REMOVAL OF BROMIDE FROM FLUE GAS DESULFURIZATION WASTEWATER USING SILVER MODIFIED BIOCHAR

by

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(Under the Direction of Valentine Nzengung)

ABSTRACT

Bromide in flue gas desulfurization (FGD) wastewater contains a significant concentration of bromide which can contaminate potable water sources. During water disinfection, bromide can form deleterious brominated disinfection by products; therefore, removing bromide from FGD wastewater is essential. To determine a cost-effective method for removing bromide from FGD wastewater, we evaluated the use of silver modified biochar in batch and column tests. We report that silver modified biochar showed promise in batch and column tests with removal efficiencies between 61% and 99% in batch tests and sustained removal efficiencies between 65% and 80% in column tests. We conclude that silver modified biochar is an effective technique for bromide removal from FGD wastewater due to specific adsorption between silver and bromide. This data may play a role in designing fixed bed adsorption systems or continuously stirred batch reactors for FGD wastewater treatment.

INDEX WORDS: bromide, flue gas desulfurization, biochar, silver modified biochar, batch test, column test, chloride, anion removal, wastewater treatment

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DEDICATION

To my family. Thank you for making me see this through to the end.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Coal combustion is a cheap and efficient process for electricity generation. In fact, over 90% of combusted coal is used to generate electricity, and coal accounted for 14% of all fossil fuel production on a heat content basis in 2020 (EIA, 2021). Coal fired power plants (CFPPs) have been a staple in energy production for the U.S. for many years; however, recent data indicates that coal usage is declining due to increased use of natural gas and the rise of alternative energy sources, such as nuclear, biomass, solar, wind, geothermal, etc. (Figure 1). Coal fired power plant capacity peaked in 2011 at 318 gigawatts (GW) and has decreased to 229 GW in 2019. Despite the declines, CFPPs are still a primary source of energy in the United States particularly in the southeast region (Figure 2) (EIA, 2020).

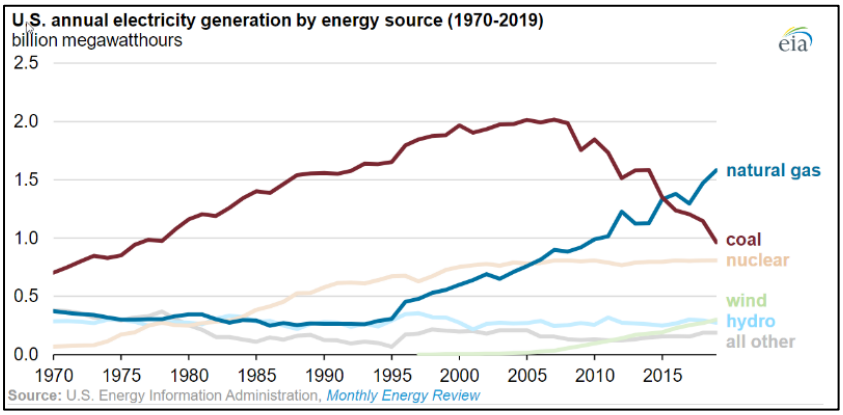

Figure 1 – Sources of energy in the United States. From EIA, (2020)

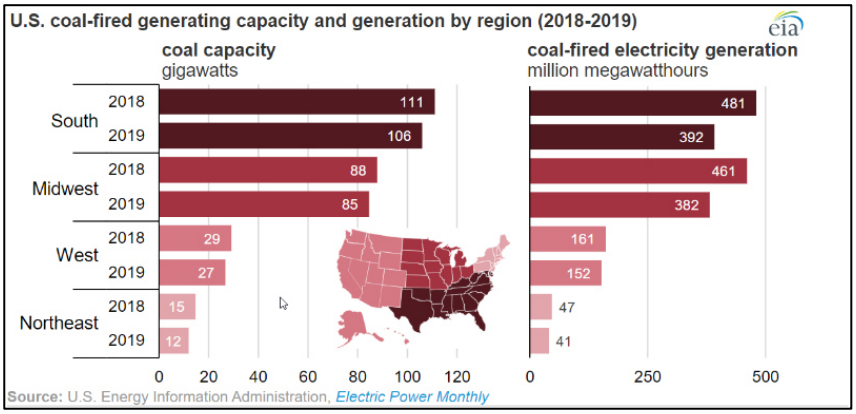

Figure 2 – Regional map of coal fired power plant electricity generation. From EIA, (2020).

Although coal is an important resource that supports daily life, the combustion gasses have negative impacts for the environment. Sulfur dioxide is a major contaminant of concern from coal combustion for electric power generation.

Sulfur Dioxide Emissions

Although carbon dioxide (CO_2) is the most notable and largest pollutant from CFPPs, another important pollutant from coal combustion is sulfur dioxide (SO_2). Most coal contains approximately 1 – 3% sulfur, which is in pyrite (FeS_2), an iron sulfide mineral, and thiophene (C_4H_4S), an organic pentagonal ring structure. The sulfur in pyrite and thiophene is in a reduced state; however, when coal is mined and subsequently burned, the sulfur is oxidized to SO_2. The +4 oxidation state of SO_2 continues to increase once it is released to the atmosphere. In the atmosphere it can react with hydroxyl radicals (·HO) to form $\cdot HSO_3$ as follows:

$$SO_2 + \cdot HO \rightarrow \cdot HSO_3 \quad (1)$$

The oxidation state of sulfur in $\cdot HSO_3$ is +5, and it can react further with O_2 and H_2O to form sulfuric acid (H_2SO_4).

$$\cdot HSO_3 + O_2 + H_2O \rightarrow H_2SO_4 + \cdot HO_2 \quad (2)$$

Sulfuric acid includes sulfur in the +6 oxidation state and is a strong acid that dissociates completely in atmospheric water and creates acid rain (Ryan, 2014). Acid rain is known to harm sensitive ecosystems and can have detrimental effects on aquatic and terrestrial ecosystems. Most aquatic species have a narrow pH range they can survive in; therefore, lowering the pH can be detrimental to aquatic organisms' survival. Acid rain can also leach minerals and nutrients from soils. Additionally, acid rain leaches aluminum from clay particles which can be toxic to plants. Furthermore, SO_2 can form fine sulfate particulates in the atmosphere that can harm human respiratory systems. Due to the harmful effects of acid rain, a method to control SO_2 emissions from CFPPs was desperately needed. To reduce air pollution and acid rain, flue gas desulfurization was developed as a method for removing SO_2 from flue gasses at CFPPs.

Flue Gas Desulfurization

A common FGD process is a wet scrubbing system that requires spraying an alkaline slurry on upwelling flue gas that contains SO_2 (Figure 3).

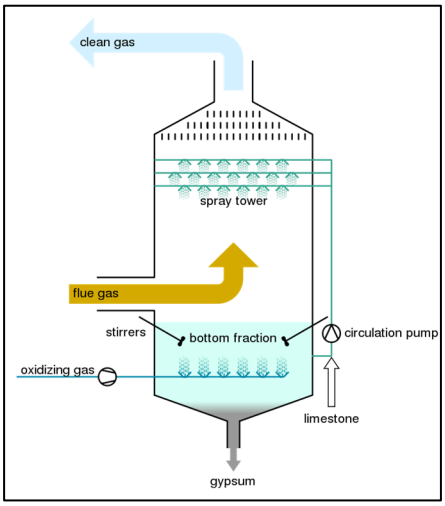

Figure 3 – Wet scrubbing FGD system (ASD reports, 2015).

The sulfur is removed by the formation of gypsum solids through the following chemical reactions (Higgins et al., 2009).

$$CaCO_3\ (s) + SO_2\ (g) \rightarrow CaSO_3\ (s) + CO_2\ (g) \quad (3)$$

$$2CaSO_3\ (s) + O_2\ (g) \rightarrow 2CaSO_4\ (s) \quad (4)$$

The gypsum solids can be removed and reused for commercial wallboard manufacturing, agricultural lime substitute, road construction, or backfill material for mine site reclamation; although, most of it unfortunately ends up in landfills (Alvarez-Ayuso et al., 2006). Once the solids are removed, the FGD water can be re-used for further SO_2 removal. The resulting wastewater tends to contain high chloride concentrations of up to 12,000 milligrams per liter (mg/L), and corrosion of the metal FGD tank may occur. Therefore, the water must be purged in order to sustain the infrastructure of the FGD system (Higgins et al. 2009). This purge water is FGD wastewater which contains harmful elemental contaminants and must be treated.

The FGD wastewater chemical composition can be influenced by differences in coal composition, type of scrubber, and the gypsum dewatering system. Concentrations of acidic gasses (e.g., chlorides, fluorides, and sulfates) vary depending on the type of coal used. Metals such as arsenic, mercury, boron, cadmium, selenium, and zinc also are present in varying concentrations depending on the parent coal material. Minor amounts of clay in the coal can contribute aluminum to the FGD wastewater, and the main source of iron is from the corrosion of balls in the ball mill utilized to crush limestone for the aqueous slurry (Higgins et al. 2009).

Treatment of FGD wastewater is conducted at the coal fired powerplant in order to comply with National Pollutant Discharge Elimination System (NPDES) requirements. A basic treatment system may include methods for clarification, total suspended solids (TSS) removal,

heavy metal precipitation, and filtration. Any further tertiary treatment will be contaminant specific (Higgins et al., 2009).

Contaminant of Concern in FGD – Bromide

Bromide is a naturally occurring halide ion in group 7 of the periodic table. In nature, bromine occurs in multiple oxidation states, with the most widespread being the negative univalent bromide anion. In natural waters, bromide concentrations are highest in closed hypersaline lakes with concentrations in the 10^3 mg/L range. Sea water contains an average of approximately 65 mg/L bromide. Natural surface waters can contain bromide concentrations that range from less than 1 mg/L to >100 mg/L, depending on the environment. Arid environments typically have higher concentrations of bromide than coastal environments due to rapid evaporation of water which concentrates any dissolved constituents. In groundwater, concentrations of bromide are commonly low, ranging from <1 mg/L to 30 mg/L, but in hypersaline groundwater the range is from 50 mg/L to ~2,600 mg/L (Winid, 2015).

In FGD wastewater, bromide concentrations commonly fall between 10 to 200 mg/L and typically come from calcium bromide (CaBr) salts added in order to reduce gaseous mercury emissions. In 2015, the Mercury and Air Toxics Standards (MATS) was implemented to control gaseous emissions of mercury and other metals. The MATS requirements resulted in the installation of many wet scrubbing systems at CFPPs. The addition of CaBr helps solubilize mercury by converting it into Hg^{2+}, a more water-soluble ion (McTigue et al. 2014). The mercury emission control method increases the amount of bromide discharged to the natural environment in FGD wastewater.

Even higher bromide concentrations can occur if the coal is naturally enriched with bromine. In general, bituminous coal has higher amounts of bromine, while lignite and sub-

bituminous coal have lower amounts of bromine. Bituminous coal also has high amounts of sulfur, which make it cheaper than low-sulfur coal; therefore, the more cost-effective bituminous coal will have more bromide (McTigue et al. 2014). Several studies have analyzed bromine levels in coal, and coal can contain negligible amounts of bromine down to 0.12 milligrams per liter (mg/L) (Peng and Wu, 2014), but can reach concentrations above 1,300 mg/L (Vassilev et al., 2000).

Health Impact of Brominated Compounds

Most surface water and groundwater do not contain concentrations of bromide that exceed 0.2 mg/L; therefore, bromide as an ion is not a direct concern for public health since the LD_{50} (dose killing 50% of organisms) is 3,500 – 7,000 milligrams per kilogram (mg/kg). Meanwhile, during potable water disinfection, bromide can form various disinfection by products (DBPs) that are more toxic than the bromide ion (Winid, 2015). For example, when oxidative water treatment occurs with chlorine or ozone, bromide can be oxidized to hypobromous acid (HOBr) which can then react with natural organic matter (NOM) to form mutagenic organobromine species such as bromoform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoacetic acid (Karanfil et al., 2008; Winid, 2015). These species are included in the total trihalomethanes (TTHMs) and the five haloacetic acids (HAA5) regulated by the EPA. Other unregulated disinfection by products such as halonitromethanes, haloamides, and haloacetonitriles will also be generated with increasing bromide concentration (Krasner et al. 2006; Pressman et al. 2010). Additionally, ozonation can transform bromide to bromate (BrO_3^-). Bromate is a regulated carcinogenic DBP with an EPA maximum contaminant level (MCL) of 0.01 mg/L (EPA, 2010; Winid, 2015). Numerous DBPs exists beyond what is stated above, and many have several routes of exposure such as ingestion,

inhalation, and skin adsorption. DBPs, specifically trihalomethanes, have been associated with increased risk of bladder cancer, and other DBPs have a slight correlation with negative effects on fetal growth (Villanueva, 2015). In general, brominated DBPs are more toxic and carcinogenic than their chlorinated analogues; thus, brominated DBPs should be kept to a minimum in water treatment (Richardson et al. 2003).

The disinfectants/disinfection byproduct rule (D/DBPR) of the USEPA sets stringent regulations on DBPs released in effluent including guidelines for maximum allowable concentrations and sampling procedures. Stage 2 of the D/DBPR requires utility companies to adhere to MCLs for four individual trihalomethanes (i.e., chloroform, bromodichloromethane, Dibromochloromethane, and Bromoform) and the sum of all four trihalomethanes listed cannot exceed 0.08 mg/L. The five haloacetic acids (i.e., Monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid) also have MCLs and the sum of the five listed haloacetic acids cannot exceed 0.60 mg/L (EPA, 2010).

A common strategy for DBP minimization is to remove the precursors of DBPs such as bromide. By removing the DBP precursors, the amount of various DBPs can be reduced; therefore, reducing time and money spent removing the DBPs before water distribution (Watson et al., 2012). Due to negative effects of brominated DBPs, the removal of bromide from wastewater that can potentially contaminate drinking water sources is critical.

Bromide Discharge Regulations

Many wastewater effluents have discharge limits that are strictly enforced or recommended by regulatory agencies. These limits are calculated by toxicologists that model the fate of different contaminants in the human body; therefore, a regulatory objective is directly influenced by the health-based objective.

The EPA 2015 final rule for steam electric generating power plants established a limitation of 0.2 micrograms per liter (μg/L) for bromide in FGD wastewater effluent for power plants participating in the voluntary incentives program (VIP). The stringent limitation is required in exchange for an extension until 2028 to meet compliance. Although numerical limits were not proposed beyond what is necessary for the VIP program, three treatment options for bromide were put forward to the EPA to reduce bromide discharges in FGD wastewater. The three methods are 1) zero liquid discharge such as thermal treatment or membrane filtration, 2) reverse osmosis, and 3) monitoring bromide levels in discharge and providing data to state permitting authorities to come up with site specific discharge limits. The current 2020 final rule solicits commentary about cost effective methods for bromide removal as well as methods for removing other halides that may form DBPs (EPA, 2020). Clearly, the EPA recognizes the need for bromide removal from FGD wastewater, and as such research must be conducted on cost effective methods for bromide removal.

Existing Bromide Removal Techniques

Several methods are available for removing bromide from water. A literature review by Watson et al. (2012), concludes that the three primary techniques for bromide removal from water are membrane techniques, electrochemical techniques, and adsorption techniques.

Membrane techniques such as reverse osmosis and nanofiltration remove the most amount of bromide but are cost prohibitive due to the expensive membranes and high energy input necessary to maintain high pressures. Additionally, with a wastewater containing a high ionic strength such as FGD wastewater, the reverse osmosis and nanofiltration process will yield small amounts of permeate (clean water) and significant quantities of concentrated brine solution, meaning even more membranes will be needed to continually treat the brine solution

which reduces membrane life and is not cost effective. Membrane techniques appear to be well suited for drinking water purification or in special circumstances where desalination of seawater must occur, but not for high ionic strength FGD wastewater treatment. Electrochemical techniques such as electrolysis capacitive deionization are also cost prohibitive and require high energy inputs to treat wastewater. The electrochemical techniques are promising for bromide removal, but further research would be necessary for a scaled-up system to be applied at a coal fired power plant. Adsorption techniques are also promising; however, some common techniques for monovalent ion removal such as ion exchange membranes and resins are cost prohibitive and not suitable for large quantities of FGD wastewater. Additionally, some sorbents such as pristine activated carbon and soils have little effectiveness for removing bromide, are not specific enough to target bromide in a complex wastewater or are too expensive to produce. Clearly there is variability in the effectiveness, applicability, and cost of different sorbents. Adsorption is likely the simplest method and easiest to apply but requires that appropriate sorbents be identified and evaluated.

Recent peer reviewed literature reveals the state of the art regarding bromide removal from water. Nanofiltration, evaluated by Lin et al. (2020), only removed a maximum of 28.3% bromide, while bromate, was better removed by the membrane due to its larger size not being able to penetrate the membrane. Membrane capacitive deionization, evaluated by Dorji et al. (2020), removed between 68% to 70% of bromide from an initial concentration of 0.3 mg/L. Bromide selective ion exchange resins, evaluated by Soyluoglu et al. (2020), removed up to 93% bromide from an initial concentration of 0.25 mg/L, although the removal efficiency decreased as the chloride to bromide ratio increased. AgCl-superfine activated carbon, evaluated by Ateia et al. (2019) removed 94 +/- 3% bromide from groundwater with an initial concentration of 2.0

mg/L and between 84% to 86% bromide from surface water with an initial concentration of 1.04 mg/L. In general, increasing the chloride and natural organic matter content in solutions will reduce bromide removal efficiencies. Although the results from previous research are promising, it is critical to identify a cost-effective alternative for bromide removal from FGD wastewater.

The objective of this research is to evaluate the efficacy of silver modified biochar for removal of bromide from FGD wastewater. A secondary objective is to monitor chloride concentrations since chlorides are commonly two orders of magnitude higher than bromide in FGD wastewater and strongly compete for sorption sites due to similar ionic potential.

CHAPTER 2

PHYSICO-CHEMICAL CHARACTERISTICS OF BIOCHAR

Biochar Structure

Biochar is a carbonaceous adsorbent material produced by pyrolysis of organic waste biomass. Sources of biomass can include hard and soft wood, straw, animal and municipal wastes, plant residues/wastes, and algal biomass to name a few (Jeong et al. 2016). After pyrolysis, a black carbonaceous material is obtained which is similar to activated carbon (AC) and contains macropores (>50nm), mesopores (2-50nm), and micropores (<2nm) (Kazemi Shariat Panahi et al. 2020). Carbonaceous biochar can be used in the environmental industry as an adsorbent for organic or inorganic contaminants as well as for agricultural soil supplements (Ahmad et al. 2014; Jeong et al. 2016).

The pore size distribution in biochar is important for its utility because it plays a role in the transport of species to and from adsorption sites. For example, micropores (<2nm) give rise to the highest surface area and contribute substantially to the adsorption of small molecules (Kazemi Shariat Panahi et al. 2020). The pyrolysis temperature and heating rate have been shown to affect the microporosity of biochar. Pyrolysis temperatures between 400 degrees Celsius (°C) and 850 °C yield higher microporous structure, while temperatures >850 °C have decreased microporosity (Li et al. 2019; Zhang et al. 2004). The decreased microporosity at higher temperatures is likely due to the thin pore walls between micropores being destroyed (Zhang et al. 2004). Pyrolysis of biochar using a fast-heating rate can cause melting which forms macropores (>50 nm), while a slow heating rate enhances microporosity (Cetin et al. 2004). Moreover, mesopores (2 – 50nm) and macropores act as channels for adsorbable solutes to travel

through to micropores; thus, all pore types play a specific role in the adsorption capacity of biochar.

Biochar characteristics are variable and depend on the pyrolysis temperature and original biomass/feedstock composition. Characteristics of biochar that are affected by pyrolysis temperature include total biochar yield, ash content, pH, surface area, carbon content, and nutrient content (N, S, O concentrations). In general, increasing pyrolysis temperature yields lower amounts of biochar (Hossain et al. 2011) and increases the amount of ash content (Cantrell et al. 2012; Song and Guo, 2012). Biochar produced at higher temperatures also has a higher pH than low temperature biochar (Hossain et al. 2011; Yuan et al. 2011; Cantrell et al. 2012; Song and Guo, 2012; Li et al. 2019). The higher pH at higher pyrolysis temperatures is likely due to decomposition of hydroxyl bonds in the biochar structure (Li et al. 2019). Biochar carbon content and surface area increase with increasing pyrolysis temperature, while the nutrient content (e.g., nitrogen, sulfur, and oxygen) decreases (Hossain et al. 2011; Cantrell et al. 2012; Song and Guo, 2012). The biomass composition can vary between lignin rich and cellulose rich. Lignin is very recalcitrant and degrades at temperatures between 280 – 500 °C, and the resulting biochar contains a macroporous structure (Joseph et al. 2007). Cellulose is easily degraded at temperatures between 200 – 260 °C, and the resulting biochar contains a microporous structure (Downie et al. 2009; Joseph et al. 2007).

Biochar Adsorption Characteristics

The adsorption capacity and remediation potential of biochar is affected by the amount of oxygen containing functional groups such as carboxyl groups, hydroxyl groups, and phenolic groups (Figure 4). Other N-based functional groups have also been detected in biochar (Leng et al. 2019). Examples of inorganic N-functional groups include NH_4-N, NO_2-N and NO_3-N while

organic N-functional groups may be pyridinic, pyrrolic, graphitic, amine, amide, and/or nitrile groups (Leng et al. 2019). When producing biochar, higher temperatures (>700 ºC) have been shown to decrease the number of functional groups and the cation exchange capacity (CEC) (Li et al. 2017). The lowered CEC at higher temperatures is likely due to removal of acidic functional groups (Li et al. 2019). Jeong et al. (2016) concluded that a pyrolysis temperature of 550 ºC was ideal for adsorption due to high biochar stability and maximum CEC as well as no lignin decarboxylation or demethoxylation. Additionally, the amount of hydrophobic sorption sites as well as non-pyrolyzed organic matter can affect the adsorption capacity of biochar. Hydrophobic contaminants have a high affinity for hydrophobic sites and non-pyrolyzed organic matter associated with the biochar.

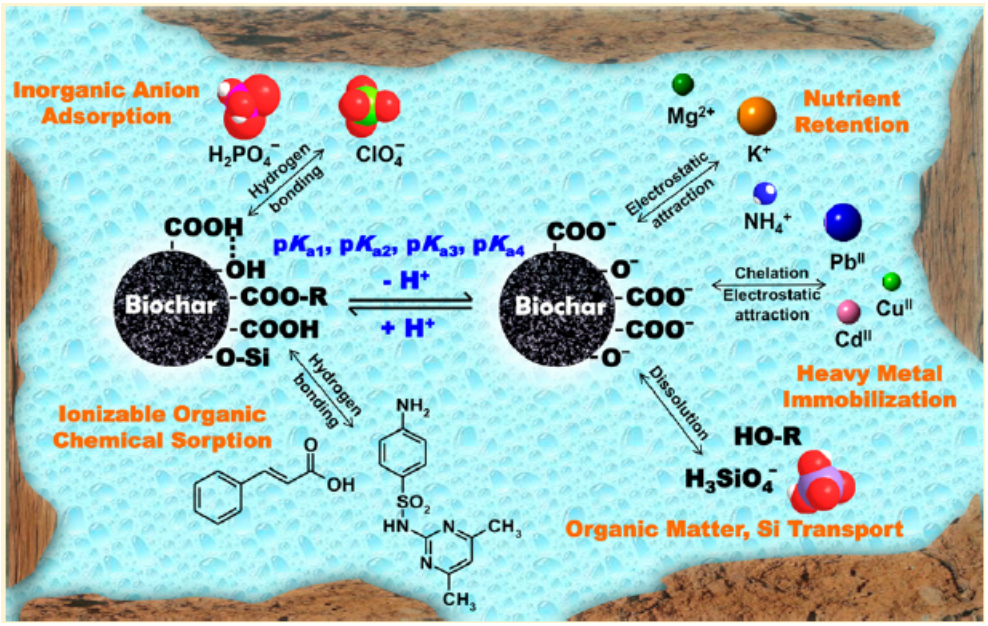

Figure 4 – Biochar functional groups and applications for environmental remediation. From Chen et al. (2015).

Modified Biochar

Further modifications can be made to biochar to tailor its physical and chemical characteristics and solve specific environmental problems. Several methods are available to modify the surface of biochar. These methods include activation with steam, oxidizing agents, alkaline agents, acids, metals, clays, microorganisms, and organic compounds (Sizmur et al. 2017).

Of these methods, modification with metal shows most promise for removal of anions such as bromide. Since bromide is negatively charged and pristine biochar carries an overall negative charge, it is unlikely that bromide would be adsorbed to pristine biochar due to the low anion exchange capacity and inherent repellency of negative charges. Therefore, a modification with metals is necessary to raise the amount of bromide sorption. Modification with metals is performed by immersing the biochar in metal nitrate or metal chloride salt solutions (typically 0.25 – 0.5 M). After the immersion of biochar, it is filtered and dried at temperatures between 50 ºC – 300 ºC to volatilize NO_2 and Cl_2 gasses. The ideal metal modified biochar will have an even distribution of metal on the porous biochar surface.

Metal modified biochar may be useful for bromide removal from FGD wastewater. Previous research by Favero, (2020) found that iron modified biochar showed promise for bromide removal in batch and column tests. Batch tests by Favero, (2020) indicated that iron modified peanut hull biochar could remove 32 – 34% of bromide from FGD wastewater and iron modified bamboo biochar had the highest bromide loading of 241 mg/kg. A column test by Favero, (2020) indicated that iron modified bamboo biochar could remove bromide from FGD wastewater; although, removal efficiency quickly decreased and reached 90% breakthrough after 3 pore volumes. Although these results are promising, further research is warranted to confirm

these results and find more effective methods for the treatment of large volumes of FGD wastewater.

Biochar modified with silver is likely useful for bromide removal since silver is known to complex with halides and form insoluble precipitates. No previous research has been conducted using silver modified biochar to remove bromide from FGD wastewater; however, other silver modified materials have been tested for bromide removal from freshwater (Table 1). Previous research has examined silver modified carbon spheres (Gong et al., 2013), activated carbon (Chen et al., 2017), aerogels (Sanchez Polo et al., 2007), and polymeric cloth (Polo et al., 2016) as well as silver amended coagulation (Gan et al. 2018). Silver modified porous carbon spheres (Gong et al. 2013) removed 98% of bromide from freshwater with an initial bromide concentration of 200 μg/L and silver modified activated carbon (Chen et al. 2017) removed 85 – 93% of bromide from freshwater with an initial bromide concentration of 300 μg/L, indicating that high removal efficiencies occur when using silver modified highly porous carbonaceous material. In contrast, silver modified aerogels only removed 60 - 71% of bromide (Sanchez-Polo et al. 2007), silver amended coagulation removed 20 – 90% of bromide from natural water with bromide concentrations ranging from 47 to 426 μg/L (Gan et al. 2018), and silver modified polymeric cloth removed 0.83 – 1.46 mg Br^-/g Ag^+ cloth from an initial concentration of 2.5 x 10^{-5} M bromide (Polo et al. 2016). It is apparent that the highest removal of bromide comes from using carbonaceous materials as a vessel for silver modification; therefore, investigations using silver modified biochar are warranted. Due to the cost effectiveness of biochar and the success of previous research using silver modified materials, this study intends to use silver modified biochar as a method for removing bromide from FGD wastewater.

Silver is likely the key element necessary for bromide removal; although, in the FGD wastewater bromide removal may be inhibited by the high relative amount of chloride. The formation of silver salts and their respective solubility constants are shown in the following reactions (Gledhill and Malan, 1953)

$$Ag^{+} + Br^{-} \rightarrow AgBr(s) \quad K_{sp} = 5.4 \times 10^{-13} \tag{5}$$

$$Ag^{+} + Cl^{-} \rightarrow AgCl(s) \quad K_{sp} = 1.8 \times 10^{-10} \tag{6}$$

Since the K_{sp} of AgBr(s) is much lower than the K_{sp} of AgCl(s), the formation of AgBr(s) is more likely to occur; however, the exceedingly high chloride concentration may inhibit the formation of AgBr(s). Although, an ion exchange between bromide and chloride can occur according to the reaction (7) below.

$$AgCl(s) + Br^{-} \rightarrow AgBr(s) + Cl^{-} \tag{7}$$

The reaction indicates that bromide can exchange with chloride in water, although a high chloride concentration may hinder or reverse the above reaction.

Table 1 – Previous research using silver modified materials for bromide removal.

Author	**Method**	**Contaminant**	**Initial Concentration**	**Removal Amount**
Chen et al. (2017)	Ag-Activated Carbon	Bromide	300 μg/L	85 – 94%
Gan et al. (2018)	Ag-amended coagulation	Bromide	Cl:Br ratios of 15 – 886	40%
Gong et al. (2013)	Ag-porous carbon spheres	Bromide	200 μg/L	94%
Polo et al. (2016)	Ag-polymeric cloth	Bromide and Iodide	2.5×10^{5} M	0.83 – 1.46 mg Br^{-} /g Ag cloth
Sanchez-Polo et al. (2007)	Ag-aerogels	Bromide and Iodide	150 μg/L	60 – 71%

CHAPTER 3

MATERIALS AND METHODS

Wastewater

Multiple batches of FGD wastewater were collected from a coal fired power plant in the southeast United States. Powerplant employees collected the wastewater directly from the FGD blowdown prior to clarification; therefore, the wastewater contained high levels of suspended solids. The wastewater was collected in clean plastic 20 or 40-liter (L) sampling containers. FGD wastewater was transported from the power plant to the Riverbend Research Laboratory at the University of Georgia. At the laboratory, the wastewater sat at room temperature for 2-3 days while the suspended solids settled. Once the suspended solids settled, the wastewater was decanted, filtered through P8 filter paper, and stored in the freezer for long term storage at a temperature of -8.7 °C until the time of use when the samples were thawed in a refrigerator at 14 ºC. Freezing and refrigeration was used as a preservation method to inhibit any chemical changes from occurring in the FGD wastewater.

A sample of the filtered FGD wastewater was collected in a 500 milliliter (mL) polyethylene Nalgene container and transported to the University of Georgia Soil Plant and Water laboratory for a baseline analysis which included major cations and anions.

Biochar Modification

Five different varieties of biochar were used throughout the experiments: bamboo, bone, hardwood, softwood, and peanut hull (Figure 5).

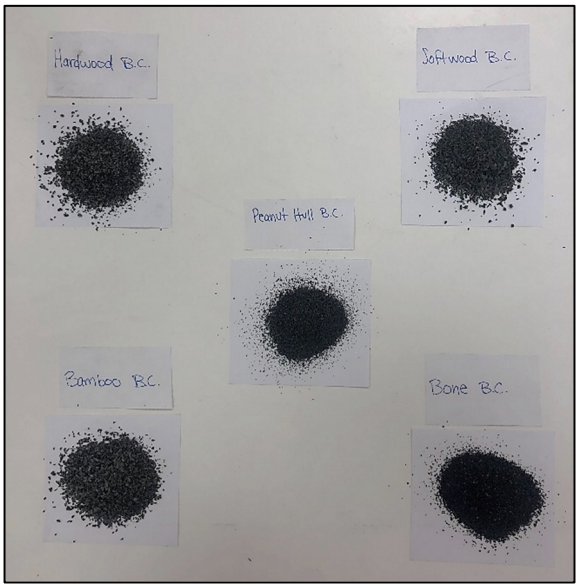

Figure 5 – Five feedstocks for biochar used throughout this study. Hardwood, softwood, peanut hull, bamboo, and bone.

