Final Report Alternative Biosorbent Design and Implementation



Corn Corps

CENE 486C 5/7/19

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List of Abbreviations

AMD (Acid Mine Drainage) DI (deionized) EBCT (Empty Bed Contact Time) EPA (Environmental Protection Agency) MCL (Maximum Contaminant Level) rpm (revolutions per minute) ICP-MS (Inductively Coupled Plasma Mass Spectrometry) ND (non-detect) BDST (bed-depth service time) GAC (granular activated carbon)

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1.0 Project Introduction

The Alternative Biosorbent Design and Implementation project is a research-based engineering project that aims to assess the viability of using corn cobs as a biosorbent for removing cadmium from drinking water. The removal of cadmium through low-cost treatment alternatives, such as waste corn, is necessary because traditional treatment technologies (such as activated carbon) tend to be expensive [1].

Corn cobs have the potential to remove cadmium and provide clean drinking water economically, while simultaneously converting a waste product into a resource. Heavy metal contaminants, like cadmium, can enter drinking water supplies through a variety of natural and anthropogenic sources, such as the erosion of mineral deposits and via acid mine drainage (AMD). These metals can pose serious threats to human health when ingested due to their toxicity and cause various diseases and disorders, such as kidney failure. Cadmium is also classified as a potential human carcinogen [2]. While emerging research on biosorbents has been pursued in Asia and in the Middle East, limited research has currently been conducted regarding biosorbents in the United States [3].

This project expands upon a NASA Space Grant research project awarded to a Northern Arizona University undergraduate student during the 2017-2018 school year, which first tested the effectiveness of corn cob biosorbent removal. This research showed promise, yielding removal efficiencies of up to 51%. However, some inconsistencies prompted further corn biosorbent research [4]. Thus, the Alternative Biosorbent Design and Implementation project intends to expand upon the original results to include a more detailed isotherm for untreated corn, an isotherm for cadmium removal by corn treated with nitric acid, and pilot-scale test of a corn cob adsorption tower. Full-scale design impacts and a feasibility assessment for the adsorption tower are also included to determine the viability.

1.1 Objectives

There are several objectives for this research project.

- A. Prepare the corn biosorbent for testing. A portion of the corn is treated with nitric acid to determine if nitric acid-treated corn increases sorption potential. Previous literature found that nitric acid treatment of corn increased cadmium adsorption capacity by 62%. This higher adsorption capacity is attributed to an increase in the number of binding sites on the surface of the corn particles [5].
- B. Measure the removal of cadmium by treated and untreated corn cobs under ideal conditions and develop adsorption isotherms for treated and untreated corn.
- C. Construct a bench-scale adsorption tower prototype to assess the feasibility of corn cobs in an adsorption tower.
- D. Determine whether the prototype can achieve the desired level of cadmium removal from an initial concentration of 75 μ g/L to the EPA's Maximum Contaminant Level (MCL) of 5 μ g/L.
- E. Scale up the tower design to predict full-scale effectiveness and analyze the feasibility of implementing this technology in real applications.

1.2 Previous Research Conducted at NAU

During the 2017-2018 academic school year at NAU, the NASA space grant funded an environmental engineering undergraduate student to test the validity of corn cobs as a biosorbent for removing cadmium from water. Corn cobs were dried for 24 hours at 100 °C, then pulverized using a food processor, and sifted through a 250 µm sieve. One gram of the corn biosorbent was then added to 300 mL of cadmium solution. Initial concentrations of 10 ug/L, 25ug/L and 80 ug/L were tested using the HACH 8017 Dithizone Method to determine removal efficiencies. Testing returned promising results of up to 51% removal (Table 1.1) [4].

Removal Efficiencies		
Initial Concentrations (ug/L)	Average Removal (%)	
10	9	
25	42	
80	51	

Table 1.1. Removal efficiencies by mass for each tested concentration – Spring 2019

The validity of the isothermal model (Appendix A, Figure A.1) has limitations because the isotherm model was produced from only three concentrations – a very small sample size – and several tests yielded higher final concentrations than the starting concentrations. There was likely experimental and/or analytical error, possibly due to a lack of familiarity with the HACH 8017 method. However, the research showed cadmium removal potential.

1.3 Constraints and Limitations

This project is limited to testing the removal of cadmium using the ground corn cob biosorbent. Cadmium was tested in an aqueous solution and was the only constituent, as opposed to a mixture of metals in solution, which would be a more likely scenario in a real application. Only the cob portion of sweet corn was investigated for sorption potential. Cadmium removal by feed corn was not investigated, nor was removal by kernels or husks.

2.0 Testing and Analysis Methods

2.1 Corn Biosorbent Preparation

A standard method was not followed for preparation of the corn cob biosorbent because none currently exist. Therefore, methods were adapted from a variety of literature that prepared corn biosorbents [4]. Approximately 200 grams of corn biosorbent were prepared for use. First, the husks were removed, then the corn cobs were rinsed to remove surface impurities. The cobs were then cut into 2-inch sections with the kernels still present at this point (Figure 2.1).



Figure 2-1. Fresh corn being cut into 2-inch pieces

The corn was placed in a drying oven at 180 °C for 24 hours or until the corn was thoroughly dried (Figure 2.2). The dried corn was de-kernelled by hand (Figure 2.3), and a pestle and mortar were used to break the cob pieces apart.



Figure 2-2. Corn after being dried for 24 hours



Figure 2-3. Dried corn de-kernelled

These pieces were then pulverized in a food processor (Figure 2.4). The corn was sieved through a 250 μ m (#60) sieve to maximize surface area for greater sorption potential (Figure 2.5).



Figure 2-4. Pulverizing the dried corn cobs



Figure 2-5. Sieving the pulverized corn through a 250 um sieve

2.2 Corn Biosorbent Treatment

Approximately 45 grams of the pulverized cob were treated with nitric acid to determine if acid treatment increases sorption potential. This procedure was adapted from previous literature and guidance from Dr. Terry Baxter [3]. The corn was treated by first saturating the ground cobs with 1.0 M nitric acid (HNO₃) solution for 12 hours on a rotary shaker. The corn/nitric acid mixture was poured into centrifuge tubes and centrifuged for 20 minutes at 3000 rpm (revolutions per minute). The top layer of liquid in the tubes was poured off into waste bottles. Deionized water was added into the centrifuge tubes and placed back into the centrifuge for further rinsing. The water/nitric acid residue was dumped into the waste bucket again. From this point, the corn was treated two separate ways due to pH problems encountered through experimentation. A standard procedure was created, which aimed at returning the corn to a neutral pH.

The treated corn was created by combining two different batches in the following manner. The first batch nitric acid-treated corn was scooped into evaporating dishes and oven dried at 80° C for 12 hours. The corn was then treated with sodium hydroxide in a manner identical to the nitric acid treatment phase. This batch of corn turned out to be extremely basic (pH >11). Thus, the basic corn was combined with a second batch of corn that had only been treated with nitric acid. By mixing the two batches for 12 hours on the shaker table, a neutral pH was achieved.

After the high pH issue was noted in the first batch, the next batch of corn treatment was executed by treating the corn with nitric acid and titrating the corn until pH 7 was achieved. First, deionized (DI) water was combined with the acidic corn to create a slurry. 19.8 M sodium hydroxide was then titrated into the slurry to a pH of 7. The solution was put onto the rotary shaker table for 12 hours to ensure that the pH of the liquid solution was the same as the pH of the corn. The corn was then separated from the liquid using a glass fiber filter and dried at 80 °C.

Photographs outlining all stages of corn treatment attempted for this project can be found in Appendix B.

2.3 Testing the Removal of Cadmium using HACH 8017

Five initial cadmium concentrations of 10 μ g/L, 20 μ g/L, 35 μ g/L, 50 μ g/L, and 75 μ g/L were tested at room temperature to determine the removal efficiency of corn. This range of concentrations was selected to determine if cadmium-contaminated water may be treated to the EPA's MCL standard for cadmium (5 μ g/L). These concentrations also reflect realistic cadmium concentrations in contaminated drinking water sources. For instance, cadmium concentrations in the groundwater of some western regions of India were found to be 40 μ g/L and 70 μ g/L [6]. The World Health Organization reported the maximum concentration range falls within the testable limits of the HACH 8017 Dithizone Method (0.7 μ g/L to 80 μ g/L) [8]. The following experimental matrix (Table 2.1) displays the initial cadmium concentration tested, whether or not the corn utilized in the test was treated, and the number of replicates tested.

