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AQUEOUS ZINC REMOVAL USING NANOPARTICLE TREATED NATURAL FIBERS

by

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Abstract

The objective of this thesis research is to evaluate and enhance a recently developed water treatment technology. The technology was previously successful in removing airborne mercury from coal fired power plant flue gas, and has since been demonstrated to remove aqueous copper and cadmium. The technology uses natural coconut fibers impregnated with metal nanoparticles using a proprietary technique. A series of batch tests determined that both the treated and untreated natural fibers were capable of removing over 90% of aqueous zinc from a synthetic solution made by dissolving $ZnCl_2$ salts in deionized water. Further testing with a bench scale continuous flow reactor demonstrated that the treated fibers were capable of removing up to 70% of aqueous zinc with an EBCT of ten minutes. Further testing could prove the technology a viable and cost-effective alternative solution for treating industrial wastewater.

Keywords: Water Treatment, Adsorption, Zinc, Natural Fiber

Dedication

I would like to thank my parents for their unwavering support and encouragement. Thanks especially to my little brother for providing many excellent conversations when I needed a diversion. Finally, my friends who shared the struggle should also share the glory. I could not have done it without all of you.

Acknowledgements

I would like to thank the members of my committee, Dr. Bill Drury, Dr. Kumar Ganesan, and Dr. Butch Gerbrandt, without whom this research would not have been possible. Thanks also to Pankajam Ganesan, Jeanne Larson, and Gary Wyss for their invaluable assistance with laboratory and analytical work.

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1. Introduction

Environmental engineering is a profession dedicated to the protection and promotion of human health and the natural environment. In pursuit of that goal, environmental engineers develop and test new technologies to improve the efficiency and reduce the cost of waste treatment practices. Much research has gone into means of using biomass as waste treatment media (Lim, Teng, Ibrahim, Ahmad, & Chee, 2012) (Volesky, 1987) (Banat, Al-Asheh, & Mohai, 2000). The technique presented in this thesis uses coconut fibers, an agricultural waste, impregnated with metal nanoparticles to remove toxic heavy metals from water. This research focuses on removing aqueous zinc.

1.1. Background Information

Zinc is a metallic element commonly used in many manufacturing processes. It is used to produce die-casts, essential to the automobile and hardware industries, and is used extensively to galvanize other metals to prevent rusting. Zinc oxide is also used in the production of paints, rubbers, pharmaceuticals, plastics, textiles, electrical equipment, and many other common products. In small amounts, zinc is an essential nutrient. The average human takes in approximately 15 milligrams per day (Royal Society of Chemistry, n.d.).

Consumption of excess zinc can cause gastrointestinal distress and alterations to the hematological system in humans. Animal studies have shown zinc to cause lesions on the liver, kidneys, and pancreas (Agency for Toxic Substances and Disease Registry (ATSDR), 2005).

Zinc contamination of water occurs primarily from mine operations and wastes. Groundwater monitoring in mining impacted Butte, Montana showed zinc concentrations ranging from 0.42 mg/L up to 408 mg/L (Gammons, Shope, & Duaime, 2005). Zinc is also a component in paints and dyes, and can leach into water distribution systems from pipes and fittings (TSC Water Treatment Engineering Team, 2009). Other sources of aqueous zinc include runoff from galvanized materials on roofs and materials released from vehicles, especially from motor oils and hydraulic fluid. Zinc concentrations in these sources have been reported to be as high as 0.63 mg/L (Golding, 2006).

The Environmental Protection Agency (EPA) sets primary drinking water standards based on human health and aquatic life and secondary standards based on aesthetics or comfort. The water quality standards for zinc are shown in Table I I.

Table I: EPA National Recommended Water Quality Criteria

Criteria	Standard (ppm)
Aquatic Life	0.12
Human Health	7.40
Organoleptic Criteria	5.00

(EPA, n.d.)

1.2. State of the Art

Water treatment options for removing dissolved solids are many and varied. Some of the more commonly used treatment techniques are adsorption, ion exchange, and reverse osmosis.

1.2.1. Adsorption

Adsorption is a mass transfer operation where aqueous phase substances accumulate on a solid phase adsorption media. Activated carbon is one of the most common adsorption media, especially for drinking water treatment. The water treatment technique examined in this research is an adsorption process.

During the adsorption process, the dissolved constituent, the adsorbate, is transported into the porous adsorbent media by diffusion. The adsorbate is then adsorbed onto the active sites of the adsorbent. Adsorption phenomena are divided into either chemisorption or physical adsorption. Chemisorption involves electron exchange, creating a chemical bond between the adsorbate and the surface of the adsorbent. Chemisorption is rarely used in water treatment. Physical adsorption is a rapid process caused by several binding mechanisms, most notably van der Waals forces. Physical adsorption is also reversible, which enables regeneration of the adsorbent for re-use. However, carbons for water treatment are seldom regenerated because complete restoration of adsorption capacity cannot be achieved and new activated carbon is inexpensive (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012). Reactivation for water treatment purposes only makes economic sense if carbon usage is greater than 150,000 kg/yr (Sontheimer, Crittenden, & Summers, 1988).

Physical adsorption is dependent on three competing interactions. Adsorbate-surface interactions determine the strength of the attraction of the adsorbate to the adsorbent and are the driving forces for adsorption. Adsorbate-water interactions and water-surface interactions tend to oppose adsorption based on the solubility of the adsorbate and the surface chemistry of the adsorbent. For water treatment purposes the single most important factor for successful adsorption process is the number of adsorption sites available for the adsorbate, commonly called active sites, and the number of active sites of the adsorbent is dependent on surface area and pore size. Surface area and pore size have an inverse relationship, the smaller the pores are for a given volume of pores, the greater the surface area that is available for adsorption. Additionally, pore size determines the size of the adsorbate that can be adsorbed, a phenomenon known as steric effects. While pore size determines what adsorbates can be adsorbed, surface area more directly determines the amount of adsorbate that can be adsorbed. Commercially available activated carbon typically has a surface area of around 1000 m^2/g as measured by the Brunauer, Emmett, and Teller (BET) method (Table 15-2, 2012).

There are three main types of commercially used adsorbents: zeolites, synthetic polymeric adsorbents, and activated carbon. Activated carbon is the most commonly used adsorbent due to its low cost and high availability. Any natural, carbonaceous material can be used to manufacture activated carbon and the activation processes are typically inexpensive. Activated carbon production involves two processes, pyrolytic carbonization and activation. Carbonization releases volatile components from the carbonaceous material and causes graphite to form as well as creating a more porous structure. The activation step increases porosity and the average size of the micropores. Activated carbon is produced either by chemical or physical activation, with chemical activation combining the carbonization and activation processes and physical activation accomplishing them as discrete steps.

Chemical activation uses dehydrating chemicals that are added to the cellulose containing raw material at elevated temperatures. The whole is then heated, cooled, and the activating chemicals extracted. This process results in low density carbons with a low proportion of micropores, making them unsuitable for removing micropollutants without further treatment.

Physical activation is more commonly used to produce carbons for water treatment. Usually this is a thermal activation process that uses a gaseous activating agent, usually steam, pumped through the previously pyrolytically carbonized material at high temperatures. This process burns off mass from the char, causing more pores to open and existing pores to widen. The amount of mass burnoff can be controlled by using particular activating agents and by changing the length or temperature of thermal activation. For most thermally activated carbons, 40 to 50 percent mass burnoff produces the maximum surface area per weight. At that point most pores are open and further activation only enlarges the existing pores resulting in a decrease in total surface area.

1.2.2. Ion Exchange

Ion exchange is a process where dissolved ionic contaminants are removed by replacing them with an ion of like charge that does not cause health or aesthetic issues. The majority of U.S. ion exchange systems are small installations at individual homes, but increased concern over adverse health effects from ionic contaminants such as, radium, fluoride, nitrate, and others, has increased demand for full scale ion exchange water treatment applications.

Ion exchange is the exchange of an aqueous phase ion for a solid phase ion. For most water treatment ion exchange applications, the solid phase ion exchanger is a synthetic polymeric resin in the form of spherical beads consisting of a crosslinked polymer network. The surface of the polymers is covered in functional groups with a fixed charge. Associated with each functional group is a counter-ion of opposite charge that is free to move within the pores of the polymer matrix but remains electrostatically associated with the functional group to maintain electroneutrality. When the exchange resin is immersed in a solution containing contaminant ions of the same charge as the mobile counter-ions, concentration differences cause the counter-ions to diffuse into solution. The contaminant ions are then drawn to the functional groups of the resin to maintain electroneutrality.

1.2.3. Reverse Osmosis

Reverse Osmosis (RO) is a membrane process that directs a high-pressure feed stream across a semi-permeable membrane. Water passes through the membrane leaving the feed side with a high concentration of contaminants and the permeate side with extremely pure water. The high concentration of solutes in the feed stream can exceed the solubility product of the various salts causing scaling on the membrane surface, which can permanently damage the membrane. Suspended particulates can also interfere with RO systems, either by clogging the feed stream or accumulating on the membrane. For these reasons, RO systems almost always require pretreatment of the feed water. The high pressure concentrate is typically a waste stream that may require treatment before disposal. The permeate stream, though very pure, typically requires posttreatment to remove dissolved gasses and adjust pH. Although the EPA has designated RO a best available technology for removing many inorganic compounds, including toxic metals, alternative technologies are frequently more cost effective for treating specific contaminants.

1.3. Thesis Statement

The objective of this thesis research was to evaluate and enhance a previously developed water treatment technology that uses natural fibers impregnated with metal nanoparticles to remove heavy metals from water. This research focuses specifically on the treatment technique's effectiveness at removing zinc contamination and explores both treated natural fibers (TNF) and untreated natural fibers (NF).

2. Literature Review

A review of scholarly literature indicates that, while toxic metal ions can be effectively removed by conventional treatments such as precipitation, filtration, and membrane processes, such processes are frequently expensive (Rao, Parwate, & Bhole, 2002) (Sohail, Ali, Khan, & Rao, 1999), and, at least for zinc removal, less efficient than biosorption (Amuda, Giwa, & Bello, 2007). Although much research has been done on the effectiveness of bio-adsorbent materials, much more work is required to better understand and demonstrate the technology (Bailey, Olin, Bricka, & Adrian, 1999).

Previous research at Montana Tech established several important factors for examining the effectiveness of the natural fibers, treated and untreated, in removing heavy metals from wastewater. A chemical analysis of the fibers was performed to determine the presence of eight metals anticipated to be targets for future testing. The results of the chemical analysis are shown in Table III.

Table II: Concentration of metals present in natural fibers
Adapted from (Larson, 2013)

Analyte	Concentration (mg/kg)	Detection Limit (mg/kg)
Aluminum	36.100	15.000
Arsenic	None detected	0.300
Cadmium	0.045	0.020
Chromium	6.250	0.400
Copper	16.400	0.250
Lead	0.187	0.040
Zinc	5.960	0.600
Mercury	None detected	0.997

The presence of target metals in the fibers could cause leaching of metal contaminants from the fibers to the water. No such leaching has been observed (Larson, 2013).

Specific surface area is a useful metric for comparing sorbents. Higher specific surface area generally indicates more effective adsorption. A Quantachrome Monosorb Rapid Surface Area Analyzer (QMRSAA) made available through the Montana Tech Metallurgical and Materials Engineering Department was used to determine the BET specific surface area of the natural fibers. The BET analysis determined a specific area of 50.2 m^2/g for the NF and 177.3 m^2/g for the TNF (Larson, 2013). Another experiment testing coconut husk for adsorbent potential found a BET surface area of 1.97 m^2/g for coconut thread ground in a mortar and pestle (Hasany & Ahmad, 2006).

Adsorption rates of metal ions are affected by the pH of the wastewater. Experiments with the NF and TNF for cadmium adsorption indicated that adsorption efficiencies for both treated and untreated fibers are highest at neutral pH (Rediske, 2014). Other researchers using bioadsorption to remove aqueous zinc found that maximum zinc removal efficiency was at pH 6 (Amuda, Giwa, & Bello, 2007) (Salim, Al-Subu, Abu-Shqair, & Braik, 2003).

One advantage adsorption has over other water treatment methods is that the sorbent can frequently be regenerated, allowing the recovery of valuable metals and reuse of the sorbent material. Quantitative recovery of zinc was demonstrated using chitosan-coated coconut shell carbon (Amuda, Giwa, & Bello, 2007), but research using green coconut shell in a fixed-bed column reactor indicated that reusing the adsorbent resulted in reductions greater than 70% of removal capacity for nickel, zinc, and copper (Sousa, et al., 2010).

3. Methods

Two experiments were conducted to evaluate the performance of the natural fibers, treated and untreated, in removing aqueous zinc. The first experiment was a static jar test or batch test used to develop adsorption isotherms for the filter media. The second experiment consisted of continuous flow tests using a bench scale reactor to simulate the fiber's performance in real situations. The experiments were conducted using zinc solutions made from zinc chloride ($ZnCl_2$) salt and deionized (DI) water, for the batch tests, or tap water, for the continuous flow tests. The samples from each experiment were analyzed using Inductively Coupled Plasma – Optic Emission Spectroscopy (ICP/OES) to determine the zinc concentration.