Except for the peanut hull biochar, all biochar samples were purchased from commercial vendors not affiliated with the University of Georgia (Table 2). Prior to all experiments the biochar was dried and sieved to 500µm < X < 2mm (Figure 6).

Figure 6 – Particle size of biochar (500 µm < X < 2mm) used in batch and column tests.

Table 2 – Different biochar types and pyrolysis temperature.

Feedstock	Commercial Name	Vendor	Pyrolysis Temperature (°C)
Hardwood	Made to Order	BioChar Central	600
Softwood	Made to Order	BioChar Central	600
Bamboo	Made to Order	BioChar Central	600
Aged Bones	BONE CHAR 2060-BC	Charcoal House	Not Available
Peanut Hulls	-	Produced In-house	500

Biochar modification started by mixing biochar with 40 mL of boiling deionized (DI) water for every gram of biochar. Each biochar sample was washed three times to remove soluble impurities and very fine particulates from the biochar surface. After washing the biochar, it was left to dry in the oven at 105 ºC. Standard drying time was 24 hours; however, large quantities would sometimes take up to 48 hours to completely dry. Once dried, the modification using ferric chloride ($FeCl_3$) or silver nitrate ($AgNO_3$) was conducted.

Preparation of Ferric Iron Modified Biochar

All five types of biochar were modified with iron by mixing 10 mL of 0.5 M $FeCl_3$ solution per gram of biochar for 12 hours using a stir bar. After 12 hours the $FeCl_3$ solution was filtered from the biochar using a vacuum filter and P8 filter paper. The biochar was then dried for 24 hours at 105 ºC. Once completely dried, it was rinsed with DI water 10 times. Each rinse consisted of 40 mL DI water per gram of biochar. The rinsed biochar was dried at 105 ºC for 24 hours.

Preparation of Silver Modified Biochar

All five types of biochar were modified with silver nitrate ($AgNO_3$). For batch tests, one gram of washed biochar was mixed with 10 mL of 0.5 M $AgNO_3$ solution (10:1 V/M ratio) for

12 hours. For column tests, 250 grams of washed biochar was mixed with 1000 mL of 0.5 M $AgNO_3$ solution (4:1 V/M ratio) for 12 hours. After 12 hours the $AgNO_3$ solution was filtered from the biochar using a vacuum filter and P8 filter paper. The filtered $AgNO_3$ liquid was collected and stored in tightly sealed clean mason jars for further use. The biochar was then dried for 24 hours at 105 ºC. Once completely dried, it was rinsed with DI water 10 times. Each rinse consisted of 40 mL DI water per gram of biochar. The rinsed biochar was dried at 105 ºC for 24 hours.

Batch Sorption Experiments

Batch sorption tests were conducted to determine bromide removal efficacy. Several batch tests were conducted using FGD wastewater. A known mass (0.5 or 1.0 grams) of each type of biochar was mixed with 40 mL FGD wastewater in a 50 mL polypropylene centrifuge tube (Falcon 2098 Blue Max and ThermoScientific Nunc conical tubes). Replicates of all experiments were prepared. Additionally, 40 mL of FGD wastewater and 40 mL of DI water were used for quality control. The centrifuge tubes were placed on a rotating shaker at a speed of 3.3 revolutions per minute (rpm) for 24 hours to attain equilibrium. After 24 hours, the samples were placed in a centrifuge for 20 minutes at 2,000 rpm to separate the biochar from the solution phase.

Subsequently, the maximum loading of bromide onto each biochar was performed. Loading tests were conducted with silver modified softwood, silver modified hardwood, silver modified bone, and silver modified peanut hull biochar. Different masses of biochar including 0.025, 0,05, 0.1, 0.25, 0.5, 0.75, 1.0, and 1.25 grams of each type of biochar were mixed with 40 mL of FGD wastewater in clean 50 mL polypropylene centrifuge tubes. The mass of the biochar was varied instead of the concentration of bromide because it was necessary to maintain the

chemical composition of the FGD wastewater; therefore, extra chemicals were not added to the FGD wastewater. The centrifuge tubes were placed on a rotating shaker for 24 hours at a speed of 3.3 rpm and samples were collected in 20 mL polyethylene scintillation vials. All mass loading experiments were performed in triplicate.

To obtain data required to estimate cost effectiveness, additional batch tests were conducted to measure the lowest concentration of $AgNO_3$ required for optimum bromide removal by silver modified biochar. Biochar was modified by mixing 5 grams of pristine biochar and 20 mL of $AgNO_3$ with varying concentrations. The spectrum of $AgNO_3$ concentrations were 0.5 M, 0.3 M, 0.2 M, 0.1 M, and 0.0 M. The biochar was soaked for 12 hours in the different concentrations of $AgNO_3$ and then dried in the oven at 105 ºC for 24 hours. All experiments were conducted in triplicate.

Samples from batch tests were collected from the centrifuge tubes using 10 mL polypropylene syringes (BD 10 mL syringe luer lock Tip or Norm-Ject 10 ml) with polyethersulfone or cellulose acetate syringe tip filters (VWR 25 millimeter [mm] syringe filter with 0.45 or 0.22 μm membrane). A 40 mL sample collected in polypropylene centrifuge tubes was separated into two 20 mL polyethylene scintillation vials. One vial was retained for in house pH measurement following EPA method 150.1 (Thermoscientific Orion VersaStar Pro pH meter). The second sample was placed on ice and delivered to the UGA Soil, Plant, and Water laboratory for the analysis of bromine and chloride. The samples were accompanied by FGD wastewater samples as untreated control samples and deionized water blank samples for quality control.

Fixed Bed Column Experiments

Column tests were conducted using transparent plastic columns with a length of 75 cm, an interior diameter of 10 cm, and total volume of 5.9 L (Figure 7).

Figure 7 - Photos of plastic columns used in the column experiments.

Two plastic end caps were fitted into the columns with ports for the inlet and outlet wastewater streams. The top and bottom ends of the column contained 5 centimeters (cm) of clean quartz sand and two layers of cheese cloth to hold the treatment media in place and for filtration of any suspended sand particles. Treatment media for different column tests consisted of silver modified softwood biochar, silver modified hardwood biochar, silver modified bone biochar, and surfactant modified zeolites. Silver modified biochar was prepared as stated in the earlier section on modified biochar preparation, and the zeolites were used as supplied from St. Cloud Mining Company (14x40 SMZ 6%). The columns were filled by dumping the treatment media from the top of the column and then tapping the sides of the column with a rubber mallet

until no further settling was visually observed. FGD wastewater was pumped through the column using a peristaltic pump (Masterflex Console Drive) and polyethylene tubing (Masterflex Tygon Tubing 7.9 mm ID) from the bottom to the top of the column. The peristaltic pump was turned on and the FGD wastewater completely filled the tubing prior to attachment to the inlet port.

Effluent from the column tests was sampled at fixed volumes every 500 mL (0.15 pore volumes) or 1000 mL (0.31 pore volumes) or at fixed times e.g., every 15, 30, or 60 minutes. Each sample consisted of 50 mL of wastewater collected in clean centrifuge tubes directly from the column outlet. Samples for analysis were collected from the centrifuge tubes in duplicate using 10 mL polypropylene syringes. Polyethersulfone or cellulose acetate syringe filters were used to remove particulate material from the samples. Samples were placed in 20 mL polyethylene scintillation vials, put on ice, and then delivered to the UGA Soil, Plant, and Water laboratory for analysis.

Sample Analysis

The UGA Soil, Plant and Water laboratory conducted analyses of bromide and chloride ions using a DIONEX DX500 modular chromatography system. An IonPac AS4A column was used for common anions separation with suppressed conductivity detection. In order to suppress the background carbonate eluent conductivity, an SRS-II self-regenerating suppressor (DX500 system) was used, which enhanced analyte sensitivity resulting in significant improvements in analyte detection limits ranging from 20 µg/L to 200 µg/L.

Data Analysis – Batch Sorption Tests

The percent bromide and chloride removed from the FGD wastewater by the modified biochar was calculated using equation (8).

$$Percent\ Removal = \frac{(C_o - C_e)}{C_o}\ x\ 100 \quad \text{---------- (8)}$$

Where C_o is the initial concentration (mg/L) of bromide or chloride in the untreated FGD wastewater, and C_e is the final concentration (mg/L) in each batch treatment.

The maximum loading of bromide was calculated using equation (9).

$$q_e = \frac{(C_o - C_e)\, x\, V}{M} \quad \text{---------- (9)}$$

Where q_e is the amount of bromide adsorbed to the biochar after 24 hours equilibration (mg bromide/kg biochar), C_o is the initial concentration (mg/L) of bromide in FGD wastewater, C_e is the final concentration (mg/L) of bromide in treated samples, V is the total volume (L) of FGD wastewater in the centrifuge tube, and M is the mass (kg) of biochar added to the centrifuge tube.

The relative percent difference (RPD) for each set of replicates batch samples was calculated using equation (10).

$$RPD = \frac{S - R}{(\frac{S + R}{2})} \text{ x } 100 \quad \text{---------- (10)}$$

Where S is the sample concentration and R is the replicate concentration. RPDs of <30% were considered quality analytical samples.

Data Analysis – Column Tests

Several parameters were evaluated throughout the column test. The flow rate of the FGD wastewater through the column was calculated by filling a graduated cylinder with FGD wastewater for 1 minute using a peristaltic pump. The flow rate was fixed throughout each column test; however, since the flow rate can change throughout the course of a column test, minor adjustments to the flow rate at the pump were made to ensure a consistent flow throughout the column test. The time of first flow, which is when the column becomes fully saturated and the first drop of effluent appears, was determined as the amount of time it took from the initial

influent FGD wastewater to be released at the effluent port of the column. The porosity of the column was calculated using the flow rate, time of first flow, and total media volume.

$$\varphi = \frac{(F_r \cdot t_{ff})}{V_{tot.\ media}} \quad \text{---------- (11)}$$

Where φ is porosity (%), F_r is the flow rate (mL/min), t_{ff} is the time of first flow (min), and $V_{tot\ media}$ is the volume of total media in the column (mL).

The Contact Time (CT) was used to determine the residence time for the column experiments. CT was calculated using the total media volume ($V_{tot.\ media}$), the porosity (φ), and the flow rate (F_r).

$$CT = \frac{V_{tot.\ media} \cdot \varphi}{F_r} \quad \text{---------- (12)}$$

The total number of pore volumes treated during each column test was estimated using the total media volume ($V_{tot.\ media}$), the porosity (φ), and the total amount of water treated ($V_{tot.\ water}$).

$$Total\ Pore\ Volumes = \frac{V_{tot.\ water}}{V_{tot.\ media} \cdot \varphi} \quad \text{---------- (13)}$$

Where $V_{tot.\ water}$ is the total volume of FGD water treated during the column test (mL).

Duplicates of selected samples from each column test were collected for quality control analysis. The duplicate samples were evaluated using the RPD method (Equation 10).

Biochar Characterization

Biochar was characterized via scanning electron microscopy (SEM) with energy dispersive spectroscopy for examination of biochar structure and elemental mapping analysis. Additionally, biochar was analyzed with x-ray diffraction (XRD) to confirm silver attached to the biochar and to examine any mineral phases formed after treatment. The specific surface area was analyzed to see how silver modification affects the surface area and to evaluate the effect of surface area on the biochar removal capability of bromide. Samples of 1) pristine biochar

without any modification, 2) silver modified biochar before column tests (pre-treatment), 3) silver modified biochar after column tests (post-treatment), and 4) silver modified biochar after maximum loading tests were characterized with scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD). Additionally, some of the samples had specific surface area tests, cation exchange capacity analyses, and Fourier Transform Infrared Spectroscopy analysis.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy

The SEM analysis was conducted on a FE-SEM Thermo Fisher Teneo microscope with an Everhart-Thornley detector (ETD) or concentric backscatter detector (CBS). SEM stage height was set at 10 mm with a spot size of 10 μm and a voltage of 10 kV. These parameters enabled the use of energy-dispersive X-ray spectroscopy (EDS), which allowed for mapping of elements within the frame of the SEM image. The EDS was conducted using an Oxford XMax detector and the AZtec computer software. Several SEM images beyond what is presented in the text are available in Appendix B.

X-ray Diffraction

For X-ray diffraction (XRD) analysis, sample preparation consisted of grinding the biochar into a fine powder using a mortar and pestle and then using a hydraulic press to form it into a square pellet for use in the XRD machine. XRD data was collected on a Bruker D8 Advance diffractometer operated at 40 mA and 35 kV using $Co_{K\alpha}$ radiation. Prior to sample analysis a Corundum standard (NIST SRM1976) was analyzed with scanning angles from 40° to 42°, a step increment of 0.01°, and scan rate of 0.1 seconds per step. For sample analysis, scan angles were from 2° to 70° with an increment of 0.01° at a rate of 0.1 second per step. Analysis

of the raw data was conducted using EVA software version 5.1 matching best fit patterns from the International Centre for Diffractions Data Power Diffraction File (PDF4+ 2021).

Specific Surface Area

The specific surface area for the pristine and silver modified biochar was obtained at Control Laboratories in Watsonville, CA. Biochar samples were placed in clean plastic bags and sent in the mail to Control Laboratories. The specific surface area was determined using butane adsorption. Butane activity was evaluated following the American Society for Testing and Materials (ASTM) method D 5742-95 Standard Test Method for Determination of the Butane Activity of Activated Carbon. This method uses dried activated carbon and equilibrates it with pure butane at one atmosphere pressure. The butane activity was correlated to surface area using data from McLaughlin et al (2012).

Cation Exchange Capacity

Samples of pristine biochar and silver modified biochar were analyzed for cation exchange capacity at the University of Georgia Center for Applied Isotope Studies Laboratory for Environmental Analysis (CAIS-LEA). The cation exchange capacity was measured by displacing adsorbed cations such as sodium, magnesium, potassium, and calcium with barium dichloride and measuring displaced cations with inductively coupled spectroscopy.

Fourier Transform Infrared Spectroscopy

Samples of pristine biochar and silver modified biochar were analyzed for surface functional groups using FTIR. FTIR analysis of powdered biochar samples were conducted using a Thermo Nicolet Avatar 360 FTIR System. The data was acquired using 64 scans at a resolution of 4 cm^{-1}. The data was analyzed with Thermo Nicolet's OMNIC® software.

CHAPTER 4

RESULTS

Wastewater Analysis

The FGD wastewater analysis included a suite of cations and anions (Table 3). Of the cations analyzed, calcium and magnesium were the most abundant with concentrations of 3,454 mg/L and 1,144 mg/L, respectively. This is expected since large amounts of alkaline slurry is used to desulfurize the flue gas. Additionally, the sulfur concentration was 776 mg/L, resulting from the desulfurization process. Other cations such as aluminum, phosphorus, potassium, sodium, and strontium were present in concentrations above laboratory detection limits. These elements are minor constituents of coal, and their presence in FGD wastewater is expected.

Of the anions analyzed, chloride was the most abundant and had a concentration one order of magnitude higher than sulfate and two orders of magnitude higher than bromide, fluoride, and nitrate (NO_3^- - N). Based on the concentrations of chloride and bromide, the FGD wastewater is classified as moderately saline water per USGS standards.

Table 3 – FGD wastewater baseline analysis.

Element	**Concentration (mg/L)**
Cations	
Aluminum (Al)	2.2
Antimony (Sb)	0.0085
Arsenic (As)	0.0096
Boron (B)	166
Cadmium (Cd)	<0.1
Calcium (Ca)	3,454
Chromium (Cr)	<0.1
Copper (Cu)	<0.5

Iron (Fe)	<1
lead (Pb)	<0.039
Magnesium (Mg)	1,144
Manganese (Mn)	<0.5
Mercury (Hg)	<0.0001
Molybdenum (Mo)	<0.1
Nickel (Ni)	<0.1
Phosphorus (P)	2.54
Potassium (K)	32.2
Selenium (Se)	0.0557
Silicon (Si)	<5
Sodium (Na)	48.1
Strontium (Sr)	11.7
Sulfur (S)	776
Vanadium (V)	<0.001
Zinc (Zn)	<0.5
Anions	
Bromide (Br^-)	92.7
Chloride (Cl^-)	7,700
Fluoride (F^-)	12
Nitrate Nitrogen (NO_3^- - N)	23.5
Phosphate (PO_4^{3-})	<0.7
Sulfate (SO_4^{2-})	1,535
pH	7.00 – 8.00

Red indicates contaminants of primary concern. Note that chloride is two orders of magnitude higher than the target analyte bromide.

Batch Sorption Experiments

Batch sorption testing with silver modified biochar showed promising bromide removal results. The results indicated that all four types of silver modified biochar removed bromide with efficiencies averaging between 61% and 99% using 1 grams of silver modified biochar in 40 mL of FGD wastewater with initial concentrations of 59.17 mg/L and 106.2 mg/L (Table 4). Higher pH values were observed in the batch test with the highest bromide removal (>99%) and the

lower chloride removal (2 – 9% and 35%). Lower pH values were observed in the batch test with lower bromide removal (61 – 78%) and higher chloride removal (19 – 28%). Also, the most effective iron modified biochar for bromide removal was iron modified peanut hull biochar with 25% bromide removal. This data warranted further investigation by maximum loading tests and fixed bed column tests. Complete data for all batch sorption tests are available in Appendix A, Table 1.

Table 4 – Silver modified biochar batch sorption results.

Sample Description	pH	C_o Br- (mg/L)	C_e Br^- (mg/L)	Br^- removal (%)	C_o Cl- (mg/L)	C_e Cl^- (mg/L)	Cl^- removal (%)
Ag-Softwood	7.57	59.17	16.20	73	5123	3900	24
Ag-Softwood	7.63	59.17	16.85	72	5123	3880	24
Ag-Softwood	7.17	59.17	16.95	71	5123	3800	26
Ag-Softwood	8.01	106.20	<2.5	>99	8062	7624	5
Ag-Softwood	8.05	106.20	<2.5	>99	8062	7496	7
Ag-Hardwood	7.82	59.17	13.40	77	5123	3800	26
Ag-Hardwood	7.84	59.17	14.35	76	5123	3760	27
Ag-Hardwood	7.85	59.17	15.05	75	5123	3680	28
Ag-Hardwood	8.31	106.20	<2.5	>99	8062	7742	4
Ag-Hardwood	8.36	106.20	<2.5	>99	8062	7702	4
Ag-Bamboo	7.77	59.17	16.20	73	5123	3770	26
Ag-Bamboo	7.79	59.17	15.75	73	5123	3800	26
Ag-Bamboo	7.78	59.17	16.15	73	5123	3700	28
Ag-Bamboo	8.21	106.20	<2.5	>99	8062	7356	9
Ag-Bamboo	8.23	106.20	<2.5	>99	8062	7348	9
Ag-Peanut Hull	7.16	59.17	16.85	72	5123	3820	25
Ag-Peanut Hull	7.11	59.17	19.60	67	5123	3920	23
Ag-Peanut Hull	7.09	59.17	23.05	61	5123	4130	19
Ag-Peanut Hull	7.20	106.20	<2.5	>99	8062	7938	2
Ag-Peanut Hull	7.20	106.20	<2.5	>99	8062	7930	2
Ag-Bone	8.14	106.20	<2.5	>99	8062	5266	35
Ag-Bone	8.28	106.20	<2.5	>99	8062	5288	34

C_o – initial concentration
C_e – effluent concentration

The batch samples were analyzed for trace amounts of silver leached into the solution from the biochar during the batch sorption tests. The results confirmed that trace amounts of

silver bound to the biochar were leached, and the concentrations were typically in the 500 to 600 micrograms per liter (µg/L) range. The bone biochar leached relatively higher amounts of silver (Table 5). Silver is not a regulated substance and does not have an EPA maximum contaminant level; therefore, small amounts in the µg/L range in treated effluent should not be concerning.

Table 5 – Silver concentrations in solution after batch sorption tests

Sample Description	pH	Ag^+ (µg/L)
Ag-Bamboo	8.21	595
	8.23	569
Ag-Bone	8.14	709
	8.28	826
Ag-Peanut Hull	7.20	585
	7.20	605
Ag-Hardwood	8.31	564
	8.36	562
Ag-Softwood	8.01	555
	8.05	582

Maximum loading tests were conducted using silver modified hardwood, silver modified softwood, silver modified peanut hull, and silver modified bone biochar. The maximum loading test measured adsorption capacity (q_e) which is the maximum amount of bromide adsorbed by a specific mass of sorbent at equilibrium. The percentage removed measured the fraction of bromide was removed from the wastewater. The results indicated that silver modified softwood biochar had the highest loading at 65,051 mg/kg (Figure 8). The next highest loading was silver modified bone biochar at 41,920 mg/kg (Figure 9). The highest loading for silver modified hardwood biochar was 13,439 mg/kg (Figure 10), and the highest loading for silver modified peanut hull biochar was 10,307 mg/kg (Figure 11).

From the maximum loading tests, q_e and bromide removal in percent (%) were calculated and charted together in Figures 8 – 11. Complete data for all maximum loading tests are available in Appendix A, Table 2.

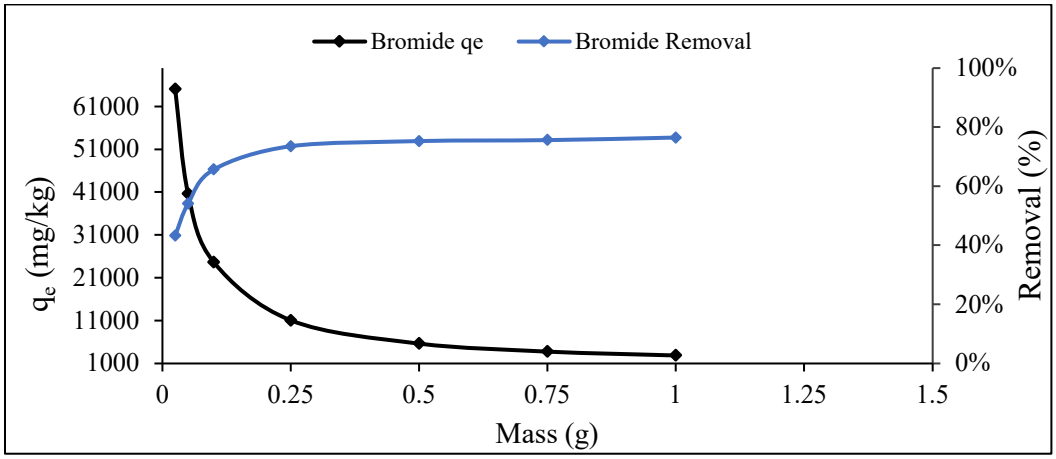

Figure 8 – Maximum loading of bromide onto silver modified softwood biochar.

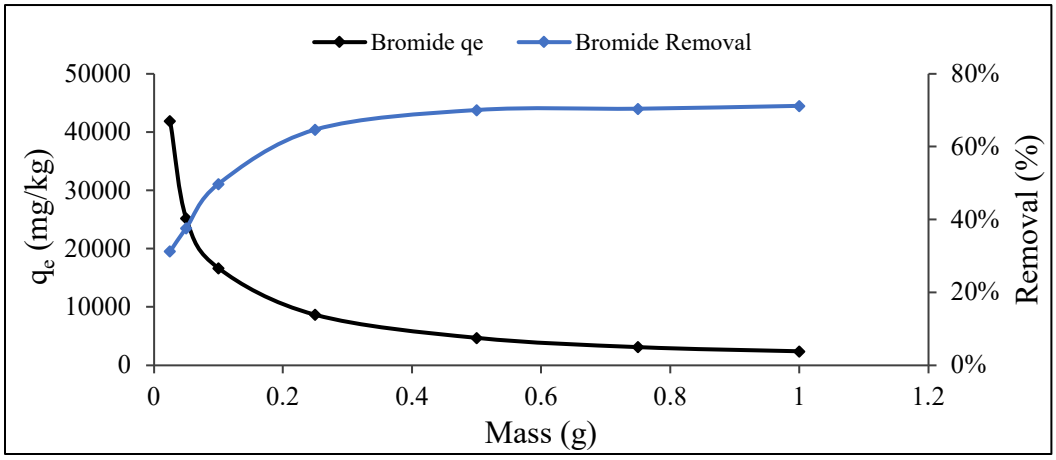

Figure 9 – Maximum loading of bromide onto silver modified bone biochar.

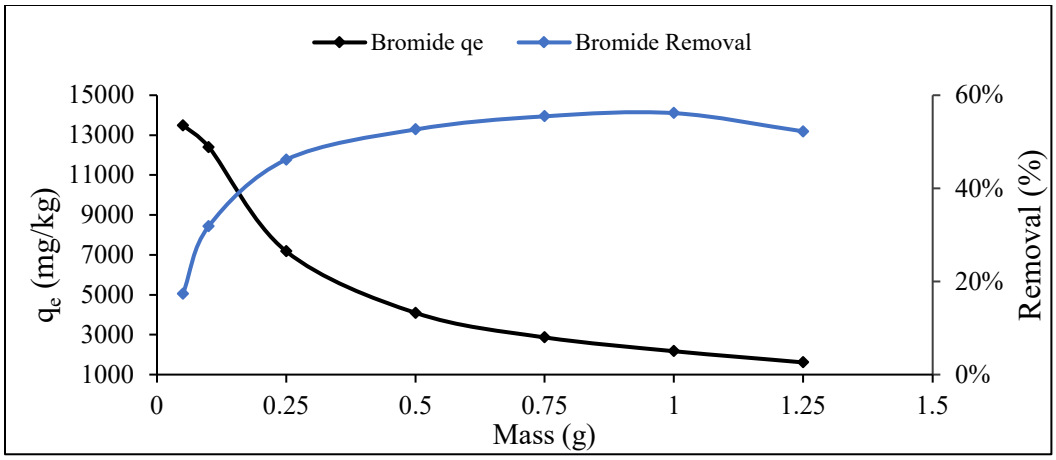

Figure 10 – Maximum loading of bromide onto silver modified hardwood biochar.

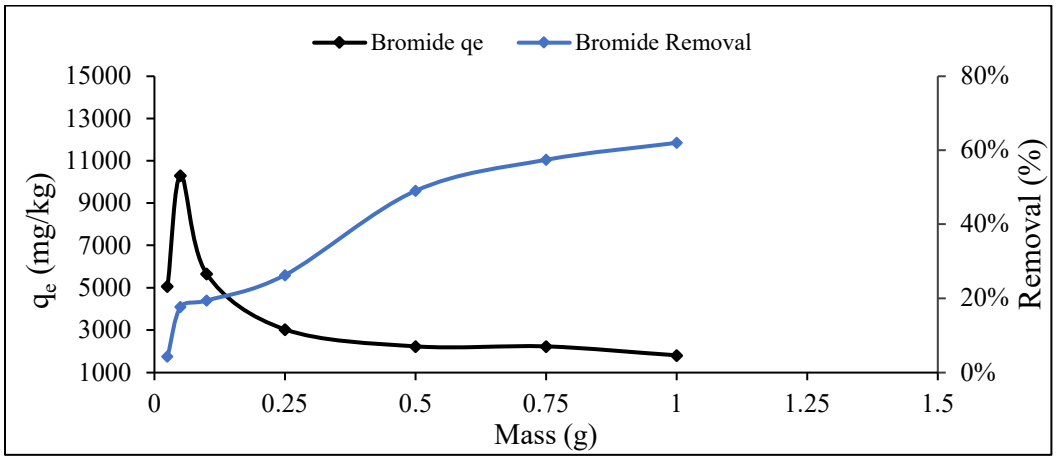

Figure 11 – Maximum loading of bromide onto silver modified peanut hull biochar.

In a subset of tests, the fraction of bromide removed from FGD wastewater by softwood biochar treated with different concentrations of silver nitrate was evaluated in batch treatments with a fixed ratio of the silver modified biochar mass to solution volume. The silver modified biochar was prepared using silver nitrate solutions at concentrations of 0.5, 0.3, 0.2, and 0.1 M and 5 grams of softwood biochar, respectively. The bromide removal from FGD wastewater slightly increased with the concentration of silver nitrate used in the softwood biochar preparation; although, the increase was not noteworthy (Table 6). This indicated that there is

likely a fixed number of sites on the pristine biochar for silver to attach to. Complete data for fixed mass and volume tests are available in Appendix A, Table 3.

Table 6 – Fixed mass and volume tests with varying concentrations of silver nitrate

Sample Description	Concentration $AgNO_3$ (M)	pH	C_o Cl^- (mg/L)	C_e Cl^- (mg/L)	Cl^- removal (%)	C_o Br^- (mg/L)	C_e Br^- (mg/L)	Br^- removal (%)
Ag-Softwood Biochar	0.5	8.24	1808.3	658	64	24.7	3.2	87
	0.5	8.18	1808.3	632	65	24.7	3.13	87
	0.5	8.22	1808.3	627	65	24.7	3.04	88
	0.3	8.11	1808.3	724	60	24.7	3.48	86
	0.3	8.10	1808.3	727	60	24.7	3.61	85
	0.3	7.9	1808.3	724	60	24.7	3.49	86
	0.3	7.9	1808.3	727	60	24.7	3.79	85
	0.2	8.04	1808.3	795	56	24.7	3.89	84
	0.2	8.09	1808.3	798	56	24.7	4.03	84
	0.2	8.16	1808.3	788	56	24.7	3.97	84
	0.1	8.08	1808.3	838	54	24.7	4.2	83
	0.1	8.10	1808.3	1040	42	24.7	4.12	83
	0.1	8.02	1808.3	1030	43	24.7	4.09	83
	0	7.73	1808.3	1785	1	24.7	18.2	26
	0	7.8	1808.3	1815	0	24.7	19.9	19
	0	7.9	1808.3	1800	0	24.7	21.1	15
	0	7.71	1808.3	1840	-2	24.7	26.8	-8

C_o – initial concentration
C_e – effluent concentration

Fixed Bed Column Experiments

Based on the effectiveness of silver modified biochar in removing bromide from FGD wastewater in batch tests, it was further evaluated for bromide removal in fixed bed columns. Column tests are conducted because the treatment efficiency is higher in column tests than in batch tests. Although silver modified bone biochar had the highest maximum loading, bone biochar is in limited supply compared to hardwood and softwood biochar. Due to ease of availability for potential full-scale treatment, column tests were conducted using silver modified hardwood and softwood biochar. The column parameters are shown in Tables 7 and 8.

Table 7 – Experimental parameters of single-phase columns.

Columns	Column 1	Column 2	Column 5
Sorption Media	1,178 grams Ag-HWB (12%) 164 grams Ag-SWB - (88%)	1,358 grams Ag-HWB (100%)	1,267 grams Ag-HWB (100%)
Wastewater	FGD [Cl] = 8,197 mg/L [Br] = 172 mg/L	50% diluted FGD [Cl] = 2,580 mg/L [Br] = 72 mg/L	FGD [Cl] = 3,850 mg/L [Br] = 73 mg/L
Flow Rate (mL/min)	100	100	55
Porosity	78%	59%	60%
Total Pore Volumes	4.7	15.7	13.1
Contact Time (min)	40	30	56

Ag-HWB – silver modified hardwood biochar, Ag-SWB – silver modified softwood biochar, [ ] – concentrations.

