar was relatively unaffected by the interfering anions as can be seen in Figures 18 and 19. In the binding studies in the absence of interfering ion the binding was approximately 80% and in the interference study for the most part the binding was observed to be close to 80%. The only observed antagonistic effect was observed in the solutions with silicate at 100 ppm and 1000 ppm as can be seen in Figure 19.

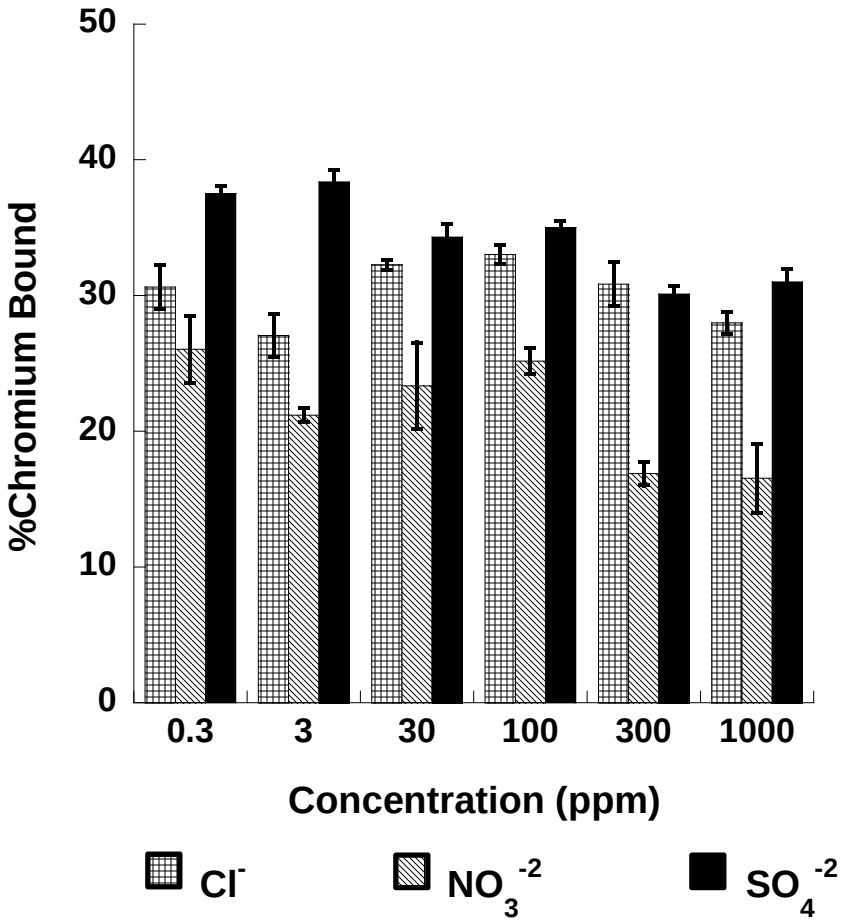

Figure 16: Anion Interference Study using Native Biochar (1)

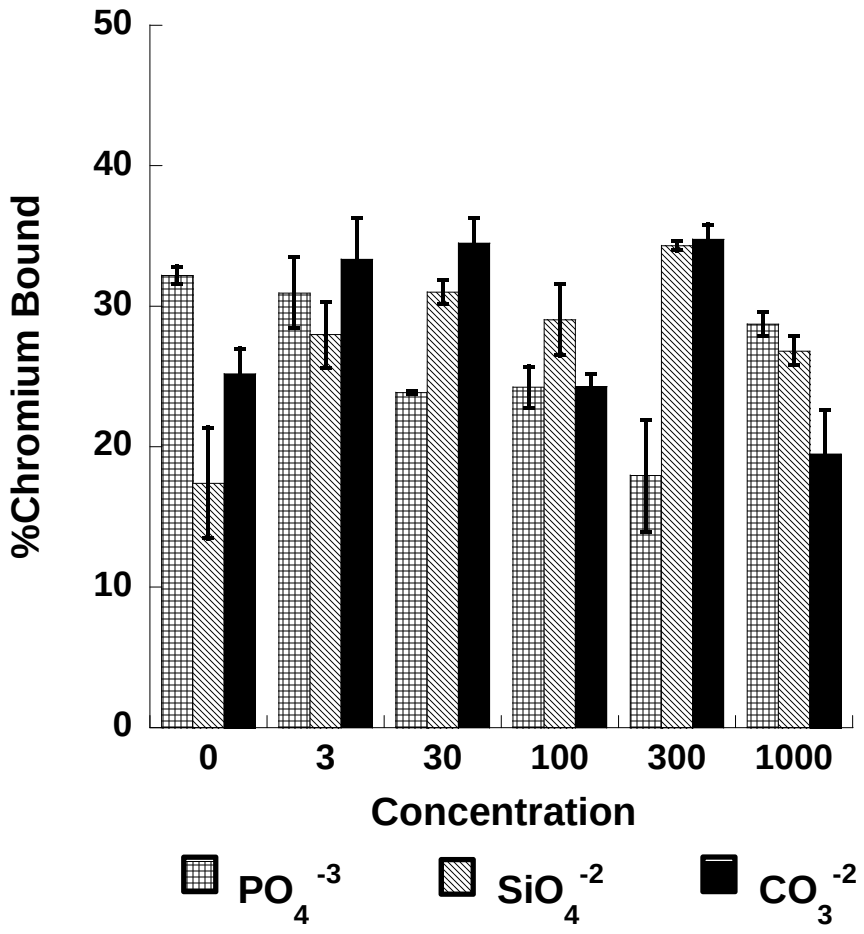

Figure 17: Anion Interference Study using Native Biochar (2)