3.1. Batch Tests

For the batch tests, 50 mL each of five different concentrations of zinc solution were placed in beakers containing either one gram of untreated natural fiber, one gram of treated natural fiber, or no natural fiber. The solutions were made by stirring a measured mass of $ZnCl_2$ salt into DI water. After pouring 50 mL of solution into the beakers to use that solution, the remainder was diluted to produce the next concentration of solution. The nominal concentration of the five different solutions are presented in Table III.

Table III: Batch test solution concentrations

Solution	Nominal Zinc Concentration (mg/L)
1	35
2	25
3	15
4	5
5	1

A 10 mL sample was taken from each beaker at zero, two, and four hours of treatment. A single direct analysis trial was performed to compare the NF to the TNF. Thereafter, dissolved metals analysis was used for four runs with TNF and four runs with NF. Only two tests were run without any filtration media, these to check for changes in zinc concentration due to factors other than the filtration media. The experimental design is summarized in Table IV.

Table IV: Batch test experimental design

Fiber	Replicate Runs	Analytical Method
NF	1	Direct
TNF	1	Direct
None	2	Dissolved Metals
NF	3	Dissolved Metals
TNF	3	Dissolved Metals

Every run consisted of five beakers each containing one of five different solutions as outlined in Table III.

3.2. Continuous Flow Tests

Previous research by Eric Larson determined that a bench scale continuous flow reactor 1.76 inches long and 2.1 inches in diameter made of PVC was best for conducting continuous flow tests with the natural fiber adsorption media. A flow rate of 10 mL/min of contaminated water was supplied by peristaltic pump for a column containing approximately 5 grams of TNF. The flow rate of 10 mL/min corresponds to an Empty Bed Contact Time (EBCT) of ten minutes (Larson, 2013). The first set of three flow through tests used a low concentration zinc solution made by dissolving 9.6 mg of $ZnCl_2$ salt in 19 L of tap water. The second set of three tests used a high concentration zinc solution made by dissolving 96.5 mg of $ZnCl_2$ salt in 19 L of tap water. The column was not filled with either DI or tap water prior to pumping. 10 mL samples were taken at various intervals over a 24 hour period. For the high zinc tests the sampling period was reduced to 12 hours. Detailed sampling schedules can be found in Table IX and Table X. It was found that the tap water contained some dissolved copper and data for copper was also collected.

3.3. Sample Preparation

Three methods of sample preparation were used when taking samples for analysis. Direct analysis was used for sampling the initial batch tests, Total Dissolved Metals analysis was used with the batch tests for developing adsorption isotherms for the adsorption media, and Total Recoverable Metals analysis was used for continuous flow tests.

3.3.1. Direct Analysis

Direct analysis is excellent for obtaining quick results for comparison between samples. The samples were prepared by adding 1 mL of trace metal grade nitric acid to a 10 mL sample. Direct analysis was used in the initial batch tests to prove the viability of the natural fibers as an adsorption media. The method allowed for fast results adequate for their purpose as only the comparison between initial and subsequent concentrations was required.

3.3.2. Total Dissolved Metals

Total dissolved metals was used during the batch tests for characterizing the adsorption media because a higher level of accuracy was desired. Total Dissolved Metals sample preparation was done in accordance with EPA methods (EPA, 1983) using the following steps.

1. 10 mL of sample was drawn using a disposable syringe
2. A 0.45 µm membrane filter was connected to the end of the syringe
3. The 10 mL water sample was injected through the membrane filter into an ICP-OES sample holder
4. 1 mL of trace metal grade nitric acid was added to the sample

3.3.3. Total Recoverable Metals

Montana DEQ Circular regulates total recoverable metals (Montana Department of Environmental Quality, Planning, Prevention, and Assistance Division, 2010). Normally, sample preparation for total recoverable metals follows EPA method 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts (United States Environmental Protection Agency, 2007), as water samples frequently contain suspended solids as well as dissolved solids. However, because the ICP/OES process only requires Microwave Assisted Digestion if the water samples contain suspended solids that might block the sample ingestion system, the microwave digestion process was avoided.

3.4. Inductively Coupled Plasma/Optical Emission Spectrometry

Metal concentration for each sample was analysed with an Inductively Coupled Plasma-Optical Emission Spectrometer. ICP/OES is the combination of two analytical processes into a single compact machine. The first process is the breakdown of samples into constituent atoms using the Inductively Coupled Plasma (ICP) section of the instrument. After the sample is atomized, the Optical Emission Spectrometer (OES) detects the elements and their concentrations.

The ICP consists of a quartz torch surrounded by an electrical coil followed by a tesla coil. As argon gas flows through the torch, the oscillating electrical and magnetic fields induced by the surrounding coil causes the formation of more and more argon ions. The tesla coil creates a spark that also forms argon ions, eventually resulting in an argon plasma approximately 10,000 degrees Celsius. When an aerosol sample is introduced to the argon stream, the plasma converts the constituent atoms into ions that emit discrete wavelengths of radiation.

The radiation emitted by sample ions is passed through a focusing slit with a series of mirrors that organize the waves before they are collected on a grating that separates them into individual wavelengths. The waves then pass through an order-sorting prism that further orders each wave before it comes in contact with an array detector. The array detector uses the wavelength of each wave to determine the element the wave represents and the intensity of the wave to determine the relative amount of that element in the sample (Hou & Jones, 2000).

To summarize, the ICP uses intensely hot argon plasma to break down a liquid sample causing the individual elements to release radiation. The radiation wavelengths are detected and interpreted by the OES to determine the presence and concentration of the various elements. The standard operating procedure used for this research can be found in Appendix B.

3.5. Adsorption Isotherms

The Langmuir and Freundlich isotherm equations were used to analyze the batch test results to characterize the adsorption process. The Langmuir isotherm models monolayer adsorption where a single layer of contaminant adsorbs to the active sites of the adsorbate. The Freundlich isotherm assumes multi-layer adsorption where the contaminant fills the active sites of the adsorbate material before further adsorbing onto layers of contaminant. The Langmuir isotherm is shown in equation 1 and the Freundlich isotherm is shown in equation 2.

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \tag{1}$$

where:

x is the mass of contaminant adsorbed

m is the mass of adsorbate

C_e is the equilibrium concentration of contaminant

and a and b are derived constants

$$\frac{x}{m} = K_f C_e^{1/n} \tag{2}$$

where:

x is the mass of contaminant adsorbed

m is the mass of adsorbate

C_e is the equilibrium concentration of contaminant

and K_f and $1/n$ are derived constants

The adsorption isotherms were derived using linear regression in a computer spreadsheet. The data from replicate runs of the batch tests were averaged prior to isotherm analysis.

4. Results

4.1. Batch Tests

The initial static jar tests were performed to determine the viability of natural fibers as an adsorption media. Beakers were filled with zinc solutions of various concentrations prepared from zinc chloride salt before natural fiber filters were added. Two runs of tests without any fiber added were also performed, the results of the unfiltered batch tests are in Appendix A.

4.1.1. Untreated Natural Fibers

The initial batch test was performed to determine viability of the natural fibers as an adsorption media. Figure Figure 11 shows the results of the initial uncoated fiber batch test.

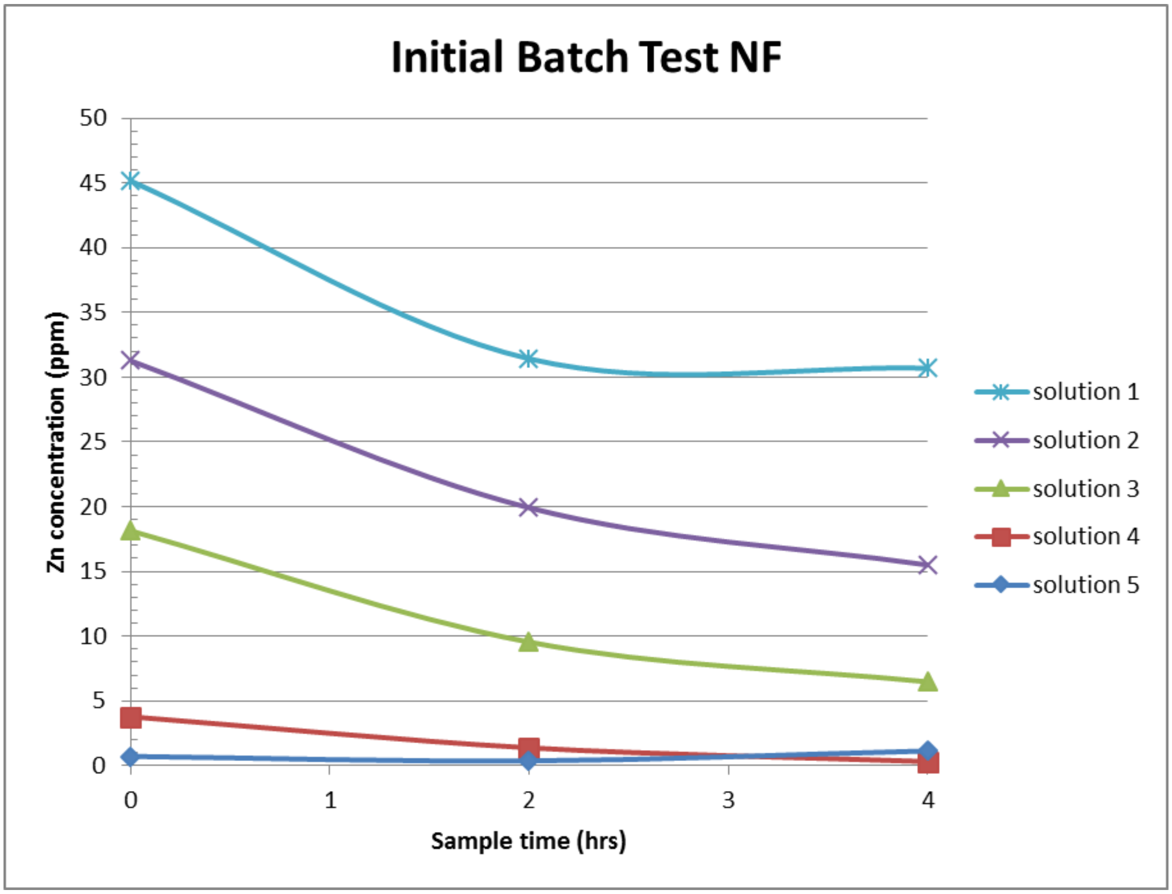

Figure 1: Initial batch test using uncoated fibers

The plot in Figure 1 shows the trend of decreased zinc concentration in the jars containing zinc solution and untreated natural fibers. Each solution showed consistent zinc removal throughout the four hour testing period with the exception of the lowest initial concentration, solution 5. The data from Figure 1 is shown in Table V.

Table V: Initial NF batch test

	Zinc Concentration (ppm)			**% removal**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	**at 4 hrs**
1	45.15	31.42	30.69	32.0%
2	31.27	19.92	15.50	50.4%
3	18.14	9.55	6.48	64.3%
4	3.79	1.39	0.32	91.6%
5	0.72	0.37	1.14	-58.4%

The data given in Table V shows the zinc removal in the five solutions by the untreated natural fibers. Percent removal after 4 hours increased as initial concentration decreased with the exception of solution 5, which had a negative removal after 4 hours. Further batch tests were performed to validate the results.

A series of three further batch tests were performed following the same procedure as the initial batch test but samples were analyzed for total dissolved metals rather than using a simple direct analysis. Figure 2 2 shows the average of the results of the three NF batch tests.

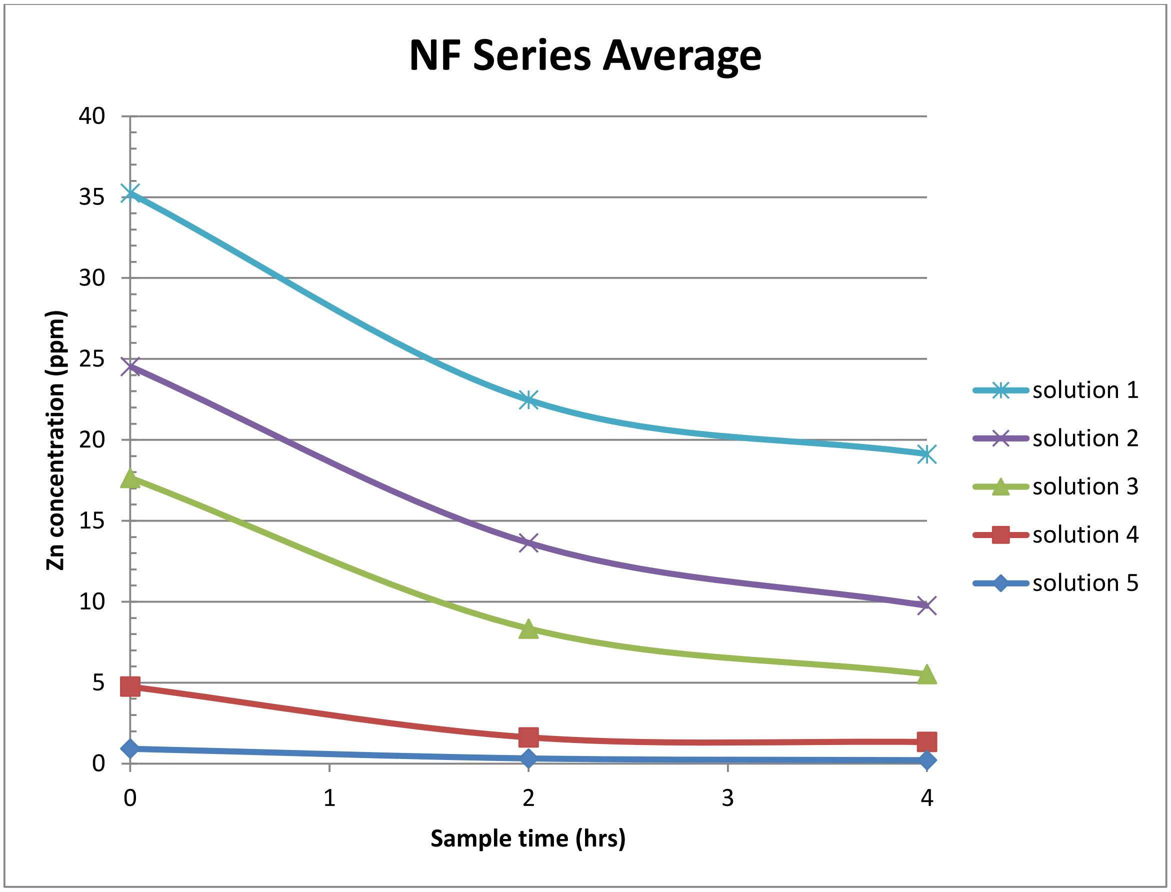

Figure 2: Natural fibers batch test series average

The plot in Figure 2 confirms the trend of zinc removal by the uncoated natural fibers. The data associated with the plot is presented in Table VI below.