Table 8 – Experimental parameters of coupled columns in series.

Columns	Column 3	Column 4
Sorption Media	1,236 grams zeolites (36%) 2,224 grams Ag-HWB (64%)	1,369 grams Ag-BNB (39%) 2,140 grams Ag-HWB (61%)
Wastewater	50% diluted FGD [Cl] = 2,503 mg/L [Br] = 66 mg/L	50% diluted FGD [Cl] = 4,654 mg/L [Br] = 132 mg/L
Flow Rate (mL/min)	100	100
Porosity (Avg. 2 columns)	63%	58%
Total Pore Volumes	8.2	12.2
Contact Time (min)	64	59

Ag-HWB – silver modified hardwood biochar, Ag-SWB – silver modified softwood biochar, [ ] – concentrations.

Column run #1 contained 88% silver modified softwood biochar and a 12% silver modified hardwood biochar. The first effluent sample collected as the treated FGD wastewater first exited the top of the column showed 83% bromide removal from an initial concentration of 172 mg/L. After the initial sample, average bromide removal stabilized at approximately 71% over 4.5 pore volumes. Meanwhile, the highest chloride removal was 61% from an initial

concentration of 8,197 mg/L, and the chloride quickly reached a 90% breakthrough prior to one pore volume (Figure 12).

Column run #2 contained 100% silver modified hardwood biochar and was used to treat the FGD wastewater diluted to 50% strength using tap water. The first effluent sample collected as the treated FGD wastewater first exited the top of the column showed 98% bromide removal from an initial concentration of 72 mg/L. After the initial sample, the average bromide removal was at approximately 77% over 8 pore volumes. Additionally, chloride reached 90% breakthrough after 3.2 pore volumes, later than in column 1 (Figure 13). The greater initial bromide removal was attributed to the 50% dilution of FGD wastewater which reduced the initial concentrations of bromide and chloride in the influent.

Column run #3 consisted of two columns in series and treated the 50% diluted FGD wastewater. In an attempt to minimize the influence of the high chloride concentration in the FGD wastewater on the removal of bromide, the first column was filled with a 15 cm layer of zeolite at the column influent and the rest of the column contained silver modified hardwood biochar. The second column contained 100% silver modified hardwood biochar. The first effluent sample collected as the treated FGD wastewater first exited the top of the column showed 100% bromide removal from an initial concentration of 66 mg/L. After the initial sample, the average bromide removal stabilized at approximately 75% over 8 pore volumes. A chloride removal of 73% was observed in the first sample; however, chloride quickly broke through to 90% within 1 pore volume (Figure 14).

Column run #4 consisted of two columns in series and used to treat the 50% diluted FGD wastewater. The first 21.5 cm of column one contained silver modified bone biochar followed by silver modified hardwood biochar. Silver modified bone biochar was evaluated based on its

ability to remove substantial amounts of chloride in addition to bromide in the batch sorption tests. The second column contained 100% silver modified hardwood biochar. The influent chloride concentration of 4,654 mg/L was removed to 44.9 mg/L, representing the highest removal of chloride observed in all column tests, likely due to the silver modified bone biochar. However, this level of removal was not sustained, and chloride quickly reached 90% breakthrough. The first effluent sample was collected as the treated FGD wastewater first exited the top of the column showed 100% bromide removal, but the bromide removal quickly stabilized at an average of 75% from 1 to 12 pore volumes (Figure 15). After column test 4 was completed, the column was drained of excess wastewater and allowed to sit overnight. Then a leaching test was conducted with tap water. A full pore volume of tap water was flushed through the column before effluent samples were collected to evaluate desorption of bromide from the biochar. The results indicate that small amounts of bromide were leached but were not a significant mass to suggest that the bromide was reversible bound (Figure 16).

Column run #5 was a single column test filled with silver modified hardwood biochar. The influent FGD wastewater contained average initial bromide and chloride concentrations of 73 mg/L and 3,850 mg/L, respectively. The first sample was collected as the treated FGD wastewater first exited the top of the column and showed an 84% removal of bromide. Bromide removal quickly decreased and stabilized at an average of 66% during column 5, which is lower than previous column tests (Figure 17). Complete data for all column tests are available in Appendix A, Table 4.

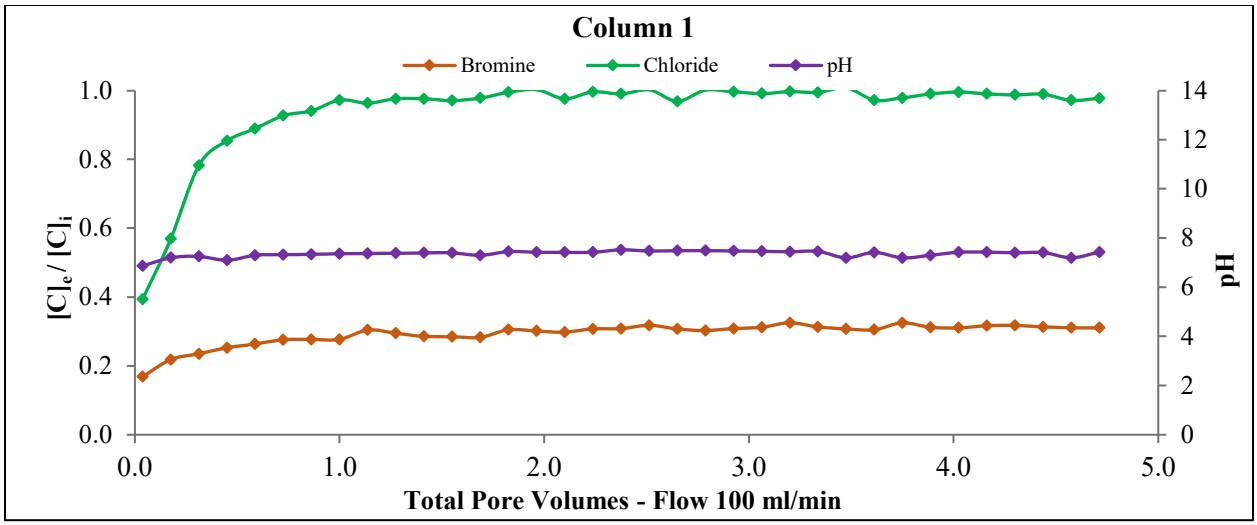

Figure 12 – Column 1. Treatment of undiluted FGD wastewater in packed bed of 88% silver modified hardwood biochar and 12% silver modified biochar. The FGD wastewater contained 8,197 mg/L chloride and 172 mg/L bromide, corresponding to a Cl:Br ratio of 47. An average bromide removal of 71% was sustained over 4.5 pore volumes, while the chloride concentrations quickly reach 90% breakthrough after ~0.5 pore volumes. $[C]_e$ = concentration in effluent. $[C]_i$ = influent concentration of FGD wastewater.

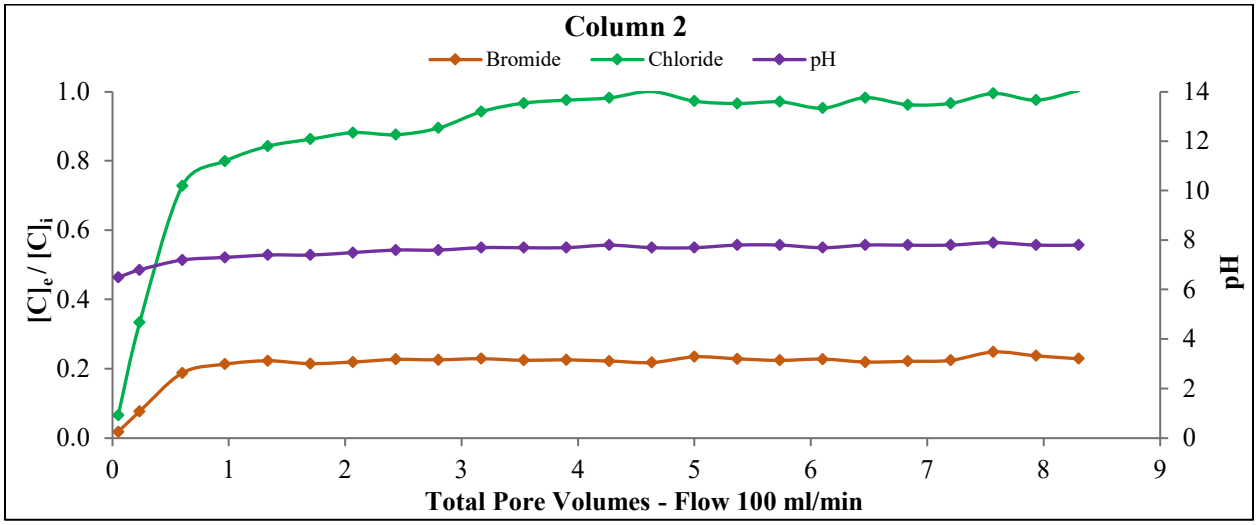

Figure 13 – Column 2. Treatment of 50% diluted FGD wastewater in packed bed of silver modified hardwood biochar. The FGD wastewater contained 2,580 mg/L chloride and 72 mg/L bromide, corresponding to a Cl:Br ratio of 35. An average bromide removal of 79% was sustained over 8 pore volumes, while the chloride concentrations quickly reach 90% breakthrough after ~3 pore volumes. $[C]_e$ = concentration in effluent. $[C]_i$ = influent concentration of 50% diluted FGD wastewater.

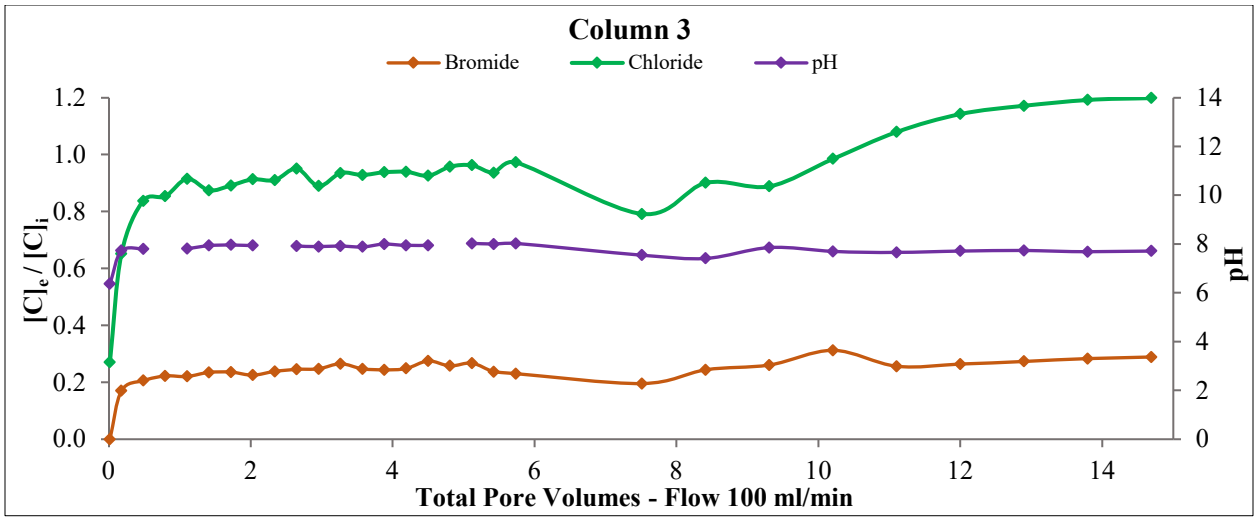

Figure 14 – Column 3. Treatment of 50% diluted FGD wastewater in packed bed of 36% zeolite and 64% silver modified hardwood biochar. The FGD wastewater contained 2,503 mg/L chloride and 66 mg/L bromide, corresponding to a Cl:Br ratio of 38. An average bromide removal of 76% was sustained over 14 pore volumes, while the chloride concentrations quickly reach 90% breakthrough after ~1 pore volume. $[C]_i$ = influent concentration of 50% diluted FGD wastewater.

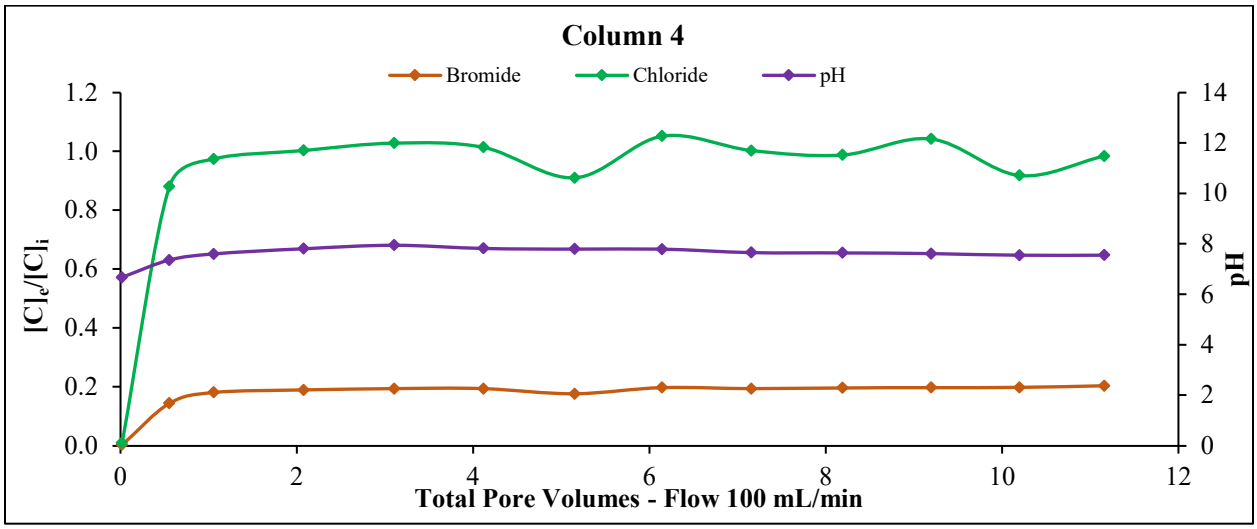

Figure 15 – Column 4. Treatment of 50% diluted FGD wastewater in packed bed of 39% silver modified bone biochar and 61% silver modified hardwood biochar. The FGD wastewater contained 4,654 mg/L chloride and 132 mg/L bromide, corresponding to a Cl:Br ratio of 35. An average bromide removal of 77% was sustained over 10 pore volumes, while the chloride concentrations quickly reach 90% breakthrough after ~1 pore volume. $[C]_e$ = concentration in effluent. $[C]_i$ = influent concentration of 50% diluted FGD wastewater.

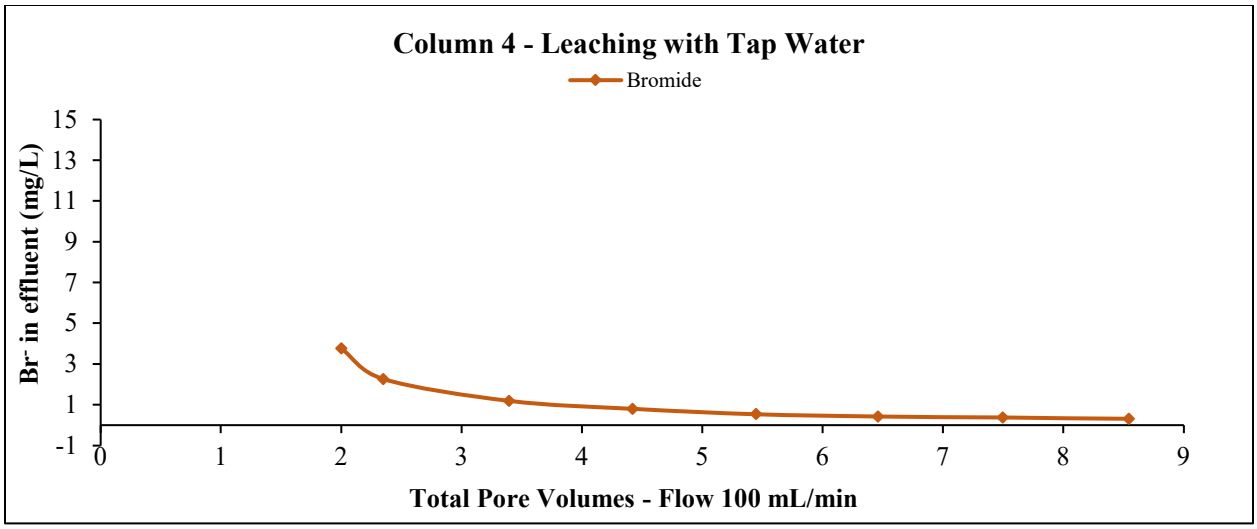

Figure 16 – Leaching of spent media in column 4. The low concentration of bromide (<1 mg/L) in the effluent suggested chemisorption as the mechanism of bromide removal by silver modified biochar.

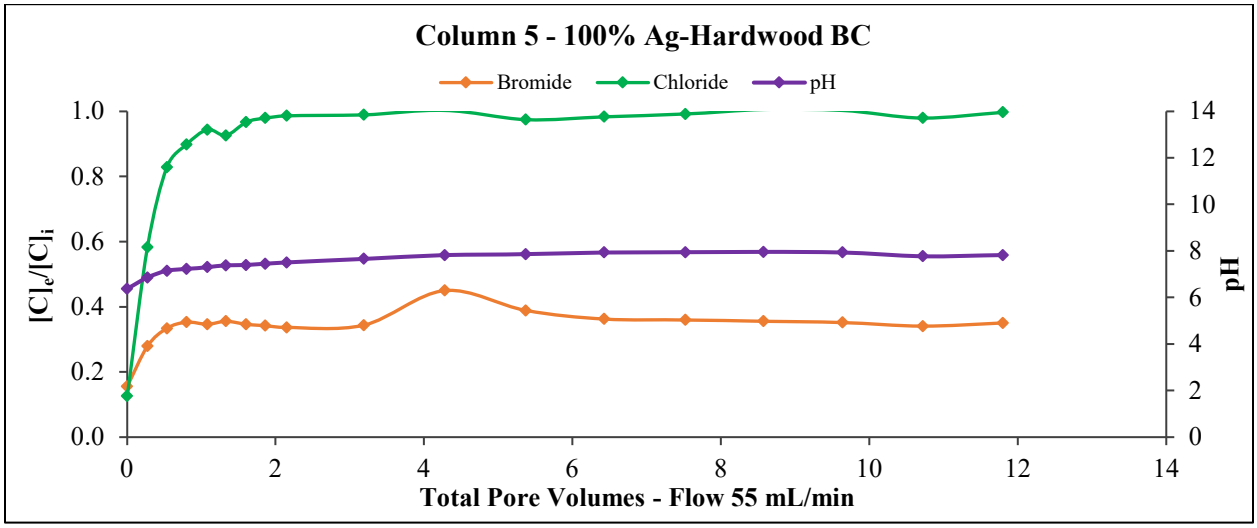

Figure 17 - Column 5. Treatment of 50% diluted FGD wastewater in packed bed of silver modified hardwood biochar. The FGD wastewater contained 3,850 mg/L chloride and 73 mg/L bromide, corresponding to a Cl:Br ratio of 52. An average bromide removal of 66% was sustained over 10 pore volumes, while the chloride concentrations quickly reach 90% breakthrough after ~1 pore volume. $[C]_e$ = concentration in effluent. $[C]_i$ = influent concentration FGD wastewater.

Biochar Characterization

The pristine and silver modified biochars were characterized by SEM and XRD methods as well as specific surface area analysis by butane adsorption. The pristine biochar was a

hardwood biochar that had been washed with boiling DI water three times. The morphology of the pristine biochar contained a highly porous almost honeycomb like structure with pore sizes ranging from >100 µm to <10 µm (Figure 18). Elemental analysis indicated that the majority of the biochar was carbon with lesser amounts of oxygen, calcium, magnesium, and potassium. These are common macronutrients for plants, and their appearance in the elemental analysis is reasonable for hardwood biochar (Figure 19). The XRD data for the pristine hardwood biochar revealed a spectrum for the mineral calcite (Figure 20). This is expected since calcium was present in the elemental analysis and likely formed calcite during preparation due to interactions with carbonate (CO_3^{2-}) in the water.

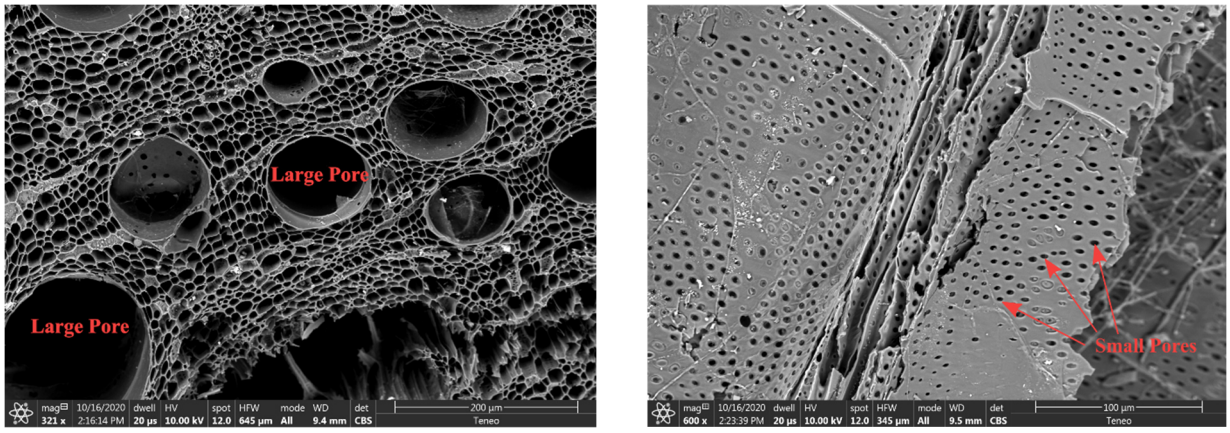

Figure 18 – SEM images of pristine hardwood biochar

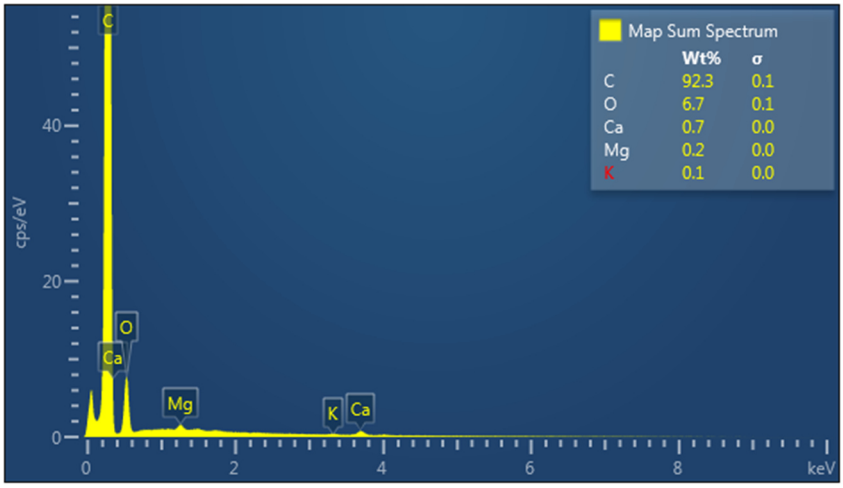

Figure 19 – Elemental analysis of pristine hardwood biochar by EDS

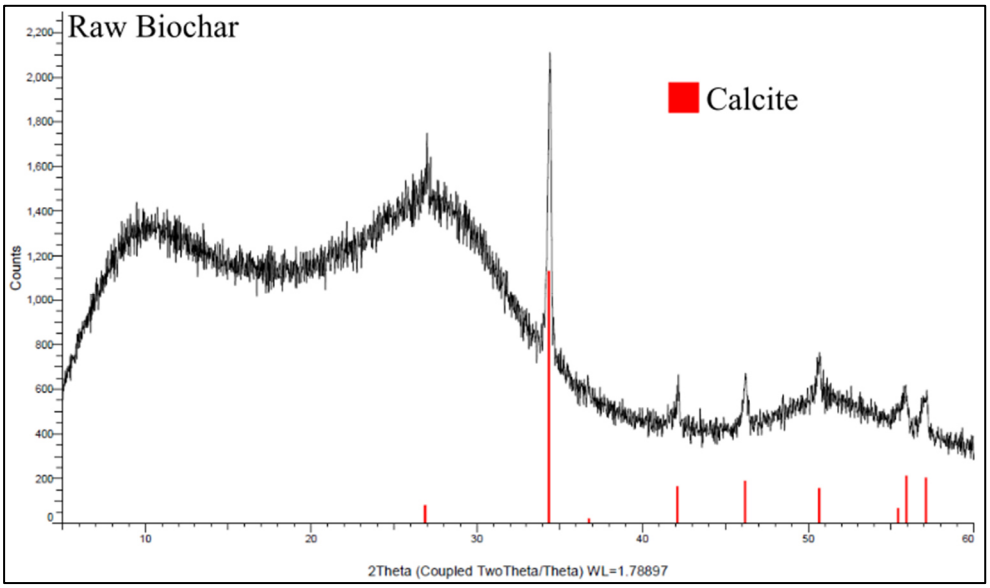

Figure 20 – XRD analysis of pristine hardwood biochar

Silver modified hardwood biochar with the highest loading of bromide in batch tests was characterized by SEM analysis since hardwood biochar was used extensively in the column tests (Figure 21A). The sample analyzed had a range of silver content from 15% to 30% weight. This indicates that the silver was easily attached onto the surface of the biochar. The surface of the biochar shows a porous structure, and the energy dispersive spectroscopy (EDS) maps indicate silver is well distributed throughout the surface of the biochar (Figure 21B). Furthermore, EDS maps of chloride and bromide were obtained. A clear association of chloride and bromide with silver is immediately apparent (Figure 21C and 21D). Although, chloride appears to be much more densely distributed than bromide, which is expected since chloride is two orders of magnitude higher in the FGD influent than bromide is.

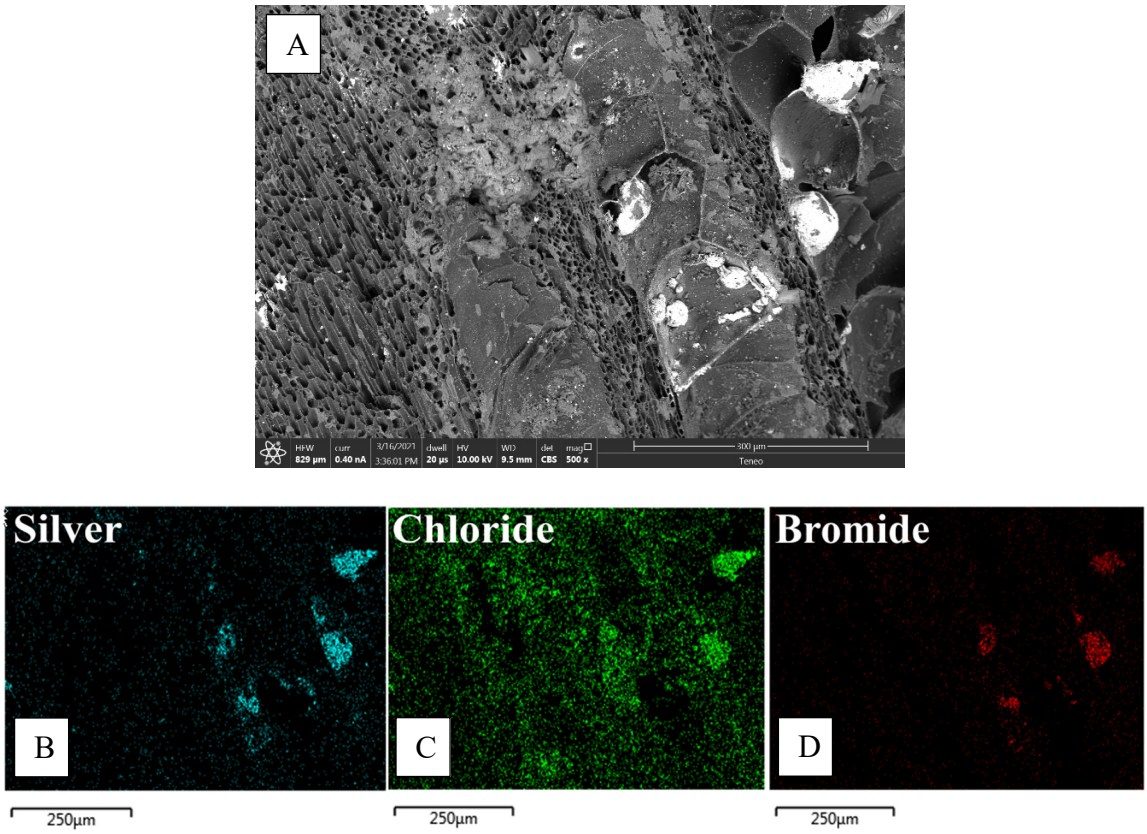

Figure 21 –SEM image and EDS maps of silver impregnated hardwood biochar after maximum loading test. A) SEM image B) EDS map of silver distribution on the biochar C) EDS map of chloride distribution on the biochar D) EDS map of bromide distribution on the biochar. Colocation of bromide and silvers appears to occur on the biochar surfaces with the highest loading of silver.

Silver modified biochar before and after treatment in columns was analyzed by SEM and XRD. A sample of silver modified hardwood biochar that had not undergone column treatment had noticeable silver particles attached to the biochar. The size range of silver particles was from approximately <5 µm to 25 µm (Figure 22A). The silver did not appear to obstruct pores to the point where solute mobility would be inhibited. The EDS map indicated that silver was well distributed on the surface of the biochar (Figure 22B). The elemental analysis indicated that most of the modified biochar was carbon with less amounts of silver, oxygen, calcium, and potassium (Figure 22C). The XRD analysis of the modified biochar showed spectra for silver and nitratine ($NaNO_3$) (Figure 23). Since biochar was soaked in $AgNO_3$ for the modification, it is likely that

silver and nitratine were artifacts of the modification process. The EDS results showed a 12.5 wt.% silver impregnation of the biochar which was confirmed in the SEM photos and EDS map.