Cadmium Experimental Matrix			
Experiment Number	Initial Concentration (µg/L)	Treated	Number of Replicates
Cd -1	10	No	3
Cd -2	20	No	3
Cd -3	35	No	3
Cd -4	50	No	3
Cd -5	75	No	3
Cd -6	10	Yes	3
Cd -7	20	Yes	3
Cd -8	35	Yes	3
Cd -9	50	Yes	3
Cd -10	75	Yes	3

Table 2.1. Experimental matrix of cadmium removal test

To test removal of cadmium by corn, a cadmium standard was first prepared for one of the established initial concentrations. A HACH 100 mg/L cadmium standard solution was diluted in a flask containing between 1200 mL and 1500 mL of deionized water. This prepared cadmium standard was divided into three Erlenmeyer flasks, each containing 300 mL of cadmium solution. 1 gram of corn was added to each flask, then placed on a rotary shaker table for 90 minutes at 250 rpm. The corn was filtered out of the solution using a vacuum apparatus and VWR® Fiber Filter 1.6 μ m. Filtrate was poured into a separatory funnel and tested in accordance to HACH Method 8017 for residual cadmium that did not adsorb to the corn (see Appendix B for the step by step method).

A liquid-liquid separation was induced by the HACH 8017 method, and the bottom layer (composed of chloroform and cadmium) was dispensed into a 10 mL cuvette. A HACH DR 3900 spectrophotometer was zeroed using a cuvette containing only chloroform. Then, the sample was analyzed in the spectrophotometer to determine the equilibrium concentration of cadmium. After the completion of each test, all glassware was washed with 6.0 N hydrochloric acid to reduce chance of contamination for the following test.

3.0 Results and Analysis

3.1 Untreated Corn Calibration Curve

A calibration curve was only developed for the untreated corn because the HACH 8017 method was used, which lacked precision due to the fact that it is based on a colorimetric analysis. The treated corn was tested using ICP-MS (due to issues encountered with HACH 8017- see section 3.2), which is much more precise, and therefore the measured values were taken to be the true values. Therefore, the development of a calibration curve was not necessary for treated corn. In total, five initial cadmium concentrations were tested using the HACH 8017 method for untreated corn: $10 \mu g/L$, $20 \mu g/L$, $35 \mu g/L$, $50 \mu g/L$, and $75 \mu g/L$. Standards for every concentration were analyzed using a DR 3900 spectrophotometer after the steps of the HACH method were completed, and the concentration readings in the

spectrophotometer were used to make a calibration curve for all data collected. These readings can be found in Table 3.1 below. The standard concentration is the initial concentration prepared, which is assumed to be the true value. The HACH method concentration is the reading returned from the DR 3900 for each standard solution. The calibration curve shown in Figure 3.1 plots these prepared concentration values against the spectrophotometer readings.

A reagent blank was tested to determine if there was any interference from the reagents in the sample readings. The reagent blank only contained the reagents, without the addition of corn or cadmium. The x-intercept of the calibration curve was set to the value of this reagent blank, or $3.4 \mu g/L$ (see Appendix E). The equation of the calibration curve was used to calculate the true value of all readings taken using the HACH 8017 method.

Standard Concentration (µg/L)	HACH Method Concentration Reading (µg/L)
10	11.7
20	22.1
35	41.1
50	49.0
75	70.0

Table 3.1. Untreated calibration curve data



Figure 3-1. Untreated corn calibration curve

The R^2 value for the calibration curve was very close to 1, indicating that the preparation of the standards and the spectrophotometer readings were fairly accurate considering that HACH 8017 is a colorimetric test.

3.2 HACH Method Complications and Solutions

The HACH Cadmium Dithizone Method 8017 was used for testing cadmium removal by untreated corn. The reliability of the data was at first questionable for various reasons, including changing concentration readings over time, the clarity of samples that were extracted from the separatory funnel, and the variability of concentration readings in differing light exposures. Many of these issues were resolved; however, the causes remain not entirely understood.

3.2.1 Clarity of Samples

Some of the cadmium solutions appeared cloudy after dispensing testing solution into the cuvette. This was attributed to the creation of air bubbles while shaking the separatory funnel to disperse reagent materials. Additional measures were therefore taken to reduce cloudiness. When dispensing solution, the topper of the separatory funnel was removed so that a vacuum was not created in the funnel as the liquid flowed through and bubbles disturbed the solution in the funnel. The tip of the funnel was also placed against the side of the cuvette (as opposed to letting it free-fall) so that there was less disturbance of the liquid when flowing.

3.2.2 Light Sensitivity

After several HACH 8017 tests were completed, it was noted that the concentration readings from the spectrophotometer dropped each time a reading was taken. Two potential causes were explored to determine the cause of the dropping values:

- 1. Light interference, either from the spectrophotometer or ambient light in the room was affecting the sample readings.
- 2. The samples in the cuvettes needed time to settle and stabilize, and as they stabilized, the concentration dropped. This was a probable cause because the separatory funnel needs to be shaken to thoroughly distribute reagent materials during the reaction time, however the shaking appeared to create microbubbles in the solution. This may have affected the ability for the light to pass through, thus creating artificially high readings.

To test these two hypotheses, a light sensitivity test was conducted at two different concentrations (5 μ g/L and 75 μ g/L). First, a standard was prepared for 75 μ g/L to test effects of light on the HACH 8017 method, and two 10 mL cuvettes were collected from separatory funnel. One of these cuvettes (cuvette B) was immediately placed in a dark cabinet next to the DR 3900. The other (cuvette A) was exposed to the light of the fume hood for a short amount of time before being placed directly in the DR 3900 spectrophotometer. Readings were taken on cuvette A every 15 seconds for the first 2.5 minutes, then every minute until 15 minutes had passed. At 15 minutes, cuvette A inside the spectrophotometer was removed and allowed to sit on the counter in the light, while cuvette B, which had been sitting in the dark up until this point, was placed in the DR 3900.

If the outside light exposure was causing the abnormal readings, cuvette B (which had been sitting in the dark for 15 minutes) should theoretically have had the same reading as

cuvette A after 15 minutes of continuous readings. However, this did not happen, as cuvette B read higher than the initial value of the light cuvette, A. Figure 3.2 demonstrates that cuvette B read 2.8 μ g/L higher than cuvette A started at initially. Readings were taken on cuvette B for another 17 minutes.



Figure 3-2. 75 µg/L Light sensitivity graphical test results

After 17 minutes of readings (t=32 minutes total elapsed time, including cuvette A), cuvette B was removed from the DR 3900 and placed back in the dark cabinet. The cuvette A that had been sitting in the light on the counter was then read again at t=32 minutes, this time higher than the previous reading at t=15 minutes. Readings for another 7 minutes resulted in a continued drop in concentration. At t=39 minutes (not shown on graph), the cuvette A was removed, and cuvette B was placed back into the DR 3900. This, too, read higher than its last reading before being taken out of the 3900 (t=32). Since the samples are only good for analysis within one hour of collection, this was the last reading that was taken.

To verify mathematically that the two data sets were statistically, significantly different, Microsoft Excel ANOVA: single factor analysis was performed. This analysis compared the two data sets' sample size and variance, and ultimately related the data's calculated F value to the F_{critical} value. Equation 3.1 below shows the calculation for the F test.

$$F = \frac{\sum n_j (\bar{x}_j - \bar{x})^2 / (k - 1)}{\sum (\sum (X - \bar{x}_j)^2) / (N - k)}$$
(3.1)

Where:

 $n_j = the sample size in the j^{th} group$

 \overline{X}_j = the sample mean in the jth group \overline{X} = the overall mean between groups k = the number of independent groups (therefore, j) N = total number of observations in the analysis (not population)

Because the F values that were calculated were higher than that of the $F_{critical}$ values, there was a statistically significant difference in the two data sets. This means that light influences the cuvette readings. To see ANOVA output tables and raw data for this process, see Appendix D. The 5 µg/L experiment was conducted in the same manner and yielded similar results. The graph for the 5 µg/L sensitivity test may be seen in Appendix D Figure D.1.

This light sensitivity test led to the conclusion that the conditions in which the cuvette are stored and the amount of time that passes before taking a reading do not have an effect on the final stabilized value; only reading the sample continuously every minute with the 515 nm light causes the sample to converge to its true value after approximately 15-30 minutes. It is unknown whether the stabilization of the readings was due to the spectrophotometer's wavelength pulse or the dissipation of the air bubbles, thereby reducing cloudiness. Regardless, this finding standardized all results and was reflected in testing methods. Concentrations for every test were read until the solutions stabilized or reached 30 minutes of readings. This stabilized value was reported as the final concentration for each test.

3.2.3 Cadmium Reading Interference and Corrections

The interference of the reagents used in the HACH method and corn were initially unknown. Therefore, additional tests were conducted to determine whether or not the reagents or the corn were causing artificially high cadmium readings by the DR 3900 spectrophotometer. A series of blanks were tested to quantify these interferences (Table 3.2).

