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Enhancement Of Retention Of Heavy Metals By Storm Water Structural Best Management Practices

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ENHANCEMENT OF RETENTION OF HEAVY METALS BY STORM WATER STRUCTURAL BEST MANAGEMENT PRACTICES

Prepared by:

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Bachelor of Science, University of North Dakota, 2016

A Thesis

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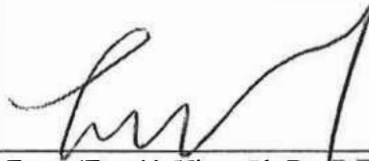
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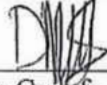
Master of Science

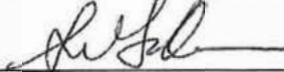Grand Forks, North Dakota

August 2019

This thesis submitted by Nicholas Reid Peterson in partial fulfillment of the requirements for the Degree of Master of Science in Civil Engineering from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Department   Civil Engineering

Degree   Master of Science

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Abstract

Batch and column experiments were performed on wide range of adsorbent materials for the adsorption of copper (II) ion from aqueous solution. The objective of this research was to determine a suitable material to be applied in urban stormwater control measures such as low impact developments that will increase the pollutant reduction efficiency of the structure, specifically increase heavy metal retention. Materials analyzed in this research are wood chips, tree leaves, rice husk, biochar, modified iron-coated sand and flocculated alum particles. Batch experiments determine the maximum adsorption capacity of each material under a range of metal and adsorbent dosages. Column experiments on the other hand are created to represent soil matrix conditions found in stormwater control measures, and to determine how much cumulative copper mass retained will be achieved before column exhaustion.

Batch adsorption experiments determined that tap flocs had the greatest copper (II) binding strength with a maximum adsorption capacity of ($q_M = 34.5$ mg/g), produced with a Langmuir isotherm model, which was followed by river flocs ($q_M = 32.16$ mg/g) > low MICS ($q_M = 16.29$ mg/g) > oxidized biochar ($q_M = 1.78$ mg/g) > biochar ($q_M = 0.41$ mg/g) > straw ($q_M = 0.31$ mg/g) > rice husk ($q_M = 0.25$ mg/g) > tree leaves ($q_M = 0.24$ mg/g) > woodchips ($q_M = 0.21$ mg/g). Whereas, column experiments indicated that modified iron-coated sand was the only adsorbent material added to a column that produced more significant retention amounts then the control alone.

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Chapter 1

1 Introduction

1.1 Problem Statement

Heavy metals have been a concern in water quality for a long-time and was one of the initial pollutants targeted for removal in the Clean Water Act. This act and its derivative regulations were successful in reducing heavy metal pollutant loading from many point-source polluters, however, was ineffective for many non-point sources like urban stormwater runoff. Urbanization has increased this problem due to more vehicles depositing heavy metals along roadways, primarily zinc, copper and lead and industrial sources, through atmospheric deposition, increasing the amount of heavy metals deposited on urban impervious surfaces. Heavy metals accumulate on impervious surfaces until sufficient rainfall mobilizes these pollutants and washes these contaminants into the stormwater sewer system where they are discharged into nearby surface water areas. This process has been referred to as the "first-flush" effect. This sudden release of heavy metals can cause a concentration spike and cause degradation of aquatic habitat downstream.

The aim of this study is to find a suitable adsorbent material that is capable of retaining heavy metals, through the process of adsorption, and could be implemented with current structural stormwater control measures such as bioretention cells to enhance heavy metal removal.

1.2 Study Focus

The focus of this research will be directed at the heavy metal copper (II) and utilize batch and column experiments to evaluate different adsorbent materials for their adsorption capacity and percent removal. Structural low impact developments (LIDs) such as bioretention cells and bioswales have been demonstrated to be effective stormwater control measures for more than a decade. Adsorbent materials capable of reducing heavy metal loadings from urban stormwater, while retaining the heavy metals through varying conditions, if incorporated into the soil media of LIDs could greatly enhance the performance of these structures.

1.3 Hypothesis

If suitable adsorbents that are capable of retaining heavy metal ions from aqueous solution are incorporated into stormwater control measures, then a reduction of heavy metal pollutant loading from urban stormwater runoff will occur downstream.

1.4 Significance of Research

The main significance of this research is for urban stormwater runoff pollutant loading reduction, especially stormwater control measures for effective stormwater management. This includes bioretention areas or rain gardens and other green infrastructure control measures. Adsorbent materials could increase the heavy metal retention of these systems and possibly make them less dependent on plant-uptake for efficient contaminant removal, which would increase removal in cold weather climates. Copper concentrations or pollutant loadings can be exceedingly high in certain urban stormwater runoffs, because of increased urbanization, altering the natural hydrology of

an area from increased impervious surface percentages, and high traffic volumes depositing copper and other heavy metals along roadway and parking lot surfaces that are then flushed into nearby waterbodies, during rainfall events, which can have negative impact on aquatic life downstream.

1.5 Research Objectives

The objective of this research is to develop a suitable sorbent material that could be used to augment current structural stormwater control measures to remove a range of stormwater contaminants such as heavy metals, nutrients and pathogens. This research focused on the removal of heavy metals or particularly copper (II) ions from aqueous solution, however it is being done in conjunction with other research focusing on the removal of nutrients or phosphates, and eventually pathogens or E. coli from urban stormwater runoff.

The primary objective of this research is to identify a suitable sorbent material with a strong adsorption capacity for copper (II) ions and favorable retention characteristics. Other important factors include determining the workability of the material and the cost associated with either the production or harvesting of the material. This is why initially many potentially recyclable biomass materials were investigated.

Chapter 2

2 Literature Review

2.1 Urbanization Stormwater Effects

Urbanization has exacerbated inherent problems mentioned above in conventional stormwater management, because the increase in impervious surfaces in an urban environment amounts to a loss of water-retaining soils and vegetation, reducing infiltration and evapotranspiration, causing radically different flow regimes of the post-development watershed (Ahieblame, L.M. et al. 2012). Roads and parking lots can be the most significant problems in stormwater management because they are usually connected impervious surfaces that have the shortest time of concentration, and experience rapid surface runoff, which combined with urban non-point sources of pollution have greatly diminished downstream aquatic habitat and water quality (NRC 2008). Some non-point sources include de-icing, fertilizer and vehicles exhaust among others. Pollutants of interest in stormwater management include nutrients, pathogens, heavy metals, hydrocarbon derivatives and other sediment related toxins (Bhaskar, A.S. et al. 2016).
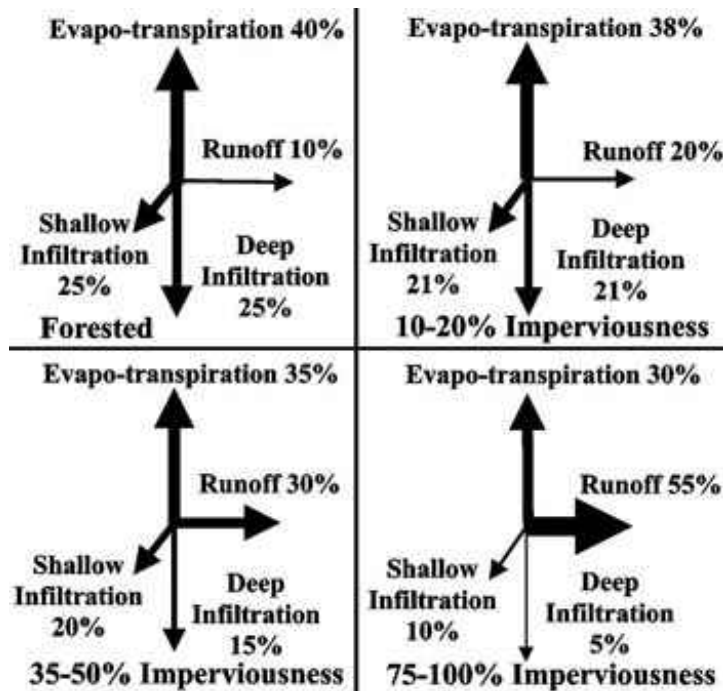
Figure 1: Hydrologic flow changes with increased impervious surfaces
(Source of image: Paul MJ & Meyer JL. 2001)

2.2 Stormwater Regulations

The Clean water Act was enacted in 1987 in the United States to address the rapidly degrading in-stream water quality of many of the nation's water bodies, because of intensive industry activities, wastewater treatment facilities, urbanization and other factors. Initially Congress passed Sec 402 (p), which formed the national pollution discharge elimination system (NPDES), which was the primary federal program to regulate the nations waterbodies, and targeted at reducing pollutant discharge from primarily point-source polluters, because volume discharges and pollutant loading were more readily defined and discernable for these sources, compared to the more elusive non-point sources. This legislation unfolded in two distinct phases (NRC 2008).

Phase I was codified in 1990 and required municipal separate storm and sewer systems (MS4's) in cities with populations greater than 100,000, and also required permitting requirements for any impactors with a defined conveyance or pipe that

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discharged into nearby waterbodies. This included major industries and wastewater

treatment plants, serving a population larger than 100,000 capita. In many ways, phase I

regulations dramatically reduced pollutant loadings into the environment. Most of the

known toxic heavy metals like arsenic and lead were eliminated from wastewater

effluents. However, this regulation failed to address the growing concern of non-point

source polluters (Reese 2009).

Phase II was developed in 1999 to begin regulations for non-point sources such as

agricultural runoff, septic tank leakage, combined sewer overflow, and stormwater runoff

(Tillet 2016). It widened the scope of MS4's permittees or local communities that were

required to develop stormwater control measures (SCM) to combat the negative impacts

or stressors of stormwater discharge on the environment such as erosion from increased

water flow and velocity due to urbanization increasing the percent impervious surfaces in

many urban environment, and the transportation or entrainment of contaminants

deposited on those impervious surfaces from de-icing, fertilizers and vehicle exhaust into

nearby rivers, lakes and estuaries, which potentially could be harmful to aquatic life

(NRC 2008) . Stormwater control measures were developed largely on a state-wide

policy and comprised of a "one-size-fit-all" application. These measures have come to be

known informally as best-management-practices (BMP's) and utilized either structural

methods like retention/detention basins, or non-structural methods, depending on the

local stormwater conditions, and climatic expectations.

2.3 Stormwater Control Measures (SCM)

Early urban stormwater management practices and control measures that emerged

after the conclusion of WWII centered around the principle of efficient drainage or

conveying stormwater runoff as quickly as possible away from urban areas to prevent

flooding of roadways and infrastructure, through curb and pipe conveyance. It was a

"damage avoidance" management program that unfortunately had unanticipated

consequences of increasing storm peak flow downstream, caused by altering the natural

hydrologic cycle. These adverse effects included increased flow volume and velocity,

reduced infiltration, and thereby increased pollutant loading and channel erosion, causing

aquatic habitat degradation downstream (Bhaskar, A.S. et al. 2016). It wasn't until

around the 1970s that focus on centralized stormwater management ponds and detention

basins became in vogue, and were implemented to reduce the downstream peak

stormflow by retaining stormwater for an extended period of time, thereby extending the

lag time of the peak flow, and allowing for the settling of saturated sediments, improving

water quality discharging into nearby receiving waterbodies (Dietz 2007). This approach

has generally been termed conventional development control measures, and colloquially

as "end-of-pipe" practices or conventional pass-through treatment.
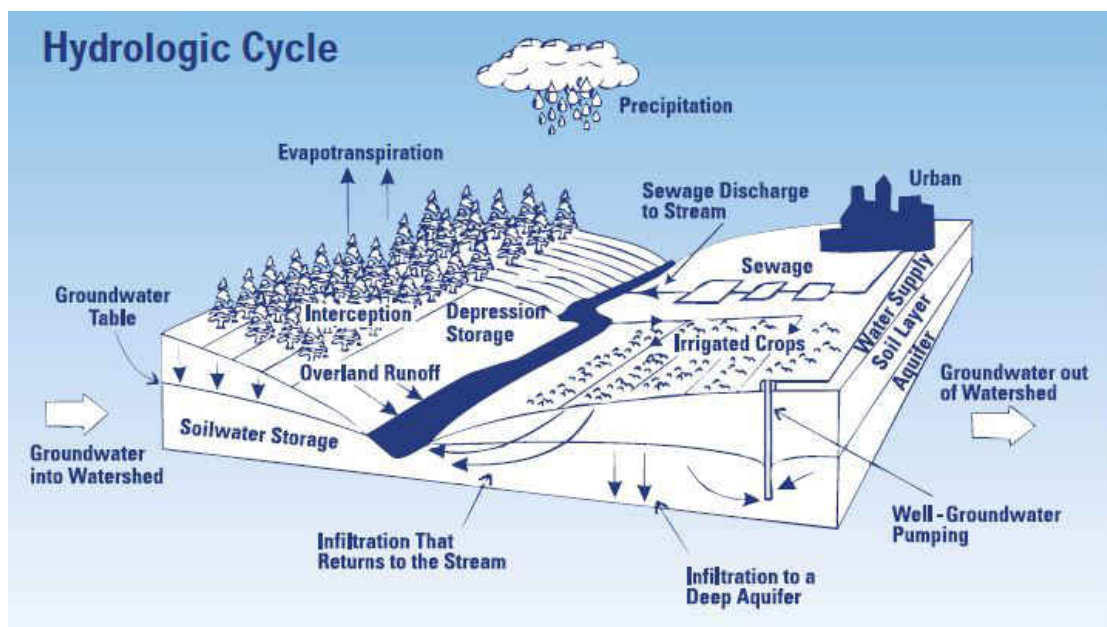
Figure 2: Hydrologic Cycle. (Source of image: M.L. Davis and Cornwell, D.A. Introduction to Environmental Engineering 1991)

In stormwater management as the rain continues or storm size increases management priorities shift between five levels 1.) infiltration, 2.) pollution reduction, 3.) erosion reduction, 4.) flood reduction, 5.) floodplain management. Each phase is associated with a general storm event. For instance, levels 1-3 are grouped for small storm events or 1 year – 2 hour storms on the IDF curve. Infiltration serves as groundwater recharge and reuses, because it extends the baseflow recession curve, and is important for water conservation during dry inter-storm intervals (Reese 2009). After rainfall exceeds a certain threshold soil becomes sufficiently saturated to allow for pooling and surface runoff, which mobilizes any settled contaminants into the stormflow. This process has been termed the "first-flush" effect and is a major source of pollutant loading from stormwater to nearby water bodies, because small storms (< 27mm) account for a significant proportion of the annual stormwater volume (Dietz 2007). These small storms have been difficult to manage for reduction of pollutant loading through conventional treatments. Erosion reduction is caused by excessive stormwater flow velocity, which is directly related to stormflow volume, and happens when the shear force of the bank or bed is surpassed. Streambank erosion is a certainty; however, the time for channel erosion and course change to occur differs. Flood reduction and floodplain management are considered usually for 2 year- 24 hour and 100 year-24 hour storm return periods and could be called severe flood scenarios Erosion reduction can be accomplished with conventional extended detention in stormwater management facilities for upwards of 12-24 hours (Reese 2009).

The common thread for levels 1-3 or infiltration, pollution reduction, and erosion reduction is stormflow volume. If the surface runoff volume is reduced, then adverse consequences that have been attributed to post-development hydrology and have not been solved completely with conventional stormwater management are reduced. The last levels fall in a different scope from this research but can be properly managed with conventional techniques, accurate stormwater management master plans and best management practices (NRC 2008).

Low-impact design (LID) practices are capable of reducing stormwater volume through increased infiltration or groundwater recharge, stream bank protection and water quality enhancement. This approach focuses on green designs that encourage a return to pre-development hydrology or that can mimic natural hydrology as much as possible (Dietz 2007). LID practices include reducing impervious surfaces, increasing the time of concentration, reducing soil compaction and erosion during urbanization, public education and infrastructure-based stormwater facilities. Structural LID control measures encompass a wide range of treatment systems from infiltration based designs such as bioretention cells (BRC) or rain gardens, porous pavements, bioswales, green roofs, etc. and reuse systems such as rain barrels. These systems either promote infiltration, detention or evapotranspiration of stormwater or more likely a combination of these processes (Bhaskar, A.S. et al. 2016). This is achieved with treatment at the source through changes of the soil regime and vegetation type to mimic pre-development hydrology. There is good evidence to suggest that LID control measures can treat the "first-flush" small storms that cause significant pollutant loading to nearby waterbodies annually. Cold weather effects on the efficiency of BMPs in Grand Forks, ND was

investigated and found that nutrient removal was high, however other contaminant removals such as heavy metals was not significant. This is important because stormwater control measures may not have the same performance efficiency and use in different climatic and soil conditions (Lim, Y.H et al. 2016). Three main LIDs may have application with this research 1). bioretention cells, 2.) bioswales and 3.) green roofs.
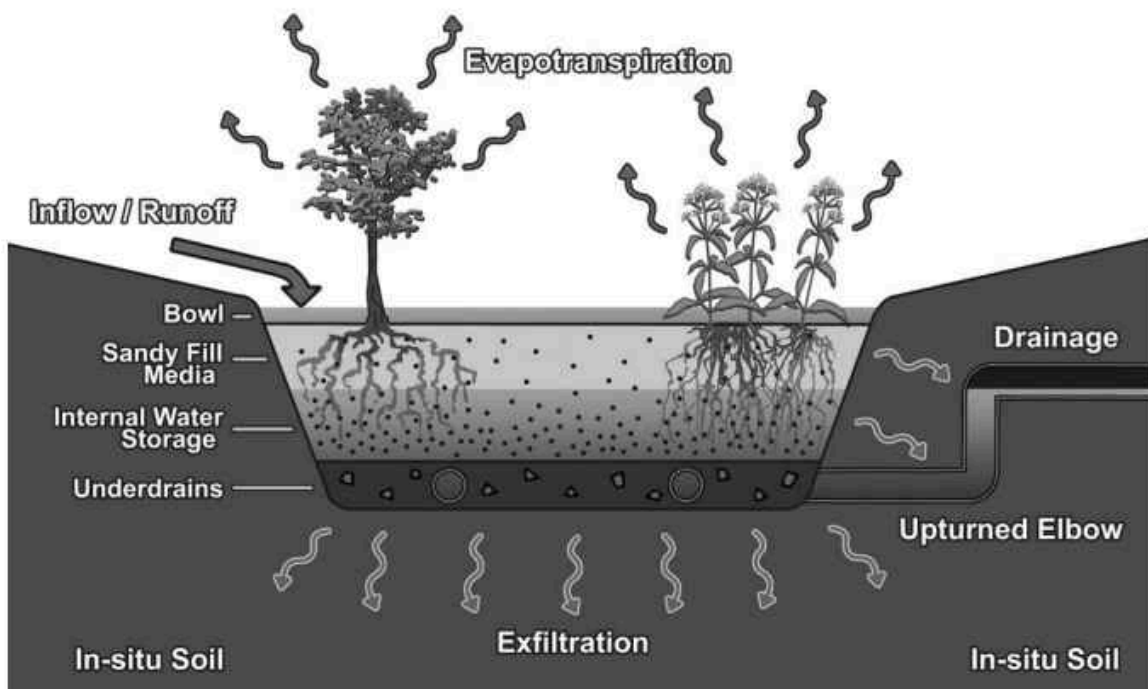
Figure 3: Bioretention cell (Source of image: Shawn Kennedy, NCSU)

