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CHARACTERIZATION OF HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS USING NATURAL FIBER IMPREGNATED WITH METALLIC NANOPARTICLES

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CHARACTERIZATION OF HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS USING NATURAL FIBER IMPREGNATED WITH METALLIC NANOPARTICLES

By
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Abstract

Heavy metals are found in varying concentrations in anthropogenically influenced water sources including waste water discharge from mining operations. The heavy metals need to be removed to meet applicable discharge standards and to eliminate potential health effects. There has been substantial research recently in the field of water treatment technologies to produce low-cost materials that have metal-binding capabilities. The goal of this research is to characterize the toxic metal removal capabilities of a novel, low cost water treatment system.

This research uses a natural fiber substrate and incorporates specific nanometallic particles to remove toxic heavy metals from water. Natural fiber (NF) and metallic nanoparticle treated fiber (MNP) were subjected to various concentrations of copper, cadmium, nickel, and zinc. The research included kinetic experiments, adsorption isotherm experiments, and flow through column tests.

The results indicated that the fibers performed consistently well in removing copper with all metal removal efficiencies between 41%-58% for NF and 56%-77% for MNP in a mixed metal solution where the metals were each present at 1 mg/L. NF and MNP were both found to follow a pseudo first order kinetic adsorption model and had processes that followed Langmuir and Freundlich isotherms. MNP was able to reduce initial metals concentrations of 1 mg/L by 50% in 10-30 minutes whereas NF took 20-50 minutes. Metal adsorption is mass transfer limited and concentration gradients appear to be the driving force behind the adsorption rate.

Flow through column tests using synthetic mixtures of the four metals of concern, showed consistently high reduction in copper ranging from 78%-90%. Zinc consistently had the lowest removal efficiency and ranged between 24%-62%. A fortified mine tailing water solution with metals was also tested and removal efficiencies reached as high as 87%. MNP performed better overall in experimentation than NF. The fiber filter system is proven to be effective for treating heavy metal contamination from industrial waste streams.

Keywords: adsorption; heavy metals; water treatment; ion exchange; coir fibers; nanoparticles removal efficiencies

Dedication

I would like to say thank you to my family as well as to my boyfriend Derek for all of the love and support throughout this project. I would also like to thank my friends Garrett and Dylan and Professor Jeanne Larson who helped me in so many ways.

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**Committee Chair

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Glossary of Terms

Term	Definition
Coir Fiber	Coarse fibers harvested from the husks of coconuts
MNP	Metallic Nanoparticle Treated Coir Fiber
NF	Natural or Untreated Coir Fiber
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
ICS	Ion Chromatography System
US-EPA	United States Environmental Protection Agency
MCL	Maximum Contaminant Level
MDL	Minimum Detection Limit
MTDEQ	Montana Department of Environmental Quality

1. Introduction

Heavy metals are a common industrially sourced water contaminant that impacts ground and surface water across the world. There has been substantial research recently in the field of water treatment technologies to develop low-cost and sustainable materials that have metal binding capabilities. Industrial and agricultural by-products are of particular interest as substrates to remove metals. A variety of materials that have been examined in the past includes: rice husks, fly ash, peat moss, zeolites, clay, soft coal, and coir fibers. The goal of this research is to characterize the toxic metal removal capabilities of a novel low cost adsorption system.

1.1. Project Background

1.1.1. Pollution Problem

Although heavy metals are naturally occurring in the Earth’s crust, most environmental contamination and exposure to humans result from anthropogenic activities including mining, smelting, industrial production, and agricultural use (Haslego, 2010). Due to worldwide population growth, the demand for clean water has increased significantly. There is a growing demand for sustainable technology that allows efficient removal of metals from aqueous systems. The United States Environmental Protection Agency (US-EPA) defines heavy metals as “metallic elements with high atomic weight”, and it is understood that heavy metals pose significant health threats when they are released into the environment (EPA, 2000). These heavy metals have negative effects on aquatic flora and fauna as well as the potential for bioaccumulation. Since humans are at the top of the food chain, bioaccumulation increases the risk for toxic exposures. Table I shows heavy metals ranked in order of decreasing environmental risks.

Table I. Ranking of risks associated with various metals in the environment (Haslego, 2010)

Relative Priority	Environmental Risk
High	Cd Pb Hg
Medium	Cr Co Cu Ni Zn
Low	Al Fe

In this research four heavy metals are being studied; cadmium, copper, nickel, and zinc. These metals are capable of causing environmental and human health effects when present in the environment at unsafe levels. Metals persist in the environment and have the potential to enter water resources used for consumption by humans (Haslego, 2010). Cadmium and copper are among the contaminants regulated by the US EPA's National Primary Drinking Water Regulations and have legally enforceable standards that apply to public water systems (EPA, 2016). Zinc is listed in the National Secondary Drinking Water Regulations because it is responsible for causing a metallic taste when present above the secondary maximum contaminant level (MCL). Table II summarizes the US EPA Drinking Water Standards, Montana Department of Environmental Quality (MT-DEQ) aquatic life standards and health effects associated with each metal.

Table II. Standards and health effects for relevant metals (EPA, 2016) (Barakat, 2011)

Metal Of Concern	Drinking Water Standard (mg/L)	Aquatic Life Standards (ug/L) @ 25 mg/L Hardness (12)		Health Effects
		Acute	**Chronic**	
Cadmium	0.005	0.52	0.097	kidney damage, renal disorder, itai-itai, probable carcinogen
Copper	1.3	3.79	2.85	liver or kidney damage, Wilson disease, insomnia
Nickel	N.A	145	16.1	dermatitis, nausea, human carcinogen
Zinc	5	37	37	depression, lethargy, neurological signs, copper deficiency

1.1.2. Heavy Metal Treatments

Current methods to reduce heavy metals in water include: chemical precipitation, membrane filtration, coagulation-flocculation, ion exchange, and adsorption. Previous research conducted at Montana Tech suggests that coir fibers are able to remove heavy metals through a combination of adsorption and ion exchange mechanisms (Rediske, 2014).

1.1.2.1. Chemical Precipitation

Chemical precipitation is a widely used, proven technique for heavy metal removal. The process involves manipulating the chemistry of an aqueous system to encourage contaminants that are either dissolved or suspended to settle out of the solution as a solid. Once this occurs, the solid precipitant can be filtered, centrifuged or otherwise separated from the liquid. Dissolved and suspended metals are commonly precipitated from aqueous solutions as metal hydroxides through the addition of lime or sodium hydroxide (EPA , 2000). The advantages of chemical precipitation include low capital costs and simple operation procedures. The disadvantages include the generation of sludge and the additional costs associated with sludge disposal (Barakat, 2011).

1.1.2.2. Membrane Filtration

Membrane filtration processes such as reverse osmosis and nanofiltration were first developed for the creation of potable water. Recently they have been adapted to treat industrial wastewater for heavy metals. In order to preserve the filtration membranes, feed solution must be pretreated to optimize pH, remove physical media, and add anti-precipitant chemical controls. However, these processes have revealed instability of the membrane. These factors limited its use in treating waste water. The advantages of using a membrane system include small space requirement for operation, low pressure operation, and a high degree of separation selectivity (Barakat, 2011).

1.1.2.3. Coagulation – Flocculation

Coagulation and flocculation processes are used together to destabilize colloidal particles by adding a coagulant and disturbing the existing charges in the water, allowing the particles to undergo flocculation for easier removal. Despite being a good option for heavy metal removal, coagulation-flocculation processes have high operating costs due to chemical consumption and generates large amounts of sludge. Electrocoagulation is another alternative to traditional techniques that allows for less sludge generation but, it also creates a floc of metallic hydroxides which would require further purification (Barakat, 2011).

1.1.2.4. Ion Exchange

Ion exchange operates by exchanging equivalent ions on the solid phase adsorbent for an unwanted ion in the water. The goal of the treatment is to replace more hazardous materials in bulk phase with less hazardous materials exchanged from the ion exchange resin. Two components that are very important to ion exchange media are their engineering and physical properties (Crittenden, 2012).

The engineering properties include the ion exchange capacity of the resin and the resins' selectivity. Physical properties are characteristics of the resin that include swelling, durability, moisture, density and other factors that determine how useful the resin will be in water treatment processes (Crittenden, 2012).

Exchange capacity is the property of an ion exchange resin that quantifies the number of counter ions that can be exchanged into the resin. Selectivity refers to the way that different resins prefer certain ions over others in aqueous solutions. The selectivity is driven by physical and chemical characteristics of the exchanging ions as well as the resin itself.

There are two basic types of ion exchange resins; strong acid cation exchangers (SAC) and strong base anion exchangers (SBA). Strong acid cation resins are useful in removing all cation species (such as many heavy metals). They usually operate by exchanging either H^+ or Na^+ ions for the equivalent metal ions. This means that H^+ and Na^+ ions enter the fluid in exchange for the metals being removed. Ion exchange processes can be extremely efficient but are extremely pH dependent, and have a high capital and operating cost (Crittenden, 2012).

1.1.2.5. Adsorption

Adsorption is a mass transfer process in which contaminants in the liquid phase are accumulated on the surface of a solid phase adsorption material. The substance that is removed from the bulk solution is referred to as the *adsorbate* and the solid which collects the adsorbate is referred to as the *adsorbent*. Important factors that are involved in adsorption are surface area, and pore size. In general, the surface area and pore size are inversely related.

The term adsorption is actually a more general term used to describe two kinds of interaction between the adsorbate and the adsorbent. These interactions are referred to as chemisorption (chemical adsorption) and physisorption (physical adsorption).

Chemisorption is based on electrostatic forces between the adsorbent and adsorbate and is caused by covalent or electrostatic chemical bonds. These have a shorter bond length then physisorption and higher bond energy (Kelesoglu, 2007). The enthalpy of chemisorption is much greater than that of physisorption and the reaction is usually exothermic (Crittenden, 2012). In chemisorption the adsorbate is chemically bonded to the adsorbent so desorption is not usually possible and the adsorbate is bound at a specific site on the adsorbent. Chemisorption is also associated with monolayer adsorption because the adsorbate must be able to access a site on the surface of the material.

Physisorption is much more common than chemisorption in water treatment processes (Crittenden, 2012). Physisorption is caused by weak forces between molecules including dipole-dipole interactions, dispersion interactions and hydrogen bonding. In physisorption, the adsorbate is not fixed to a specific spot on the adsorbent and desorption is possible. Physisorption is also associated with multilayer adsorption since the adsorbate does not require direct access to the surface of the adsorbent.

There are three types of adsorbents that are commercially available for water contaminants: zeolites, synthetic polymeric adsorbents, and activated carbon (Crittenden, 2012)**.** Activated carbon is the most common of the three and comes in either a granular or powdered form. At present, the predominant application of adsorption in the United Stated is for taste and odor removal from water (Crittenden, 2012).

Adsorption is a practical and highly researched option for metal removal. The advantages include low cost, ease of operation, a wide operational pH range, and promising advancements in adsorption technology may make it one of the most environmentally sustainable options. Traditionally, sources of adsorbents are activated carbon, silica gel, and alumina, because these materials offer enormous surface areas per unit mass. The disadvantages may include low selectivity and the production of waste products (Crittenden, 2012).

1.1.3. Coir Fibers

Previous research performed at Montana Tech has shown that natural coir fiber (NF), and natural coir fiber treated with metallic nanoparticles (MNP) are effective in removing toxic metals from solution. The mechanisms involved are likely a combination of both adsorption and ion exchange processes. NF and MNP are shown below in Figure 1 and 2 respectively.

Figure 1. Natural Fibers (NF)

Figure 2. Metallic Nanoparticle Treated Fibers (MNP)

1.1.3.1. Properties of Coir Fiber

Coir fiber from coconut husks are an important agricultural waste product in countries like India, Tanzania, Kenya, Bangladesh, Burma, Thailand, Sri Lanka, Nigeria, Ghana, and Malaysia. Natural coir fiber has been examined for a variety of applications ranging from use in household textiles, gardening, sound adsorption, and heavy metal removal. (Alam, 2014)

Coir fibers are appropriate candidates for heavy metal removal in aqueous solutions due to their physical and chemical properties. Physically, coir fibers are 0.1-1.5mm in diameter and are of various lengths. They are durable, with a recorded elongation range of 30% before failure and will swell up to 5% of their diameter in water, equating to about 8 times their weight (Yoneda, 2012). Significant physical characteristic of coir fiber is that they are porous and have a very large surface area, which provides contaminants with many active sites on the surface to perform adsorption/ion exchange processes. According to a BET analysis performed in 2013, NF has a specific surface area of 50.2 m^2/g and MNP has a specific surface area of 177.3 m^2/g (Larson, 2013).

Chemically, coir fibers are composed of 45.84% lignin, 43.44% cellulose, 0.25% hemi-cellulose, 3.0% pectin, 5.25% water soluble compounds, and 2.22% ash. Coir fiber has a pH near neutral, ranging between 5.2 to 6.8 which makes it an attractive material for water treatment applications (Mathew, 2008).

A comparison of fiber surface morphology was examined using scanning electron microscopy by Eric Larson in 2013. This process allowed for a more thorough understanding of the physical properties of both types of fibers through a visual inspection of the fibers at varying magnifications as shown in Figures 3 through 8.

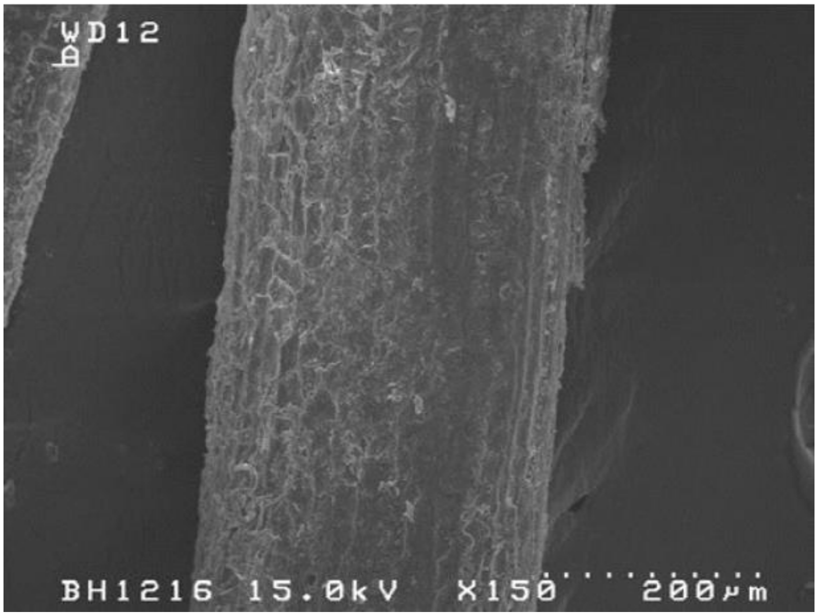

Figure 3. NF X150 magnification (Larson, 2013)

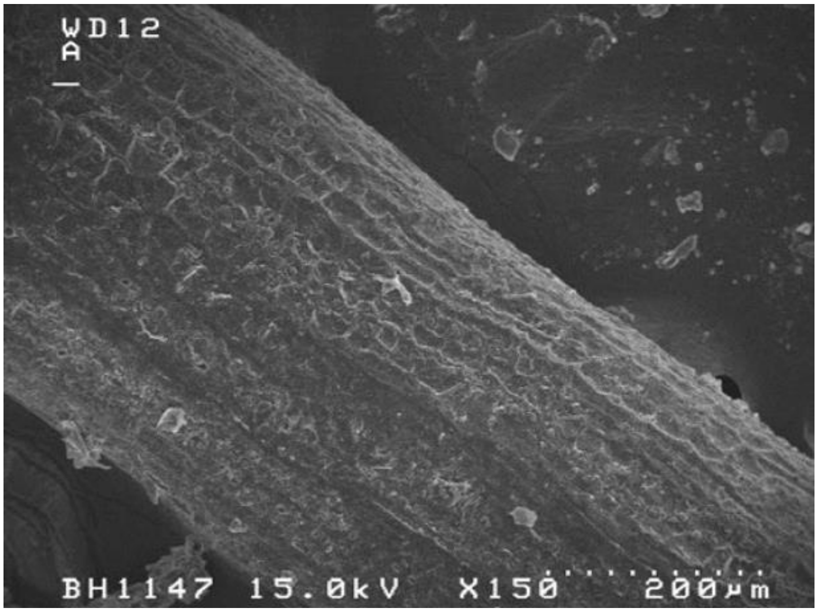

Figure 4. MNP X150 magnification (Larson, 2013)

At a magnification of X150 it is apparent that the two fibers are very similar in structure. They both have a somewhat coarse texture with visible cell wall structures.

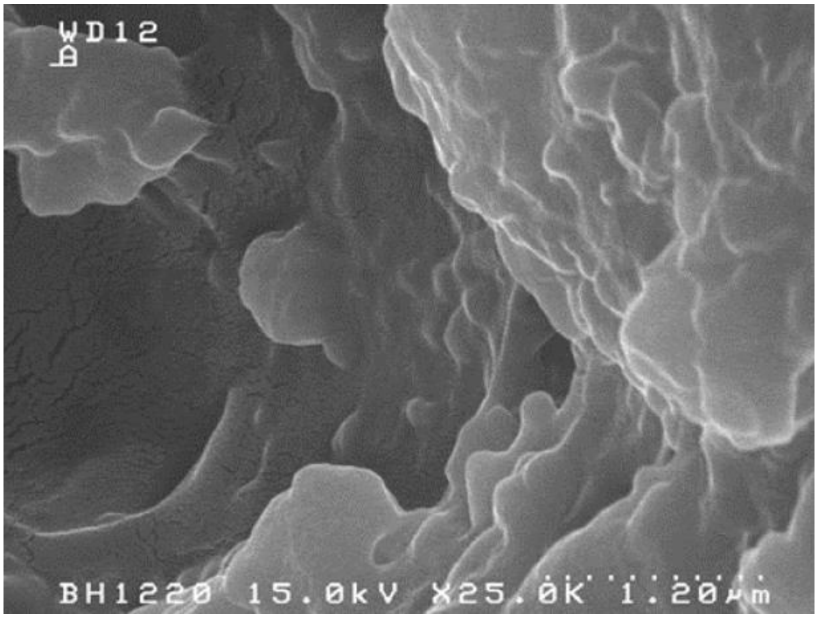

Figure 5. NF X25K magnification (Larson, 2013)

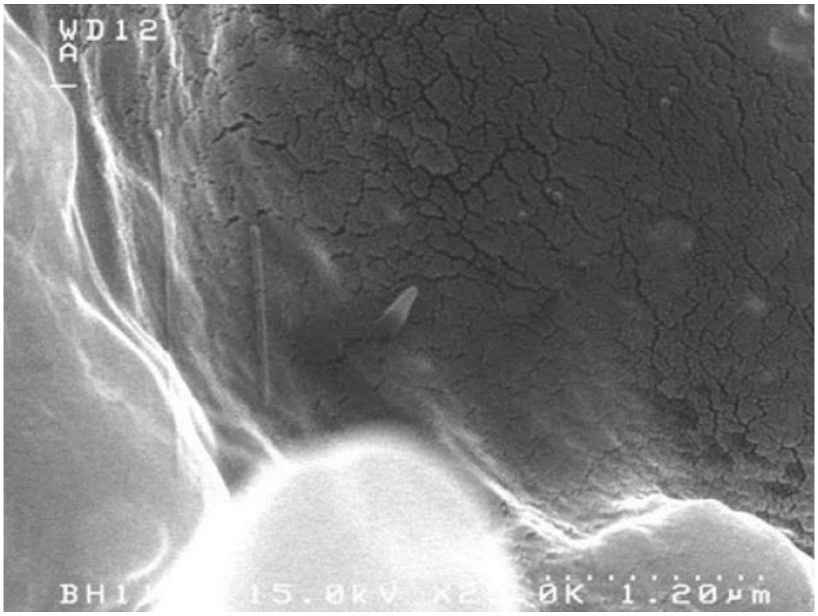

Figure 6. MNP X25K magnification (Larson, 2013)

At a magnification of 25,000X shown in Figures 5 and 6, the fibers begin to show more significant differences in surface structure. Both fibers appear to show deep pits that could be demonstrating pore spaces within the structure as well as similar ridges along the walls of the structure. It appears that the MNP have some foreign features attached to their surface in the form of a long rod-like structure and a protruding finger-like structure. This could be attributed to the metallic nanoparticle coating applied to the MNP.

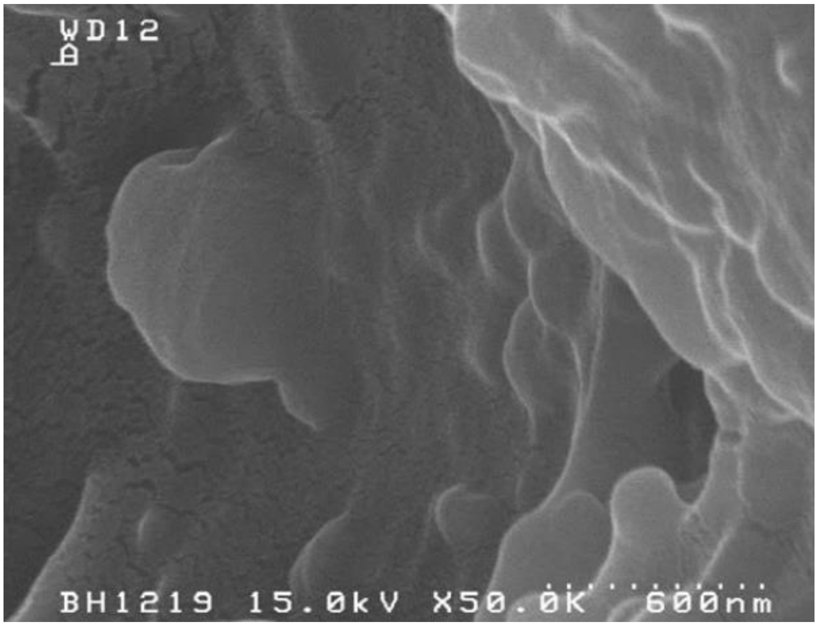

Figure 7. NF X50K magnification (Larson, 2013)

Figure 8. MNP X50K magnification (Larson, 2013)

At a magnification factor of 50,000X shown in Figures 7 and 8, more differences in the two fibers are revealed. There is more significant cracking on the surface of the MNP and the small structures become more apparent. This cracked texture and additional surface structures help account for the increased surface area of the fibers.

1.1.4. Previous Research – External Sources

Research has been conducted to evaluate coir fiber and other natural materials for use in heavy metal removal applications. While these data are relevant, it is difficult to compare due to the variations in experimental conditions such as metal species, temperature, pH, loading, time, and other factors that control overall fiber performance.

A study performed by affiliates of the United States Department of Agriculture (USDA) Forest Service compared coir fibers against materials such as spruce, sugarcane bagasse, kenaf bast, kenaf core, and cotton for its heavy metal removal as a function of each product's lignin content. The study suggested that tannin and lignin present in the materials are the active sites for attachment of heavy metal cations. The lignin was extracted from each product with various solvents, tested separately from the rest of the structure. Coir fibers have the highest lignin content compared to other products. It was found that all of the fibers with greater than 10% lignin contents adsorbed metals effectively. Products with low lignin content had poor results. It was concluded that overall performance could be more dependent on cell wall chemistry and architecture (Beom-Goo Lee, 2004).

1.1.5. Previous Research – Montana Tech

Montana Tech has produced various projects that used nanoparticle treated coir fiber to treat and remove heavy metals. Research initially began with an examination of mercury in air streams. The coir fibers were employed in the air streams to effectively scrub mercury from coal fired flue gas. This research showed over 90% mercury removal in the laboratory as well as in a flue gas from a coal fired power plant. This research is ongoing and promising results have made nanoparticle treated coir fiber an attractive research material for heavy metal removal.

Research then moved into aqueous solutions when Larson evaluated the removal of copper from aqueous solutions using the same MNP. Larson's thesis was titled "Evaluating the Performance of Natural Fibers Impregnated with Metallic Nanoparticles to Remove Copper from Aqueous Media." It was found that the treated fiber was able to reduce copper by 44.5% and zinc by 89.2% from contaminated storm water during a 24 hour continuous flow test (Larson, 2013).

Aqueous contamination research continued in 2014 with a project by Rediske, titled "The Characterization of the Adsorption of Cadmium from Aqueous Solutions Using Natural Fibers Treated with Nanoparticles." Rediske tested the fibers' performance on cadmium removal under various pH, metal concentration and fiber loading conditions. It was found that NF and MNP were able to remove between 0.2–1.4 mg/L at initial concentrations of 0.75 mg/L to 5 mg/L and that the fiber load was inversely proportional to the fiber mass and the initial cadmium concentration. It did not appear that pH had any significant effect on the adsorbent loading. (Rediske, 2014)

Rediske also observed that the heavy metal removal process consisted of two adsorption mechanisms. One process began as soon as the fibers contacted the contaminated solution and the second process began when the concentration profile leveled off, and the rate of adsorption decreased dramatically. During work with cadmium adsorption, it was noted that during the first mechanism of adsorption, calcium (Ca) and magnesium (Mg) concentrations increased in the solution. This suggested that removal was taking place using an ion exchange process. It was also noticed that during the second mechanism, no increase in these other elements occurred;

suggesting that the second method could be physisorption controlled by van der Waals forces. When NF was used, the Ca and Mg concentrations leveled off, whereas with the MNP, they decreased in the second mechanism. Rediske suggested that the MNP adsorbed Ca and Mg ions as well as cadmium during the second mechanism. (Rediske, 2014)

1.2. Objectives

The objective of this thesis research was to characterize the effectiveness of natural and treated coir fibers in the adsorption of multiple toxic heavy metals from an aqueous solution.

One objective was to evaluate two types of fibers, the first was natural coir fiber (NF) and the second was treated fiber which has been impregnated with metallic nanoparticles (MNP). Both fibers were evaluated to establish a comparison of which fiber type allowed for more effective removal of heavy metals.

The second objective was to quantify removal of four heavy metals commonly found in waters associated with the mining industry. Copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn) were chosen and it was the intent of this thesis to characterize the effectiveness of these fibers in the presence of multi-metal solutions. This project specifically focused on the dissolved form of these metals as they were deemed harder to remove and more hazardous. Experiments were conducted to establish an understanding of adsorption kinetics and the loading capacity of the fibers. This was accomplished by performing a series of static batch tests followed by the design and construction of a flow through bench scale application.

2. Experimental Approach

This section outlines experimental parameters and variables considered during experimentation. Research included batch test experiments as well as continuous flow column tests. Experimental parameters and considerations for each are described below.

2.1. Experimental Parameters

During both batch test and continuous flow experimentation, the following parameters were considered: time, temperature, pH, initial metal concentration, fiber/water ratio, and type of fiber.

2.1.1. Time

Time is a major factor in the adsorption of metals from water until equilibrium partitioning or exhaustion is reached. Previous research revealed that the fibers would do the bulk of their adsorption within the first two hours of contact with the water (Larson, 2013; Rediske, 2014). Experimental time was 8 hours for kinetics experiments and removal was evaluated more frequently during the first two hours of experimentation and then less frequently as time progressed. This gave a detailed concentration profile of the most efficient part of the process.

Isotherm experiments were timed so that the equilibrium partitioning was reached before the final sample was collected. Rediske (2014) conducted isotherm experiments out to ten days. Based on Rediske’s results it was deemed reasonable to reduce this time to 24 hours to gain the most critical data. Any additional removal past this time was very minimal and 24 hours was determined reasonable for a real world application to reduce contaminant levels to acceptable ranges.

Continuous flow experiments were designed to have an empty bed residence time of 30 minutes. Flow rate was set at 10 mL/minute which accounted for 15 minutes of contact between the fibers and the water in each column. This was determined to be sufficient time to achieve desirable removal efficiencies based on results from the batch test experiments.

2.1.2. Temperature

Temperature is an important consideration, especially when conducting isotherm evaluations. A consistent temperature of 20°C was maintained throughout experimentation to eliminate any variation in the characteristics of solutions and fibers. In order to accomplish this, 18 MΩ water was stored in an incubator at 20°C before use in experimentation. In addition, experiments were conducted in the incubator whenever possible.