Table VI: Untreated natural fibers series average

	Zinc Concentration (ppm)			% removal
Solution	**0 hrs**	**2 hrs**	**4 hrs**	**at 4 hrs**
1	35.25	22.47	19.12	45.8%
2	24.53	16.64	9.76	60.2%
3	17.66	8.35	5.53	68.7%
4	4.76	1.62	1.33	72.0%
5	0.92	0.32	0.21	77.2%

Table VI shows the zinc removal by the untreated natural fibers from averaging three series of batch tests. The data for the individual series may be found in Appendix A.

4.1.2. Treated Natural Fibers

The initial batch test was performed to determine viability of the treated natural fibers as an adsorption media. Figure 3 shows the results of the initial treated natural fiber batch test.

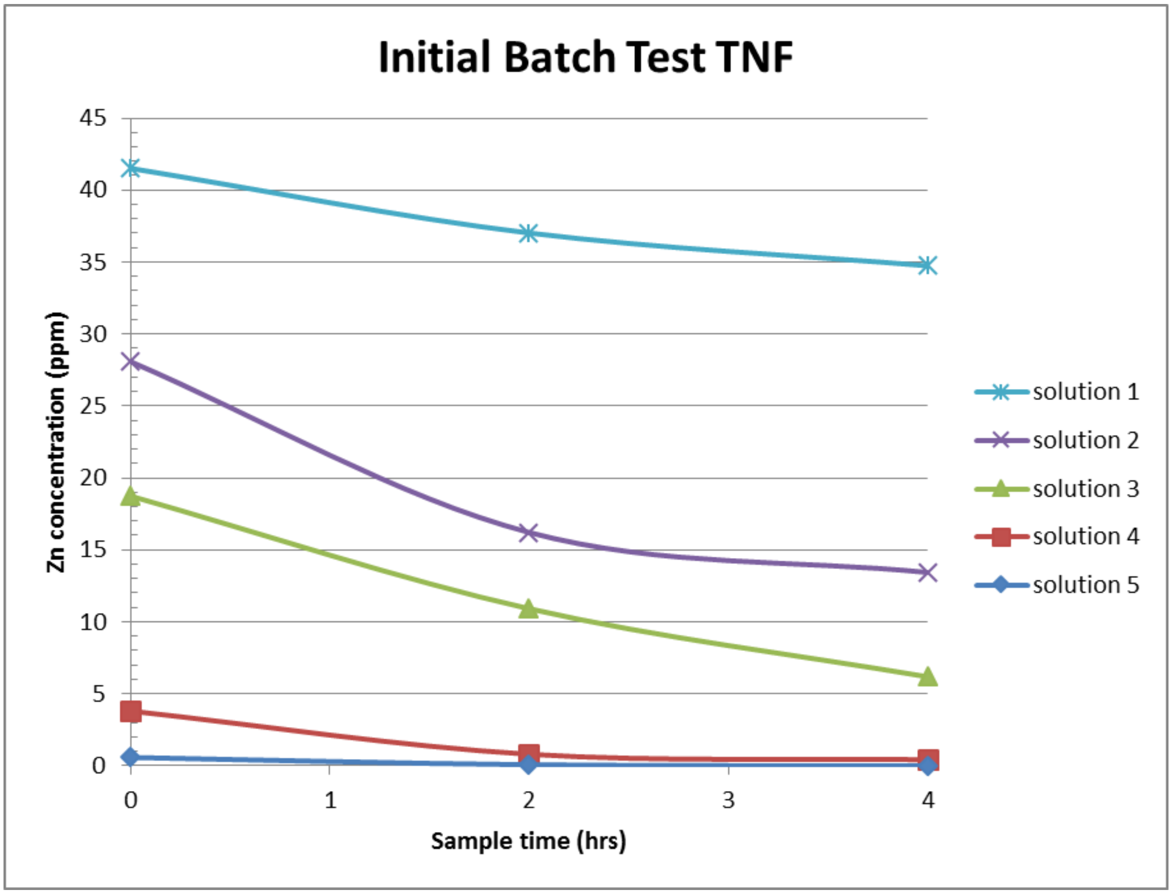

Figure 3: Initial batch test using treated natural fibers

The plot in Figure 3 shows the trend of decreased zinc concentration in the jars containing zinc solution and treated natural fibers. Each solution showed consistent zinc removal. The data from Figure 3 is shown in Table VII.

Table VII: Initial TNF batch test

	Zinc Concentration (ppm)			% removal at 4 hrs
Solution	**0 hrs**	**2 hrs**	**4 hrs**	
1	41.51	37.02	34.74	16.3%
2	28.08	16.21	13.43	52.2%
3	18.74	10.91	6.18	67.0%
4	3.80	0.80	0.42	88.9%
5	0.57	0.07	0.00	99.8%

The data given in Table VII shows the zinc removal in the five solutions by the treated natural fibers. Percent removal after 4 hours increased as initial concentration decreased. Zinc removal by the treated natural fibers was higher than removal by untreated fibers as seen by comparing Table V with Table VII. Further batch tests were performed to validate the results.

A series of three batch tests were performed following the same procedure as the initial batch test but samples were analyzed for total dissolved metals rather than using a simple direct analysis. Figure 4 shows the average of the results of the three TNF batch tests.

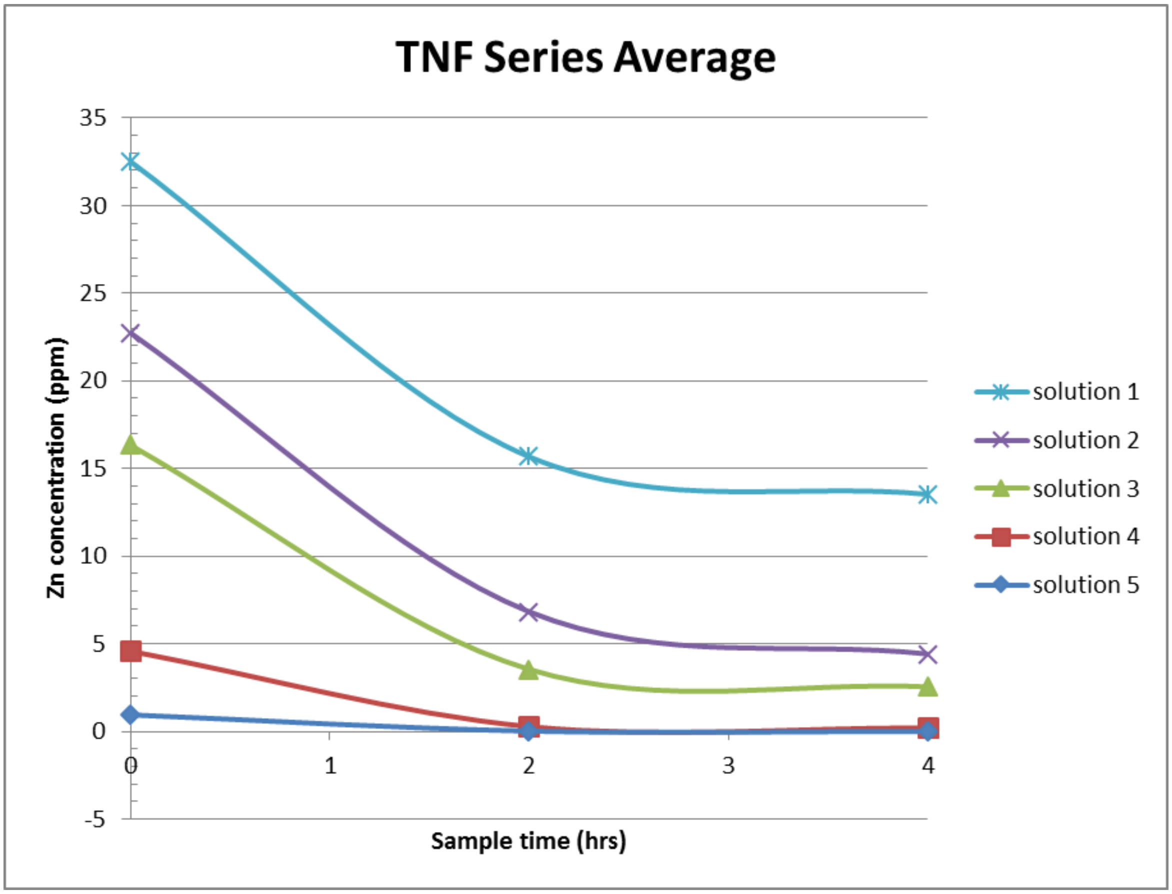

Figure 4: Treated fibers batch test series average

The plot in Figure 4 confirms the trend of zinc removal by the treated natural fibers. The data associated with the plot is presented in Table VIII VIII below.

Table VIII: Treated natural fibers series average

	Zinc Concentration (ppm)			% removal
Solution	**0 hrs**	**2 hrs**	**4 hrs**	**at 4 hrs**
1	32.51	15.68	13.53	58.4%
2	22.73	6.83	4.42	80.6%
3	16.33	3.55	2.55	84.4%
4	4.58	0.28	0.20	95.6%
5	0.94	0.02	0.00	99.5%

Table VIII shows the zinc removal by the treated natural fibers from the average of three series of batch tests. The data for the individual series may be found in Appendix A.

4.2. Continuous Flow Tests

Though the natural fibers perform well in batch treatment, the most economically viable option for commercial application of the natural fiber adsorption media would likely be for continuous flow reactors (Cooney, 1999). Bench scale continuous flow tests were performed to simulate the fiber's performance in flow through conditions.

4.2.1. Low zinc concentration

The first set of continuous flow tests consisted of three trials performed with zinc concentrations between 0.3 and 0.45 mg/L. The results of the low concentration trials are shown in Figure 5: Continuous flow test low concentration Figure 5.

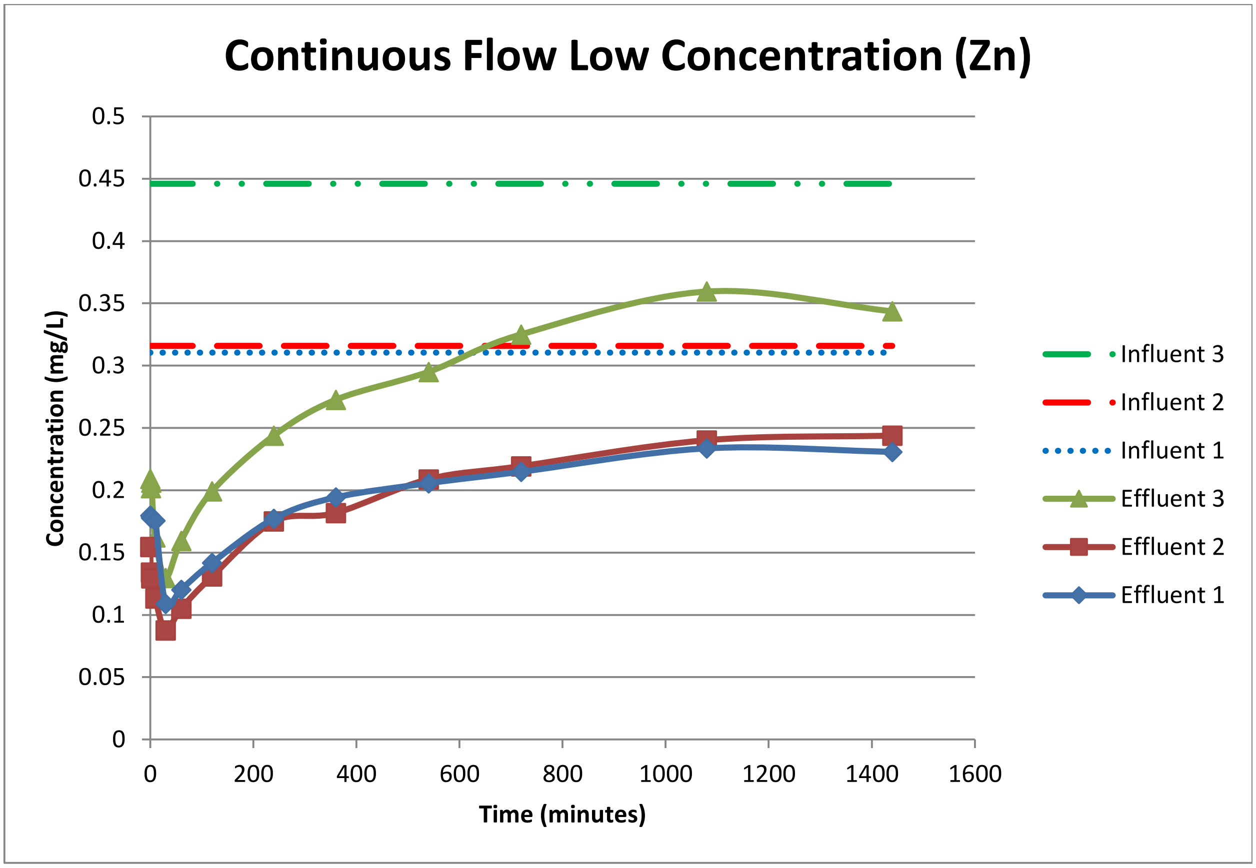

Figure 5: Continuous flow test low concentration zinc data

Figure 5 shows the concentration of zinc on the vertical axis with the time of sampling on the horizontal axis. The dashed horizontal lines indicate the concentration of zinc in the source solution and the solid lines represent samples taken at the outlet of the reactor. In each trial the lowest effluent concentration was found at the thirty minute sample. By the end of the 24 hour testing period, the effluent concentration was less than 77% of the influent concentration. The data in Figure 5 is presented in Table IX.