Figure 4: Bioswale (Source of image: Michigan Water Council)
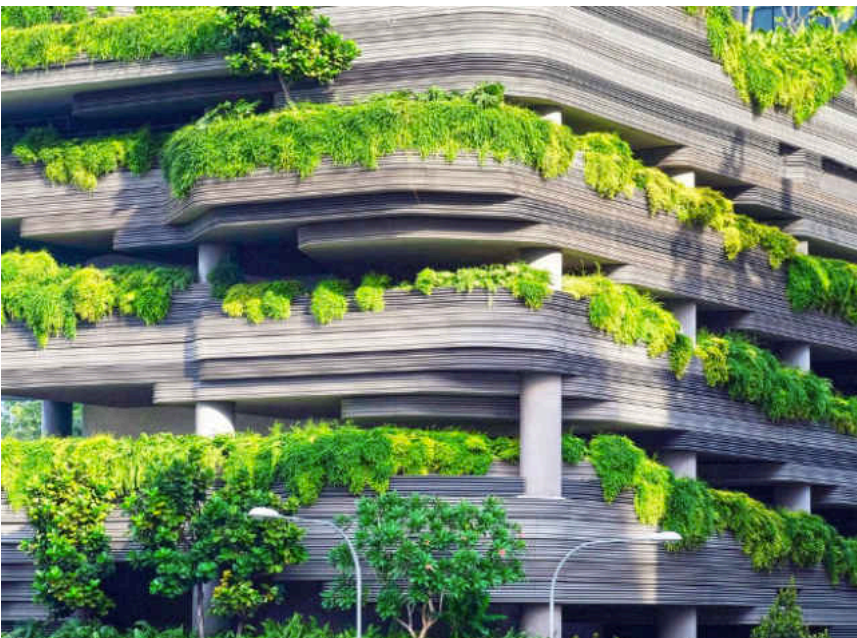
Figure 5: Green roof (Source of imaget: Jasmine O'Donoghue, Architecture & Design)

2.4 Toxicity

      Copper is an essential micronutrient to living systems, however, like anything, can be harmful in too high of a dosage. Copper-toxic effects on human beings include reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, and diarrhea (Farooq et al. 2010). However, more concerns with stormwater runoff and copper toxicity involve adverse impacts to aquatic ecosystems when tolerance levels are exceeded. In general, free copper ion species has the highest toxicity to aquatic organisms. Observations have been made that copper toxicity greatly decreases in harder water, which could be explained by complex formation between copper species and alkalinity, because a general rule is as hardness increases alkalinity in turn increases (Snoeyink and Jenkins 1980). This has to do with the bioavailability of copper. Copper is most effectively complexed by carbonate minerals and iron-manganese oxide minerals, and tend to become coated to sediments, and therefore have relatively lower mobility than other heavy metals. Excess chlorine concentrations decrease copper adsorption on sediments, because of competing ions for chelation, which increase copper solubility and mobility (John and Leventhal 2004).
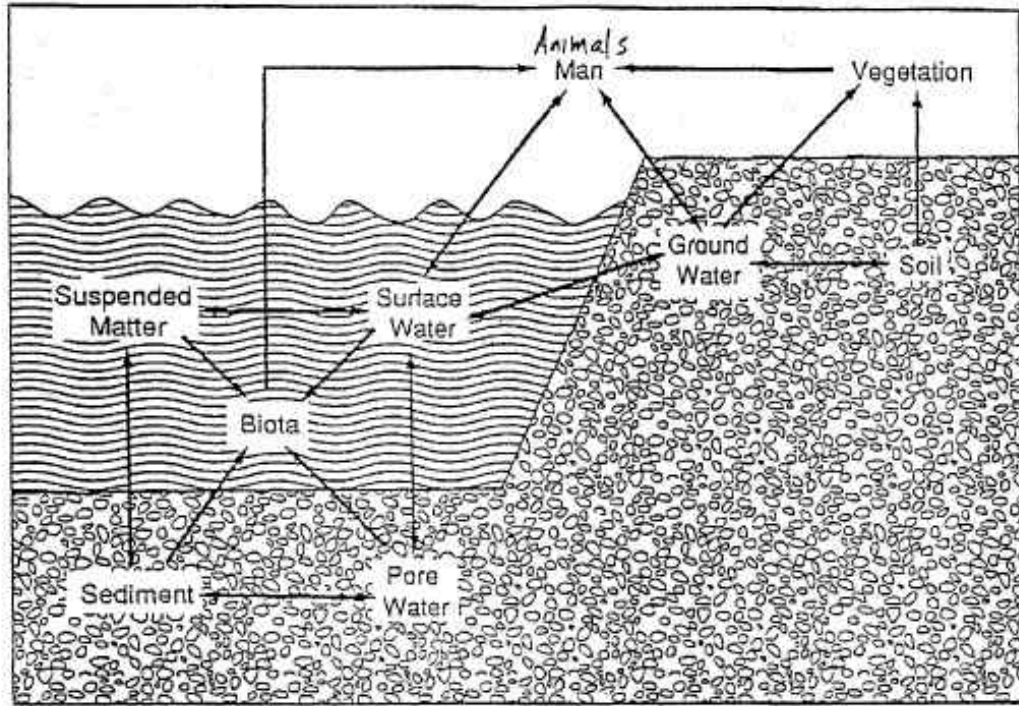
Figure 6: Man, metal and environment relationship (Source of image: Salomons and

Forstner 1988)

2.5 Types of Adsorbents

There are many different types of potential adsorbents that have been effective at removing heavy metals and include clay minerals, activated carbon, carbon nanotubes, biosorbents, metal oxides, zeolites and other.

Activated Carbon

Activated carbon has high porosity and high specific surface area and is made from readily available carbon sources such as coal, wood and agricultural waste products (Zhao, G. et al. 2011). The microporosity of activated carbon creates a surface area above 3000 m^2 per gram. It has many applications in water treatment and is capable of

removing trace heavy metals from solution. It is a relatively low-cost material and has a high metal-sorption potential.

Carbon Nanotubes

Recently carbon nanotubes (CNTs) have acquired much interest, because of CNTs enhanced surface sorption properties that are effective in removing different heavy metal ions in solution (Zhao, G. et al. 2011). Members of the fullerene family, that are allotropic or composed of cylindrical graphene sheets that are rolled into a tube. CNTs have been shown to possess high adsorption capacities for heavy metals in laboratory batch experiments that exceed traditional adsorbent materials. This has been associated with the material's high porosity, light mass density and hallow structure, and the enhanced surface properties which create strong interactive forces between heavy metals and CNTs. However, the lack of large-scale application studies and the high cost of the material have limited the growth and application of CNTs in water treatment and heavy metal removal. (Ihsanullah et al. 2016)

Biosorbents

This collection of sorbents has gained a lot of attention in recent years, and the category is wide and varied because it contains any sorbent material that contains biomass, which is any plant or animal matter, usually grown or derived from energy from the sun. The main distinction in biosorbents is whether dead biomass or living biomass is being used. The difference between these two occurs in available biosorption mechanisms, mainly that living biomass still has cell metabolism (Veglio and Beolchini

1997). However, it has been determined that dead cells accumulate an equal or greater amount of heavy metals than living cells in adsorption processes and that toxicity problems and nutrient requirements are eliminated with dead biomass application (Bailey, S.E. et al. 1999). Therefore, only dead biosorbents will be considered in this research.

Dead biomass can be aquatic or terrestrial in origin. Examples of aquatic biomass that have been extensively researched include chitosan, which is a crustacean from seafood processing, and seaweed. Terrestrial biosorbents are generally derived from plant-based agricultural waste materials that are rich in lignin, cellulose and tannin content. Advantages of these biosorbents include low-cost, high-efficiency, minimized sludge production, regeneration or sorbent, no additional nutrients required and the possibility of metal recovery (Zhao, G. et al. 2011). Many functional groups important in the metal binding process are found in the molecules of biomass, which are strong chelates and have a high affinity for metal complexion (Sud and Kaur 2008). Some active functional groups include acetamido groups, carbonyl, phenolic, polysaccharides, amido, amino, sulphydryl carboxyl groups alcohols, and esters. The active functional groups present depend on the type of biomass, and what components are present (e.g. lipids, proteins, sugars, starches, etc.). For example, bark-based biosorbents are tannin-rich materials, and polyhydroxy polyphenol groups have been shown to be the active species in the adsorption process. Whereas lignin-based biosorbents that form the structural component of plants have polyhydric phenols and other functional groups that are active (Bailey, S.E. et al. 1999). This demonstrates the immense variability in biosorbents, and the mechanisms of adsorption that are critical.

Metal Oxides / Clay Minerals / Zeolites

The natural weathering of primary minerals produces many secondary hydrous oxide minerals, which include Fe-oxides, Mn-oxides, that have functioned as important adsorbents in natural waters and soils. Other examples include TiO_2, γ-AlOOH and γ-Al_2O_3 etc. (Zhao, G. et al. 2011). Oxide minerals can act as a heavy metal sink in groundwater, and after conditions change, be a constant source of heavy metals to surrounding solution. Primary sorption mechanisms are ion exchange and are strongly pH dependent (Smith, K.S. 1999).

Clay minerals have long been known to possess strong heavy metal adsorption behavior, and are also natural weathering products of primary minerals, producing aluminosilicates which are composed of mixtures of fine-grained clay minerals, crystals of other minerals and metal oxides. Clay complexes have a porous structure and high specific surface area and produce strong physiochemical interactions between dissolved species (Uddin, M.K. 2017). Since clays are found with natural coatings of metal oxides and organics in natural systems, it has been difficult to assess the actual contribution the clay-sized minerals have in the metal sorption process (Smith, K.S. 1999).

Hydrated aluminosilicates referred to as zeolites are highly porous naturally occurring minerals that have been used as adsorbents. Zeolites possess a unique framework that is a three dimensional with a negatively charged lattice structure, that gives it a strong ion-exchange capacity and specific surface area important in metal-sorption processes (Zhao, G. et al. 2011). Zeolites occur naturally but are also manufactured industrially on a large scale.

Edwards and Benjamin in 1989 studied iron hydroxide coated sand as an adsorbent filter media in treating heavy metal bearing wastes. This method entailed modifying sand media by applying a ferrihydrite coating, through precipitation reactions between ferric nitrate and a strong concentrated base (Edwards and Benjamin 1989).

Other

There is a variety of other materials that have been demonstrated to have success in the sorption of heavy metal ions from solution. Any materials with high surface area, active functional groups, high sorption ability, easy separation from aqueous solution, low price and negligible environmental impacts may be attractive as an adsorbent in heavy metal ion removal from solution (Zhao, G. et al. 2011).

2.5 Kinetics

Kinetics is essential in heavy metal adsorption because most sorption mechanisms require a certain amount of contact time before equilibrium is established. However, in most natural systems equilibrium is rarely obtained, so the reaction rate controls the extent of the reaction because there is insufficient contact time for many sorption mechanisms (Snoeyink and Jenkins 1980). Most heavy metal sorption reactions proceed rapidly initially then significantly decrease in later stages until equilibrium is achieved. Kinetic models that have been suggested in heavy metal adsorption include first-order and second-order (irreversible), first-order and second-order (reversible) and pseudo-first-order and pseudo-second-order models (Ho 2006). These reactions are generally reversible for non-metabolism dependent sorption mechanisms, and different

mechanisms can become dominant under different solution conditions (Veglio and Beolchini 1997).

2.6 Thermodynamics

Thermodynamic parameters such as Gibb's free energy (G), entropy (S) and enthalpy (H) are estimated by equilibrium constants that change with solution conditions such as temperature and pressure. The equation for Gibb's free energy (G) given by thermodynamic principles is,

$$G = H - ST$$

Where T is temperature and R is the universal gas constant. Entropy (S) is the degree of disorder or randomness in a system, and enthalpy (H) is the total energy content of an element or compound (Snoeyink and Jenkins 1980).

However, if the reaction is conducted in constant temperature, then the expression becomes,

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

This equation determines whether the reaction is spontaneous or non-spontaneous. Essentially if Gibbs free energy is negative ($\Delta G < 1$), then the reaction will proceed spontaneously, and oppositely if ($\Delta G > 1$), then the reaction cannot proceed spontaneously. This is important because it specifies whether or not a reaction requires external energy to proceed (i.e. non-spontaneous), or if the reaction will occur without any external assistance (i.e. spontaneous). Prior research has indicated that most heavy metal adsorption is spontaneous, and the degree of spontaneity increases with temperature (Uslu and Tanyol 2006).

On another note, most copper sorption mechanisms have been observed to be endothermic in nature, which means that heat is taken up, compared to exothermic reactions that release heat. This implies that the amount of copper adsorption is directly proportional to temperature (Zhao, G. et al. 2011). Entropy (S) will generally increase after adsorption because there is more order for heavy metal ions near the surface of the adsorbate then after the heavy metals are adsorbed onto the surface. This increase in randomness due to adsorption is caused by an increase of rotational and translational energy among molecules. Therefore, heavy metal adsorption will likely be spontaneous at and above room temperatures (Argun et al. 2007).

2.7 Sorption Mechanisms

Metal ions that are removed from solution by sorption processes can be classified as either extracellular accumulation/precipitation, which is sorption taking place near the sorbent surface, and surface sorption/precipitation, which understandably is happening on the surface of the sorbent. For living biomass biosorbents there can also be metabolism dependent intracellular accumulation, but that will not be explored any further in this study. Physiochemical interactions between the heavy metal ions and the active functional groups on the surface are the primary mechanisms in these non-metabolism dependent metal-sorption processes and can account for physical adsorption, ion-exchange and complexion interactions (Ngah et al. 2011).

The formation of surface charge is responsible for most of the sorption mechanisms, because any solid surface acquires a charge in an aqueous environment, which forms an electric potential at the solid-solution phase also called an electrical

double-layer (Smith, K.S. 1999). There are three principle formations of surface electrical charge 1.) chemical reactions at the surface, 2.) the crystalline imperfection and 3.) active surface groups (Stumm and Morgan 1995). There is a variable surface electric charge, which is dependent on the constituents of the surrounding aqueous solution, and constant surface electric charge which is independent of the surrounding aqueous solution. Variable charge is usually produced because many surface groups located on organic matter and hydrous metal oxides are ionizable. Whereas constant surface charge is attributable to clay minerals, which have structural lattice imperfections that produce a net-negative charge potential (Smith, K.S. 1999). Many parameters will influence what mechanisms are active and dominant and can occur simultaneously (Veglio and Beolchini 1997).
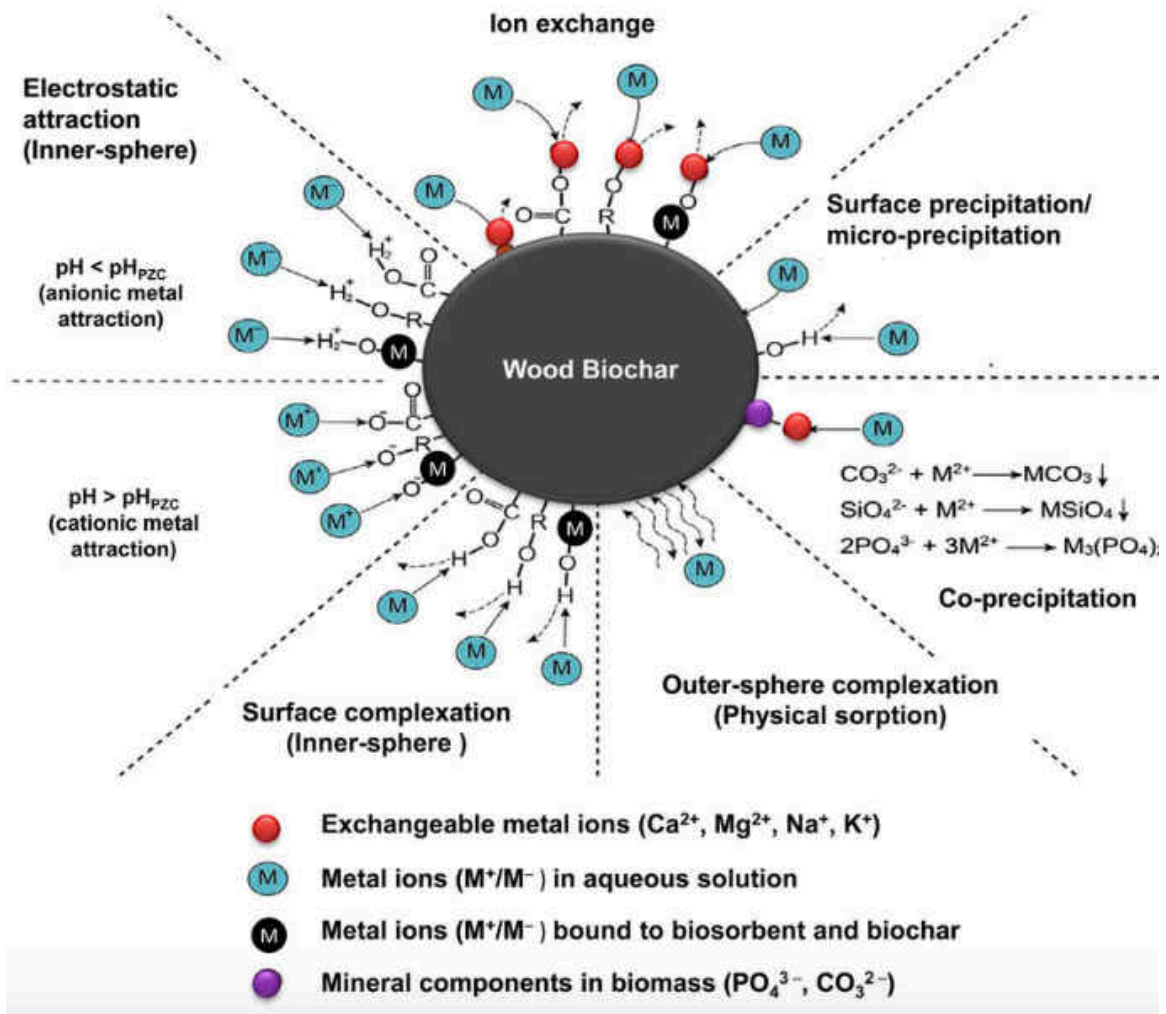
Figure 7: Biosorption mechanisms for wood biochar (Source of image: Nabeel Khan Niazi, University of Agriculture Faisalabad)

Physical adsorption (electrostatic)

This group of interaction phenomena is electrostatic in nature and depend on van der Waals' forces, and the associated intermolecular forces between molecular charged ions, dipoles and hydrogen atoms. These interactions account for behavior between ions in solution encountering a charged solid surface. (Veglio and Beolchini 1997) Many adsorbents have charged solid surfaces, for instance, metal oxides, clay minerals, etc. however, there are also many biosorbents that can become charged under varying solution conditions. For example, in chitosan adsorption of heavy metals, it was

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suggested that electrostatic interactions may be responsible for part of sorption process and was caused by the protonation of amine groups at low pH, which at high pH hydroxyl competition would reduce these electrostatic interactions. (Ngah et al. 2011). Electrostatic interactions have also been suggested to be the dominant adsorption mechanism for a range of biosorbents.

Ion-exchange (cationic metal exchange)

In heavy metal ion removal from solution by an adsorbent, this mechanism can also be referred to as cationic metal exchange because it is only considering cations in solution. This process involves the exchange of metal ions with counter ions on the active surface groups of the sorbent material.

Complexion

This is the removal of a metal ion from solution by the complex coordination on the sorbent surface after interaction between the metal ion and active functional groups. Lewis acid-base system can generally explain the relationship between the functional groups or ligands and the metal species. The functional groups generally being the Lewis base or electron donor, and the metal species being the Lewis acid, or an electron acceptor. Functional groups can be either neutral, positively or negatively charged, and include ligands containing sulfur, phosphorus, nitrogen, and oxygen electron donors (Snoeyink and Jenkins 1980). Biosorbents active functional groups usually include acetamido groups, carbonyl, phenolic, polysaccharides, amido, amino, sulphydryl carboxyl groups alcohols and esters (Bailey, S.E. et al. 1999). Rate of chelate formation

can either be labile (very fast) or inert (very slow), however, this does not indicate

complex stability. Although, as the number of attachment points between the ligand and

metal ion increases, complex stability generally increases and is called the chelate effect.