2.1.3. pH

Since metal ions are less soluble in basic conditions, pH becomes an important factor to control in order to evaluate metal treatment processes. On the whole, an acidic pH ranging from 2-6 is effective for metal removal by adsorbents from biological wastes, including coir fibers (Barakat, 2011). Rediske (2014) found that a pH ranging between 3 and 9 had little effect on cadmium adsorption. It was summarized that the adsorbent load will have the same relationship with the mass of fiber between pH values of 3 to 9 (Rediske, 2014).

Considering the literature and conclusions made by Rediske, a pH of 3 was maintained as a base for experimentation. This value ensured that metals stayed in solution and were being removed by adsorption processes instead of precipitation, as well as provided acidic conditions to aid the performance of the fibers.

2.1.4. Initial Metal Concentration

It was established through literature review and previous research at Montana Tech that the initial metal concentration will influence the efficiency of adsorption due to concentration gradients. In general, as metal concentration increases, the loading on the fiber increases.

In this research, four metal species were tested (Cu^{2+}, Cd^{2+}, $Ni^{+}2$, and Zn^{2+}). They were tested as independent metal solutions and as a mixed solution of four metals. A concentration of 1 mg/L (1ppm) of each metal was used for all individual and mixed metal tests.

2.1.5. Fiber/Water Ratio

During experimentation, a ratio of 1 gram of fiber per 100 mL of water was utilized for kinetic experiments. However, for conducting the isotherm experiments the fiber mass was varied between 0.25 – 2.5 grams per 100 mL to determine equilibrium loading values. For the continuous flow column tests, 10 grams of fiber was packed into each column to treat approximately 1L of water per experiment.

2.1.6. Type of Fibers

The two types of fibers tested in this research were natural fiber (NF) and metallic nanoparticles treated fiber (MNP). The NF was purchased from the Carlsbad Manufacturing Corporation in Carlsbad, California. No pretreatment was done before using this fiber. MNP were developed using the NF as a base and then attaching nanoparticles of a particular metal using an in house procedure developed at Montana Tech. The particular metal and the process whereby it was attached to NF will not be discussed. Whenever possible, identical tests were performed with both NF and MNP to compare the performance of the two fibers.

3. Experimental Methods

3.1.1. Material Preparation

Natural fibers and MNP were provided by the Environmental Engineering Department at Montana Tech.

All metal solutions were prepared using 1000 mg/L stock solutions of the respective metals preserved in nitric acid. The stock solutions were diluted with 18MΩ de-ionized water obtained from the Montana Bureau of Mines and Geology located on the Montana Tech campus.

Labware utilized for experimentation included disposable plastic beakers, 20 mL syringes, 0.45 μm filters, and a 10 mL pipette with disposable plastic tips. These items were used only once to ensure that no cross contamination occurred between experiments. Any glassware used for mixing or during experimentation was acid washed in a solution of 10% HCl, and rinsed thoroughly with DI water between each use.

3.1.2. Kinetic Experiments

During the kinetic experiments, Cu, Cd, Ni, and Zn were examined individually in solutions as well as in a mixture that contained all four metals. Tests were performed using both NF and MNP. To perform these tests, two grams of specified fiber were added to 200 mL of each solution in 250 mL disposable plastic beakers. The beakers were sealed with Parafilm and left undisturbed between sampling. Each beaker was swirled by hand to mix the water before each sample to ensure the sample was representative of the entire solution.

A 10 mL sample was collected from each beaker at specific intervals starting with half hour, one hour, two hours and then every three or four hours after that. Once collected, the samples were filtered with a syringe and 0.45 μm filters, and acidified with trace metal grade nitric acid before analysis. The samples were stored at 4°C and analyzed within 48 hours of collection as outlined by EPA Method 200.7.

3.1.3. Adsorbent Load/Isotherm Experiments

In general, adsorption isotherms relate the amount adsorbed on the fiber to the concentration remaining in the solution. Adsorbent load capacity and isotherm parameters were developed using batch tests that examined equilibrium loading rates of different fiber/water ratios. Fibers ranging between 0 to 5 grams and 200 mL of the multiple metal solution containing 1 mg/L of all four metals were added to Erlenmeyer flasks. The initial pH, temperature, and metal concentrations of the solution were recorded along with the initial mass of fiber in each flask. The experimental set-up is shown in Figure 9.

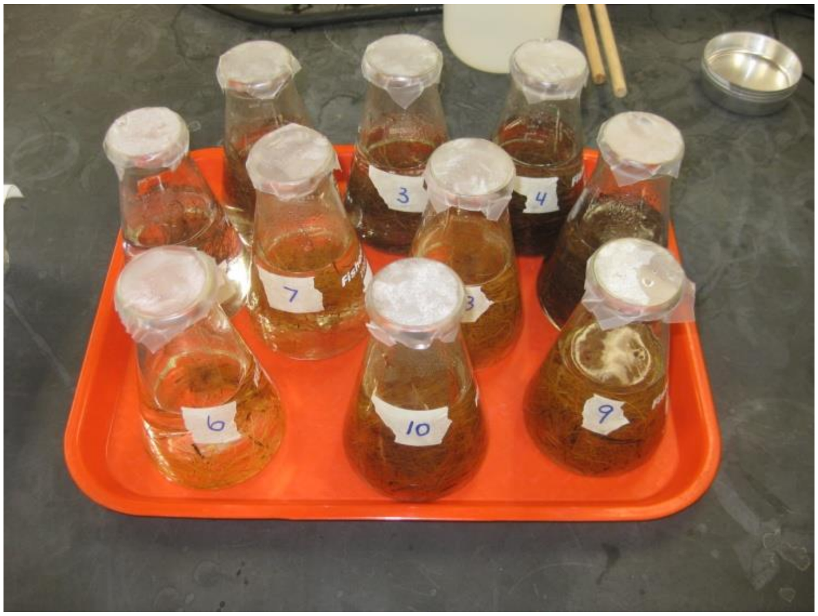

Figure 9. Adsorbent load and isotherm experimental setup

The flasks were then sealed with Parafilm and placed on a shaker table inside of an incubator at 20˚C for 24 hours. A shaker table was utilized to increase the rate of contact between the metal contaminants and the fibers. After 24 hours, a 10 mL sample of the solution was extracted using a sterile syringe and was filtered using a 0.45 μm filter. The solution was acidified with 1% trace metal grade nitric acid by volume before analysis was performed.

3.1.4. Continuous Flow Column Tests

A bench scale system consisted of two vertical columns connected in series with an upward flow. The columns were made of 1.5” clear composite plastic pipe, and were connected with 3/8”rubber tubing. The ends were sealed with white plumbing caps. Ten grams of designated fiber was weighed and packed into each column and compressed to a consistent 5.5 inch height to ensure uniform density. The fiber was held in place within the tube by an aluminum plate and metal spring. The column test apparatus is shown in Figure 10.

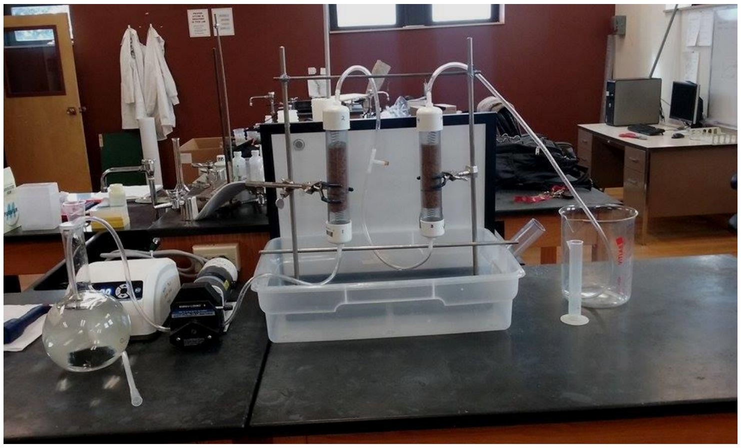

Figure 10. Continuous flow column test apparatus

Contaminated water was contained in a beaker at the start of the system and the rubber tubing was placed into the solution. A 10 mL sample was then collected from this beaker using a 10 mL pipette before experimentation began to quantify the initial concentrations of metals in the prepared solution. The sample was filtered with a 0.45 μm filter and acidified with trace metal grade nitric acid. The water was then pumped with a peristaltic pump through the columns and was collected in another beaker at the end of the system.

The peristaltic pump was maintained at a flow rate of approximately 10 mL/min. A stop watch was used to verify that the contact time between the fibers and the water was approximately the desired value of 15 minutes per column. Once the water filled the first column, a sample was collected 5 minutes after the water passed the sample port of the first column. A 10 mL sample was then collected to represent the effluent from the first column. The last sample was taken 5 minutes after water started flowing into the effluent beaker; this represented the effluent from the system. The entire bench scale system was disassembled and acid washed before it was packed with new fibers between each test.

3.1.5. Digestion of Fibers

Fibers were digested and analyzed to quantify the amount of metals adsorbed during the column test, and to provide a chemical composition of each type of fiber.EPA method 3050B was followed to carry out the acid/base digestion of the NF and MNP to better understand the composition of each fiber. EPA method 200.2 was used to perform the digestion of 0.45 μm filters used for filtering samples to analyze total recoverable metals used in the mass balance process. The digested liquid from both digestions was then analyzed to determine elemental composition using Montana Tech Environmental Engineering Department’s Thermo iCAP 6500 Duo-View Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

3.1.6. Mass Balance Procedure

In order to understand the distribution of metals in the column test, the fibers and the filters (with which samples were filtered) were digested as described, and analyzed for metals in addition to the water samples. These digested substrates were then analyzed for heavy metals as well as major anions using an ICP-OES and a Dionex Ion Chromatography system (IC) respectively.

4. Experimental Analysis

All samples were analyzed on campus in the Montana Tech Environmental Engineering Analytical Laboratory. The metals analysis was performed using the ICP-OES. A SEAL Analytical BD50 Block Digestion System was used to digest the samples and an ICS was used to analyze major anions. Table III summarizes the parameters being evaluated and the instruments.

Table III. Experimental parameters, instrumentation, and corresponding EPA Methods

Parameter	Instrumentation	EPA Method
pH, Temperature	Fisher Scientific AP115 pH Meter	N.A.
Dissolved Heavy Metals	Thermo Scientific iCAP 6500 Series ICP-OES	EPA 200.7
Digestion of Total Recoverable Heavy Metals	SEAL Analytical BD50 Block Digestion System	EPA 200.2
Acid Digestion of Coir Fibers	SEAL Analytical BD50 Block Digestion System	EPA 3050B
Major Anions	DIONEX ICS 2100 Ion Chromatography System	EPA 300.0

4.1. Sample Preparation

4.1.1. Total Dissolved Metals

For analysis on the ICP-OES, samples were collected using a 10 mL pipette and a disposable syringe. As discussed, each sample was filtered and acidified to maintain a consistent 1% nitric acid matrix that was used for all sample, blanks, and calibration standards.

4.1.2. Total Recoverable Metals

Analysis of total recoverable metals was performed during the mass balance procedure. In order to prepare samples for total recoverable metal analysis, a Block Digestion System was used to digest 0.45 μm filters used in the mass balance experiments. After digestion, the samples were allowed to cool to below 25°C before analytical analysis.

4.1.3. Major Anions

In preparation for analysis using the IC for major anions, samples were filtered through a 0.45 um filter and diluted to an appropriate concentration for accurate analysis. Samples were analyzed within 48 hours of collection without preservation, as outlined in EPA method 300.0.

4.2. Equipment Methods

4.2.1. ICP-OES Method (EPA Method 200.7)

An ICP-OES was utilized to quantify concentrations of dissolved heavy metals. This equipment has a low detection limit for elements with greater atomic masses, such as the metals being studied. This instrument was chosen due to the high number of elements that it examines simultaneously, along with its high sample throughput.

The ICP-OES was calibrated before each use to ensure the accuracy of results. A five-part dilution (0, 0.1, 0.5, 1.0, 2.0 ppm) was prepared from SPEX CertiPrep QC21 standard and the solutions were used to calibrate the instrument. The software creates a calibration curve of known concentrations versus elemental specific wavelength. Care was taken during calibration to maintain a percent difference of less than 10% for accurate results. Once calibrations were acceptable, the samples were analyzed. Three repeat injections of 1 mL of sample were analyzed and the reported value is the mean concentration.

4.2.2. Block Digestion Methods

The block digestion system was used to perform the total recoverable metals analysis used in the mass balance calculations, as well as to determine the chemical composition of both types of fibers following EPA Methods 200.2 and 3050B respectively. For both analyses, acid-based digestions were used to convert the original sample into a liquid analyte. A SEAL BD50 Analytical Block Digestion System was utilized because of its recommended use in EPA Method

200.2 titled *"Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements."*

Prior to analysis, the block digestion system was calibrated to within +/- 0.5° C. The system was then set up to increase in temperature at a rate of 1° C/minute and maintain a temperature of 95° C (+/-1° C) for the duration of the procedure. After completion, the samples were allowed to cool to below 25° C.

4.2.3. IC Method

A Dionex Ion Chromatography System was used to analyze anions. This system was used because it can inexpensively and accurately quantify high concentrations of particular anions simultaneously. The IC system utilizes an anion column with a nutrient specific retention time. The Thermo Scientific Chromeleon software plots the resulting retention time versus the measured specific conductivity, with the area under the resulting curve representing the concentration of the analyte in mg/L.

The ICS was calibrated before each use using a five part dilution of a pre-made standard. The dilution was used to create a five point calibration curve to ensure accuracy of results. EPA Method 300.0 "*Determination of Inorganic Anions by Ion Chromatography"* was used during the operation of this equipment.

4.3. Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) measures were followed to reduce contamination during experimentation and analysis. Contamination in any experiment could be attributed to the glassware used for experimentation, laboratory conditions, human error, contaminated fibers, contaminated chemicals, and other sources. The bench scale experiments were especially prone to contamination due to the amount of equipment that was directly involved in the process. This included plastic tubing and columns, metallic springs and plates used to hold the fibers in place, glue, caulking and other adhesives, and the rubber O-rings placed on the inside of the columns. Great care was taken in disassembling and acid washing the equipment before each experiment but many sources of contamination still existed. In order to quantify the contamination, various duplicates and sample blanks were performed with each analysis.

4.3.1. Sample Duplicates

Experimental duplicates were collected at the same time as the original sample to quantify variability of the experiment. One duplicate was collected per sampling event; with one duplicate being added for every ten percent of samples if the sampling included more than 10 samples. In addition, each experiment was repeated at least twice but in some cases, three times to ensure the reproducibility of the results. Lab duplicates were prepared from the original sample and were processed identically to the original sample to quantify the instrument variability. A duplicate was analyzed at least once every sample run.

4.3.2. Sample Blanks

Experiment blanks were used to verify the extent of lab contamination in the samples. These blanks consisted of testing coir fiber in DI water and also served as a way to observe contaminants released by the fibers into the water. Lab reagent blanks were used to classify background contamination in the DI water used to prepare experimental solutions. When mine water was being evaluated, a reagent blank was collected from the initial mixture as well.

Lab fortified blanks were used to determine error in the sample methodology and the accuracy of the instrumentation. A lab fortified blank was included with each sample run.

4.3.3. Calibration Standards

Calibration standards were used to calibrate the instruments before each sample run. Standards were prepared using stock solutions and 18 MΏ DI water. They were then used to produce a multipoint calibration curve which ensured accurate results.

5. Theory

5.1. Adsorption Kinetics

Kinetics refers to the rate at which the adsorbent removes adsorbate from the solution. It is important to understand the rate of removal of metals to gain an understanding of the mechanisms involved. Information about kinetics will also help to obtain design parameters such as residence time, flow rates, and sizing of the system.

5.1.1. Removal Efficiency

Removal efficiencies were calculated based on the decreasing concentrations of metals in the aqueous solution at each sample time interval using Equation 1:

$$Percent\ Removal\ Efficiency = (C_{TI} - C_{TF})/C_{TI} * 100 \tag{1}$$

where C_{TI} is the initial concentration of metal (mg/L) and C_{TF} is the final concentration of metal left in the aqueous solution (mg/L).

It is important to note that removal of 10 mL of solution at each sample event while the mass of fibers remains constant, changes the solution to fiber ratio. Therefore, the results are used for relative performance of the two fibers.

5.1.2. Kinetic Models

Kinetic models are useful in determining the nature of the adsorption process. In this analysis, Lagergren's pseudo first order and Ho pseudo second order kinetic model were considered. The general kinetic model for adsorption is shown in Equation 2:

$$dq_t/dt = k(q_e - q_t)^n \tag{2}$$

where dq_t/dt is the change in load with respect to time (mg adsorbate/g adsorbate/day), k is the rate constant and n is the constant that defines the reaction order, q_e is the adsorbent load at equilibrium and q_t is the adsorbent load at some time t (Criddenten, 2012).

5.1.2.1. Lagergren's Pseudo First Order Model

The pseudo first order kinetic equation has been widely used to predict metal adsorption kinetics (Criddenten, 2012). The rate equation for pseudo first order is shown in Equation 3 and is derived from the general kinetic model by setting n=1:

$$dq_t/dt = k_1(q_e - q_t)^1 \tag{3}$$

where k_1 is the pseudo first order rate coefficient (min^{-1}), and the quantity of fibers remains constant while the loading (mg/g) of dissolved ions changes. The term pseudo is used to imply that the amount of fibers is assumed to remain constant and that the rate is only dependent on the metal load on the fibers (Kelesoglu, 2007).

Equation 3 is integrated to give Equation 4 in a linear form as:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \tag{4}$$

where t is time in minutes.

If the reaction is first order, plotting $ln\ (q_e - q_t)$ versus t will give a linear plot. The negative value of the slope from this plot will then give the value for the pseudo first order rate constant, k_1 (Kelesoglu, 2007).

5.1.2.2. Ho Pseudo Second Order Model

The adsorption data can further be analyzed using a second order model such as the Ho pseudo second order model. When modeling a second order adsorption process, it is assumed that the adsorption capacity is proportional to the load of adsorbate on the adsorbent.

The equation for second order reactions is derived from Equation 2 and is shown in Equation 5:

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the second order rate constant (mg/g/day) (Kelesoglu, 2007).

The linearized version of Equation 5 gives Equation 6 and if plotting ($1/q_t$) versus t yields a linear trend, the process is second order.

$$1/q_t = 1/k_2 + (1/qe)t \tag{6}$$

It should also be mentioned that in theory, adsorption processes will either be pseudo first or pseudo second order but they cannot be mixed.

5.2. Adsorbent Load

The adsorbent load represents the mass of adsorbate that is adsorbed to the adsorbent material on a mass basis. The general equation for adsorbent load is given in Equation 7:

$$q_t = (V/M)*(C_o - C_t) \tag{7}$$

where q_t is the adsorbent load at a time t (mg adsorbate/g adsorbent), V is the volume of solution (L), M is the mass of adsorbent used (g), C_o is the initial metal concentration (mg/L) and C_t is the concentration of metals in solution (mg/L) at time t (Crittenden, 2012).

5.3. Isotherms

One way that adsorption can be analyzed is through the use of adsorption isotherms. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among the liquid and solid phases (Crittenden, 2012). The two most common isotherm models used in metal adsorption research are the Freundlich Isotherm and the Langmuir Isotherm.

5.3.1. Freundlich Isotherm

Freundlich isotherms are based on the assumptions that there is almost no limit to the amount of adsorbate that can be adsorbed and that it occurs as multilayer adsorption. The empirical formula for the Freundlich isotherm is shown below:

$$q_e = K_f C_e^{1/n} \tag{8}$$

where q_e is the amount adsorbed per unit mass of adsorbent at equilibrium (mg/g) or (mol/g), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/g) or (mol/L), K_f is the empirical Freundlich constant or capacity factor, 1/n is the Freundlich exponent.

5.3.2. Langmuir Isotherm

Langmuir isotherms are based on the assumption that there are a fixed number of active sites and therefore, that adsorption capacity is finite. This correlates best with the idea of monolayer adsorption. The empirical formula for the Langmuir Isotherm is shown below:

$$q_e = (QbC_e)/(1+bC_e) \tag{9}$$

where q_e is the amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/l), Q is the empirical Langmuir constant (mg/g), and b is the empirical Langmuir constant.

6. Results and Discussion

6.1. Kinetics Experiments

6.1.1. Removal Efficiencies

The concentration of metals left in solution in parts per million (ppm) versus the time in minutes that the solution has been in contact with the fibers is shown in the following figures. All solutions began with a concentration of 1-1.5 mg/L of the metal. Figures 11-18 display the concentration profiles of individual metals for natural and treated fibers. Each test was performed in duplicate.

6.1.1.1. Natural Fibers (NF)

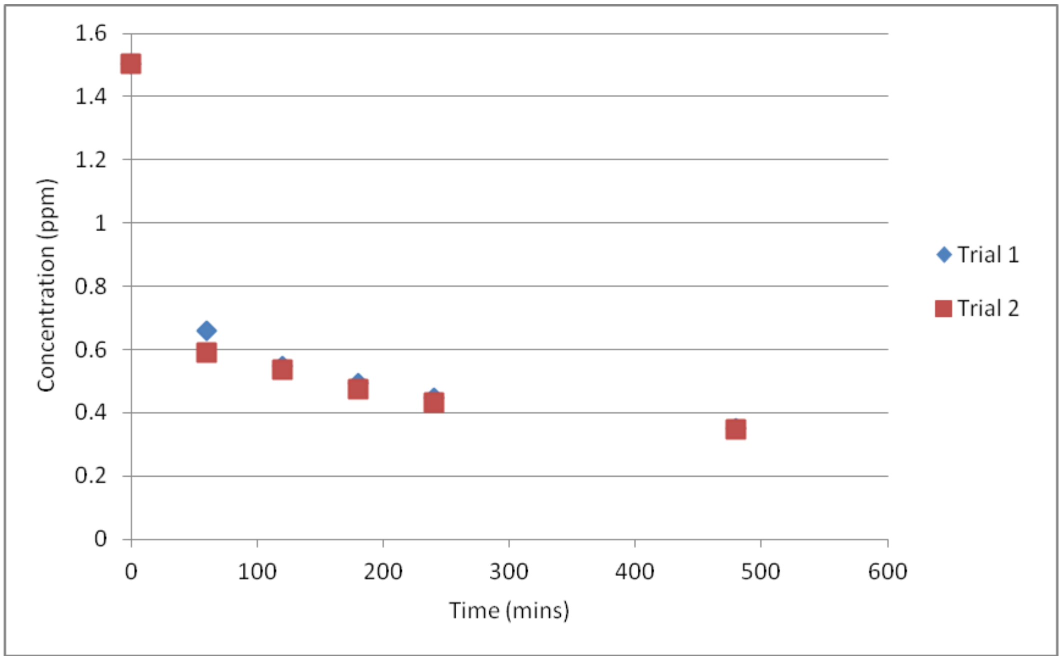

Figure 11. Concentration profile showing copper removal during treatment with NF

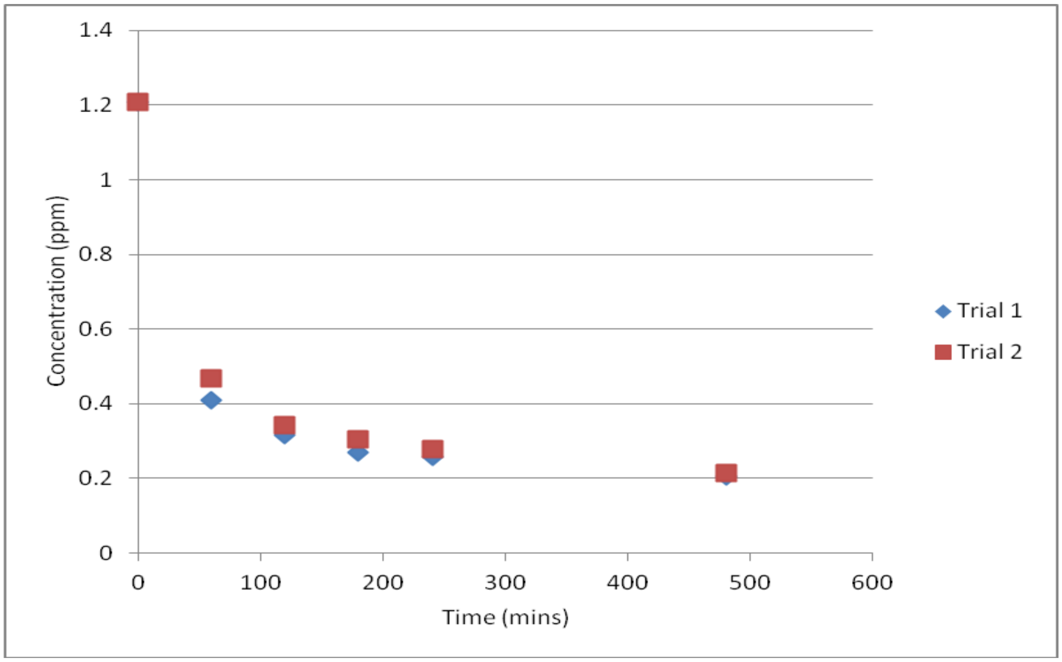

Figure 12. Concentration profile showing cadmium removal during treatment with NF