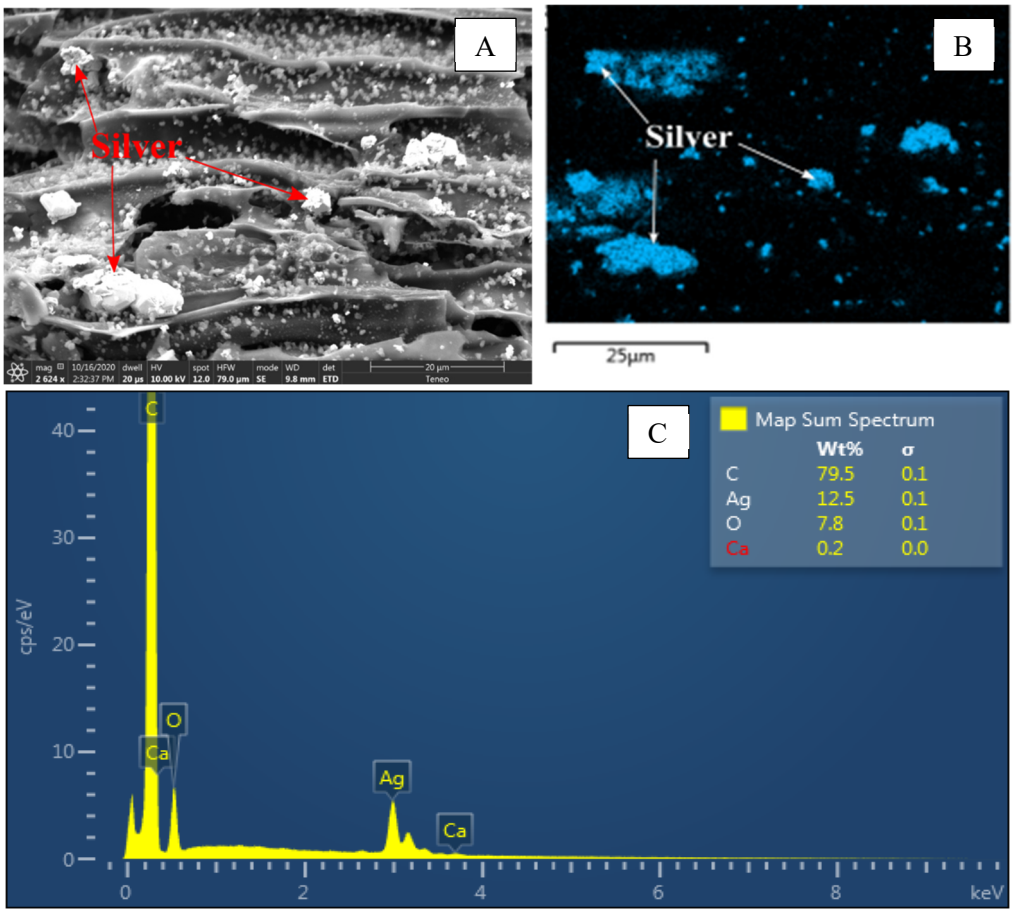

Figure 22 – SEM image and EDS analysis of silver modified hardwood biochar prior to column treatment. A) SEM image of silver modified hardwood biochar prior to treatment in column 2. B) EDS map of silver loaded onto biochar. C) Elemental analysis of silver modified hardwood biochar

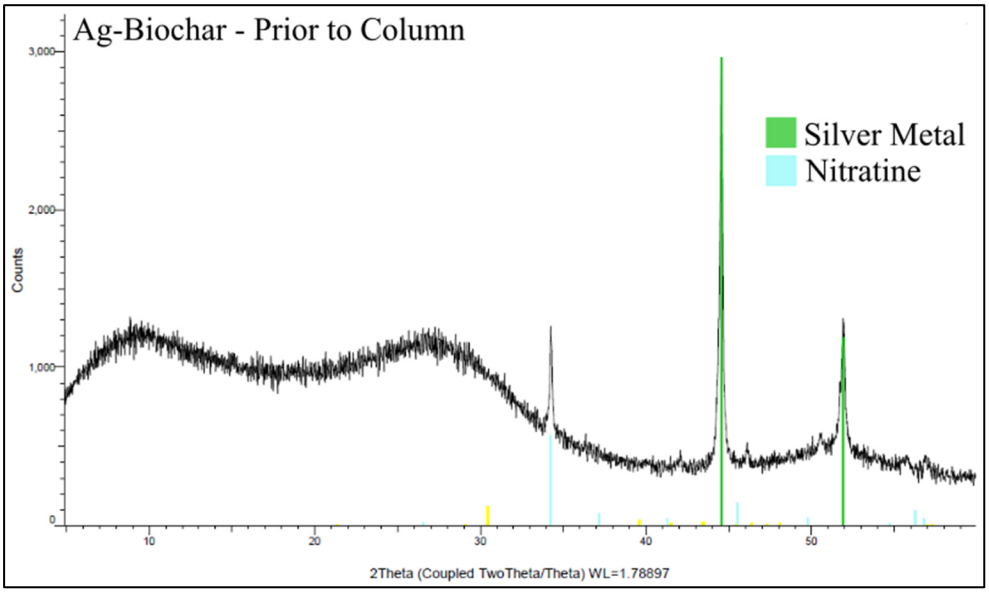

Figure 23 – XRD spectrum of silver modified hardwood biochar prior to column test. High intensity peaks of silver and lower intensity peaks of nitratine ($NaNO_3$) are artifacts of the modification process with $AgNO_3$.

A sample of silver modified softwood biochar that had been used as treatment media in column 1 had a similar morphology as the silver modified hardwood biochar in previous images. Noticeable silver particles were attached to the biochar (Figure 24A). The size range of silver particles were approximately <5 µm to 25 µm. The elemental analysis indicated that most of the modified biochar was carbon with less amounts of silver and oxygen; however, there were trace (defined as 0.1 wt.% or less) amounts of bromine detected, indicative of bromide sorption (Figure 24B). Large amounts of chlorine were detected as well, and its association with silver is displayed in the EDS maps (Figure 24C and 24D). The XRD spectrum for the silver modified softwood biochar that was used as treatment media contained spectra for chlorargyrite and silver (Figure 25). This is important since chlorargyrite is the silver chloride mineral phase. Since chlorargyrite is present, it is likely that the removal of chloride and bromide is due to mineral phase formation indicating non-reversible chemisorption. Additionally, there is free silver present, and not associated with chlorargyrite (Figure 24). This silver is likely unavailable for

additional bromide removal due to blockage of access to the silver in smaller micropores and mesopores.

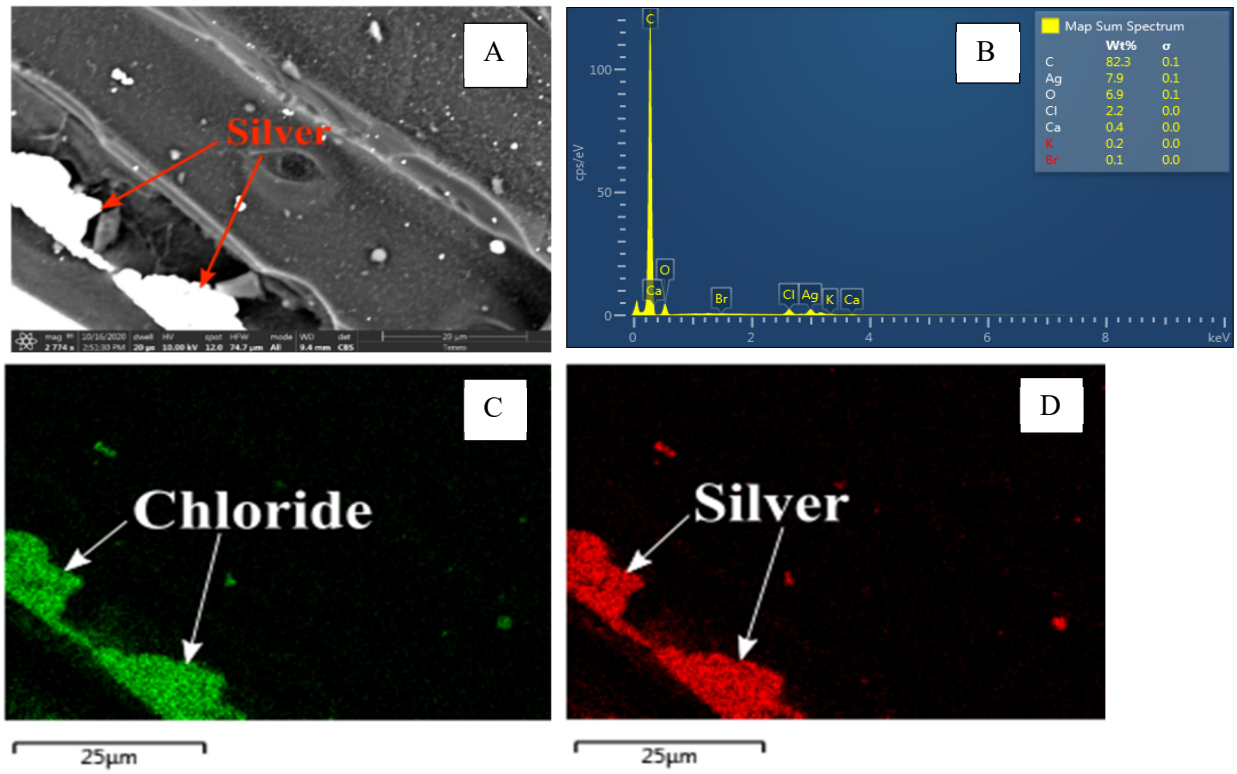

Figure 24 –SEM image and EDS analysis of silver modified softwood biochar after column treatment A) SEM image of silver modified softwood biochar after treatment in column 1. B) elemental analysis of silver modified softwood biochar after treatment showing both Cl and Br. C) EDS map showing locations of chloride. D) EDS map showing locations of silver. Both Ag and CL are colocated on the biochar similar to the colocation in Figure 20.

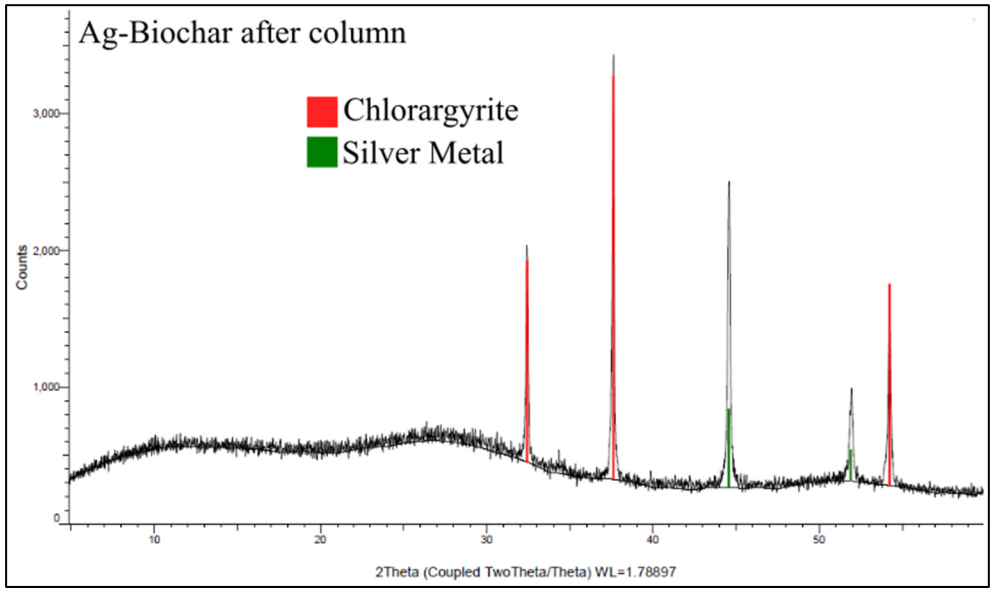

Figure 25 - XRD spectrum for silver modified softwood biochar after column treatment. Chlorargyrite is present due to AgCl (s) complexes. Silver metal is present and likely available for further sorption.

The specific surface area of the biochar was calculated by the butane adsorption method at Control Laboratories in Watsonville, CA. Overall, the surface area decreased slightly after the modification with silver (Table 9). This is likely due to silver particles attached to the biochar reducing surface area.

Table 9 – Specific surface area analysis results for pristine and silver modified biochars

Biochar Type	**Surface Area (m^2/g)**
Pristine Bamboo	257
Ag-Bamboo	219
Pristine Hardwood	308
Ag-Hardwood	227
Pristine Bone	234
Ag-Bone	228
Pristine Peanut Hull	165
Ag-Peanut Hull	145
Pristine Softwood	274
Ag-Softwood	218

Of note is that a higher surface area does not correlate with a higher maximum loading of the different silver modified biochars. This indicates that surface area does not play a key role in bromide removal. A more important parameter is likely the porous structure of the biochar. This includes silver sorption sites within micropores (<2nm) and mesopores (2 – 50 nm). Bromide movement into the micropores and mesopores may be inhibited by larger polyatomic anions such as sulfates (SO_4^{2-}) and nitrates (NO_3^-) as well as the excessive chlorides in solution. Therefore, there is some unreacted silver unavailable for bromide sorption. This unreacted silver can be seen in the XRD spectrum of Figure 25. Since XRD requires powdering the sample, the unreacted silver was exposed during the mechanical grinding to create a biochar powder. Laboratory data for specific surface area analysis from control laboratories is included in Appendix C.

The cation exchange capacity was measured at CAIS-LEA. The results indicated that the silver modified biochar had a similar cation exchange capacity to the pristine biochar (Table 10). The silver modified peanut hull biochar had the highest cation exchange capacity and both the pristine and silver modified bone biochar had the lowest cation exchange capacity. Laboratory data for cation exchange capacity is included in Appendix D.

Table 10 – Cation exchange capacity of pristine and modified biochars

Biochar Type	**CEC (meq/100g)**
Pristine Bamboo	4.2
Ag-Bamboo	5.05
Pristine Bone	3.22
Ag-Bone	3.34
Pristine Hardwood	5.47
Ag-Hardwood	5.87
Pristine Peanut Hull	5.18
Ag-Peanut Hull	6.88
Pristine Softwood	6.25
Ag-Softwood	5.42

The surface functionality was determined through FTIR analysis. The FTIR analysis indicated that the pristine bamboo, hardwood, and softwood biochars were not markedly different from one another. The overall shape of the curve was sloping from high absorbance at low wavenumbers to lower absorbance at higher wavenumbers. Large amount of IR absorption occurred in the low wavenumber range likely due to C=C, C-H, and aromatic functional groups. The pristine bone biochar had marked absorption peak at 1025 cm^{-1} indicating possible ether or phosphate functional groups. The pristine peanut hull biochar had a marked peak at 1050 cm-1 indicating possible ether functional groups and a broad peak between 1500 – 1700 cm-1 which is likely various carbonyl functional groups (e.g., esters, ketone, aldehyde, and carboxylic acids). Of note is that the FTIR spectra of the pristine biochar and the silver modified biochars are not markedly different. Indicating that the functionality does not change after modification. FTIR spectra for all biochars are included in Appendix E.

CHAPTER 5

DISCUSSION

Overall, silver modified biochar was much more effective than pristine and iron modified biochar for the removal of bromide from FGD wastewater with removals ranging from 61% to 99% in batch tests, and sustained removal of 65% to 80% bromide over more than 10 pore volumes in column tests. Of note is that the largest coal fired power plants are in the eastern states that border the Ohio River. An examination of tree distribution maps throughout the United States shows a wide abundance of many pine and cedar species in the eastern United States (Little, 1971). Therefore, silver modified hardwood and softwood biochar are likely the best cost-effective candidates for full scale treatment due to the ease of availability and satisfactory performance in batch and column tests.

In batch tests, the iron modified peanut hull biochar was the best of the iron modified biochars and removed 25% of an initial 106 mg/L bromide from FGD wastewater which is similar to results obtained by Favero, (2020). Unlike chemisorption by silver modified biochar, it is likely that the bromide adsorbed by iron modified biochar is reversibly adsorbed.

To evaluate the role of silver loading onto the biochar, multiple batch tests were performed with a fixed mass of biochar treated with different concentrations of silver nitrate. The test results indicated that biochar treated with higher concentrations of silver nitrate had slightly higher removals of bromide. However, in order to maintain cost effectiveness, the lower concentrations of silver nitrate are preferred. For example, batch tests using biochar modified with silver nitrate concentrations of 0.1, 0.2, and 0.3 M had bromide removals of between 83 to

86%. However, increasing the concentration of silver nitrate in the modification process to 0.5 M only increased the removal to 87 to 88%. Therefore, a balance must be obtained between cost effectiveness and bromide removal efficiency. Lower concentrations of silver nitrate (0.1, 0.2, and 0.3 M) appear to be satisfactory for biochar modification and bromide removal.

The results using silver modified biochar are consistent with previous research using other carbonaceous materials as platforms for silver modification. Previous research by Gong et al. (2013) removed 94% of bromide from a 200 µg/L bromide solution; although, when Gong et al. (2013) increased the chloride concentration to 50 mg/L, the bromide removal decreased to 9%. Chen et al. (2017) obtained 85 – 94% of bromide removal from a 300 µg/L initial bromide solution. Chen et al. (2017) also tested the effect of competing anions with a solution containing 247 µg/L bromide and 10 mg/L chloride. In this situation the bromide removal was 83.5% (Table 11). It should be noted that the research by Gong et al. (2013) and Chen et al. (2017) was conducted using simplified synthetic wastewater, while this research was conducted with a complex FGD wastewater. The results of this study do however contrast with the results of Chen et al. (2017) and Gong et al. (2013) since substantial bromide removal occurred even with chloride levels that were one to two orders of magnitude higher in the FGD wastewater. Chen et al. (2017) and Gong et al. (2013) suggested that high chloride concentrations greatly inhibit the removal of bromide. Remarkably, the silver modified biochar in this study achieved 61 – 98% bromide removal from FGD wastewater in batch tests with remarkably high chloride to bromide concentration ratios of 76 and 86. In this study, the higher bromide removal occurred in the FGD wastewater that also had a higher bromide concentration. The greater removal may be attributed to the lower chloride to bromide ratio of 76 in the batch test with the initial chloride and bromide concentrations of 5,123 and 59.17 mg/L respectively compared to 86 for the batch test with the

initial chloride and bromide concentrations of 8,062 and 106 mg/L respectively. The pH may also play a role since the batch test with higher bromide removal had higher pH values.

Table 11 - Comparison to previous results by Gong et al. (2013) and Chen et al. (2017)

Author	Method	Br removal (%)	Initial Br Concentration	Initial Cl Concentration
Gong et al. 2013	Ag-Porous Carbon Spheres	9%	200 ug/L	50 mg/L
Chen et al. 2017	Ag-Activated Carbon	83.5%	247 ug/L	10 mg/L
Rajaeian et al. 2018	Ag-Activated Carbon	53 – 98%	6, 2, and 1 mg/L	-
Current Study	Ag-Biochar	61 - 77%	59 mg/L	5,123 mg/L
Current Study	Ag-Biochar	99%	106 mg/L	8,062 mg/L

The batch tests provided a better understanding of the relative effectiveness of the modified and unmodified biochar. The silver modified bone biochar removed substantially higher amounts of chloride and bromide simultaneously, indicating a strong affinity for both. The high removal capabilities of the silver modified bone biochar may be due to the porous structure of the bone biochar. This may be the case since bones are not a lignocellulosic biomass but are composed of primarily hydroxyapatite and collagen.

The maximum loading tests indicated that the silver modified softwood biochar could load the highest amount of bromide with 65.1 g bromide/kg biochar. The maximum loading tests are useful when evaluating the total amount of wastewater that can be treated before the silver modified biochar treatment media is exhausted. For example, if 1 kg of silver modified biochar is used with a maximum loading capacity of 65.1 g/kg and the FGD wastewater has a bromide concentration that varies between 20 to 175 mg/L, which is a typical range observed in this research, then the total volume of water capable of being treated can be calculated.

1 kg biochar	65.1 g bromide / kg biochar	1 L / 0.020 g bromide	3,255 L wastewater treated
1 kg biochar	65.1 g bromide / kg biochar	1 L / 0.175 g bromide	372 L wastewater treated

This dimensional analysis indicates that the silver modified softwood biochar with a maximum loading of 65,051 mg/kg could treat between 372 and 3,255 L of wastewater depending on the initial concentration of bromide in solution. Lower initial concentrations of bromide and a lower Cl^-: Br^- ratio will allow a greater volume of FGD wastewater to be treated prior to exhaustion of the treatment media.

Column tests sustained bromide removal efficiencies between 65% to 80% over several pore volumes. In all column tests, continual removal of bromide occurred after chloride had reached 90% breakthrough, with chloride to bromide ratios of 48, 36, 38, 35, and 53 in columns 1, 2, 3, 4, and 5, respectively. The chloride to bromide ratio tends to affect the amount of bromide that can be continuously removed during a column test. The column tests conducted with influent having a higher chloride to bromide ratio showed a lower removal of bromide over time. For example, column test 2 had a chloride to bromide ratio of 36 and a sustained removal of bromide of approximately 77%. In contrast, column test 5 which had a chloride to bromide ratio of 53 had a sustained bromide removal of only 64%. This suggests that a higher chloride to bromide ratio in the influent may result in lower bromide removal throughout a column test. Figure 26 shows the relationship between chloride to bromide ratio versus the average percent removed in the five different column tests. The column tests provided evidence that bromide removal from the FGD wastewater was influenced to a lesser extent by the type of silver biochar and instead by the chloride to bromide ratio and the amount of silver loaded onto the biochar.

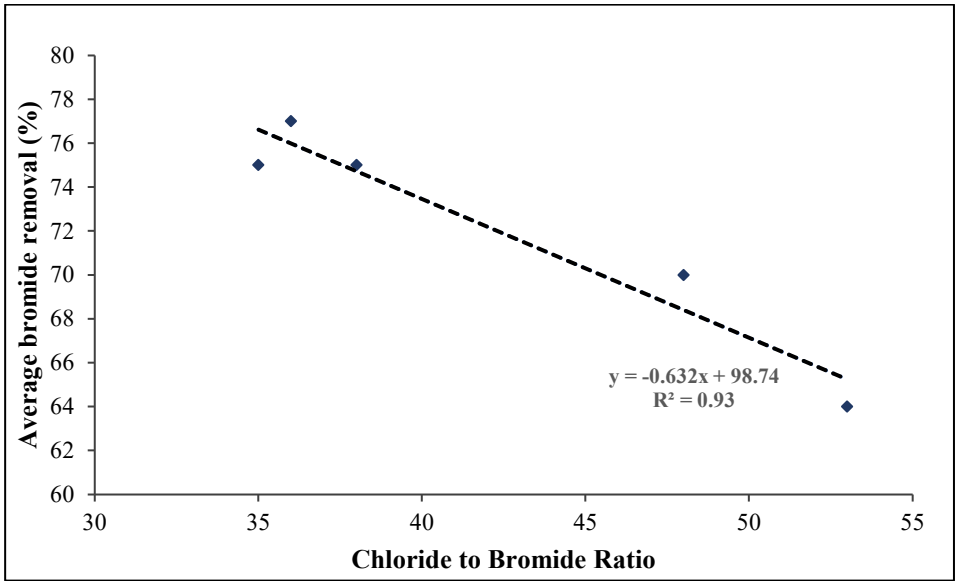

Figure 26 – The relationship between chloride to bromide ratio and average percent bromide removal in five different column tests. Higher chloride to bromide ratios yields lower average percent removals of bromide throughout column tests.

The effect of chloride on bromide removal was studied in batch tests by Gong et al (2013) and by Chen et al. (2017) and confirm results regarding the chloride to bromide ratio. Gong et al. (2013) found that bromide removal decreased with increasing chloride concentrations (Figure 27). Chen et al. (2017) also found that chloride had an inhibitory effect on bromide removal. At a chloride concentration of 10 mg/L, approximately 83.5% of bromide was removed, and at a chloride concentration of 200 mg/L, only 7.0% of bromide was removed.

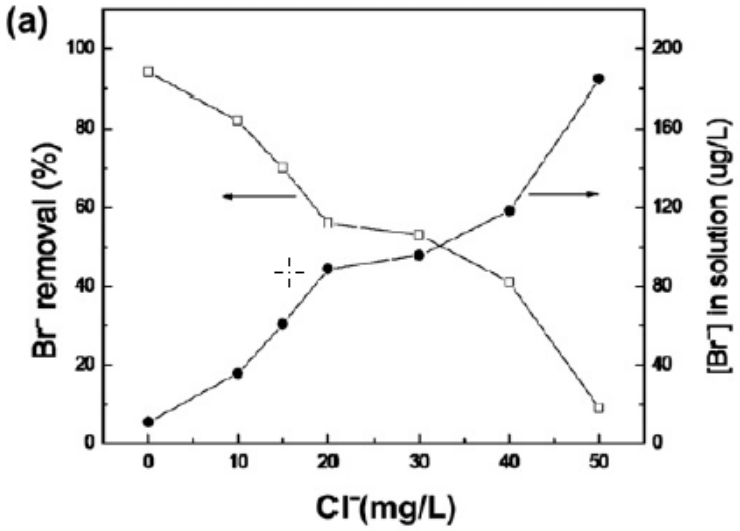

Figure 27 – Effect of chloride on bromide removal in a batch test by Gong et al. (2013).

Typically, the contact time plays a significant role in solute removal with longer contact times removing greater amounts of solute. Contact times can be increased by lowering the flow rate or increasing the column length. These column tests revealed that contact time did not affect the removal of bromide. This can be seen in Figures 28 and 29. Figure 28 shows that contact times are not related to the average percentage of bromide removed. Figure 29 shows a comparison of effluent bromide concentrations between column 2, a single column experiment, and column 3, an experiment with two columns in series. This shows that the doubled contact time could remove more bromide initially, however, it could not remove substantially more bromide over multiple pore volumes than a single column.

This is expected because of the fast kinetics of formation of silver chloride and silver bromide. Silver chloride and silver bromide both can be precipitated almost instantaneously in the laboratory using a silver nitrate solution; thus, the kinetics of formation are extremely fast. The kinetics show that the contact time has little effect on the removal of bromide; thus, the treatment system is very much controlled by the level of chlorides.

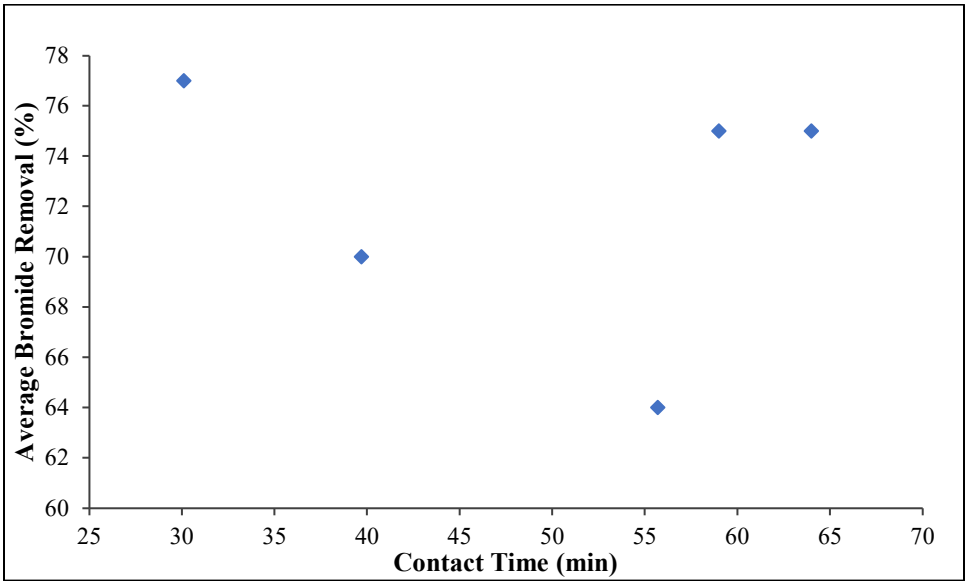

Figure 28 – The relationship between contact time and average bromide removal. The percent removal does not depend on the contact time between the FGD wastewater and the treatment media.

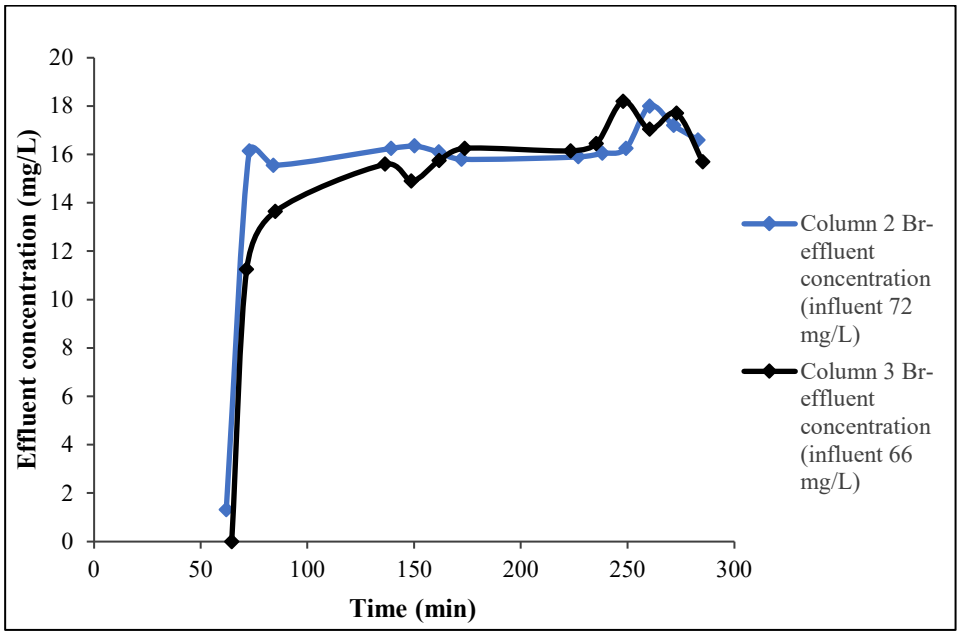

Figure 29 – Effluent bromide concentrations from column 2 (single column) and column 3 (two columns in series). The effluent concentration of bromide is similar between the two even though column 3 has twice the amount of treatment media and a doubled contact time.

A possible mechanism for bromide removal in column tests after one pore volume is anion exchange of chloride for bromide following equation 7:

$$AgCl\ (s) + Br^- \rightarrow AgBr\ (s) + Cl^- \quad (7)$$

This can be explained by examining the difference in electronegativity between the silver chloride bond and the silver bromide bond. The difference in electronegativity between silver and chloride is 1.23 and for silver and bromide it is 1.03; therefore, silver bromide has more covalent character and is a more stable bond. Additionally, silver chloride has a higher solubility than silver bromide. The K_{sp} of silver chloride is 5.4×10^{-13} and the K_{sp} of silver bromide is 1.8×10^{-10}. This shows that the sustained removal of bromide over several pore volumes in the column tests could be explained by continual anion exchange of chloride by bromide. Furthermore, the specific adsorption of bromide over chloride can be attributed to silver being a "soft" type B metal with a nd^{10} electron configuration. Type B metals have a higher tendency to complex with halides of lower electronegativities ($I^- > Br^- > Cl^- > F^-$), suggesting that silver will prefer to complex with bromide over chloride (Ahrland, 1958).

Note that when the first flow of effluent is sampled, both chloride and bromide concentrations are markedly low, which is due to the initial saturation of the silver modified biochar sorption sites. After about 1 pore volume, the chloride reaches 90% breakthrough indicating that no further removal of chloride is occurring; however, bromide removal stabilizes at between 65% to 80% throughout the remainder of the column tests (up to 12 pore volumes). The continual removal of bromide indicates that chloride initially bound to the Ag-biochar surface is exchanging for bromide over time.