Competition between ligands and metal ions can occur, and generally the chelate with the

greatest stability is favored. Similarly, competition between cations or heavy metal ions

can also occur for coordination sites (Snoeyink and Jenkins 1980). The complexion of

metals by dissolved ligands can either enhance or inhibit sorption reactions (Davis and

Leckie 1978).

Precipitation

Sometimes referred to as dissolution-precipitation reactions generally occur in

three phases 1.) nucleation, 2.) crystal growth and 3.) agglomeration. The degree of

supersaturation required determines when precipitation of the solid will occur. Chemical

interactions between the metal and sorbent surface may cause precipitation of a solid.

Complex formation can increase the solubilization of heavy metals, depending on

whether the complex is soluble or insoluble (Snoeyink and Jenkins 1980). The difference

between ion exchange or complexion adsorption mechanism to precipitation is that a

single monolayer is created at the solid-solution interphase during adsorption, whereas a

three-dimensional lattice structure is created during solid formation on the surface. Some

researchers have argued that some sorption phenomena on biomass have been suggested

to be caused by ion exchange mechanisms. However, biosorbent precipitation may occur

if there is an accumulation of metals within the diffuse parts of the electrical double-

layer. (Schneider et al. 2001)

<u>2.8 Sorption Factors</u>

There are many important factors in physiochemical sorption such as pH, contact time, adsorbent dosage and initial metal concentration. Other factors that will not be addressed are particle size, ligand complex, temperature etc.

pH

pH is a significant variable in adsorption processes because it characterizes the species of the adsorbate, and charge of the solution. Most adsorption mechanisms are related to charge (i.e. complexion and cation exchange). The pH of the solution can alter the surface charge of active functional groups, and in effect increase or decrease the adsorption capacity. Previously reported results for biosorption have indicated high sorption of copper (II) ions for a pH between 5 and 7 (Grimm et al. 2008). Figure 8 demonstrates a maximum copper (II) ion adsorption around pH = 5.8. It also was mentioned that the pH was kept low to eliminate any precipitation that would impact the results. This research was interested in biosorption of copper on treated sawdust (Meena, A.K. 2008).
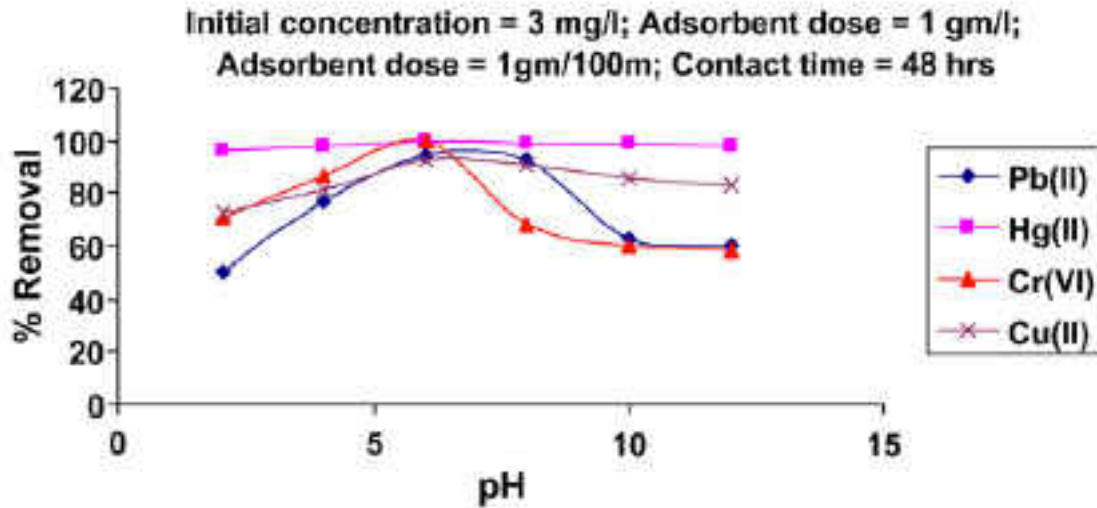
Figure 8: Effect of pH on copper biosorption. (Source of image: A.K. Meena et. al 2008)

It should be mentioned that this is probably not the optimal pH in all cases. Prior observation has indicated that this is the most optimal pH range for the adsorption of copper (II) ions. Most natural waters fluctuate within pH range between 6.5 – 8.5, which is low to moderately alkaline. These to some degree alkaline conditions commonly found in natural waters change the copper speciation in solution. In Figure 9 the copper speciation in natural waters with inorganic carbon present is given. Free copper (II) ion is only a dominant species in a solution with pH < 6.5. Otherwise at greater pH values, copper begins forming complexes, in this case with inorganic carbon (Snoeyink and Jenkins 1980). Copper is known to form stable complexes with organic matter in natural waters (Blecken et al. 2011).
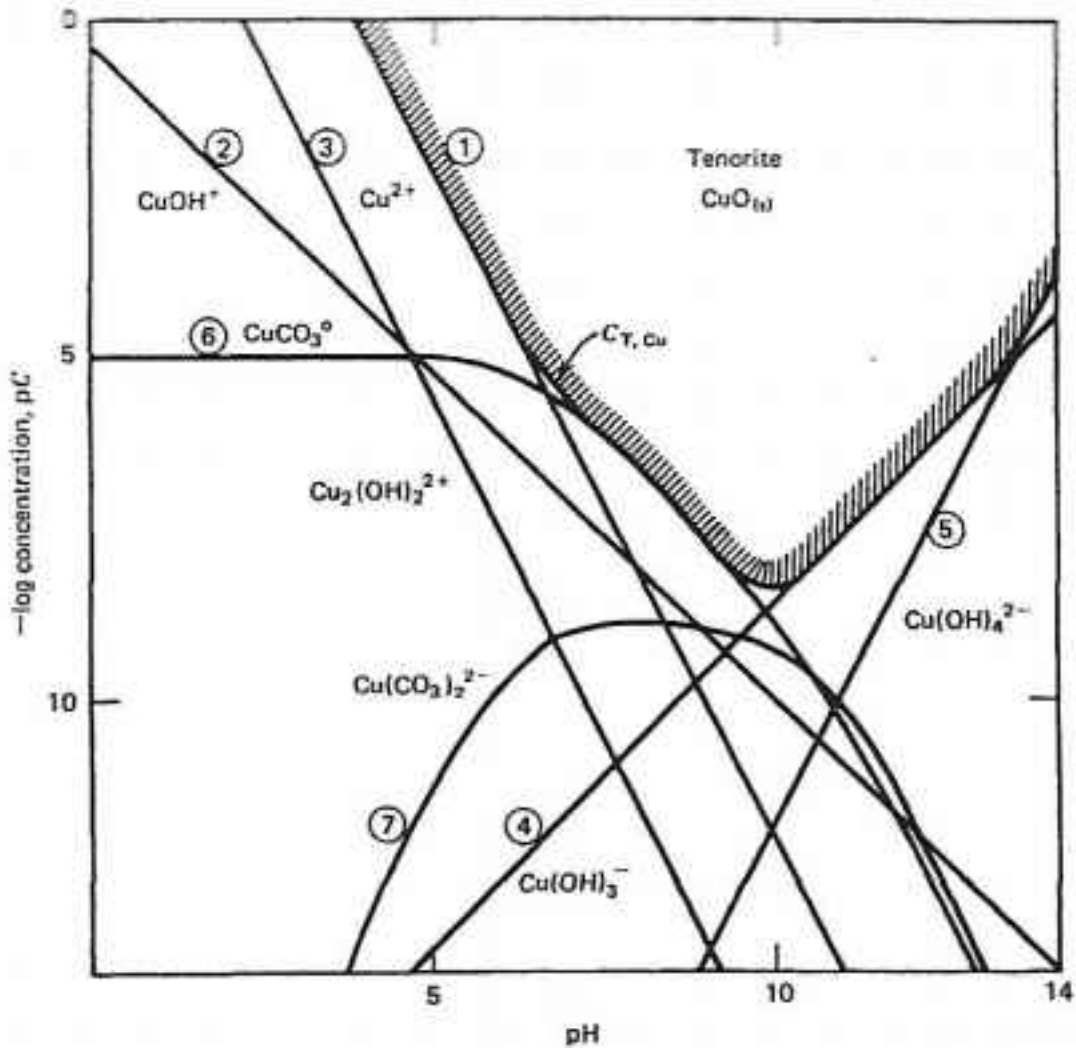
Figure 9: Copper speciation in natural waters with inorganic carbon (Source of image: Snoeyink and Jenkins 1980)

Contact time

Contact time is another important factor in metal adsorption because equilibrium is rarely obtained in natural waters. Therefore, rate or kinetics is paramount, and the time of contact dictates the extent of the reaction (Snoeyink and Jenkins 1980). It has been observed that many copper biosorption reactions are pseudo-second-order models. This

means there is initially a rapid adsorption phase followed by a gradual adsorption phase that extends until equilibrium is reached (Grimm et. al 2008). This is shown in Figure 10 where adsorption of copper (II) rapidly increases for contact times less then 1 hour then gradually decreases. It has been reported that contact times between 42-72 hours are optimal for most biosorption reactions. This estimation could change for other adsorbents, depending on the rate of reactions.
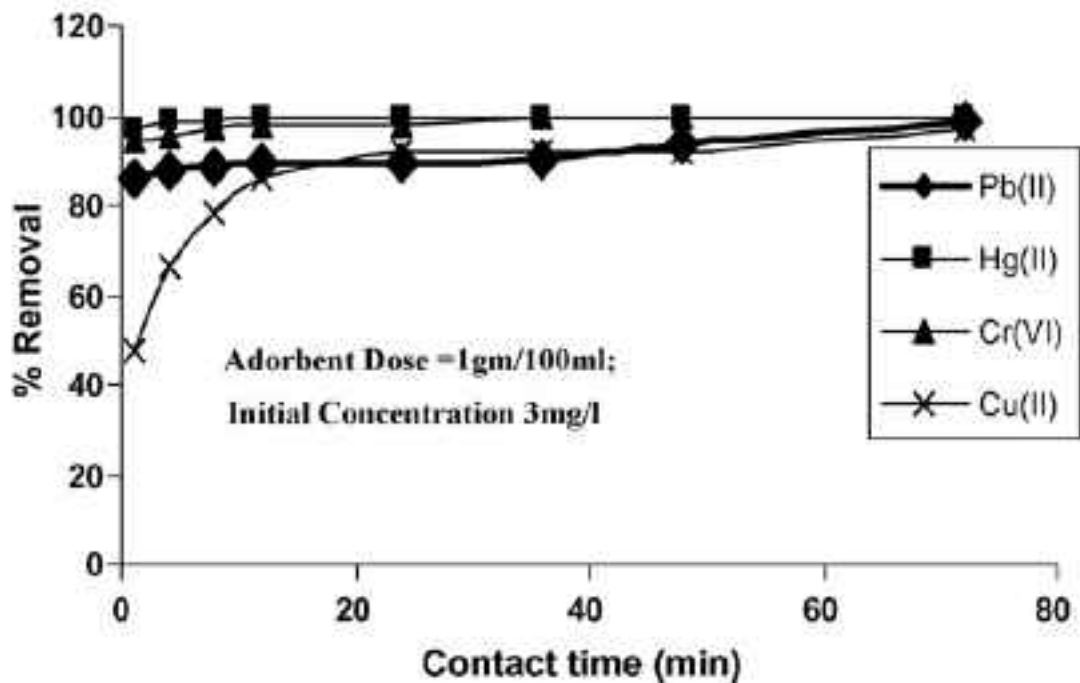
Figure 10: Effect of contact time on biosorption (Source of image: A.K. Meene et al (2008))

Adsorbent Dosage and Initial Metal Concentration

These factors are inherently related and generally in adsorption are directly proportional to the percentage removal of heavy metals. For instance, as adsorbent dosage or the mass of adsorbent increases the percentage removal of the heavy metal

increases. This can be attributed to the increase in surface area and active adsorption sites present (Meena, A.K. 2008). Similarly, yet in a different direction, as initial metal concentration increases percentage removal decreases. This is due to there being insufficient adsorption sites with the increase in metal concentration, and the adsorbent becomes exhausted (Grimm et al. 2008). This relationship becomes important in generating isotherms with high ranges of equilibrium concentrations. As the initial metal concentration increases the adsorbent dosage must increase, and vice-versa.

Chapter 3

3 Methodology

3.1 Materials

Adsorbent

     Inorganic and organic adsorbents were used in this study. Organic adsorbents sometimes referred to as biomass, that were used are tree leaves, woodchips, wheat straw, wheat husk, rice husk, and biochar. Inorganic adsorbents used were alum flocs and modified iron-coated sand (MICS). It should also be noted that humic acid and fluvic acid standards sourced from the Suwannee River were also briefly used in this research.

Collection and Sampling

     Some biomass samples were collected from natural areas located on the University of North Dakota Campus, these materials were tree leaves and woodchips. Tree leaves were collected in the Fall from a cottonwood tree (*Populus deltoides*) and woodchips were collected from a recently cut down white poplar tree (*Populus alba*). Biomass that was ordered from internet retailers included wheat straw and rice husk, while wheat husk was obtained from the North Dakota Mill, which is a local mill in Grand Forks, ND.

Adsorbent Treatment

Any biomass that was collected from natural sources such as wood chips, tree leaves, required treatment before use in any experiments because the material was unsanitary. Wood chips and tree leaves were initially rinsed with a dilute 0.1M HCl solution for a period of time. Afterwards, the biomass was placed in individual 2L beakers and immersed with hot water to remove the lignin content, especially from the tree leaves. It was observed that a dark green solution, similar to that produced by the steeping of green tea was produced from the treatment of tree leaves, and more of a yellow solution was produced from the treatment of wood chips. After several cycles of rinsing the runoff became clear and the biomass was ready to be dried at 70° C.

Adsorbent Preparation

Modified iron-coated sand (MICS) was produced in the lab. The sand used was laboratory grade Ottawa 20-30 mesh with nearly spherical grains. Ferrihydrate coating was applied to the sand through a redox reaction between ferric chloride and sodium hydroxide solutions. The reaction equation is as follows,

$$FeCl_3 + 3NaOH \xrightarrow{yields} Fe(OH)_3 + 3NaCl$$
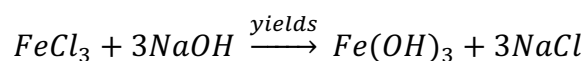
This product yields a 1:3 ratio, or for one mole ferric chloride hexahydrate, there must 3 moles of NaOH strong-base for the reaction to completely proceed to the right and form all products.

This method was adapted from prior work done by Marc Edwards and Mark Benjamin in 1989. For the low-MICS sand (0.0001 mol/g), which implies that there are

10^{-5} moles of Fe^{3+} ion per gram of sand, 10 ml of 0.5 M FeCl3 solution was added to 50 grams of sand and 150 ml deionized water. Then gradually 30 ml of 0.5 NaOH solution was added, which caused the iron to precipitate, and a portion of the precipitate attached to the sand. Then the solution was dried at 110° C and periodically stirred for 36 hrs. The sand was rinsed and drained with water until runoff was clear, then the sand was dried once more at 110° C for 24 hrs. The sand was then sieved using a no. 8 sieve, which removed any debris or any excess precipitate from the sand. Only a single coating was applied to the sand. In order to produce the high-MICS sand (0.0005 mol/g), 50ml of 0.5M $FeCl_3$ solution was added to 50 grams of sand, and 750 ml deionized water, and then gradually 150 ml of 0.5 NaOH solution was added, in essence all solution volumes were multiplied by 5, whereas everything else remained the same, in particular, the amount of sand.

Aluminum flocs or wastewater treatment residuals were produced in the lab, using a 6-paddler jar tester. Two liters of Red River water is placed into each beaker, and then 15 ml of 10 g/L alum sulfate solution would be added to each beaker, which was then rapidly mixed at 140 rpm for 1 min, and then gradually mixed at 40 rpm for 10 min. To obtain the alum flocs, the solution was left to settle, and then gradually the supernatant was poured from the beaker until finally, only the flocs in solution remained. These flocs were condensed using a centrifuge that could rotate four 25 ml test tubes. Then these test tubes were dried at 80° C until all water was removed from the floc. After that the flocs were ground with mortar and pestle until the flocs were finely crushed. It should be remarked that after the flocs were crushed it was exceedingly difficult to weigh the flocs, because of the high surface charge of the material, the flocs tended sticking to the

laboratory metal spoon and other utensils, particularly in the winter time, when there was less moisture in the air.

Table 1: Adsorbent type, source, preparation and treatment

Adsorbent Type	Source	Preparation	Treatment
Woodchips	UND Campus	No	Yes
Tree Leaves	UND Campus	No	Yes
Straw	Online	No	No
Rice Husk	Online	No	No
Biochar	Produced in Lab	No	No
Oxidized Biochar	Produced in Lab	Yes	No
Tap Flocs	Produced in Lab	Yes	No
River Flocs	Produced in Lab	Yes	No
Iron Modified Sand	Produced in Lab	Yes	No

Metal Solution

Copper solutions were produced for both column experiments and batch adsorption experiments, and usually included spiking a measured amount of stock $CuCl_2$ solution, to create a specified initial copper concentration. The copper solution was made from analytical grade $CuCl_2$.

Initial batch experiments were conducted with DI water and buffered with bicarbonate, to remove any interference or unaccounted for variables that may be present in Red River water. The buffered solution was prepared at $2x10^{-3}$ M HCO_3 concentration, which was meant to simulate alkalinity found in natural surface waters. Laboratory grade sodium bicarbonate ($NaHCO_3$) was used to produce a buffered solution. To produce a 2 L buffered solution at $2x10^{-3}$ M HCO_3, 0.336 gram $NaHCO_3$ was required.

Red River water was used for batch experiments later on in the research and fixed-bed column experiments. This was collected at 47°56'30.29"N and 97° 2'55.64"W which is where a rock dam is located on the Red River just North of the City of Grand

Forks, ND, which is a best management practice. This site was selected for the easy accessibility, there is a boat launch near the dam, and more importantly that parts remain unfrozen on the river during the winter, because of the water turbulence passing over the rock dam. The collected surface water was then filtered using a vacuum pump and filter apparatus. Whatman 1004-042 grade 4 qualitative filter paper was used, which had a diameter of 4.25 cm and pore size of 25 μm. This is the standard filter paper used in water analysis. This filter paper was effective at removing the majority of suspended solids, and substantially reduced the turbidity of the water, which was essential because any turbidity in the water would affect the measurements from the spectrophotometer.

3.2 Batch Adsorption Experimental Methods

Experimental Procedure

Batch adsorption experiments were performed by contacting a given mass of adsorbent, or adsorbent dosage with either 25 – 50 ml of copper ion solution at a given concentration, typically between 5 – 40 mg/L copper (II) within a 50 ml standard test tube. The initial copper concentration and adsorbent dosage were determined to produce the highest ranged isotherm, which would be the greatest range of equilibrium concentrations to adsorption capacities, more on that late. The sorption process was conducted at a pH between 5-7 for bicarbonate buffered solutions and a pH between 8 – 8.5 for Red River solutions, which is near the higher pH range for average surface waters. Test tubes were then loaded onto a laboratory Glas-Col rotator for anywhere between 24-72 hrs. Any necessary pH adjustments would take place after this time. Then the samples were analyzed with a Hach spectrophotometer model DR 2000 for free copper (II) ion

concentration. It should be mentioned that in similar research usually a flame atomic adsorption (FAA) instrument was used to measure the heavy metal concentration of the solution.