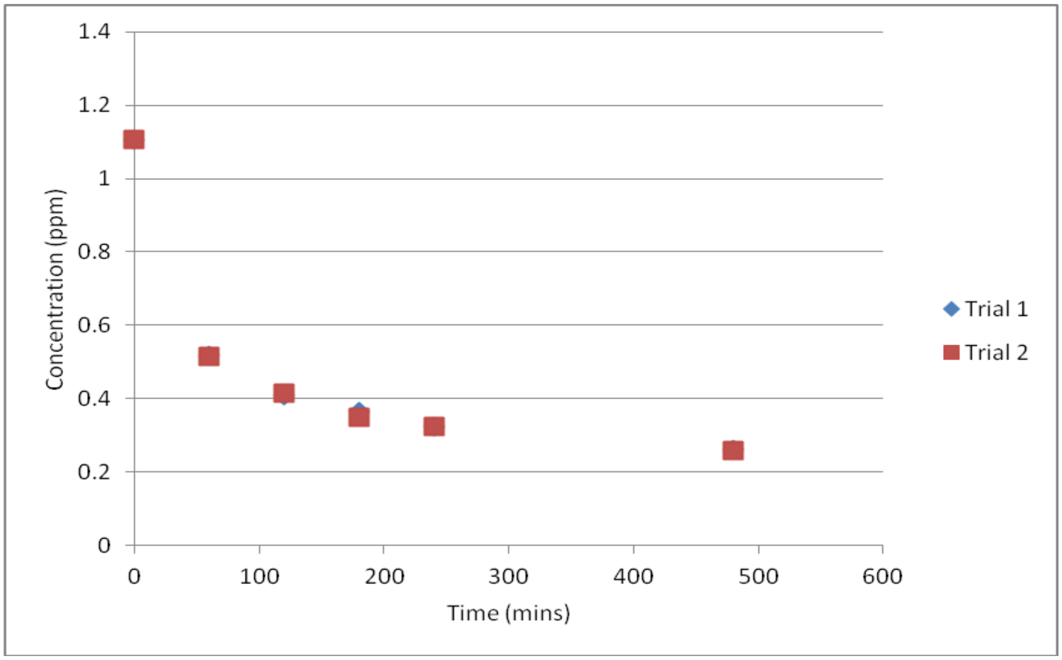

Figure 13. Concentration profile showing nickel removal during treatment with NF

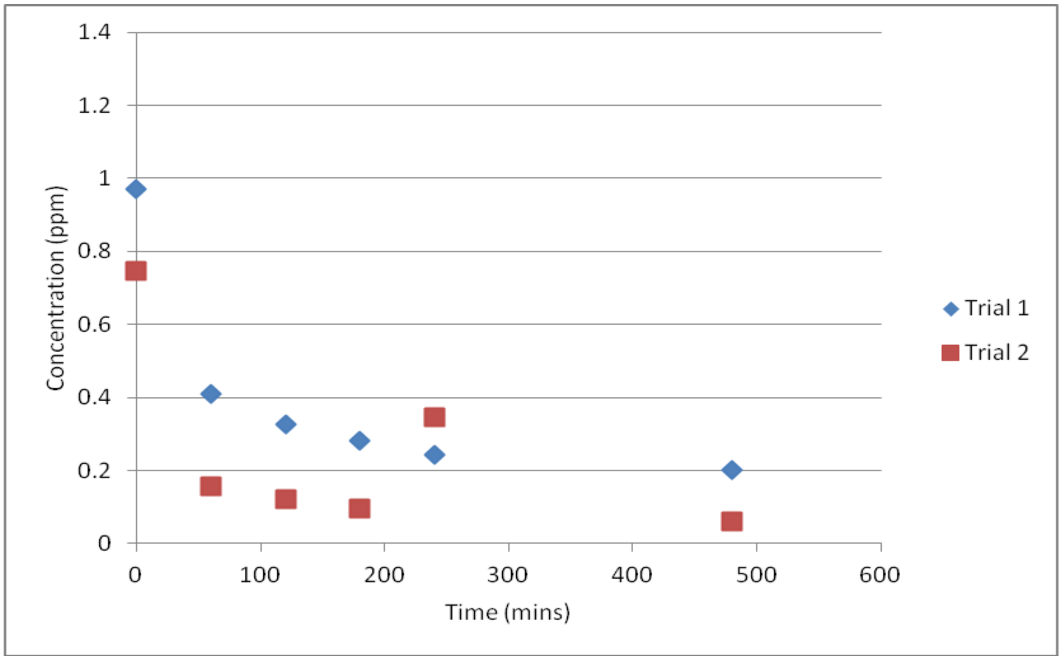

Figure 14. Concentration profile showing zinc removal during treatment with NF

6.1.1.2. Metallic Nanoparticle Treated Fiber (MNP)

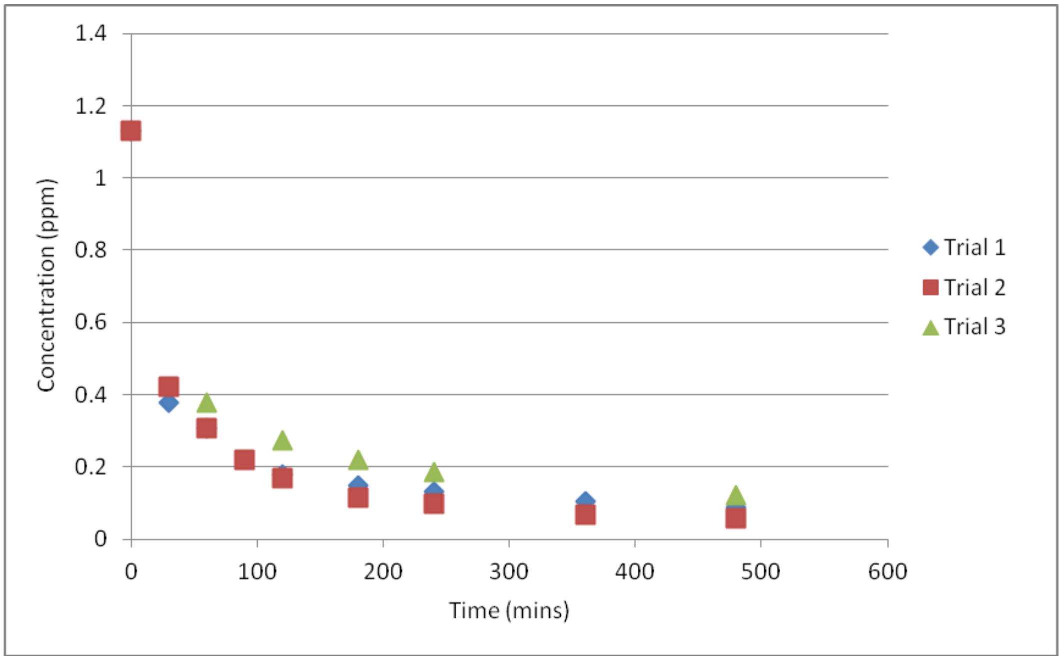

Figure 15. Trend showing concentration profile of copper during treatment with MNP

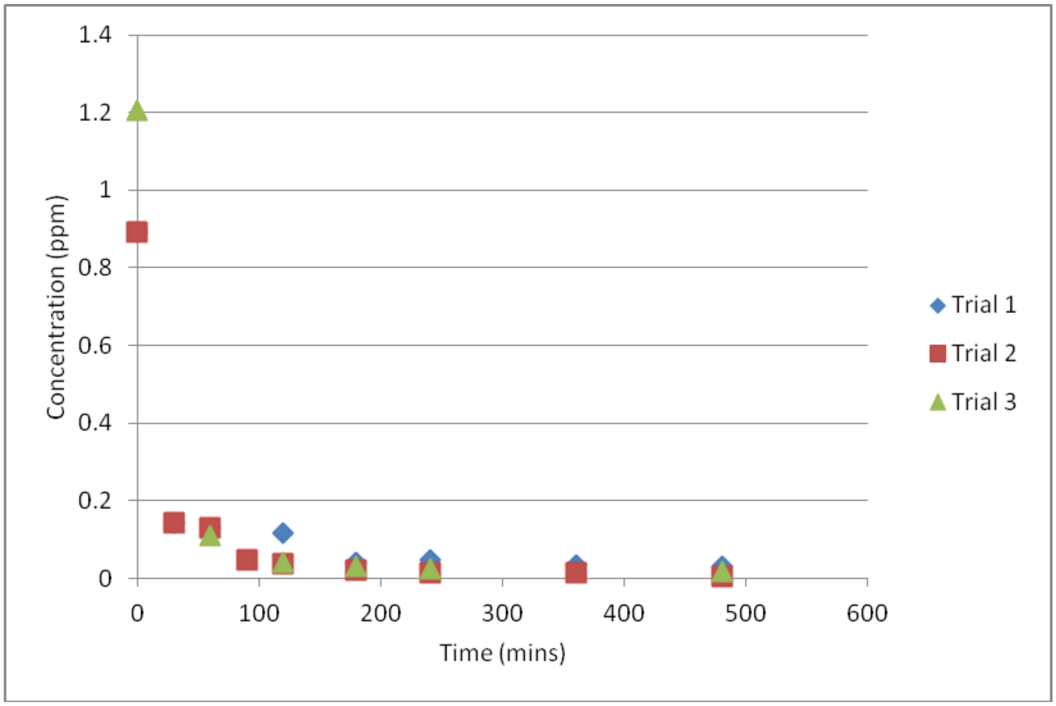

Figure 16. Trend showing concentration profile of cadmium during treatment with MNP

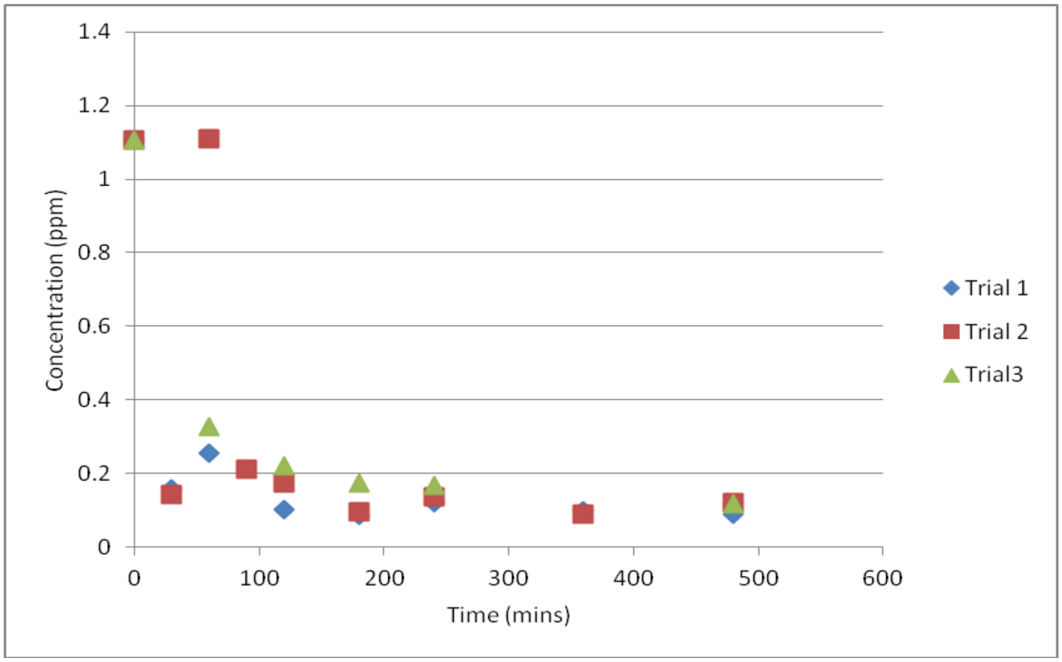

Figure 17. Trend showing concentration profile of nickel during treatment with MNP

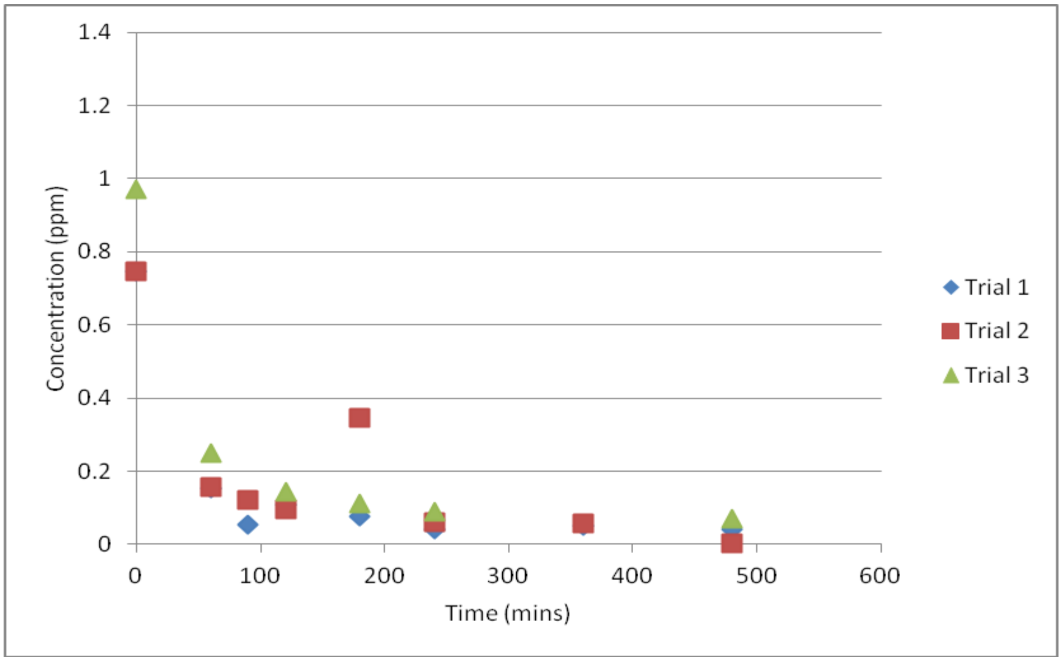

Figure 18. Trend showing concentration profile of zinc during treatment with MNP

Trends in both NF and MNP are similar and demonstrate that metals are adsorbed much faster at the beginning of the contact between the solution and the fiber. The time taken for 50% reduction in the initial concentration for each metal with the NF and MNP is given in Table IV.

Table IV. Time in Minutes for 50% Reduction in Initial Metal Concentration

Metal of Concern	Time for 50% metal Reduction by NF (min)	Time for 50% metal Reduction by MNP (min)	% change from NF to MNP
Copper	30	20	+33%
Cadmium	50	10	+80%
Nickel	50	30	+40%
Zinc	20	30	-33%

This table shows that the MNP was able to reduce the initial metal concentration by 50% in 10-30 minutes where the time range was between 20-50 minutes for the NF.

Figures 19 and 20 show adsorption trends in a multiple metal solution. In Figure 20, it is seen that cadmium, nickel, and zinc show desorption from the fibers while copper continues to be removed. This suggests that after the active sites are filled, copper may be preferentially exchanged for the other metals, demonstrating that copper may be removed at higher efficiencies than the other three metals tested.

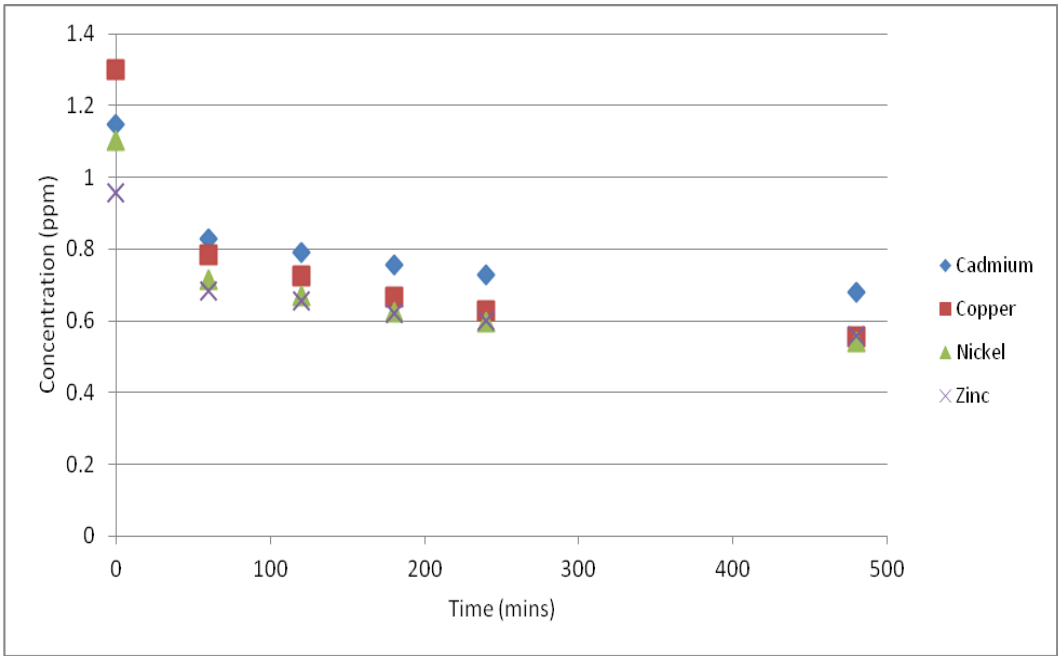

Figure 19. Averaged concentration profile of removal of metals from a mixed solution of copper, cadmium, nickel and zinc by NF

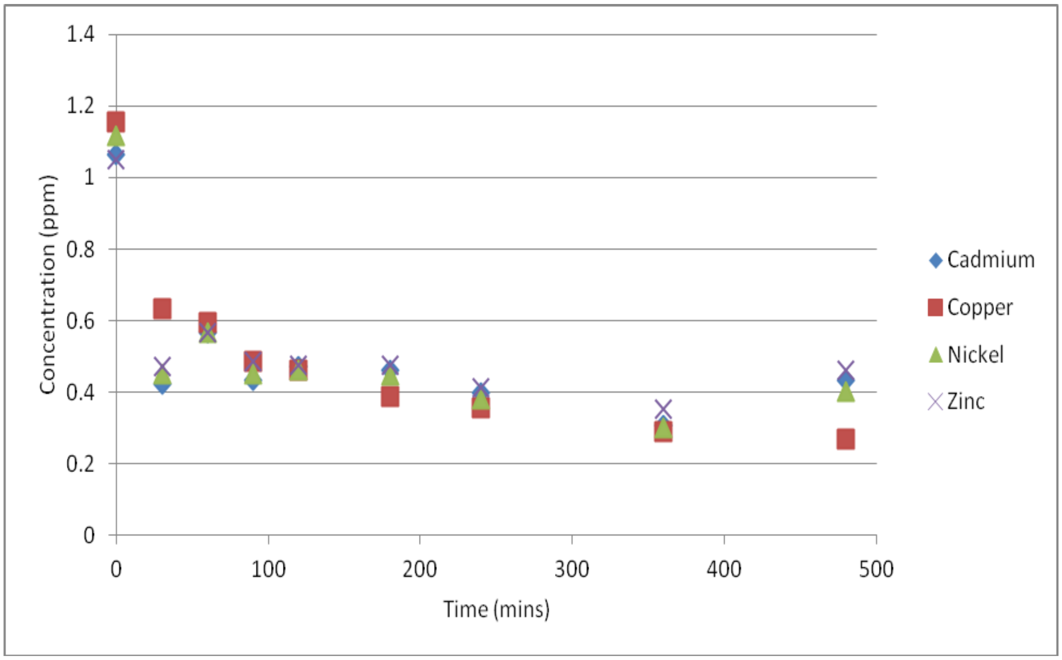

Figure 20. Average concentration profile of metals from a mixed solution of copper, cadmium, nickel and zinc during treatment with MNP

Kinetic experiments using each type of fiber were conducted on each metal, as well as on a mixed solution of the four metals. The removal efficiencies achieved in each condition after 8 hours were calculated (Table V). The results of the metal removal efficiency after 8 hours are shown graphically in Figure 21. The metal loading of fibers on a mass to mass basis (mg of metal removed per gram of fiber) was also calculated (Table VI). This method is more accurate than simple removal efficiencies because it accounts for the removal of volume from the solution with each sample.

Table V. NF and MNP removal efficiency for individual metals vs. metals from a mixed solution

NF and MNP Metal Removal Efficiency (%) after 8 hours								
	Cu		Cd		Ni		Zn	
Fiber Type	NF	MNP	NF	MNP	NF	MNP	NF	MNP
Single Metal Soution	77%	93%	84%	98%	78%	90%	78%	96%
Mixed Metal Soution	58%	77%	41%	59%	51%	64%	41%	56%

Table VI. NF and MNP loading for individual metals vs. metals from a mixed solution

NF and MNP Metal Loading (mg/g) after 8 hours								
	Cu		Cd		Ni		Zn	
Fiber Type	NF	MNP	NF	MNP	NF	MNP	NF	MNP
Single Metal Soution	0.110	0.112	0.096	0.096	0.080	0.096	0.071	0.076
Mixed Metal Soution	0.069	0.082	0.044	0.062	0.052	0.069	0.037	0.058

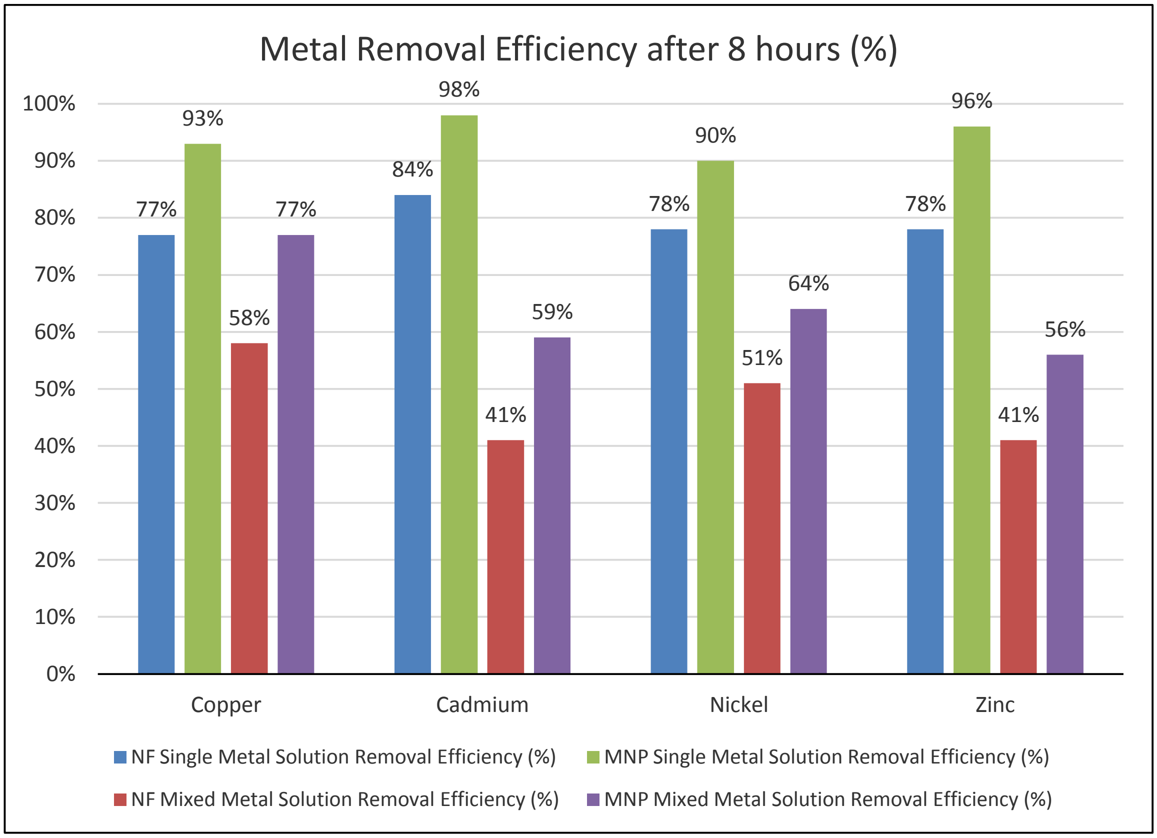

Figure 21. Metal removal efficiency after 8 hours for mixed and single metal solutions

The results indicate that the metal removal ranged from 77-84% for NF with single metal solutions while the removal lowered to 41-58% with multi-metal solutions. Similarly for MNP, the removal efficiency ranged from 90-98% for single metal solutions while the removal efficiency lowered to 56-77% with the multi-metal solution. The results also indicated that the MNP performed better than the NF, in terms of removal efficiency and the amount of metal removal per mass of fiber.

The efficiency and adsorbent load in the NF and MNP was higher when the metals were treated individually versus when the metals were treated in a mixture solution. This is likely due to competition between the metals for access to active sites on the fibers

6.1.2. Kinetic Models

The kinetic experiments demonstrated that the pseudo first order kinetic model fit the data better than the pseudo second order model. The pseudo first order model produced straight line fits while the pseudo second order model did not (Figures 22-33). The remaining pseudo second order figures can be found in Appendix C.

The R^2 values ranged from 0.9736 – 0.9984 for the NF and single metals solutions and had a value of 0.999 for copper in a mixed metal solution. The R^2 values for the MNP ranged between 0.8299 – 0.9930 for single metal solutions and had a value of 0.9020 for copper in a mixed metal solution.