Table IX: Zinc concentration for low zinc continuous flow trials

	Zinc Concentration (mg/L)		
Time (minutes)	**Trial 1**	**Trial 2**	**Trial 3**
Initial	0.3104	0.3159	0.4459
0	0.1797	0.1545	0.2091
1	0.1781	0.1339	0.2017
2	0.1777	0.1295	0.2061
10	0.1756	0.1133	0.1623
30	0.1088	0.0876	0.1297
60	0.1202	0.105	0.1593
120	0.1417	0.1309	0.1991
240	0.1772	0.175	0.2439
360	0.1943	0.1818	0.2726
540	0.2057	0.2088	0.2950
720	0.2149	0.2193	0.3251
1080	0.2337	0.2401	0.3595
1440	0.2309	0.2438	0.3436

Table IX shows the time of sampling and the effluent concentration of each sample as well as the influent concentration for the three low concentration continuous flow trials. The copper concentration data for the low zinc concentration trials is shown in Appendix A in Figure 19 and Table XX.

4.2.2. High zinc concentration

The second set of continuous flow tests was conducted with concentrations greater than 2 mg/L. The data collected for the high zinc concentration trials is presented in Figure 6 and Table X.

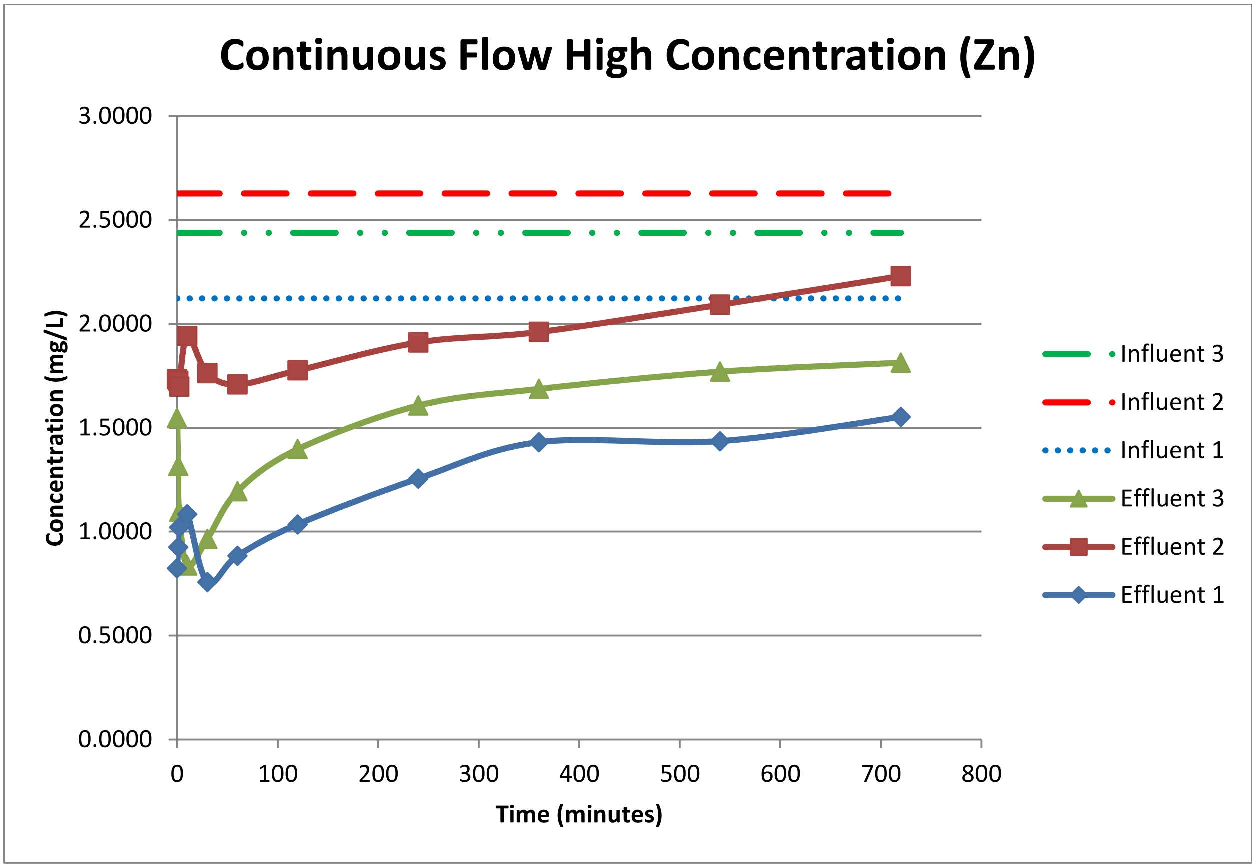

Figure 6: Continuous flow test high concentration zinc data

The dashed horizontal lines in Figure 6 indicate the concentration of zinc in the source solution and the solid lines represent samples taken at the outlet of the reactor. Due to the much higher influent concentration flowing through a reactor with the same amount of fiber (approximately 5g) the total run time was reduced from 24 hours to 12 hours. The relatively large zinc concentration compared to fiber mass may have caused the variation in the trend lines before 100 minutes compared to the smooth curves seen in Figure 5.

Table X: Zinc concentration for high zinc continuous flow trials

	Zinc Concentration (mg/L)		
Time (minutes)	**Trial 1**	**Trial 2**	**Trial 3**
Initial	2.12	2.63	2.44
0	0.822	1.734	1.547
1	0.925	1.726	1.316
2	1.021	1.698	1.096
10	1.084	1.942	0.836
30	0.756	1.763	0.964
60	0.882	1.709	1.194
120	1.035	1.776	1.397
240	1.255	1.911	1.607
360	1.430	1.961	1.687
540	1.435	2.092	1.770
720	1.552	2.230	1.813

Table X shows the time of sampling and the effluent concentration of each sample as well as the influent concentration for the three high concentration continuous flow trials. While the low concentration trials consistently had minimum effluent concentration at the 30 minute sample, there is no definite pattern shown in the high concentration data. Trial 1 has a minimum at 30 minutes, Trial 2 has a minimum at 2 minutes, and the lowest effluent concentration for Trial 3 occurred at 10 minutes. The high concentration copper data is shown in Appendix A in Figure 20 and Table XXI.

4.3. Adsorption Isotherms

In an effort to characterize the adsorption process of zinc by the natural fibers, both treated and untreated, Langmuir and Freundlich isotherms were developed for both averaged sets of batch tests.

4.3.1. Natural Fiber Isotherms

Previous research suggested that the NF adsorption would better fit the Freundlich isotherm, indicative of multilayer adsorption (Larson, 2013). Figure 7 7 shows the Langmuir isotherm for the NF batch tests and Figure 8 shows the Freundlich isotherm.

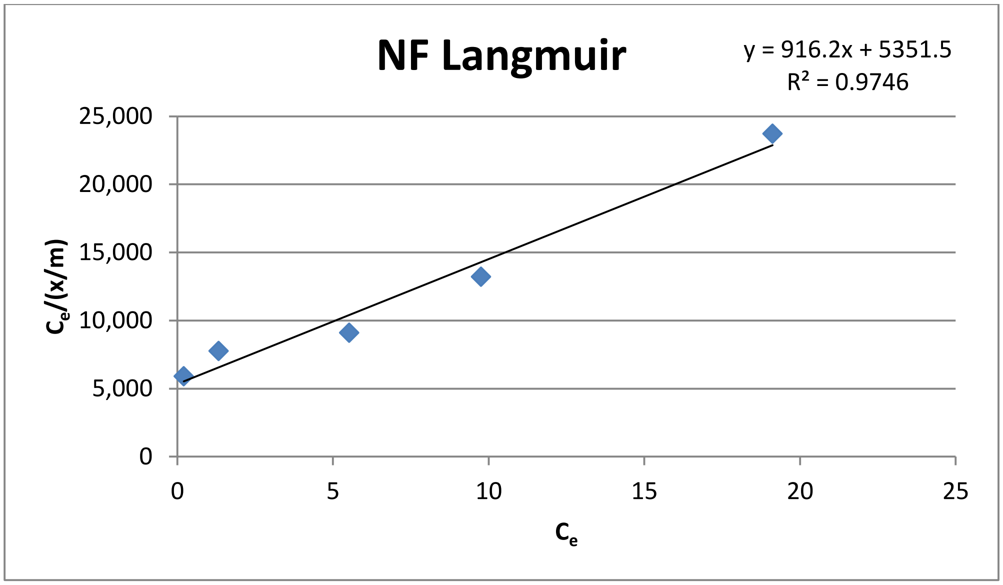

Figure 7: NF Langmuir Isotherm

The linear regression shown in Figure 7 indicates a high correlation between the data and the Langmuir isotherm. The correlation coefficient of 0.9746 strongly suggests that the NF batch tests were undergoing monolayer adsorption.

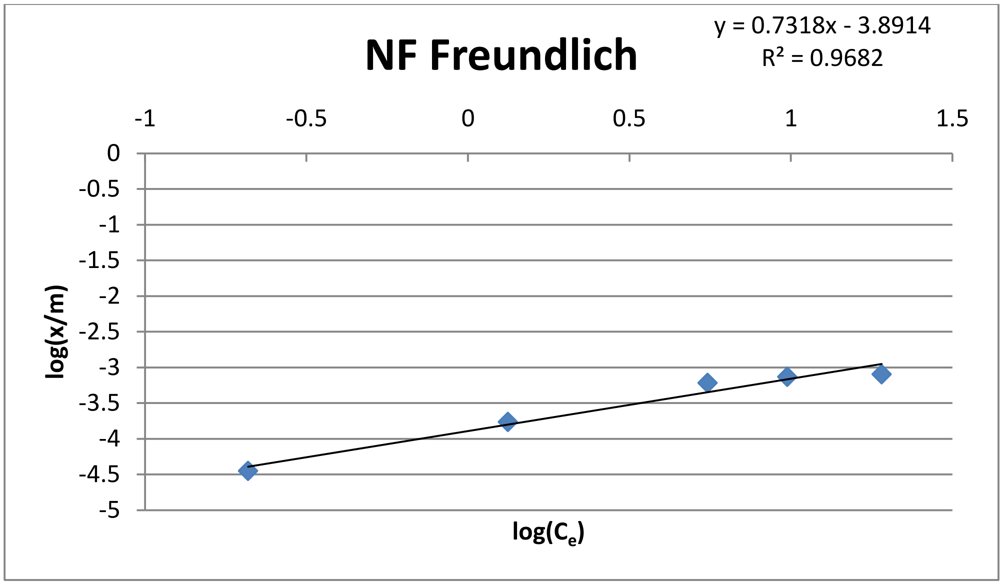

Figure 8: NF Freundlich Isotherm

The Freundlich linear regression for the NF tests indicated a high correlation with an R^2 value of 0.9682 as shown in Figure 8 8. The high correlation between the data with both equations makes it difficult to draw firm conclusions about the dominant adsorption process.

4.3.2. Treated Natural Fiber Isotherms

Based on previous research it was anticipated that the TNF would undergo monolayer adsorption and therefore more closely correlate to the Langmuir isotherm (Larson, 2013). Figure 9 and Figure 10 show the linear regression plots for the Langmuir and Freundlich isotherms respectively.