The pH was important because high sorption of copper ions is found for a pH between 5 -7 and avoids metal precipitation that may occur in more alkaline conditions. This was a challenge because although the solutions were buffered with 2×10^{-3} HCO_3 solutions, significant pH changes were sometimes observed at the end of the experiment and required pH corrections with either 0.1M HCl or 0.1M NaOH titration, to keep the beginning and end pH measurements the same. For Red River water samples, no pH adjustment was needed, because the buffering capacity of the water was high enough to keep the pH relatively constant throughout the entirety of the experiment. However, there were concerns with copper metal precipitation, which would limit the comparative meaning between results obtained, using Red River water and buffered solutions.

Adsorption Models

The general adsorption models for batch reaction experiments where sufficient time is given for equilibrium to be reached are Langmuir and Freundlich isotherm models. These adsorption models linearize the basic adsorption equation,

$$q_e = (C_i - C_e)V/M$$

Where q_e is the mass of adsorbed metal per mass of media, C_i is the initial metal concentration, C_e is the equilibrium metal concentration, V is the volume of the solution and M is the mass of the media.

Langmuir model is given as,

$$\frac{1}{q_e} = \frac{1}{(K_L Q_M)}\frac{1}{C_e} + \frac{1}{Q_M}$$

Where Q_M is the maximum adsorption capacity and K_L is a constant. The slope and y-intercept of this linearized equation are $1/(K_L Q_M)$ and $1/Q_M$, respectively. Some assumptions that are made for this adsorption model include,

1. Adsorbate surface consists of a certain number of active sites, that only a single molecule can be adsorbed to.

2. No lateral interaction of adsorbed molecules, so the heat of adsorption is constant

3. Adsorbed molecule remains at the active site until desorption

4. Only a monolayer can be formed (i.e. molecules cannot deposit onto already adsorbed molecules) (Ho 2006)

Freundlich model is given as,

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$$

Where K_F is the adsorption capacity and n is the affinity of adsorption. Affinity is the strength of the binding interaction between the ligand and central metal ion (Demirbus 2008). The main limitation of this model is that it is purely an empirical model and does not have any theoretical basis.

The success of these models in describing the adsorption process can be measured by the corresponding r^2 value of the linearization. Therefore, these values can be averaged, and the most accurate model can be determined. However, it is possible that some models may more accurately predict the adsorption capacity of differing material, depending on the type of material and the dominant adsorption mechanism.

3.3 Fixed-Bed Column Experimental Methods

Experimental Setup

Resprep polypropylene tubes with a reservoir capacity of 75 ml were used as columns for the experiment, and approximately had an external dimeter of 3 cm, with a wall thickness of 0.2 cm and length of 13 cm. These tubes had to be modified in lab to service as a function. This was done by drilling a small hole at the top of the tube, so that an effluent tube could be connected. Columns were attached to stand with clamps and supports and connected with tubing through a Cole Parmer Masterflex peristaltic pump system into a storage tank. The flow rate was determined by filling a 25 ml graduated cylinder and measuring the time that elapsed to fill the graduated cylinder. Then the flow dial was adjusted accordingly, until the desired flow rate was produced.

Columns were manufactured in lab and consisted of a subbase, and mixture of sand and adsorbent. Subbase consisted of large coarse sand, which was added to prevent any sand or adsorbent from falling into the influent tube, this sand was collected between sieves no 8 and no 10 or standard particle size of 2 – 2.38 mm approximate diameter. In some cases, glass beads were also added at the top of the column to prevent any adsorbent from floating. Laboratory grade Ottawa 20-30 mesh sand was then placed on top of the subbase with the adsorbent either well-mixed or layered in the sand. In all columns 15 grams of subbase was used, and 40 grams of laboratory grade sand was placed in each column, with varying amounts of adsorbent added. The only exception to this would be for the modified iron-coated sand columns, which only had 20 grams non-coated laboratory grade sand added. This was meant to replicate natural sandy soil

conditions and soil matrices found in stormwater best management practices. The control

for these experiments consisted of a column with 15 grams subbase and 40 grams

laboratory grade sand with no adsorbent added. This was used to compare results from

adsorbent columns.

Table 2: Column sequences 1-4 parameters

No.	Type	Adsorbent mass (g)	Sand mass (g)	Flow (ml/min)	Feed concentration (mg/L)
1	Woodchips	0.5	40	5 ± 1.0	5.25 ± 0.25
	River flocs	0.5	40	5 ± 1.0	5.25 ± 0.25
	Biochar	0.5	40	5 ± 1.0	5.25 ± 0.25
	Control	-	40	5 ± 1.0	5.25 ± 0.25
2	River flocs	0.103	40	5 ± 1.0	5.25 ± 0.25
	Control	-	40	5 ± 1.0	5.25 ± 0.25
3	Mixed Low-MICS	20	20	5 ± 1.0	1.1 ± 0.1
	Layered Low-MICS	20	20	5 ± 1.0	1.1 ± 0.1
4	High-MICS	20	20	5 ± 1.0	1.1 ± 0.1
	Control	-	40	5 ± 1.0	1.1 ± 0.1
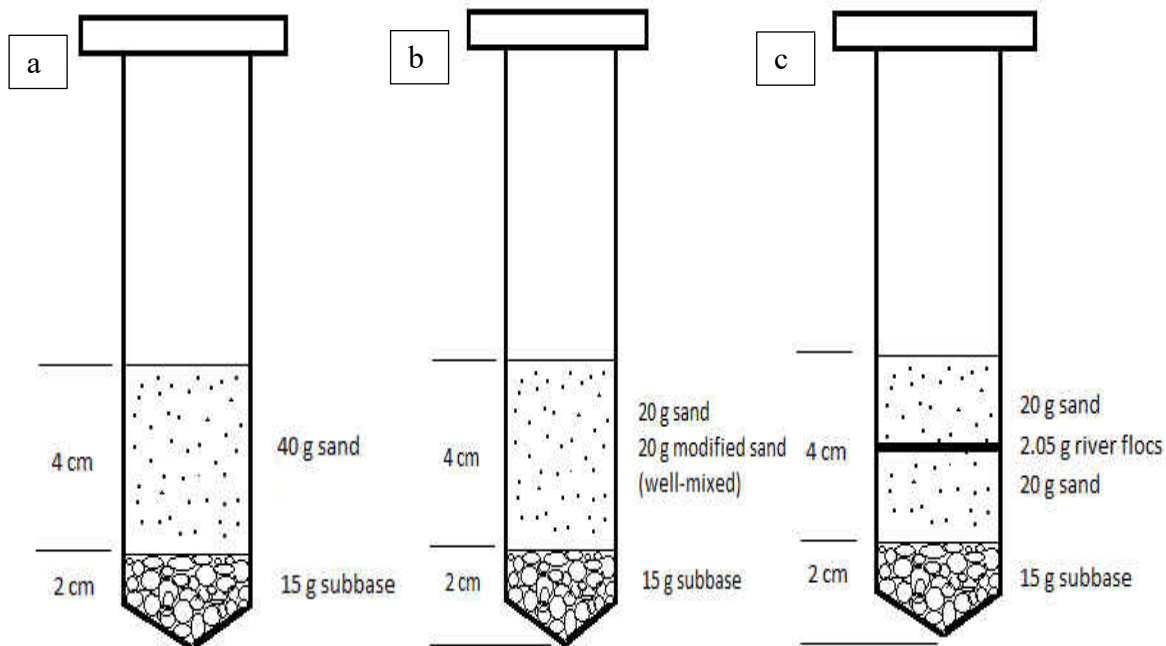
Figure 11: Column profile view (a: control; b: modified iron-coated sand (MICS); c: river flocs)

Experimental Procedure

The experiment was conducted with the following variables,

1. bed height (6 cm)
2. flow rate of solution (5 ± 1.0 ml/min)
3. influent concentration of pollutant (1-5.5 mg/L Cu (II) ions)

The fixed-bed column experiment started by pumping a known concentration of metal solution from a storage tank through the column at a fixed flow rate with a column with a known bed height, and a known mass of adsorbent within the column. The effluent or metal solution downstream of the column was collected at varying intervals and analyzed using spectrophotometry Hach model DR 2000 copper bicinchoninate method. The

samples were collected and analyzed normally until the column reached near

breakthrough where the metal concentration in the effluent was no longer changing.

Then a desorption cycle would begin, which would simulate a backwash, where

filtered Red River water was pumped, under similar conditions as the adsorption cycle,

through the column. The filtered Red River water had no significant copper (II)

concentrations, however because of low turbidity an initial concentration of 0.05 mg/L

copper (II) ion was measured. This value would later be subtracted from all effluent

concentration measurements. After the column was regenerated another adsorption cycle

would follow. This process would usually contain anywhere between 3-5

adsorption/desorption cycles if a column was seriously considered.

1 : Feed storage
2 : Pump
3. Rotameter
4 : Column
5. Delivery line
6. : Sample collection
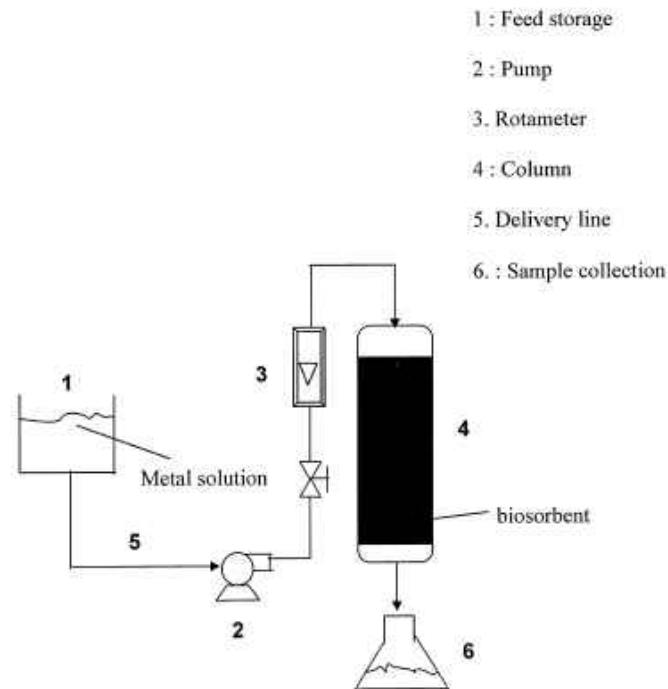
Fig. 1. Experimental set-up.

Figure 12: Example of column experiment set-up (Source of image: Z. Zulfadhyly et al.,

Environmental Pollution

Analytical Modelling

Analysis of column experiment data was conducted with area under the curve estimations, using the computer software Origin, which was used to determine the cumulative mass retained of copper (II) ion on the adsorbent surface. This information then could be used to determine breakthrough points and the period that the column becomes completely saturation or exhaustion.

Chapter 4

4.1 Results

Batch Adsorption Experiments

These experiments were conducted with a range of different parameters such as pH, adsorbent mass, adsorbate dosage, solution volume and type. It should be noted that adsorbent mass and solution volume are related variables that correspond to the adsorbent dosage. Other parameters as contact time and temperature were kept constant at around 48 hours and 25°C, respectively. Batch experiment parameters are given in Table 4, and the corresponding adsorbent type isotherm linearization model abbreviations are given in Table 3. Many results were not included because of either different parameter being used for the same adsorbent. For example, in the beginning of the research most solution types were created with buffered DI water, in order to reduce any unaccounted variables that may be present in surface water, however later in the research filtered surface water was used to give more credible results to solution characteristics present in stormwater runoff. In these cases, results are given for the experiments that yielded the best trend-line. Some results were removed as outliers (see Appendix A).

Table 3: Abbreviation legend

Abbreviation	Name
MICS	Modified iron-coated sand
WC	Woodchips
S	Straw
TL	Tree leaves
RH	Rice husk
OB	Oxidized biochar
B	Biochar
TF	Tap flocs
RF	River flocs
L	Langmuir
F	Freundlich

Table 4: Batch experiment parameters

Type	Mass (g)	Volume (ml)	Dosage (mg/L)	Solution	pH
Low-MICS	0.2 - 1.0	50	1.1	River water	8.0 ± 0.1
WC	1.0	35	3.2 – 8.2	Buffered DI water	5.8 ± 0.1
S	0.3 – 1.0	35	1.9 – 8.2	Buffered DI water	5.8 ± 0.1
TL	1.0	35	4.6 – 8.2	Buffered DI water	5.8 ± 0.1
RH	0.025 – 0.1	50	1.8	River water	8.0 ± 0.1
OB	0.1 – 1.21	50	4.4	River water	8.0 ± 0.1
B	0.08 – 0.7	50	1.8 – 3.12	River water	8.0 ± 0.1
TF	0.005 – 0.05	50	13.2	Buffered DI water	5.8 ± 0.1
RF	0.01 – 0.11	25	13.2	River water	8.0 ± 0.1

Isotherms
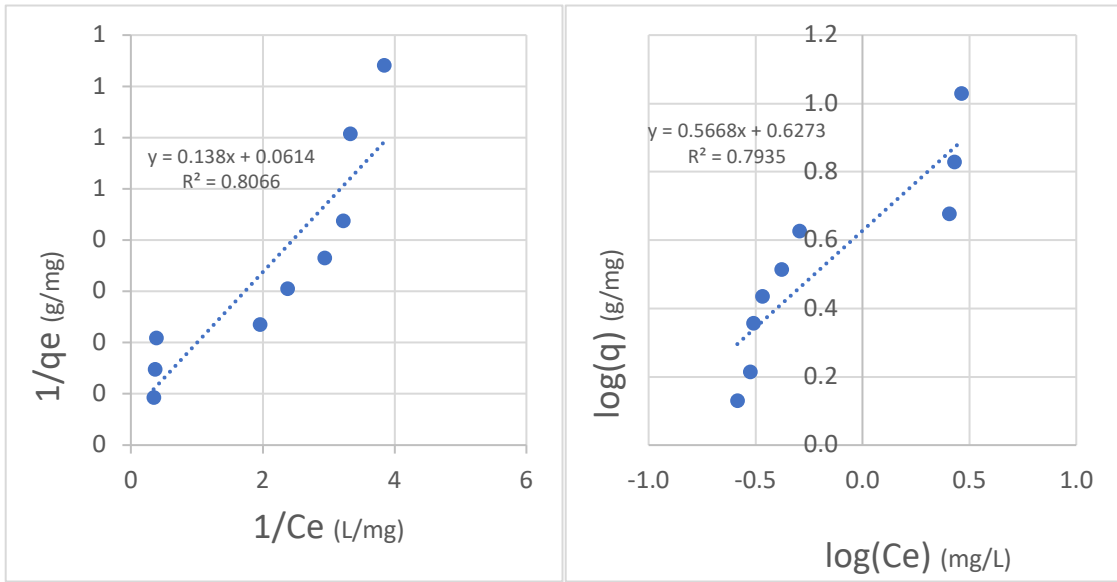
Figure 13: Low-modified iron coated sand (MICS) isotherms (Left: IMS-Langmuir model; Right: IMS-Freundlich model)
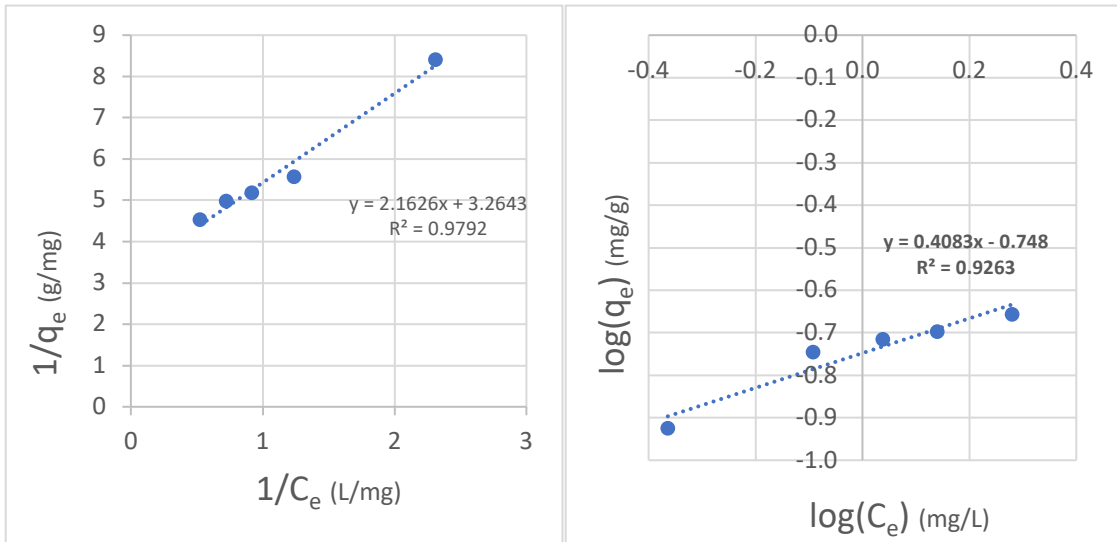
Figure 14: Woodchips isotherms (Left: WC-Langmuir model; Right: WC-Freundlich model)