6.1.2.1. NF Trends

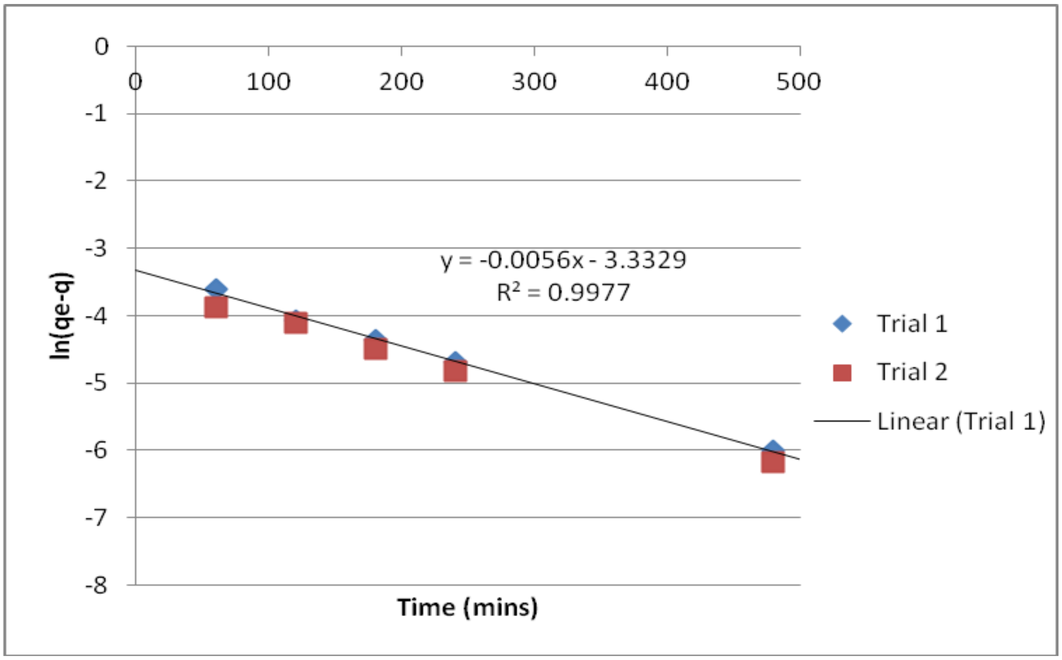

Figure 22. Pseudo first order plot, NF, copper

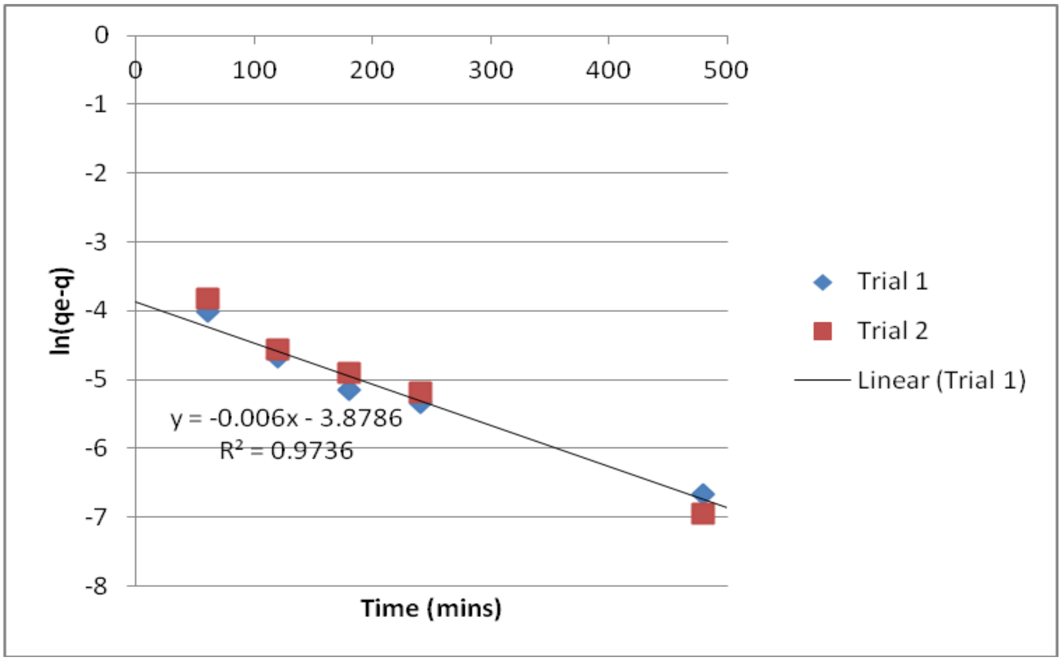

Figure 23. Pseudo first order plot, NF, cadmium

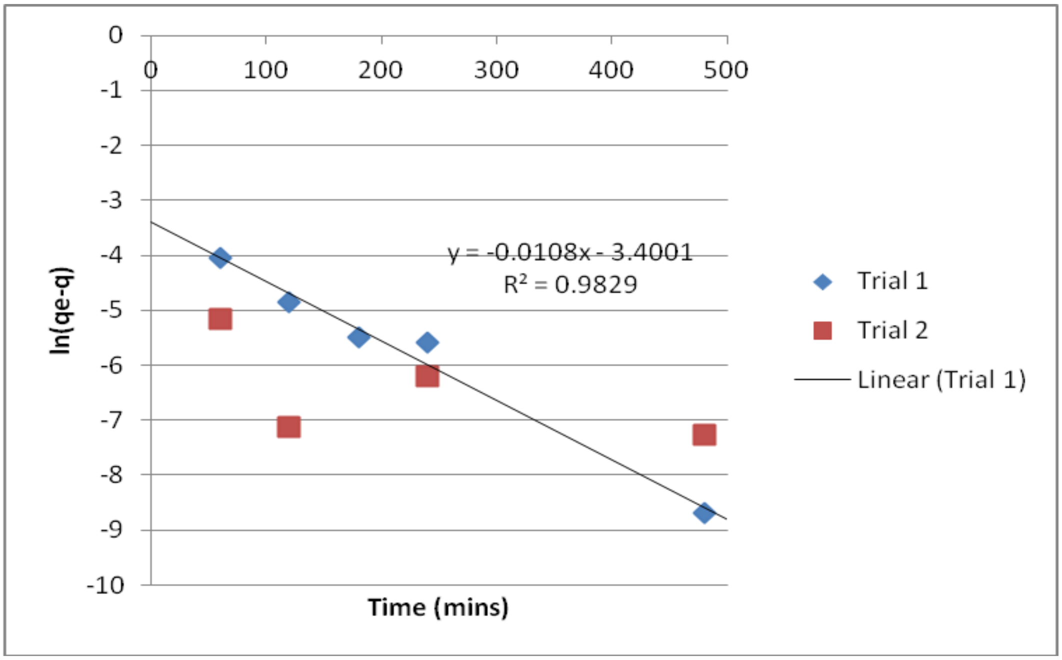

Figure 24. Pseudo first order plot, NF, nickel

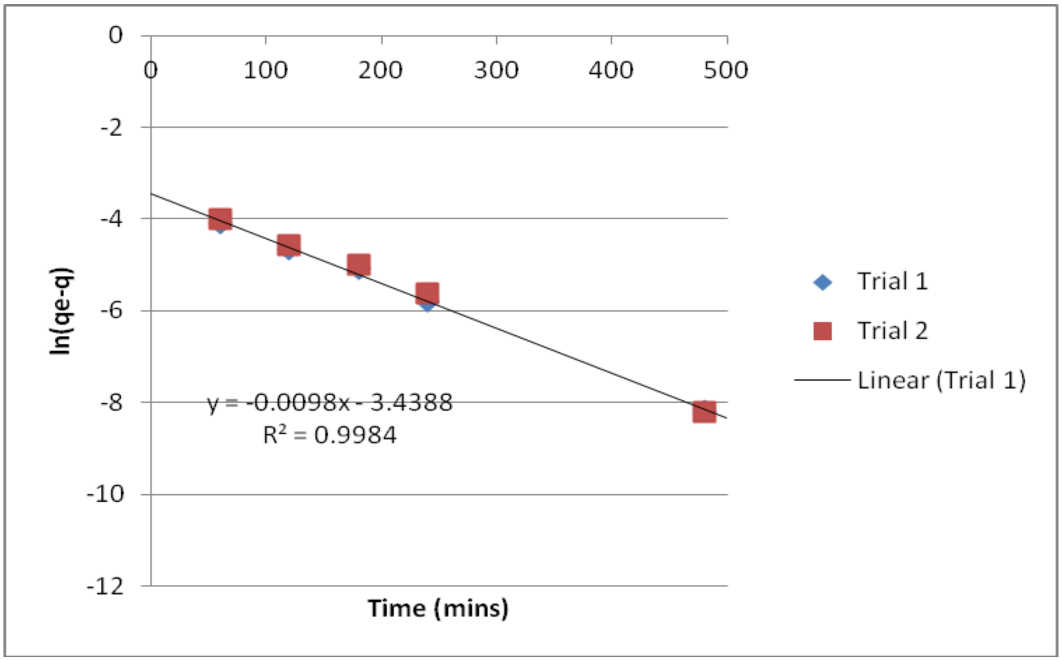

Figure 25. Pseudo first order plot, NF, zinc

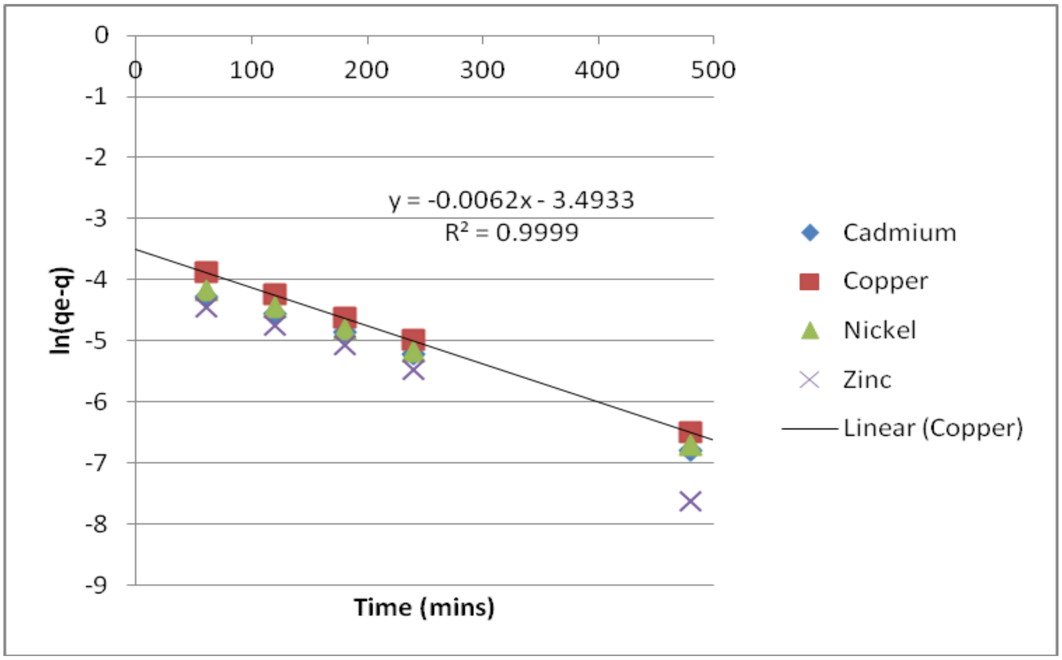

Figure 26. Pseudo first order plot, NF, mixed solution

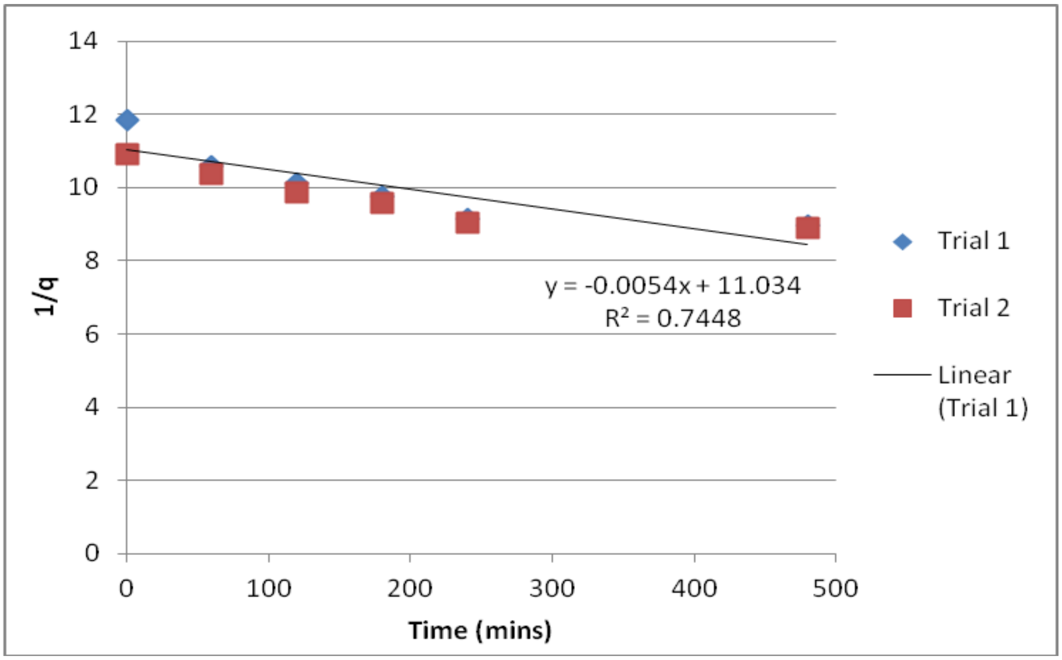

Figure 27. Pseudo second order plot, NF, copper

6.1.2.2. MNP Trends

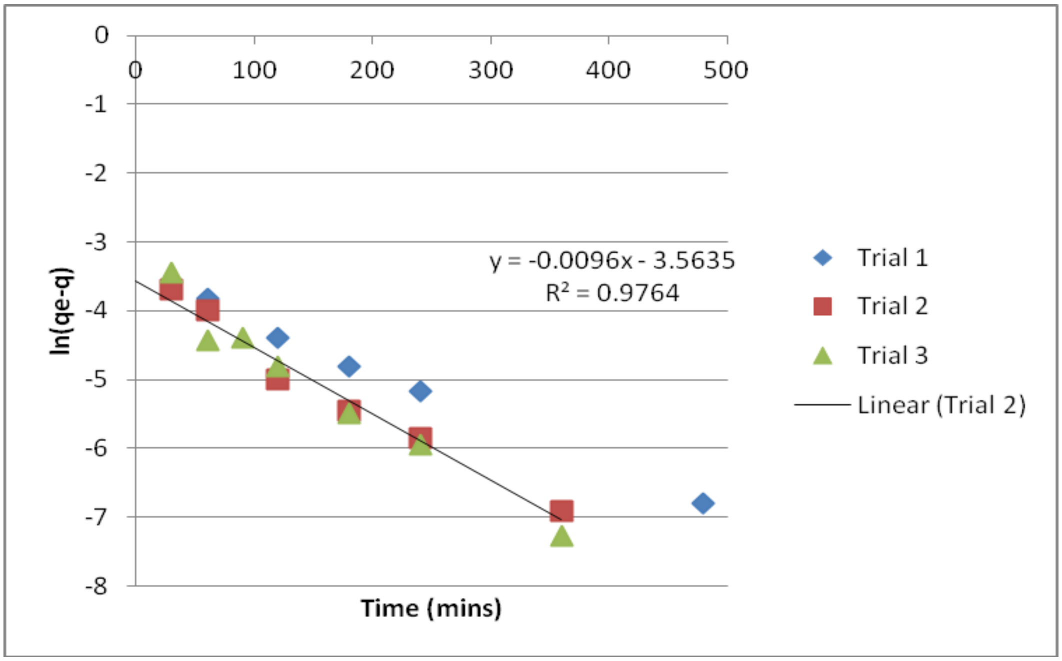

Figure 28. Pseudo first order plot, MNP, copper

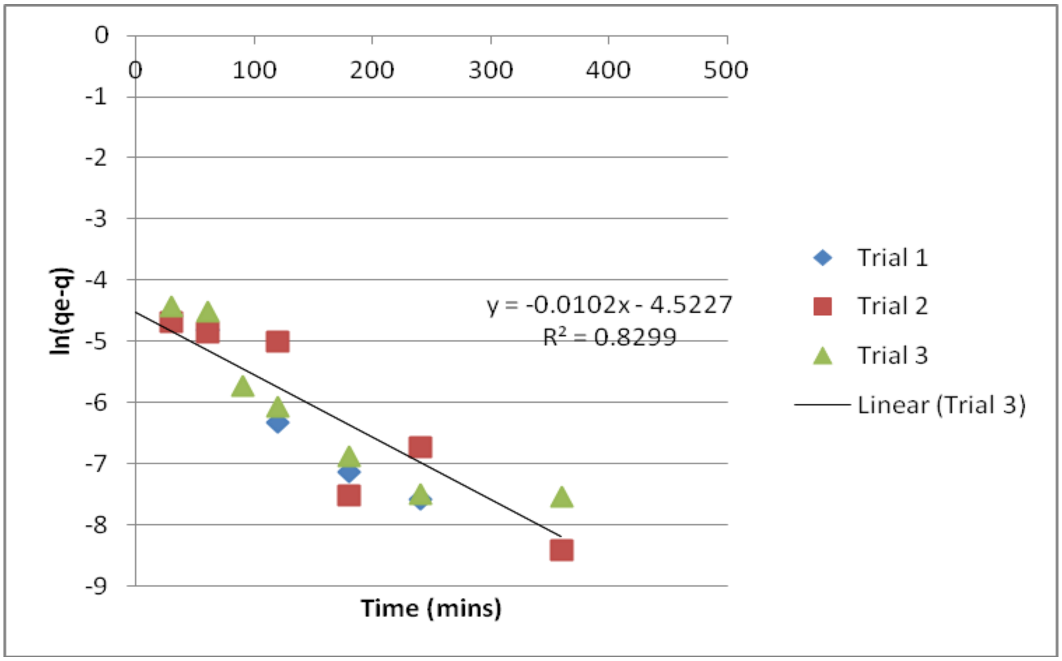

Figure 29. Pseudo first order plot, MNP, cadmium

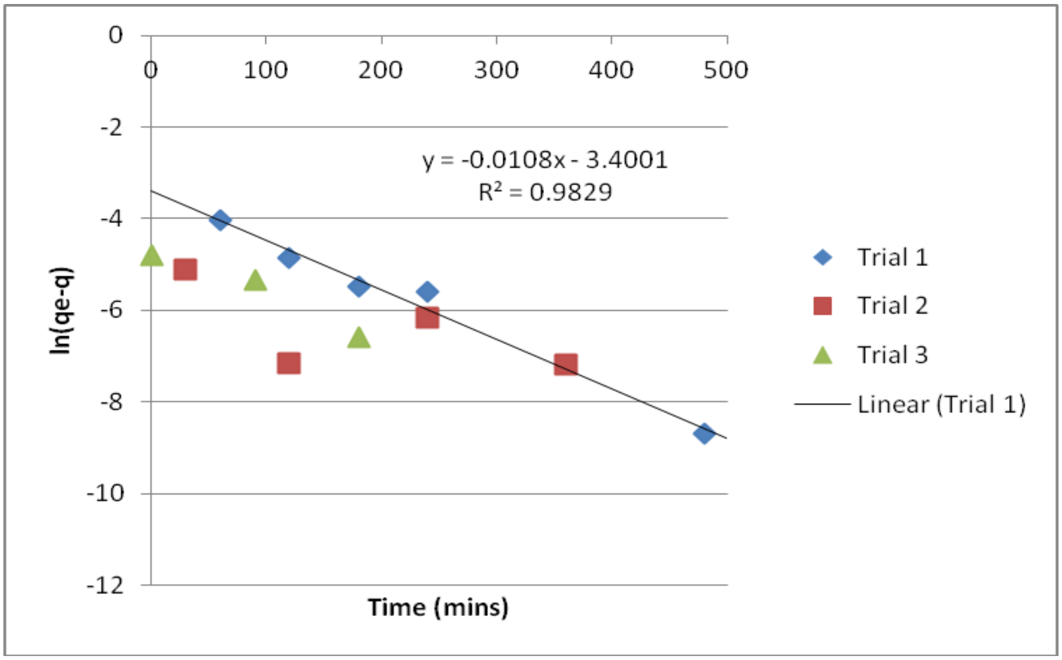

Figure 30. Pseudo first order plot, MNP, nickel

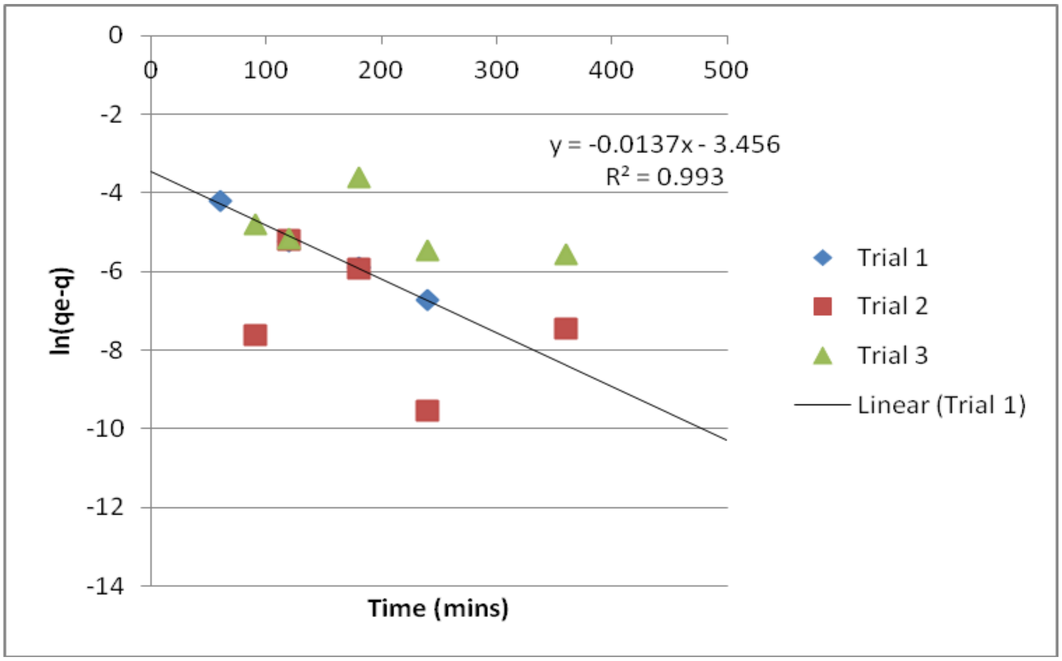

Figure 31. Pseudo first order plot, MNP, zinc

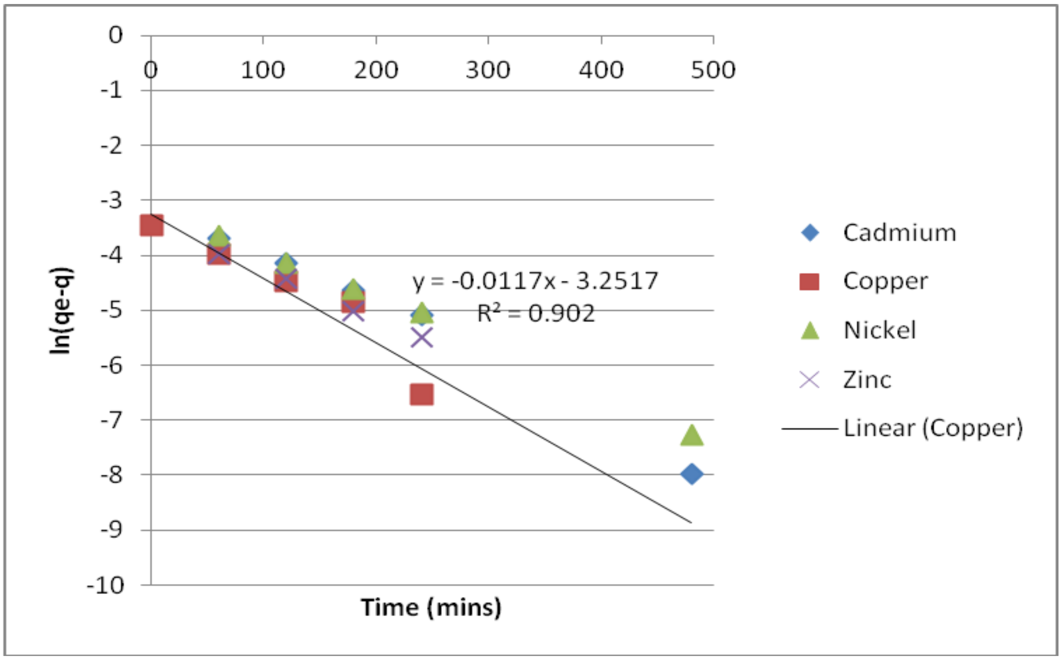

Figure 32. Pseudo first order plot, MNP, mixed solution

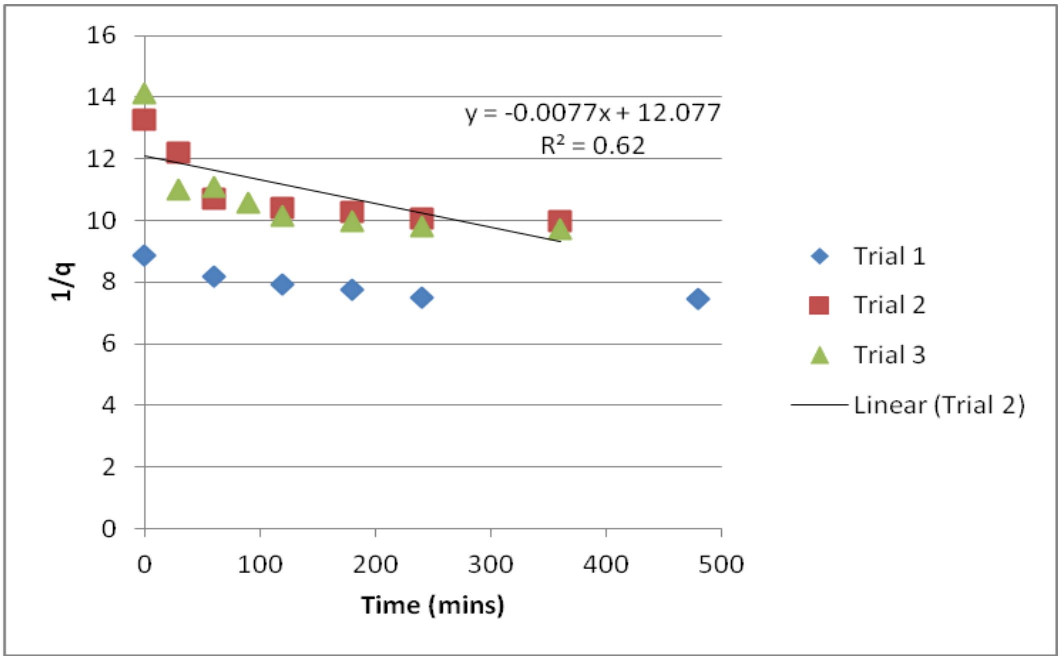

Figure 33. Pseudo second order plot, MNP, copper

Slopes and y-intercepts from the linear regressions (Figures 22-33) and additional figures in Appendix E were used to calculate the rate constants for each first order experiment. The slope is the measurement of the mass transfer rate constants. Rate constants for individual metals as well as mixed solutions are compared in Table VII and shown in Figure 34.

Table VII. Pseudo first order rate constants for NF and MNP

Pseudo first order rate constants (min^{-1})								
	Cu		**Cd**		**Ni**		**Zn**	
Fiber Type	**NF**	**MNP**	**NF**	**MNP**	**NF**	**MNP**	**NF**	**MNP**
Single Metal Solution	0.0056	0.0096	0.0060	0.0102	0.0108	0.0108	0.0098	0.0137
Mixed Metal Solution	0.0062	0.0117	0.0061	0.0104	0.0061	0.0087	0.0077	0.0085

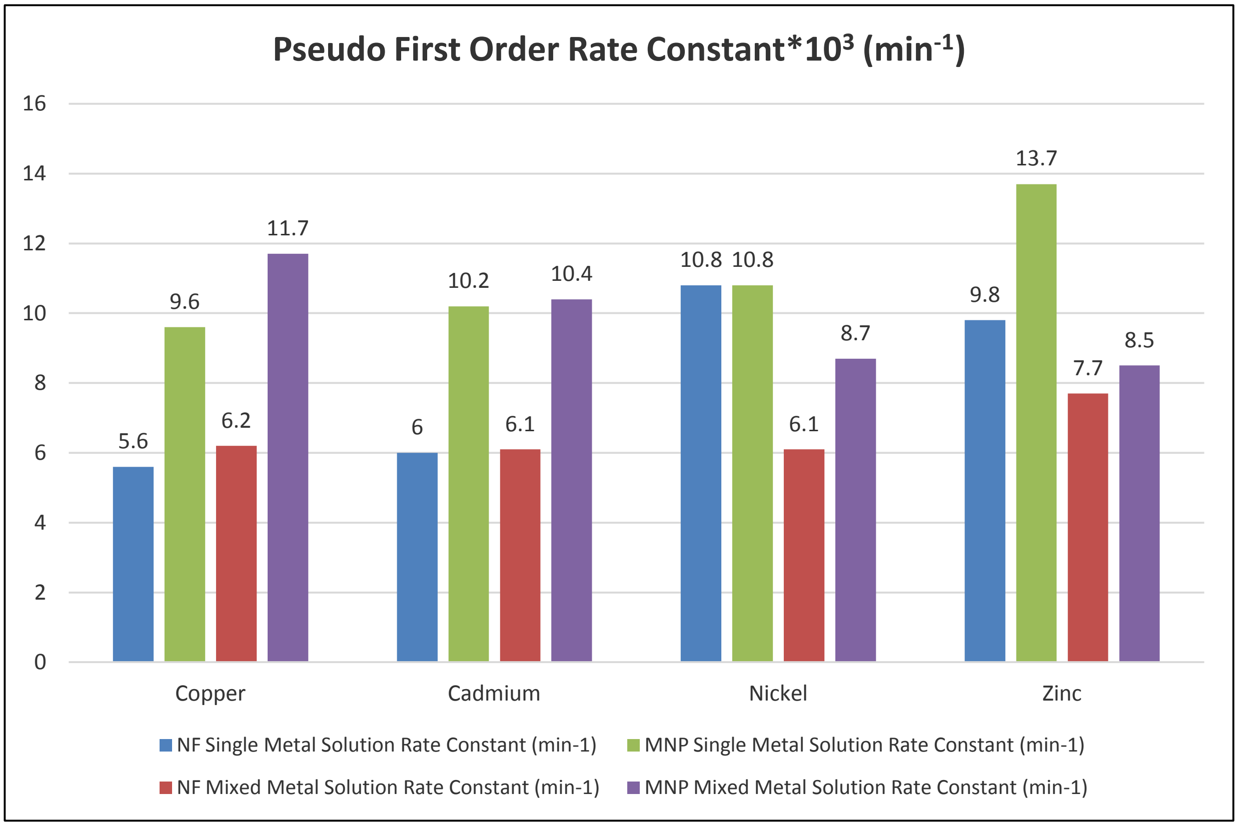

Figure 34. Pseudo first order rate constant *10^3 (min^{-1})

The rate constants reveal that MNP consistently remove heavy metals faster than NFs. Copper was removed faster by both types of fiber when it was treated in a mixture of metals than when it was removed alone. Cadmium removal by the MNP had higher rate constants than the NF. Nickel and Zn were both removed faster individually than in a mixed solution, independent of fiber type.

These results lead to the conclusion that the MNP prefer Cu and Cd over other metals in the mixed solution. Nickel and Zn are not adsorbed as readily when copper is present and removal efficiencies for those two metals decrease in a mixed solution.

6.1.3. Adsorption Kinetics Discussion

A concentration gradient is created between the fiber surface and the metal ions in solution. Due to the mechanisms of Brownian motion, the metal ions will diffuse from areas of high concentration (such as the bulk solution) to areas of low concentration (such as the surface of the fibers) (Criddenton, 2012). As more ions are removed from the bulk solution, the system eventually reaches an equilibrium where concentrations in the bulk solution are low enough that the diffusion no longer drives the ions to move towards the fiber surface.

This can be explained through Fick's Law which is given in Equation 10 and 11:

$$J_A = -D_{AB}(\Delta C_A/\Delta z) \tag{10}$$

$$C_A = C_{bulk} - C_{surface} \tag{11}$$

where J is the mass flux of component A due to diffusion, (mg/m^2/sec), D_{AB} is the diffusion coefficient of component A in solvent B (m^2/s), C_A is concentration of component A (mg/L), and z is the distance in direction of concentration gradient (m).

The change in concentration is the difference between the concentration of metals in the bulk solution and the concentration of metals collected on the fibers. The concentration of metals at the surface is assumed to be 0 because the metals are said to be adsorbed on the fibers. The simplified Fick's equation is given in Equation 12:

$$J = -D_{AB}(C_{bulk}/\Delta x) \tag{12}$$

Therefore, flux (or rate of diffusion) is proportional to the concentration of metals in the bulk solution (Criddenton, 2012). This law explains why metals are adsorbed much faster between zero and 50 minutes than compared to 50 to 480 minutes. It also suggests that the mechanism used by the fibers is physisorption since the rate and adsorbent load appears to be dictated by concentration gradients.

6.2. Adsorbent Load

The adsorbent load was examined further to determine the ideal amount of fibers needed to treat a given volume of water. Additional experiments were performed on both types of fibers using a mixed solution of 1 mg/L of all four metals of concern.

For the MNP, it was found that as fiber mass increased the copper load decreased. When about 0.5 grams of fiber was added to 200 mL of solution, the copper loading was about 0.25 mg/g. This was by far the highest loading achieved by any of the metals. These results are consistent with the data in section 6.1.1 which shows that Cu is adsorbed preferentially over Cd, Ni, and Zn.

As fiber mass increased the load of cadmium, nickel, and zinc initially increased but after a small peak at about 1.5 grams of fiber, the loading of these three metals declined as well. This could show that when the fiber mass was low, so many of the adsorption sites were occupied by copper that there were few sites to adsorb Cd, Ni, and Zn. For fiber masses greater than 1.5 grams, little copper was left in solution after most of the adsorption occurred to there was available adsorption sites for Cd, Ni, and Zn. This trend is shown in Figure 35.