Blank Type	Application	Solution Description
Chloroform	This blank was used to zero out the	Chloroform was the blank material
Blank	spectrophotometer before every	because chloroform is the solvent in the
	sample reading.	HACH method.
Reagent	The reagent blank was used to	The reagent blank was created by only
Blank	determine if any interferences were	running deionized water through the
	occurring due to HACH reagents.	HACH method and testing the result.
	This value was subtracted from the	
	concentration readings of the	
	prepared standards.	
Method	The method blank was used to	The method blank was created by
Blank	determine if any interferences were	running only corn filtrate through the
	occurring due to the corn in the	HACH method and testing the result.
	water. This value was subtracted	The filtrate was created by adding 1
	from the concentration readings of	gram of corn to 300 mL of deionized

the sample filtrate spectrophotometer	water and shaking the solution for 90
readings.	minutes.

Ultimately, the development of the three blanks revealed that there were consistent interferences caused by the reagents and the corn. The reading for each blank is displayed in Table 3.3 below.

Blank Type	Stabilized Concentration (µg/L)
Chloroform	0.0 (baseline)
Reagent	3.4 (n=2)
Method	2.5 (n=2)

Table 3.3. Blank readings for HACH Method 8017

The stabilized method blank concentration was determined by taking the average of two method blank tests' final readings (see Appendix E for raw data), and the stabilized reagent blank concentration was determined from a single reagent blank test that is recommended to be completed once for every new reagent set by HACH. Since only one reagent batch was used for the duration of the HACH 8017 tests, only one reagent blank test was conducted. The results in Table 3.3 indicate that the reagents cause spectrophotometer readings to be 3.4 μ g/L higher than the true cadmium value, and the corn cob residual causes an additional 2.5 μ g/L increase to the true cadmium value reading in the DR 3900.

Sample concentrations were first adjusted by subtracting out the value obtained for the method blank (see Table 3.2) to account for interference of both the corn and the reagents in the DR 3900 spectrophotometer readings. The average concentration for each set of triplicates was calibrated using the equation of the trendline shown in Figure 1, which sets the intercept to the value of the reagent blank in order to correct for the interference caused by the reagents. These calculations are summarized in the equations below.

$$x = \frac{(y-3.4)}{0.9189} \tag{3.1}$$

Where:

x=the true cadmium concentration value ($\mu g/L$) y= DR 3900 spectrophotometer reading ($\mu g/L$)

This equation was used to calibrate final concentration values to the calibration curve trendline.

Final Concentration = Final Reading
$$\left(\frac{\mu g}{L}\right) - 2.5 \mu g/L$$
 (3.2) Where:

 $2.5 \ \mu g/L$ is the method blank concentration

This equation was used to correct for corn cob interference in each individual sample reading.

3.3 Isotherms and Percent Removal

Adsorption isotherms were developed for both treated and untreated corn in order to plot the amount of contaminant sorbed per unit mass of corn, q, against the equilibrium concentration of contaminant in the bulk fluid at a constant temperature. These isotherms can be used to determine the mass of corn required to treat a contaminated water source to a specified final concentration. The mass sorbed was calculated by multiplying the change in concentration ($\mu g/L$) by the volume of solution (0.3 L) to obtain the μg sorbed. Since 1 gram of corn was used for this method, the $\mu g/g$ sorbed to the corn was equivalent to the mass sorbed. The isotherms were developed at room temperature (≈ 25 °C) since a standard water treatment process would typically operate within this temperature range. Removal efficiencies for each process were calculated using Equation 3.5.

$$q = \frac{(C_{initial} - C_{final}) * V}{m}$$
(3.4)

Where:

q=mass sorbed ($\mu g/g$) $C_{initial}$ = initial cadmium concentration of the sample ($\mu g/L$) C_{final} = final concentration of cadmium in the sample once equilibrium has been reached ($\mu g/L$) V= sample volume (L), in this case 0.3 L m= mass of corn (g), in this case 1 gram

This equation was used to calculate the adsorption capacity, which was plotted on the y-axis of the isotherm models.

Removal Efficiency (%) =
$$\frac{C_{initial} - C_{final}}{C_{initial}} * 100$$
 (3.5)

This equation was used to then calculate the removal efficiency for each of the five different initial concentrations. An average of these values was taken to obtain the overall average removal efficiency.

3.3.1 Untreated Corn Isotherm and Removal

For the untreated corn, the HACH 8017 method was used for testing. The experimental matrix showing the number of replicates for each test is reiterated in Table 3.4. The corrected equilibrium concentrations resulting from average removal efficiency were determined by taking the mean of the removal efficiencies for each concentration. In Appendix F, Table F.1 shows the raw data for the experiment without calibrating readings and Table F.2 shows the final stabilized reading. To account for the interference of the dissolved solids from the corn, the concentration of the method blank ($2.5 \mu g/L$) was subtracted from every sample reading. Table 3.4 describes the equilibrium data, which was plotted in the isotherm.

Experiment Number	Initial Concentration (µg/L)	Number of Replicates
Cd -1	10	3
Cd -2	20	3
Cd -3	35	3
Cd -4	50	3
Cd -5	75	3

Table 3.4. Untreated corn experimental matrix

Table 3.5. Calibrated final cadmium readings for HACH testing of untreated corn

Prep'd Initial Conc. (ug/L)	EQ Conc. Sample A (ug/L)	EQ Conc. Sample B (ug/L)	EQ Conc. Sample C (ug/L)
10	2.6	X*	1.3
20	2.6	3.6	4.9
35	10.3	11.5	11.1
50	X**	9.8	11.5
75	24.8	18.2	18.0

*This sample was accidentally discarded before analysis

**This sample was prepared incorrectly

Table 3.6. Results- untreated corn isotherm

Prep'd Initial Conc. (ug/L)	Average EQ Conc. (ug/L)	Standard Deviation	95% Confidence Interval (±)	Removal Efficiency (%)
10	1.93	0.85	2.11	81
20	3.67	1.05	2.62	82
35	10.96	0.57	1.41	69
50	10.65	4.59	11.41	79
75	20.31	3.58	8.90	73

The cadmium equilibrium concentration (final concentration listed in Table 3.3) was plotted against the mass of cadmium sorbed to the corn cob in order to produce the isotherm model below (Figure 3-3).



Figure 3-3. Untreated corn linear isotherm model

As shown in Figure 3.3, the linear isotherm model has an R^2 value of 0.7419, and therefore is determined to be an accurate model. A comparable Freundlich power isotherm model could not be developed due to the equilibrium concentration of the first data point being equal to 0 μ g/L; however, the high R^2 of the trend line in Figure 3.3 validates the linear model.

One concentration batch had a low standard deviation (35 μ g/L), and therefore a rather narrow confidence interval in relation to the initial concentration. However, most concentrations had significant standard deviations, and therefore had wider confidence intervals.

It can be seen from Table 3.4 that in some cases the confidence intervals are nearly as high as the calibrated final concentrations themselves. Using the data collected from the experimental methods, the average removal efficiency of cadmium was 76% across all tested concentrations. The range of the removal efficiencies for all samples was 52% to 100%.

3.3.2 Treated Corn Isotherm and Removal

The initial plan was to use the HACH Method 8017 to evaluate the treated corn's ability to remove cadmium. However, the problems from the HACH 8017 method outlined in section 3.2 intensified further, which resulted in invalid data. In summary, the spectrophotometer measured higher final concentrations than the initial standard concentrations, even though samples did not develop pink the coloration characteristic of cadmium presence. Additionally, samples appeared to be very cloudy, resulting in artificially high readings.

As the HACH method was unable to produce reliable data, alternative testing methods were pursued. The team subcontracted cadmium testing to Western Technologies, Inc. to complete the treated corn isotherm. Western Technologies further subcontracted the

cadmium testing to Pace Analytical, a water quality testing facility in Phoenix, AZ, who conducted cadmium analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Samples were collected in 250 mL vials containing nitric acid to preserve cadmium concentrations during transport. Samples were uniquely identified according to the time of collection as specified on the chain of custody form. In Table 3.7, the experimental matrix of the concentrations test is displayed. Duplicates were sent for analysis, instead of triplicates, due to budgetary limitations and the increased accuracy of ICP-MS testing. Table 3.8 shows the finalized results of the treated corn. Lab results and the chain of custody forms can be seen in Appendix H.