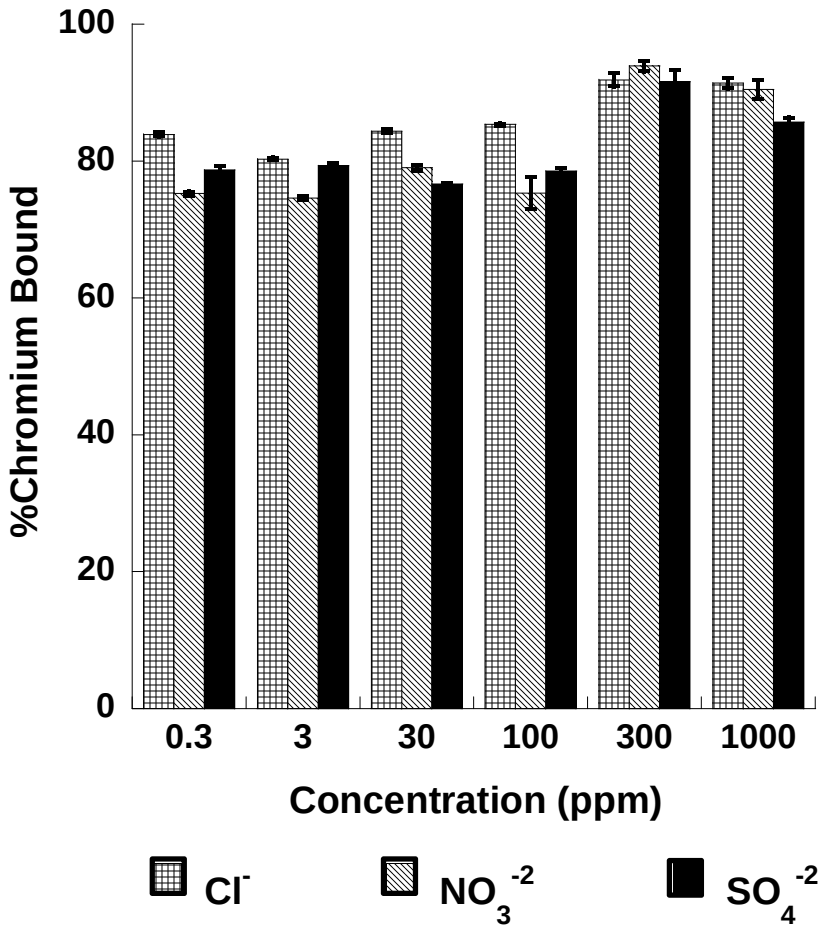

Figure 18: Anion Interference Study using Amino Modified Biochar (1)

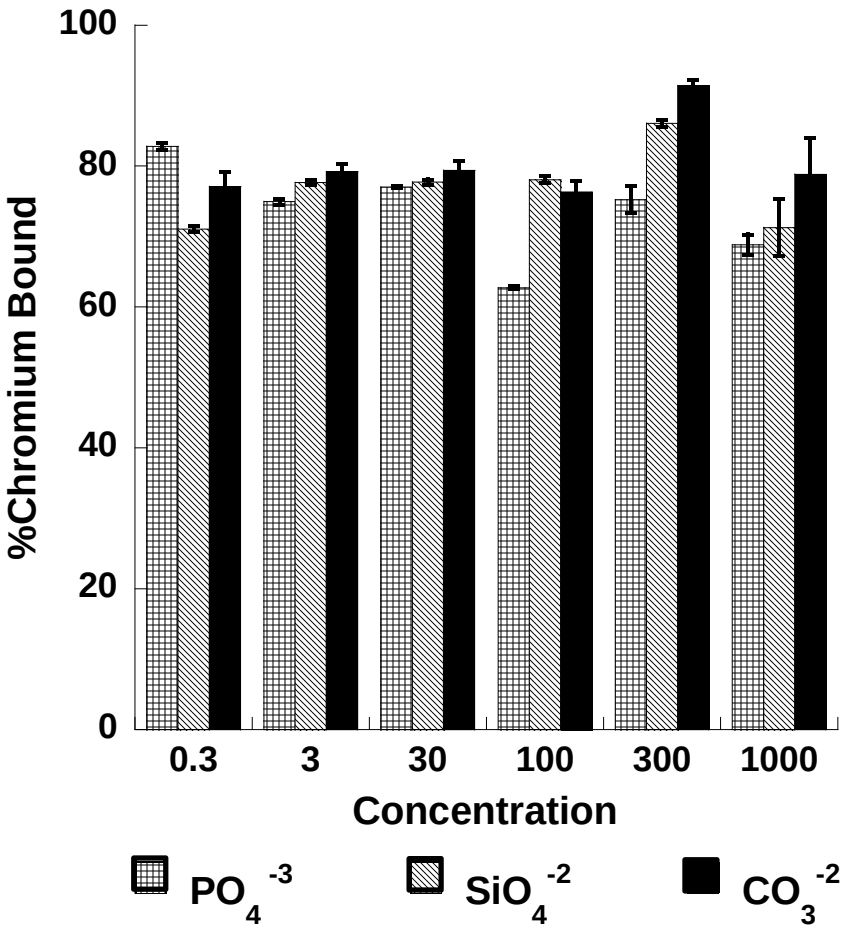

Figure 19: Anion Interference Study using Amino Modified Biochar (2)