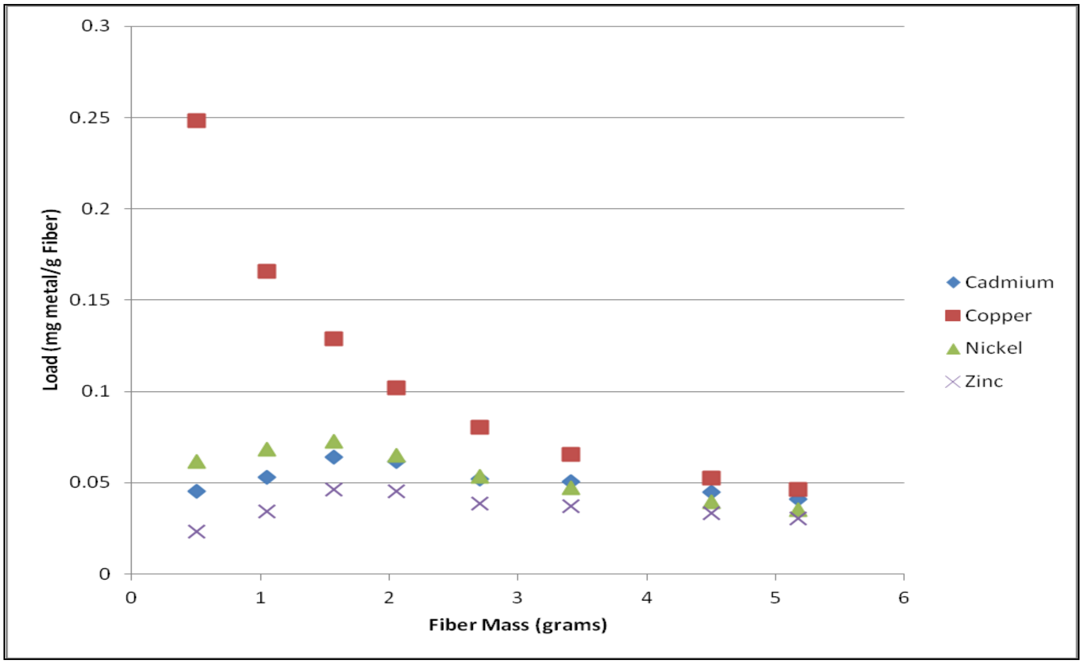

Figure 35. Trend in MNP load as a function of fiber mass. Temperature maintained at 20°C, pH of 3, and initial metal concentrations of 1 mg/L Cu, Cd, Ni, Zn.

The NF showed similar trends. The maximum copper adsorption attained was 0.21 mg/g of fiber and the loads decreased with each increase in fiber mass. Cadmium, nickel, and zinc loads decreased consistently with the highest loading being attained at approximately 1.5 grams in 200 mL of solution. Figure 36 demonstrated the trend in loading versus fiber mass for NF.

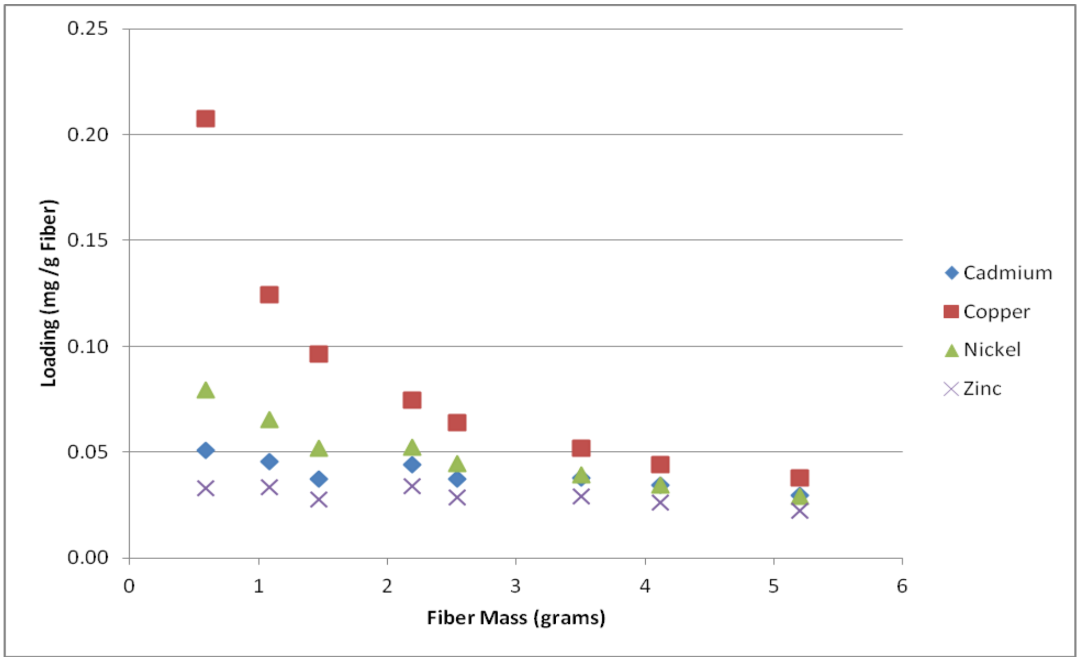

Figure 36. Trend in NF load as a function of fiber mass. Temperature maintained at 20°C, pH of 3, and initial metal concentrations of 1 mg/L Cu, Cd, Ni, Zn.

This trend shows that loading is inversely related to fiber mass. This is consistent with the conclusions made by Rediske for cadmium adsorption and indicated once more that the process is likely mass transfer driven.

The significance of the copper loading over other metals may be explained by the apparent preference of both types of fibers to remove copper over other metals. This could be caused by a number of factors including surface charges on the fibers, pore volume, size, and orientation, and other chemical and physical properties that affect preferential adsorption.

6.2.1. Adsorption Isotherms

The experimental procedures and methods for adsorption experiments were utilized to generate Freundlich and Langmuir isotherms for individual metal solutions. It was found that each metal was unique and that both types of fibers followed different isotherms.

Figures 35 through 42 represent the best fitting isotherm model for each metal. The best fitting model was established using the least square method and choosing the model with the highest R^2 value. Values of greater than 0.500 were considered acceptable for demonstrating a relationship in the data and values greater than 0.800 were preferred. The Langmuir and Freundlich isotherms for each metal can be found in Appendix F that did not meet the required R^2 value.

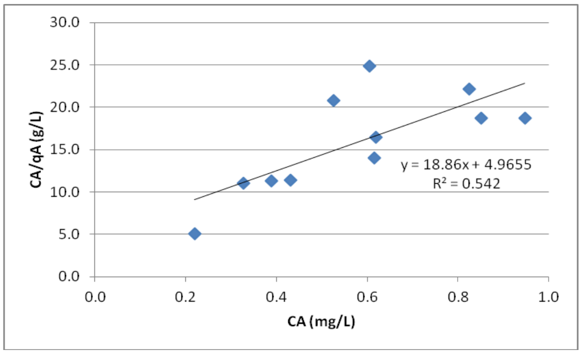

Figure 37. Langmuir isotherm for NF demonstrating trends in CADMIUM removal from a mixed solution of Cu, Cd, Ni, and Zn

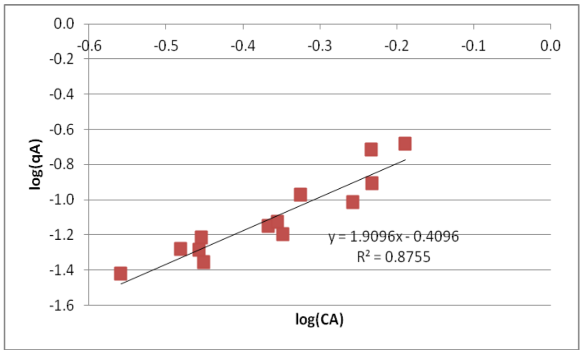

Figure 38. Freundlich isotherm for NF demonstrating trends in COPPER removal from a mixed solution of Cu, Cd, Ni, and Zn

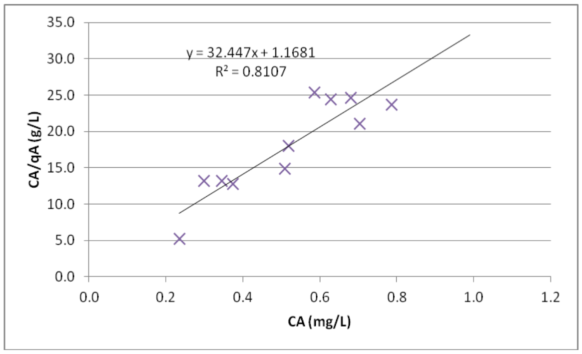

Figure 39. Langmuir isotherm for NF demonstrating trends in ZINC removal from a mixed solution of Cu, Cd, Ni, and Zn

Copper fits better with a Freundlich isotherm model with an R^2 value of 0.8755 while cadmium and zinc more closely follow Langmuir isotherms with R^2 values of 0.542 and 0.8107 respectively. Nickel did not follow either model. The trends show that the mechanisms used in copper removal are different from that of the other three metals. Since Freundlich isotherms are associated with multilayer adsorption, this could explain why copper loading is higher when less fiber is present. Therefore, it is likely that copper uses a multilayer adsorption process. Another explanation could be that copper only appears to be multilayer due to preferential adsorption over the other metals. It could give the impression of having infinite adsorption sites when really it just began replacing other substances on the surface of the fibers.

Similar results were seen for multiple metal experiments with MNP. The results are shown in Figures 35-38.

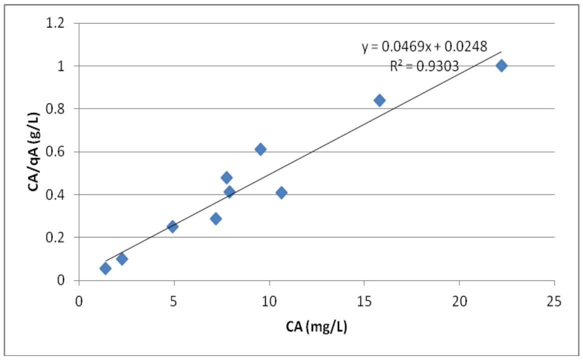

Figure 40. Langmuir isotherm for MNP demonstrating trends in CADMIUM removal from a mixed solution of Cu, Cd, Ni and Zn

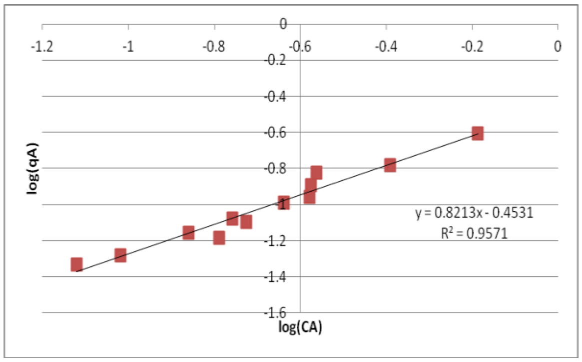

Figure 41. Freundlich isotherm for MNP demonstrating trends in COPPER removal from a mixed solution of Cu, Cd, Ni and Zn

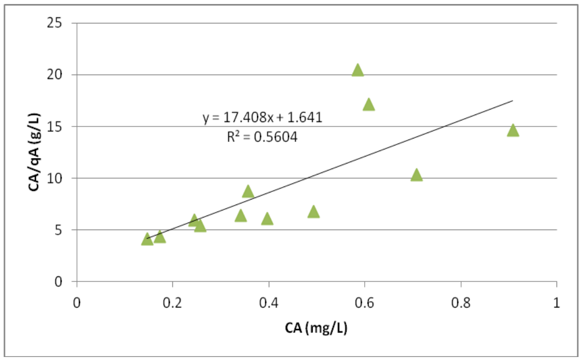

Figure 42. Langmiur isotherm for MNP demonstrating trends in NICKEL removal from a mixed solution of Cu, Cd, Ni, and Zn

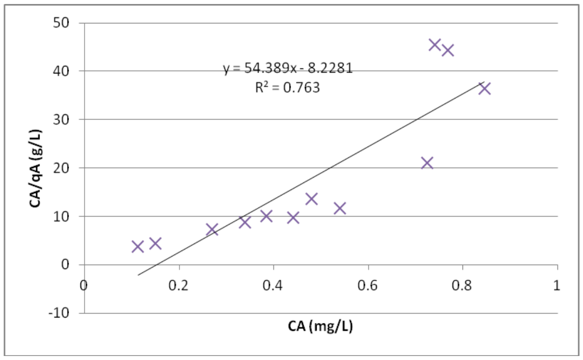

Figure 43. Langmuir isotherm for MNP demonstrating trends in Zinc removal from a mixed solution of Cu, Cd, Ni, and Zn

Results show that when copper, cadmium, nickel, and zinc were removed from an aqueous solution by MNP; copper will follow a Freundlich isotherm model with an R^2 value of 0.9571, while cadmium, nickel and zinc will more closely follow Langmuir models with R^2 values of 0.9303, 0.5604, and 0.7630 respectively.

The Langmuir constants were evaluated for cadmium, nickel, and zinc and Freundlich constants were evaluated for copper from the above results using Equation 8 for Freundlich and Equation 9 for Langmuir isotherms.

Table VIII. Langmuir Isotherm constants for heavy metal ion adsorption

Fiber Type	Metal	b_A	Q (mg/g)	R^2
MNP	Cadmium	1.891	21.322	0.9303
	Nickel	10.608	0.057	0.5604
	Zinc	-6.610	0.018	0.7630
NF	Cadmium	3.798	0.053	0.5420
	Nickel	3.679	0.064	0.2199
	Zinc	27.778	0.031	0.8107

Table IX. Freundlich Isotherm constants for heavy metal ion adsorption

Fiber Type	Metal	K_f	1/n	R^2
MNP	Copper	0.3523	0.8213	0.9571
NF	Copper	0.3894	1.9096	0.8755

6.3. Fiber Characterization

NF and MNP were digested to analyze the composition of the fibers as well as to conduct a mass balance on the flow through system.

Coir fiber naturally contains trace levels of heavy metals so a digestion analysis was performed to give approximate background levels of metals in the fibers. The heavy metal content in the coir fiber changes based on where the coconuts were grown, when they were harvested and other environmental factors. Table X lists the concentration of various metals and other elements present in a representative sample of NF and MNP used for this research.

Table X. Metals Present in NF and MNP

Metal	NF Concentration (mg/kg)	MNP Concentration (mg/kg)
As	None Detected	0.302
Be	None Detected	None Detected
Ca	244	0.052
Cd	None Detected	1.86
Co	None Detected	0.306
Cr	None Detected	6.39
Cu	2.46	None Detected
Fe	63.6	None Detected
Li	None Detected	0.088
Mg	698	NA
Mn	16.9	1.76
Mo	None Detected	0.506
Ni	0.546	None Detected
Pb	None Detected	0.257
Sb	0.197	0.084
Se	2.32	0.546
Sr	8.75	14.40
Ti	0.003	0.861
Tl	None Detected	None Detected
V	None Detected	0.819
Zn	6.28	6.86

During this process, the fibers were also analyzed for major anions. Table XI lists the concentrations of major anions found in a representative sample of NF and MNP used for this research.

Table XI. Major Anions Present in NF and MNP

Anion	NF Concentration (mg/kg)	MNP Concentration (mg/kg)
Cl	961	4370
SO_4	28900	26600
Br	38.7	52.9
F	96.1	92.4
NO_3	90.2	53.1

6.4. Continuous Flow Column Experiments

Once initial experimentation was completed, a bench scale flow through system was designed to test the performance of the fibers. Table XII summarizes design specification of the bench scale system

Table XII. Design parameters and dimensions of continuous flow through system

Parameter	Dimensions
Flow Rate	10 mL/min
Total Water Volume of System	825 mL
Mass of fiber/Column	10 g
Length of Fiber/ Column	5.5 – 6”
Empty Bed Residence Time/Column	15 min
Diameter of Columns	1.5”
Length of Each Column	12”

The bench scale was examined for contamination prior to use by allowing DI water to soak for 24 hours as well as flowing 1.5L of DI water through the system and examining the water before and after contact with the system.

The flow through system consisted of two columns, each packed with 10 grams of fiber. Experiments were conducted using NF in both columns and NF in the first column followed by MNP in the second column. The NF-NF system was tested using the synthetic water containing 1 mg/L concentrations of copper, cadmium, nickel, and zinc. The NF-MNP system was tested using 1 mg/L and 2 mg/L synthetic solution and also Mine Tailing Water (MTW) obtained from a mining company.

The MTW was analyzed for metals of concern. It was determined that the concentrations of metals in the mine tailing water were too low for this experiment. Therefore, MTW was fortified with a mixed four metal solution of 1 mg/L of each of the four study metals. The composition of MTW mixed with synthetic solution is given in Appendix J.

The results of these experiments are shown in Table XIII. With NF in both columns, the results showed that all four metals were removed at high efficiencies. Copper reduction was relatively high at 88.6% and zinc was the lowest with 62.1%.

Tests followed with NF in the first column followed by MNP in the second column. This set up was tested with mixed solutions of 1 mg/L, 2 mg/L, and fortified MTW. The idea behind the second set up was to have the NF remove the bulk of the contaminants and use the MNP as a finishing step. This design would be preferred for a full scale design because NF would treat the water with the higher concentration gradients and leave the more effective MNP to tackle the residual metals that were harder to remove. This is also advantageous because if this process were scaled up, it would reduce the amount of MNP required.

Contrary to the results of the batch experiments (Sections 6.1, 6.2), the MNP continuous flow system did not outperform the NF system. While copper removal remained high at 78% - 90%, the other three metals were removed much more efficiently with the NF system under the same conditions. The fact that removal efficiency of cadmium, nickel, and zinc increased with increasing concentration indicates that the metal removal is driven by concentration gradients and that initial metal concentration will influence removal efficiency.

Experiments with the MNP system were focused on a real world application of these fibers and utilized mine tailing water (MTW) instead of the synthetic mixture of metals used in the previous experiments. The mine tailing water had very low levels of heavy metals initially, so 1 mg/L of all four metals was added to the water to make it comparable to the other experiments. The solution pH was maintained at 3 and all other variables were treated identically to previous experiments. The advantage of the mine tailing water was that it included a more complex water composition, including anions and salts that allowed the fibers to demonstrate their performance with more contaminants.

Table XIII. Performance of bench scale flow through system in removal of heavy metals of concern

Fiber Type	Solution	Copper Reduction	Cadmium Reduction	Nickel Reduction	Zinc Reduction
NF-NF	1 mg/L Cu, Cd, Ni, Zn	88.6%	68.2%	73.8%	62.1%
NF-MNP	1 mg/L Cu, Cd, Ni, Zn	77.9%	33.2%	36.8%	24.3%
NF-MNP	2 mg/L Cu, Cd, Ni, Zn	90.3%	69.7%	64.3%	61.1%
NF-MNP	Modified Mine Tailing Water	87.0%	9.3%	20.0%	0.27%

The modified mine tailing water showed once again consistent removal of copper, at 87%. As Table XIII demonstrates, the cadmium, nickel, and zinc reduction suffered. Figure 44 represents the decrease in metal concentration decrease through the bench scale flow through process.

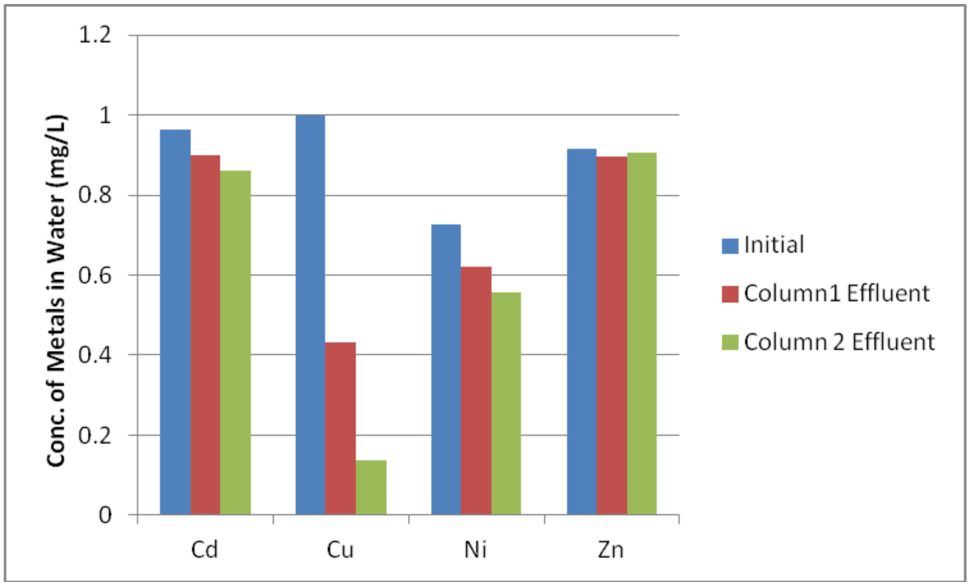

Figure 44. Concentration decrease in each column during NF-MNP bench scale experiment with fortified MTW

The most likely reason that the fibers did not perform as well on in this application could be because the water contained chloride and sulfate, 1380 mg/L and 1800 mg/L respectively as well as levels of nitrate and bromide, 11 mg/L and 60 mg/L respectively. It is most likely that the performance was affected by competition of the metals with major cations such as Ca^{2+} and Mg^{2+} which are capable of occupying some adsorption sites when present in high enough concentrations. These constituents, as well as others that were not analyzed could be responsible for limiting access of the metals to the surface of the fibers.

6.5. Mass Balance

The mass balance was performed on the bench scale system with NF in both columns. The fibers were removed from each column following experimentation and digested to quantify the amount of metal that was removed by the fibers and to prove that the fibers were accountable for the reduction of metals from the initial solution. Equation 13 was used to calculate the mass balance.

$$\textit{Metals In} = \textit{Metals out} \tag{13}$$

$$\textit{Initial Dissolved Metals} = \textit{Metals from Column 1 Digested Fibers} + \textit{Metals from Column 1 Sample Filter} + \textit{Metals from Column 2 Digested Fibers} + \textit{Metals from Column 2 Sample Filter} + \textit{Metals from Final Solution} \tag{14}$$

Table XIV demonstrates the mass of each metal recovered in each column of the bench scale system.

Table XIV. Mass balance on bench scale system, NF-MNP (+ is additional, - is loss)

	Cadmium	**Copper**	**Nickel**	**Zinc**
Initial (mg)	0.936	0.938	0.909	0.853
Column 1 (mg)	0.519	0.507	0.442	0.388
Column 2 (mg)	0.258	0.179	0.217	0.156
Final Water (mg)	0.220	0.130	0.156	0.223
Removal Efficiency	76%	86%	83%	74%
BALANCE (mg)	+0.060	-0.121	-0.095	-0.086
% Recovered	106%	87%	90%	90%

Copper, nickel and zinc each had about a 90% recovery rate and cadmium was recovered at 106%. Although this is within 10%, the error also could have been due to losses during the digestion process.

As expected, more metal was removed by the first column than the second due to concentration gradients. This experiment demonstrates that coir fiber does remove dissolved heavy metals from aqueous solutions.

7. Conclusions

The purpose of this research was to characterize the adsorption of copper, cadmium, nickel, and zinc from aqueous solutions using natural fiber and natural fiber treated with metallic nanoparticles. Both natural and treated coir fibers demonstrated affinity for heavy metal removal however, the MNP performed better overall. The research included kinetic experiments, adsorption isotherm experiments, and flow through column tests. The results are summarized here.

7.1. Adsorption Kinetics

Kinetics experiments were used to determine rates of removal for individual metals as well as a mixture of four metals. Using solutions with initial concentrations of 1-1.5 mg/L, removal efficiencies of 77%-82% were achieved for single metal solutions and 41%-58% were achieved for mixed metal solution with NF in an 8 hour period. MNP achieved removal efficiencies of 90%-98% for single metal solutions and 56%-77% for mixed metal solution under the same conditions. A 50% reduction in initial concentration was seen in 20-50 minutes with the NF compared to 10-30 minutes with the MNP. This showed that the MNP worked 33-80% faster than the NF for all metals expect zinc.

Kinetic models were used to determine rate constants for NF and MNP based on the kinetic experiments. Both fiber types were found to follow a pseudo first order rate model. As expected, MNP had consistently higher rate constants than the NF. NF pseudo first order rate constants had a range of 0.0056-0.0108 min^{-1} for single metal solutions compared to MNP which had a range of 0.0096-0.0137 min^{-1}. NF mixed metal solution rate constants had a range of 0.0061-0.0077 min^{-1} and MNP rate constants had a range of 0.0085-0.0117 min^{-1} showing that MNP performed better.

7.2. Adsorbent Load

Adsorbent load experiments were conducted to determine the optimum mass of fibers that could be used to treat a set volume of water. Experiments showed that fiber loading is inversely related to fiber mass. Isotherms were used to evaluate the adsorption of copper, cadmium, nickel, and zinc from a mixed solution. It was found that for both NF and MNP, copper removal was adequately modeled by a Freundlich isotherm and cadmium, nickel, and zinc more closely followed a Langmuir isotherm. For the Langmuir isotherms, the b_A constants were as high as 28 L/mg for NF and 11 L/mg for MNP. The Langmuir Q values ranged from 0.031-0.064 mg/g and 0.018-21.322 mg/g for the MNP. For Freundlich isotherms, 1/n values were 1.9 for NF and 0.8213 for MNP. The K_f constant was approximately 0.4 $(mg/g)(L/mg)^{1/n}$ for both fiber types. These experiments revealed that within both types of fibers, the mechanism of copper removal appears to be different from the other metals. Since Freundlich isotherms are associated with multilayer adsorption, this could indicate that copper uses a multilayer adsorption process or that it is preferentially adsorbed over other metals, making it appear to utilize multilayer adsorption.

7.3. Flow through Column Tests

The bench scale system was designed as a way to test the performance of NF and MNP in a flow through column application. Two different experimental set-ups were tested, the first being NF loaded in both columns and the second being NF followed by MNP.

The NF-NF system was tested with 1 ppm mixed metal solution and the best removal efficiency was seen in copper at 89% and the lowest was zinc at 62% reduction. These experiments proved that the fibers could be used in a flow through application successfully.

The NF-MNP system was tested using mixed metal solutions of 1 mg/L, 2 mg/L and fortified mine tailing water fortified with synthetic metal solutions. Results showed that metal reductions ranged from 24%-78% for 1 mg/L solutions, and 61%-90% for 2 mg/L solutions. Using the fortified MTW, the metal reduction ranged from 0.27%-87%. Copper reduction was consistently higher than the other three metals throughout flow through column experiments while zinc reduction was consistently the lowest.

7.4. Future Research

This research reveals that both NF and MNP are capable of treating toxic heavy metals from aqueous solutions. The results of this research produce the following possibilities for future research.

Further research could be performed to optimize the flow through column system and then to design a pilot scale plant. It would be beneficial to determine the optimum flow rate, fiber mass and packing technique that would yield the best metal reduction results. In addition to this, further testing would be beneficial to determine breakthrough points and quantify value such as volume of water treated per mass of fiber.

Finally, research should be conducted to determine the ability of NF and MNP to treat other metals of concern in the presence of other contaminants. This testing would be beneficial to a real world application because it would give a better idea of how the fibers will perform when exposed to real water from industrial sources.