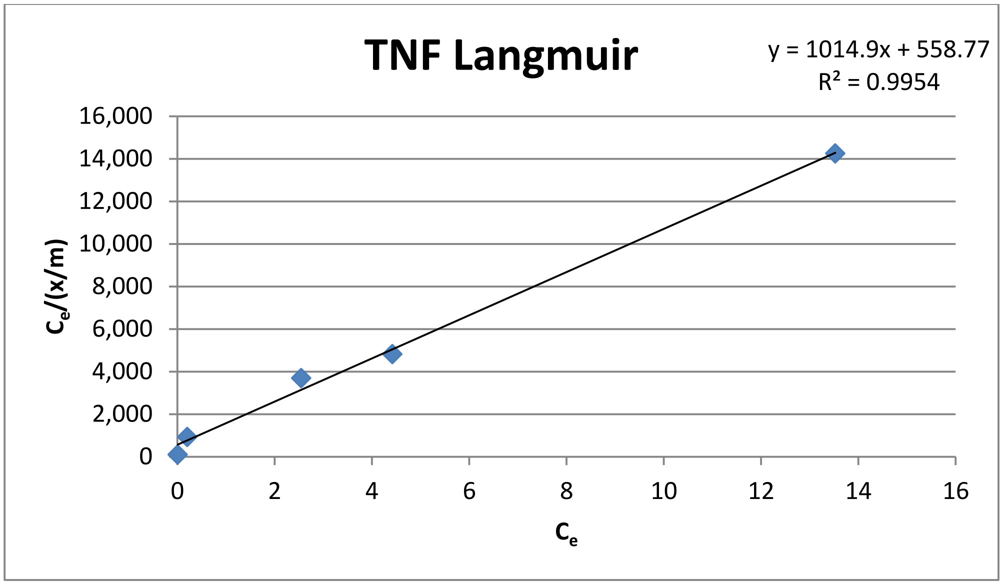

Figure 9: TNF Langmuir Isotherm

The linear regression in Figure 9 results in a high 0.9954 R^2 value, strongly suggesting that the TNF experiences monolayer adsorption.

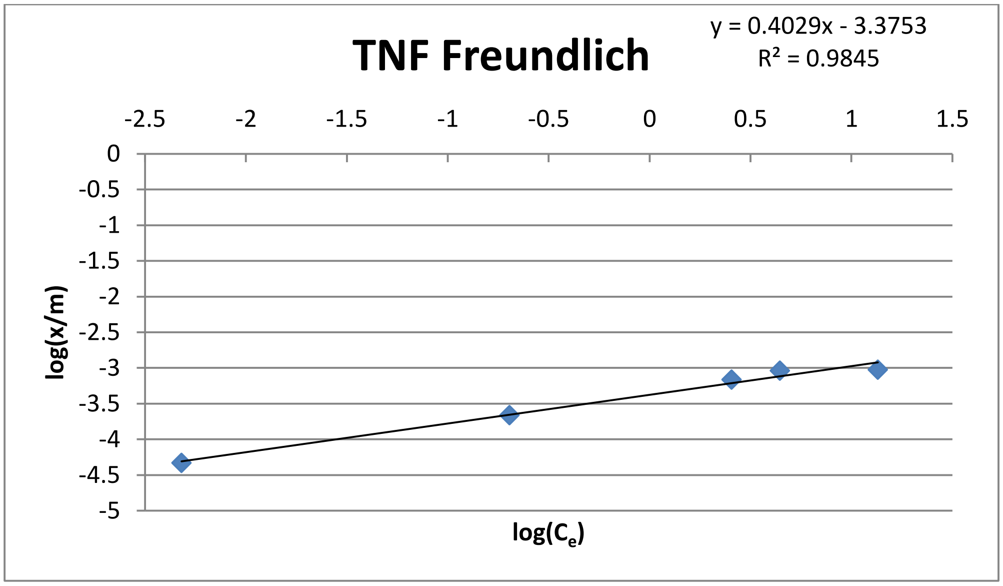

Figure 10: TNF Freundlich Isotherm

Figure 10 shows a high correlation between the data and the Freundlich equation with a correlation coefficient of 0.9845, only slightly lower than the data's correlation with the Langmuir isotherm. Once again it is difficult to draw sound conclusions.

The isotherm coefficients for the Langmuir and Freundlich equations were calculated for both the TNF and the NF, the results are shown in Table XI.

Table XI: Adsorption isotherm coefficients

	Langmuir		**Freundlich**	
Fiber	**a**	**b**	**K_f**	**1/n**
NF	0.001091	0.171204	0.000128	0.7318
TNF	0.000985	1.816311	0.000421	0.4029

Because each equation is derived from only five data points, each being the average of three runs, the results of the isotherm analysis are not statistically significant. However, relative comparisons can still be made between the two fibers and between the two equations.

5. Conclusions

Several experiments were conducted to further the knowledge of the natural fiber and treated natural fiber as adsorption media for treating zinc contamination in water. The significant conclusions from this work are summarized below.

- The batch tests demonstrated that both the treated and untreated natural fibers are effective in removing zinc contamination from water. A range of aqueous zinc concentrations between approximately 40 mg/L zinc and 0.5 mg/L zinc showed a consistent trend of zinc removal by the natural fibers. The TNF showed removal efficiencies above 90% after 4 hours of treatment time with an initial zinc concentration of 5 mg/L or lower.
- The continuous flow tests showed that up to 70% zinc removal could be accomplished using treated natural fibers in a packed column reactor. Longer run times and higher removal could be reached by larger reactors with a more favorable ratio of contaminant concentration to adsorbent mass. The continuous flow tests also confirmed that the TNF adsorbent will remove multiple contaminant ions simultaneously
- Both NF and TNF had good correlations with both Langmuir and Freundlich isotherms. The NF data correlated slightly better with the Langmuir isotherm with an R^2 of 0.975 compared to 0.968 for the Freundlich isotherm, but no clear conclusion can be drawn. The TNF had a Langmuir correlation of 0.995 and a Freundlich correlation of 0.984, once again providing no basis for drawing valid conclusions.

6. Future work

The research presented here supports the use of the natural fibers as a water treatment technique and suggests the following possibilities for future research.

- Additional research into the natural fiber’s ability to remove other contaminants
- Research of the fiber’s performance in water with multiple contaminants of concern
- Determination of the breakthrough point and treatment capacity of the natural fibers
- Optimization of the continuous flow reactor, perhaps with multiple treatment stages using untreated fibers as a ‘pre-treatment’ before passing the water to the treated natural fibers for final treatment

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8. Appendix A

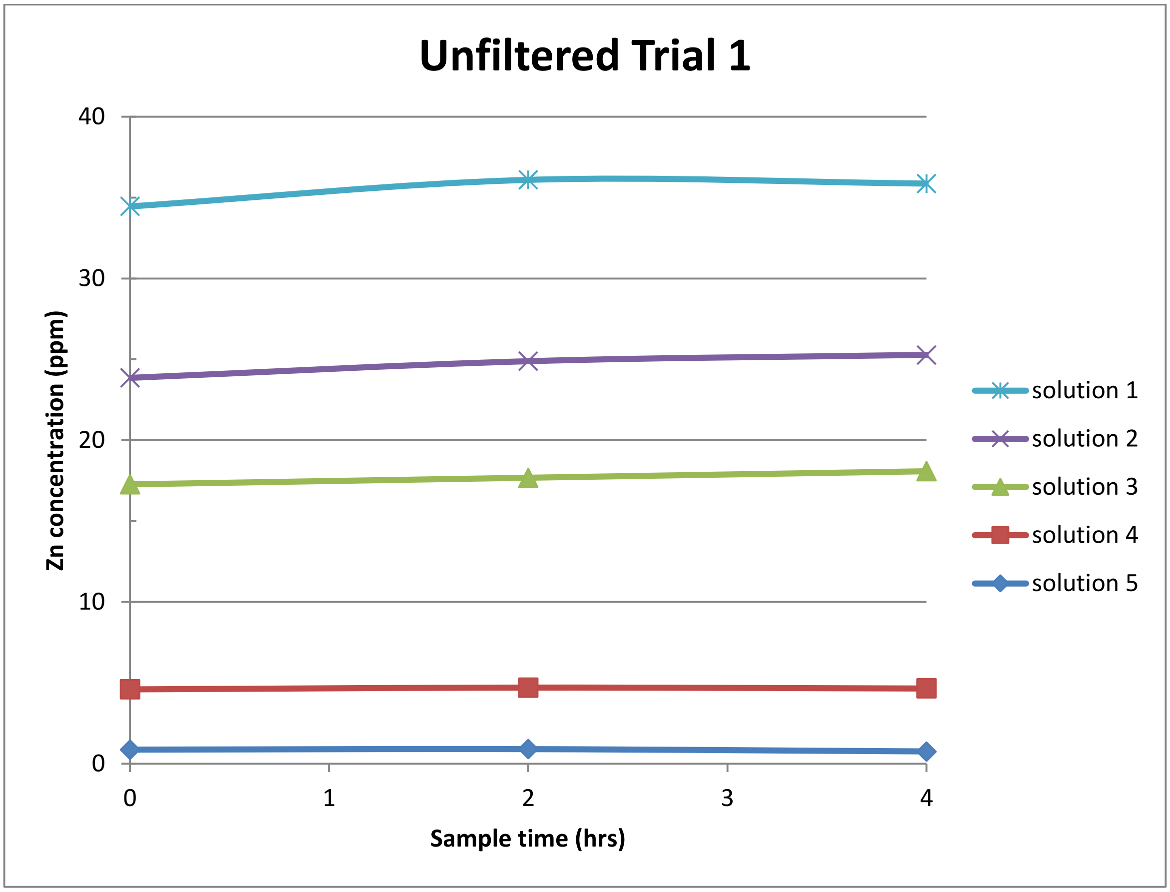

Figure 11: Unfiltered batch test first run

Table XII: Unfiltered batch test first run data

	Zinc Concentration (ppm)			**% removal at 4 hrs**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	
1	34.45	36.10	35.87	-4.1%
2	23.86	24.88	25.27	-5.9%
3	17.27	17.68	18.08	-4.7%
4	4.60	4.71	4.65	-1.1%
5	0.87	0.90	0.76	13.6%

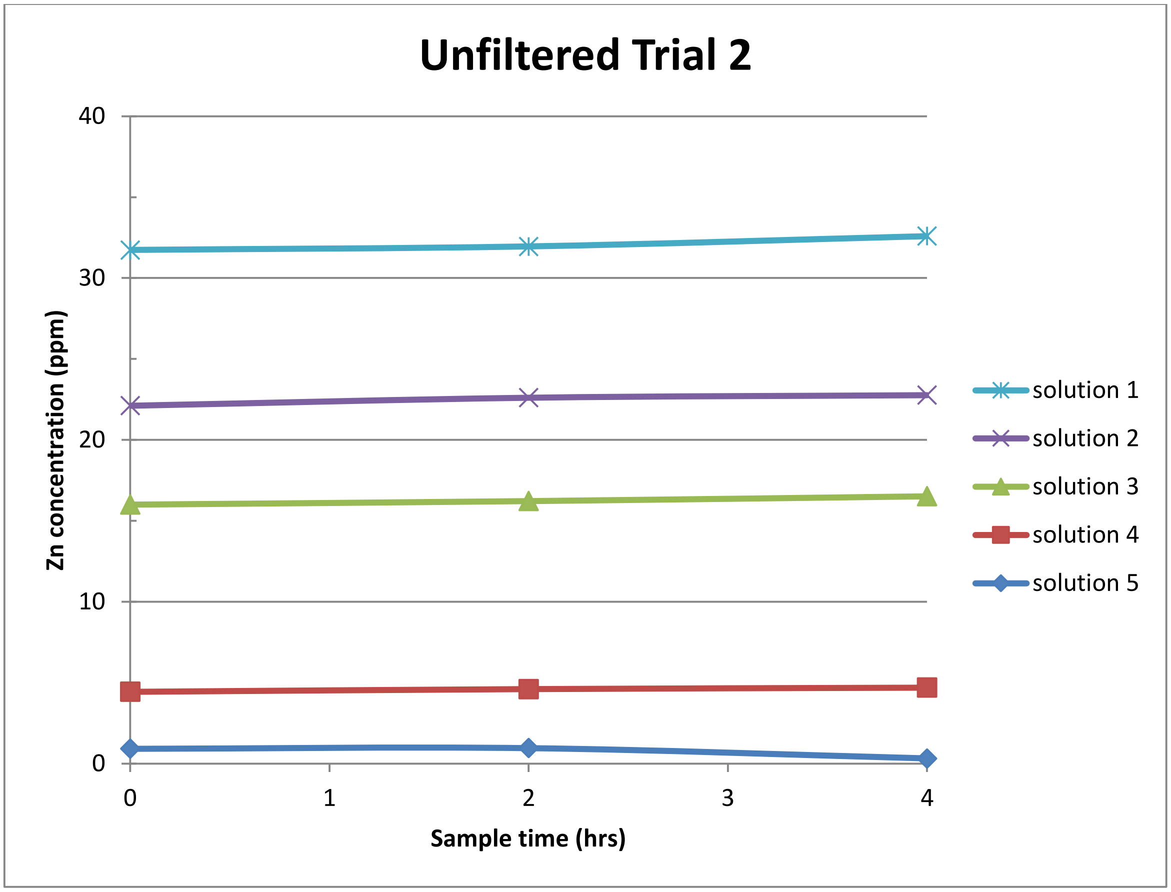

Figure 12: Unfiltered batch test second run

Table XIII: Unfiltered batch test second run data

	Zinc Concentration (ppm)			**% removal**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	**at 4 hrs**
1	31.73	31.95	32.59	-2.7%
2	22.11	22.61	22.77	-3.0%
3	16.00	16.22	16.52	-3.3%
4	4.43	4.60	4.69	-5.8%
5	0.91	0.96	0.32	65.1%