For the native Biochar, the cation solutions, at pH 4, the monovalent cations had a slight antagonistic effect with the binding of Cr(III) in the presence of high concentrations of single valent cations. However, a synergistic effect was observed in the solutions with high concentrations of divalent cations, the binding was observed to increase, as shown in Figure 20. The binding in the presence of the high concentration in the presence of the divalent cations increased from 80% without interferences to approximately 100%. The amino modified biochar showed slight synergistic effects at low concentrations of the interfering cations. However, at higher concentrations antagonistic effects were observed. The binding during the pH study, in

the absence of divalent cationic interferences was around 95% binding whereas in the presence of high concentrations 300 ppm and 1000ppm of Ca^{2+} and Mg^{2+} the binding of the Cr(III) is dramatically decreased, as seen in Figure 21.

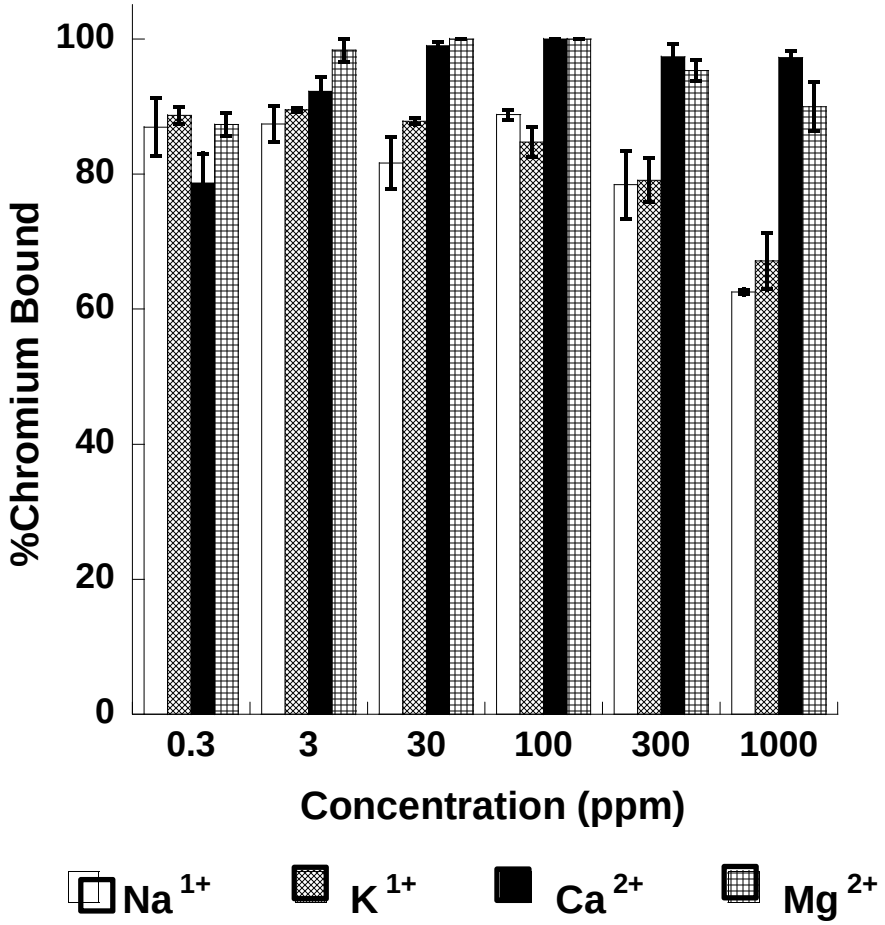

Figure 20: Cation Interference Study using Native Biochar

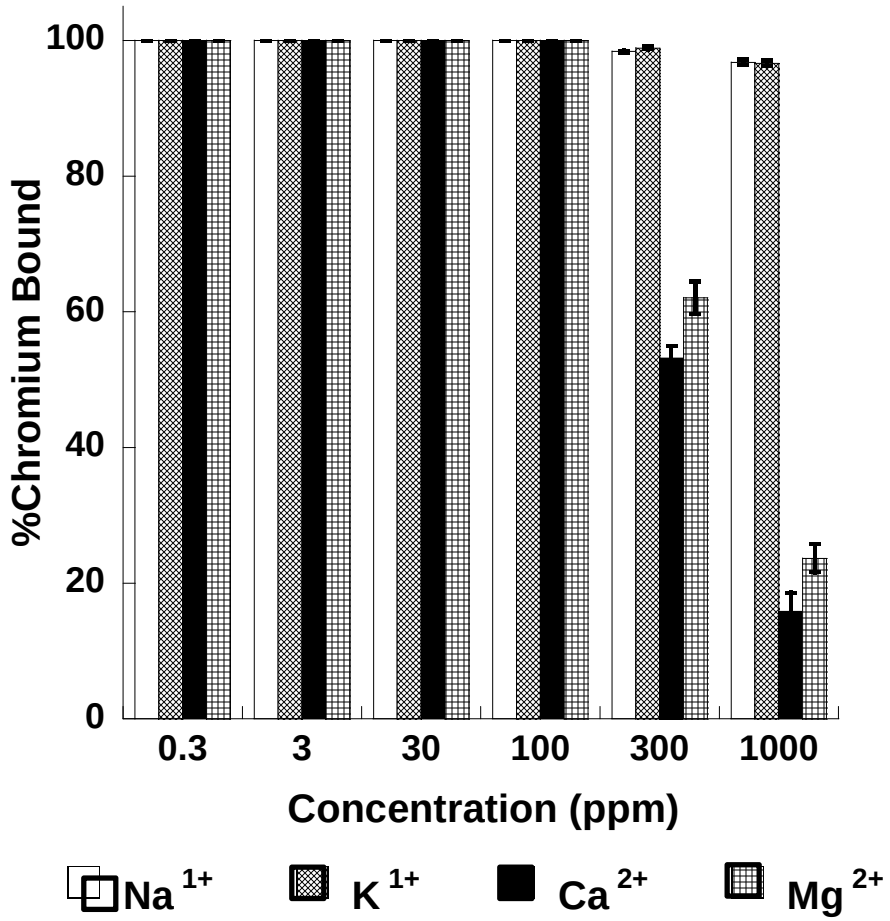

Figure 21: Cation Interference Study using Amino Modified Biochar

Finally, interference studies of combined anions and combined cations were performed to determine the effects on the Cr(VI) and Cr(III) binding to the native and amino modified biochar materials. Figure 22 shows the Cr(VI) and Cr(III) binding results for the native biochar. The combination of all the anions in solution showed a decrease in binding as the concentrations of the anions was increased, to be less than 20% at the 1000 ppm concentration of all anions. Whereas the cation interference combination showed a slight increase in the binding of the Cr(III) in comparison to the pH studies. The results of the Cr(VI) and Cr(III) binding to the amino modified in the presence of the combined interferences are shown in Figure 23. They

showed slight increases for the Cr(VI) binding up to anion concentrations of 100 ppm. However, above the 100 ppm the Cr(VI) binding was decreased greatly. Similarly, the binding of the Cr(III) to the amino biochar in the presence of the combined cations show increasing binding up to a cation concentration of 100 ppm and then was dramatically decreased thereafter. Both the native biochar and the amino modified biochar show a preference in the binding of Cr(VI) and Cr(III) over similar charged ionic species in solution. The Cr(VI) and Cr(III) concentrations are extremely small comparted to the interference concentrations at the 1000 ppm combined cation reaction give a cation: Cr ratio of 23,425 to 1 and binding of the Cr is still observed. Whereas in the anion interferences solution at the 1000 ppm concentration an anion: Cr ratio of 16,085 to 1. Even at the high ratio of anion to Cr(VI) the binding of Cr(VI) is still observed to occur [33].