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Appendix A: Minimum Detection Limits

Table A. ICP-OES Minimum Detection Limits

Element	Minimum Detection Limit (mg/L)
Arsenic	0.0020
Beryllium	0.0025
Calcium	0.1229
Cadmium	0.0018
Cobalt	0.0014
Chromium	0.0017
Copper	0.0025
Gold	0.0015
Iron	0.0023
Lithium	0.0013
Magnesium	0.0053
Manganese	0.0238
Mercury	0.0851
Molybdenum	0.0018
Nickel	0.0024
Lead	0.0019
Antimony	0.0017
Selenium	0.0058
Strontium	0.0067
Titanium	0.0010
Thallium	0.0019
Vanadium	0.0018
Zinc	0.0016

Appendix B: Kinetics Raw Data

Table B, I. Raw data from MNP kinetics experiments

Experiment Number	Fiber Type	pH	1 ppm Soln.	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
1	MNP	3	Cu	0	<MDL	1.505	<MDL	0.0518
1	MNP	3	Cu	60	<MDL	0.3796	<MDL	0.006
1	MNP	3	Cu	120	<MDL	0.2727	<MDL	0.005
1	MNP	3	Cu	180	<MDL	0.221	<MDL	0.0038
1	MNP	3	Cu	240	<MDL	0.1872	<MDL	0.004
1	MNP	3	Cu	480	<MDL	0.1219	<MDL	0.0026
1	MNP	3	Cu	720	<MDL	0.1034	<MDL	0.0019
2	MNP	3	Cu	0	0.0003	1.131	0.0002	0.00675
2	MNP	3	Cu	30	0.0001	0.37755	0.0004	0.0095
2	MNP	3	Cu	60	<MDL	0.30755	0.0004	0.00685
2	MNP	3	Cu	120	<MDL	0.1791	0.0005	0.00495
2	MNP	3	Cu	180	0.0001	0.1485	0.0006	0.00305
2	MNP	3	Cu	240	<MDL	0.1303	0.0002	0.00155
2	MNP	3	Cu	360	<MDL	0.1032	0.0003	0.01035
2	MNP	3	Cu	480	0.0001	0.0878	0.0005	0.002
3	MNP	3	Cu	0	0.0003	1.131	0.0002	0.00675
3	MNP	3	Cu	30	0.0002	0.4235	0.0006	0.0046
3	MNP	3	Cu	60	<MDL	0.2113	0.0003	0.0035
3	MNP	3	Cu	90	0.0001	0.21785	0.0005	0.00575
3	MNP	3	Cu	120	0.0001	0.16735	0.0003	0.0015
3	MNP	3	Cu	180	0.0001	0.1161	0.0004	0.00235
3	MNP	3	Cu	240	<MDL	0.0967	0.0003	0.00375
3	MNP	3	Cu	360	<MDL	0.06905	0.0004	0.0054
3	MNP	3	Cu	480	<MDL	0.05835	0.0003	0.0008
4	MNP	3	Cd	0	1.207	<MDL	<MDL	0.0305
4	MNP	3	Cd	60	0.1116	<MDL	<MDL	0.0034
4	MNP	3	Cd	120	0.042	<MDL	<MDL	0.0024
4	MNP	3	Cd	180	0.0295	<MDL	<MDL	0.0017
4	MNP	3	Cd	240	0.0256	<MDL	<MDL	0.0016
4	MNP	3	Cd	480	0.0184	<MDL	<MDL	0.0006
4	MNP	3	Cd	720	0.0151	<MDL	<MDL	<MDL
5	MNP	3	Cd	0	0.8921	<MDL	0.0002	0.00955
5	MNP	3	Cd	30	0.1431	0.0001	0.0003	0.0056
5	MNP	3	Cd	60	0.1293	<MDL	0.0002	0.003
5	MNP	3	Cd	120	0.1163	<MDL	0.0005	0.0089

Experiment Number	Fiber Type	pH	1 ppm Soln.	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
5	MNP	3	Cd	180	0.0397	<MDL	0.0002	0.0022
5	MNP	3	Cd	240	0.0482	<MDL	0.0003	0.0036
5	MNP	3	Cd	360	0.0345	<MDL	0.0001	0.00275
5	MNP	3	Cd	480	0.0311	<MDL	0.0002	0.00255
6	MNP	3	Cd	0	0.8921	<MDL	0.0002	0.00955
6	MNP	3	Cd	30	0.1427	<MDL	0.0002	0.0065
6	MNP	3	Cd	60	0.1329	<MDL	0.0004	0.0097
6	MNP	3	Cd	90	0.0476	<MDL	0.0004	0.00195
6	MNP	3	Cd	120	0.0366	<MDL	0.0001	0.0028
6	MNP	3	Cd	180	0.0208	<MDL	0.0003	0.0008
6	MNP	3	Cd	240	0.0144	<MDL	0.0003	0.0002
6	MNP	3	Cd	360	0.0141	<MDL	0.0003	0.00125
6	MNP	3	Cd	480	0.0059	<MDL	0.0001	<MDL
7	MNP	3	Ni	0	<MDL	<MDL	1.106	0.0514
7	MNP	3	Ni	60	<MDL	<MDL	0.3287	0.0048
7	MNP	3	Ni	120	<MDL	<MDL	0.2213	0.0032
7	MNP	3	Ni	180	<MDL	<MDL	0.1744	0.0019
7	MNP	3	Ni	240	<MDL	<MDL	0.169	0.0024
7	MNP	3	Ni	480	<MDL	<MDL	0.1183	0.0024
7	MNP	3	Ni	720	<MDL	<MDL	0.1155	0.002
8	MNP	3	Ni	0	0.0007	<MDL	1.108	0.00795
8	MNP	3	Ni	30	<MDL	<MDL	0.1575	0.00145
8	MNP	3	Ni	120	<MDL	<MDL	0.1026	0.00095
8	MNP	3	Ni	180	<MDL	<MDL	0.0876	0.00035
8	MNP	3	Ni	240	<MDL	<MDL	0.1199	0.0036
8	MNP	3	Ni	360	<MDL	<MDL	0.1009	0.0012
8	MNP	3	Ni	480	<MDL	<MDL	0.0893	0.01915
9	MNP	3	Ni	0	0.0007	<MDL	1.108	0.00795
9	MNP	3	Ni	90	<MDL	<MDL	0.2115	0.0038
9	MNP	3	Ni	120	0.0001	<MDL	0.1741	0.0032
9	MNP	3	Ni	280	<MDL	<MDL	0.0949	0.11165
9	MNP	3	Ni	240	<MDL	<MDL	0.1383	0.0014
9	MNP	3	Ni	360	<MDL	<MDL	0.0908	0.00045
9	MNP	3	Ni	480	<MDL	<MDL	0.1206	0.00405
10	MNP	3	Zn	0	<MDL	<MDL	<MDL	0.9695
10	MNP	3	Zn	60	<MDL	<MDL	<MDL	0.2506
10	MNP	3	Zn	120	<MDL	<MDL	<MDL	0.1437
10	MNP	3	Zn	180	<MDL	<MDL	<MDL	0.111
10	MNP	3	Zn	240	<MDL	<MDL	<MDL	0.0905
10	MNP	3	Zn	480	<MDL	<MDL	<MDL	0.0692

Experiment Number	Fiber Type	pH	1 ppm Soln.	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
10	MNP	3	Zn	720	<MDL	<MDL	<MDL	0.0739
11	MNP	3	Zn	0	<MDL	<MDL	0.0002	0.74595
11	MNP	3	Zn	90	<MDL	<MDL	0.0002	0.05295
11	MNP	3	Zn	120	<MDL	<MDL	0.0006	0.1079
11	MNP	3	Zn	180	<MDL	<MDL	0.0003	0.07505
11	MNP	3	Zn	240	<MDL	<MDL	0.0004	0.04285
11	MNP	3	Zn	360	<MDL	<MDL	0.0002	0.0497
11	MNP	3	Zn	480	<MDL	<MDL	0.0001	0.04135
12	MNP	3	Zn	0	<MDL	<MDL	0.0002	0.74595
12	MNP	3	Zn	90	<MDL	<MDL	0.0002	0.12295
12	MNP	3	Zn	120	<MDL	<MDL	0.0003	0.0956
12	MNP	3	Zn	180	<MDL	<MDL	0.0003	0.3458
12	MNP	3	Zn	240	<MDL	0.004	0.0002	0.06145
12	MNP	3	Zn	360	<MDL	<MDL	0.0002	0.05775
12	MNP	3	Zn	480	<MDL	<MDL	0.0926	0.0023
13	MNP	3	Mix	0	1.148	1.299	1.101	0.9565
13	MNP	3	Mix	60	0.762	0.661	0.7132	0.6544
13	MNP	3	Mix	120	0.6588	0.5167	0.6025	0.5796
13	MNP	3	Mix	180	0.5804	0.4257	0.5264	0.5133
13	MNP	3	Mix	240	0.5346	0.3765	0.4805	0.4802
13	MNP	3	Mix	480	0.4514	0.2868	0.3982	0.4191
13	MNP	3	Mix	720	0.4457	0.2623	0.3867	0.4215
14	MNP	3	Mix	0	1.024	1.083	1.125	1.0985
14	MNP	3	Mix	30	0.401	0.6811	0.4316	0.44785
14	MNP	3	Mix	60	0.4473	0.56675	0.4728	0.49945
14	MNP	3	Mix	90	0.19	0.4781	0.1985	0.2136
14	MNP	3	Mix	120	0.3334	0.4199	0.3431	0.37395
14	MNP	3	Mix	180	0.3824	0.357	0.3859	0.43395
14	MNP	3	Mix	240	0.2086	0.3314	0.2078	0.2396
14	MNP	3	Mix	360	0.2501	0.27455	0.2429	0.2885
14	MNP	3	Mix	480	0.3496	0.24605	0.3308	0.40155
15	MNP	3	Mix	0	1.024	1.083	1.125	1.0985
15	MNP	3	Mix	90	0.6782	0.4916	0.7044	0.75605
15	MNP	3	Mix	120	0.4242	0.44565	0.4358	0.4749
15	MNP	3	Mix	180	0.4229	0.3859	0.4271	0.47745
15	MNP	3	Mix	240	0.4582	0.36725	0.458	0.5172
15	MNP	3	Mix	360	0.3678	0.30695	0.3596	0.41895
15	MNP	3	Mix	480	0.498	0.27675	0.4795	0.56955
16	NO Fibers	3	Mix	60	1.012	1.0705	1.109	1.079
16	NO Fibers	3	Mix	120	1.012	1.0735	1.113	1.082

Experiment Number	Fiber Type	pH	1 ppm Soln.	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
16	NO Fibers	3	Mix	240	1.022	1.071	1.124	1.098
16	NO Fibers	3	Mix	360	0.8811	1.0905	0.9735	0.9523
16	NO Fibers	3	Mix	480	0.9939	1.032	1.089	1.0705

Table B,II. Raw data from NF kinetics experiments

Experiment Number	Fiber Type	pH	1 ppm Solution	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
1	NF	3	Cu	0	<MDL	1.505	<MDL	0.0518
1	NF	3	Cu	60	<MDL	0.66	<MDL	0.0119
1	NF	3	Cu	120	<MDL	0.5493	<MDL	0.0112
1	NF	3	Cu	180	<MDL	0.4948	0.0029	0.0123
1	NF	3	Cu	240	<MDL	0.447	<MDL	0.01
1	NF	3	Cu	480	<MDL	0.35	<MDL	0.0176
1	NF	3	Cu	720	<MDL	0.309	<MDL	0.0203
2	NF	3	Cu	0	<MDL	1.505	<MDL	0.0518
2	NF	3	Cu	60	<MDL	0.5885	<MDL	0.0114
2	NF	3	Cu	120	<MDL	0.5374	<MDL	0.013
2	NF	3	Cu	180	<MDL	0.474	<MDL	0.011
2	NF	3	Cu	240	<MDL	0.4314	<MDL	0.0134
2	NF	3	Cu	480	<MDL	0.3463	<MDL	0.0089
2	NF	3	Cu	720	<MDL	0.3114	<MDL	0.0099
3	NF	3	Cd	0	1.207	<MDL	<MDL	0.0305
3	NF	3	Cd	60	0.4109	<MDL	<MDL	0.0082
3	NF	3	Cd	120	0.3151	<MDL	<MDL	0.005
3	NF	3	Cd	180	0.2697	<MDL	<MDL	0.0051
3	NF	3	Cd	240	0.2573	<MDL	<MDL	0.0041
3	NF	3	Cd	480	0.2065	<MDL	<MDL	0.0069
3	NF	3	Cd	720	0.1853	<MDL	<MDL	0.0087
4	NF	3	Cd	0	1.207	<MDL	<MDL	0.0305
4	NF	3	Cd	60	0.4684	<MDL	<MDL	0.0057
4	NF	3	Cd	120	0.343	<MDL	<MDL	0.0051
4	NF	3	Cd	180	0.3045	<MDL	<MDL	0.0047
4	NF	3	Cd	240	0.2796	<MDL	<MDL	0.0054
4	NF	3	Cd	480	0.2137	<MDL	<MDL	0.0043
4	NF	3	Cd	720	0.1978	<MDL	<MDL	0.0057
5	NF	3	Ni	0	<MDL	<MDL	1.106	0.0514
5	NF	3	Ni	60	<MDL	<MDL	0.5198	0.0135
5	NF	3	Ni	120	<MDL	<MDL	0.4081	0.012
5	NF	3	Ni	180	<MDL	<MDL	0.3655	0.0111
5	NF	3	Ni	240	<MDL	<MDL	0.3248	0.0104

Experiment Number	Fiber Type	pH	1 ppm Solution	Time	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)
5	NF	3	Ni	480	<MDL	<MDL	0.2613	0.0099
5	NF	3	Ni	720	<MDL	<MDL	0.2494	0.0115
6	NF	3	Ni	0	<MDL	<MDL	1.106	0.0514
6	NF	3	Ni	60	<MDL	<MDL	0.5161	0.0103
6	NF	3	Ni	120	<MDL	<MDL	0.4149	0.0088
6	NF	3	Ni	180	<MDL	<MDL	0.351	0.0071
6	NF	3	Ni	240	<MDL	<MDL	0.3245	0.0091
6	NF	3	Ni	480	<MDL	<MDL	0.2589	0.0075
6	NF	3	Ni	720	<MDL	<MDL	0.2413	0.0081
7	NF	3	Zn	0	<MDL	<MDL	<MDL	0.9695
7	NF	3	Zn	60	<MDL	<MDL	<MDL	0.4088
7	NF	3	Zn	120	<MDL	<MDL	<MDL	0.3268
7	NF	3	Zn	180	<MDL	<MDL	<MDL	0.2833
7	NF	3	Zn	240	<MDL	<MDL	<MDL	0.2417
7	NF	3	Zn	480	<MDL	<MDL	<MDL	0.2028
7	NF	3	Zn	720	<MDL	<MDL	<MDL	0.1981
8	NF	3	Zn	0	<MDL	<MDL	<MDL	0.9695
8	NF	3	Zn	60	<MDL	<MDL	<MDL	0.4492
8	NF	3	Zn	120	<MDL	<MDL	<MDL	0.3629
8	NF	3	Zn	180	<MDL	<MDL	<MDL	0.3155
8	NF	3	Zn	240	<MDL	<MDL	<MDL	0.2747
8	NF	3	Zn	480	<MDL	<MDL	<MDL	0.2271
8	NF	3	Zn	720	<MDL	<MDL	<MDL	0.2225
9	NF	3	Mix	0	1.148	1.299	1.101	0.9565
9	NF	3	Mix	60	0.7984	0.7685	0.6846	0.659
9	NF	3	Mix	120	0.7616	0.7002	0.6425	0.6264
9	NF	3	Mix	180	0.7273	0.6404	0.5992	0.5973
9	NF	3	Mix	240	0.6947	0.6012	0.566	0.569
9	NF	3	Mix	480	0.6342	0.5251	0.5031	0.5164
9	NF	3	Mix	720	0.6155	0.4999	0.483	0.5082
10	NF	3	Mix	0	1.148	1.299	1.101	0.9565
10	NF	3	Mix	60	0.8573	0.8006	0.7429	0.7058
10	NF	3	Mix	120	0.8209	0.7463	0.695	0.6838
10	NF	3	Mix	180	0.783	0.6932	0.6521	0.6465
10	NF	3	Mix	240	0.7645	0.6563	0.6267	0.6333
10	NF	3	Mix	480	0.7276	0.5849	0.579	0.6035
10	NF	3	Mix	720	0.7253	0.5637	0.5673	0.6117
11	No Fiber	3	Mix	0	1.148	1.299	1.101	0.9565
11	No Fiber	3	Mix	240	1.105	1.267	1.058	0.8894
11	No Fiber	3	Mix	720	1.119	1.282	1.07	0.9078