Figure 15: Straw isotherms (Left: S-Langmuir model; Right: S-Freundlich model)
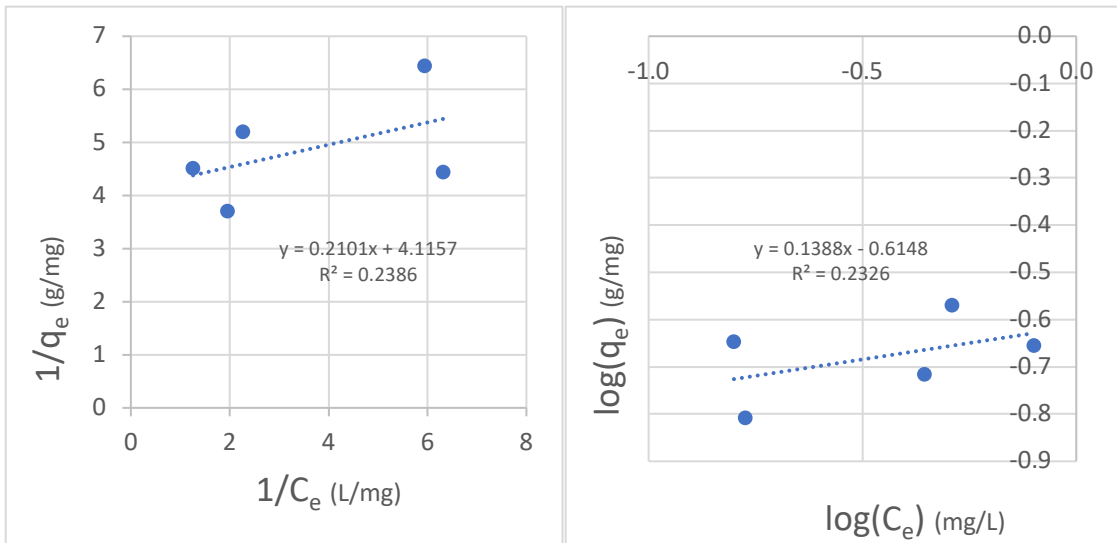
Figure 16: Tree leaves isotherms (Left: TL-Langmuir model; Right: TL-Freundlich model)
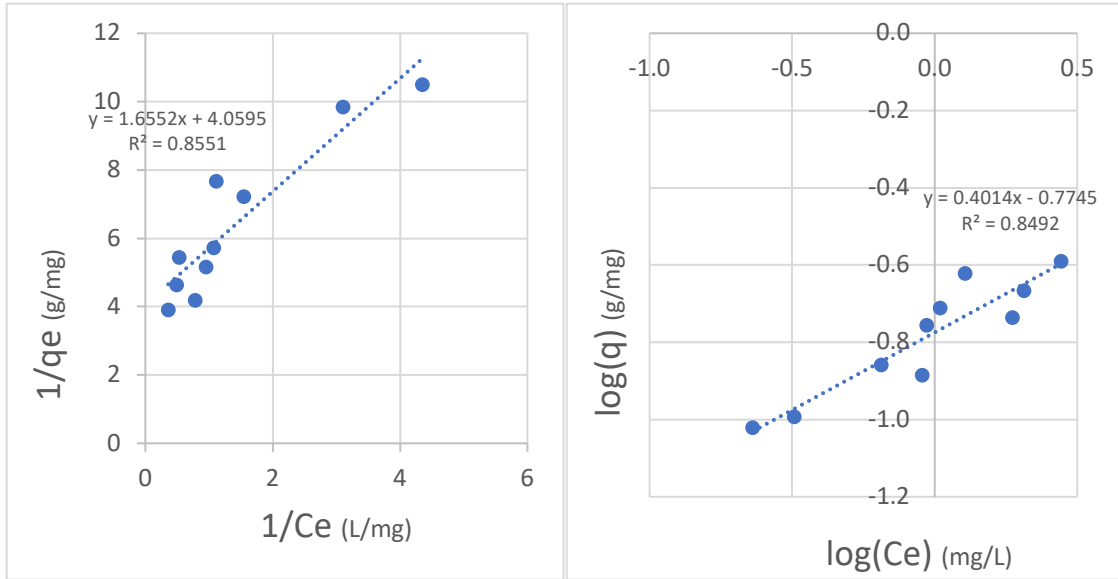
Figure 17: Rice husk isotherms (Left: RH-Langmuir model; Right: RH-Freundlich model)
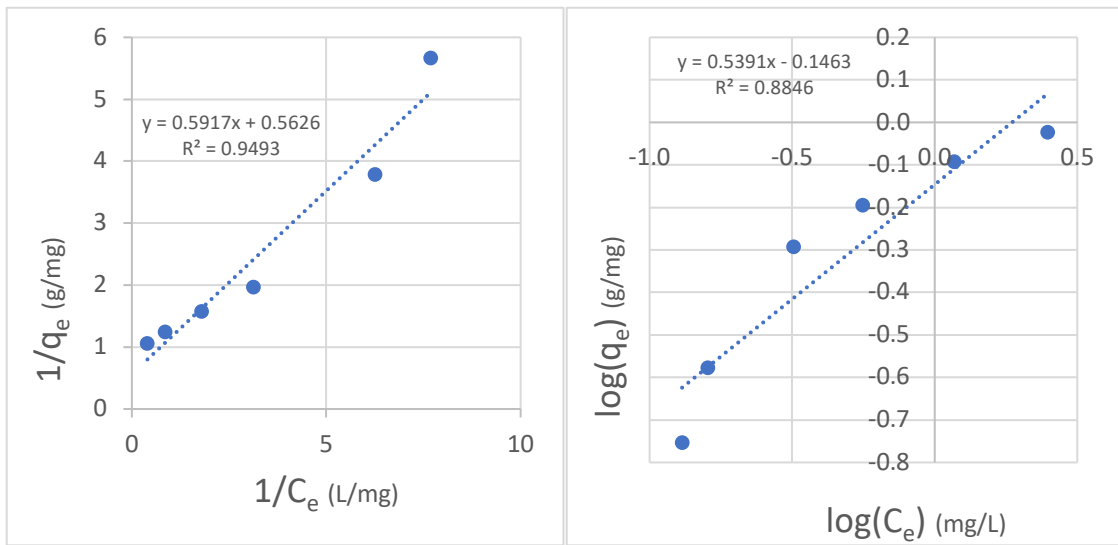
Figure 18: Oxidized biochar isotherms (Left: OB-Langmuir model; Right: OB-Freundlich model)
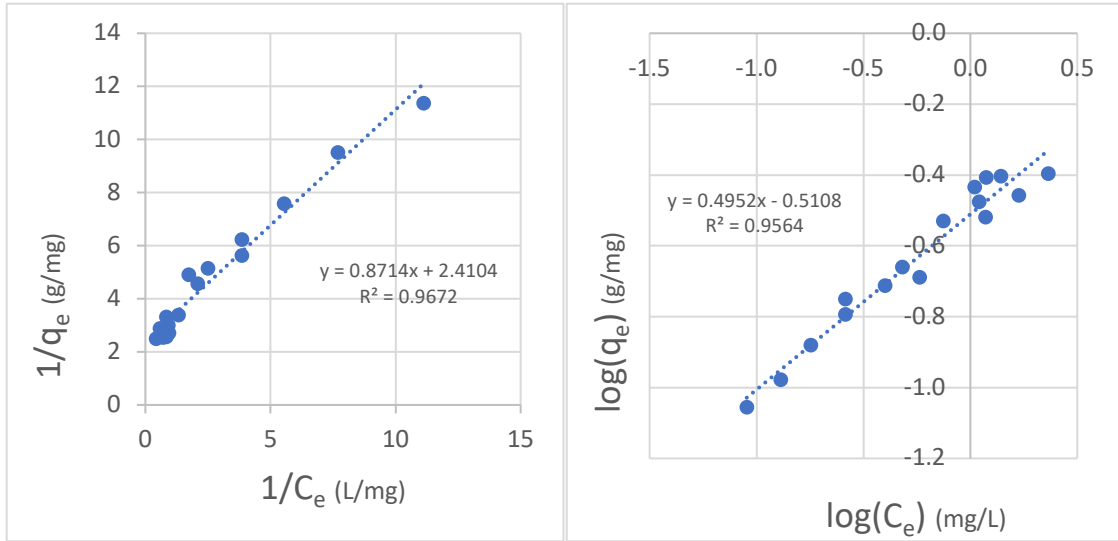
Figure 19: Biochar isotherms (Left: B-Langmuir model; Right: B-Freundlich model)

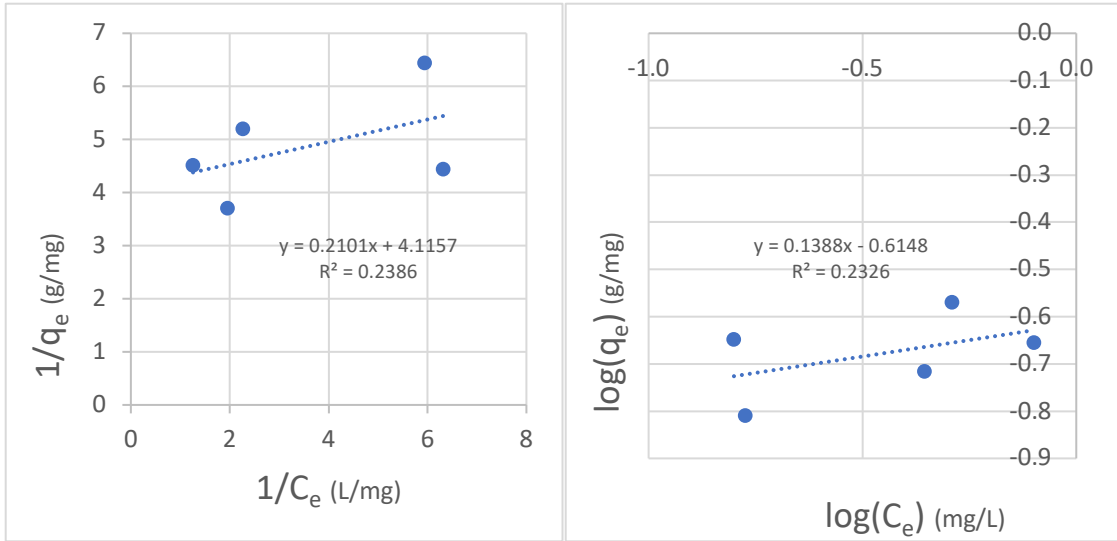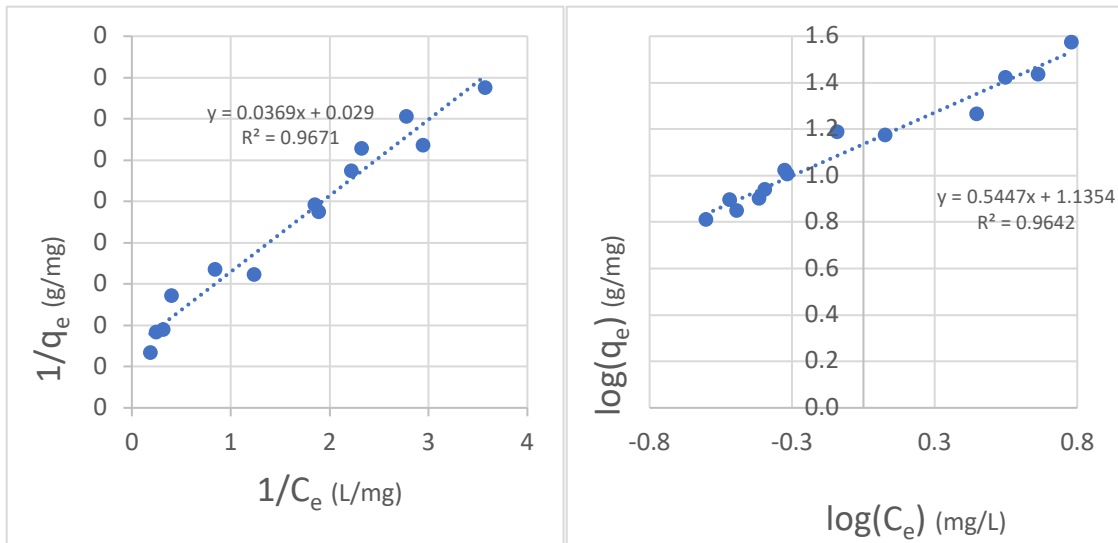*Figure 20: Tap water flocs isotherms (Left: TF-Langmuir model; Right: TF-Freundlich model)*
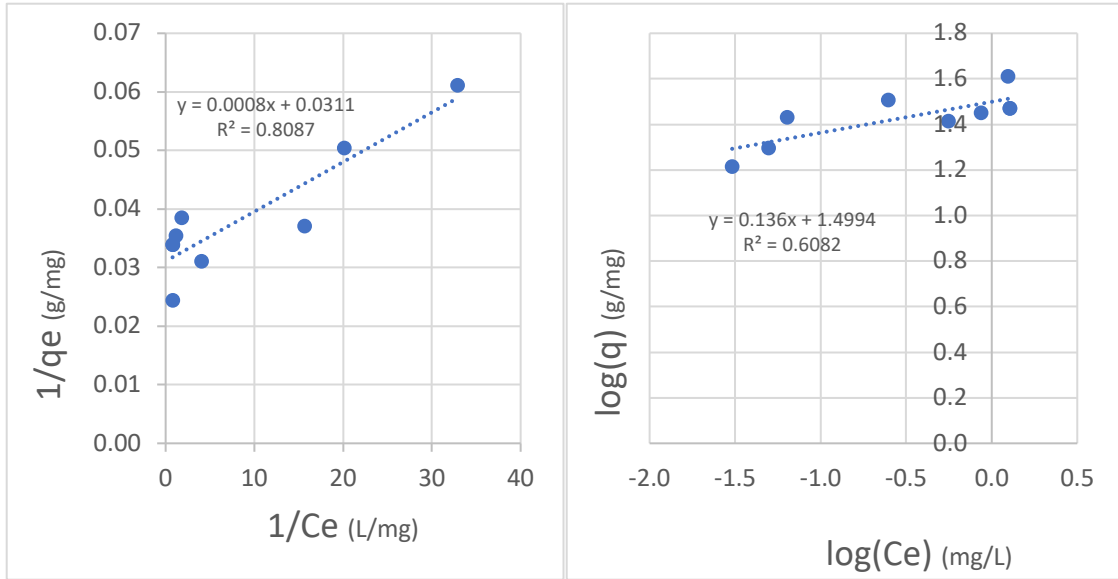
Figure 21: River water flocs isotherms (Left: RF-Langmuir model; Right: RF-Freundlich model)

Isotherm Constants

Table 5: Langmuir isotherm constants

Sorbent Material	Langmuir Constants		
	q_e (mg/g)	K_L (L/mg)	R^2
Low-MICS	16.29	0.44	0.81
River flocs	32.16	36.72	0.81
Tap flocs	34.50	0.79	0.97
Biochar	0.41	2.77	0.97
Oxidized biochar	1.78	0.95	0.95
Rice husk	0.25	2.45	0.86
Straw	0.31	1.51	0.98
Woodchips	0.21	6.85	0.83
Tree leaves	0.24	19.59	0.24
		avg	0.82

Table 6: Freundlich isotherm constants

Sorbent Material	Freundlich Constants		
	K_F	n	R^2
Low-MICS	4.24	1.76	0.79
River flocs	31.58	7.35	0.61
Tap flocs	13.66	1.84	0.96
Biochar	0.31	2.02	0.96
Oxidized biochar	0.71	1.85	0.88
Rice husk	0.17	2.45	0.93
Straw	0.18	2.45	0.93
Woodchips	0.19	3.44	0.89
Tree leaves	0.24	7.20	0.23
		avg	0.79

Humic Substances

Table 7: Humic and fulvic acid with river flocs adsorption comparison

Sample		Acid Volume (mL)	Acid mass (mg)	River Floc mass (g)	pH	Volume (ml)	C_i (mg/L)	C_e (mg/l)	q_e (mg/L)
Control		0	0	0.03	6.0	25	13	0.663	10.33
Humic Acid (HA)	1	0.125	12.5	0.03	6.0	25.125	13	0.15	10.76
	2	0.25	25	0.03	6.0	25.250	13	0.31	10.68
	3	0.5	50	0.03	6.0	25.500	13	0.37	10.73
	4	1	100	0.03	6.0	26.000	13	0.25	11.05
	5	2	200	0.03	6.0	27.000	13	0.3	11.43
	6	3	300	0.03	6.0	28.000	13	0.37	11.78
	7	5	500	0.03	6.0	30.000	13	0.37	12.63
Fulvic Acid (FA)	8	0.125	12.5	0.03	6.0	25.125	13	0.3	10.64
	9	0.25	25	0.03	6.0	25.250	13	0.23	10.74
	10	0.5	50	0.03	6.0	25.500	13	0.41	10.7
	11	1	100	0.03	6.0	26.000	13	0.26	11.04
	12	2	200	0.03	6.0	27.000	13	0.34	11.39
	13	3	300	0.03	6.0	28.000	13	0.54	11.63
	14	5	500	0.03	6.0	30.000	13	0.32	12.68

MICS Variation

Table 8: Different MICS concentration comparison

Sample	MICS (Fe mol/ grams of sand)	Mass (g)	pH	C_i (mg/L)	C_e (mg/l)
1-3	2.5×10^{-5}	1.0	8.6 ± 0.1	1.07	0.89
4-6	5.0×10^{-5}	1.0	8.6 ± 0.1	1.07	0.97
7-9	1.0×10^{-4}	1.0	8.6 ± 0.1	1.07	0.76
10-12	2.5×10^{-4}	1.0	8.6 ± 0.1	1.07	0.79
13-15	5.0×10^{-4}	1.0	8.6 ± 0.1	1.07	0.77

Fixed-Bed Column Experiment

There were four main column experiments performed in this research. Column experiment 1 was a preliminary experiment that compared adsorbents that yielded high adsorption capacities, during batch adsorption experiments. Column experiment 2 ran a river floc column and control column for three adsorption/desorption cycles. In part due to the unsatisfactory results from the river floc, and other adsorbent columns from column experiment 1 and 2, iron-coated modified sand was produced in lab and analyzed. Column experiment 3 compared layered and well-mixed low-iron modified sand. Column experiment 4 ran a high-iron modified sand and control column for multiple adsorption/desorption cycles and extended some cycles for long time durations to determine column saturation points.

Column Sequence 1
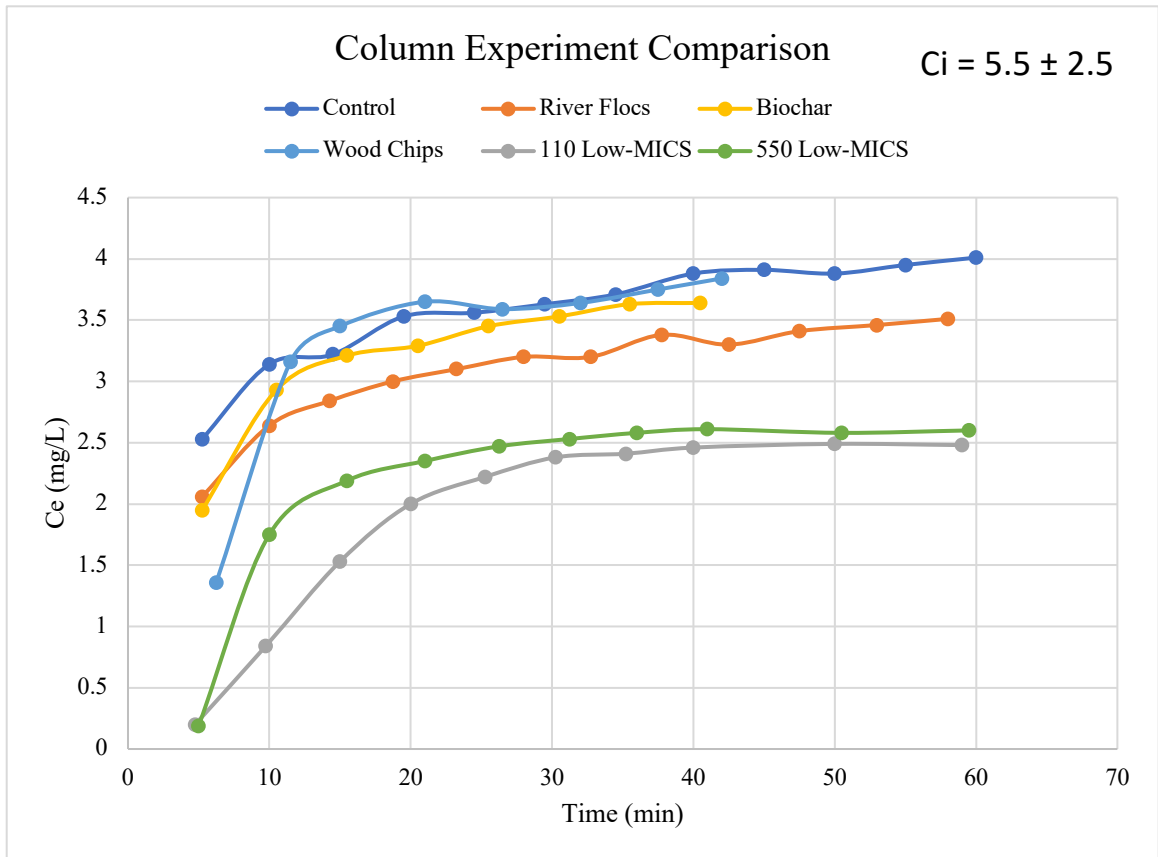
Figure 22: Initial column experiments for suitable adsorbents