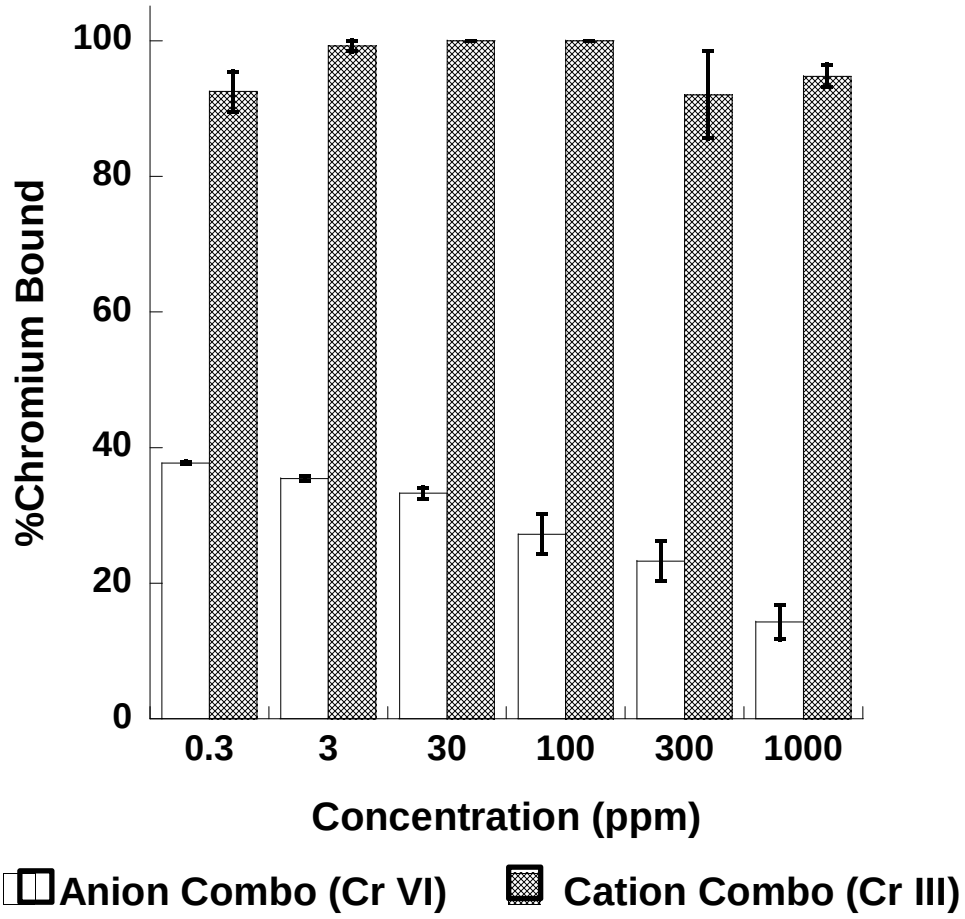

Figure 22: Interference Combo Studies using Native Biochar

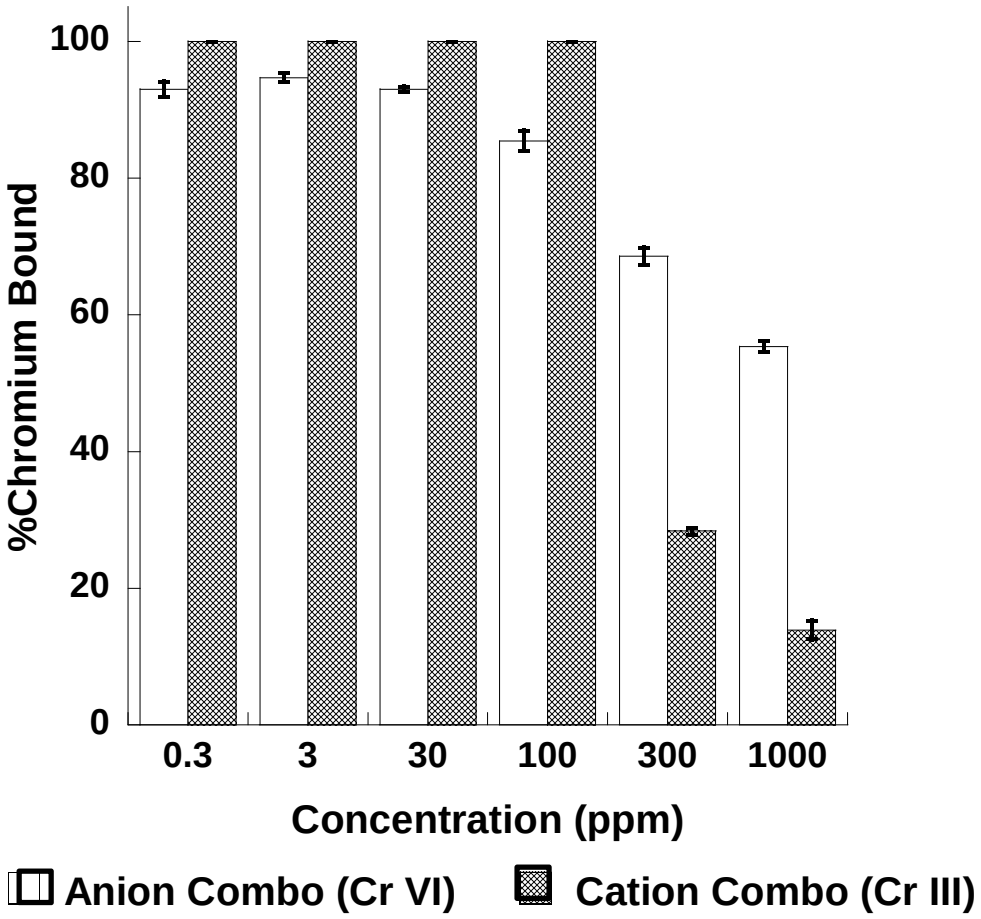

Figure 23: Interference Combo Studies using Amino Modified Biochar

CHAPTER V

CONCLUSIONS

Through the initial material sourcing to processing and production of the chosen bio-material; the primary objectives of the present study were

1. To produce a biochar material that was cheap and abundant
2. To chemically modify the biomaterial surface with amino groups
3. To investigate the effectiveness of the biochar for chromium removal
4. To investigate the thermodynamics of chromium binding

The chosen biomass material was pineapple skin for the production of biochar, the advantages of using pineapple skins for biochar production were the minimal processing of the starting material and ease of production. The biomass, pineapple skins, also provided advantageous opportunities for upcycling since the majority of consumers and industries, producing pineapple waste, have limited recyclable options for this material. Provided with this criteria, the pineapple skin was highly favorable for biochar production.

Following production of the native and amino modified biochar materials FTIR-ATR, SEM, and EDS mapping were performed to obtain general function group and surface morphology information. The results showed that the amino functionalization of the material surface was successful. The SEM imaging showed the retention of cellular structure despite the harsh conditions the material was exposed to during grinding and pyrolization; while EDS

mapping provided a visual representation of elemental correlation in chromium bounded biochars. These two techniques were supplemental to the FTIR-ATR spectra in confirmation of both the successful amination of the biochar and the effectiveness of chromium binding from solution under the various solution conditions.

The pH binding studies for Cr (III) and Cr (VI) with native biochar were consistent with previous reported studies found in literature. The Cr(III) did not bind well at low pHs whereas the Cr(VI) did not bind well at high pHs. The optimal binding for Cr (III) was found to occur at pH 4 whereas the optimum binding for Cr (VI) was found to occur at pH 2. Chemical modification of the surface of bio-based materials has been shown to change the way metal ions interact with the surface of a bio-material changing optimal binding pH as well as binding capacities. The amination or amino modification was performed with the intention of changing the optimum binding pH of the Cr(VI) as well as the binding capacity. The pH studies with amino modified biochar and Cr(VI) showed the desired change in the behavior with the effect of pH. Cr(VI) showed a dramatic change in the pH profile studies, it was found to be almost pH independent, very high removal values were observed at all pH's investigated. In addition, the Cr(III) binding occurred at lower pH, and became pH independent above pH 3.