Appendix C: Kinetics Graphs

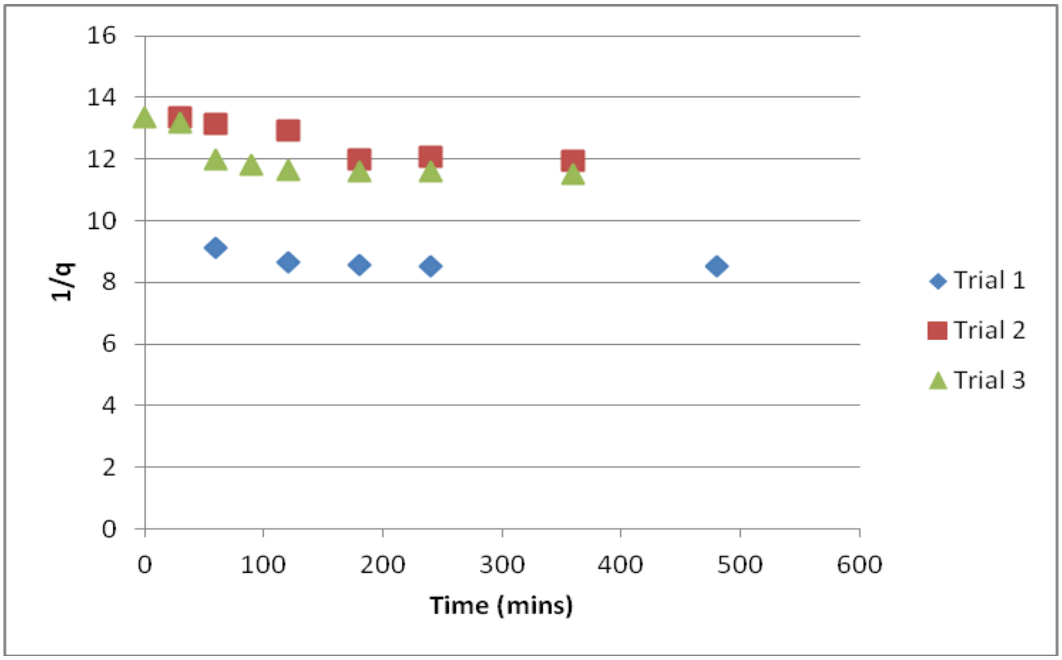


Figure C,1. Pseudo second order plot, MNP, cadmium

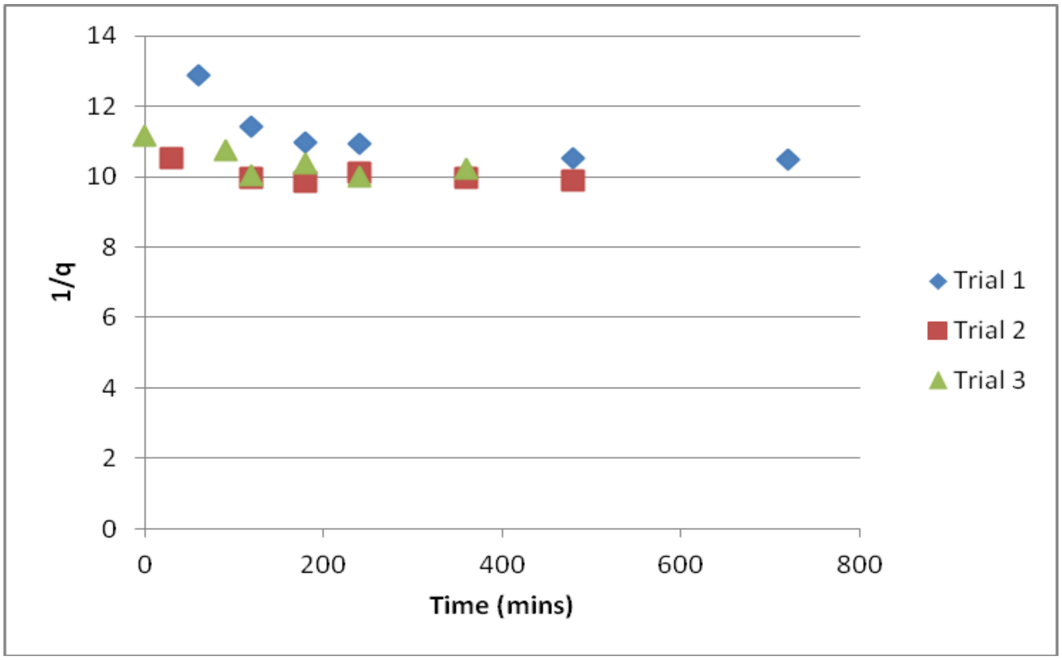


Figure C,2. Pseudo second order plot, MNP, nickel

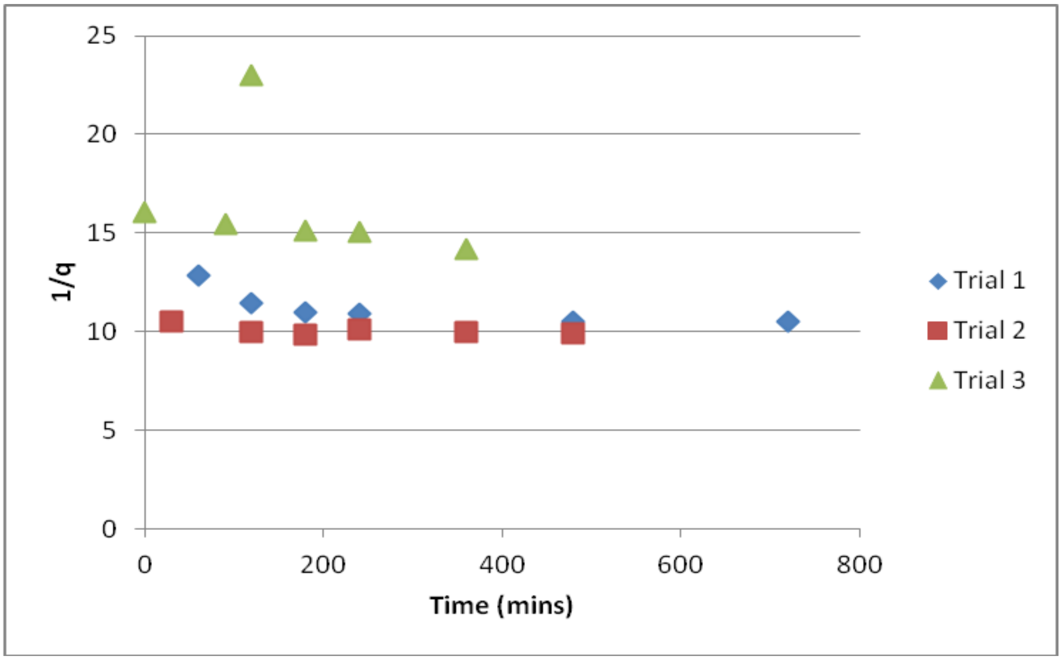


Figure C,3. Pseudo second order plot, MNP, zinc

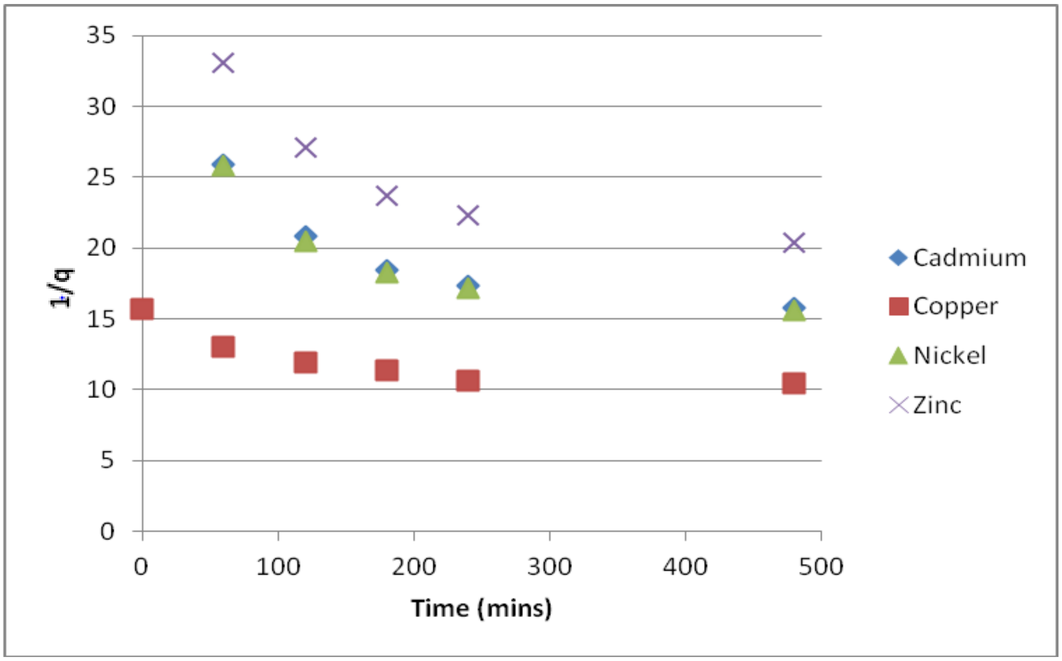


Figure C,4. Pseudo second order plot, MNP, mixed solution

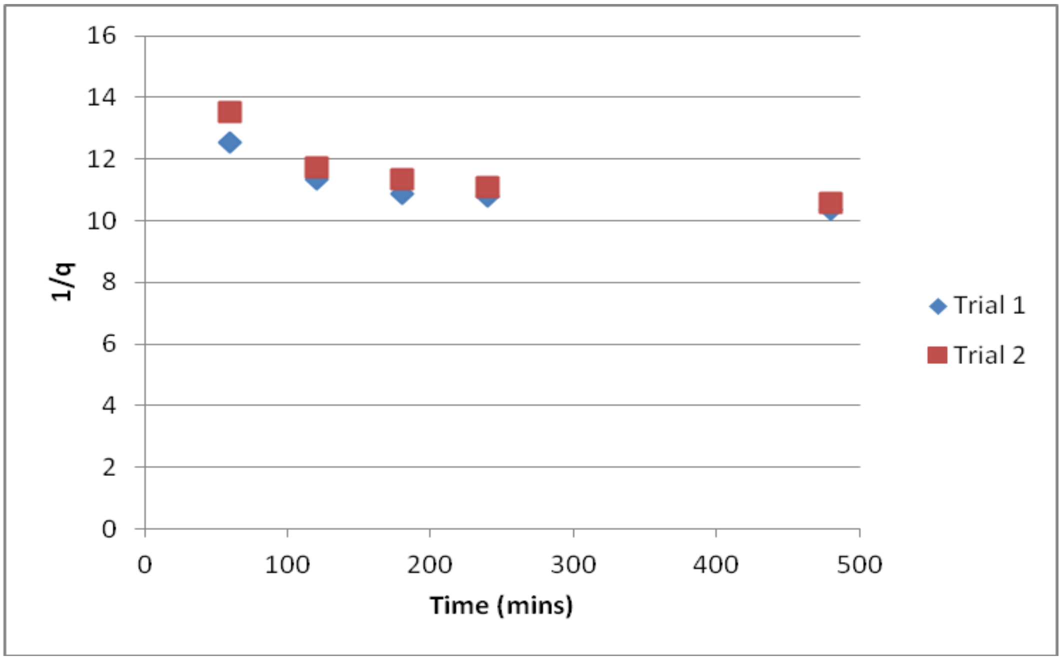


Figure C,5. Pseudo second order plot, NF, cadmium

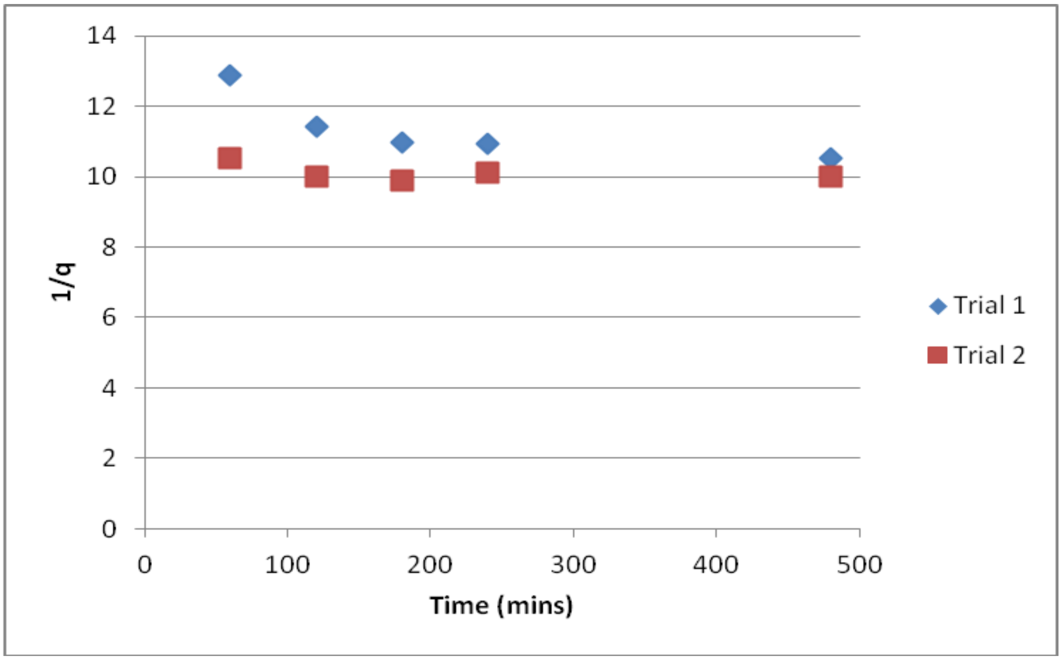


Figure C,6. Pseudo second order plot, NF, nickel

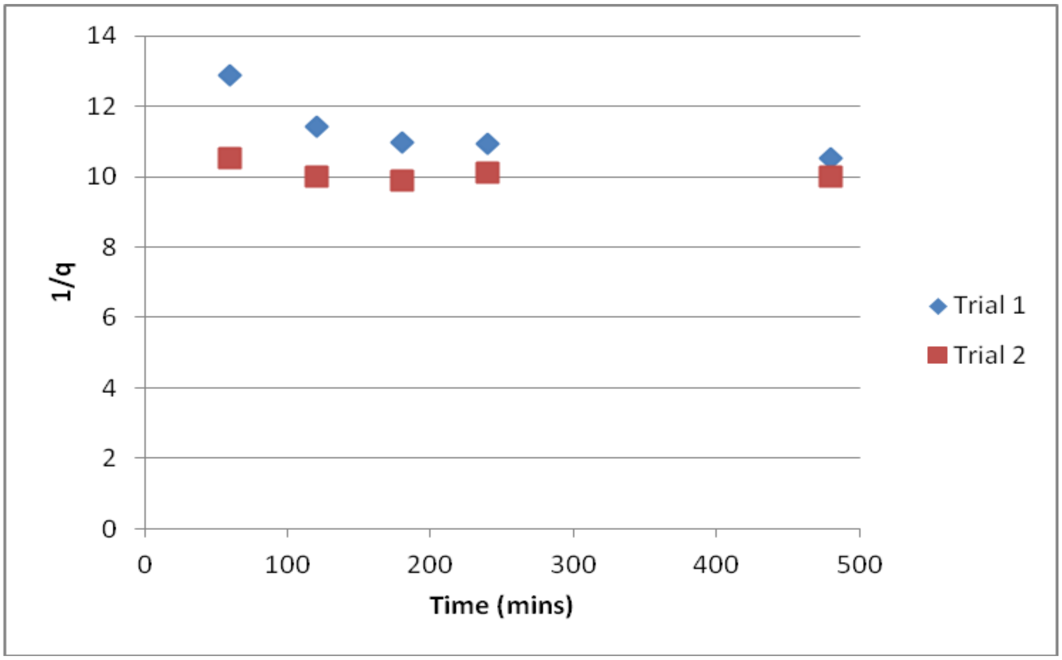


Figure C,7. Pseudo second order plot, NF, zinc

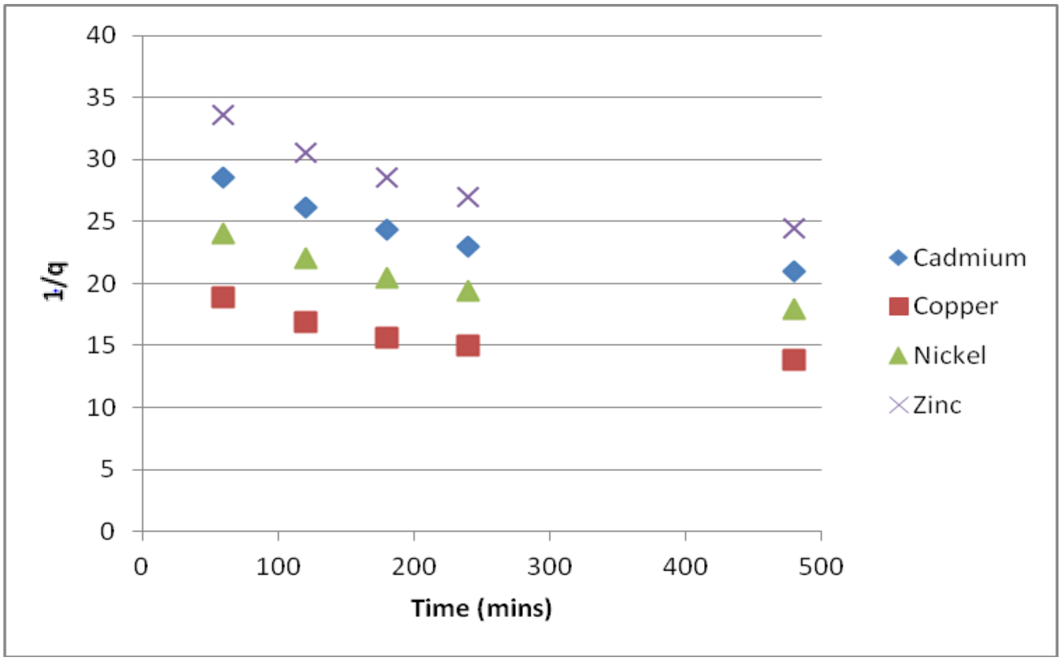


Figure C,8. Pseudo second order plot, NF, mixed Solution

Appendix D: Adsorbent Load Raw Data

Table D,I. Raw data from adsorbent load experiments

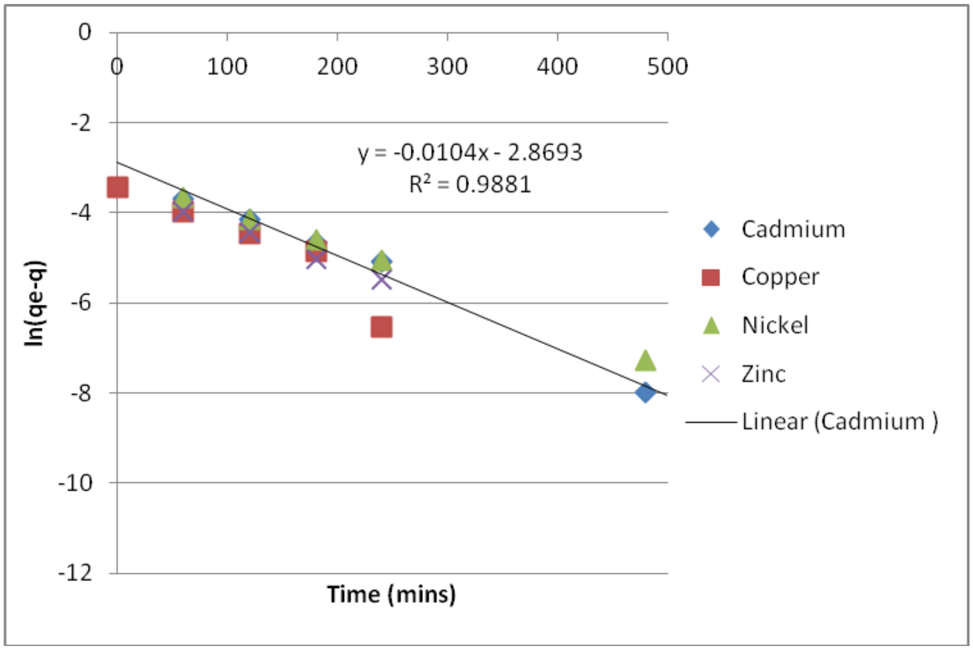
Sample Name	Fiber Type	Mass of Fiber (g)	Volume (L)	Metal in 1 ppm Mixed Solution	Initial Conc. (mg/L)	Final Conc. CA (mg/L)
1	NF	0.5019	0.2	Cu	1.0675	0.5847
2	NF	1.1135	0.2	Cu	1.0675	0.4730
3	NF	1.802	0.2	Cu	1.0675	0.4292
4	NF	2.357	0.2	Cu	1.0675	0.3515
5	NF	2.7962	0.2	Cu	1.0675	0.3304
6	NF	0.592	0.2	Cu	1.2610	0.6471
7	NF	1.084	0.2	Cu	1.2610	0.5865
8	NF	1.4685	0.2	Cu	1.2610	0.5526
9	NF	2.1915	0.2	Cu	1.2610	0.4414
10	NF	2.544	0.2	Cu	1.2610	0.4486
11	NF	3.4998	0.2	Cu	1.2610	0.3492
12	NF	4.1197	0.2	Cu	1.2610	0.3538
13	NF	5.1963	0.2	Cu	1.2610	0.2763
14	NF	0	0.2	Cu	1.2610	1.2830
15	NF	2	0.2	Cu	0	<MDL
16	MNP	1.0527	0.2	Cu	1.0675	0.2738
17	MNP	1.465	0.2	Cu	1.0675	0.2635
18	MNP	2.1429	0.2	Cu	1.0675	0.17475
19	MNP	2.673	0.2	Cu	1.0675	0.1379
20	MNP	0.5054	0.2	Cu	1.277	0.65
21	MNP	1.0493	0.2	Cu	1.277	0.4063
22	MNP	1.5706	0.2	Cu	1.277	0.2663
23	MNP	2.055	0.2	Cu	1.277	0.2296
24	MNP	2.7041	0.2	Cu	1.277	0.188
25	MNP	3.4085	0.2	Cu	1.277	0.1627
26	MNP	4.4992	0.2	Cu	1.277	0.0959
27	MNP	5.1745	0.2	Cu	1.277	0.0757
28	MNP	0	0.2	Cu	1.277	1.293
29	MNP	2	0.2	Cu	0	<MDL
1	NF	0.5019	0.2	Cd	0.8238	0.9473
2	NF	1.1135	0.2	Cd	0.8238	0.8238
3	NF	1.802	0.2	Cd	0.8238	0.6044
4	NF	2.357	0.2	Cd	0.8238	0.5257
5	NF	2.7962	0.2	Cd	0.8238	0.2191
6	NF	0.592	0.2	Cd	1.0970	0.9470

Sample Name	Fiber Type	Mass of Fiber (g)	Volume (L)	Metal in 1 ppm Mixed Solution	Initial Conc. (mg/L)	Final Conc. CA (mg/L)
7	NF	1.084	0.2	Cd	1.0970	0.8510
8	NF	1.4685	0.2	Cd	1.0970	0.8242
9	NF	2.1915	0.2	Cd	1.0970	0.6151
10	NF	2.544	0.2	Cd	1.0970	0.6194
11	NF	3.4998	0.2	Cd	1.0970	0.4315
12	NF	4.1197	0.2	Cd	1.0970	0.3882
13	NF	5.1963	0.2	Cd	1.0970	0.3269
14	NF	0	0.2	Cd	1.0970	1.1150
15	NF	2	0.2	Cd	0.0000	<MDL
16	MNP	1.0527	0.2	Cd	0.8238	0.725
17	MNP	1.465	0.2	Cd	0.8238	0.6958
18	MNP	2.1429	0.2	Cd	0.8238	0.4108
19	MNP	2.673	0.2	Cd	0.8238	0.288
20	MNP	0.5054	0.2	Cd	1.116	1.002
21	MNP	1.0493	0.2	Cd	1.116	0.8381
22	MNP	1.5706	0.2	Cd	1.116	0.6126
23	MNP	2.055	0.2	Cd	1.116	0.4801
24	MNP	2.7041	0.2	Cd	1.116	0.4124
25	MNP	3.4085	0.2	Cd	1.116	0.2499
26	MNP	4.4992	0.2	Cd	1.116	0.1015
27	MNP	5.1745	0.2	Cd	1.116	0.0569
28	MNP	0	0.2	Cd	1.116	0.0569
29	MNP	2	0.2	Cd	1.116	0.0569
1	NF	0.5019	0.2	Ni	0.7944	0.8417
2	NF	1.1135	0.2	Ni	0.7944	0.6721
3	NF	1.802	0.2	Ni	0.7944	0.4740
4	NF	2.357	0.2	Ni	0.7944	0.4175
5	NF	2.7962	0.2	Ni	0.7944	0.1740
6	NF	0.592	0.2	Ni	1.0500	0.8152
7	NF	1.084	0.2	Ni	1.0500	0.6949
8	NF	1.4685	0.2	Ni	1.0500	0.6676
9	NF	2.1915	0.2	Ni	1.0500	0.4779
10	NF	2.544	0.2	Ni	1.0500	0.4809
11	NF	3.4998	0.2	Ni	1.0500	0.3615
12	NF	4.1197	0.2	Ni	1.0500	0.3437
13	NF	5.1963	0.2	Ni	1.0500	0.2940
14	NF	0	0.2	Ni	1.0500	1.0570
15	NF	2	0.2	Ni	1.0500	<MDL

Sample Name	Fiber Type	Mass of Fiber (g)	Volume (L)	Metal in 1 ppm Mixed Solution	Initial Conc. (mg/L)	Final Conc. CA (mg/L)
16	MNP	1.0527	0.2	Ni	0.7944	0.6077
17	MNP	1.465	0.2	Ni	0.7944	0.5851
18	MNP	2.1429	0.2	Ni	0.7944	0.3569
19	MNP	2.673	0.2	Ni	0.7944	0.2452
20	MNP	0.5054	0.2	Ni	1.065	0.9086
21	MNP	1.0493	0.2	Ni	1.065	0.7072
22	MNP	1.5706	0.2	Ni	1.065	0.4925
23	MNP	2.055	0.2	Ni	1.065	0.3973
24	MNP	2.7041	0.2	Ni	1.065	0.3422
25	MNP	3.4085	0.2	Ni	1.065	0.2574
26	MNP	4.4992	0.2	Ni	1.065	0.1723
27	MNP	5.1745	0.2	Ni	1.065	0.1466
28	MNP	0	0.2	Ni	1.065	0.1466
29	MNP	2	0.2	Ni	1.065	0.1466
1	NF	0.5019	0.2	Zn	0.8593	0.9903
2	NF	1.1135	0.2	Zn	0.8593	0.8532
3	NF	1.802	0.2	Zn	0.8593	0.6279
4	NF	2.357	0.2	Zn	0.8593	0.5867
5	NF	2.7962	0.2	Zn	0.8593	0.2343
6	NF	0.592	0.2	Zn	0.8843	0.7862
7	NF	1.084	0.2	Zn	0.8843	0.7034
8	NF	1.4685	0.2	Zn	0.8843	0.6814
9	NF	2.1915	0.2	Zn	0.8843	0.5098
10	NF	2.544	0.2	Zn	0.8843	0.5188
11	NF	3.4998	0.2	Zn	0.8843	0.3736
12	NF	4.1197	0.2	Zn	0.8843	0.3448
13	NF	5.1963	0.2	Zn	0.8843	0.2980
14	NF	0	0.2	Zn	0.8843	0.9042
15	NF	2	0.2	Zn	0.8843	0.0044
16	MNP	1.0527	0.2	Zn	0.85925	0.7681
17	MNP	1.465	0.2	Zn	0.85925	0.7402
18	MNP	2.1429	0.2	Zn	0.85925	0.47975
19	MNP	2.673	0.2	Zn	0.85925	0.3393
20	MNP	0.5054	0.2	Zn	0.9044	0.8457
21	MNP	1.0493	0.2	Zn	0.9044	0.7239
22	MNP	1.5706	0.2	Zn	0.9044	0.5395
23	MNP	2.055	0.2	Zn	0.9044	0.4409
24	MNP	2.7041	0.2	Zn	0.9044	0.3852

Sample Name	Fiber Type	Mass of Fiber (g)	Volume (L)	Metal in 1 ppm Mixed Solution	Initial Conc. (mg/L)	Final Conc. CA (mg/L)
25	MNP	3.4085	0.2	Zn	0.9044	0.2697
26	MNP	4.4992	0.2	Zn	0.9044	0.1491
27	MNP	5.1745	0.2	Zn	0.9044	0.1125
28	MNP	0	0.2	Zn	0.9044	0.1125
29	MNP	2	0.2	Zn	0.9044	0.1125

Appendix E: Pseudo First Order Plots



FigureE,1. Pseudo first order plot, MNP, Mixed solution, cadmium trend

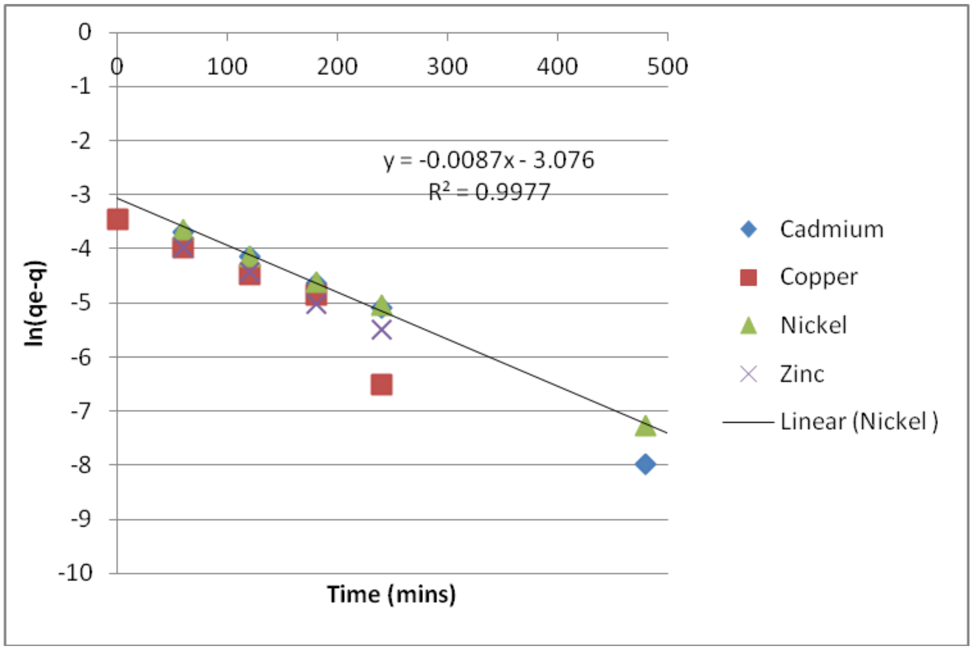


Figure E,2. Pseudo first order plot, MNP, Mixed solution, nickel trend

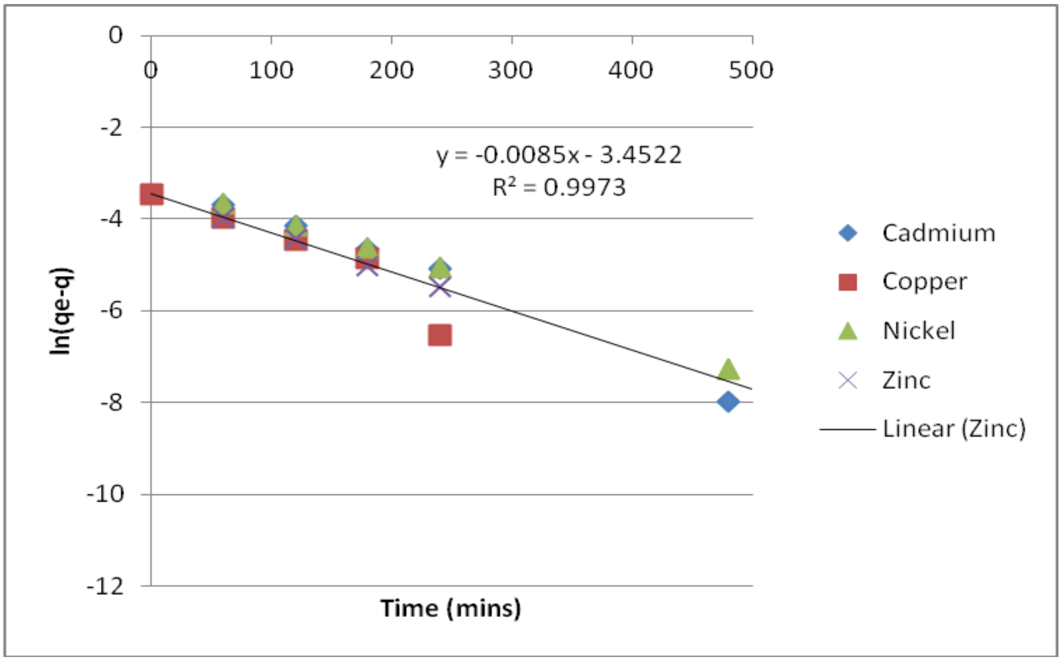
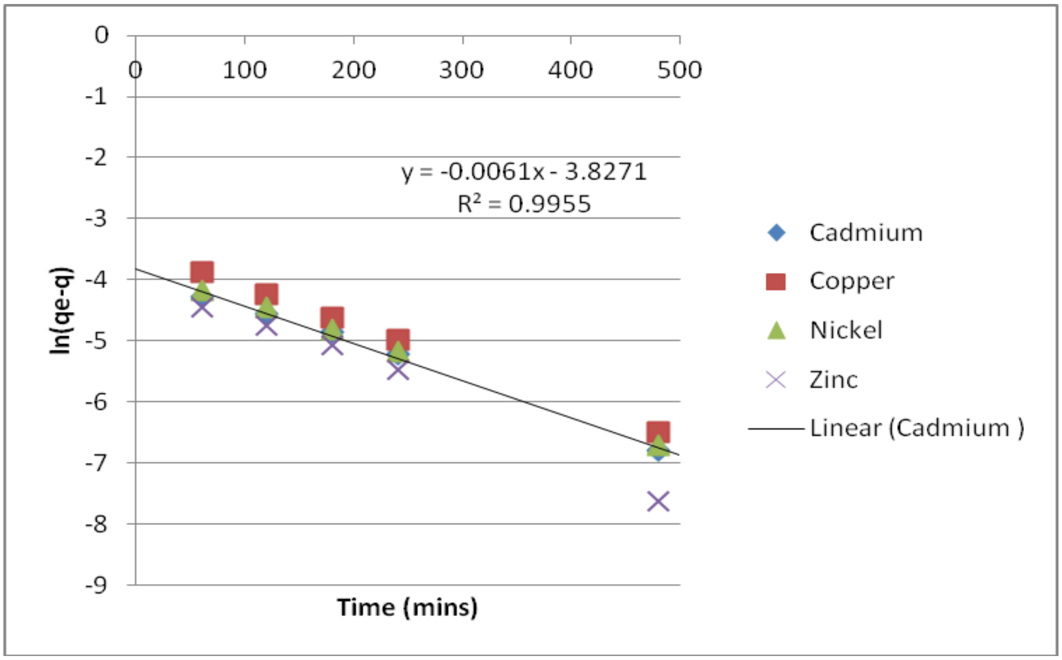
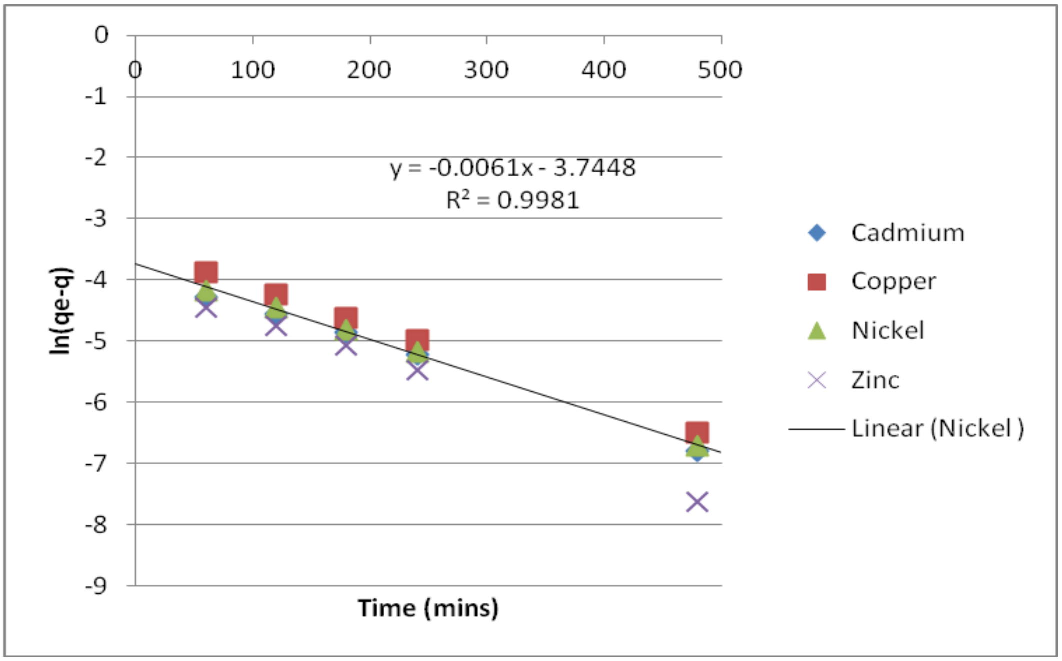


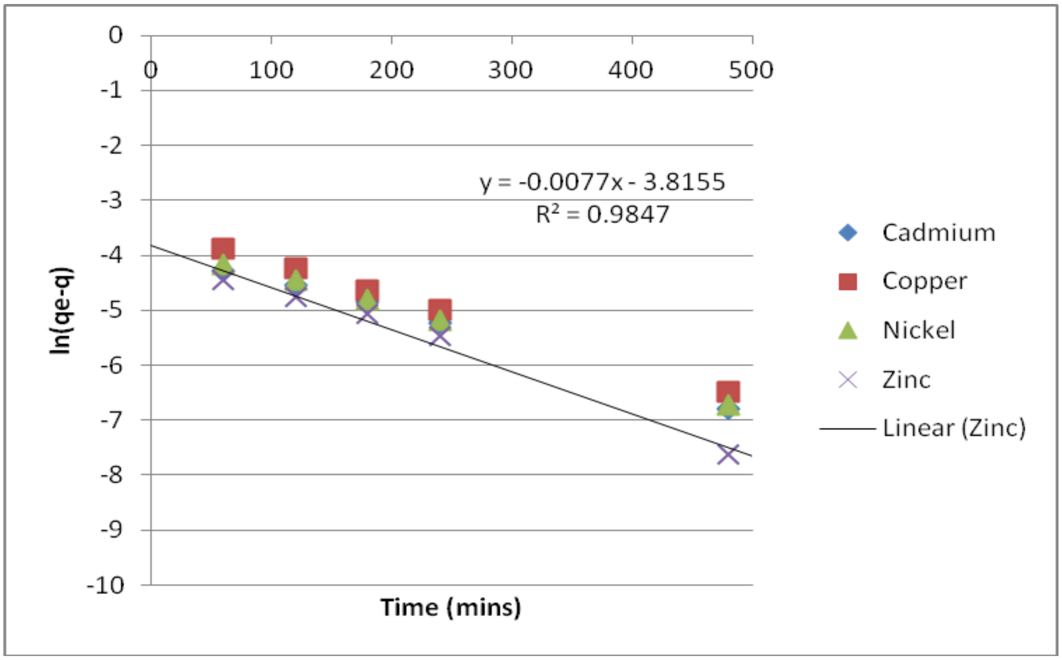
Figure E,3. Pseudo first order plot, MNP, Mixed solution, zinc trend