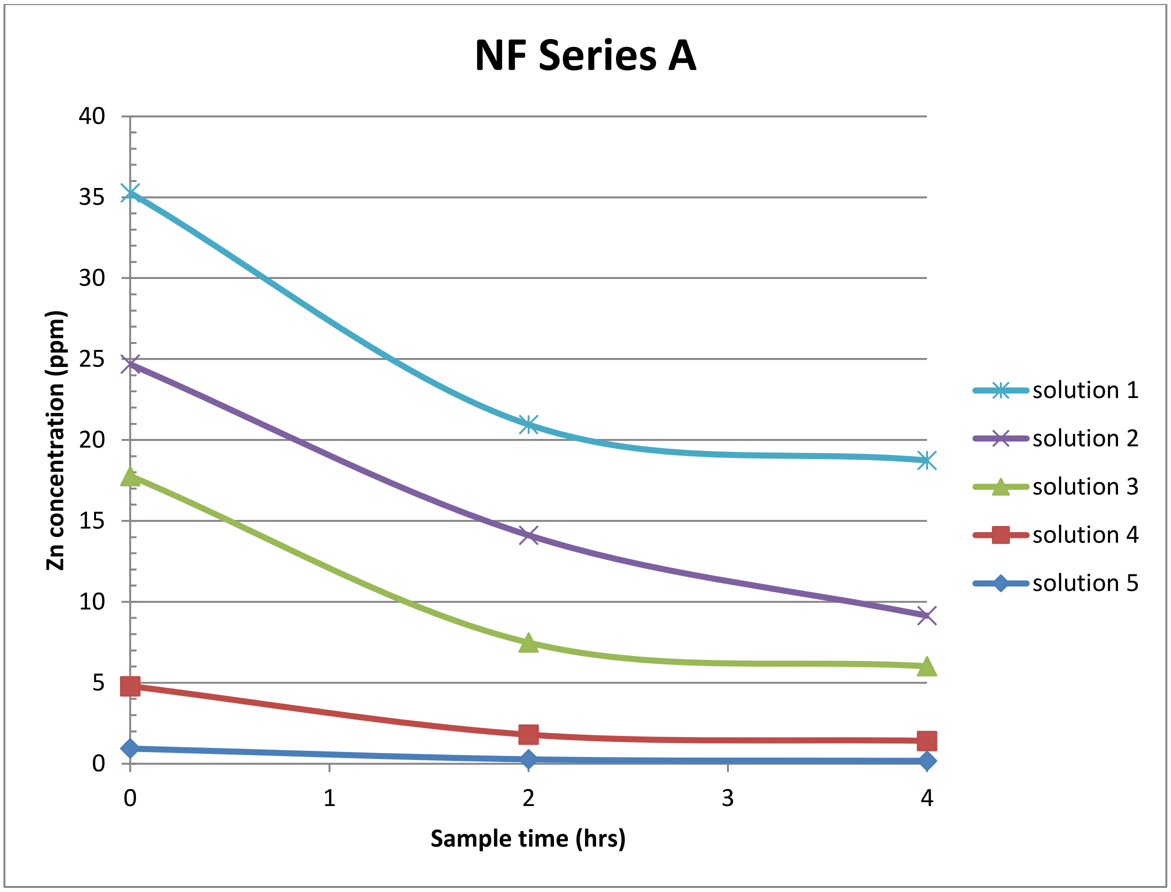

Figure 13: Natural fiber batch test series A

Table XIV: Natural fiber batch test series A data

	Zinc Concentration (ppm)			**% removal at 4 hrs**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	
1	35.27	20.95	18.73	46.9%
2	24.68	14.12	9.15	62.9%
3	17.77	7.49	6.02	66.1%
4	4.79	1.79	1.41	70.7%
5	0.94	0.26	0.17	82.0%

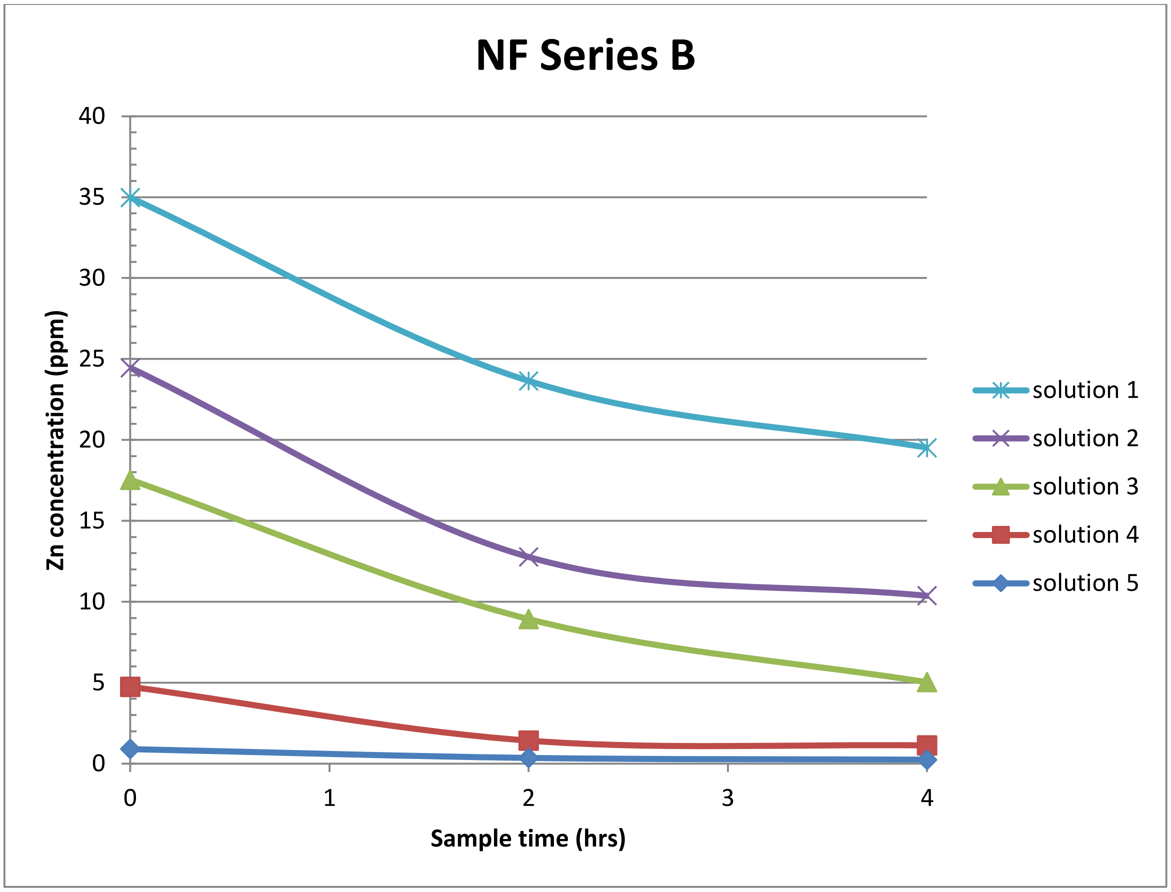

Figure 14: Natural fiber batch test series B

Table XV: Natural fiber batch test series B data

	Zinc Concentration (ppm)			% removal at 4 hrs
Solution	0 hrs	2 hrs	4 hrs	
1	34.98	23.64	19.51	44.2%
2	24.46	12.77	10.37	57.6%
3	17.54	8.93	5.027	71.3%
4	4.745	1.42	1.123	76.3%
5	0.9034	0.3496	0.2389	73.6%

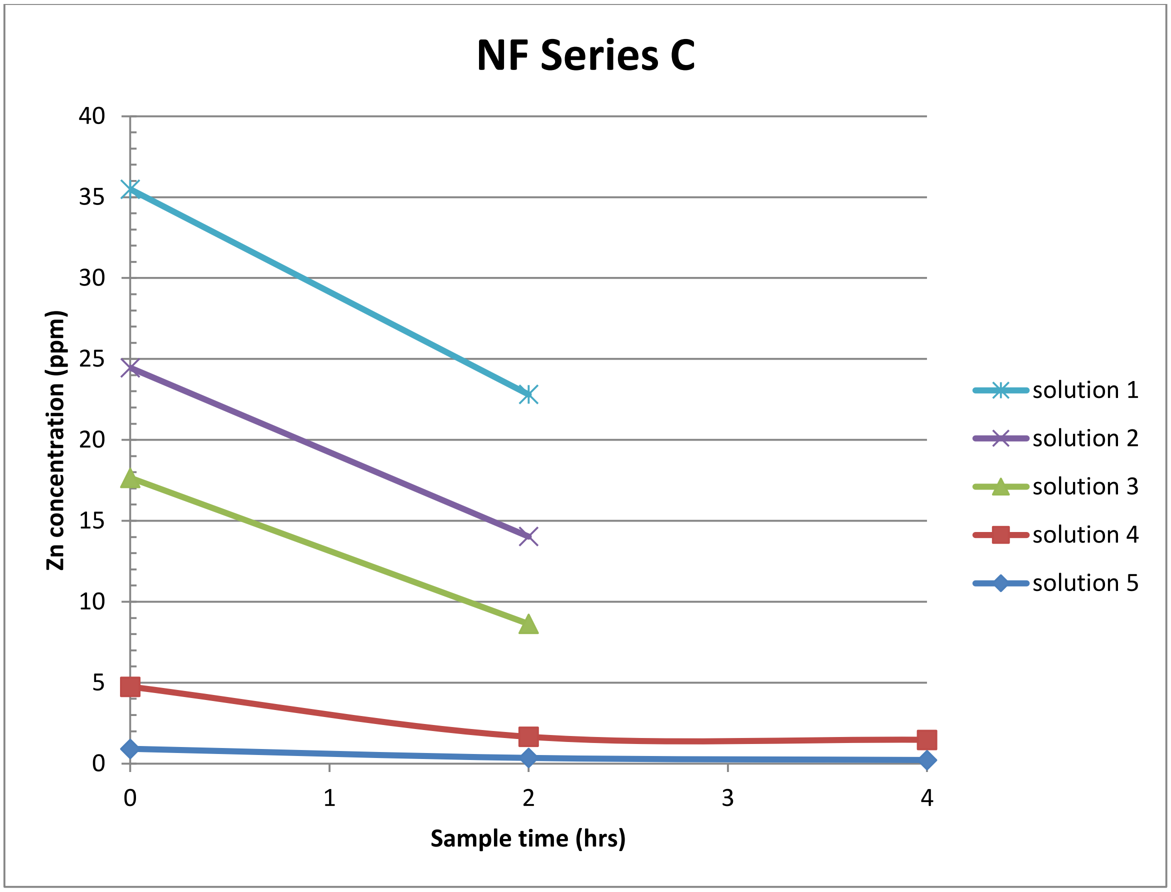

Figure 15: Natural fiber batch test series C

Table XVI: Natural fiber batch test series C data

	Zinc Concentration (ppm)			% removal at 4 hrs
Solution	0 hrs	2 hrs	4 hrs	
1	35.49	22.81	-	-
2	24.46	14.03	-	-
3	17.66	8.63	-	-
4	4.74	1.65	1.46	69.2%
5	0.91	0.35	0.22	75.9%

The missing data in Figure 15 and Table XVI are the result of a software crash causing the loss of data for the 4 hr samples from solutions 1 through 3 for the natural fiber series C tests.