Kinetic and thermodynamic data provided general information about the reactive properties of the material. A comparison, between the native and amino modified biochar and their interactions with Cr(VI) and Cr(III) were in agreement with their thermodynamics found in the literature. The reaction between Cr(III) and the native biochar showed favored binding with a decrease in temperature, indicating an exothermic reaction was occurring. Whereas Cr(VI) binding to the native biochar was found to follow a exothermic reaction process, with the binding increasing with increasing temperature based on the rates of reaction determined from the

kinetics studies. The activation energy for the Cr(VI) as determined to 18.4 kJ/mol which indicates a chemisorption process is occurring. Alternatively the Cr(III) binding to the native biochar had an activation energy of 11.4 kJ/mol which, is close to the border between chemisorption, physisorption, and ion-exchange. The binding of the Cr(VI) ions to the amino modified biochar followed an opposite trend to the rate of the reaction decreased with increasing temperature indicating an exothermic reaction was occurring, The activation energy for the binding of Cr(VI) to the amino modified biochar was determined to be 19.50 kJ/mol. The trend in the Cr(III) remained constant, with an endothermic reaction and a determined activation energy of 37.90 kJ/mol. The increase in the Cr(III) activation energy indicates a change in the binding process to a facilitated sorption mechanism. The thermodynamics of the binding supported the data collected from the kinetics studies. The Cr(VI) binding to the native biochar was occurring through an endothermic process as the ΔG values became more negative with increasing temperature and the ΔH was positive. Whereas the Cr(III) binding to the native biochar was endothermic with ΔG values decreasing with increasing reaction temperature and the ΔH of the process was negative. Alternatively, the binding of the Cr(VI) to the amino modified biochar was observed to have ΔG values that increased with increasing temperature and a ΔH which was negative indicating an endothermic process. The Cr(III) binding to the amino modified biochar followed the same as the native biochar with ΔG increasing with increasing temperature and a negative ΔH. The binding capacity of the biochar materials were found to be enhanced after the amino modification of the biochar. The binding capacity increases observed for Cr(VI) binding to the biochar after amino modification were 20 times or more at similar temperatures. The binding capacity increases observed for Cr(III) binding to the biochar after amino modification were again 20 at similar temperatures. The combination of the

thermodynamics data and the binding capacity data indicate that the amino modification has changed the binding process for Cr(VI) from a simple sorption to potentially a redox mechanism.

The interference studies over all highlighted that certain ions, such as silicates and phosphates, can have antagonistic effects towards the binding of Cr(VI) to the both the native and amino modified biochar materials. There were also apparent antagonistic effects of the high concentration anion matrices, which are supported by the negative effects observed on the binding in individual anion studies with Cr(VI). Alternatively cation interferences showed some positive effects on the binding of Cr(III) to the native and amino modified biochar materials. These effects were only observed at concentrations at or below 100ppm. At concentration above 100ppm were found a negative effect on Cr(III) binding was observed. The change in binding in the presence of interfering ion indicates that there is a limit of the concentration of interfering ions before the functional groups biochar become unable to interact as effectively with chromium ions in solution. However, the Cr(VI) and Cr(III) concentrations are extremely small comparted to the interference concentrations. For example, at the 1000 ppm combined cation reactions a cation: Cr ratio of 23,425 to 1 and yet binding of the Cr(III) is still observed. Whereas in the combined anion interferences solution at the 1000 ppm concentration, an anion: Cr ratio of 16,085 to 1, yet Cr(VI) is still binding. The binding at such high concentrations of interfering ions indicates some preference to bind Cr over other ions in solution.

Overall, the properties of the native and amino modified biochar materials derived from the batch studies allows for the understanding of the chemical functionalization process and their effects on traditional biochar materials. Future study of material types, particle sizes, pyrolization temperatures, and functionalization techniques will further the depth of understanding for this specific water remediation technique. The benefits of discovering new

absorbent materials for water remediation purposes is key in maintaining crucial potable water supplies around the world.

REFERENCES

[1] Perlman, Howard. "The World's Water." *Where Is Earth's Water?* The USGS Water Science School, 02 Dec. 2016. https://water.usgs.gov/edu/earthwherewater.html.

[2] United States of America. Environmental Protection Agency. *Chromium - Hazard Summary*. Environmental Protection Agency., Jan. 2000. https://www.epa.gov/sites/production/files/2016-09/documents/chromium-compounds.pdf.

[3] Gupta, Vinod K., and Imran Ali. *Environmental Water: Advances in Treatment, Remediation and Recycling*. 1st ed. Amsterdam: Elsevier, 2013.

[4] Wittmann, Gottfried T. W., and Ulrich Forstner. *Metal Pollution in the Aquatic Environment*. 2nd ed. Berlin Heidelberg New York: Springer-Verlag, 1981.

[5] Gore, Andrea C. "Heavy Metals as Endocrine-Disrupting Chemicals." *Endocrine-disrupting Chemicals: From Basic Research to Clinical Practice*. Totowa, NJ: Humana, 2007. 112.

[6] Iavicoli, Ivo, Luca Fontana, and Antonio Bergamaschi. "The Effects of Metals as Endocrine Disruptors." *Journal of Toxicology and Environmental Health, Part B* 12.3 (2009): 206-223. *National Center for Biotechology Information*. doi: 10.1080/10937400902902062.

[7] EPA. "National Primary Drinking Water Regulations." *Ground Water and Drinking Water*. Environmental Protection Agency, 22 Mar. 2018. www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.