Experiment Number	Initial Concentration (µg/L)	Number of Replicates
Cd -6	10	2
Cd -7	20	2
Cd -8	35	2
Cd -9	50	2
Cd -10	75	2

Table 3.7. Treated corn cadmium experimental matrix

Initial Conc (ug/L)	Sample A Final Conc (ug/L)	Sample B Final Conc (ug/L)
8.47	ND	ND
25.6	ND	1.05
35.4	1.28	1.35
48.4	1.43	1.92
70.6	2.2	2.11

Table 3.8. Final cadmium readings for ICP-MS Testing of treated corn

Table 3.9. Results for the treated corn isotherm

Initial Conc (ug/L)	Average Final Conc (ug/L)	Standard Deviation	95% Confidence Interval (±)	Removal Efficiency (%)
8.47	N/A	N/A	N/A	N/A
25.6	1.05	N/A	N/A	96
35.4	1.32	0.05	0.44	96
48.4	1.68	0.35	3.11	97
70.6	2.16	0.06	0.57	97

Similar to the untreated corn cadmium testing, concentrations were prepared to be 10, 20, 35, 50, and 75 μ g/L. Because of the accuracy of ICP-MS analytics, the results of the

prepared standard were taken as the true concentration and used for the isotherm and the calculation of removal efficiency (Table 3.8).

Table 3.9 shows that both the final readings for the first concentration (10 μ g/L) were measured as non-detected (ND). Additionally, one equilibrium concentration for the second concentration tested (20 μ g/L) was measured ND. The limit of detection for ICP-MS is 1 μ g/L, as specified by Pace Analytical. It is highly probable that the true values for the cells listed as "ND" in Table 3.6 range anywhere between 0 to 1 μ g/L. Because precise values for the concentrations listed as ND were unavailable, those cells were not used in producing the treated corn isotherm. In total, 10 samples were prepared to produce the treated corn isotherm, but due to the limits of detection for ICP-MS, only 7 samples produced usable data. Figure 3.4 below shows the treated corn isotherm.



Figure 3-4. Treated corn linear isotherm model

Comparatively, the treated corn isotherm had a higher R^2 value (0.8522) than that of the untreated corn (0.7419). While the R^2 value is only marginally improved for the treated corn, the removal efficiency was noticeably higher for treated corn. The average removal efficiency for treated corn was 97% while the average removal efficiency for untreated corn was 77%. Because the treated corn was much more effective at removing cadmium, it was used for the prototype design.

4.0 Prototype Development and Pilot Testing

An adsorption tower prototype was designed according to the schematic shown in Figure 4.1. A pre-constructed column from the NAU Environmental Lab was used for the adsorption tower design. A peristaltic pump was used to pump water through the column so that none of the pump components would be contaminated by cadmium. Centrifugal pumps move water through the impeller, which would contaminate the inside of the pump; peristaltic pumps move water by compressing replaceable tubing. A Y-fitting was installed in the tubing preceding the pump to easily switch between the flows of cadmium-contaminated water and deionized (DI) water.



Figure 4-1. Prototype Design Schematic

Treated corn was used in the prototype due to its higher removal efficiency. To verify the capacity of the prepared corn biosorbent, two parameters were initially selected. First, the influent concentration was set to 75 μ g/L, as this concentration is within the upper range for a mine spill where cadmium is present [7]. The target effluent concentration was set at 5 μ g/L because this is the EPA's MCL for cadmium. Based on the target effluent concentration and the treated corn isotherm, the adsorption ratio of cadmium to treated corn was determined to be 43.4 μ g/g (Equation 4.1).

$$q = KC_e \tag{4.1}$$

Where: $C_e = 5 \ \mu g/L$ $K = 8.6817 \ L/g$ (taken from isotherm)

Based on the adsorption ratio of 43.3 μ g/g, the capacity of the treated corn was calculated (Equation 4.2).

$$Capacity = \frac{q}{\Delta c}$$
(4.2)
Where:
$$q = 43.3 \ \mu g/g \Delta C = 70 \ \mu g/L$$

The capacity of the treated corn was calculated to be 1.61 grams of treated corn per liter of contaminated water (Equation 4.2). After completing treated corn isotherm testing, 2.5 grams of treated corn remained available for use in the prototype. Based on 2.5 grams of treated corn being used in the column, 1.55 L of contaminated water could be treated.

The length and diameter of the column was measured, then filled with 2.5 grams of corn. The volume of corn used was calculated by multiplying the cross-sectional area of the column by the bed depth, or height of the corn. The flow rate was determined by timing how long it took 25 mL

to flow through the column. The empty bed contact time (EBCT), which is the amount of time that the contaminant is in contact with the biosorbent, thus allowing adsorption and removal to occur, was calculated using Equation 4.4 below. The values for each of these parameters can be found in Table 4.1. The prototype is shown in Figure 4.2 below.

$$EBCT = \frac{V}{Q} \tag{4.4}$$

Where:

EBCT= Empty bed contact time (sec) V= Bulk volume of corn in adsorption column (mL) Q= Flow rate through the column (mL/sec)

Table 4.1. Adsorptio	n column final	design values
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Column Parameter	Value
Diameter (in)	1
Length (in)	8
Mass of corn (g)	2.5
Bed depth (in)	0.9
Volume of corn (mL)	11.58
Flow rate (mL/sec)	0.54
Empty Bed Contact Time (sec)	21



Figure 4-2. Adsorption column

Water was pumped into the prototype via 3/8" clear vinyl tubing using a Cole Parmer MasterFlex L/S Peristaltic pump set at 20 rpm in order to maintain a constant pressure head above the packed corn. The full prototype set up is displayed in Figure 4.3.



Figure 4-3. Adsorption tower prototype set up

A salt test was performed before a cadmium run to determine the time it takes for the water in the cadmium reservoir to reach the effluent collection point. To perform the salt test, a brine solution was run through the prototype system. The amount of time that it took the salt to reach a conductivity meter at the effluent point was the amount of time it took for cadmium to reach the effluent sampling point. Once the flow splitter was switched from DI water to cadmium, it took three minutes for the salt to register at the conductivity meter.

For the pilot test, a 3000 mL standard of 75 μ g/L was prepared in the volumetric flask shown in Figure 4.3. An initial sample was taken for measurement of the inlet concentration. DI water was pumped through the system until flow stabilized, and then the aqueous cadmium solution was pumped through the adsorption tower. 25 mL samples were collected at the outlet using a graduated cylinder. The samples were placed in sample bottles provided by Western Technologies and sent for ICP-MS analysis.

Originally, the intention was to perform two column tests. The first test was intended to serve as a preliminary run to ensure that breakthrough and exhaustion occurred over the course of the test. Only five samples were planned for collection during this test. However, during the first column test, the flow visibly channelized through the corn material due to the impact of the water after falling through the column (Figure 4.4). To mitigate this issue in the following testing attempt, glass beads were added to the column to break up the flow of water and reduce the force of impact (Figure 4.5).



Figure 4-4. Failed column test due to channelized flow (outlined in red)



Figure 4-5. Plastic beads used to reduce channelization by absorbing the impact of water

After the failed first attempt, project time constraints only allowed for one more column test. This was because the turn-around time to receive data following sample shipment was 5-7 days between samples being sent and data being received from Western Technologies. To ensure the new column test would produce a breakthrough curve with usable data, a new sampling plan was created in which 50 evenly-spaced samples were collected over the course of 2500 mL of contaminated water flow.

To ensure the best possible use of project funds, every other sample was shipped for testing, resulting in the analysis of 25 samples total. The remaining 25 samples were collected and refrigerated. If the initial 25 samples did not provide enough data for the breakthrough curve, more samples would be shipped for testing. After sending the initial 25 samples, it was

determined the breakthrough curve had adequate data (Figure 4.6). Lab results may be seen in Appendix I.



Figure 4-6. Breakthrough curve produced from the column test

The data from column test revealed that the influent concentration was 82.2 μ g/L. The concentration of cadmium in the first 400 mL of treated water was not detected (ND). Based on a linear interpolation between 400 and 500 mL of volume treated, the volume at which the concentration of cadmium would be equal to 5 μ g/L occurs at 457 mL.

The corn was considered to be exhausted at 75% of the influent concentration because additional conclusions could not be drawn about what would happen past the final data point measured without further testing.

5.0 Scale-Up: Designing Three Adsorption Columns in Series

In order to scale up the prototype design for full-size implementation, three columns were designed in series to allow for prolonged biosorbent usage. This is because subsequent columns have the ability to catch the breakthrough of the previous column and continue to treat the contaminated water to an effluent concentration below $5 \mu g/L$ after the first column has been exhausted [9]. This also allows for redundancy so that one column can be taken off-line for corn cob biosorbent replacement or regeneration at any time.

This design was achieved by developing a breakthrough curve for three columns in series. Because of scope and resource limitations of the project, a pilot test was not run for three columns in series. The data from the original pilot test was extrapolated to create a breakthrough curve for this scenario. These curves assume that had three columns been tested, the additional columns would behave identically to the first column. This assumption would require further testing and verification before executing full-scale implementation.