Column Sequence 2

River Floc and Control Column Experiment

Control ■   River Floc ●

Ci = 5.5 mg/L
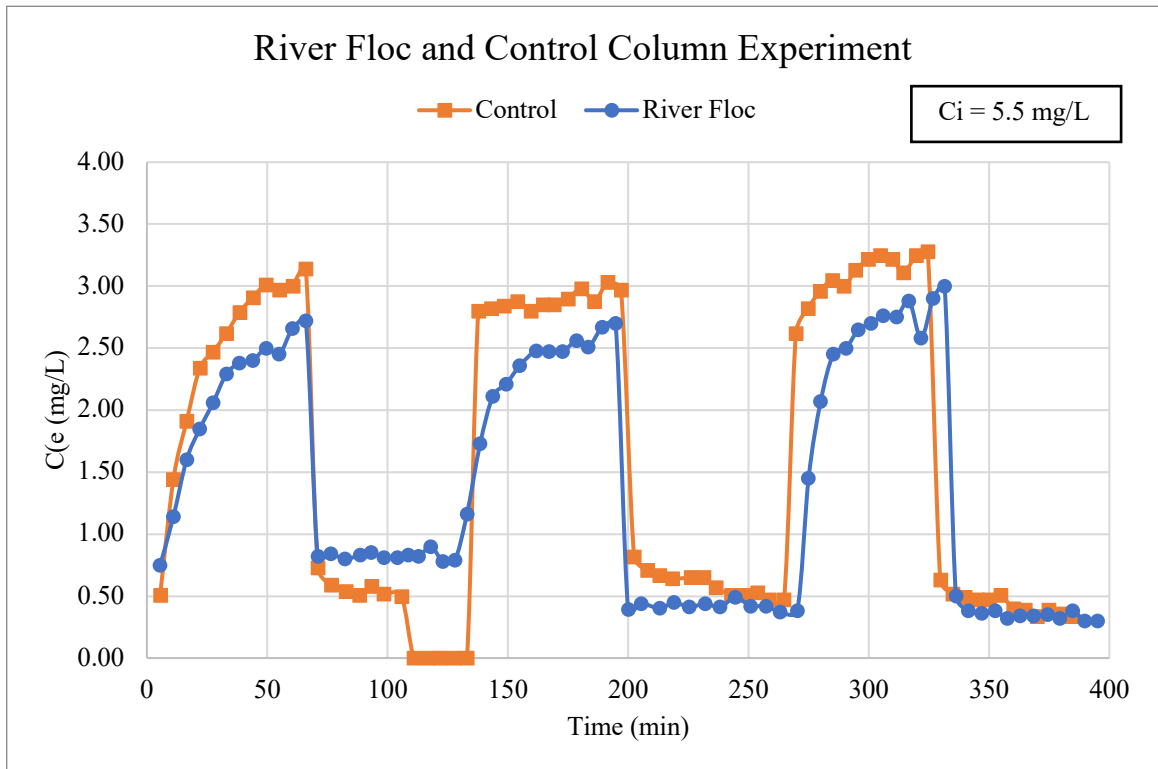
Figure 23: River floc and control column experiment

River Flocs Retained

Area under Ci   Area under Ce   Retained (mg)
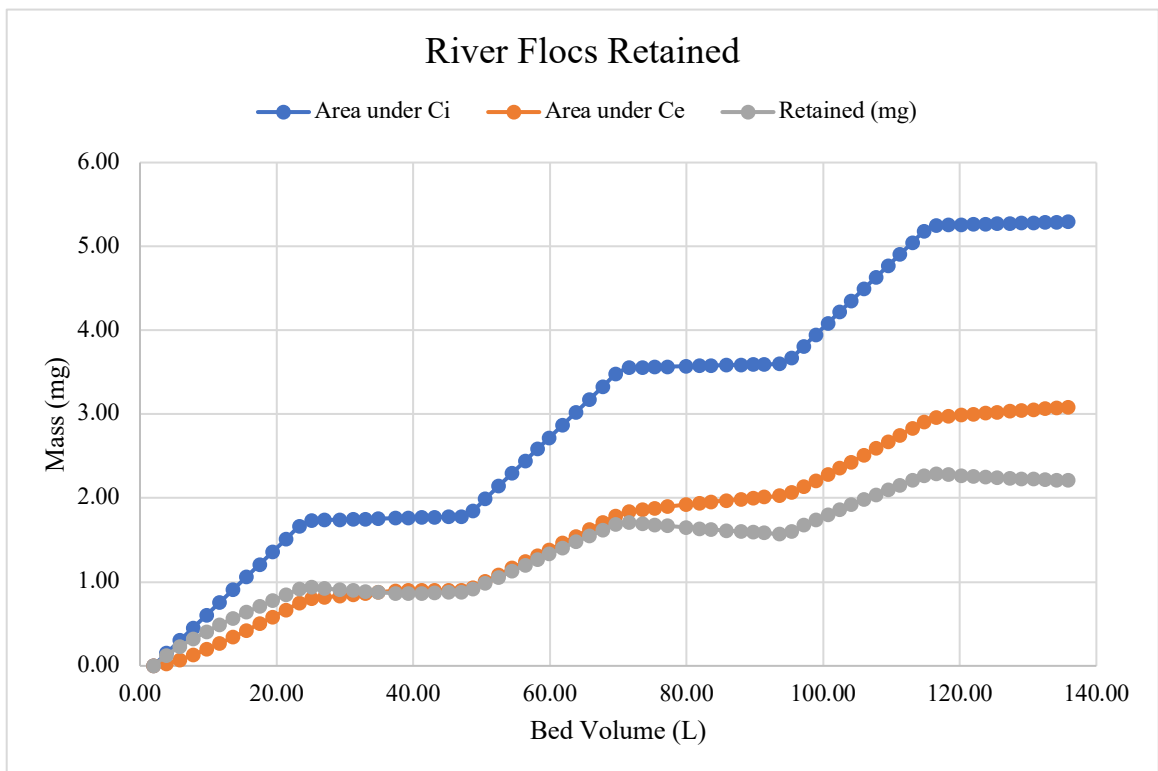
Figure 24: River floc cumulative mass retained
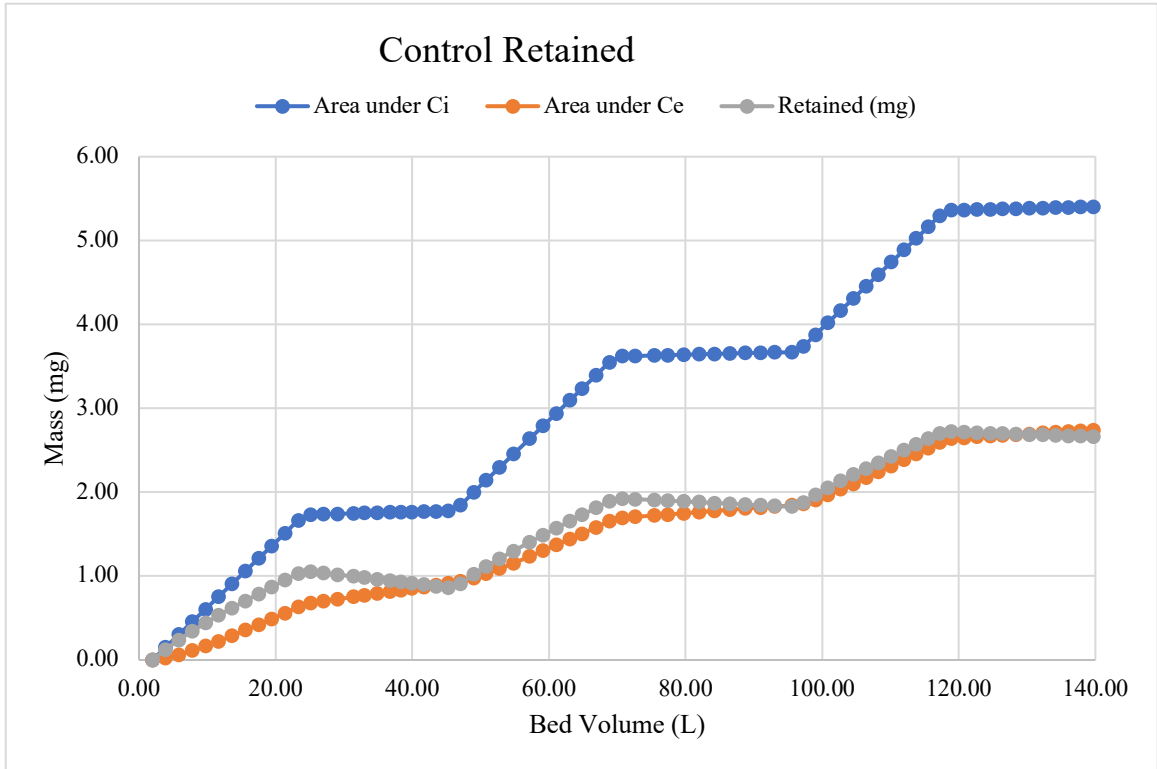
Figure 25: Control cumulative mass retained
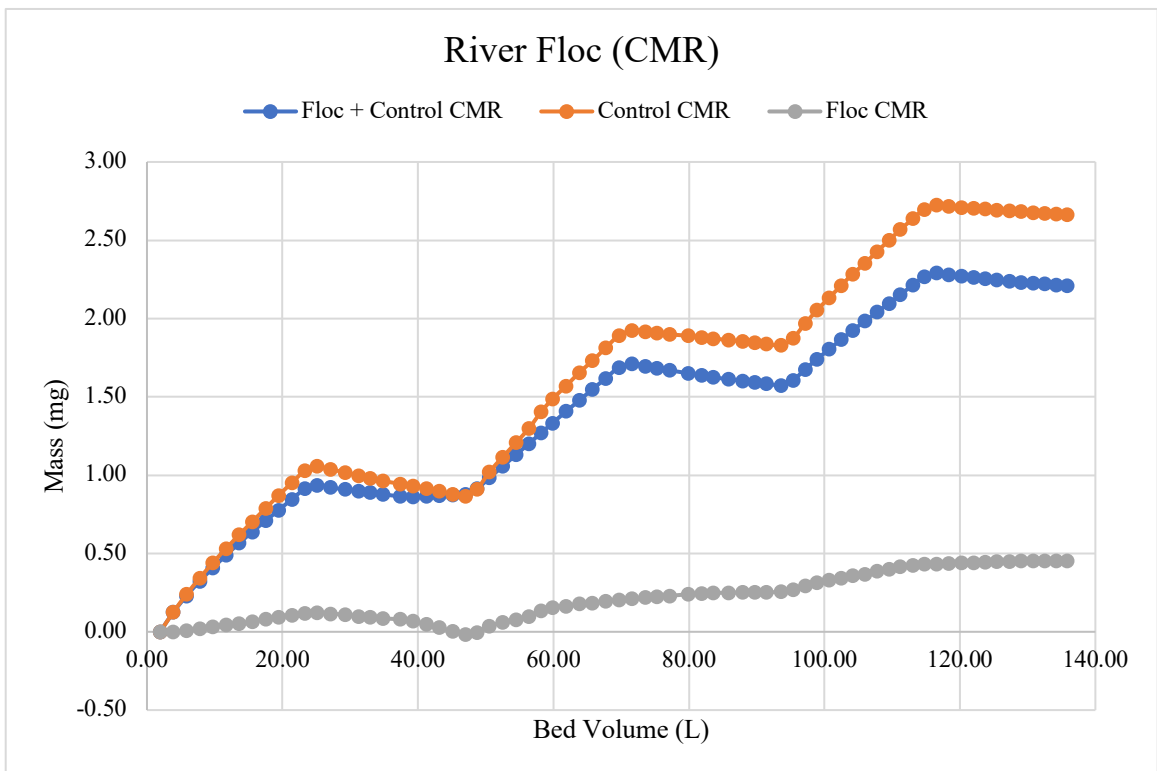
Figure 26: Control and river floc cumulative mass retained difference

Column Sequence 3
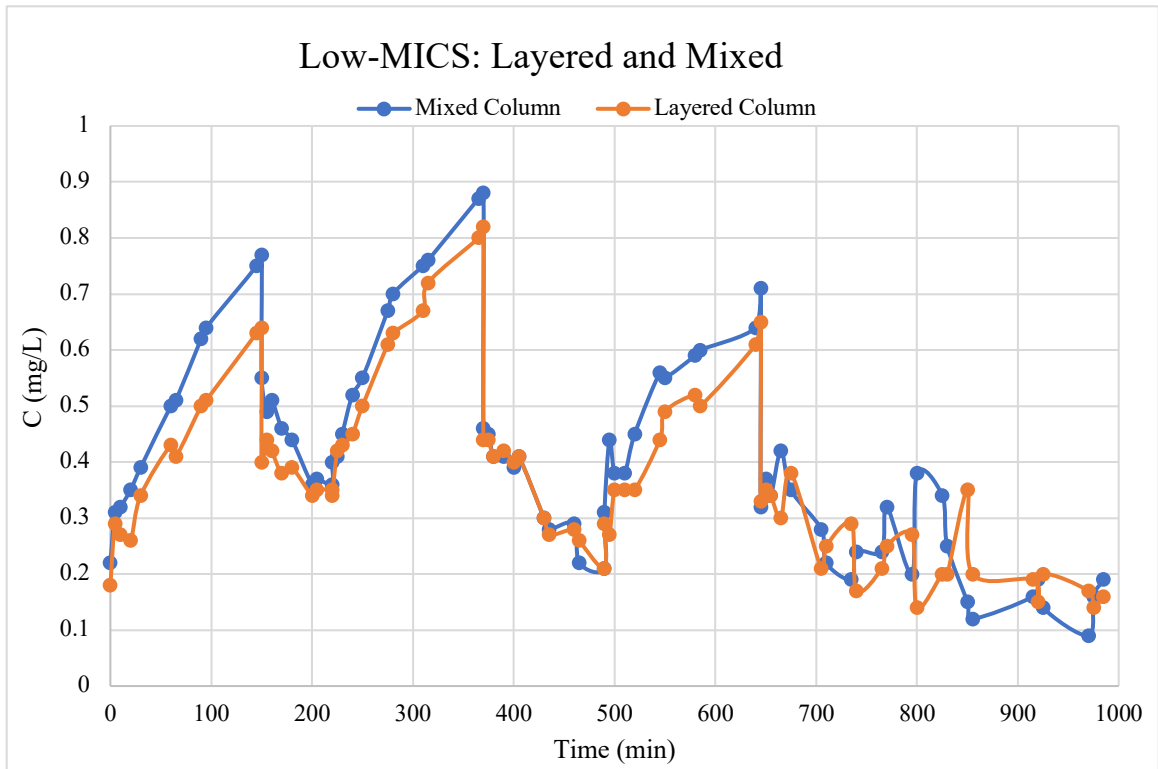
Figure 27: Mixed and layered low-iron modified sand column experiment
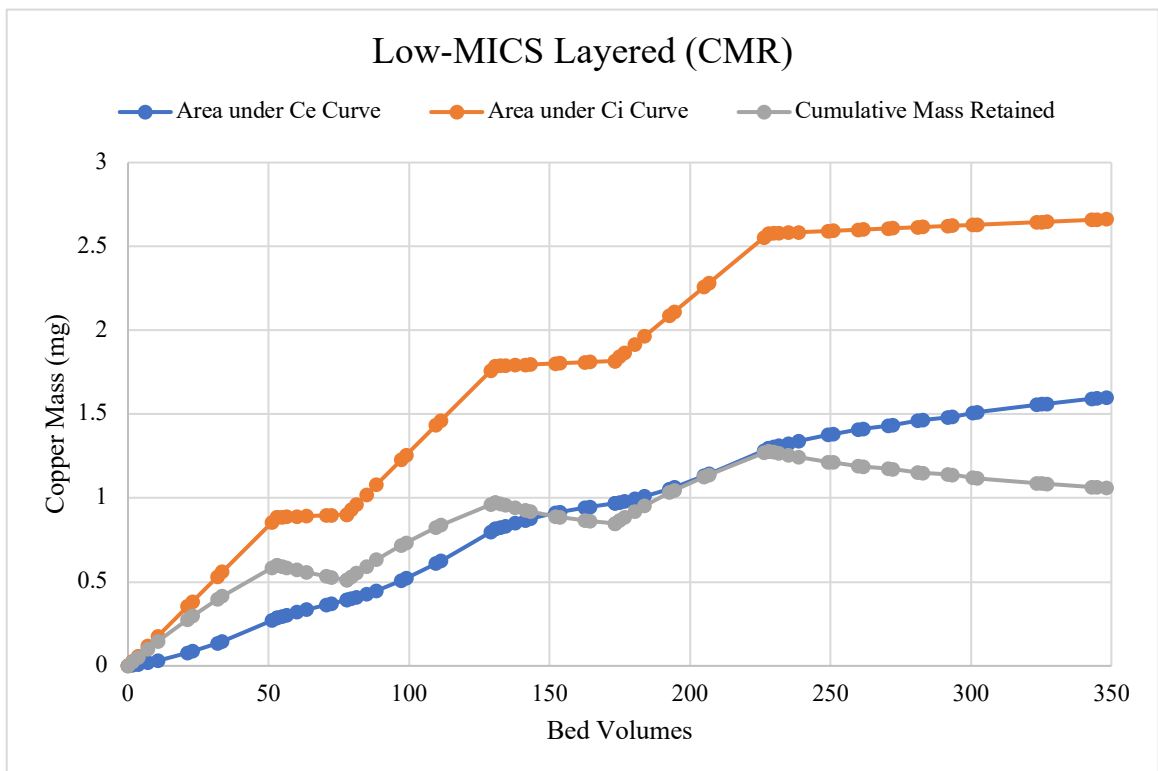
Figure 28: Low-iron modified sand cumulative mass retained column experiment