FigureE,4. Pseudo first order plot, NF, Mixed Solution, cadmium trend

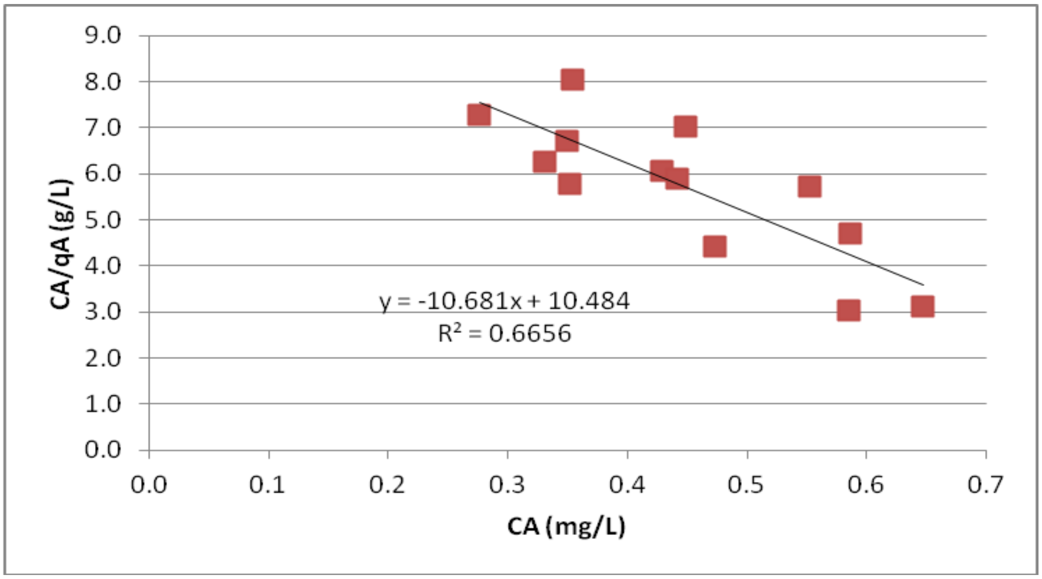


FigureE,5. Pseudo first order plot, NF, Mixed solution, nickel trend



FigureE,6. Pseudo first order plot, NF. Mixed Solution, zinc trend

Appendix F: Isotherm Plots with R^2 values < 0.500



FigureF,1. NF Copper Langmuir isotherm plot

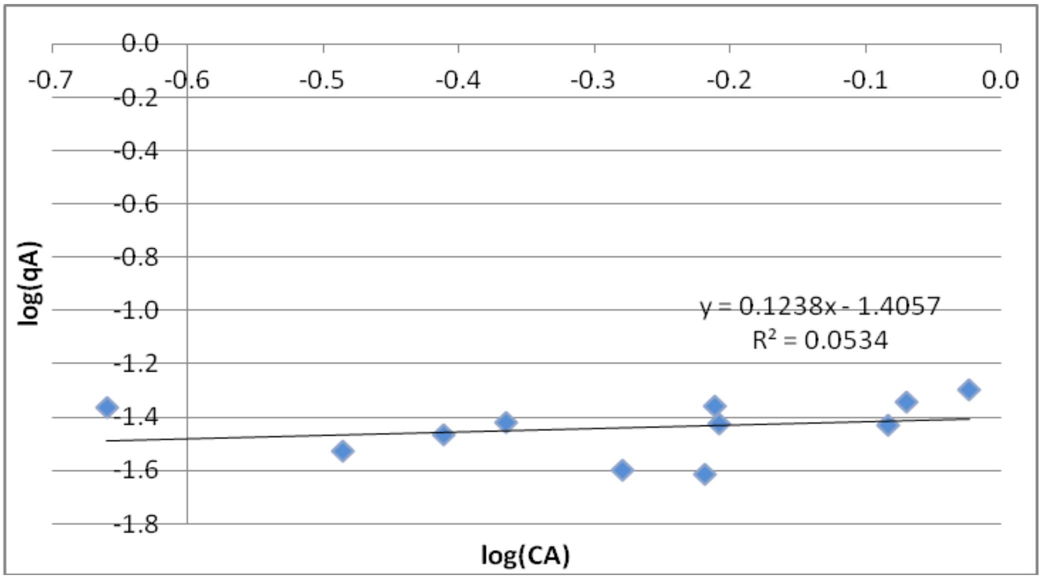


Figure F,2. NF Cadmium Freundlich isotherm plot

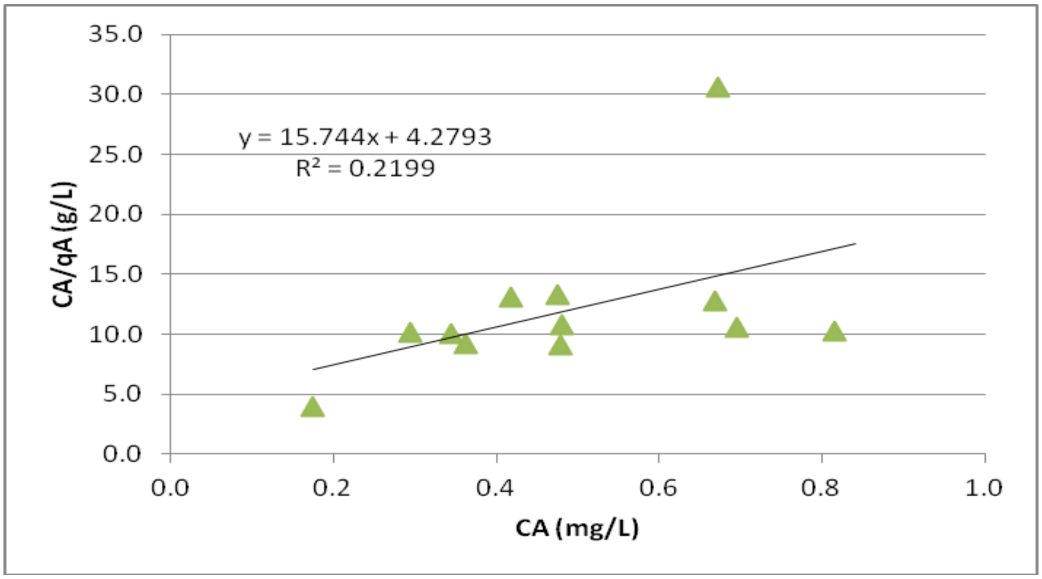
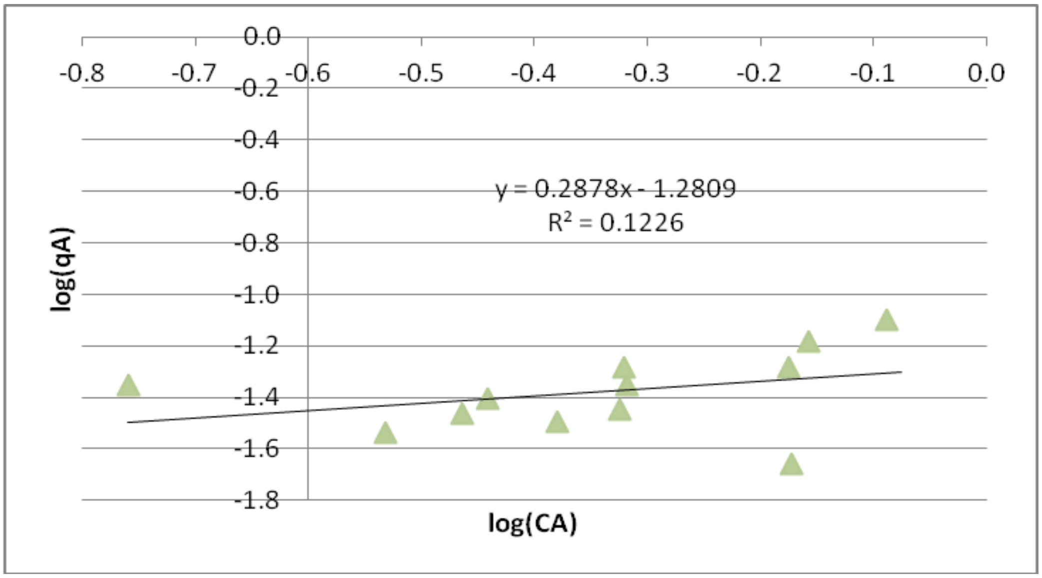


Figure F,3. NF Nickel Langmuir isotherm plot



FigureF,4. NF Nickel Freundlich isotherm plot

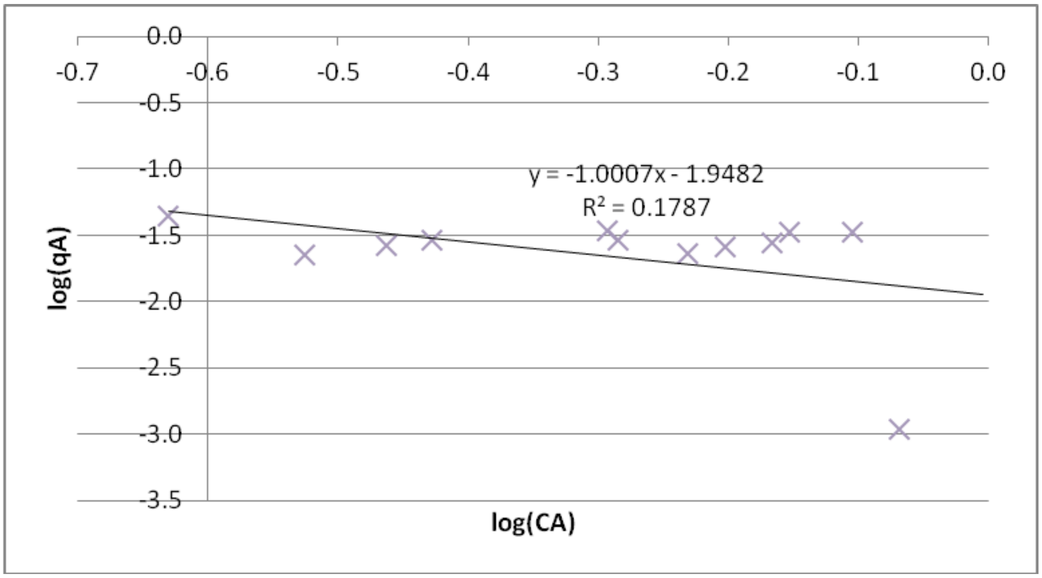


Figure F,5. NF Zinc Freundlich isotherm plot

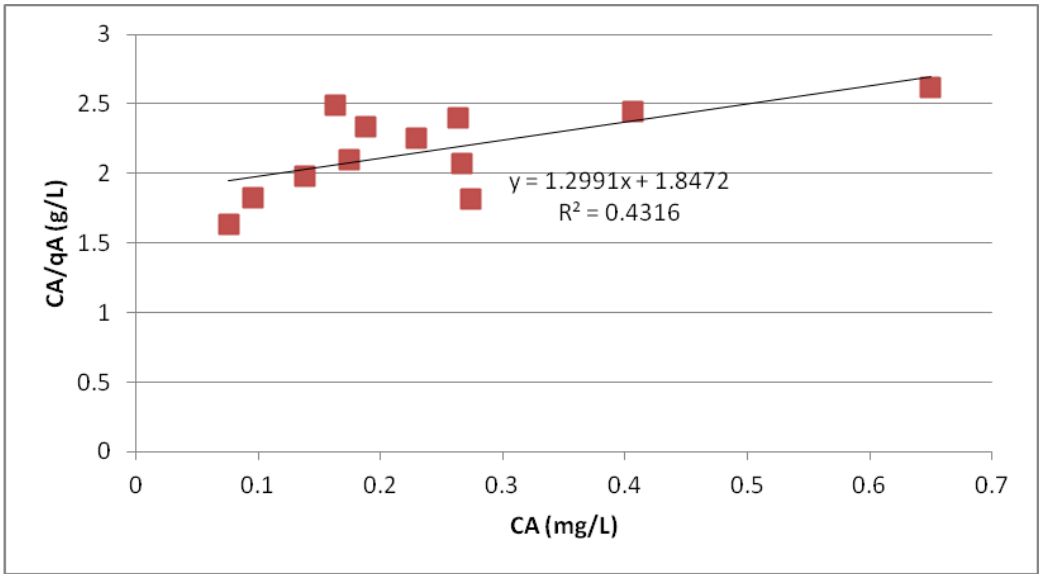


Figure F,6. MNP Copper Langmuir isotherm plot

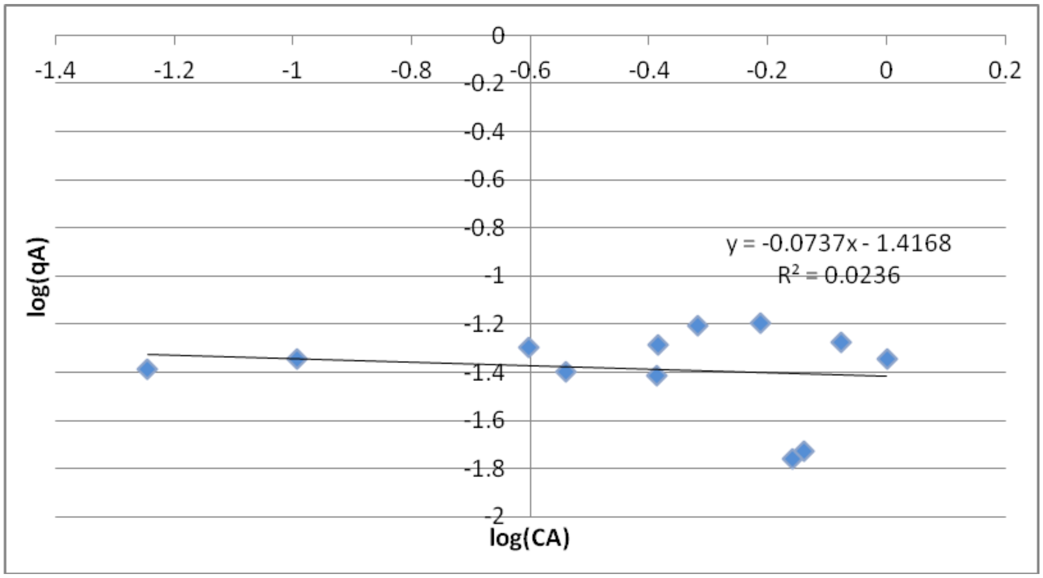


Figure F,7. MNP Cadmium Freundlich isotherm plot

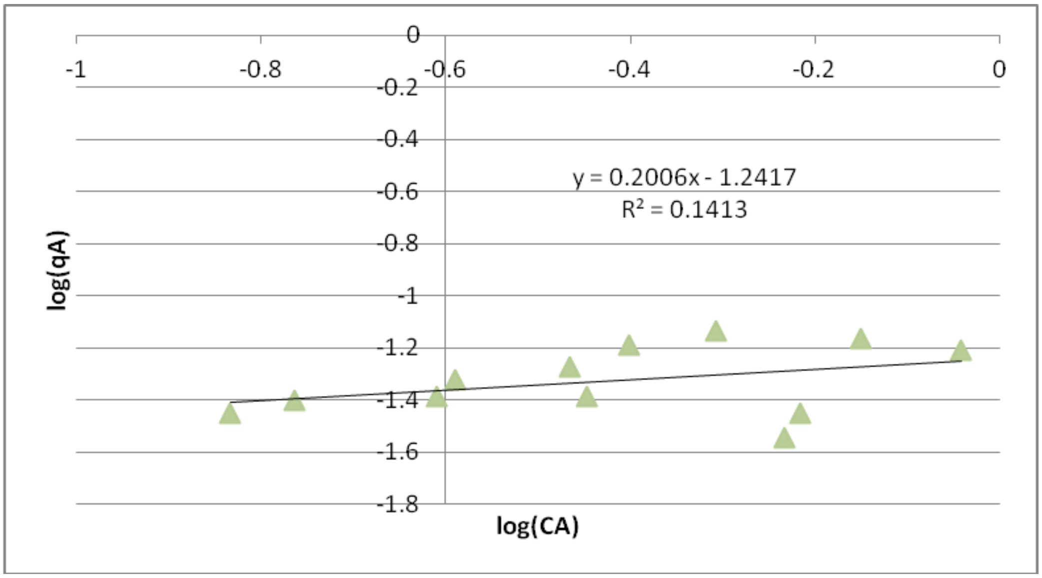
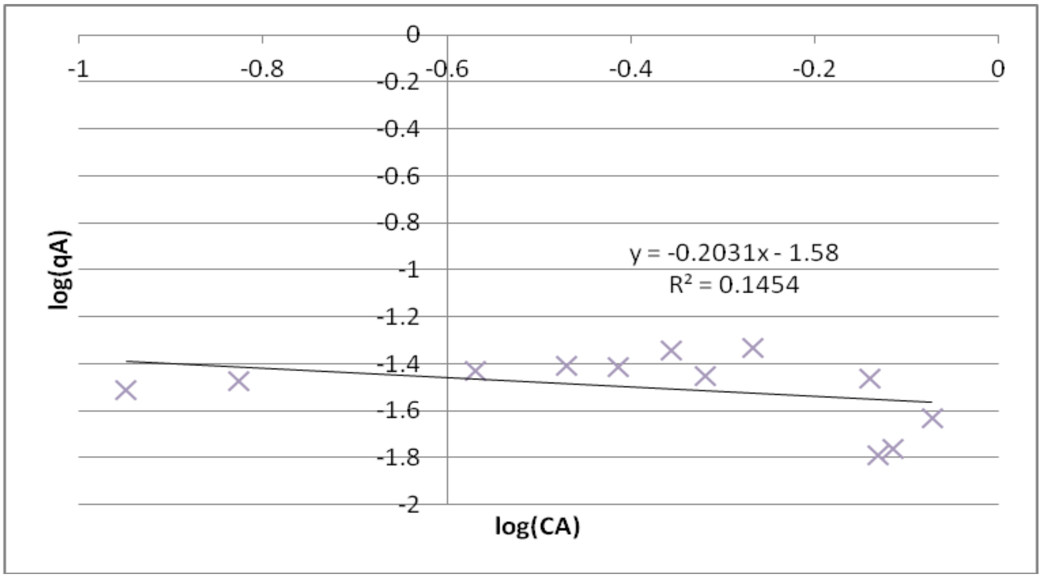


Figure F,8. MNP Nickel Freundlich isotherm plot



FigureF,9. MNP Zinc Freundlich isotherm plot

Appendix G: Digestion Raw Data

Table G. Sample MNP Digestion

Metals	MNP Digest Concentration	Mass of Fiber	Volume	Mass of Metal	Digestion Correction	Digestion Correction	MNP
	mg/L	grams	L	mg	mg/L	Mg	mg/g
Al1670	0.0215	2.069	0.055	0.0011825	0.4567	0.0251185	<MDL
Be3130	<MDL	2.069	0.055	<MDL	<MDL	<MDL	<MDL
Cd2288	0.0024	2.069	0.055	0.000132	0.0004	0.000022	5.31658E-05
Co2286	0.068	2.069	0.055	0.00374	<MDL	<MDL	0.001868777
Cr2835	0.0645	2.069	0.055	0.0035475	0.0538	0.002959	0.000284437
Cu3247	0.2423	2.069	0.055	0.0133265	0.0018	0.000099	0.006393185
Fe2599	5.678	2.069	0.055	0.31229	7.619	0.419045	<MDL
Hg1849	<MDL	2.069	0.055	<MDL	<MDL	<MDL	<MDL
Li6707	0.0014	2.069	0.055	0.000077	<MDL	<MDL	9.03818E-05
Mg2795	12.53	2.069	0.055	0.68915	0.0948	0.005214	0.330563557
Mn2576	0.1791	2.069	0.055	0.0098505	0.1139	0.0062645	0.001733204
Mo2020	<MDL	2.069	0.055	<MDL	<MDL	<MDL	0.000499758
Ni2216	<MDL	2.069	0.055	<MDL	0.0087	0.0004785	<MDL
Pb2203	0.0076	2.069	0.055	0.000418	<MDL	<MDL	0.000260512
Sb2068	0.0109	2.069	0.055	0.0005995	0.0071	0.0003905	0.000101015
Se1960	0.0382	2.069	0.055	0.002101	0.0183	0.0010065	0.000529
Sr4077	0.539	2.069	0.055	0.029645	<MDL	<MDL	0.014384002
Ti3349	0.0319	2.069	0.055	0.0017545	<MDL	<MDL	0.000874577
Tl1908	<MDL	2.069	0.055	<MDL	<MDL	<MDL	<MDL
V_3093	0.0205	2.069	0.055	0.0011275	<MDL	<MDL	0.00080812
Zn2138	0.2835	2.069	0.055	0.0155925	0.0314	0.001727	0.006701547

Appendix H: Bench Scale Raw Data

Table H. Raw data for bench scale analysis

Experiment	Fiber Type	Solution	Sample Name	Cd2288	Co2286	Cu3247	Fe2599	Hg1849	Li6707	Mn2576	Mo2020	Ni2216	Pb2203	Sb2068	Se1960	Sr4077	Ti3349	V_3093	Zn2138
1	NF-NF	1 ppm Mix	Initial	1.197	<MDL	1.052	<MDL	0.1077	<MDL	<MDL	<MDL	1.161	<MDL	<MDL	<MDL	<MDL		0.0007	1.118
1	NF-NF	1 ppm Mix	Column1	0.8562	<MDL	0.3814	1.521	0.0357	0.0008	0.0761	<MDL	0.7522	0.0658	<MDL	<MDL	0.0935		0.0194	0.8461
1	NF-NF	1 ppm Mix	Column 2	0.4004	<MDL	0.0941	0.8318	0.0255	0.0035	0.0792	<MDL	0.353	0.0267	<MDL	<MDL	0.1155		0.0357	0.4124
2	NF-NF	1 ppm Mix	Initial	1.091	-0.0016	1.094	<MDL	0.0186	<MDL	<MDL	<MDL	1.048	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1.008
2	NF-NF	1 ppm Mix	Column 1	0.5789	<MDL	0.426	0.0805	0.0405	0.0023	0.0241	<MDL	0.4926	<MDL	<MDL	<MDL	0.091	<MDL	0.0309	0.6205
2	NF-NF	1 ppm Mix	Column 2	0.2507	<MDL	0.1313	0.1116	<MDL	0.0096	0.0405	<MDL	0.2393	<MDL	<MDL	<MDL	0.1541	<MDL	0.0628	0.3252
3	NF-MNP	1 ppm Mix	Initial	1.478	<MDL	1.73	<MDL	0.0241	<MDL	<MDL	<MDL	1.45	<MDL	<MDL	<MDL	<MDL	<MDL	0.0039	1.38
3	NF-MNP	1 ppm Mix	Column 1	1.765	<MDL	1.194	0.1847	<MDL	0.0038	0.0383	<MDL	1.506	<MDL	<MDL	<MDL	0.1529	<MDL	0.0314	1.704
3	NF-MNP	1 ppm Mix	Column 2	0.9881	0.0073	0.3824	0.3293	0.0193	0.0032	0.0427	<MDL	0.9168	0.0001	<MDL	<MDL	0.1338	<MDL	<MDL	1.044
4	NF-MNP	2 ppm Mix	Initial	2.181	<MDL	2.25	0.0263	0.0436	0.0138	<MDL	<MDL	2.076	<MDL	<MDL	<MDL	0.0056	0.0321	<MDL	2.052
4	NF-MNP	2 ppm Mix	Column 1	0.0038	<MDL	<MDL	<MDL	0.0677	<MDL	<MDL	<MDL	0.0028	<MDL	0.0004	<MDL	<MDL	<MDL	0.0189	1.327
4	NF-MNP	2 ppm Mix	Column 2	0.6623	0.0062	0.2179	0.3361	<MDL	0.011	0.0392	<MDL	0.7417	0.0003	<MDL	<MDL	0.1059	0.0153	<MDL	0.7974
5	NF-NF	1 ppm Mix	Initial	0.7978	<MDL	0.8112	0.0058	0.0231	0.0056	<MDL	<MDL	0.7597	<MDL	<MDL	<MDL	0.0014	0.0069	<MDL	0.7826
5	NF-NF	1 ppm Mix	Column1	0.5373	<MDL	0.5086	0.1569	0.0154	0.0235	0.0313	<MDL	0.4175	0.0005	<MDL	<MDL	0.1172	0.028	<MDL	0.536
5	NF-NF	1 ppm Mix	Column 2	0.2846	<MDL	0.094	0.1248	0.0168	0.0194	0.0452	<MDL	0.1768	<MDL	<MDL	<MDL	0.146	0.0176	<MDL	0.3128
6	NF-MNP	MTW	Initial	0.9634	0.0067	1	<MDL	<MDL	0.1644	2.76	1.517	0.7258	<MDL	0.0079	0.0115	<MDL	<MDL	0.7004	0.915
6	NF-MNP	MTW	Column 1	0.9004	0.0076	0.4317	0.0501	<MDL	0.1656	2.658	0.3086	0.6222	<MDL	0.0077	0.0113	<MDL	<MDL	0.6834	0.8954
6	NF-MNP	MTW	Column 2	0.8594	0.013	0.1364	0.5101	<MDL	0.1673	2.633	0.1139	0.5575	<MDL	0.0082	0.0092	<MDL	<MDL	0.6774	0.9067
7	NF-MNP	MTW	Initial	0.9634	0.0067	1	<MDL	<MDL	0.1644	2.76	1.517	0.7258	<MDL	0.0079	0.0115	<MDL	<MDL	0.7004	0.915
7	NF-MNP	MTW	Column 1	0.9393	0.0081	0.3894	0.0457	0.0388	0.1578	2.81	0.2581	0.6691	<MDL	0.0087	0.0126	3.482	<MDL	0.7103	0.9321
7	NF-MNP	MTW	Column 2	0.8875	0.017	0.123	0.3904	<MDL	0.1539	2.757	0.1546	0.6032	<MDL	0.009	0.0103	3.433	<MDL	0.6713	0.9134

Appendix I: Mass Balance Raw Data

Table I. Mass balance raw data

Sample	Initial Metals	Column 1	Column 2	Metal in Final Water	Unaccounted
	mg	mg	mg	mg	mg
Al1670	<MDL	3.3406897	2.607073	1.5407242	-7.4890641
As1890	<MDL	0.001855313	0.00285	0.0003656	-0.00754591
Be3130	<MDL	0.002530612	0.003574	<MDL	-0.0074294
Cd2288	0.936375	0.51898703	0.257924	0.2199492	-0.06048521
Co2286	<MDL	0.002548042	0.002384	<MDL	-0.00534469
Cr2835	<MDL	0.026415838	0.030857	0.001749	-0.06100186
Cu3247	0.938025	0.507264097	0.178958	0.1301908	0.121612556
Fe2599	<MDL	<MDL	<MDL	<MDL	1.013193718
Hg1849	0.013365	<MDL	<MDL	0.0276492	0.7483694
Li6707	<MDL	0.004835439	0.012965	0.011159	-0.03060945
Mn2576	<MDL	<MDL	<MDL	0.0219894	0.209093633
Ni2216	0.90915	0.441529494	0.217073	0.1558792	0.094668166
Pb2203	<MDL	0.01009534	0.009078	<MDL	-0.01956204
Sb2068	<MDL	<MDL	<MDL	<MDL	0.003963814
Se1960	<MDL	<MDL	<MDL	0.0044	0.032430565
Sr4077	<MDL	0.084496112	0.102192	0.10217	-0.29075552
Ti3349	<MDL	0.01253195	0.063628	0.01359	-0.091647
Zn2138	0.85305	0.387938304	0.156445	0.2228188	0.085847514

Appendix J: Mine Tailing Water Chemical Composition

Table J. Mine Tailing Water Chemical Composition

METALS	**MTW Concentration (mg/L)**
Aluminum	12.5725
Arsenic	0.005075
Gold	0.005733
Beryllium	<MDL
Calcium	<MDL
Cadmium	<MDL
Cobalt	0.005725
Chromium	<MDL
Copper	0.009025
Iron	0.014925
Mercury	<MDL
Lithium	0.15565
Magnesium	<MDL
Manganese	3.06025
Nickel	<MDL
Lead	<MDL
Antimony	0.005075
Selenium	0.01
Strontium	3.73225
Titanium	<MDL
Thallium	<MDL
Vanadium	0.6118
Zinc	0.006225
ANIONS	**MTW Concentration (mg/L)**
Fluoride	5.53
Chloride	1383.203
Sulfate	1812.8265
Nitrate	11.3135
Bromide	61.016

SIGNATURE PAGE

This is to certify that the thesis prepared by Samantha Hutcheson entitled "Characterization of Heavy Metal Removal from Aqueous Solutions Using Natural Fiber Impregnated with Metallic Nanoparticles" has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Tech of The University of Montana, on this 2nd day of May, 2016.

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