It was assumed that it would take approximately 3 minutes for the effluent of the first column to be pumped up to the inlet of the second column and flow through the length of the tower. This approximation was based on the time it took for the water to travel from the cadmium reservoir



through the prototype. The final breakthrough curve for three columns in series is displayed in Figure 5.1.

Figure 5-1. Breakthrough curve for three columns in series

The values for the time each column reached breakthrough (6% of the influent concentration, or $5 \mu g/L$) and exhaustion (75% of the influent concentration) were determined from these breakthrough curves. These values are displayed in Table 5.1. The cumulative bed depth is the total height of corn that the water has passed through as it moves through multiple columns.

		Service Time % contamina	e, minutes, for ant remaining
Column #	Cumulative Bed Depth (m)	6%	75%
1	0.023	12.5	76
2	0.046	98	159
3	0.069	162.5	221

Table 5.1. Bed-depth service time

For the design scale up, the Bohart-Adams method was used to determine adsorption zone velocity and corn cob usage rate of the pilot test setting. A bed-depth service time curve was developed (Figure 5.2), which displays the cumulative bed depth as the water flows through each column on the x axis and the service time in minutes on the y axis (values from Table 5.1). The upper line represents 75% of the feed concentration, and the lower line represents 6% of the feed concentration, or breakthrough.



Figure 5-2. Bed-depth service time curves

The height of the adsorption zone was determined by measuring the horizontal distance between these two curves, which was 0.017 meters. The adsorption zone is the volume within the bed where adsorption takes place. The slope of the 6% line (breakthrough) was modeled using the Bohart-Adams equation (Equation 5.1) [9]. The slope of this equation provides a measure of the velocity of the adsorption zone, and the y-intercept represents the time required for an adsorption zone to pass through the critical bed depth.

 $t = aX + b \tag{5.1}$

Where:

t= time required to reach 94% cadmium removal (from 82.2 μ g/L to 5 μ g/L) a= slope (h/m) X= depth in column (m) b= intercept (h)

The values of a and b for this form of the equation were obtained from the slope equation of the 6% BDST line. The units for a and b were converted from minutes to hours in order to match the form of the Bohart-Adams method. These values are displayed in Table 5.2.

Bohart Adams a and b Values Obtained From BDST Curve			
Parameter	In Terms of Minutes	In Terms of Hours	
a	3280.8 min/m	54.68 h/m	
b	-59 min	-0.938 h	

Table 5.2. Values obtained for a and b from BDST curves

The velocity of the adsorption zone was then calculated by taking the inverse of the BDST curve slope (Equation 5.2) [9]. This resulted in a velocity of 0.018 m/h.

$$v = \frac{1}{a} \tag{5.2}$$

Where:

v= adsorption zone velocity (m/h) a= 54.68 m/h (from BDST curve and Table 5.2)

Other in-depth Bohart-Adams parameter calculations, such as critical bed depth, can be found in Appendix J. These values are not presented here because they are theoretical, are only based on a single experiment, and do not directly influence the final design.

The biosorbent utilization rate was calculated using Equation 5.3 [9]. The utilization rate indicates how much of the biosorbent is exhausted per unit time as water flows through the column. For the pilot test, this value was 2.22 grams per hour, or 53 grams per day.

Biosorbent Utilization Rate =
$$A * v * \rho$$
 (5.3)
Where:
A= cross sectional area of the column (m²)
v= adsorption zone velocity (m/h)
 ρ = dry bulk density of the corn [unit weight], 239,190 g/m³

The number of columns for the scaled-up design was calculated using Equation 5.4 [9]. This number was rounded to the nearest whole number, which resulted in the need for two columns in series. Three columns were designed in series in order to allow for redundancy.

$$n = \left(\frac{AZ}{h}\right) + 1 \tag{5.4}$$

Where:

AZ= adsorption zone height, 0.017 m from BDST Curves h= bed height (m) ρ = dry bulk density of the corn [unit weight], 239,190 g/m³

The scale-up was then designed using a flow rate of 50,000 gallons per day (gpd), which is a typical design flow rate seen for rural communities, such as on the Hopi Reservation [10]. The design flow rate and the original loading rate of the lab columns were used to calculate a new cross-sectional area. This area was used to calculate the corn cob utilization rate of the full-scale design (Equation 5.3), which resulted in a usage rate of 216 kg/day.

The dimensions of the column were then adjusted for a 30 day service time, resulting in a larger column design where corn would only need to be replaced every month as opposed to a smaller design where the corn would need to be replaced daily. This was done using Equation 5.5 [11].

$$V = \frac{(CCUR*COP)*S.F.}{\rho}$$
(5.5)

Where:

V= adsorption column volume (m³)

CCUR= Corn cob utilization rate (g/day) COP= Change out period (days) S.F.= safety factor for backwashing, typically 1.2 ρ = dry bulk density of the corn [unit weight], 0.23919 g/cm³

A change-out period of 30 days was selected as the service time for corn cob biosorbent replacement. This resulted in the need for a bed volume of 27 m³. A height of 4 meters was chosen arbitrarily, which resulted in a corresponding diameter of 3 meters. A 2-meter plastic bead layer will be placed on top of the corn layer in order to disperse flow and prevent channelization. These beads will need to have a lower density than the corn in order to allow for proper operation after backwashing.

Off-the-shelf contactors for adsorption can typically hold from 70 to 9100 kg of adsorbent material [11]. The load limit for hauling off waste material is also typically 9100 kg [11]. Due to shipping restrictions, vessel diameters also rarely exceed 12 feet (3.6 m), while their length is generally limited to 50 feet (15 m) [12]. Therefore, the main design constraints for the scale-up was a maximum biosorbent mass in the column of 9100 kg, a maximum diameter of 3.6 meters, and a maximum height of 15 meters. Because the column designed will only require 6480 kg of biosorbent material and has a 3 meter diameter and 6 meter height, the column design is considered valid. The final design parameters can be seen in Table 5.3, and the design schematic can be seen in Figure 5.3. All hand calculations for the final design may be seen in Appendix K.

Design Results			
n	3	columns	
Loading Rate	1.2	m/h	
Area	7	m ²	
Diameter	3	m	
Bed Height	4	m	
Bed Volume	27	m ³	
Bead Height	2	m	
Total Vessel Volume	41	m ³	
Empty Bed Contact Time	3.4	h	
Corn Cob Utilization Rate	216	kg/day	
Service Time	30	days	
Mass of Corn Required	6473	kg	

Table 5.3.	Final	design	parameters
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Figure 5-3. Schematic of scaled up adsorption tower design

6.0 Cost Benefit Analysis

In order to best determine the viability of corn cobs as a biosorbent for heavy metal removal, the total cost of using this material for water treatment needs to be examined. This cost benefit analysis compares the cost of corn cobs to the most commonly used technology for adsorption treatment, granular activated carbon (GAC). It considers both the cost per kilogram of implementation of each material as well as a lifetime analysis of implementing an adsorption contact vessel containing each adsorption medium.

This analysis assumes that industrially-produced and pre-crushed corn cob waste will be used for the corn cob biosorbent. Pre-crushed corn cob is typically used as animal feed and will be purchased in bulk for the purpose of this analysis. The purchased corn will require further grinding down to 250 microns. Nitric-acid treated corn will also require further processing, including immersion in 1N nitric acid for 12 hours, titration with 1N sodium hydroxide, and oven drying at 80°C for 12 hours.

6.1 Corn Cob Biosorbent Cost

This analysis assumes that the corn cobs will be purchased from the animal feed industry. Partially ground corn cob costs \$201.25 per ton. The bulk corn cob waste price was gathered from various sources that sell ground corn cobs for livestock feed [13]. The estimates for each process were found using large-scale industrial equipment. Table 6.1 shows the breakdown of the cost of using treated corn as a biosorbent. To dry the treated corn in a drying oven at 80°C for 12 hours, 18 kWh [14] of energy is required. This energy dries 4.3 kg of corn biosorbent when using a Fisher Scientific Lab drying oven (Catalog No. S43015).

55 kWh of energy are estimated to grind one kilogram of corn down to 250 microns [15] using a Maize grinder model M6FFC-800 from Henan Kingman M&E Complete Plant. The cost of nitric acid is \$0.002 per mL when diluted to 1N [16], and the cost of sodium hydroxide 1 N is \$0.02 per mL [17]. For 30 grams of corn, 200 mL of nitric acid (1N) was used in the preparation of the treated corn which is the largest component of the production cost. Then, 2 mL of sodium hydroxide was used to titrate the corn to a neutral pH. Overall, it would cost \$15.42 to produce one kilogram of treated corn. The calculation breakdown for

each process is located in Appendix H. Figure 6.1 displays the breakdown of the treated corn cob biosorbent cost per kilograms base off the parameters above.