Bromide removal using silver modified biochar likely occurs due to specific chemisorption. As shown in the EDS map of biochar from column 2 (Figure 24), trace amounts

of bromide were present on the biochar, although a bromargyrite spectrum was not observed in the XRD data (Figure 25) and an intense spectrum for chlorargyrite was observed. Since bromide and chloride are similar ions, it is likely that bromargyrite was also formed in trace amounts but was masked by the exceedingly high chlorargyrite formed because of the high concentrations of chloride in the FGD wastewater. Due to the large amounts of chlorargyrite formed, the flow of wastewater could possibly be affected by the clogging of pores that could lower bromide removal efficiency.

The characterization of the pristine and modified biochar through specific surface area, CEC, and FTIR indicate that the surface area, CEC, and surface functional groups are less important than the pore structure of the biochar. The specific surface area did not vary much between different biochar varieties with different maximum loading values. The CEC also did not vary much between pristine and silver modified biochar. This is expected when examining the FTIR spectra that indicated little change in functionality between pristine biochar and silver modified biochar.

CHAPTER 6

CONCLUSION

To prevent the formation of brominated DBPs during water disinfection, the effectiveness of silver modified biochar was evaluated for the removal of bromide from FGD wastewater. Silver modified biochar showed high effectiveness in batch and column tests. In batch tests, bromide removal of between 61% to >99% from initial concentration of 59.17 and 106.2 mg/L was achieved, and in column tests, sustained bromide removal of 70 – 80% of influent bromide concentration between 66 to 172 mg/L was achieved for up to 12 pore volumes treated. In batch tests, greater bromide removal occurred with FGD wastewater that had a higher pH level. The silver modified biochar could adsorb marked quantities of bromide onto its surface. The maximum loading of bromide onto the silver modified biochar surface was 65,051 mg/kg using the silver modified softwood biochar. The surface area did not correlate with the maximum loading, suggesting that the surface area likely plays a subordinate role to the pore structure and pore size distribution. The column tests indicated that continuous removal of bromide occurs due to anion exchange of chloride for bromide at the silver sorption sites. Lastly, the bromide removal efficiency in the column tests decreased as the chloride to bromide ratio in the wastewater increased.

This work contributes to the overall body of knowledge on bromide removal coal combustion residuals by 1) showing data using actual FGD wastewater from a coal fired power plant, 2) revealing that the surface area of the silver modified biochar does not correlate with the maximum loading on bromide to the Ag-biochar; thus, the pore size distribution and connectivity

in the biochar likely determines the efficacy of bromide loading, and 3) providing a simple biochar modification method that can be used by other researchers to corroborate the results and for large scale production and use at the field scale.

Recommended Future Research

Further research could include tests conducted at the temperatures of the FGD wastewater at CFPPs, which would yield more realistic results for scale up from the bench to the field. Evaluating the effect of temperature is necessary because previous research by Gong et al. (2013) indicated that higher temperature increased both bromide removal efficiency and bromide loading; however, reaching equilibrium at a higher temperature takes a longer time. This study only evaluated the leaching of bromide from modified hardwood biochar in one column test; therefore, more research on leaching of bromide and chloride from different modified biochar types is warranted. Furthermore, a more extensive characterization of the biochar is necessary to optimize the efficacy of the metal modified biochar. An analysis of pore structure and pore size distribution is warranted since it likely plays a role in the maximum loading of bromide onto the biochar. The determination of the point of zero charge on the silver modified biochar is also necessary because it will allow a clearer evaluation of the effect of pH on the removal of bromide. The most effective and optimized media could be used in full scale treatment systems to remove bromide from FGD wastewater. A full scale completely stirred tank reactor (CSTR) is likely better suited for this treatment due to the low cost of a CSTR system. Also, mechanical agitation in a CSTR should reduce particle sizes continuously, allowing more unreacted silver sorption sites to be exposed and used for bromide adsorption. Additionally, a CSTR should be more efficient than continuous flow through column treatment because reduction in the effective porosity and mineral precipitate formation is not likely to limit media performance as in a column treatment configuration. In a flow through reactor, insoluble precipitates may form on

the surface of the biochar reducing the effective porosity and permeability of silver modified biochar.

It is necessary to evaluate methods for regeneration of the silver modified biochar. Previous authors have regenerated silver modified materials through hydrogen streams (Gong et al. 2013) or dilute ammonia solutions (Sanchez-Polo et al. 2007). After regeneration, the removed bromide may be useful for creating bromine-based chemicals.

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Batch Sorption Tests - Appendix A Table 1

Sample ID	Sample Description	Size Fraction	Mass (g)	FGD Volume (mL)	pH	Ce Br⁻ (mg/L)	Br⁻ RPD (%)	Br⁻ remov. (%)	C_CT (mg/L)	CT RPD (%)	CT remov. (%)
Set 1 Analysis completed April 20, 2020											
A-1S	Silver impr. Softwood Biochar	Unsieved/Raw	1	40	7.57	16.2		73	3900		24
A-2S	Silver impr. Softwood Biochar	Unsieved/Raw	1	40	7.63	16.85		72	3880		24
A-3S	Silver impr. Softwood Biochar	Unsieved/Raw	1	40	7.17	16.95		71	3800		26
A-4H	Silver impr. Hardwood Biochar	Unsieved/Raw	1	40	7.82	13.4		77	3800		26
A-5H	Silver impr. Hardwood Biochar	Unsieved/Raw	1	40	7.84	14.35		76	3760		27
A-6H	Silver impr. Hardwood Biochar	Unsieved/Raw	1	40	7.85	15.05		75	3680		28
A-7B	Silver impr. Bamboo Biochar	Unsieved/Raw	1	40	7.77	16.2		73	3770		26
A-8B	Silver impr. Bamboo Biochar	Unsieved/Raw	1	40	7.79	15.75		73	3800		26
A-9B	Silver impr. Bamboo Biochar	Unsieved/Raw	1	40	7.78	16.15		73	3700		28
A-10P	Silver impr. Peanut Hull Biochar	Unsieved/Raw	1	40	7.16	16.85		72	3820		25
A-11P	Silver impr. Peanut Hull Biochar	Unsieved/Raw	1	40	7.11	19.6		67	3920		23
A-12P	Silver impr. Peanut Hull Biochar	Unsieved/Raw	1	40	7.09	23.05		61	4130		19
DI-S	Deionize water w/ Softwood Biochar	Unsieved/Raw	1	40	4.99	<0.25		-	0.0006		-
DI-H	Deionize water w/ Hardwood Biochar	Unsieved/Raw	1	40	5.95	<0.25		-	2.37		-
DI-B	Deionize water w/ Bamboo Biochar	Unsieved/Raw	1	40	5.02	<0.25		-	0.001		-
DI-P	Deionize water w/ Peanut Hull Biochar	Unsieved/Raw	1	40	3.78	<0.25		-	0.0006		-
Blank DI	Deionized water blank	-	1	40 mL DI	5.32	<0.25		-	1.23		-
Blank FGD1	FGD Leachate Control	-	-	40	6.88	81.75		-	5440		-
Blank FGD2	FGD Leachate Control	-	-	40	6.89	49.95		-	5020		-
Blank FGD3	FGD Leachate Control	-	-	40	6.91	45.8		-	4910		-
				Leachate Control Averages		59			5123		
Set 2 Analysis completed June 17, 2020											
Ba-1	Pristine Bamboo Biochar	500um<X<2.0mm	1	40	7.52	75.7		29	8054		0
Ba-2	Pristine Bamboo Biochar	500um<X<2.0mm	1	40	7.54	68.3		36	6212		23
	Average				7.529	72.000	10.3%		7133.000	25.8%	
Ba-3	Iron Impr. Bamboo Biochar	500um<X<2.0mm	1	40	2.27	95.8		10	7992		1
Ba-4	Iron Impr. Bamboo Biochar	500um<X<2.0mm	1	40	3.23	96.3		9	7220		10
	Average				2.749	96.050	-0.5%		7606.000	10.1%	
Ba-5	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.21	<2.5		98	7356		9
Ba-6	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.23	<2.5		98	7348		9
	Average				8.22	5.00	0.0%		7352	0.1%	
Bo-1	Pristine Bone Biochar	500um<X<2.0mm	1	40	7.01	84.4		21	7764		4
Bo-2	Pristine Bone Biochar	500um<X<2.0mm	1	40	6.86	96.2		9	6988		13
	Average				6.934	90.300	-13.1%		7376.000	10.5%	
Bo-3	Iron Impr. Bone Biochar	Fine Sand - Med. Sand	1	40	3.83	100.6		5	7770		4
Bo-4	Iron Impr. Bone Biochar	Fine Sand - Med. Sand	1	40	3.77	75.8		29	7634		5
	Average				3.803	88.200	28.1%		7702.000	1.8%	
Bo-5	Silver Impr. Bone Biochar	Fine Sand	1	40	8.14	<2.5		98	5266		35
Bo-6	Silver Impr. Bone Biochar	Fine Sand	1	40	8.28	<2.5		98	5288		34
	Average				8.21	5.00	0.0%		5277	-41.7%	
PHB-1	Pristine Peanut Hull Biochar	0.038mm<X<2.0mm	1	40	7.74	80		25	7574		6
PHB-2	Pristine Peanut Hull Biochar	0.038mm<X<2.0mm	1	40	7.74	96		10	7888		2
	Average				7.738	88.000	-18.2%		7731.000	-4.1%	
PHB-3	Iron Impr. Peanut Hull Biochar	0.038mm<X<2.0mm	1	40	6.70	78.9		26	6830		15
PHB-4	Iron Impr. Peanut Hull Biochar	0.038mm<X<2.0mm	1	40	6.63	80.7		24	8062		0
	Average				6.667	79.800	-2.3%		7446.000	-16.5%	
PHB-5	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.20	<2.5		98	7938		2
PHB-6	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.20	<2.5		98	7930		2
	Average				7.20	5	0.0%		7934.000	0.1%	
H-1	Pristine Hardwood Biochar	500um<X<2.0mm	1	40	7.43	108.4		-2	8020		1
H-2	Pristine Hardwood Biochar	500um<X<2.0mm	1	40	7.37	104.8		1	7978		1
	Average				7.398	106.600	3.4%		7999.000	0.5%	
H-3	Iron Impr. Hardwood Biochar	500um<X<2.0mm	1	40	3.93	72.9		31	8518		-6
H-4	Iron Impr. Hardwood Biochar	500um<X<2.0mm	1	40	3.97	109.2		-3	8450		-5
	Average				3.949	91.050	-39.9%		8484.000	0.8%	
H-5	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.31	<2.5		98	7742		4
H-6	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.36	<2.5		98	7702		4
	Average				8.33	5	0.0%		7722.000	0.5%	
S-1	Pristine Softwood Biochar	500um<X<2.0mm	1	40	7.26	107.2		-1	8120		-1
S-2	Pristine Softwood Biochar	500um<X<2.0mm	1	40	7.20	108.6		-2	7776		4
	Average				7.229	107.900	-1.3%		7948.000	4.3%	
S-3	Iron Impr. Softwood Biochar	500um<X<2.0mm	1	40	3.83	76.2		28	8466		-5
S-4	Iron Impr. Softwood Biochar	500um<X<2.0mm	1	40	3.81	101.4		5	8216		-2
	Average				3.822	88.800	-28.4%		8341.000	3.0%	
S-5	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.01	<2.5		98	7624		5
S-6	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.05	<2.5		98	7496		7
	Average				8.03	5	0.0%		7560.000	1.7%	
C-DI	Deionized water blank	-	-	40 mL DI	6.92	<0.3		-	0.307		-
C-FGD	FGD leachate control	-	-	40	6.88	106.2		-	8062		-
Set 3 Analysis completed July 17, 2020											
Spent AgNO3 - 1st round											
S-1	Silver Impr. Softwood Biochar	500um<X<2.0mm	0.5	40	8.351	0.913		95	907.75		10
S-2	Silver Impr. Softwood Biochar	500um<X<2.0mm	0.5	40	8.301	0.883		96	780.75		23
	Average				8.326	0.898	3.3%		844.250	15.0%	
S-3	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.323	8.208		59	636.25		37
S-4	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.389	8.295		58	611.5		40
	Average				8.356	8.252	-1.1%		623.875	4.0%	
H-1	Silver Impr. Hardwood Biochar	500um<X<2.0mm	0.5	40	8.377	8.018		60	843		17
H-2	Silver Impr. Hardwood Biochar	500um<X<2.0mm	0.5	40	8.488	8.37		58	875.75		13
	Average				8.433	8.194	-4.3%		859.375	-3.8%	
H-3	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.322	8.39		58	742.25		27
H-4	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.294	7.925		60	762		25
	Average				8.308	8.158	5.7%		752.125	-2.6%	
PHB-1	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	0.5	40	7.985	9.165		54	905.5		10
PHB-2	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	0.5	40	7.832	9.46		53	908.25		10
	Average				7.909	9.313	-3.2%		906.875	-0.3%	
PHB-3	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.613	8.168		59	775.25		23
PHB-4	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.838	1.403		93	762.5		25
	Average				7.726	4.786	141.4%		768.875	1.7%	
Ba-1	Silver Impr. Bamboo Biochar	500um<X<2.0mm	0.5	40	8.282	8.605		57	879.5		13
Ba-2	Silver Impr. Bamboo Biochar	500um<X<2.0mm	0.5	40	7.747	9.66		52	865.75		14
	Average				8.015	9.133	-11.6%		872.625	1.6%	
Ba-3	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.685	8.39		58	719		29
Ba-4	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.54	8.233		59	734.75		27
	Average				8.613	8.312	1.9%		726.875	-2.2%	
Bo-1	Silver Impr. Bone Biochar	20 x 60 mesh	0.5	40	8.531	18.658		6	373.25		63
Bo-2	Silver Impr. Bone Biochar	20 x 60 mesh	0.5	40	8.394	9.82		51	365		64
	Average				8.463	14.239	62.1%		369.125	2.2%	
Bo-3	Silver Impr. Bone Biochar	20 x 60 mesh	1	40	8.028	<0.25		99	0.339		100
Bo-4	Silver Impr. Bone Biochar	20 x 60 mesh	1	40	8.254	<0.25		99	0.667		100
	Average				8.141	0.500	0.0%		0.503	-65.2%	
C-FGD	FGD Leachate control	-	-	40	8.361	19.94		-	1010.75		-
C-DI	Deionized water blank	-	-	40 mL DI	9.049	<0.25		-	<0.25		-
Set 4 Analysis completed											
Spent AgNO3 - 2nd round											
S-1	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.333	7.27		55	649		35
S-2	Silver Impr. Softwood Biochar	500um<X<2.0mm	1	40	8.276	6.94		57	648		35
	Average				8.305	7.105	4.6%		648.500	0.2%	
H-1	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.518	6.69		58	692		31
H-2	Silver Impr. Hardwood Biochar	500um<X<2.0mm	1	40	8.349	6.54		59	694		31
	Average				8.434	6.615	2.3%		693.000	-0.3%	
PHB-1	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.153	0.74		95	776		23
PHB-2	Silver Impr. Peanut Hull Biochar	500um<X<2.0mm	1	40	7.244	0.73		95	765		24
	Average				7.20	0.74	136.1%		770.5	142.8%	
Ba-1	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.371	7.67		52	754		25
Ba-2	Silver Impr. Bamboo Biochar	500um<X<2.0mm	1	40	8.481	7.06		56	751		25
	Average				8.426	7.365	8.3%		752.500	0.4%	
Bo-1	Silver Impr. Bone Biochar	20 x 60 mesh	1	40	8.337	7.84		51	215		79
Bo-2	Silver Impr. Bone Biochar	20 x 60 mesh	1	40	8.481	7.01		56	252		75
	Average				8.409	7.425	11.2%		233.500	-15.8%	
C-DI	Deionized water blank	-	-	40 mL DI	6.28	<0.25		-	<0.25		
C-FGD1	FGD Leachate control	-	-	40	8.173	15.84		-	1001		
C-FGD2	FGD Leachate control	-	-	40	8.283	16.29		-	1006		-
				Leachate Control Averages		**16.065**			**1003.5**		-
											-

Maximum Loading Data - Appendix A, Table 2

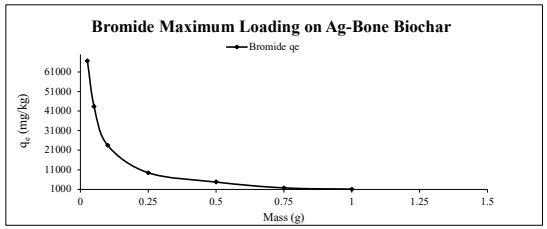
Set 1 - Ag Bone Biochar

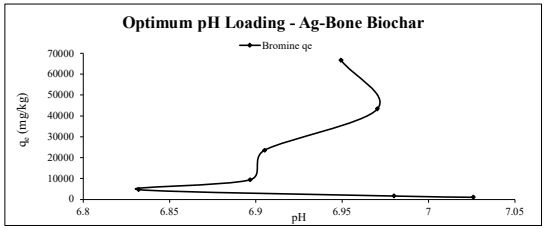
Sample ID	Size Fraction	Mass (g)	FGD Volume (L)	Dose (g/L)	pH	Ce Br^- (mg/L)	Br^- remov. (%)	q_e Br^- (mg/kg)	C_e Cl^- (mg/L)	Cl^- remov. (%)	q_e Cl^- (mg/L)
Bo-1	500µm<X<2.0mm	0.025	0.04	0.625	7.02	43	49	65120.0	3880.7	2	134075
Bo-2	500µm<X<2.0mm	0.025	0.04	0.625	6.893	41.12	51	68128.0	3902.63	2	98987
Bo-3	500µm<X<2.0mm	0.025	0.04	0.625	6.935	42	50	66720.0	3839.93	3	199307
Bo-4	500µm<X<2.0mm	0.05	0.04	1.25	7.056	29.9	64	43040.0	3883.01	2	65189
Bo-5	500µm<X<2.0mm	0.05	0.04	1.25	6.923	29.75	64	43160.0	3796.96	4	134029
Bo-6	500µm<X<2.0mm	0.05	0.04	1.25	6.932	28.95	65	43800.0	3857.75	3	85397
Bo-7	500µm<X<2.0mm	0.1	0.04	2.5	6.896	24.7	70	23600.0	3837	3	50875
Bo-8	500µm<X<2.0mm	0.1	0.04	2.5	6.964	25	70	23480.0	3855	3	43631
Bo-9	500µm<X<2.0mm	0.1	0.04	2.5	6.855	25.4	70	23320.0	3858.46	3	42415
Bo-10	500µm<X<2.0mm	0.25	0.04	6.25	6.937	24.25	71	9512.0	3784.81	5	28750
Bo-11	500µm<X<2.0mm	0.25	0.04	6.25	6.935	25.2	70	9360.0	3761.17	5	32532
Bo-12	500µm<X<2.0mm	0.25	0.04	6.25	6.818	24.8	70	9424.0	3783.93	5	28891
Bo-13	500µm<X<2.0mm	0.5	0.04	12.5	6.82	23.95	71	4780.0	3641.32	8	25854
Bo-14	500µm<X<2.0mm	0.5	0.04	12.5	6.813	24.25	71	4756.0	3492.86	12	37731
Bo-15	500µm<X<2.0mm	0.5	0.04	12.5	6.863	24.05	71	4772.0	3627.36	9	26971
Bo-16	500µm<X<2.0mm	0.75	0.04	18.75	6.971	52.5	37	1664.0	3881.47	2	4428
Bo-17	500µm<X<2.0mm	0.75	0.04	18.75	7.018	52	38	1690.7	3884.69	2	4256
Bo-18	500µm<X<2.0mm	0.75	0.04	18.75	6.951	52	38	1690.7	4176.52	-5	-11308
Bo-19	500µm<X<2.0mm	1	0.04	25	6.988	56	33	1108.0	4059.41	-2	-3797
Bo-20	500µm<X<2.0mm	1	0.04	25	7.006	56.5	32	1088.0	3941.76	1	909
Bo-21	500µm<X<2.0mm	1	0.04	25	7.084	60	28	948	3917.61	1	1875
B	-	-	DI blank	-	-	<0.25	-	-	<0.25	-	-
C-1	-		0.04	-	7.231	82.1	2	-	3956.08	0	-
C-2	-		0.04	-	7.187	83	1	-	3950.02	0	-
C-3	-		0.04	-	7.071	86	-3	-	3987.39	-1	-
			FGD Leachate Control Averages			83.7			3964.5		

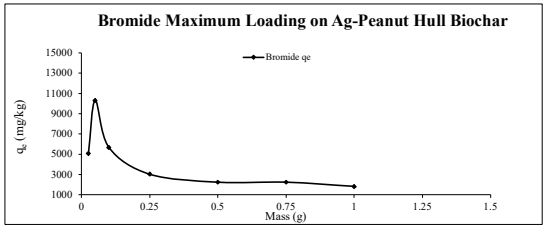
Set 2 - Ag Peanut Hull Biochar

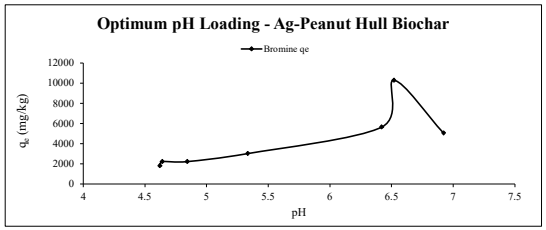
Sample ID	Size Fraction	Mass (g)	FGD Volume (L)	Dose (g/L)	pH	Ce Br^- (mg/L)	Br^- remov. (%)	q_e Br^- (mg/kg)	C_e Cl^- (mg/L)	Cl^- remov. (%)	q_e Cl^- (mg/kg)
PHB-1	500µm<X<2.0mm	0.1	0.04	0.625	-	57.5	21	6133	3912.99	-4	-61865
PHB-2	500µm<X<2.0mm	0.1	0.04	0.625	6.42	59	19	5533	4087.32	-9	-131597
PHB-3	500µm<X<2.0mm	0.1	0.04	0.625	-	59.5	18	5333	3848.1	-2	-35909
PHB-4	500µm<X<2.0mm	0.25	0.04	1.25	5.534	54.8	25	2885	3622.13	4	21791
PHB-5	500µm<X<2.0mm	0.258	0.04	1.25	5.291	53.4	27	3013	3917.86	-4	-24734
PHB-6	500µm<X<2.0mm	0.25	0.04	1.25	5.177	52.8	28	3205	3879.55	-3	-19396
PHB-7	500µm<X<2.0mm	0.5	0.04	2.5	4.896	38	48	2787	3914.64	-4	-12505
PHB-8	500µm<X<2.0mm	0.5	0.04	2.5	4.846	37.4	49	2835	3894.78	-4	-10916
PHB-9	500µm<X<2.0mm	0.5	0.04	2.5	4.788	35.9	51	2955	3844.29	-2	-6877
PHB-10	500µm<X<2.0mm	0.75	0.04	6.25	4.645	31.6	57	2199	3886.82	-3	-6853
PHB-11	500µm<X<2.0mm	0.75	0.04	6.25	4.667	30.6	58	2252	3870.89	-3	-6003
PHB-12	500µm<X<2.0mm	0.75	0.04	6.25	4.608	30.8	58	2242	3882.58	-3	-6627
PHB-13	500µm<X<2.0mm	0.05	0.04	12.5	6.357	58.5	20	11467	3918.19	-4	-127891
PHB-14	500µm<X<2.0mm	0.05	0.04	12.5	6.56	60	18	10267	3913.66	-4	-124267
PHB-15	500µm<X<2.0mm	0.05	0.04	12.5	6.641	61.35	16	9187	3991.49	-6	-186531
PHB-16	500µm<X<2.0mm	0.025	0.04	18.75	6.9	69.5	5	5333	3909.38	-4	-241685
PHB-17	500µm<X<2.0mm	0.025	0.04	18.75	6.929	69.5	5	5333	3899.41	-4	-225733
PHB-18	500µm<X<2.0mm	0.025	0.04	18.75	6.937	70	4	4533	3884.57	-3	-201989
PHB-19	500µm<X<2.0mm	1	0.04	25	4.723	28.05	61	1791	3819.26	-2	-2437
PHB-20	500µm<X<2.0mm	1	0.04	25	4.585	27.4	62	1817	3854.62	-3	-3852
PHB-21	500µm<X<2.0mm	1	0.04	25	4.554	27.5	62	1813	3868.6	-3	-4411
B		-			-						
C-1	-	-	0.04	-	6.986	69.5	-		3842.38	-	-
C-2	-	-	0.04	-	7.05	69.5	-		3555.98	-	-
C-3	-	-	0.04	-	7.283	79.5	-		3876.62	-	-
			FGD Leachate Control Averages			72.8			3758.3		

Duplicates		Br^- conc. (mg/L)	Average of dups.	RPD	Cl^- conc. (mg/L)	Average of dups.	RPD
PHB-1a	PHB-1 duplicate	58	57.8	-0.9%	3828.93	3871.0	2.2%
PHB-3a	PHB-3 duplicate	57.5	58.5	2.6%	3932.77	3890.4	-2.2%
C-1a	C-1 duplicate	69.2	69.4	0.0%	3882.63	3862.5	-1.0%









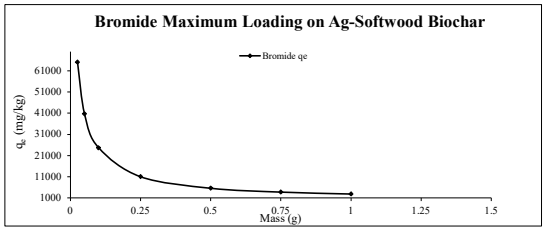
Set 3 - Ag Softwood Biochar - Analysis completed August 21, 2020

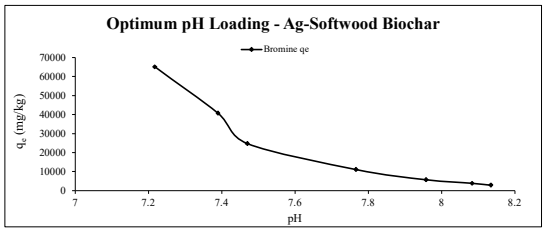
Sample ID	Size Fraction	Mass (g)	FGD Volume (L)	Dose (g/L)	pH	Ce Br- (mg/L)	Br- remov. (%)	qe Br- (mg/g)	Ce Cl- (mg/L)	Cl- remov. (%)	qe Cl- (mg/L)
S-19	500µm<X<2.0mm	0.025	0.04	0.625	7.192	51.5	45.2	67984.0	3928.66	-0.8	-51776.0
S-20	500µm<X<2.0mm	0.025	0.04	0.625	7.259	51	45.7	68784.0	3898.62	-0.1	-3712.0
S-21	500µm<X<2.0mm	0.025	0.04	0.625	7.201	57.5	38.8	58384.0	3886.56	0.2	15584.0
S-16	500µm<X<2.0mm	0.05	0.04	1.25	7.334	43.95	53.2	40032.0	3829.99	1.7	53048.0
S-17	500µm<X<2.0mm	0.05	0.04	1.25	7.397	42.6	54.7	41112.0	3659.49	6.1	189448.0
S-18	500µm<X<2.0mm	0.05	0.04	1.25	7.439	42.9	54.4	40872.0	3896.31	0.0	-8.0
S-1	500µm<X<2.0mm	0.1	0.04	2.5	7.526	30.95	67.1	25216.0	3829.97	1.7	26532.0
S-2	500µm<X<2.0mm	0.1	0.04	2.5	7.435	32.45	65.5	24616.0	3934.85	-1.0	-15420.0
S-3	500µm<X<2.0mm	0.1	0.04	2.5	7.449	33.4	64.5	24236.0	3899.83	-0.1	-1412.0
S-4	500µm<X<2.0mm	0.25	0.04	6.25	7.777	24.5	73.9	11118.4	3766.34	3.3	20793.6
S-5	500µm<X<2.0mm	0.25	0.04	6.25	7.764	25	73.4	11038.4	3796.14	2.6	16025.6
S-6	500µm<X<2.0mm	0.25	0.04	6.258	7.758	25.2	73.2	11006.4	3743.05	3.9	24520.0
S-7	500µm<X<2.0mm	0.5	0.04	12.5	8.009	23.1	75.4	5671.2	3659.99	6.1	18904.8
S-8	500µm<X<2.0mm	0.5	0.04	12.5	7.864	23.4	75.1	5647.2	3691.82	5.2	16358.4
S-9	500µm<X<2.0mm	0.5	0.04	12.5	8.001	23.3	75.2	5655.2	3621.17	7.1	22010.4
S-10	500µm<X<2.0mm	0.75	0.04	18.75	8.135	22.4	76.2	3818.1	3509.26	9.9	20642.1
S-11	500µm<X<2.0mm	0.75	0.04	18.75	8.041	23.3	75.2	3770.1	3451.76	11.4	23708.8
S-12	500µm<X<2.0mm	0.75	0.04	18.75	8.074	23.05	75.5	3783.5	3517.64	9.7	20195.2
S-13	500µm<X<2.0mm	1	0.04	25	8.133	22.2	76.4	2871.6	3378.87	13.3	20697.2
S-14	500µm<X<2.0mm	1	0.04	25	8.173	22.2	76.4	2871.6	3391.2	13.0	20204.0
S-15	500µm<X<2.0mm	1	0.04	25	8.098	22	76.6	2879.6	3437.1	11.8	18368.0
C-1	-	-	0.04	-	7.14	92.5	1.6	-	3928.93	-0.8	-
C-2	-	-	0.04	-	7.103	94.47	-0.5	-	3905.54	-0.2	-
C-3	-	-	1.04	-	7.172	95	-1.1	-	3854.43	1.1	-
C-DI 1	-	-	-	-		<0.25	-	-	<0.60	-	-
			FGD Leachate Control Averages			94.0			3896.3		

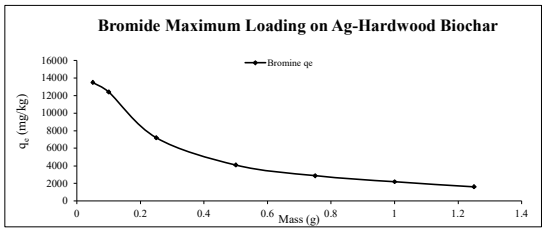
Set 4 - Ag Hardwood Biochar - Analysis completed on March 04, 2021