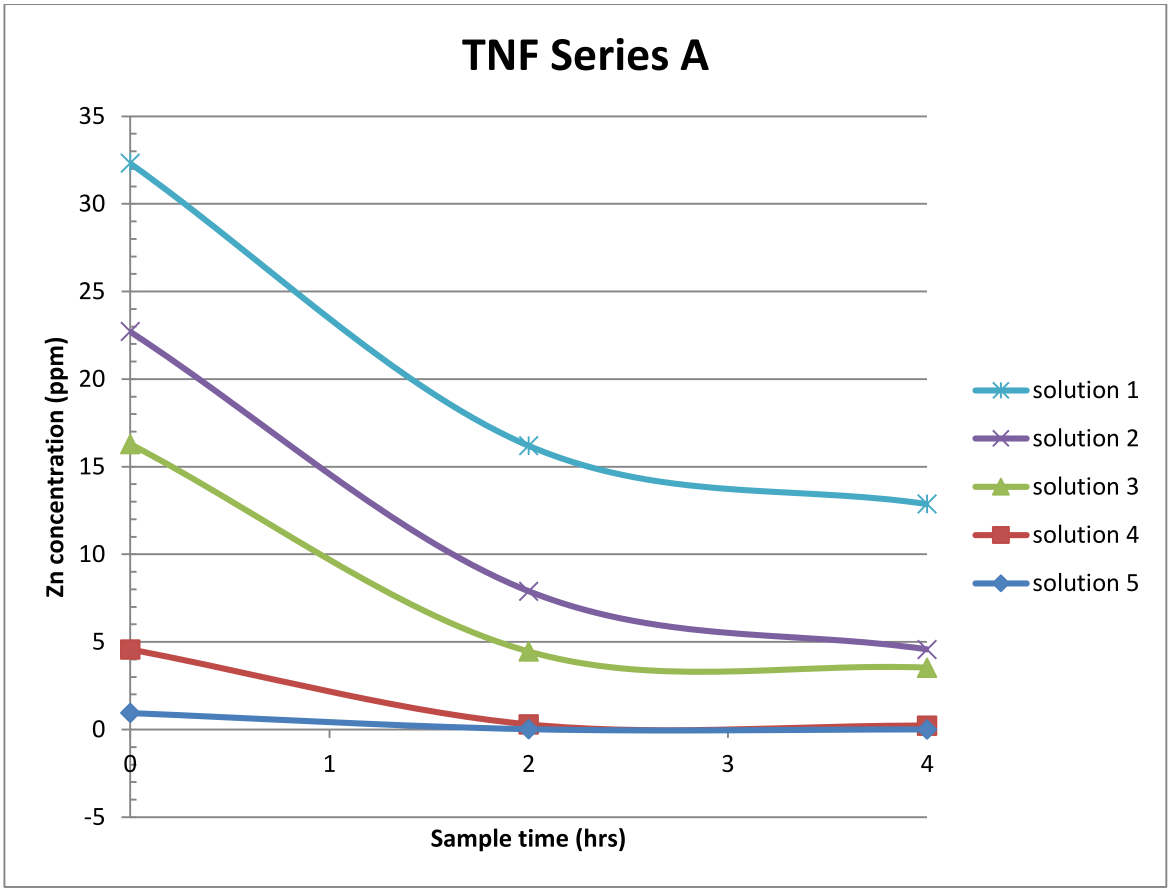

Figure 16: Treated fiber batch test series A

Table XVII: Treated fiber batch test series A data

	Zinc Concentration (ppm)			**% removal at 4 hrs**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	
1	32.32	16.20	12.87	60.2%
2	22.72	7.90	4.57	79.9%
3	16.30	4.46	3.53	78.3%
4	4.57	0.30	0.23	95.0%
5	0.94	0.02	0.01	99.2%

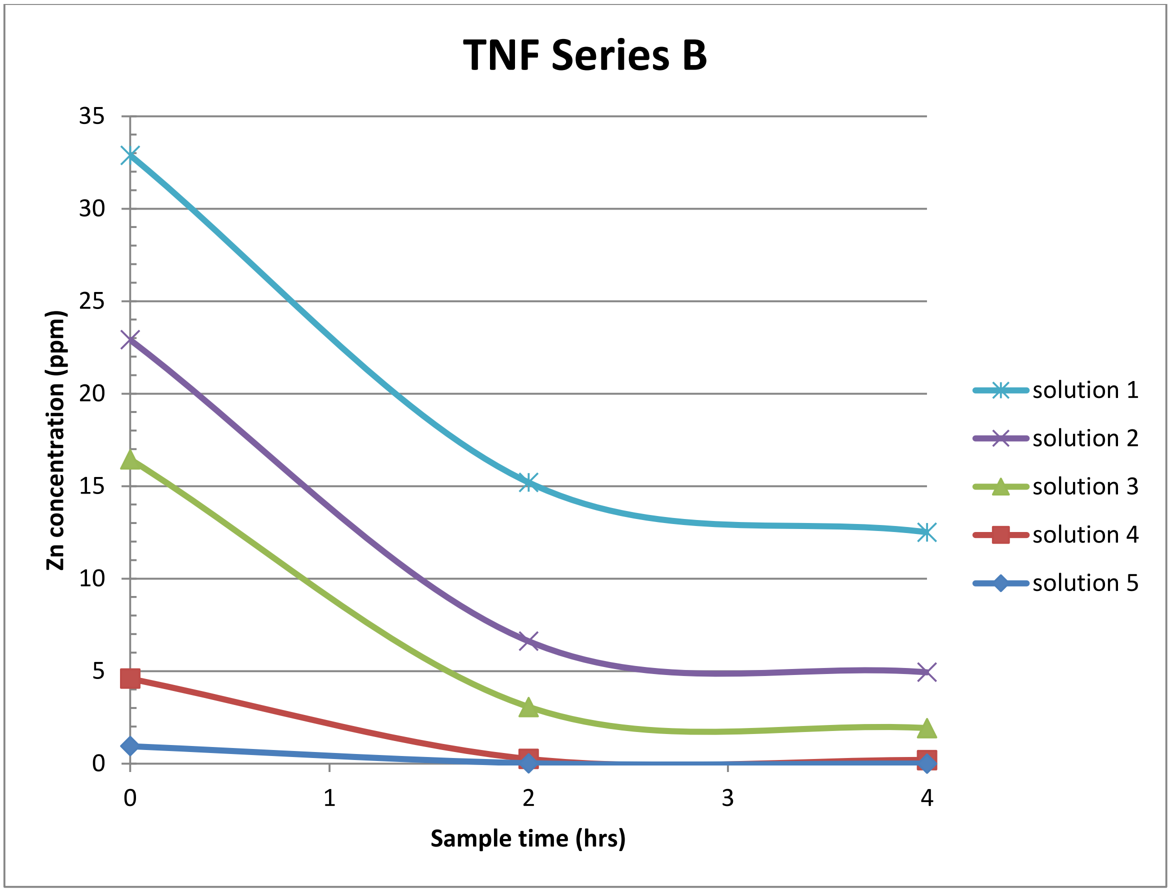

Figure 17: Treated fiber batch test series B

Table XVIII: Treated fiber batch test series B data

	Zinc Concentration (ppm)			**% removal at 4 hrs**
Solution	**0 hrs**	**2 hrs**	**4 hrs**	
1	32.89	15.2	12.51	62.0%
2	22.91	6.618	4.936	78.5%
3	16.45	3.064	1.915	88.4%
4	4.596	0.248	0.1904	95.9%
5	0.9427	0.0201	0.0021	99.8%

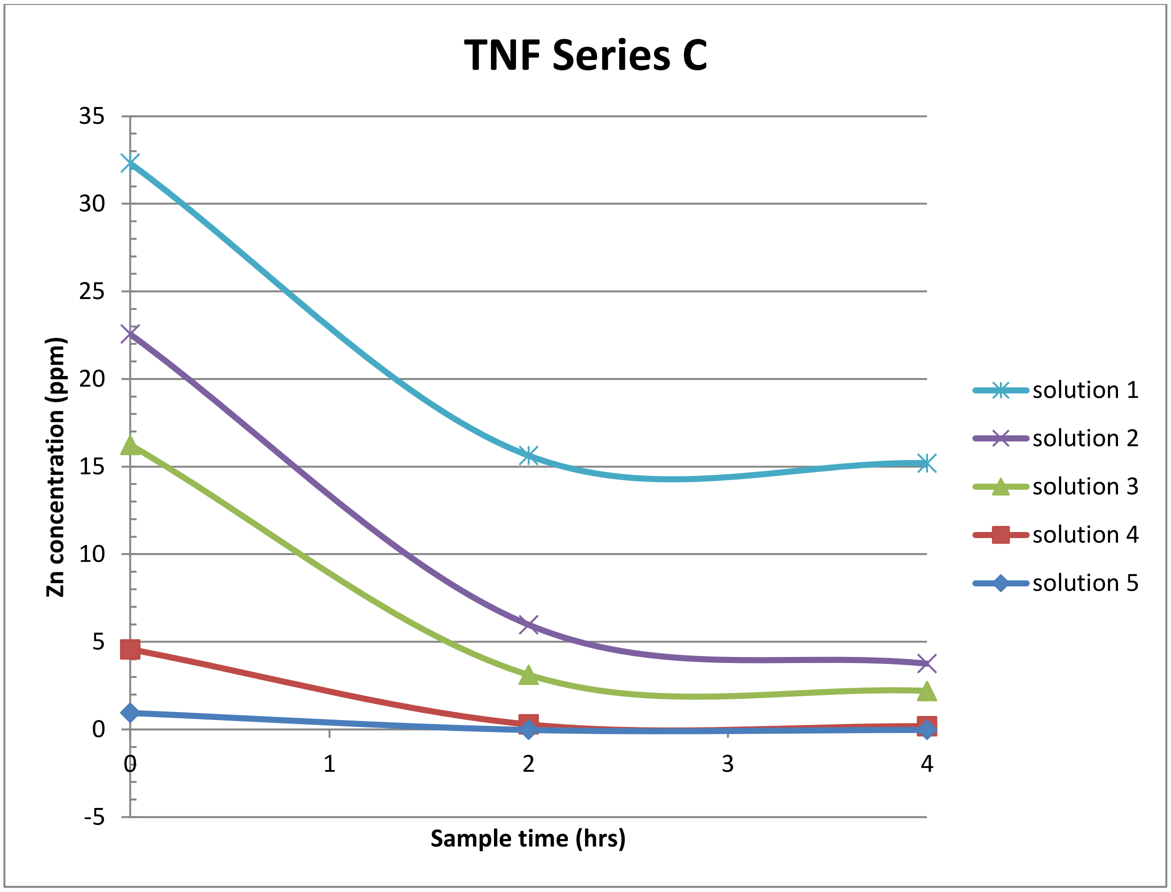

Figure 18: Treated fiber batch test series C

Table XIX: Treated fiber batch test series C data

	Zinc Concentration (ppm)			% removal
Solution	**0 hrs**	**2 hrs**	**4 hrs**	**at 4 hrs**
1	32.32	15.63	15.2	53.0%
2	22.57	5.977	3.754	83.4%
3	16.24	3.116	2.196	86.5%
4	4.571	0.2902	0.1908	95.8%
5	0.9494	-0.0222	-0.0206	102.2%

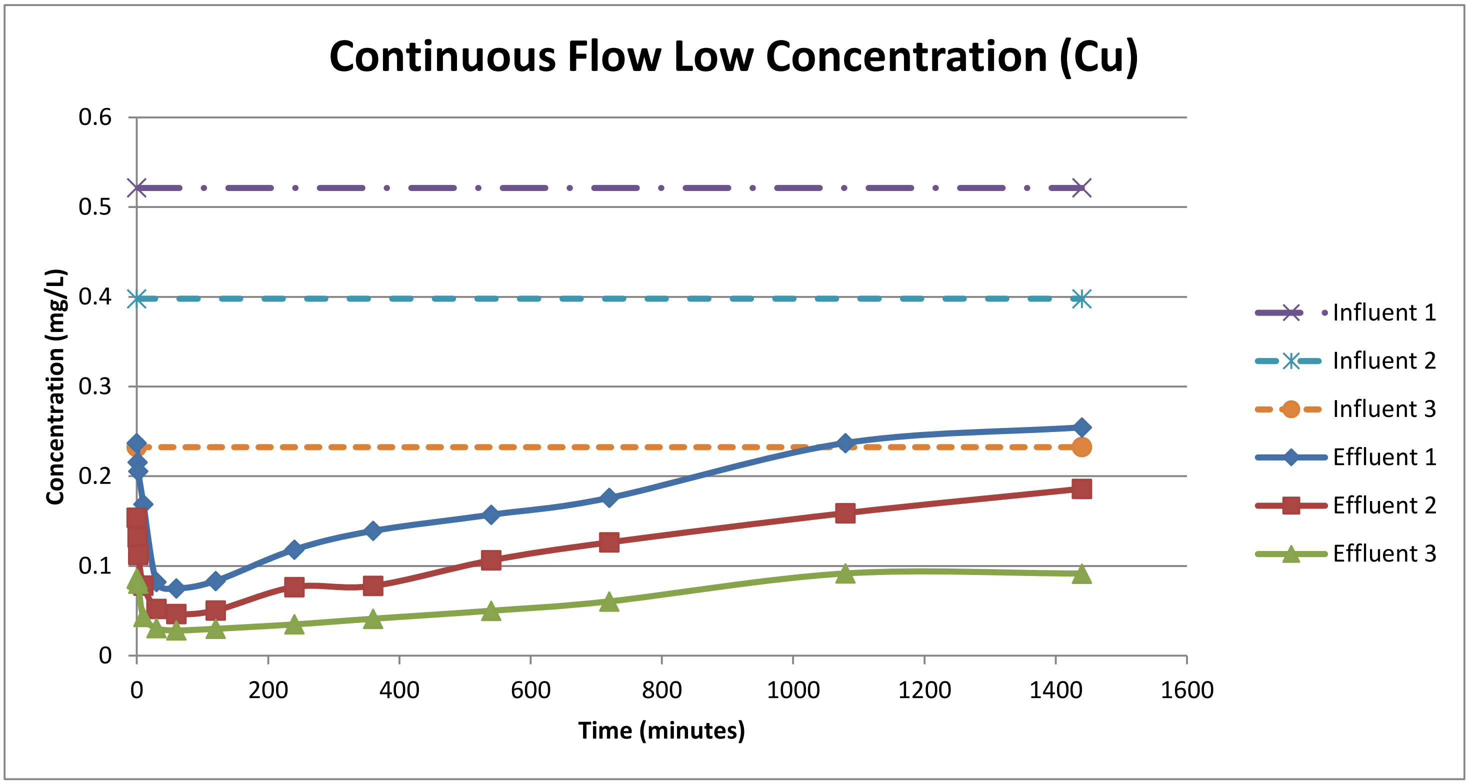

Figure 19: Copper concentrations for low zinc continuous flow trials

Table XX: Copper concentrations for low zinc continuous flow trials data

	Copper Concentration (mg/L)		
Time (minutes)	**Trial 1**	**Trial 2**	**Trial 3**
Influent	0.5213	0.3978	0.2325
0	0.2369	0.1538	0.0862
1	0.2153	0.1317	0.0849
2	0.2054	0.1125	0.0802
10	0.1687	0.0781	0.0432
30	0.0822	0.052	0.0308
60	0.0750	0.0463	0.0282
120	0.0832	0.0504	0.0300
240	0.1182	0.0765	0.0349
360	0.1390	0.0777	0.0412
540	0.1570	0.1062	0.0501
720	0.1758	0.1262	0.0605
1080	0.2370	0.1588	0.0916
1440	0.2544	0.1859	0.0915