Cost Analysis of Treated Corn Cob Biosorbent per 1000 kg					
Process	Material	Unit Cost	Amount	Net Price	
Sourcing	Corn Cob Waste (kg)	\$0.22	1,000 kg	\$222	
Grinding	kWh	\$0.12	11 kWh	\$1	
Treatment	Nitric Acid (L)	\$1.95	6,667 L	\$13,022	
	Sodium hydroxide (L)	\$16.70	133 L	\$2,227	
Drying	kWh	\$0.12	1402 kWh	\$168	
Total Cost per 1000 kg				\$15,418	

Table 6.1. Cost analysis of treated corn cob biosorbent

For the untreated corn, there is a dramatic cost reduction (Table 6.2). The preparation process is significantly cheaper for untreated corn due to the elimination of the cost of treatment, most notably the cost of nitric acid. These calculations are based on the same bulk buying price and grinding process as the treated corn.

Table 6.2. Cost	analysis for	untreated	corn
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Cost Analysis of Untreated Corn Cob Biosorbent per 1000 kg				
Material/Process	Net price			
Corn Cob Waste (kg)	\$0.22	1000 kg	\$222	
Grinding energy(kWh) \$0.12 11 kWh		\$1		
Total Cost per 1000 kg			\$223	

6.2 Corn Cob Biosorbent Comparison to Granulated Activated Carbon

In order for the corn cob biosorbent to be established as a viable alternative to GAC, there needs to be a clear difference in economics or performance. Table 6.3 presents a direct comparison of GAC to corn cob biosorbent. The average cost of GAC was taken from 10 different sources (calculation shown in Appendix I), and the cost of treated corn was taken from Table 6.1 above. The main contribution to the cost of treated corn production was the use of nitric acid, which required 200 mL to treat 30 grams of corn using the current method. This method also only resulted in a net production of 15 grams of treated corn.

Table 6.3 also compares the amount of each adsorbent required to purify 1,000 L of water contaminated with 75 μ g/L of cadmium, and the overall cost necessary to clean up this spill using each substance. Both types of corn cob biosorbent are cheaper than using activated carbon. The removal efficiency of cadmium by GAC was researched by Karnib et al [18]. This journal's Freundlich isotherm model constants were used to perform the calculations for this example scenario.

Comparison of Adsorbents					
	Corn Cob Biosorbent (Treated)	Corn Cob Biosorbent (Untreated)	Granulated Activated Carbon		
Cost per kg	\$15.42	\$0.22	\$14.33		
Removal Efficiency	96%	76%	86%		
Kg of corn required to treat 1000 L of 75 ug/L Cd water	1.6	17.1	2.4		
Cost to treat 1000L at 75 ug/L	\$24.86	\$3.76	\$34.86		

Table 6.3. Adsorbent Cost Comparison [14]

An important aspect to consider for the cost of an adsorbent material is whether or not it can be regenerated, which is a process that uses either thermal or chemical methods to remove the contaminants sorbed to the surface of the adsorbent and reopen sites on the surface for further adsorption. GAC typically runs out of regeneration cycles and needs to be replaced after 5 years of use [12]. There is no data available for the regeneration ability of a corn biosorbent specifically, but other research explores biosorbent regeneration of olive tree pruning used for lead removal. This indicates that an average biosorbent could effectively be regenerated for a total of 20 cycles approximately 400 minutes per cyle removing with a solution of 2 g/L of lead for 5 grams of biosorbent until complete exhaustion [19].

Overall, corn cob biosorbent treatment must be refined to be implemented in a large-scale treatment process that results in a less expensive product than GAC. However, corn cob has a much higher removal efficiency than GAC for cadmium, which in some cases may offset its higher cost. It is also worth noting that untreated corn shows great potential as an extremely inexpensive method for removing heavy metals despite not being the main focus of this research, and thus could have great potential for application in rural communities. The method of treatment for nitric acid-treated corn must be further refined to reduce its cost in order for it to be an economically viable option. This would make it more competitive as a biosorbent replacement for GAC. Additionally, there is no research on corn biosorbent regeneration, which must be better defined for corn cobs in order for a truly accurate economic comparison to occur.

6.3 Life Cycle Analysis for Corn Cob Biosorbent vs. GAC Adsorption Columns

In the research article A simulation study of the removal efficiency of granular activated carbon on cadmium and lead, the following data in Figure 6.1 was tested and measured for cadmium and activated carbon removal in a column 2.5 centimeters in diameter and 0.75 meters in bed height [20]. The breakthrough and BDST curves for this data are shown in Figure 6.2. It should be noted that the flow rate for the activated carbon pilot test was much lower than this research (thus resulting in a higher empty bed contact time), and that the influent concentration was in the mg/L range compared to the μ g/L range for the corn. Corn

should therefore be tested with more similar conditions to carbon in order to obtain the most accurate cost comparison possible.

Flow rates (ml/min)	EBCT (min)	Influent concentration, C _o (ppm)	Effluent concentration, C (ppm)	Adsorption percentage (%)
4.06	9.07	20.54	0.0987	99.52
5.25	7.02	20.54	2.054	90.00
9.05	4.07	20.54	5.7512	72.00

Efficiency of cadmium removal at different flow rates by GAC packed in column



Figure 6-1. GAC Data from External Pilot Study [20]

Figure 6-2. Breakthrough curve (left) and BDST curves (right) for GAC and cadmium

This article defines the slope of the BDST curve, a, using equation 6.1.

$$a = \frac{N_o}{C_o} \tag{6.1}$$

Where:

a= slope (m/h) N_o= adsorptive capacity (mg/L) C_o= influent concentration (mg/L)

A value of 1552.60 mg/L was provided for N_0 [20]. Substituting this value for N_0 and 20.54 mg/L for C_0 returned an a value of 75.59 m/h. Although the BDST curve is given in terms of EBCT (h), all of these values can be converted to cumulative bed depth by multiplying by the loading rate. After this conversion, the ratio of change in y to change in x remains the same.

The carbon usage rate was then calculated using Equation 5.3. This study used granular activated carbon (GAC) manufactured by Kekwa Indah Sdn Bhd in Nilai. Looking up the product revealed that the material has a bulk density of approximately 500 grams per liter [21]. This results in a carbon usage rate of 3.24 grams per hour, or 77.92 grams per day.

From this point, two identical vessels based on the scale-up design were compared for the cost analysis of corn cob biosorbent versus activated carbon. The usage rate of the carbon was adjusted for the 7 m^2 surface area of the design vessel. This results in a carbon usage rate

of 328 kg/day. Equation 5.5 was used to solve for the service time of the vessel if activated carbon was used as the adsorption media. The design results for the carbon vessel are displayed in Table 6.4. Because the bulk density of activated carbon is much larger than that of corn, the same volume of 27 m³ can hold a mass of carbon almost twice that of the corn. However, since the usage rate is also much higher for activated carbon compared to corn, the service time is only prolonged by 5 days despite twice as much mass being used.

Design Results				
n	3	columns		
Loading Rate	1.2	m/h		
Area	7	m^2		
Diameter	3	m		
Bed Volume	27	m ³		
Total Vessel Volume	41	m ³		
Empty Bed Contact Time	3.4	h		
Carbon Utilization Rate	328	kg/day		
Service Time	35	days		
Mass of Carbon Required	13,500	kg		

Table 6.4. Final design parameters for comparable carbon vessel

Table 6.5 displays major cost differences between corn cob and carbon, considering that all vessel, equipment, and general labor costs will be the same for each vessel. These costs come from the price of the adsorbent material, and the cost for disposal. For this analysis, it was assumed that treated corn waste would be disposed of in a hazardous waste landfill, while activated carbon would be hauled off-site for regeneration and resale by a third party and virgin activated carbon would be added to the tower for each replacement (typical for many GAC fixed-bed operations). The capital and annual costs for a GAC adsorption column are shown in Table 6.6, while Table 6.7 shows the capital and annual costs for a treated corn adsorption column. The lifetime of the vessel was considered to be 20 years [12]. Calculation methods for the vessel cost be seen in Appendix O.