Column Sequence 4
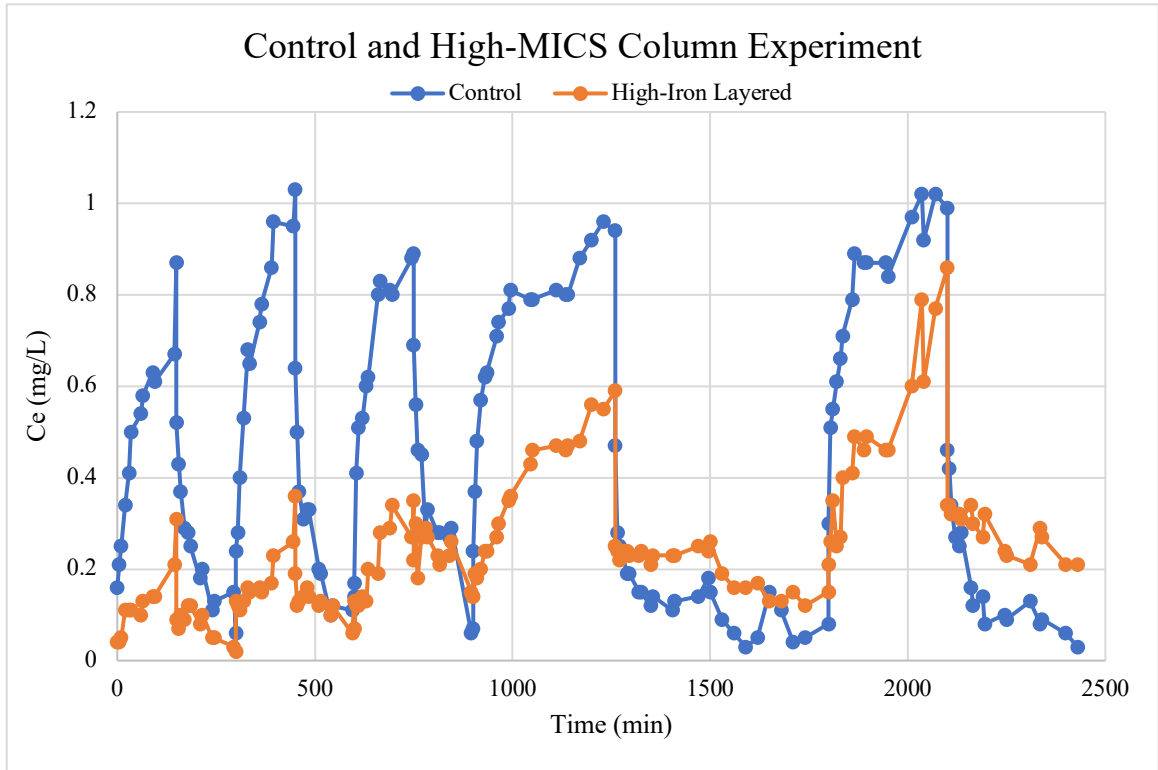
Figure 29: High-iron modified sand and control column experiment
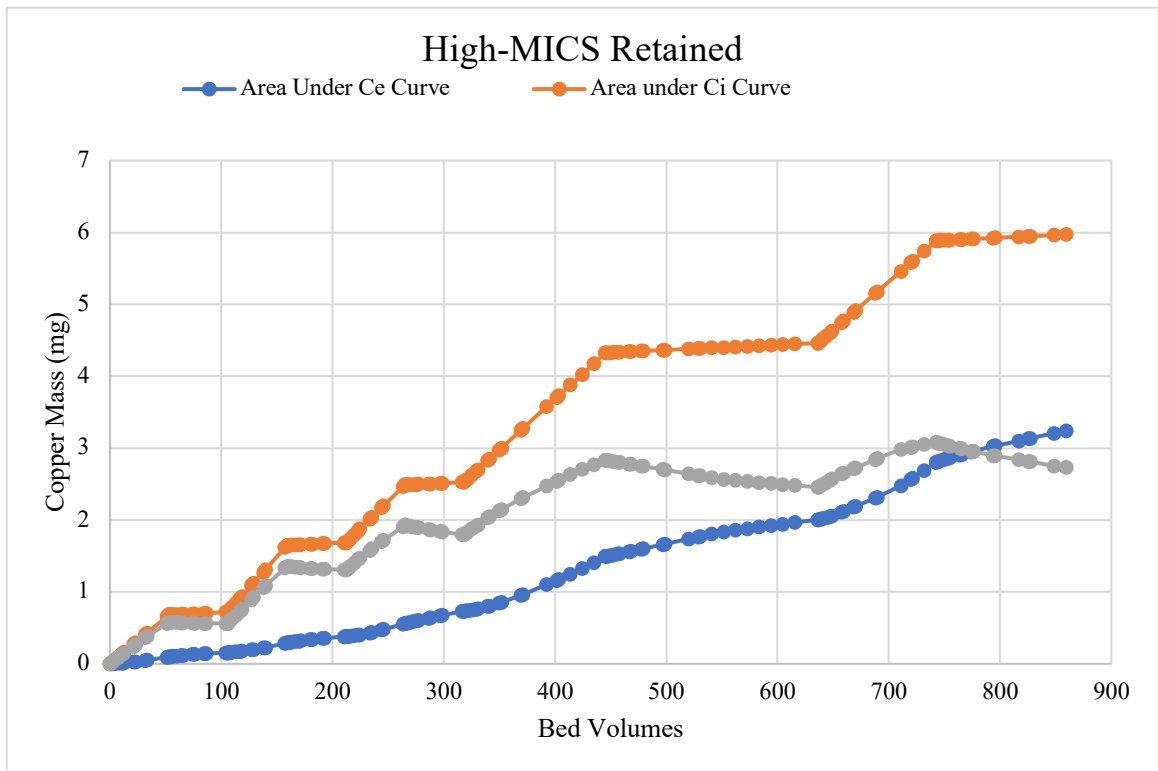
Figure 30: High-iron modified sand cumulative mass retained
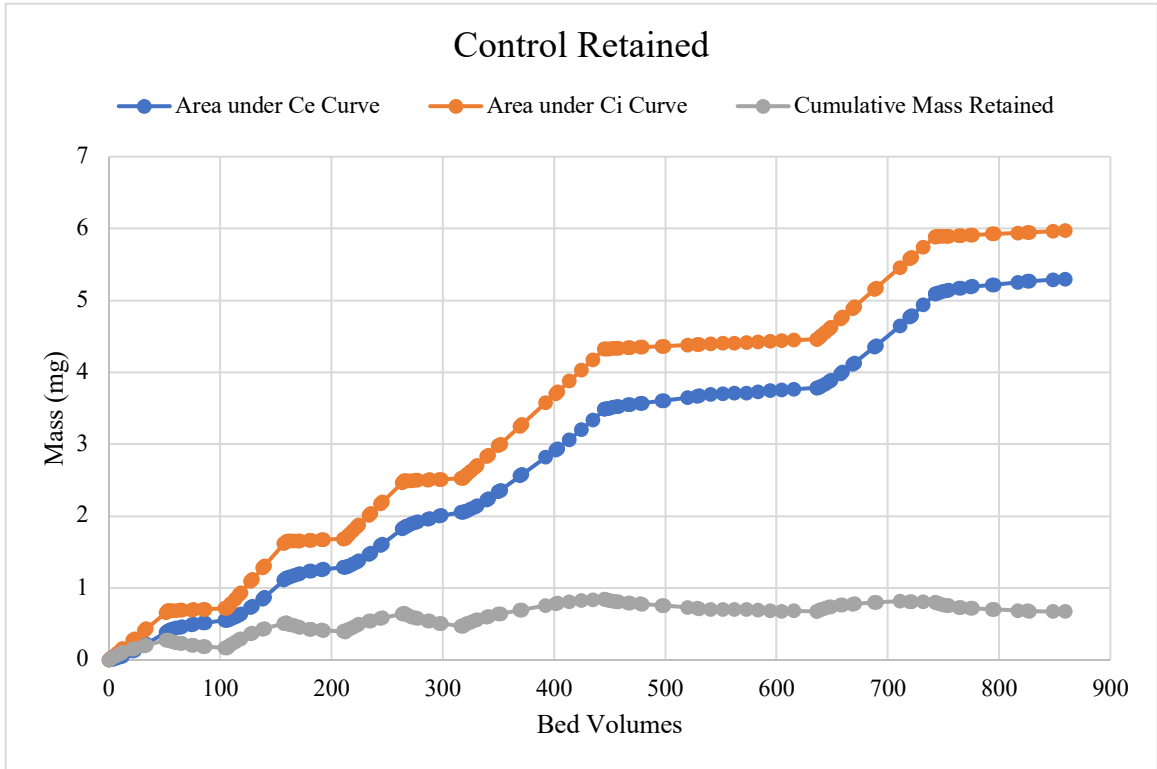
Figure 31: Control cumulative mass retained
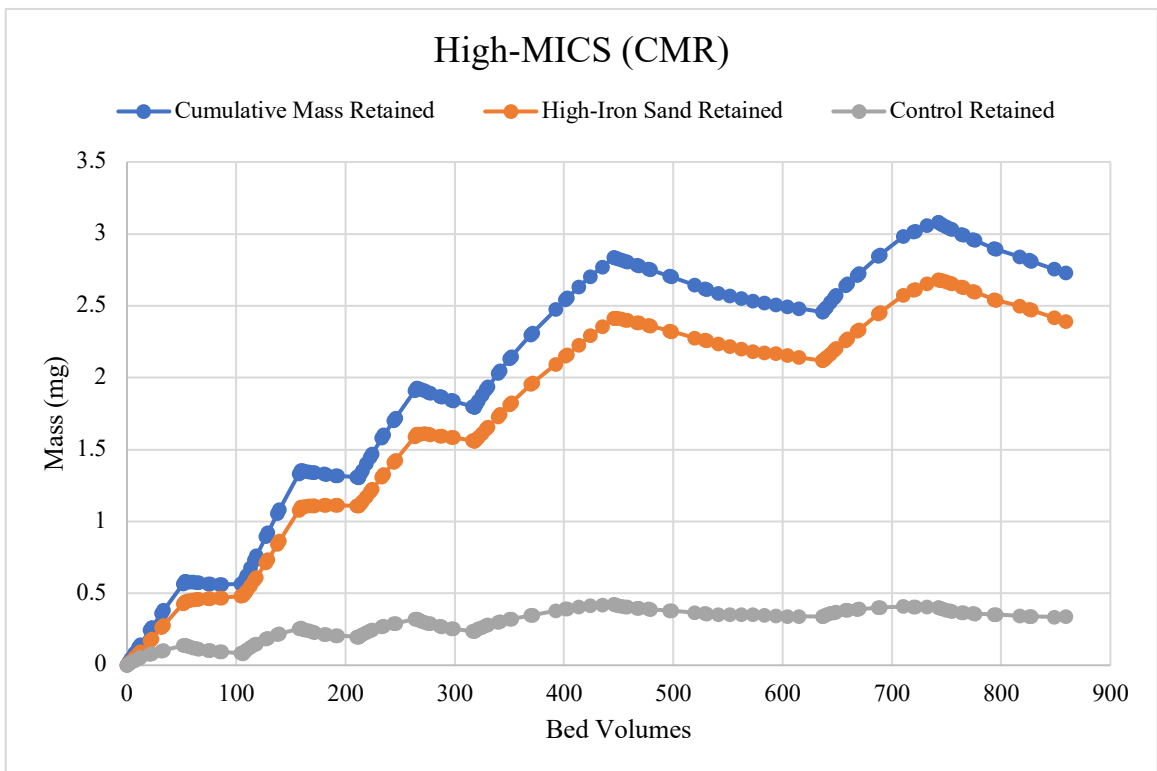
Figure 32: High-iron modified sand and control cumulative mass retained difference

4.2 Discussion

Batch Adsorption Experiments

Isotherms Models

For the batch adsorption experiments, the resultant Langmuir and Freundlich constants are given below. It is apparent from the r^2 values that both models adequately linearized the results. Except for some anomalies which will be discussed later, most of the adsorbents had high r^2 values.

The rank order for maximum adsorption capacities (q_M) obtained from the Langmuir equations are as follows; tap flocs (q_M = 34.5 mg/g) > river flocs (q_M = 32.16 mg/g) > low MICS (q_M = 16.29 mg/g) > oxidized biochar (q_M = 1.78 mg/g) > biochar (q_M = 0.41 mg/g) > straw (q_M = 0.31 mg/g) > rice husk (q_M = 0.25 mg/g) > tree leaves (q_M = 0.24 mg/g) > woodchips (q_M = 0.21 mg/g).

Table 9: Ranked Langmuir maximum adsorption capacities (q_M)

Rank	Sorbent Material	Langmuir Constants		
		q_M (mg/g)	K_L (L/mg)	R^2
1	Tap flocs	34.50	0.79	0.97
2	River Flocs	32.16	36.72	0.81
3	Modified Sand	16.29	0.44	0.81
4	Oxidized Biochar	1.78	0.95	0.95
5	Biochar	0.41	2.77	0.97
6	Straw	0.31	1.51	0.98
7	Rice Husk	0.25	2.45	0.86
8	Tree Leafs	0.24	19.59	0.24
9	Woodchips	0.21	6.85	0.83
			avg	0.82

The rank order of the adsorption capacities (K_F) for the Freundlich isotherms are river flocs (K_F = 31.581) > tap flocs (K_F = 13.66) > low MICS (K_F = 4.24) > oxidized biochar (K_F = 0.71) > biochar (K_F = 0.31) > tree leaves (K_F = 0.24) > woodchips (K_F = 0.19) > straw (K_F = 0.18) > rice husk (K_F = 0.17). Affinity (1/n) values estimate the binding strength of the material and should range between 0.2 – 0.9. Therefore, n values closest to 1.0 would have the greatest affinity copper (II) ion. This of course excludes any values < 1.0, because that would produce an affinity (1/n) value greater than 1.0, which is not possible, in regard to the Freundlich equation. The adsorbent with the greatest affinity was low-MIC (n=1.76) then tap flocs (n = 1.84), oxidized biochar (n=1.85), biochar (n=2.02), straw (n = 2.45), rice husk (n = 2.49), woodchips (n = 3.44), tree leaves (n = 7.2) and river flocs (n = 7.35).

Table 10: Ranked Freundlich adsorption capacities

Rank	Sorbent Material	Freundlich Constants		
		K_F	n	R^2
1	River flocs	31.581	7.35	0.61
2	Tap flocs	13.66	1.84	0.96
3	Low MICS	4.239	1.76	0.79
4	Oxidized biochar	0.714	1.85	0.88
5	Biochar	0.31	2.02	0.96
6	Tree leaves	0.24	7.20	0.23
7	Woodchips	0.19	3.44	0.89
8	Straw	0.179	2.45	0.93
9	Rice husk	0.168	2.49	0.85
			avg	0.79

Humic Substance Effects (Alum flocs)

The relationship between humic substances and metals is not well understood, because of the many differences in structure and chemical structure between humic substances that can be found in natural waters. However, empirically it is known that humic groups such as fluvic and humic acid can significantly change the speciation of heavy metals in natural waters between particulate and dissolved states (Snoeyink and Jenkins 1980). This is the reason why batch adsorption experiments were conducted with fluvic and humic acid collected from the Suwannee River in Georgia, which is standardized humic substances for laboratory research. In the experiment 0.3 g of flocs were added with a varying amount of humic or fluvic acid prior adding the initial copper (II) metal concentration. It was thought that the humic substance might bind with alum flocs and increase the adsorption capacity of the material. However, it is apparent in Figure 33 that the addition had negligible effect in increasing adsorption. However, sample sizes were small, and not repeated so the results are inconclusive.
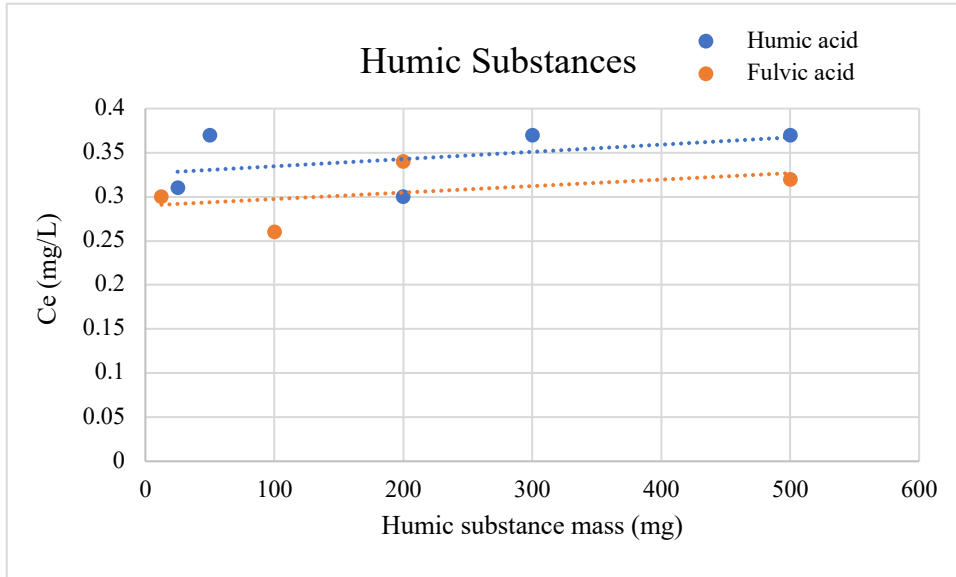
Figure 33: Humic substance comparison

Oxidation Effects (Biochar)

Oxidation of biochar was done in the lab by heating the biochar to 400° C in the oven for a period of 30 min. This process was meant to increase the oxygen-containing functional groups on the surface of the biochar, which theoretically should increase adsorption. This hypothesis was found to be correct oxidized biochar having a greater copper-binding ability (q_M = 1.78 mg/g) then regular biochar (q_M = 0.41 mg/g). This was an interesting finding, because it meant that existing functional groups on the surface of biochar were further activated, or potentially new surface groups were created in the process. This would mean that more surface complexion would occur as a result of oxidation. Unfortunately, this experiment was completed post-column trials, because it would have been interesting to determine how the oxidized surface maintained its integrity and activation throughout repeated adsorption/desorption cycles in column experiments. Although regular biochar did not perform much better than the control in

column experiments. It is possible that the oxidized biochar could have had a high

enough affinity for copper (II) ion and quick enough reaction rate to reduce the negative

effects such as reduced contact time that the column experiment presents.

Iron Concentration Effects (MICS)

Modified iron-coated sand was produced in lab, following a similar method that

Edwards and Benjamin created in 1989. However, the method instead of performing

titration into a 10^{-2} M $Fe(NO_3)_3$ solution that was meant to form several coats of

ferrihydrite. The method was simplified by conducting the precipitation in a single phase

by pouring weak base into a solution of 10^{-2} M $Fe(NO_3)_3$. Other publications had

indicated different iron (III) concentrations used to coat the sand, so this was replicated in

the lab. Three different initial concentrations of iron (III) were evaluated (1.) 0.025 M

$Fe(NO_3)_3$, (2) 0.05 M $Fe(NO_3)_3$, (3) 0.1 M $Fe(NO_3)_3$, (4) 0.25 M $Fe(NO_3)_3$ and (5) 0.5 M

$Fe(NO_3)_3$. These batches each created around 50 grams of sand, so the iron precipitate

coated onto the sand could be given as (mol/g) or Fe^{3+} moles / grams of sand. If 100

percent efficiency is assumed for the iron precipitate attachment to sand, which is

probably far from accurate, being more around 30 percent according to Benjamin and

Edward, then each batch could be categorized as (1) 2.5 x 10^{-5} mol/g, (2) 5 x 10^{-5} mol/g ,

(3) 1 x 10^{-4} mol/g, (4) 2.5 x 10^{-4} mol/g and (5) 5 x 10^{-4} mol/g. It is established that 1 x

10^{-4} mol/g corresponds to low MICS and 5 x 10^{-4} mol/g corresponds to high MICS. The

results from the batch experiments indicated that adsorption increases between 2.5 x 10^{-5}

mol/g to 1 x 10^{-4} mol/g concentrated MICS, however the adsorption plateaus afterwards

between 1 x 10^{-4} mol/g and 5 x 10^{-4} mol/g. It should be mentioned that the method

developed by, Benjamin and Edwards included drying the MICS at 550 °C. However, the

MICS sand that was produced using this method, and analyzed in column sequence 1 had

the iron-coated shells dissolve after only a couple adsorption/desorption cycles. This is

the reason why the method was altered so that the MICS was dried at 110 °C, which

increased the longevity of the iron-coated shell.
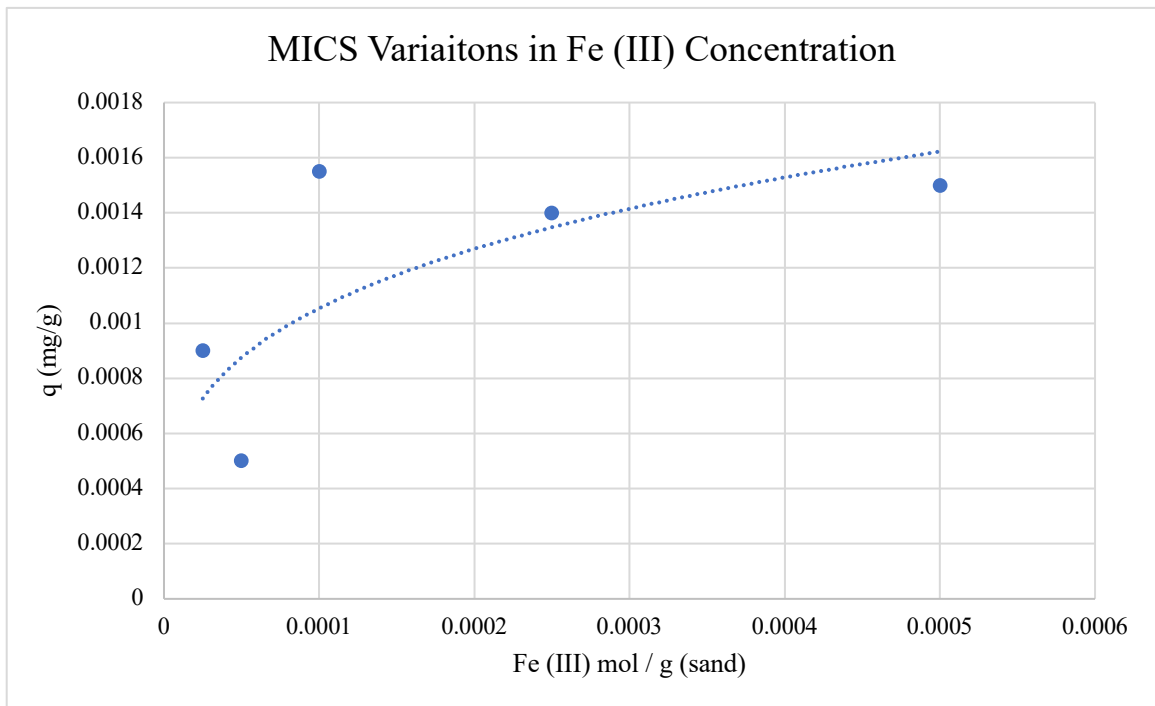
Figure 34: Variations in amount of Fe(III) precipitated for MICS production

This indicated that after 1×10^{-4} mol/g that the sand granules had been sufficiently

coated, so that any further increase in iron-oxide precipitate would not attach to the sand

granules. However, it could be that if the method put forward by Edwards and Benjamin

was used that more coatings could have been produced. Nevertheless, it was established

that low MICS or 1×10^{-4} mol/g was suitable concentration. This conclusion was

questioned, though from the column experiment results between low MICS and high MICS, which will be discussed in further detail later. Lastly, it should be noted that the process of MICS production was highly variable, because it could not be accurately determined what percentage of the iron-oxide actually attached itself to form a coating on the sand.