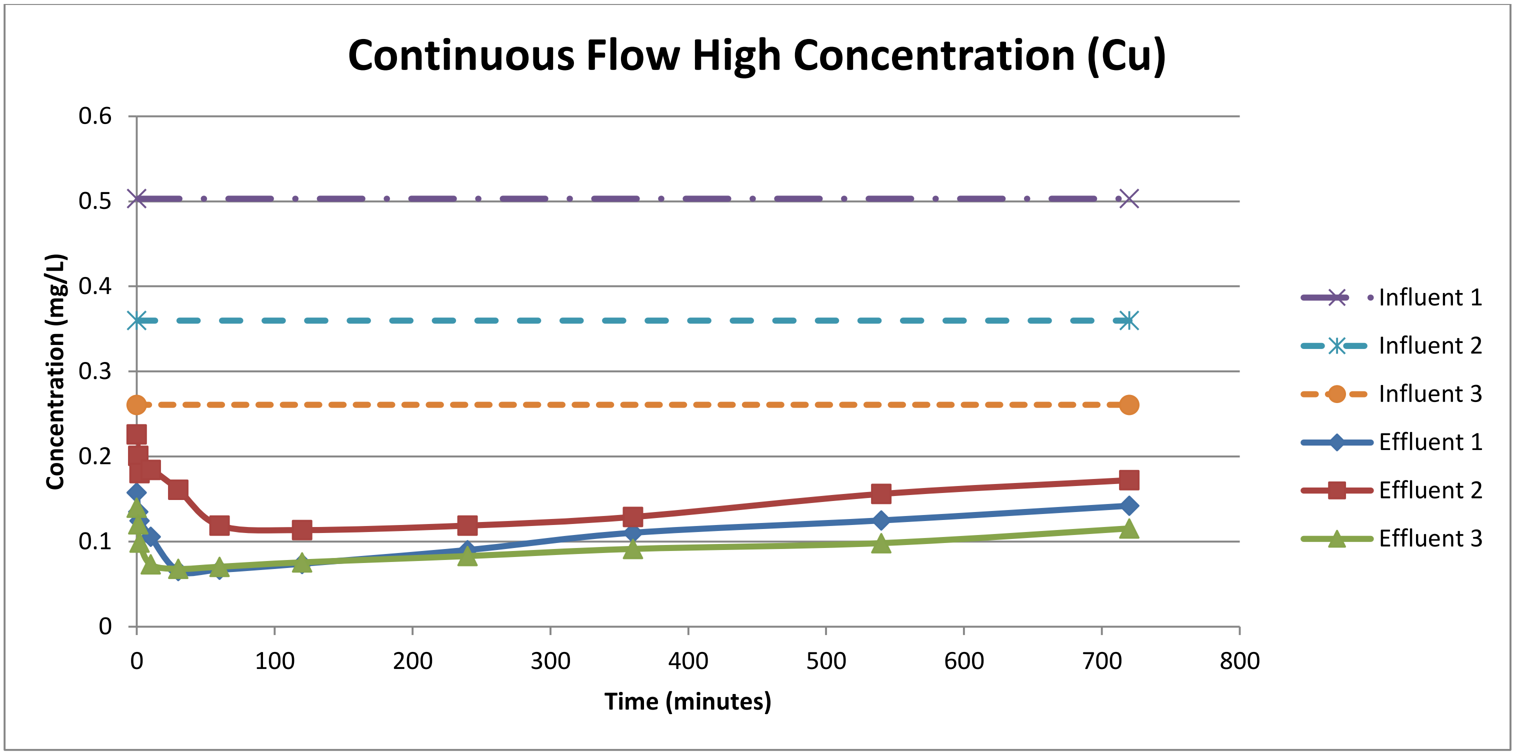

Figure 20: Copper concentration for high zinc continuous flow trials

Table XXI: Copper concentrations for high zinc continuous flow trials data

	Copper Concentration (mg/L)		
Time (minutes)	**Trial 1**	**Trial 2**	**Trial 3**
Influent	0.5031	0.3599	0.2606
0	0.1577	0.2261	0.1397
1	0.1350	0.2006	0.1201
2	0.1243	0.1803	0.0990
10	0.1058	0.1842	0.0731
30	0.0655	0.1609	0.0679
60	0.0667	0.1189	0.0704
120	0.0738	0.1134	0.0756
240	0.0900	0.1187	0.0830
360	0.1103	0.1289	0.0914
540	0.1248	0.1559	0.0982
720	0.1421	0.1721	0.1155

10. Appendix B

ICP-OES Procedures &Sequences

Operation:

1) **Turn On ICP-OES**
    a. Allow for 5 minutes for initial set-up before turning on Computer
2) **Check Argon Flow**
    a. Check pressure valves
        i. Should be at **90 psi** on left gauge
        ii. **Purge for 2 hours** prior to Plasma ignition
        iii. Keep Argon flow running all of the time
        iv. Note: Argon usage is 4-5 times faster when Plasma is ignited
        v. Record Pressure and Time In Logbook
            1. Fill in as you go along

Example Table:

Argon Tank	**Time**	**Pressure (psi)**
On	9:00 AM	1500
Plasma On	11:07 AM	1450
Start	11:27 AM	1400
End	12:43 PM	1250

3) **Turn on Computer**
4) **Turn Chiller on**
    a. This should turn the #2 light on in the POP window
    b. Check water level (red float). Should be in the middle
    c. Run approximately for **5 min** to reach 17.0 C
    d. Check weekly for algal growth (3 water filters, 1 air filter)
5) **Assemble ICP-OES Parts**
    a. Set peristaltic tubing
        i. Black/black - drain- right to left (go underneath peristaltic pump at first)
        ii. Orange/black- intake – right to left
        iii. Place one tab into the “catch” then pull tightly over the pump
        iv. Align tubes into “grooves” Make sure the tubes do not twist
        v. Align so that the tab faces outward (allows for Max contact on both sides of tab)
        vi. Clamp on (Do Not over tighten) Approx. 5 turns clockwise from loose is ok.
            1. Adjust Tension until there is a consistent flow of “Bubbles” in sample drain tubing.
            2. Reference inlet and outlet of spray chamber for troubleshooting
        vii. 3rd channel is there for use of an inline internal addition unit (leave open for us)
        viii. Check tubing once a week
            1. May be cloudy, if clogged then replace tube
    b. Assemble Sample introduction system
        i. Insert Nebulizer into Metal body assembly (if Necessary)
        ii. Clamp Spray Chamber on to the elbow joint
        iii. Make sure Inlet and outlet tube attach to glass nebulizer gas flow chamber
            1. Clean gas flow chamber via Methanol/Syringe Method as needed

        - iv. Close Plasma Chamber Door (Red Handle)
    - c. Check System flow schematically for errors before performing water test
        - i. If sample drain tubing is aligned backward on the peristaltic pump, it will draw contaminated liquid from the reservoir back into the system!

6) **Initialize Software**
    - a. iTEVA Control Center icon
    - b. Username – Steve (Create your own)
        - i. Initialize instrument buffering
    - c. Control Center is now Open
    - d. Open Analyst
        - i. Icon on Left side of Control center
    - e. Select method
        - i. Highlight Method, click OK
        - ii. If Creating New, Reference Method Set-Up Section later in this paper)
    - f. Select Sequence Automation
        - i. From bottom left of 3 tabs
    - g. Click Auto-Session
        - i. New Auto-Sampler
    - h. Click New
    - i. Enter Number of Samples to be analyzed (1-240)
    - j. Click OK
    - k. Click OK again

7) **Perform Water Flow Test**
    - a. Turn on Auto-Sampler
        - i. Power button on back right of machine
        - ii. Make sure a 5% HNO3 solution is hooked up
    - b. Click Yellow Icon on Top Right of Sequence Automation Page
        - i. This will connect the Auto-sampler to the ICP-OES Software
    - c. Right Click on Untitled (CETAC…)
    - d. Left click on Auto-Locate All
    - e. All Samples, including Cal Standards should become highlighted
    - f. Right Click over S-1
    - g. Select Go To S-1 … Method Blank
        - i. Make sure this is the location of the DI water (full)
        - ii. Sipper will automatically move into location
    - h. Open Plasma Status Window
        - i. Flame ICON on Bottom Right part of Analyst
    - i. Change Pump rate from 0 to 50 rev/ min
        - i. Select OK
        - ii. Adjust tensioning screws so that there is a consistent flow of bubbles in sample drain tubing.
            - 1. Note: Sample intake tubing should not have bubbles
            - 2. Reference inlet and outlet of spray chamber for troubleshooting
        - iii. Once correct, You may stop to conserve DI Water
            - 1. Just change Pump Rate back to 0 rev/min

8) **Check Instrument Status**
    - a. Select Instrument Status from bottom Left in Plasma Status window
    - **b.** Optics Temp should be at 38 C (mirror alignment)

- **c.** Camera Temperature should be at -47C (cannot run at Temps <-35C)
- d. Chiller Temperature should be at 17 C
- e. Record these three temperatures in logbook
- f. Make sure everything is Green (Except for Plasma, this will turn Green after next step)

Example Table:

ICP-OES	**Temp C**
Chiller	16.8
Optics	38.0
Camera	-46.78

9) Plasma Ignition (If experienced, skip to step d)

- a. Note Before Ignition: Watch Plasma stream carefully when first lighting
  - i. Plasma stream should be long solid and green.
  - ii. If flame seems short OPEN DOOR IMMEDIATELY this will cut off plasma stream
  - iii. Plasma Stream Characteristics should be Long and Green
    - 1. If initial Plasma stream is short and flickering, OPEN DOOR IMMEDIATELY
    - 2. If Plasma Stream initially is Short and Orange, OPEN DOOR IMMEDIATELY
- b. Note during ignition: Check Pressure Gauge
  - i. Pressure Gauge may “peg out” after initial ignition
  - ii. Gauge will drop back to Zero before Plasma ignition
    - 1. This is when you will have to watch the Plasma Chamber Window to check for proper ignition, make sure plasma chamber door is closed!
  - iii. Once Ignited, this will return to 0.3
    - 1. If there is a leak in the Nebulizer the system pressure will drop
    - 2. If there is a clog, the system pressure will go up, possibly caused by: dirt, crystals, or fiber in the system
- c. Note: If you have to open the door, or the plasma goes out on its own, that is ok
  - i. Just reset the machine
  - ii. It is possible the Analyst function will Freeze at this step, if this happens
    - 1. This is ok, just Close the software, re-open, and continue at Step 6.
  - iii. Click on and refer to any error messages provided
    - 1. Must click on error message before you can continue
  - iv. Adjust alignment of torch (not necessary if initially lighted properly, and Plasma cut-out sometime after initial ignition)
  - v. Start over from next step
- d. **Click Plasma On**
  - i. From Plasma Status Window, (above Instrument Status)
  - ii. Watch Plasma Stream as noted above
  - iii. Plasma stream should be long solid and green.
- e. Run loaded Blank Standard (2mg/l Zn) for 5 minutes (Optics alignment)
- f. Run DI for 2 minutes (loaded blank purge)

10) Run Samples

- a. Label all samples before initializing Sample Run
  - i. Select ICON that looks like an Excel Spreadsheet
    - 1. To the left of the connect auto-sampler ICON

- b. Press Play
- c. Let auto-sampler run until all samples are finished
    - i. View current Results in Analyst
    - ii. Watch Sampling Location in Sequence Automation

11) Shut down system

- a. After Sampling
    - i. Run DI water through system for 2 minutes
    - ii. Return sipper probe back to home
        1. Right click over home, in auto-session Tab, select Go To Home
    - iii. Click Plasma Off
        1. Flame ICON, Plasma Status Window
    - iv. Turn off AutoSampler
    - v. Disconnect Tubing
    - vi. Wait approx. 5 min for Quartz Torch to cool down
    - vii. Open Plasma Chamber door
    - viii. Detach spray chamber

12) Export Data to Flash Drive

- a. Open Publisher
    - i. From Original Control Center, IOCN below Analyst IOCN
- b. Select Report
- c. Select New
- d. Left Click Sample Report, Select OK
- e. Left Click button “Find Samples Analyzed between” (quickest), Select Search
- f. Select all appropriate Samples (Select All = quickest) Select OK
- g. Select Report
- h. Export
- i. Choose Location (Preferably a Flash Drive)
- j. Give Data a Label
- k. Change Report file from Crystal .rpt to Microsoft Excel file .xls
- l. Select Save
- m. Safely Remove Hardware From Computer

13) Turn off All Appropriate Equipment

SIGNATURE PAGE

This is to certify that the thesis prepared by Daniel Zieske entitled “Aqueous Zinc Removal Using Nanoparticle Treated Natural Fibers” has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Tech of The University of Montana, on this 5th day of May, 2015.

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