[8] Wang, Chuanhua, Lingfeng Gu, Xiaoyan Liu, Xinying Zhang, Liya Cao, and Xiaoxin Hu. "Sorption Behavior of Cr(VI) on Pineapple-peel-derived Biochar and the Influence of Coexisting Pyrene." *International Biodeterioration & Biodegradation* 111 (2016): 78-84. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0964830516301275.

[9] Ma, Ying, Wu-Jun Liu, Nan Zhang, Yu-Sheng Li, Hong Jiang, and Guo-Ping Sheng. "Polyethylenimine Modified Biochar Adsorbent for Hexavalent Chromium Removal from the Aqueous Solution." *Bioresource Technology* 169 (2014): 403-08. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0960852414009791?via%3Dihub.

[10] Zhou, Lu, Yunguo Liu, Shaobo Liu, Yicheng Yin, Guangming Zeng, Xiaofei Tan, Xi Hu, Xinjiang Hu, Luhua Jiang, Yang Ding, Shaoheng Liu, and Xixian Huang. "Investigation of the Adsorption-reduction Mechanisms of Hexavalent Chromium by Ramie Biochars of Different Pyrolytic Temperatures." *Bioresource Technology* 218 (2016): 351-59. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0960852416309191.

[11] Cantu, Yvette, Abril Remes, Alejandra Reyna, Denise Martinez, Jahaziel Villarreal, Hilda Ramos, Samantha Trevino, C. Tamez, A. Martinez, T. Eubanks, and J.g. Parsons. "Thermodynamics, Kinetics, and Activation Energy Studies of the Sorption of Chromium(III) and Chromium(VI) to a Mn3O4 Nanomaterial." *Chemical Engineering Journal* 254 (2014): 374-83. *National Center for Biotechnology Information*. https://www.ncbi.nlm.nih.gov/pubmed/25097453.

[12] Valle, J. P., B. Gonzalez, J. Schulz, D. Salinas, U. Romero, D. F. Gonzalez, C. Valdes, J. M. Cantu, T. Eubanks, and J. G. Parsons. "Sorption of Cr(III) and Cr(VI) to K 2 Mn 4 O 9 Nanomaterial a Study of the Effect of PH, Time, Temperature and Interferences." *Microchemical Journal* 133 (2017): 614-21. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0026265X17303430.

[13] Selomulya, C., V. Meeyoo, and R. Amal. "Mechanisms of Cr(VI) Removal from Water by Various Types of Activated Carbons." *Journal of Chemical Technology & Biotechnology* 74.2 (1999): 111-22. *Wiley Online Library*. https://onlinelibrary.wiley.com/doi/abs/10.1002/%28SICI%291097-4660%28199902%2974%3A2%3C111%3A%3AAID-JCTB990%3E3.0.CO%3B2-D.

[14] Azimi, Arezoo, Ahmad Azari, Mashallah Rezakazemi, and Meisam Ansarpour. "Removal of Heavy Metals from Industrial Wastewaters: A Review." *ChemBioEng Reviews* 4.1 (2017): 37-59. *Wiley Online Library*. https://onlinelibrary.wiley.com/doi/full/10.1002/cben.201600010.

[15] Barakat, M.a. "New Trends in Removing Heavy Metals from Industrial Wastewater." *Arabian Journal of Chemistry* 4.4 (2011): 361-77. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S1878535210001334.

[16] Gunatilake, S. K. "Methods of Removing Heavy Metals from Industrial Wastewater." *Journal of Multidisciplinary Engineering Science Studies* 1.1 (2015): 12-18. *Semantic Scholar*. https://pdfs.semanticscholar.org/428f/d34c37f3b95900d80119e5726d3e17a73ace.pdf.

[17] Ahluwalia, Sarabjeet Singh, and Dinesh Goyal. "Microbial and Plant Derived Biomass for Removal of Heavy Metals from Wastewater." *Bioresource Technology* 98 (2007): 2243-257. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0960852405005675.

[18] Agrafioti, Evita, Dimitrios Kalderis, and Evan Diamadopoulos. "Arsenic and Chromium Removal from Water Using Biochars Derived from Rice Husk, Organic Solid Wastes and Sewage Sludge." *Journal of Environmental Management* 133 (2014): 309-14. *National Center for Biotechnology Information*. https://www.ncbi.nlm.nih.gov/pubmed/24412594.

[19] Dakiky, M., M. Khamis, A. Manassra, and M. Mer'eb. "Selective Adsorption of Chromium(VI) in Industrial Wastewater Using Low-cost Abundantly Available Adsorbents." *Advances in Environmental Research* 6.4 (2002): 533-40. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S109301910100079X.

[20] Mohan, Dinesh, Shalini Rajput, Vinod K. Singh, Philip H. Steele, and Charles U. Pittman. "Modeling and Evaluation of Chromium Remediation from Water Using Low Cost Bio-char, a Green Adsorbent." *Journal of Hazardous Materials* 188.1-3 (2011): 319-33. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0304389411001762.

[21] Kahraman, Havva Tutar, and Erol Pehlivan. "Cr 6 Removal Using Oleaster (Elaeagnus) Seed and Cherry (Prunus Avium) Stone Biochar." *Powder Technology* 306 (2017): 61-67. *Research Gate*. https://www.researchgate.net/publication/309561946_Cr6_removal_using_oleaster_Elaeagnus_seed_and_cherry_Prunus_avium_stone_biochar.