Errors

The linearization was acceptable for both models, however certain errors may have occurred for low modified iron-coated sand (MICS), river flocs, woodchips, rice husk and tree leaves. Some of these errors could be attributed to leaching of the adsorbent into solution, causing a change in color of the solution. This is important because the concentrations were measured with Hach colorimeter, which utilizes solution color to directly measure concentration, and assumes that a concentration of zero corresponds to a clear solution. For example, biosorbents like woodchips and tree leaves continued to leach tannins and other organics into solution even after several rounds of treatment with dilute 0.1M HCl. River flocs would produce a brown solution most likely caused by the leaching of sediments retained in the floc matrix, and low MICS would leach excess iron into solution from the coating, causing the solution to hue red. These solution color changes only occurred when a significant dosage of adsorbent was added, and the change was usually low, however was enough to affect the results.

Another possibility was the presence of suspended particulate from the adsorbents sometimes present in solution that would not settle. This usually occurred for biochar and oxidized biochar when the adsorbent dosage was increased substantially to extend the

isotherm. The solution could not be filtered, because then the copper (II) ions would also be filtered, instead the supernatant had to be carefully collected, avoiding any suspended particulates.

Other sources of error include the possibility of interference from iron and aluminum ions in solution for the copper measurement, using the Hach spectrophotometer. However, these concentrations were kept below the maximum iron and aluminum concentrations recommended in the Hach methods for interference to not occur, so this is probably not a source of error. It should also be mentioned that flame atomic adsorption (FAA) is traditionally used in similar published research, which would negate any solution coloration effects.

Fixed-Bed Column Experiments

It was previously stated that the column parameters included a flow rate of 5 ± 1.0 ml/min, because it would most closely replicate the natural flow rate through sand media, which is what the column was primarily composed of. This flow rate limited the contact time of the adsorbent and passing copper (II) ions, which meant kinetic factors and reaction rates would be most important in determining how much copper would be absorbed in the column. Every column experiment, except column experiment 3, because it was a comparative study, included a control which was a column filled with laboratory grade sand. This was used as a benchmark for other columns in determining whether or not there was any increase in adsorption. However, since the initial metal concentration and other parameters varied from one column experiment to another, separate controls had to be created for each trial. Surface water collected from the Red River was used for

all column experiments but was filtered to remove turbidity. This included both the adsorption cycle, which was copper spiked surface water, and the desorption cycle which was a simulated backwash with non-spiked surface water. This was meant to simulate wet and dry periods experienced in stormwater hydrology, and also to determine how much copper would be retained on the adsorbent surface, during the desorption phase.

Column Sequence 1

This was a general column trial to compare adsorbents that had acceptable adsorption capacities, determined from isotherm profiles, in non-equilibrium conditions. The results from Figure 22 were quite surprising, because of how marginal many of the adsorbents with good adsorption capacities performed compared to the control. This column was run with an initial metal concentration of 5.5 Cu^{2+} mg/L, during the adsorption cycle, which is quite high. However, it was thought that given a high concentrated metal feed any adsorption that would occur in the column would be measured. However, it should be noted that as the metal concentration increased the adsorbent dosage probably should have increased as well.

It was determined that the only suitable adsorbents that could continue with column testing were river flocs and low MICS. The river flocs were kept simply because of how high the maximum adsorption capacity was for the material. The materials initial column run was unremarkable at best. It was difficult to ascertain how much iron-oxide was attached to sand, in order to estimate how much adsorbent was being used, because all other adsorbents examined were measured to 0.5 grams. However, if a 30 percent efficiency is assumed for the amount of iron precipitate that would attach to the sand,

then around 0.32 grams of Fe (III) would have been on the sand granules in the initial trial.

Low MICS was initially produced with two different methods. The 550°C low MICS (0.0001 mol/g) is like what the name implies, the sand was dried in the oven at 550°C, because the thought was that the high temperatures would crystallize the iron-coating possibly hardening it, giving it more strength and durability. The 110°C low MICS is similar, but it was dried at 110°C. It was quickly discovered that the 550°C low MICS sand could only survive a couple adsorption/desorption cycles before the majority of the iron-coating was dissolved, causing the effluent to turn red, which was undoubtedly a substantial problem. This is the reason why the 550°C low MICS was scratched, and the original method of drying at 110°C was kept.

Column Sequence 2

This column trial is similar in many regards to the prior experiment; however, it only examined a floc amended column against a control column, and it was extended for multiple cycles to determine when column exhaustion would occur. In Figure 23 a profile graph of time vs effluent concentration is given for both columns. It is apparent that the curves are very similar in shape, and the percent removed (Ce/Ci) is similar. The floc amended column, which was created with 0.5 grams of dried river flocs, only minimally absorbed more than the control. In Figure 24 the mass retained curves are given for the floc amended column. This graph was created by graphing the area under the influent concentration and effluent concentration curves, which were determined using Origin software, against the column bed volume. This bed volume was calculated by dividing

the treated volume, or the effluent volume, by the active volume of the column, which

was taken as the area of the column multiplied by the length of the bed, not including the

subbase. Once this was completed the influent area and effluent area could be subtracted

to determine the cumulative copper mass retained in the column. It should be noted that

the influent area is more of a theoretical value that was based on the copper metal

concentration of the adsorption and desorption cycles. It is clear from Figure 24 that the

amount of copper retained decreases after every adsorption cycle, because the slope of

the line decreases.

In Figure 25 the same results are given but for the control column. It happens that

the retained curve and area under the effluent curve match each other. It is not certain if

this is mere coincidence, because it would be thought that the same action would have

been observed then in the floc amended column. Nevertheless, Figure 26 presents the

final results for column experiment 2, which is essentially the river floc amended column

cumulative mass retained (CMR) curve subtracted by the control CMR curve to give just

the floc CMR curve. It is clear that the river flocs only slightly enhanced the column

adsorption compared to the control. However, it can be observed that near the end of the

experiment the CMR levels off around 0.5 mg, which if taken as the point that column

exhaustion occurs, would mean that flocs have a 1:1000 ratio for every 1000 mg of flocs,

1 mg of Cu^{2+} ion would be adsorbed under the given conditions.

Column Sequence 3

This column trial was done to compare the differences between well-mixed and

layered low modified iron-coated sand (MICS) columns. These columns were composed

of 20 grams MICS, 20 grams sand and 15 grams no. 8 subbase, so everything was kept the same only 20 grams of MICS sand replaced the regular control sand. It differed from previous column sequences in that the influent copper (II) concentration, during the adsorption cycle, was reduced to 1.1 ± 1.0 mg/L. This experiment was conducted to ascertain whether or not a difference in adsorption would occur, depending on how the adsorbent was placed in the column, which would have important repercussions in any large-scale applications in LIDs, for example. It also addressed potential preferential pollutant pathing through the column, which would allow for the pollutant to bypass contact with the adsorbent, if such paths were available. It was discovered though that no discernable difference in adsorption existed between the layered and well-mixed MICS columns, which is clear in Figure 27. This was a good result, because it indirectly indicated that bioretention cells or other LIDs amended with MICS would not require to be well-mixed for optimal pollutant removal performance, which would cost more money, and also make any maintenance or removal of the MICS adsorbent tedious and labor-intensive.

In Figure 28 the cumulative mass retained (CMR) is given for the layered low MICS column. The same was not performed for the well-mixed column, because the results were similar for both columns. However, the layered low MICS did have a modestly greater copper percent removal than the well-mixed low MICS column. All the same, Figure 28 is an interesting graph, because the point of column exhaustion is quite unambiguous. Where the retained or CMR curve and effluent area curve diverge around the end of the second cycle. At this point any further copper that is removed from solution in the adsorption cycle is released in the desorption cycle. However, more bed

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volumes and cycles would have had to been completed to determine this implicitly. If 1.5 mg of Cu^{2+} ion is taken as the point of column exhaustion, then low MICS would have an approximately 1:1250 ratio of removal. For every 1250 grams of low MICS, 1 gram of Cu^{2+} ion would be removed. This of course includes the initial weight of sand into the calculation, not just the mass of the iron-coating. Since, a control was not conducted for this comparative study, because the peristaltic pump is limited to only two lines in parallel, the cumulative mass retained from just the iron-coated shell cannot be determined. However, this is uncovered in column sequence 4.

Column Sequence 4

In this final column trial, high modified iron-coated sand (MICS), or 0.005 mol/g MICS, was tested simultaneously with a control. It was an interesting result, because although it had been previously established that there was negligible difference in the adsorption capacity between low and high MICS sand, during batch adsorption experiments. Column sequence 4 demonstrated quite convincingly that there is a significant difference in the adsorption capacity. This evidence can be discerned in Figure 35, which graphs the effluent concentration vs. time profiles of layered low-MICS from column sequence 3 with the profiles of the control and high-MICS from column sequence 4. It is difficult to comprehend immediately, because the timing intervals between the adsorption/desorption cycles are different, but the peaks of the adsorption curve give clear indication of enhanced percent removal from low to high MICS.
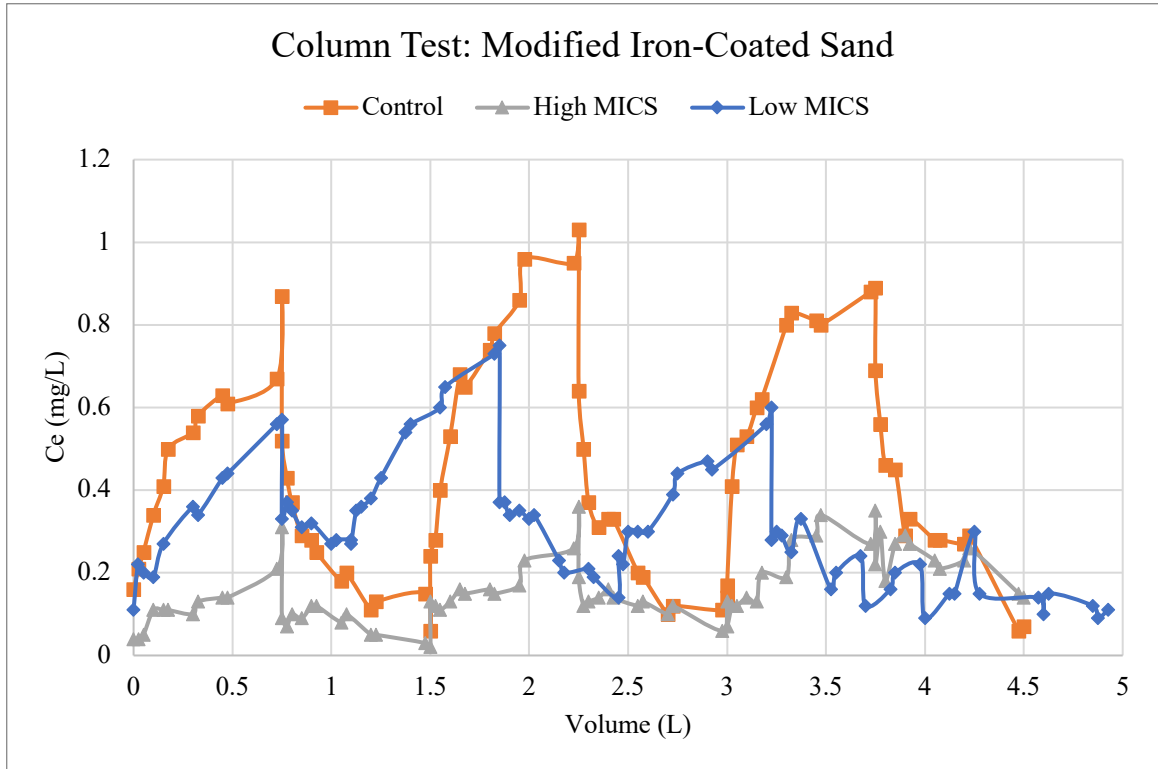
Figure 35: Column experiment C_e vs time for low-MICS, high-MICS and control

In Figure 30 and 31 the high-MICS and control cumulative mass retained (CMR) profiles are given. The high-MICS CMR continues to increase before becoming exhausted after about 750 bed volumes, which is around 500 more bed volumes than low-MICS became saturated. Intriguingly in Figure 31 it is clear-cut when the control column becomes exhausted, because the CMR curve flat-lines at around 400 bed volumes, which might suggest that the low-MICS column was not completely spent in column sequence 3. Regardless, it is apparent that the controls maximum CMR is around 0.75 ± 0.05 Cu^{2+} mg for these column conditions, because if the control from sequence 2 is examined again in Figure 25 it is obvious that the CMR is well above 0.75 mg Cu^{2+}. But that

column sequence was conducted under different parameters, namely influent copper (II) concentration.

In Figure 32 the CMR difference between the control and high-MICS is given. The procedure was only somewhat difference from that done in column sequence 2 in determining the net CMR for river flocs. In this case, only 20 grams of regular sand was used for the high-MICS column, so only ½ of the CMR from the control was subtracted from the CMR of the high-MICS column. The Figure demonstrates conclusively an improved copper adsorption ability of the high-MICS column to the control, because the CMR is negligibly reduced when the control CMR is removed.

Chapter 5

<u>5 Conclusion</u>

The development of a sorbent material capable of retaining heavy metals that could easily be incorporated into stormwater control structures is an important task, and critical to the further development and application of low-impact developments in stormwater control management design. Several materials analyzed in this research showed promise in enhancing the removal efficiencies and retentions of copper (II) ion from aqueous solution, however many of these also had noticeable shortcomings or other limitations. Here is a quick run through of the results and interpretations.

Batch adsorption experiments determined that tap flocs had the greatest copper (II) binding strength with a maximum adsorption capacity of (q_M = 34.5 mg/g), produced with a Langmuir isotherm model, which was followed river flocs (q_M = 32.16 mg/g) > low MICS (q_M = 16.29 mg/g) > oxidized biochar (q_M = 1.78 mg/g) > biochar (q_M = 0.41

mg/g) > straw (q_M = 0.31 mg/g) > rice husk (q_M = 0.25 mg/g) > tree leaves (q_M = 0.24

mg/g) > woodchips (q_M = 0.21 mg/g). The Freundlich model adsorption capacities were

similar but had minor differences, instead river flocs had the greatest adsorption capacity

at (K_F = 31.581), followed by tap flocs (K_F = 13.66) > low MICS (K_F = 4.24) > oxidized

biochar (K_F = 0.71) > biochar (K_F = 0.31) > tree leaves (K_F = 0.24) > woodchips (K_F =

0.19) > straw (K_F = 0.18) > rice husk (K_F = 0.17).

Fixed-bed column experiments were then performed on sorbents that had high

adsorption capacities, namely river flocs, modified iron-coated sand, woodchips and

biochar. Four separate column sequences were conducted, each demonstrating the

importance of the limiting factor contact time in determining heavy metal percent

removal. The only sorbent material that did not struggle under fixed-bed column trials

was modified iron-coated sand, which had very high cumulative mass retained values,

around 3 mg copper (II) ion prior to column exhaustion, which compared to the control

cumulative mass retained value of < 1mg is a significant result.

Chapter 6

6 Further Research Needed

In terms of batch and column experiments some further factors that could be considered would be the effect that different soil media (i.e. clays) and mixed metal solutions and ligand solutions. Soil conditions are an essential factor in evaluating the effectiveness of many infiltration focused LIDs, because it determines the hydrologic conductivity and degree of infiltration allowed in a particular site. Since, most of the Red River valley soil horizons are comprised of fine clays and silts it would be interesting to determine how optimal bioretention cells and bioswales would be in this region, since clays have already been shown to be effective adsorbents to many heavy metals. It would be important to access the water storage capacity of these systems as well. On another note, metal competition would be an important factor to consider because any active functional sites would favor certain species to others, depending generally on the stability constant of the complex. This competition would also occur with other pollutants such as nutrients, which would be another thing to consider.

It would also be good to conduct further research in adsorbent materials to determine projected life spans of the material and determine what type of maintenance the materials would require. This information would be important in quantifying any economic cost for the structure and material and would serve invaluably for communities

in developing stormwater management programs that would utilize more LIDs in its design.

An important consideration highlighted by the National Review Council in its review of the state of urban stormwater management in 2008 was the need for additional research on the effectiveness of difference structural stormwater control measures (SCM), such as bioretention cells, at stormwater volume-reduction in different climate and soil conditions, and to simulate the benefits that come from volume-reduction such as increased infiltration, pollutant loading reduction, reduced flow velocity, etc. Factors that would be important are seasonal differences, time between storms, pollutant loading factors, etc. Therefore, it was suggested that research move away from percent removal of pollutant measured in batch and column experiments, and instead move towards SCM simulation and performance in actual field trials.

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Appendix

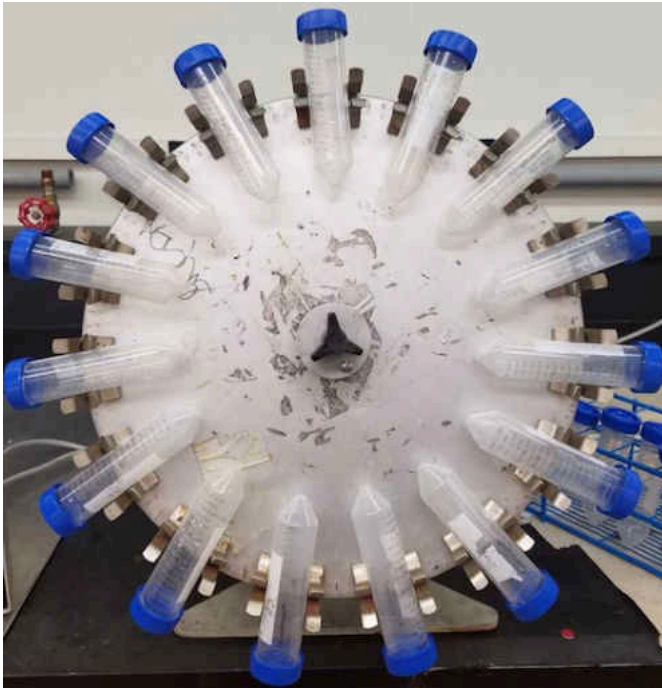**Organic Adsorbents**

Inorganic Adsorbents

MICS Concentration Variations

Hach DR 2000 Photospectrometer

Batch Experiment Rotator

550 °C Low-MICS Column

Column Experiment Set-up