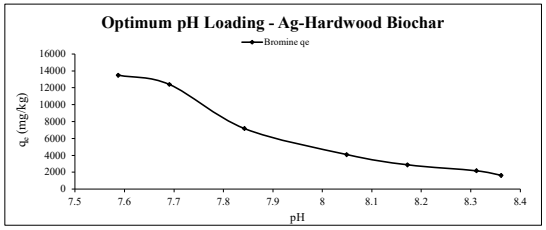
Sample ID	Size Fraction	Mass (g)	FGD Volume (L)	Dose (g/L)	pH	Ce Br- (mg/L)	Br- remov. (%)	qe Br- (mg/g)	Ce Cl- (mg/L)	Cl- remov. (%)	qe Cl- (mg/L)
S-1	500µm<X<2.0mm	0.05	0.04	1.25	7.613	84.3	13%	10.3	6648.5	-1%	-78.4
S-2	500µm<X<2.0mm	0.05	0.04	1.25	7.536	79.6	18%	14.1	6405.5	2%	116.0
S-3	500µm<X<2.0mm	0.05	0.04	1.25	7.613	77	21%	16.1	6375.5	3%	140.0
S-4	500µm<X<2.0mm	0.1	0.04	2.5	7.737	66.5	32%	12.3	6505.5	1%	18.0
S-5	500µm<X<2.0mm	0.1	0.04	2.5	7.691	64	34%	13.3	6507.5	1%	17.2
S-6	500µm<X<2.0mm	0.1	0.04	2.5	7.644	68	30%	11.7	6947.5	-6%	-158.8
S-7	500µm<X<2.0mm	0.25	0.04	6.25	7.806	52	46%	7.2	6945	-6%	-63.1
S-8	500µm<X<2.0mm	0.25	0.04	6.25	7.877	48.85	50%	7.7	7018	-7%	-74.8
S-9	500µm<X<2.0mm	0.25	0.04	6.25	7.844	56	42%	6.6	6487.5	1%	10.1
S-10	500µm<X<2.0mm	0.5	0.04	12.5	8.049	48.85	50%	3.9	6524.5	0%	2.1
S-11	500µm<X<2.0mm	0.5	0.04	12.5	8.062	43.85	55%	4.3	6904	-5%	-28.3
S-12	500µm<X<2.0mm	0.5	0.04	12.5	8.036	45.2	53%	4.2	6451.5	2%	7.9
S-13	500µm<X<2.0mm	0.75	0.04	18.75	8.156	42.65	56%	2.9	6682.5	-2%	-7.0
S-14	500µm<X<2.0mm	0.75	0.04	18.75 -		43	56%	2.9	6878	-5%	-17.5
S-14a	500µm<X<2.0mm	0.75	0.04	18.75 -		44.35	54%	2.8	6644	-1%	-5.0
S-15	500µm<X<2.0mm	0.75	0.04	18.75	8.188	43	56%	2.9	6498.5	1%	2.8
S-16	500µm<X<2.0mm	1	0.04	25	8.274	42.85	56%	2.2	6933	-6%	-15.3
S-17	500µm<X<2.0mm	1	0.04	25	8.37	41.85	57%	2.2	6854	-5%	-12.1
S-18	500µm<X<2.0mm	1	0.04	25	8.29	43	56%	2.2	6733	-3%	-7.3
S-19	500µm<X<2.0mm	1.25	0.04	31.25	8.346	42.35	56%	1.8	6925.5	-6%	-12.0
S-20	500µm<X<2.0mm	1.25	0.04	31.25	8.376	50	49%	1.5	6272	4%	8.9
S-21	500µm<X<2.0mm	1.25	0.04	31.25 -		47	52%	1.6	6929	-6%	-12.1
S-21a	500µm<X<2.0mm	1.25	0.04	31.25 -		46.3	52%	1.6	6295	4%	8.2
S-22 (cpntrol)		0	0.04		7.401	84.7			7202		
S-23 (control)		0	0.04		7.397	95.8			5450		
S-24 (control)		0	0.04		7.456	111			6999.5		
B						<0.25			<0.25		
			Control Averages			97.2			6550.5		

Duplicates		Br- conc. (mg/L)	Average of dups.	Bromide RPD	Cl- conc. (mg/L)	Average of dups.	Chloride RPD
S-14a	S-14 duplicate	44.35	43.675	-3.1%	6644	6761	3.5%
S-21a	S-21 duplicate	46.3	46.65	1.5%	6295	6612	9.6%









Fixed Mass and Volume Data - Appendix A, Table 3

Ag-Softwood Biochar

Experiment L	Analysis conducted September 2, 2020
Experiment L.1	Analysis conducted September 3,2020

	Biochar Preparation			Batch Sorption Experiment							
Sample ID	**Conc. $AgNO_3$ (M)**	**Vol. $AgNO_3$ (mL) (fixed)**	**Mass Softwood Biochar (g) (fixed)**	**Volume FGD (L)**	**Mass Softwood Biochar (g)**	**Conc. AgNO3 (M)**	**pH**	**Cl- (mg/L)**	**Cl- removal (%)**	**Br (mg/L)**	**Br removal (%)**
S-1	3	20	5	0.04	1	3.0	8.14	137	91.6%	1.0	95.5%
S-2	3	20	5	0.04	1	3.0	7.9	124	92.4%	1.0	95.7%
S-2a	**3**	**20**	**5**	**0.04**	**1**	**3.0**	**8**	**124**	**92.4%**	**1.0**	**95.7%**
S-3	3	20	5	0.04	1	3.0	8.06	69	95.8%	0.6	97.4%
S-4	2	20	5	0.04	1	2.0	8.22	158	90.3%	1.2	95.0%
S-5	2	20	5	0.04	1	2.0	8.18	120	92.7%	1.2	94.9%
S-6	2	20	5	0.04	1	2.0	8.11	74	95.5%	0.7	97.1%
S-7	1	20	5	0.04	1	1.0	8.17	420	74.3%	2.5	89.4%
S-8	1	20	5	0.04	1	1.0	8.18	398	75.7%	2.6	88.9%
S-9	1	20	5	0.04	1	1.0	8	392	76.0%	2.7	88.5%
S-9a	**1**	**20**	**5**	**0.04**	**1**	**1.0**	**8.1**	**383**	**76.6%**	**4.7**	**79.6%**
S-1	0.5	20	5	0.04	1	0.5	8.24	658	64%	3.2	87%
S-2	0.5	20	5	0.04	1	0.5	8.183	632	65%	3.13	87%
S-3	0.5	20	5	0.04	1	0.5	8.221	627	65%	3.04	88%
S-4	0.3	20	5	0.04	1	0.3	8.11	724	60.0%	3.5	85.9%
S-5	0.3	20	5	0.04	1	0.3	8.10	727	59.8%	3.6	85.4%
S-6	0.3	20	5	0.04	1	0.3	7.9	724	60.0%	3.5	85.9%
S-6a	**0.3**	**20**	**5**	**0.04**	**1**	**0.3**	**7.9**	**727**	**59.8%**	**3.8**	**84.7%**
S-7	0.2	20	5	0.04	1	0.2	8.04	795	56.0%	3.9	84.3%
S-8	0.2	20	5	0.04	1	0.2	8.09	798	55.9%	4.0	83.7%
S-9	0.2	20	5	0.04	1	0.2	8.16	788	56.4%	4.0	83.9%
S-10	0.1	20	5	0.04	1	0.1	8.08	838	53.7%	4.2	83.0%
S-11	0.1	20	5	0.04	1	0.1	8.10	1040	42.5%	4.1	83.3%
S-12	0.1	20	5	0.04	1	0.1	8.02	1030	43.0%	4.1	83.5%
S-13	0	20	5	0.04	1	0	7.73	1785	1.3%	18.2	26.4%
S-14	0	20	5	0.04	1	0	7.8	1815	-0.4%	19.9	19.5%
S-14a	**0**	**20**	**5**	**0.04**	**1**	**0**	**7.9**	**1800**	**0.5%**	**21.1**	**14.6%**
S-15	0	20	5	0.04	1	0	7.71	1840	-1.8%	26.8	-8.4%
S-10	0	20	5	0.04	1	0.0	7.67	1166	28.8%	22.7	1.6%
S-11	0	20	5	0.04	1	0.0	7.66	1344	17.9%	21.4	7.2%
S-12	0	20	5	0.04	1	0.0	7.67	1466	10.4%	21.9	5.1%
C-FGD 1	-	-	-	0.04	-	-	7.80	1810	-10.6%	23.1	-0.1%
C-FGD 2	-	-	-	0.04	-	-	7.79	1815	-10.9%	25.1	-8.8%
C-FGD 3	-	-	-	0.04	-	-	7.79	1800	-10.0%	26.0	-12.5%
C-DI 1	-	-	-	-	-	-	7.91	<1	-	<0.25	-
C-DI 2	-	-	-	-	-	-	6.80	<1	-	<0.25	-
C-DI 3	-	-	-	-	-	-	6.51	<1	-	<0.25	-
C-FGD 1	-	-	-	0.04	-	-	7.77	1610	1.6%	22.6	2.0%
C-FGD 2	-	-	-	0.04	-	-	7.77	1615	1.3%	23.0	0.3%
C-FGD 3	-	-	-	0.04	-	-	7.77	1685	-3.0%	23.6	-2.3%
C-DI 1	-	-	-	-	-	-	7.35	<0.25	-	<0.25	-
C-DI 2	-	-	-	-	-	-	6.25	<0.25	-	<0.25	-
C-DI 3	-	-	-	-	-	-	5.84	<0.25	-	<0.25	-
					Control Averages (experiment L)			**1636.7**		**23.1**	
					Control Averages (experiment L.1)			**1808.3**		**24.7**	

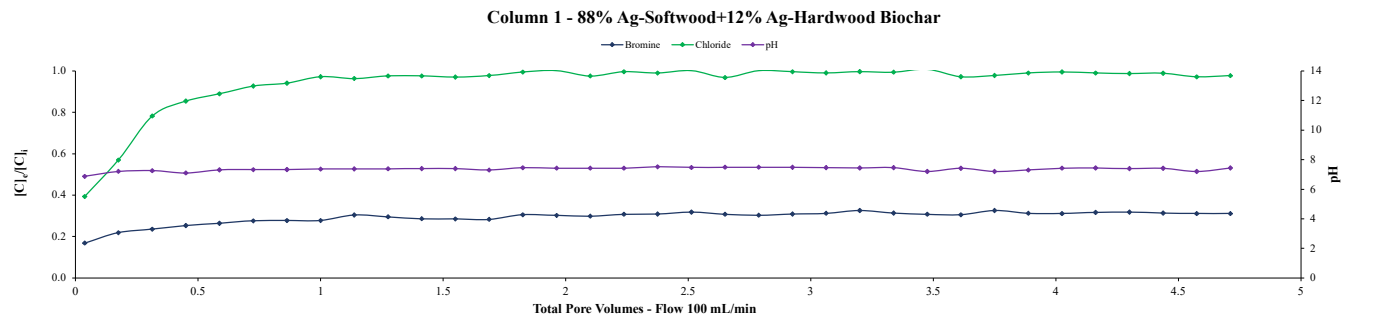
Duplicates	**pH**	**Cl- conc. (mg/L)**	**Average of dups.**	**Chloride RPD**	**Br- conc. (mg/L)**	**Average of dups.**	**Bromide RPD**
S-2a	**8**	**124**	**124**	**0.00%**	**1.0**	**0.995**	**1.01%**
S-9a	**8.1**	**383**	**387.5**	**2.32%**	**4.7**	**3.68**	**-55.98%**
S-6a	**7.9**	**727**	**725.5**	**-0.41%**	**3.8**	**3.64**	**-8.24%**
S-14a	**7.9**	**1800**	**1807.5**	**0.83%**	**21.1**	**20.5**	**-5.85%**

Column Data - Appendix A, Table 4

Column 1 - Data analyzed October 14, 2020

Sample ID	Sample Interval (mL)	Sample Vol. (mL)	pH	Bromide Ce (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride Ce/Co	Bromide removal (%)	Chloride removal (%)	time (hr:min:ss)	E. time (min)	total FGD Volume (mL)	Continuous Pore volumes
CS-01	100	50	6.871	29	0.17	3226	0.39	83%	61%	0.03	42	150	0.04
CS-02	500	50	7.205	37.6	0.22	4667	0.57	78%	43%	0.03	48	700	0.18
CS-03	500	50	7.256	40.5	0.24	6415	0.78	76%	22%	0.04	54	1250	0.31
CS-04	500	50	7.1	43.5	0.25	7005	0.85	75%	15%	0.04	59	1800	0.45
CS-05	500	50	7.305	45.4	0.26	7292	0.89	74%	11%	0.05	65	2350	0.59
CS-06	500	50	7.329	47.5	0.28	7602	0.93	72%	7%	0.05	71	2900	0.73
CS-07	500	50	7.34	47.7	0.28	7713	0.94	72%	6%	0.05	76	3450	0.86
CS-08	500	50	7.366	47.7	0.28	7972	0.97	72%	3%	0.06	82	4000	1.00
CS-09	500	50	7.376	52.4	0.30	7899	0.96	70%	4%	0.06	88	4550	1.14
CS-10	500	50	7.384	50.8	0.30	8002	0.98	70%	2%	0.07	94	5100	1.28
CS-11	500	50	7.401	49.2	0.29	8002	0.98	71%	2%	0.07	99	5650	1.41
CS-12	500	50	7.402	49	0.28	7960	0.97	72%	3%	0.07	105	6200	1.55
CS-13	500	50	7.3	48.7	0.28	8019	0.98	72%	2%	0.08	110	6750	1.69
CS-14	500	50	7.451	52.5	0.31	8157	1.00	69%	0%	0.08	117	7300	1.83
CS-15	500	50	7.427	51.9	0.30	8217	1.00	70%	0%	0.09	122	7850	1.96
CS-16	500	50	7.423	51.3	0.30	8001	0.98	70%	2%	0.09	128	8400	2.10
CS-17	500	50	7.428	52.9	0.31	8169	1.00	69%	0%	0.09	134	8950	2.24
CS-18	500	50	7.522	53.1	0.31	8118	0.99	69%	1%	0.10	140	9500	2.38
CS-19	500	50	7.476	54.7	0.32	8213	1.00	68%	0%	0.10	146	10050	2.51
CS-20	500	50	7.492	52.9	0.31	7939	0.97	69%	3%	0.11	152	10600	2.65
CS-21	500	50	7.488	52.1	0.30	8210	1.00	70%	0%	0.11	158	11150	2.79
CS-22	500	50	7.479	53.1	0.31	8167	1.00	69%	0%	0.11	164	11700	2.93
CS-23	500	50	7.464	53.7	0.31	8127	0.99	69%	1%	0.12	170	12250	3.06
CS-24	500	50	7.446	56	0.33	8174	1.00	67%	0%	0.12	176	12800	3.20
CS-25	500	50	7.46	53.9	0.31	8153	0.99	69%	1%	0.13	182	13350	3.34
CS-26	500	50	7.2	52.9	0.31	8263	1.01	69%	-1%	0.13	188	13900	3.48
CS-27	500	50	7.417	52.5	0.31	7968	0.97	69%	3%	0.13	194	14450	3.61
CS-28	500	50	7.2	56	0.33	8025	0.98	67%	2%	0.14	200	15000	3.75
CS-29	500	50	7.3	53.7	0.31	8119	0.99	69%	1%	0.14	206	15550	3.89
CS-30	500	50	7.428	53.5	0.31	8162	1.00	69%	0%	0.15	212	16100	4.03
CS-31	500	50	7.432	54.5	0.32	8119	0.99	68%	1%	0.15	218	16650	4.16
CS-32	500	50	7.403	54.7	0.32	8096	0.99	68%	1%	0.16	224	17200	4.30
CS-33	500	50	7.415	53.9	0.31	8110	0.99	69%	1%	0.16	229	17750	4.44
CS-34	500	50	7.2	53.5	0.31	7967	0.97	69%	3%	0.16	235	18300	4.58
CS-35	500	50	7.432	53.5	0.31	8015	0.98	69%	2%	0.17	241	18850	4.71
B-1 (DI water blank)		50	8.5	<0.250		<0							
LC-1 (leachate control)		50	7.3	172		8197							

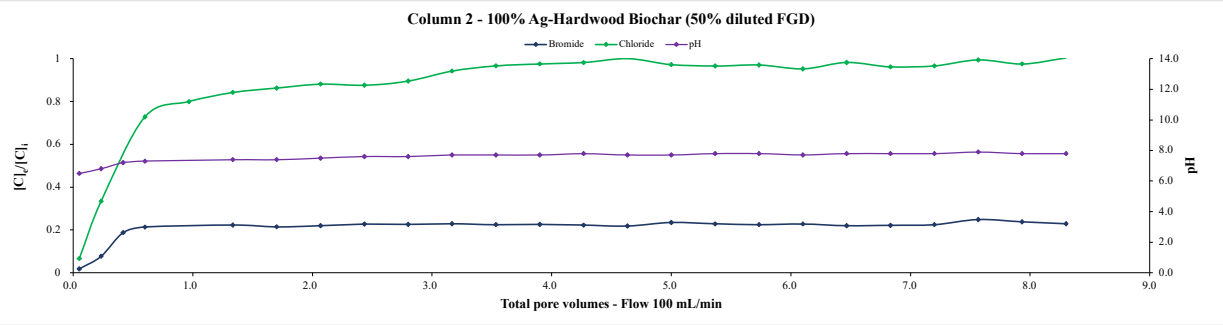
Duplicates	pH	Bromide Ce (mg/L)	Average	Bromide RPD	Chloride Ce (mg/L)	Average	Chloride RPD
CS-04b	7.2	45.9	44.7	-5.37%	7020	7012.5	-0.21%
CS-13b	7.3	48.1	48.4	1.24%	8106	8062.5	-1.08%
CS-26b	7.3	52.7	52.8	0.38%	8044	8153.5	2.69%
CS-28b	7.3	54.5	55.25	2.71%	8014	8019.5	0.14%
CS-29b	7.3	54.5	54.1	-1.48%	8137	8128	-0.22%
CS-34b	7.2	53.1	53.3	0.75%	7890	7928.5	0.97%



Column 2 - Data analyzed October 28, 2020

Sample ID	Sample Interval (mL)	Sample Vol. (mL)	pH	Bromide Ce (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride C_e/C_o	Bromide removal (%)	Chloride removal (%)	time (hr:min)	time (min)	total FGD Volume (mL)	Continuous Pore volumes
CS-01	100	50	6.5	1.32	0.02	171	0.07	98%	93%	0:32	32	150	0.05
CS-02	500	50	6.8	5.57	0.08	861	0.33	92%	67%	0:38	38	700	0.23
CS-04	1000	50	7.2	13.6	0.19	1879	0.73	81%	27%	0:50	50	1250	0.42
CS-06	1000	50	7.3	15.45	0.21	2063	0.80	79%	20%	1:02	62	1800	0.60
CS-08	1000	50	7.4	16.15	0.22	2174	0.84	78%	16%	1:12	73	4000	1.33
CS-10	1000	50	7.4	15.55	0.21	2227	0.86	79%	14%	1:24	84	5100	1.70
CS-12	1000	50	7.5	15.9	0.22	2275	0.88	78%	12%	1:34	95	6200	2.07
CS-14	1000	50	7.6	16.45	0.23	2260	0.88	77%	12%	1:46	106	7300	2.43
CS-16	1000	50	7.6	16.35	0.23	2310	0.90	77%	10%	1:57	117	8400	2.80
CS-18	1000	50	7.7	16.6	0.23	2432	0.94	77%	6%	2:08	128	9500	3.17
CS-20	1000	50	7.7	16.25	0.22	2495	0.97	78%	3%	2:19	139	10600	3.53
CS-22	1000	50	7.7	16.35	0.23	2518	0.98	77%	2%	2:30	150	11700	3.90
CS-24	1000	50	7.8	16.1	0.22	2534	0.98	78%	2%	2:41	162	12800	4.27
CS-26	1000	50	7.7	15.8	0.22	2581	1.00	78%	0%	2:52	172	13900	4.63
CS-28	1000	50	7.7	17	0.23	2510	0.97	77%	3%	3:03	183	15000	5.00
CS-30	1000	50	7.8	16.55	0.23	2492	0.97	77%	3%	3:13	194	16100	5.37
CS-32	1000	50	7.8	16.25	0.22	2505	0.97	78%	3%	3:24	205	17200	5.73
CS-34	1000	50	7.7	16.5	0.23	2458	0.95	77%	5%	3:35	216	18300	6.10
CS-36	1000	50	7.8	15.9	0.22	2535	0.98	78%	2%	3:46	227	19400	6.47
CS-38	1000	50	7.8	16.05	0.22	2483	0.96	78%	4%	3:58	238	20500	6.83
CS-40	1000	50	7.8	16.25	0.22	2494	0.97	78%	3%	4:09	249	21600	7.20
CS-42	1000	50	7.9	18	0.25	2567	0.99	75%	1%	4:20	260	22700	7.57
CS-44	1000	50	7.8	17.2	0.24	2518	0.98	76%	2%	4:31	272	23800	7.93
CS-46	1000	50	7.8	16.6	0.23	2588	1.00	77%	0%	4:43	283	24900	8.30
B-1 (DI water blank)		50	8.6	<0.250		<0.250							
B-1a (DI water blank)		50	8.8	<0.3		<0.250							
LC-1 (FGD Leachate Control)		50	7.2	72.4		2580							

Duplicates	pH	Bromide Ce (mg/L)	Average	Bromide RPD	Chloride Ce (mg/L)	Average	Chloride RPD
CS-04a	7.207	13.6	13.6	0.00%	1879	1879	0.00%
CS-26a	7.7	18.05	16.925	-13.29%	2576	2578.5	0.19%
CS-28a	7.7	16.8	16.9	1.18%	2507	2508.5	0.12%
CS-34a	7.7	21.2	18.85	-24.93%	2573	2400	-4.79%



Column 3 - Data analyzed November 18, 2020

Part 1

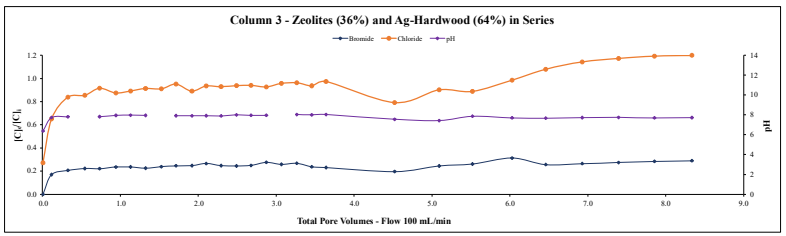
Sample ID	Sample Interval (mL)	Sample Vol. (mL)	pH	Bromide Co (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride Ce/Co	Bromide removal (%)	Chloride removal (%)	E. Time	E. Time (minutes)
CS-01	0	50	6.37	14.9	0.23	1878	0.77	77%	23%	1:11	71.5
CS-02	–4000	50	7.73	16.45	0.29	2381	0.98	72%	5%	1:25	85.0
CS-03	1000	50	7.8	15.55	0.24	2431	1.00	76%	3%	1:38	98.9
CS-04	1000	50		15.5	0.24	2381	0.98	77%	5%	1:50	111.0
CS-05	1000	50	7.81	16.75	0.26	2501	1.03	75%	0%	2:04	124.4
CS-06	1000	50	7.94	15.2	0.23	2509	1.03	77%	0%	2:16	136.4
CS-07	1000	50	7.97	16.1	0.25	2464	1.02	76%	1%	2:28	148.7
CS-08	1000	50	7.94	15.85	0.24	2390	0.98	76%	5%	2:41	161.7
CS-09	1000	50		20.3	0.31	2515	1.03	69%	0%	2:53	173.7
CS-10	1000	50	7.92	16.2	0.25	2492	1.02	75%	0%	3:06	186.8
CS-11	1000	50	7.9	16.4	0.25	2492	1.02	75%	0%	3:18	198.6
CS-12	1000	50	7.92	16.7	0.26	2472	1.02	75%	1%	3:30	210.8
CS-13	1000	50	7.89	20.8	0.32	2475	1.02	69%	1%	3:43	223.4
CS-14	1000	50	8	17.9	0.28	2518	1.04	73%	-1%	3:55	235.4
CS-15	1000	50	7.95	17.15	0.27	2511	1.03	74%	0%	4:07	247.9
CS-16	1000	50	7.95	17.35	0.27	2497	1.01	74%	2%	4:20	260.3
CS-17	1000	50		17	0.26	2539	1.04	74%	-1%	4:32	272.9
CS-18	1000	50	8.03	16.35	0.28	2535	1.04	72%	-1%	4:45	285.2
CS-19	1000	50	8	18.15	0.28	2515	1.03	73%	0%	4:56	296.9
CS-20	1000	50	8.03	17.6	0.27	2450	1.01	73%	2%	5:53	353.3
CS-23	1000	50	7.55	17.25	0.27	1969	0.80	74%	22%	6:29	390.0
CS-26	1000	50	7.42	17.05	0.26	2303	0.95	74%	8%	6:57	417.2
CS-29	1000	50	7.86	16.35	0.25	2366	0.98	75%	5%	7:29	449.8
CS-30	1000	50	7.703	19.4	0.30	2899	1.19	71%	-16%	7:57	477.4
CS-31	1000	50	7.66	19.8	0.31	2879	1.18	70%	-15%	8:27	507.3
CS-32	1000	50	7.72	20.4	0.32	2975	1.22	69%	-19%	8:57	537.2
CS-33	1000	50	7.74	20.9	0.32	3053	1.26	68%	-22%	9:26	566.7
CS-34	1000	50	7.69	20.8	0.32	2996	1.23	69%	-20%	9:57	597.4
CS-35	1000	50	7.72	22.65	0.35	2989	1.23	66%	-19%		

Part 2

Sample ID	Sample Interval (mL)	Sample Vol. (mL)	pH	Bromide Co (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride Ce/Co	Bromide removal (%)	Chloride removal (%)	E. Time	E. Time (minutes)	Total Outflow (mL)	Continuous Pore Volumes
CS-01F	0	50	6.37	0	0.00	679	0.27	100%	73%	1:04	64.6	50	0.0
CS-02F	500	50	7.73	11.25	0.17	1611	0.65	83%	35%	1:11	71.5	600	0.2
CS-03F	1000	50	7.8	13.65	0.21	2097	0.84	79%	16%	1:25	85.0	1650	0.5
CS-04F	1000	50		14.7	0.22	2137	0.85	78%	15%	1:38	98.9	2700	0.8
CS-05F	1000	50	7.81	14.6	0.22	2291	0.92	78%	8%	1:50	111.0	3750	1.1
CS-06F	1000	50	7.94	15.55	0.24	2189	0.87	76%	13%	2:04	124.4	4800	1.4
CS-07F	1000	50	7.97	15.6	0.24	2232	0.89	76%	11%	2:16	136.4	5850	1.7
CS-08F	1000	50	7.94	14.9	0.23	2287	0.91	77%	9%	2:28	148.7	6900	2.0
CS-09F	1000	50		15.75	0.24	2279	0.91	76%	9%	2:41	161.7	7950	2.3
CS-10F	1000	50	7.92	16.25	0.25	2301	0.95	75%	5%	2:53	173.7	9000	2.6
CS-11F	1000	50	7.9	16.35	0.25	2227	0.89	75%	11%	3:06	186.8	10050	3.0
CS-12F	1000	50	7.92	17.55	0.27	2342	0.94	73%	6%	3:18	198.6	11100	3.3
CS-13F	1000	50	7.89	16.35	0.25	2324	0.93	75%	7%	3:30	210.8	12150	3.6
CS-14F	1000	50	8	16.15	0.24	2349	0.94	76%	6%	3:43	223.4	13200	3.9
CS15F	1000	50	7.95	16.45	0.25	2352	0.94	75%	6%	3:55	235.4	14250	4.2
CS-16F	1000	50	7.95	18.2	0.28	2318	0.93	72%	7%	4:07	247.9	15300	4.5
CS-17F	1000	50		17.05	0.26	2398	0.96	74%	4%	4:20	260.3	16350	4.8
CS-18F	1000	50	8.03	17.7	0.27	2410	0.96	73%	4%	4:32	272.9	17400	5.1
CS-19F	1000	50	8	15.7	0.24	2344	0.94	76%	6%	4:45	285.2	18450	5.4
CS-20F	1000	50	8.03	15.25	0.23	2436	0.97	77%	3%	4:56	296.9	19500	5.7
CS-23F	6000	50	7.55	12.95	0.20	1981	0.79	80%	21%	5:53	353.3	25550	7.5
CS-26F	3000	50	7.42	16.15	0.24	2255	0.90	76%	10%	6:29	390.0	28600	8.4
CS-29F	3000	50	7.86	17.25	0.26	2225	0.89	74%	11%	6:57	417.2	31650	9.3
CS-30F	3000	50	7.703	20.65	0.31	2466	0.99	69%	1%	7:29	449.8	34700	10.2
CS-31F	3000	50	7.66	16.95	0.26	2705	1.08	74%	-8%	7:57	477.4	37750	11.1
CS-32F	3000	50	7.72	17.45	0.26	2860	1.14	74%	-14%	8:27	507.3	40800	12.0
CS-33F	3000	50	7.74	18.1	0.27	2933	1.17	73%	-17%	8:57	537.2	43850	12.9
CS-34F	3000	50	7.69	18.75	0.28	2985	1.19	72%	-19%	9:26	566.7	46900	13.8
CS-35F	3000	50	7.72	19.1	0.29	3001	1.20	71%	-20%	9:57	597.4	49950	14.7
B-1 (DI water blank)				<0.25		<0.25							

Control Samples	E. Time (hr:min)	Bromide (mg/L)	Chloride (mg/L)
LC-1	0:01	65	2396
LC-2	0:51	65.8	2450
LC-3	1:00	60.8	2460
LC-4	1:31	60.4	2377
LC-5	1:59	61	2409
LC-6	2:36	62.6	2383
LC-7	3:02	68.8	2467
LC-8	3:32	66	2445
LC-9	4:03	66.6	2502
LC-10	4:29	66.8	2482
LC-11	5:01	67.6	2472
LC-13	6:05	59.4	2486
LC-15	7:03	69	2947
LC-17	8:03	81.6	3097
LC-19	9:03	63.2	2225
LC-21	10:03	62.2	2335
	AVERAGE	66.1	2503.4
	C/Br ratio		38

Duplicates	pH	Bromide Co (mg/L)	Average	Bromide RPD	Chloride Co (mg/L)	Average	Chloride RPD
LC-2a	7.4	65.4	65.6	0.61%	2292	2371	6.66%
LC-15a	-	77.4	75.2	-11.48%	2927	2937	0.68%
CS-04a	7.5	19.95	17.425	-24.39%	2284	2282.5	-0.13%
CS-09a	7.7	17.6	18.95	14.25%	2534	2524.5	-0.75%
CS-17a	7.8	19.9	18.45	-15.72%	2474	2506.5	2.59%
CS-26a	-	16.8	16.45	-1.52%	2417	2360	-4.83%
CS-31a	-	19.65	19.725	0.76%	2844	2861.5	1.22%



Column 4 - Data analyzed February 2. 2021

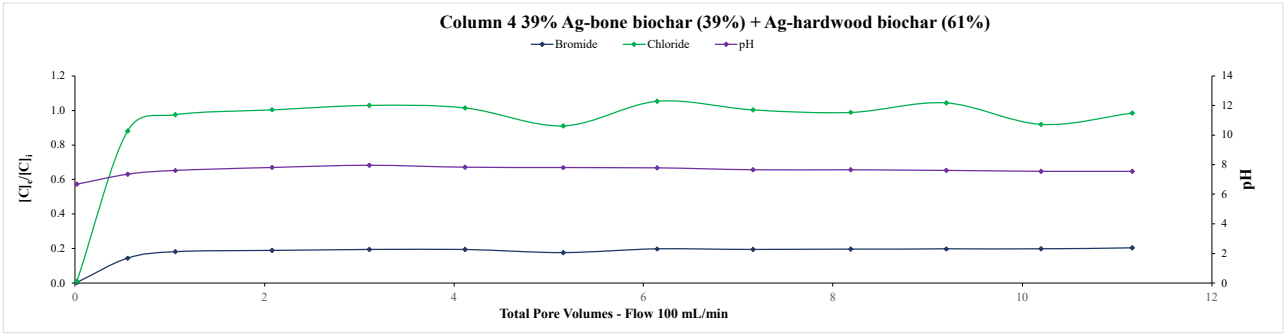
Part 2 of 2 (part 1 samples not obtained)