Major Cost Difference Comparison Between Corn Cob and Carbon					
	(Corn Cob	Carbon		
kg/Service Time		6,480		13,500	
Service Times/Year		12.2		10.4	
Cost/kg	\$	15.42	\$	14.33	
Cost/Year for Adsorbent Material	\$	1,220,000	\$	2,011,000	
Disposal Fee/kg	\$	6.70 [22]	\$	4.73 [23]	
kg Disposed/Year		79,060		140,400	
Disposal Cost/Year	\$	529,800	\$	664,100	
Total Material and Disposal Cost/Year	\$	1,749,800	\$	2,675,100	
Total Material and Disposal Cost/Lifetime	\$	34,996,000	\$	53,502,000	

Table 6.5. Major cost difference comparison for corn cob and carbon

The lifecycle analysis for the carbon column is presented in Table 6.6 below. These values are not adjusted for present worth. The first section displays the original capital cost. The next two sections show the costs per year of each component, calculating the total lifecycle cost for each section at the end. The total cost over the life of the carbon column is \$54,746,000.

Carbon					
kg carbon		13,500			
Carbon cost/kg	\$	14.33			
Vessel Cost	\$	23,500 [12]			
Auxiliary Equipment Cost	\$	30,000 [12]			
Capital Cost	\$	250,000			
Operator	\$	14,900 [12]			
Supervisor	\$	2,300 [12]			
Maintenance Labor	\$	16,500 [12]			
Maintenance Materials	\$	16,000 [12]			
Carbon Cost	\$	2,011,000			
Annual Op/Maintenance					
Cost	\$	2,060,700			
Lifecycle Op/Maintenance					
Cost	\$	41,214,000			
Disposal Cost	\$	664,100			
Lifecycle Disposal Cost	\$	13,282,000			
Total Cost	\$	54,746,000			

Table 6.6.	Carbon	column	lifecycle	analysis
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The lifecycle analysis for the corn column is presented in Table 6.7 in the same manner as the carbon column. These values are also not adjusted for present worth. The total cost over the life of the carbon column is \$35,344,000.
Corn						
kg corn		6,480				
Corn cost/kg	\$	15.42				
Vessel Cost	\$	23,500 [12]				
Auxiliary Equipment Cost	\$	30,000 [12]				
Capital Cost	\$	153,500				
Operator	\$	14,900 [12]				
Supervisor	\$	2,300 [12]				
Maintenance Labor	\$	16,500 [12]				
Maintenance Materials	\$	16,000 [12]				
Corn Cost	\$	1,220,000				
Annual Op/Maintenance						
Cost	\$	1,270,00				
Lifecycle Op/Maintenance						
Cost	\$	24,594,000				
Disposal Cost	\$	529,800				
Lifecycle Disposal Cost	\$	10,596,000				
Total Cost	\$	35,344,000				

Table 6.7. Corn column lifecycle analysis

The present worth of each column was calculated using equation 6.2.

$$P = F(1+i)^{-n}$$

Where:

P= present worth (\$) F= future worth (\$) i= interest rate, 0.05 n= number of years, 20

Table 6.8.	Present	worth o	f corn	cob	and	carbon	column
------------	---------	---------	--------	-----	-----	--------	--------

Present Worth Analysis for Corn Cob vs. Carbon							
	C	orn Cob	Carbon				
Future Worth	\$	35,344,000	\$ 54,746,000				
Present Worth	\$	13,321,000	\$ 20,634,000				

As demonstrated above, the total cost of implementing and maintaining a corn cob biosorbent tower is approximately \$7,000,000 less expensive than implementing a GAC tower containing the same amount of activated carbon when considering present worth. The main reason for this is that the treated corn column requires a significantly small amount of adsorbent material compared to GAC in order to treat the same amount of water. It should be noted that on-site regeneration reduces the cost of GAC dramatically, and more research needs to be done about the desorption of corn in order to be able to directly compare regeneration of the two adsorbents.

(6.2)

7.0 Final Design Recommendations

Ultimately, this research found that treated corn obtained the highest removal efficiency for the removal of cadmium from an aqueous solution, though this is somewhat offset by the cost of nitric acid required to treat the corn and the mass of corn lost during the treatment process. Corn cob biosorbents are a promising alternative for water treatment technologies compared to the widely-used granular activated carbon, although further research is necessary to prove this point. Further research is recommended on corn cob's ability to remove other metals (such as lead and uranium) and how a mixture of metals affects removal efficiency, since cadmium will rarely be found in a contaminated water source by itself.

Additionally, the effects of temperature and pH should be investigated to ensure that sorption occurs under a wide range of operating conditions. Untreated corn should be tested for cadmium removal using ICP-MS to obtain a better comparison to the treated corn values, since the lower removal efficiencies for the untreated corn may have been due to inaccuracies of the colorimetric HACH method and not the adsorption capacity of the corn itself. Because untreated corn is so much cheaper to produce than treated corn, it should also be evaluated in a column test. Column tests should be run in series to better simulate a real design, and ideally metal contaminants that can be measured in real-time using the given laboratory equipment should be chosen for analysis.

Finally, the possibility of desorbing the corn after it has been exhausted using different solvents should be investigated to verify the economic viability of corn cobs as a biosorbent, since this could provide a potential not only for corn reuse. Better regeneration would eliminate hazardous waste and decrease overall corn cost. There would also be potential to recover the metals that could be resold for profit. Previous research has found that 100% metal recovery of cadmium is possible for biosorbents *E. crassipes* and *C. indica* when using HNO₃ as a desorption agent [24].

The environmental, economic, and social impacts were qualitatively considered for this research project. Environmentally, the research for corn biosorbents provides an alternative to clean up cadmium contaminated drinking water, allowing for cleaner ecosystems and healthier wildlife. Additionally, by using corn cobs as a material to treat drinking water, corn cob waste could be diverted from ending up in landfills. However, because there is no research on the regeneration of a corn cob biosorbent, and any cadmium-exhausted corn would ultimately have to be placed into a hazardous waste landfill.

Economically, corn biosorbents could provide cheaper methods to purifying cadmiumcontaminated drinking water. While treated corn showed the highest cadmium removals, the most economic option to treat a contaminated water source would be using untreated corn. This is because the cost of using nitric acid and sodium hydroxide accounted for 98.9% of the unit cost for treated corn. After analyzing unit costs, untreated corn costed \$0.22/kg, while treated corn costed \$15.42/kg. Corn biosorbent production would also help provide an additional source of income for corn-growing farmers located in parts of the country near mine sites.

Socially, corn biosorbents could allow for rural communities to take pride in the fact that their locally grown corn was implemented to provide clean drinking water. Additionally, corn biosorbents could provide the means to improve the health of residents living near contaminated

water. However, there are some people in the United States that have a corn allergy. While it is rather rare, symptoms can range from mild itching to anaphylaxis. Therefore, there would need to be research to quantify the amount of residual corn solids from a treatment process to ensure the health and safety of those with a corn allergy.

8.0 Summary of Engineering Work

During the proposal phase of the project, it was anticipated that three professional roles would be needed to complete this project; a lab technician to perform all lab testing and collect data, a professional engineer to analyze data, prepare designs, and draft reports, and a senior engineer to handle all professional team interactions and finalize reports. From the proposal phase of the project, it was anticipated that the research project would require a total of 625 hours, the bulk of which would come from the lab technician (Table 8.1).

Task	SENG Hours	ENG Hours	LAB Hours	Task Total
Task 1.0 Experimental Methods	0	0	190	190
Task 1.1 Corn Biosorbent Preparation			36	36
Task 1.2 Cadmium Testing			71	71
Task 1.3 Lead Testing			83	83
Task 2.0 Isotherm Development	1	11	0	12
Task 3.0 Prototype Design	8	14	0	22
Task 3.1 Design Calculations	1	9		10
Task 3.2 Construction Drawings	1	5		6
Task 3.3 Construction	6			6
Task 4.0 Pilot Testing and Scale-up	2	12	109	123
Task 5.0 Cost Benefit Analysis	1	11	0	12
Task 5.1 Feasibility Assessment	0.5	5.5		6
Task 5.2 Assessment of Benefits	0.5	5.5		6
Task 6.0 Project Management	113	153	0	266
Task 6.1 Professional/Team Interactions	108			108
Task 6.2 Project Deliverables		79		79
Task 6.2.1 30% Report		16		16
Task 6.2.2 60% Report		20		20
Task 6.2.3 Final Report	5	10		15
Task 6.2.4 Website		20		20
Task 6.2.5 Final Presentation		8		8
TOTAL	125	201	299	625

Table 8.1. Proposed hours

The scope originally included lead testing that would be completed during the same time as the cadmium testing. It was initially estimated that it would take 3 hours to complete a batch reaction and collect cadmium and lead removal data. However, lab testing required 6 hours to complete a batch reaction and collect data. Additionally, the research project experienced a major set-back during winter break as the separatory funnel was broken, and the new order did not arrive within

the anticipated arrival date. It was also discovered that HACH method 8017 data was light sensitive, and concentrations would decrease with increasing spectrophotometer readings. Based on these project set-backs, researching lead became impossible to include in the scope. Table 9.2 shows the total actual project hours. The largest discrepancy between the projected 625 hours and the current 809 hours is the cadmium testing. It was estimated that cadmium testing would require 71 hours; however, it required 213.5.