[22] Marsh, Harry, and F. RodriÌ guez-Reinoso. "Chapter 6: Activation Processes (Chemical)." *Activated Carbon*. Amsterdam: Elsevier, 2006. 322-65.

[23] Yang, Guang-Xi, and Hong Jiang. "Amino Modification of Biochar for Enhanced Adsorption of Copper Ions from Synthetic Wastewater." *Water Research* 48 (2014): 396-405. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0043135413007598.

[24] "Infrared Spectroscopy Absorption Table." *Chemistry LibreTexts*. Libretexts, 21 July 2016. https://chem.libretexts.org/Reference/Reference_Tables/Spectroscopic_Parameters/Infrared_Spectroscopy_Absorption_Table.

[25] Li, Qi, Youyu Zhu, Pinyi Zhao, Chao Yuan, Mingming Chen, and Chengyang Wang. "Commercial Activated Carbon as a Novel Precursor of the Amorphous Carbon for High-performance Sodium-ion Batteries Anode." *Carbon* 129 (2018): 85-94. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S0008622317312307.

[26] Chen, Shile, Mengting Cheng, Ying Lang, Hongkang Wei, and Chang-An Wang. "Synthesis and Chromatic Properties of Zircon Encapsulated Ceramic Black Pigment with Carbon Sphere as Carbon Source." *Journal of the European Ceramic Society* 38.4 (2018): 2218-227. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S095522191730818X.

[27] Quan, Ying, Qinfu Liu, Shilong Zhang, and Shuai Zhang. "Comparison of the Morphology, Chemical Composition and Microstructure of Cryptocrystalline Graphite and Carbon Black." *Applied Surface Science* 445 (2018): 335-41. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S0169433218308687.

[28] Sawalha, M. F., J. I. Gardea-Torresdey, J. G. Parsons, Geoffrey Saupe, and J. R. Peralta-Videa. "Determination of Adsorption and Speciation of Chromium Species by Saltbush (Atriplex Canescens) Biomass Using a Combination of XAS and ICP-OES." *Microchemical Journal* 81.1 (2005): 122-32. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S0026265X05000196.

[29] Ahsan, M. A., S. K. Katla, M. T. Islam, J. A. Hernandez-Viezcas, L. M. Martinez, C. A. DÃaz-Moreno, J. Lopez, S. R. Singamaneni, J. Banuelos, J. I. Gardea-Torresdey, and J. C. Noveron. "Adsorptive Removal of Methylene Blue, Tetracycline and Cr(VI) from Water Using Sulfonated Tea Waste." *Environmental Technology & Innovation* (2018): n. pag. *Science Direct*. Web. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S2352186418300130#b18.

[30] Parsons, J. G., M. Hejazi, K. J. Tiemann, J. Henning, and J. I. Gardea-Torresdey. "An XAS Study of the Binding of Copper(II), Zinc(II), Chromium(III) and Chromium(VI) to Hops Biomass." *Microchemical Journal* 71.2-3 (2002): 211-19. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S0026265X02000139.

[31] Pan, Jingjian, Jun Jiang, and Renkou Xu. "Adsorption of Cr(III) from Acidic Solutions by Crop Straw Derived Biochars." *Journal of Environmental Sciences* 25.10 (2013): 1957-965. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S1001074212603052.

[32] Saha, Papita, and Shamik Chowdhury. "Chapter 16: Insight Into Adsorption Thermodynamics." *Thermodynamics*. By Mizutani Tadashi. Rijeka: InTech, 2011. 349-64.

[33] Luther, Steven, Nathan Brogfeld, Jisoo Kim, and J.g. Parsons. "Study of the Thermodynamics of Chromium(III) and Chromium(VI) Binding to Iron(II/III)oxide or Magnetite or Ferrite and Magnanese(II) Iron (III) Oxide or Jacobsite or Manganese Ferrite Nanoparticles." *Journal of Colloid and Interface Science* 400 (2013): 97-103. *Science Direct*. https://www.sciencedirect.com/science/article/pii/S0021979713001975.

[34] Parsons, J. G., K. Dokken, J. R. Peralta-Videa, J. Romero-Gonzalez, and J. L. Gardea-Torresdey. "X-ray Absorption near Edge Structure and Extended X-ray Absorption Fine Structure Analysis of Standards and Biological Samples Containing Mixed Oxidation States of Chromium(III) and Chromium(VI)." *Applied Spectroscopy* 61.3 (2007): 338-45. *SAGE Journals*. http://journals.sagepub.com/doi/abs/10.1366/000370207780220912.

[35] Gardea-Torresdey, J. I., K. Dokken, K. J. Tiemann, J. G. Parsons, J. Ramos, N. E. Pingitore, and G. Gamez. "Infrared and X-ray Absorption Spectroscopic Studies on the Mechanism of Chromium(III) Binding to Alfalfa Biomass." *Microchemical Journal* 71.2-3 (2002): 157-66. *Science Direct*. https://www-sciencedirect-com.ezhost.utrgv.edu/science/article/pii/S0026265X02000073.

[36] Lay, Peter A., and Aviva Levina. "Kinetics and Mechanism of Chromium(VI) Reduction to Chromium(III) Byl-Cysteine in Neutral Aqueous Solutions." *Inorganic Chemistry* 35.26 (1996): 7709-717. *ACS Publications*. https://pubs.acs.org/doi/abs/10.1021/ic960663a.

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