Sample ID	Elapsed Time (hr:min:ss)	Sample Vol. (mL)	pH	Bromide Ce (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride Ce/Co	Bromide removal (%)	Chloride removal (%)	Ag Ce (µg/L)	Total Outflow (mL)	Continuous Pore Volumes
CSF-1	1:00:02	50	6.87	0.51	0.003	44.9	0.010	100%	99%	28	103	0.02
CSF-3	1:31:45	50	7.21	24.8	0.144	4102	0.881	81%	12%		3275	0.56
CSF-5	2:01:26	50	7.26	31.2	0.181	4536	0.975	76%	3%		6243	1.06
CSF-7	3:01:37	50	7.10	32.6	0.190	4671	1.004	75%	0%		12262	2.08
CSF-8	4:02:16	50	7.20	33.4	0.194	4787	1.028	75%	-3%		18327	3.11
CSF-9	5:01:51	50	7.31	33.4	0.194	4720	1.014	75%	-1%	388	24285	4.12
CSF-10	6:03:04	50	7.33	30.4	0.177	4237	0.910	77%	9%		30407	5.15
CSF-11	7:01:32	50	7.34	34	0.198	4898	1.052	74%	-5%		36253	6.14
CSF-12	7:01:15	50	7.37	33.4	0.194	4668	1.003	75%	0%		42225	7.16
CSF-13	9:02:08	50	7.38	33.8	0.197	4600	0.988	74%	1%		48313	8.19
CSF-14	10:01:34	50	7.38	34	0.198	4853	1.043	74%	-4%		54257	9.20
CSF-16	11:00:36	50	7.40	34.1	0.198	4275	0.918	74%	8%	381	60160	10.20
CSF-17	11:57:24	50	7.40	35	0.203	4583	0.985	74%	2%		65840	11.16
B-1 (DI water blank)				<0.25		<0.25						

Control Samples

Sample ID	Bromide Ce (mg/L)	Chloride Ce (mg/L)
CO-1	138	4756
CO-3	138	4861
CO-5	135	4731
CO-7	123	4123
CO-9	121	4153
CO-11	139	4923
CO-13	132	5034
Average	132	4654
	Cl/Br ratio	35

Duplicates	Bromide Ce (mg/L)	Average	Bromide RPD	Chloride Ce (mg/L)	Average	Chloride RPD
CSF-7D	33.6	33.1	3.0%	4595	4633	-1.6%
CSF-11D	35.6	34.8	-4.6%	4745	4821.5	3.2%
CO-5D	105.5	120.25	24.5%	4030	4380.5	16.0%
CO-13D	141	136.5	-6.6%	4832	4933	4.1%



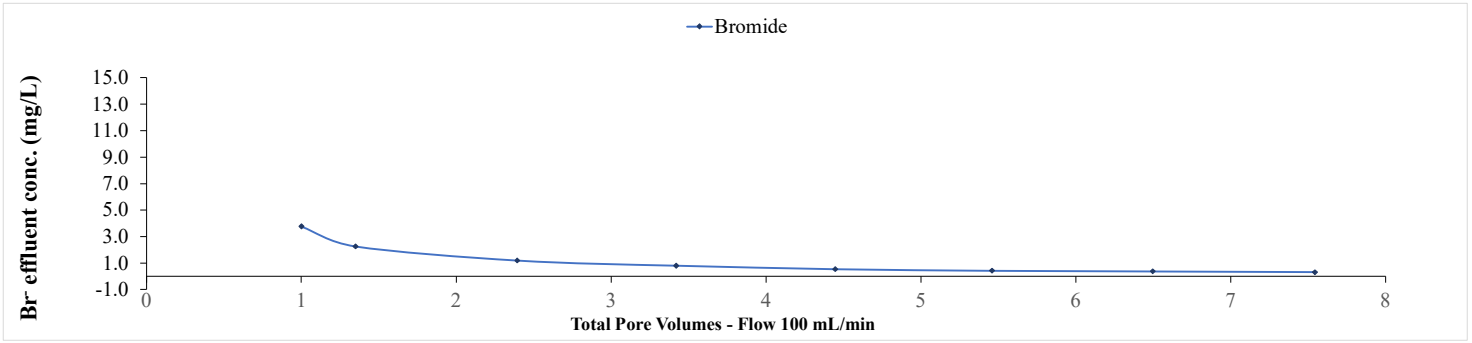
Column 4 Leaching - Data analyzed February 04, 2021

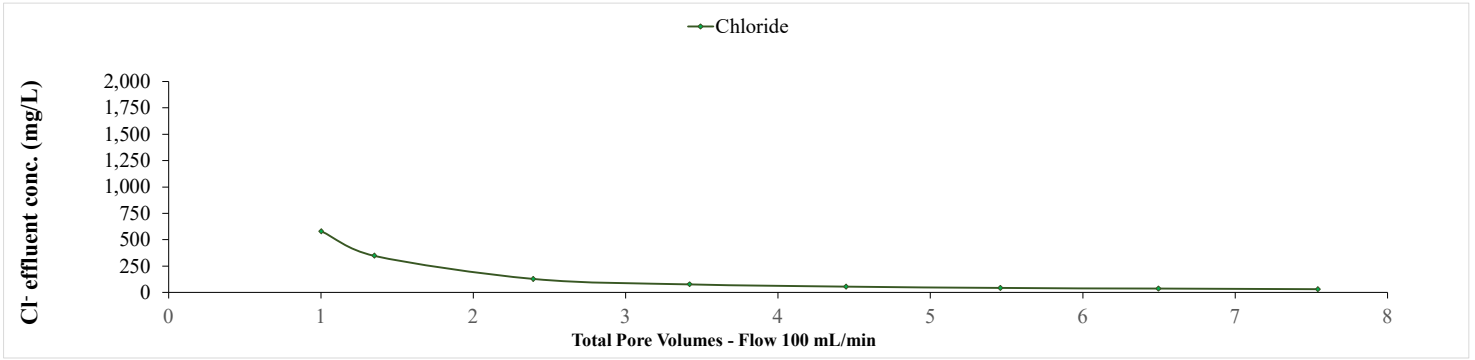
Sample ID	Elapsed Time (hr:min:ss)	Sample Vol. (mL)	pH	Bromide Ce (mg/L)	Chloride Ce (mg/L)	Total Outflow (mL)	Continuous Pore Volumes
L-1	0:38:03	50	-	-	-	-	-
L-2	0:48:14	50	-	-	-	-	-
L-3	0:58:03	50	8.102	3.76	580.4	2905	1.00
L-4	1:08:10	50	8.084	2.26	347.4	3917	1.35
L-5	1:38:26	50	8.073	1.19	126.88	6943	2.39
L-6	2:08:10	50	8.117	0.8	77.24	9917	3.42
L-7	2:37:57	50	8.156	0.54	54.02	12895	4.45
L-8	3:07:20	50	8.17	0.42	42.92	15833	5.46
L-9	3:37:25	50	8.133	0.37	35.89	18842	6.50
L-10	4:07:46	50	8.168	0.31	31.64	21877	7.54
B-1 (DI water blank)				<0.25	<0.25		

Control Samples

Sample ID	Sample Volume (mL)	Bromide Ce (mg/L)	Chloride Ce (mg/L)
CO-1	50	<0.25	9.98
CO-2	50	<0.25	9.88
CO-3	50	<0.25	9.94
CO-4	50	<0.25	9.85
CO-6	50	<0.25	9.85
CO-8	50	<0.25	9.82
CO-10	50	<0.25	9.82

Duplicates	Bromide Ce (mg/L)	Average	Bromide RPD	Chloride Ce (mg/L)	Average	Chloride RPD
L-6D	0.81	0.805	-1%	73.56	75.4	5%
L-9D	0.37	0.37	0%	37.15	36.52	-3%
CO-1D	<0.25	N/A	N/A	10.13	#REF!	#REF!





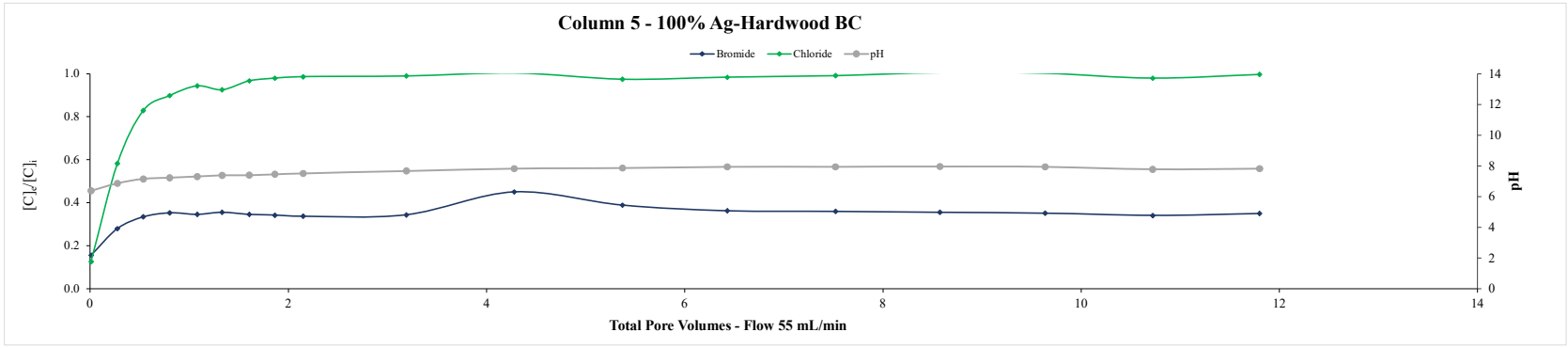
Column 5 - Data analyzed April 26, 2021

Sample ID	Elapsed Time (hr:min:ss)	Sample Vol. (mL)	pH	Bromide Ce (mg/L)	Bromide Ce/Co	Chloride Ce (mg/L)	Chloride Ce/Co	Bromide removal (%)	Chloride removal (%)	Total Outflow (mL)	Continuous Pore Volumes
CS-01	0:56:30	50	6.379	11.44	0.16	486	0.13	84%	87%	28	0.01
CS-02	1:11:23	50	6.864	20.5	0.28	2243	0.58	72%	42%	846	0.27
CS-03	1:26:02	50	7.152	24.5	0.33	3190	0.83	67%	17%	1652	0.54
CS-04	1:40:56	50	7.229	25.9	0.35	3460	0.90	65%	10%	2471	0.80
CS-05	1:56:27	50	7.307	25.4	0.35	3633	0.94	65%	6%	3325	1.08
CS-06	2:10:34	50	7.382	26.1	0.36	3564	0.93	64%	7%	4101	1.33
CS-07	2:25:51	50	7.398	25.4	0.35	3722	0.97	65%	3%	4942	1.60
CS-08	2:40:20	50	7.455	25.1	0.34	3770	0.98	66%	2%	5738	1.86
CS-09	2:56:21	50	7.507	24.7	0.34	3797	0.99	66%	1%	6619	2.15
CS-10	3:54:39	50	7.667	25.2	0.34	3809	0.99	66%	1%	9826	3.19
CS-11	4:55:36	50	7.82	33	0.45	3862	1.00	55%	0%	13178	4.28
CS-12	5:56:49	50	7.864	28.5	0.39	3752	0.97	61%	3%	16545	5.37
CS-13	6:55:56	50	7.937	26.6	0.36	3786	0.98	64%	2%	19796	6.43
CS-14	7:57:09	50	7.944	26.4	0.36	3818	0.99	64%	1%	23163	7.52
CS-15	8:56:09	50	7.963	26.1	0.36	3870	1.01	64%	-1%	26408	8.57
CS-16	9:55:38	50	7.937	25.8	0.35	3860	1.00	65%	0%	29680	9.64
CS-17	10:56:20	50	7.775	25	0.34	3771	0.98	66%	2%	33018	10.72
CS-18	11:56:48	50	7.825	25.7	0.35	3839	1.00	65%	0%	36344	11.80
B (DI water blank)				<0.25		<0.60					

Control Samples

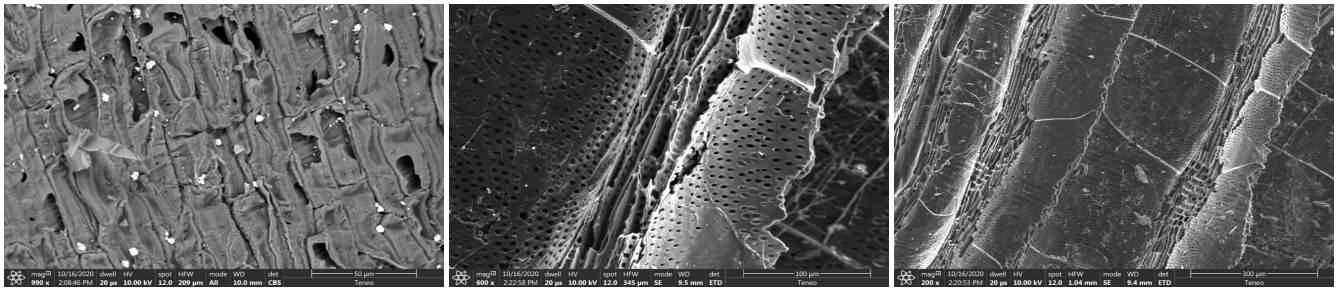
Sample ID	Sample Volume (mL)	Bromide Co (mg/L)	Chloride Co (mg/L)
L-1	50	73.25	3845.25
L-3	50	72.75	3851.74
L-5	50	72	3848.12
L-7	50	74.5	3866.99
L-9	50	73.5	3865.23
L-11	50	74	3820.18
AVERAGE		73.3	3849.6
		Cl:Br ratio	52

Duplicates	Bromide Ce	Average	Bromide RPD	Chloride Ce	Average	Chloride RPD
CS-12A	23.4	25.95	20%	2989	3370.425	23%
CS-18A	24.1	24.9	6%	3253.98	3546.35	16%

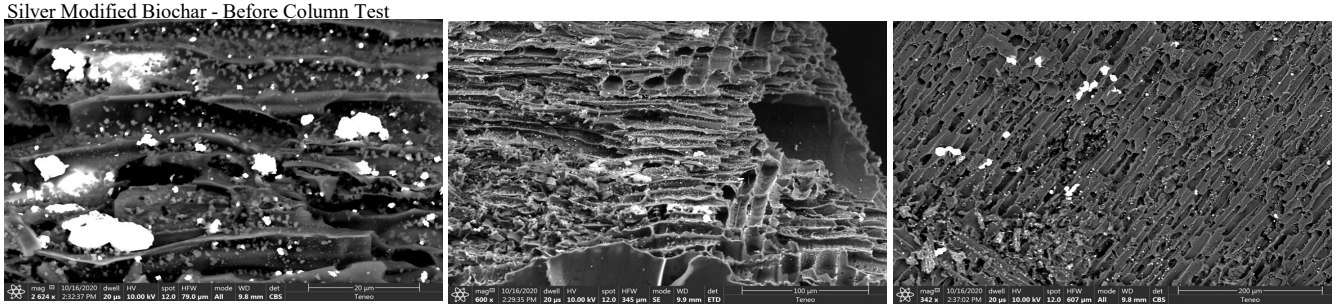


Scanning Electron Microscope Pictures from Column Tests - Appendix B, Figure 1

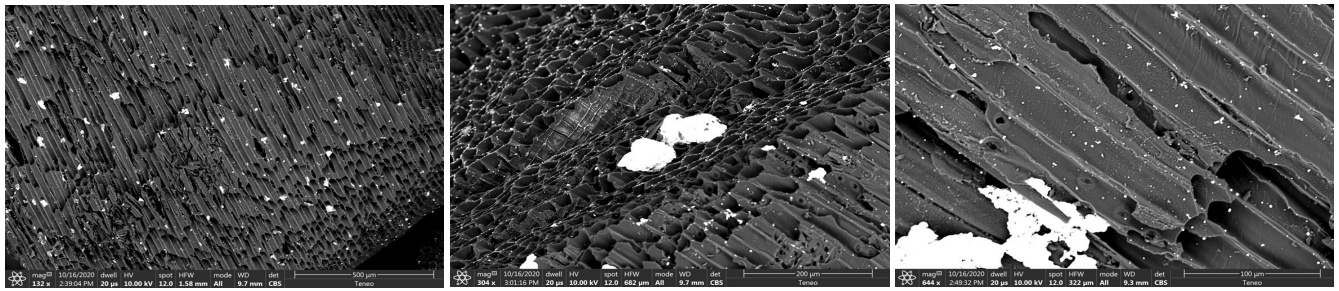
Raw Biochar



Silver Modified Biochar - Before Column Test

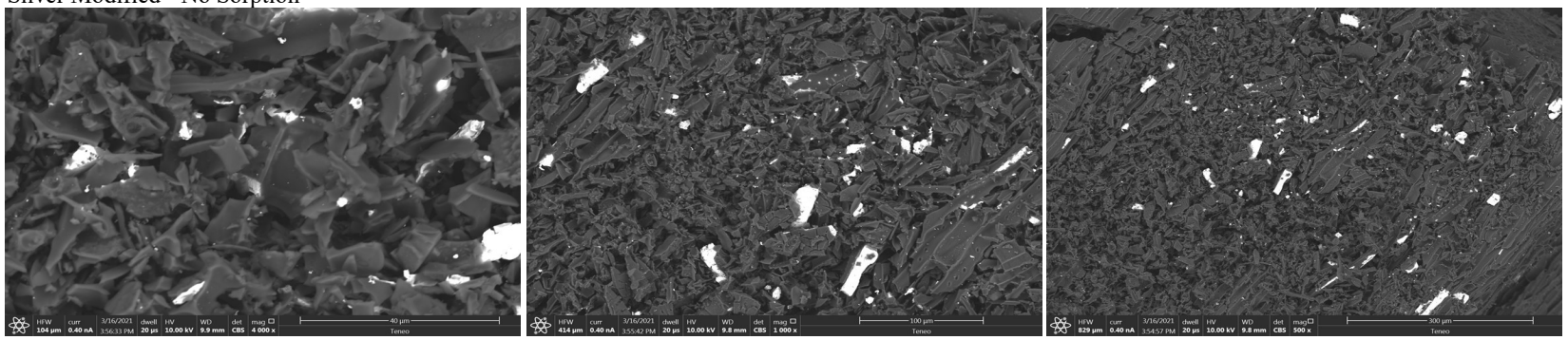


Silver Modified Biochar - After Column Test

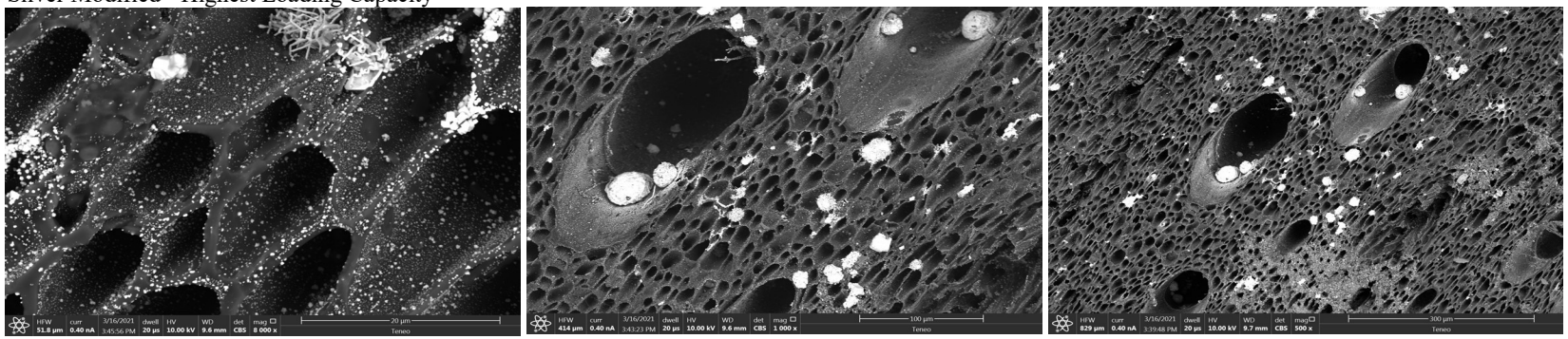


Scanning Electron Microscope Pictures from Max Loading Tests - Appendix B, Figure 2

Silver Modified - No Sorption



Silver Modified - Highest Loading Capacity



Appendix C

Specific Surface Area Analysis Data Sheets

Control Laboratories

42 Hangar Way
Watsonville, CA 95076
www.biocharlab.com
Tel: 831 724-5422
Fax: 831 724-3188

Account No.:
11478
Batch:
Jul 21 A
CODE:
Custom Report

Will Crumpacker
william.crumpacker@uga.edu
University of Georgia- Geology Department
210 Field Street, Room 308 (Geology Office)
Athens, GA 30602

Date Received: 7/11/2021
Sample ID: P-BBB
Lab ID Number: 1070248-01

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	3.9 g/100 g	C
Surface Area Correlation	257 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

Control Laboratories

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Batch:
Jul 21 A
CODE:
Custom Report

Will Crumpacker
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210 Field Street, Room 308 (Geology Office)
Athens, GA 30602

Date Received: 7/11/2021
Sample ID: P-HWB
Lab ID Number: 1070248-02

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	5.5 g/100 g	C
Surface Area Correlation	308 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Account No.:
11478
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Jul 21 A
CODE:
Custom Report

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210 Field Street, Room 308 (Geology Office)
Athens, GA 30602

Date Received: 7/11/2021
Sample ID: P-BNB
Lab ID Number: 1070248-03

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	3.2 g/100 g	C
Surface Area Correlation	234 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Account No.:
11478
Batch:
Jul 21 A
CODE:
Custom Report

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University of Georgia- Geology Department
210 Field Street, Room 308 (Geology Office)
Athens, GA 30602

Date Received: 7/11/2021
Sample ID: P-PHB
Lab ID Number: 1070248-04

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	1.0 g/100 g	C
Surface Area Correlation	165 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

Control Laboratories

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Fax: 831 724-3188

Account No.:
11478
Batch:
Jul 21 A
CODE:
Custom Report

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Athens, GA 30602

Date Received: 7/11/2021
Sample ID: P-SWB
Lab ID Number: 1070248-05

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	4.4 g/100 g	C
Surface Area Correlation	274 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

Control Laboratories

42 Hangar Way
Watsonville, CA 95076
www.biocharlab.com
Tel: 831 724-5422
Fax: 831 724-3188

Account No.:
11478
Batch:
Jul 21 A
CODE:
Custom Report

Will Crumpacker
william.crumpacker@uga.edu
University of Georgia- Geology Department
210 Field Street, Room 308 (Geology Office)
Athens, GA 30602

Date Received: 7/11/2021
Sample ID: Ag-BBB
Lab ID Number: 1070248-06

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	2.7 g/100 g	C
Surface Area Correlation	219 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

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Date Received: 7/11/2021
Sample ID: Ag-HWB
Lab ID Number: 1070248-07

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	2.9 g/100 g	C
Surface Area Correlation	227 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Date Received: 7/11/2021
Sample ID: Ag-BNB
Lab ID Number: 1070248-08

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	3.0 g/100 g	C
Surface Area Correlation	228 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Date Received: 7/11/2021
Sample ID: Ag-PHB
Lab ID Number: 1070248-09

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	0.4 g/100 g	C
Surface Area Correlation	145 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Date Received: 7/11/2021
Sample ID: Ag-SWB
Lab ID Number: 1070248-10

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	2.7 g/100 g	C
Surface Area Correlation	218 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Batch:
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CODE:
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Date Received: 7/11/2021
Sample ID: Post-AgHWB
Lab ID Number: 1070248-11

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	2.2 g/100 g	C
Surface Area Correlation	204 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Batch:
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CODE:
Custom Report

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Date Received: 7/11/2021
Sample ID: Post-AgBNB
Lab ID Number: 1070248-12

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	3.3 g/100 g	C
Surface Area Correlation	238 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Date Received: 7/11/2021
Sample ID: Post-AgPHB
Lab ID Number: 1070248-13

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	0.7 g/100 g	C
Surface Area Correlation	154 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Date Received: 7/11/2021
Sample ID: Post-AgSWB
Lab ID Number: 1070248-14

Proximate Analysis

	Dry Weight Basis	Method
Butane Activity	1.9 g/100 g	C
Surface Area Correlation	193 m^2/g	E

Methods

C ASTM D 5742-95

E Butane Activity Surface Area Correlation Based on McLaughlin, Shields, Jagiello, & Thiele's 2012 paper: Analytical Options for Biochar Adsorption and Surface Area

Analyst: Nik Zumberge

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Account No.:
11478
Batch:
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CODE:
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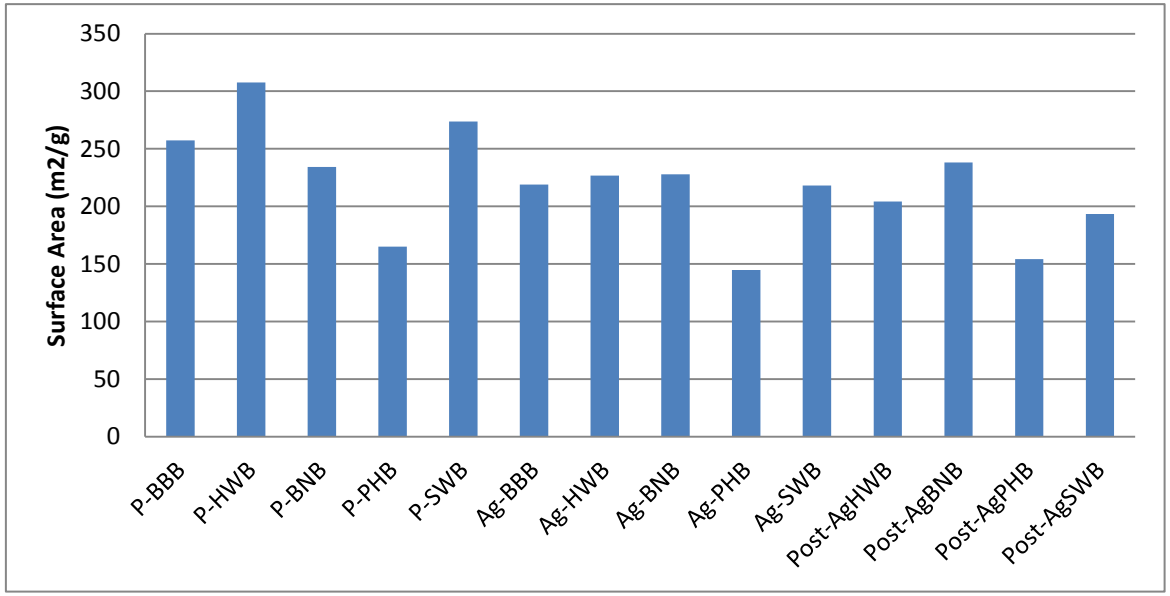
Sample ID	Client ID	Surface Area (m^2/g)
1070248-01	P-BBB	257
1070248-02	P-HWB	308
1070248-03	P-BNB	234
1070248-04	P-PHB	165
1070248-05	P-SWB	274
1070248-06	Ag-BBB	219
1070248-07	Ag-HWB	227
1070248-08	Ag-BNB	228
1070248-09	Ag-PHB	145
1070248-10	Ag-SWB	218
1070248-11	Post-AgHWB	204
1070248-12	Post-AgBNB	238
1070248-13	Post-AgPHB	154
1070248-14	Post-AgSWB	193



Analyst: Nik Zumberge

Appendix D

Cation Exchange Capacity Data Sheets

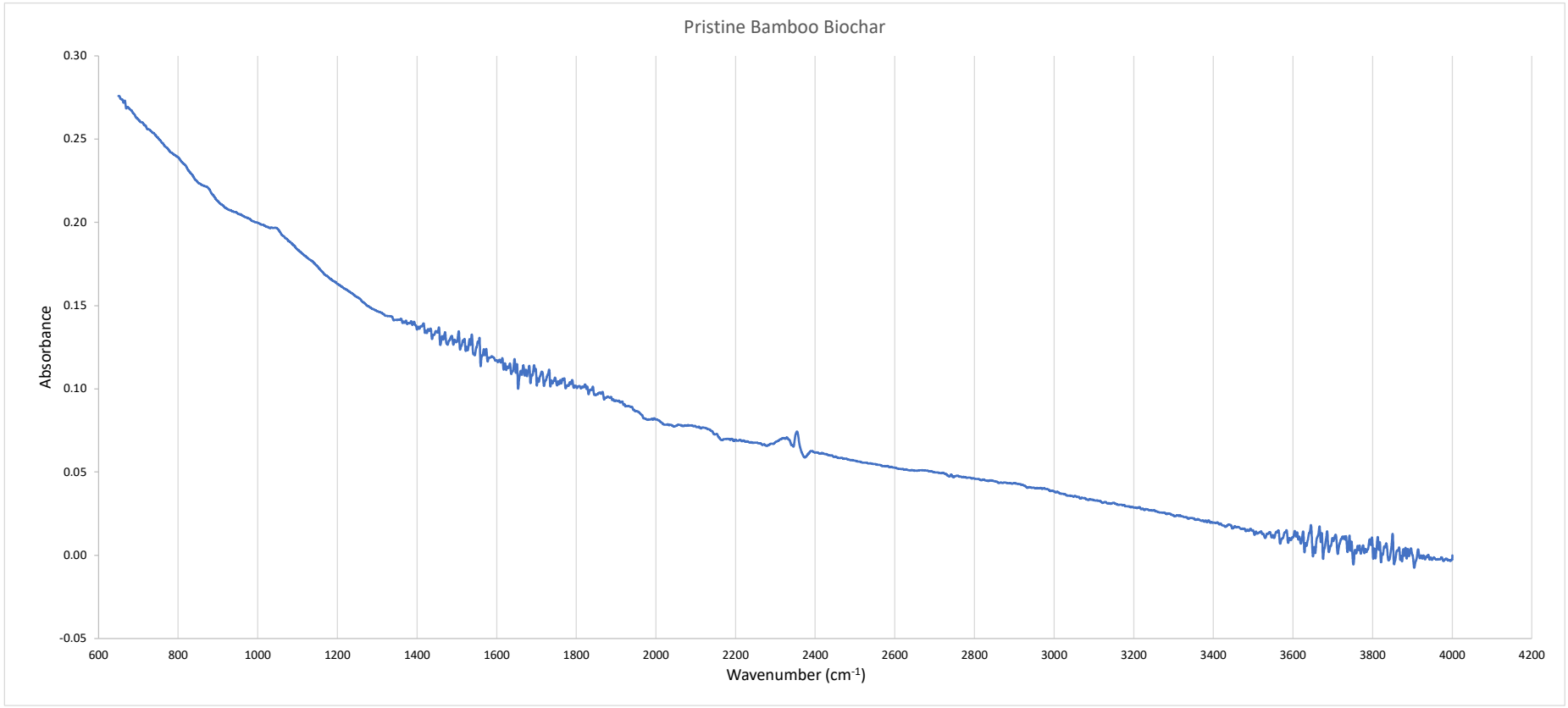
Results of the analysis of samples from William Crumpackler (Geology Dept) for CEC:

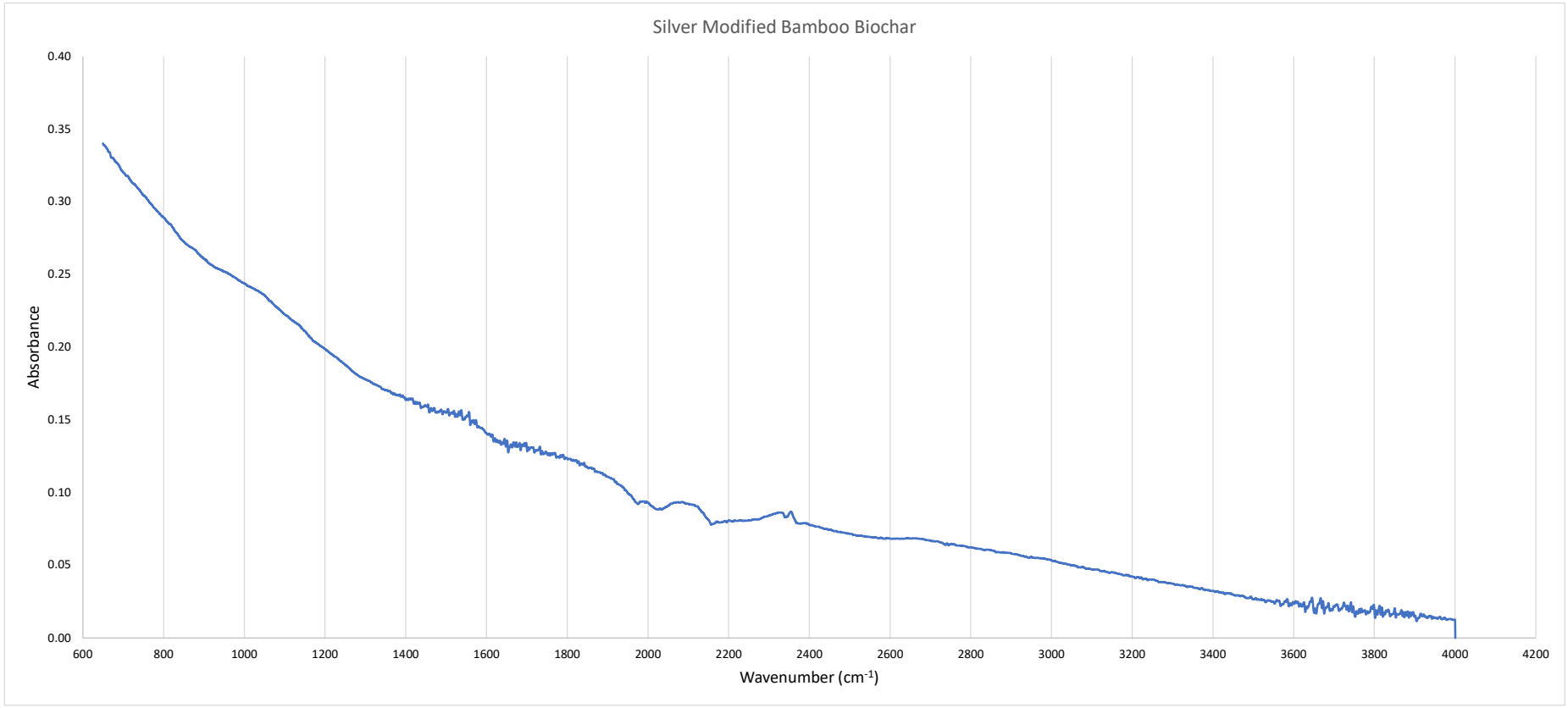
7/28/2021

		CEC	Extractable Metals			
			23Na	24Mg	39K	44Ca
Ser #	Sample ID	(meq/100g)	ppm	ppm	ppm	ppm
1	Ag-HWB	5.87	6,912.60	23,499.00	89,267.10	462,799.00
2	AG-BBB	5.05	2,676.00	23,303.80	222,881.70	95,210.80
3	Post-AgHWB	3.69	18,490.80	66,908.70	57,194.20	209,602.20
4	Post-AgPHB	12.33	16,627.20	163,306.90	87,478.90	297,195.00
5	Post-AgSWB	5.52	91,283.90	273,459.40	66,620.00	536,998.40
6	P-SWB	6.25	42,935.20	63,987.40	143,755.10	421,525.00
7	P-HWB	5.47	21,580.60	49,821.30	98,743.40	782,731.10
8	Ag-SWB	5.42	8,534.80	33,927.70	33,691.40	284,880.10
9	P-PHB	5.18	170.5	61,123.30	548,798.60	165,216.90
10	P-BNB	3.22	58,035.10	202,496.80	181.6	197,152.00
11	Ag-PHB	6.88	208.6	17,625.90	100,605.80	43,787.90
12	P-BBB	4.2	433	47,193.30	549,051.10	177,963.10
13	Ag-BNB	3.34	18,742.60	97,952.60	5,175.70	197,308.20
14	Post-AgBNB	4.15	2,663.70	178,679.60	1,019.50	504,078.10

Appendix E

Fourier Transform Infrared Spectroscopy Spectra


Pristine Bamboo Biochar
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
Wavenumber (cm-1)


Silver Modified Bamboo Biochar
Absorbance
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0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
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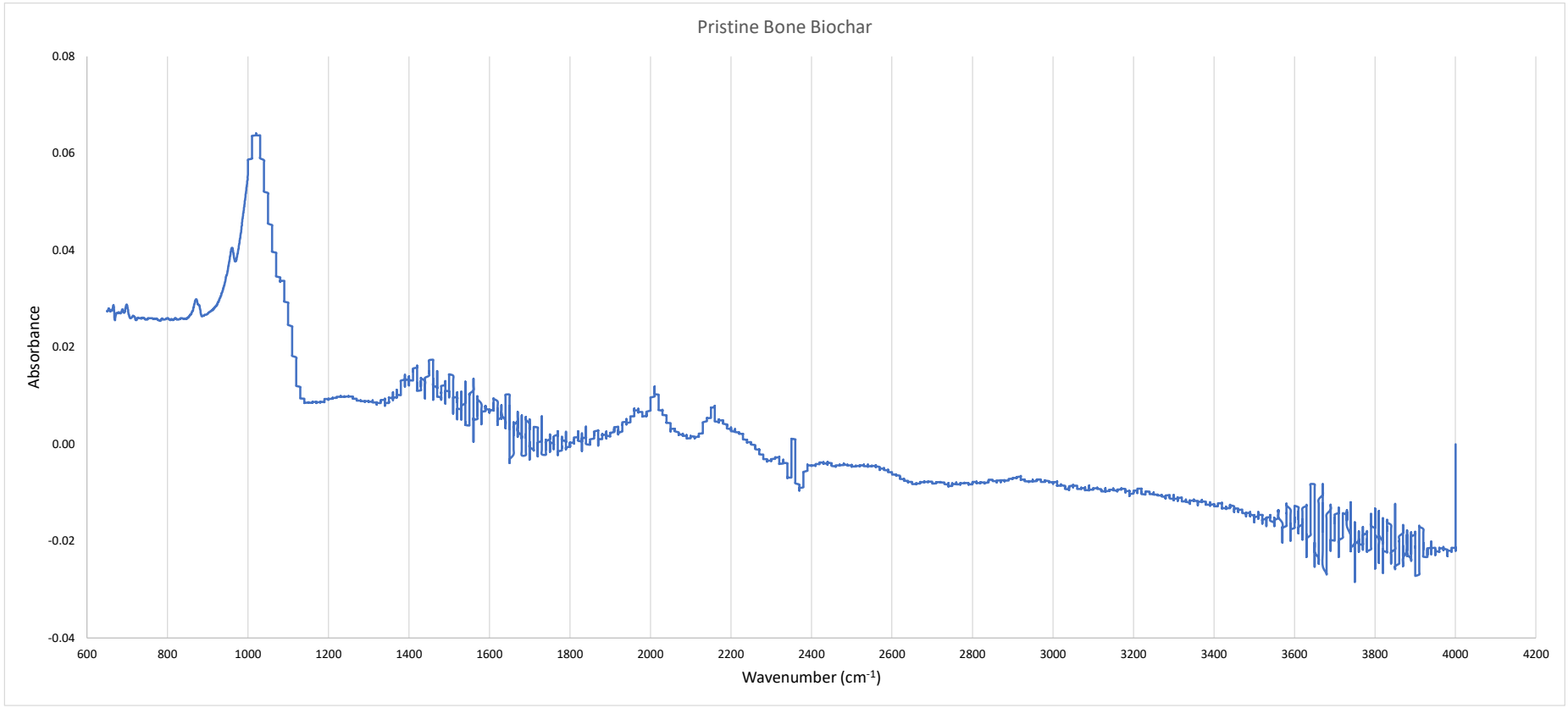
3600
3800
4000
4200
Wavenumber (cm-1)


Pristine Bone Biochar
Absorbance
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
600
800
1000
1200
1400
1600
1800
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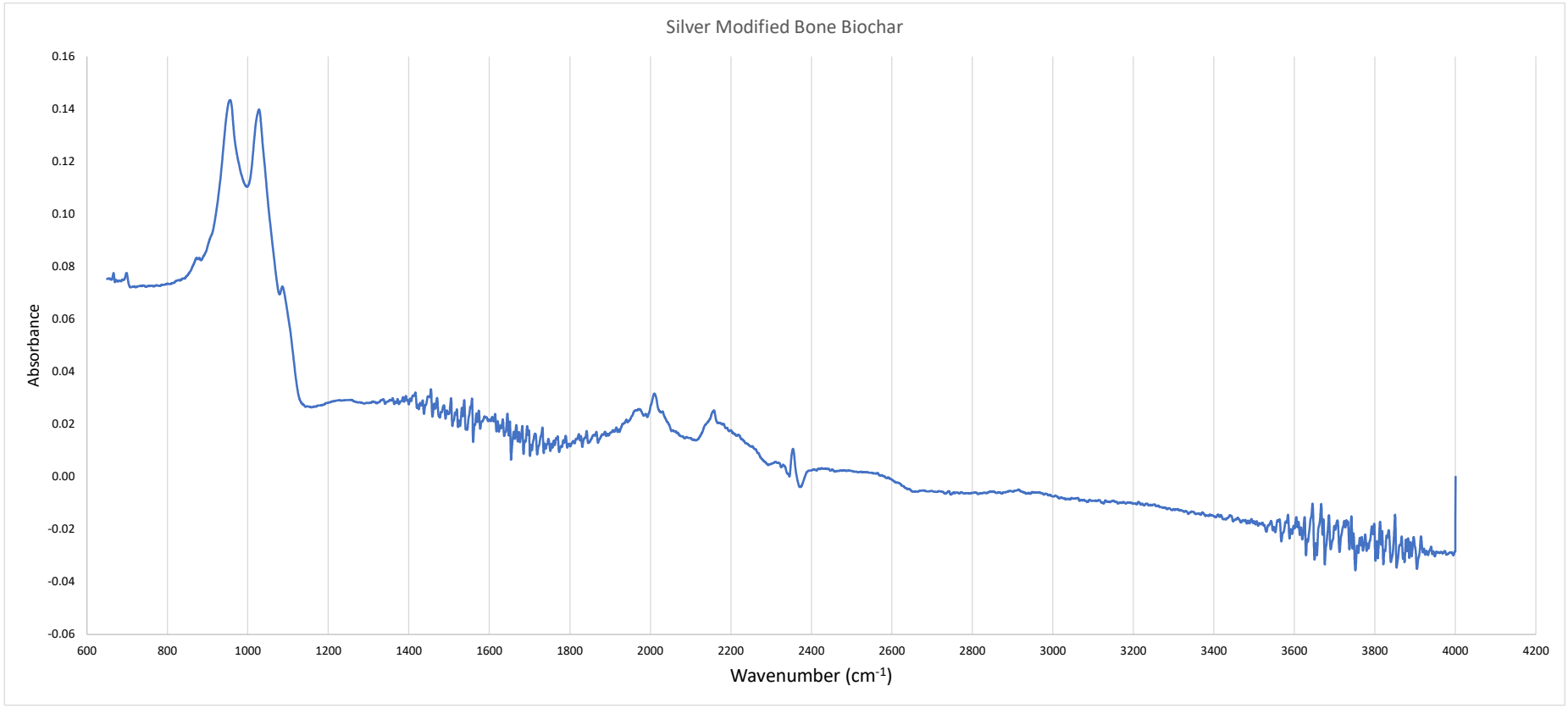
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
Wavenumber (cm-1)


Silver Modified Bone Biochar
Absorbance
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0.14
0.12
0.10
0.08
0.06
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0.00
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-0.04
-0.06
600
800
1000
1200
1400
1600
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2400
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2800
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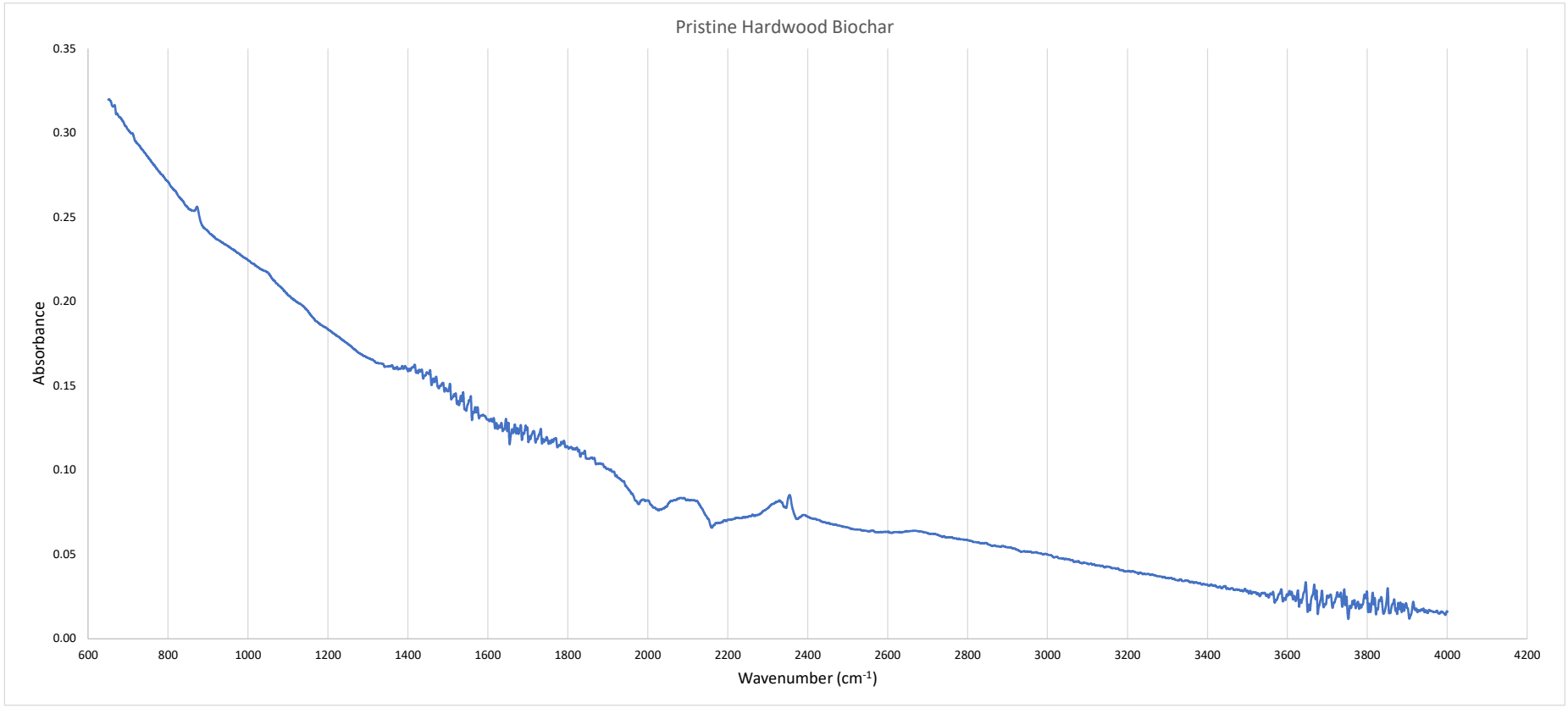
3600
3800
4000
4200
Wavenumber (cm-1)


Pristine Hardwood Biochar
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
Wavenumber (cm-1)


Silver Modified Hardwood Biochar
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
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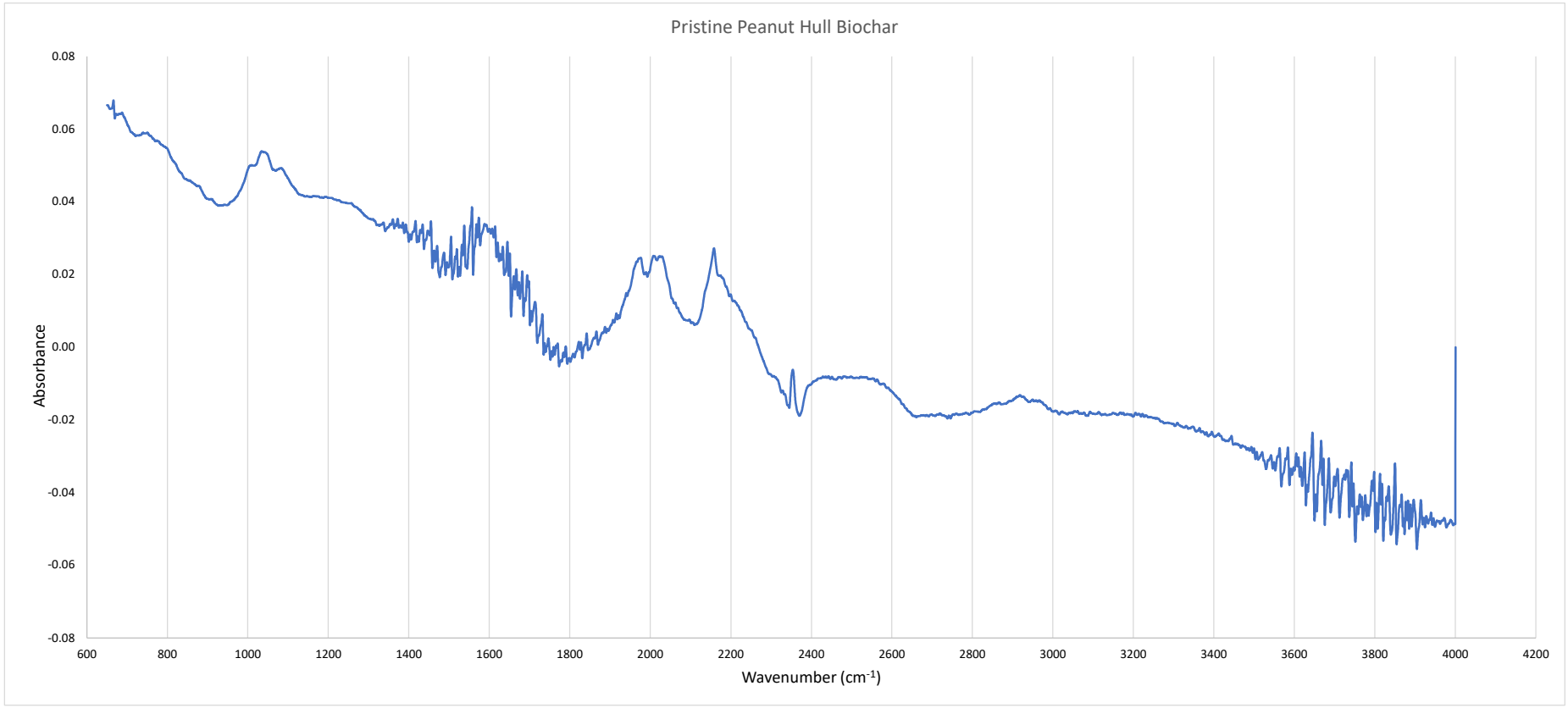
3600
3800
4000
4200
Wavenumber (cm-1)


Pristine Peanut Hull Biochar
Absorbance
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0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
600
800
1000
1200
1400
1600
1800
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2200
2400
2600
2800
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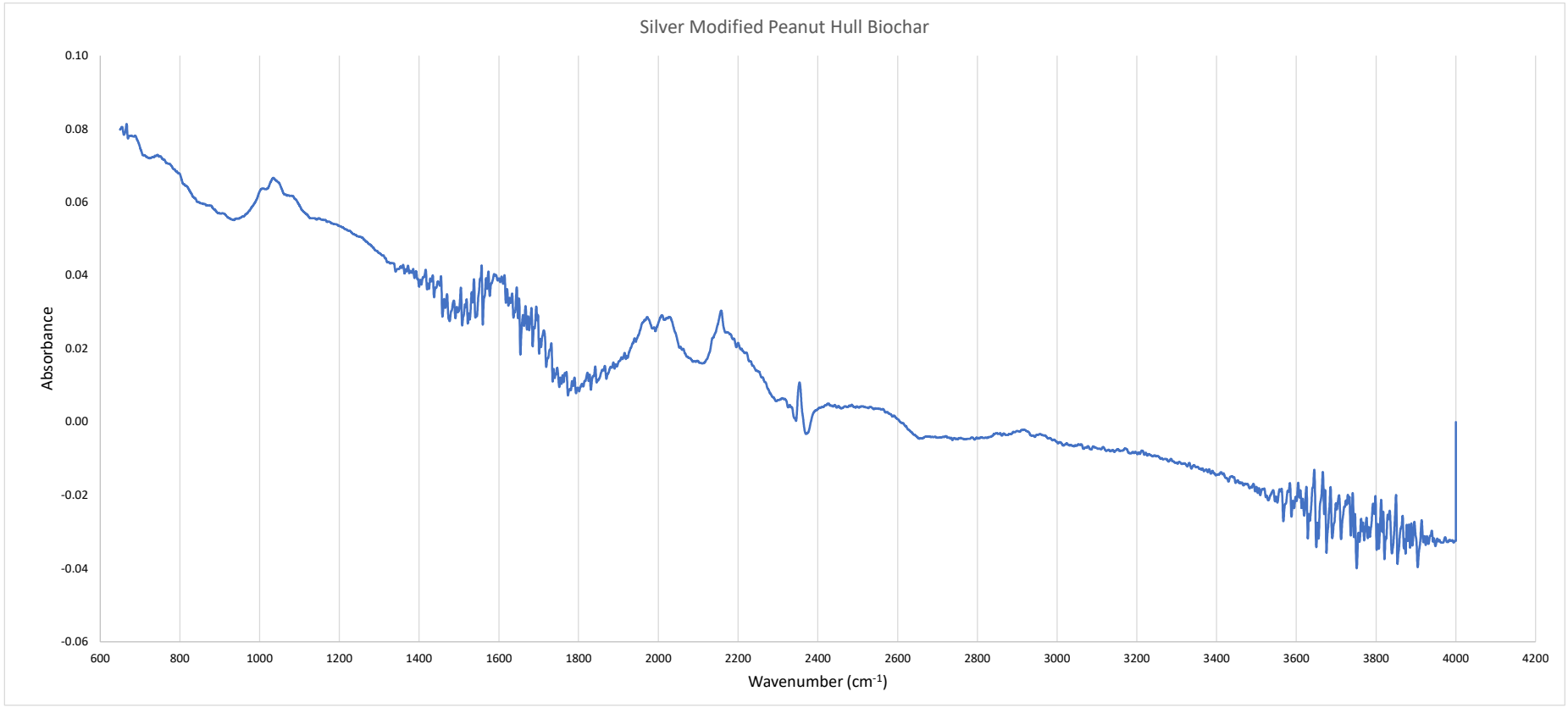
3200
3400
3600
3800
4000
4200
Wavenumber (cm-1)


Silver Modified Peanut Hull Biochar
Absorbance
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
600
800
1000
1200
1400
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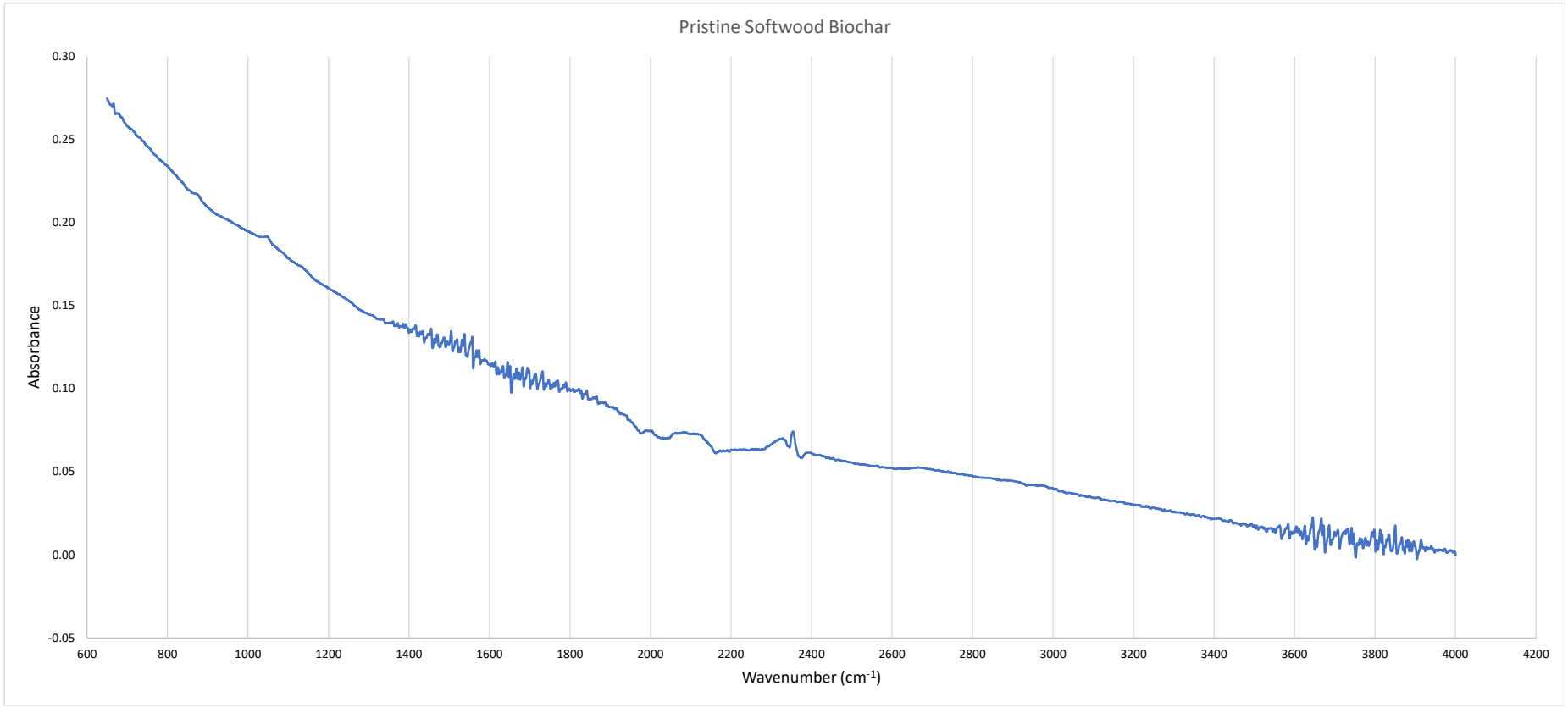
4000
4200
Wavenumber (cm-1)


Pristine Softwood Biochar
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
600
800
1000
1200
1400
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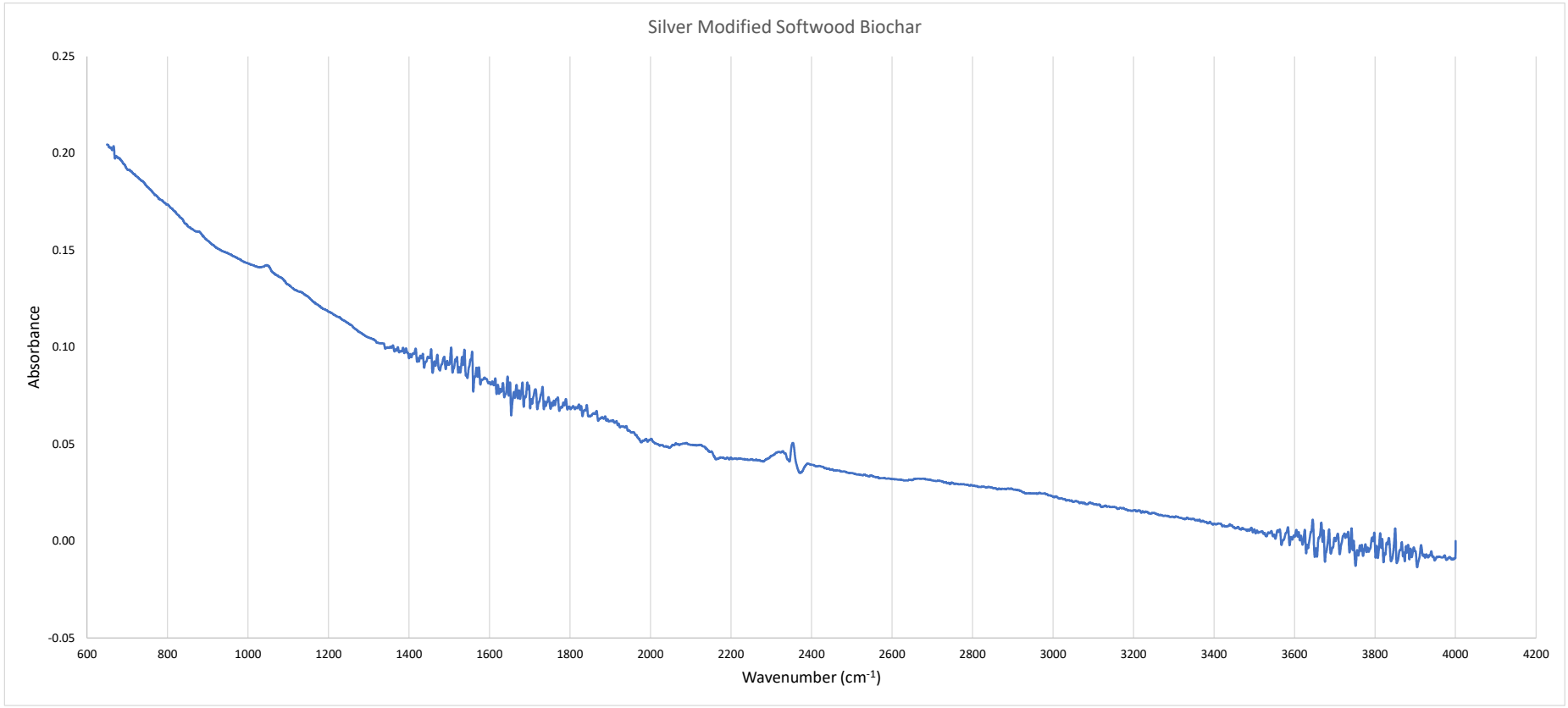
4200
Wavenumber (cm-1)


Silver Modified Softwood Biochar
Absorbance
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1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
Wavenumber (cm-1)