Task	SENG Hours	ENG Hours	LAB Hours	Task total
Task 1.0 Experimental Methods	0	18	308.5	326.5
Task 1.1 Corn Biosorbent Preparation	0	10	103	113
Task 1.2 Cadmium Testing	0	8	205.5	213.5
Task 2.0 Isotherm Development	0	7	0	7
Task 3.0 Prototype Design	0.5	72.5	8	81
Task 4.0 Pilot Testing and Scale-up	0	34.5	11.5	46
Task 5.0 Cost Benefit Analysis	2	21.5	0	23.5
Task 5.1 Feasibility Assessment	0	13.5	0	13.5
Task 5.2 Assessment of Benefits	2	8	0	10
Task 6.0 Project Management	178	147	0	325
Task 6.1 Professional/Team Interactions	95.5	32.5	0	128
Task 6.2 Project Deliverables	82.5	114.5	0	197
Task 6.2.1 30%	30.5	2.5	0	33
Task 6.2.2 60%	23.5	9	0	32.5
Task 6.2.3 Final Report	1.5	39.5	0	41
Task 6.2.4 Website	0	36	0	36
Task 6.2.5 Presentation	27	27.5	0	54.5
TOTAL HOURS	180.5	300	328	809

Table 8.2. Actual hours

The project set-backs can be seen in the Gantt charts below. Figure 9.1 shows the Gantt chart for the anticipated project schedule. This Gantt chart includes lead testing (Task 1.3) as well as prototype development (Task 3.2). Lead testing was removed from the project due to time constraints, and prototype development was not included as it was more feasible to use pre-constructed columns available in NAU's environmental engineering lab. The highlighted section in Figure 9.1 shows the critical path. Originally, it was predicted that cadmium and lead testing would only require 51 days, while both could be completed simultaneously.



Figure 8-1 – Gantt chart for the original, proposed schedule

After experiencing the project set-backs, a new project schedule was created. The major change to this schedule was the exclusion of lead testing. Figure 9.2 shows the Gantt chart for the updated project schedule. The major difference in this Gantt chart lies in the time-line for the cadmium testing. Because the separatory funnel was broken and the project waited for a new one to arrive, cadmium testing did not officially get off the ground until mid-January, even though it was anticipated to begin early December. Cadmium testing extended into mid-February due to the complications with the HACH method, whereas it was anticipated it would be finished mid-January. The red line in Figure 9.2 below shows the critical path for the project. In total, the research project will last 197 days, and the project will be complete by 5/7/19.



Figure 8-2 – Gantt chart for the updated project schedule

9.0 Summary of Engineering Costs

In Fall 2018, a proposal budget was created to predict the cost of engineering services to complete this research project. The cost of engineering services included hourly rates from three

different professional roles; a lab technician for all lab work, and professional engineer to analyze data and prepare designs, and a senior engineer to handle team management and professional interactions. It was predicted in Fall 2018 that the project would cost \$64,064 to complete (Table 9.1).

1.0 Personnel					
Classification	Hours	Rate, \$/hr	Cost		
SENG	125	120	\$15,000		
ENG	201	90	\$18,090		
LAB	299	55	\$16,445		
Total			\$49,535		
2.0 Supplies					
Item	Quantity	Cost Each	Cost Total		
Syringe Pump	1	300	\$300		
Cadmium Reagents	56	6.80	\$381		
Lead Reagents	63	7.52	\$474		
Acrylic Plexiglass (2'x6')	1	14	\$14		
Corn Cobs	60	1	\$60		
Ninja Food Processor	1	20	\$20		
PPE	4	90	\$360		
Lab Rental Fee	45 days	286/day	\$12,870		
Total			\$14,479		
3.0 Subcontracting					
Subcontractor		Cost			
Engineering Fabrication Shop		\$50.00			
Total			\$50.00		
Project Total					
			\$64,064		

Table 9.1. Proposal budget from Fall 2018

The bulk of the projected costs were the hourly rates for each of the professional roles for the project. Due to lab complications, set-backs, and necessary additional testing, personnel hours were much higher than originally anticipated. The total hours spent on this project was 809 hours. The actual project cost was \$79,834. Table 9.2 shows the running total for the actual project's cost.

1.0 Personnel							
Classification	Hours	Rate, \$/hr	Cost				
SENG	180.5	120	\$21,660				
ENG	300.5	90	\$27,045				
LAB	328	55	\$ 18,040				
Total			\$ 66,745				
2.0 Supplies							
Item	Quantity	Cost Each	Cost Total				
Cadmium Reagents	36	\$7	\$245				
Corn Cobs	60	\$ 1	\$60				
Ninja Food Processor	2	\$ 20	\$40				
PPE	4	\$90	\$360				
Lab Rental Fee	41	286/day	\$ 11,726				
Total			\$12,430				
3.0 Subcontracting							
Subcontractor		Cost					
Western Technologies Inc.	\$659						
Total	\$659						
Project Total							
			\$ 79,834				

Table 9.2. Actual budget expenses

10.0 Conclusion

The potential of use corn cobs as a biosorbent to remove cadmium from drinking water was researched for this capstone project. The potential of nitric-treated treated corn was also investigated for its effectiveness to increase cadmium removal by sorption. It was discovered from the experimental testing that both treated and untreated corn can achieve notable cadmium removal efficiencies. Based on the concentration parameters specified for the prototype design, treated corn was approximately eleven times more effective than untreated corn at removing cadmium from drinking water. Because of this advantage, treated corn was selected for column testing. During the column test, treated corn achieved nearly 100% cadmium removal for the first 450 mL. Because the projected treatable volume was 1,500 mL, it is recommended that additional column testing be performed using lower flow rates to increase EBCT.

Because of the promising results discovered from this research, further research is recommended in several areas. First, untreated corn should be tested using ICP-MS to obtain more accurate data to produce an isotherm. Additionally, because untreated corn yielded a far lower cost input than treated corn per kilogram, it is recommended that untreated corn be tested in a column to study breakthrough. Using breakthrough data for untreated corn, a treatment unit could be scaled up and economically analyzed for comparison to treated corn.

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12.0 Appendices Appendix A: Preliminary Research Results Spring 2018

Cadmium Experimental Matrix					
Experiment	Initial Concentration (C_i) (μ g/L)				
1	10				
2	10				
3	10				
4	25				
5	25				
6	25				
7	80				
8	80				
8	80				

Table A.1. Spring 2018 NASA Space Grant experimental matrix

Table A.2. Initial and final cadmium concentration (Spring 2018)

Test Results								
Test 1 Test 2 Test 3								
C _i (ug/L)	C _f (ug/L)	C _f (ug/L)	C _f (ug/L)					
10	11.08*	7.13	14.41*					
25	14.67	33.41*	14.41					
80	42.95	28.84	45.52					

* Final concentrations higher than initial concentrations due to analytical error



Figure A.1. Preliminary adsorption isotherm of Spring 2018 research

Appendix B: Pictures of the Treated Corn Biosorbent Preparation Process

Figures B.1 through B.7 display the first round of corn treatment, which produced the extremely basic batch of corn shown in Figure B.8.



Figure B.1. Untreated corn added to nitric acid solution



Figure B.2. Acid-treated corn poured into evaporating dish after being placed on rotary shaker



Figure B.3. Acid-treated corn after being dried for 24 hours at 80 °C



Figure B.4. Acid-treated corn added to sodium hydroxide solution



Figure B.5. Base-treat corn centrifuged after shaking to separate solids



Figure B.6. Base-treated corn placed in evaporating dishes



Figure B.7. Final result first batch of treated corn after drying and pulverizing



Figure B.8. Extremely basic pH of first batch of treated corn

A second batch of corn was started since the first batch only produced approximately 9.5 grams. Once the pH problems with the first batch were realized, it was combined with this second batch after evaporation occurred. This produced the neutral-pH treated corn shown in Figure B.12, which was placed in an evaporating dish and dried to be used as a final product.



Figure B.9. Second batch of untreated corn mixed with nitric acid on rotary shaker



Figure B.10. Second batch of treated corn centrifuged



Figure B.11. Second batch of treated corn placed in evaporating dish



Figure B.12. Second batch of treated corn pH neutralized after mixing with first batch

A third batch of corn was treated with nitric acid, centrifuged, and titrated with base until reaching a neutral pH, then oven dried. This was determined to be the most efficient method for treating the corn cobs. The final treated corn is shown in comparison to the untreated corn in Figure B.15.



Figure B.13. Third batch of treated corn after mixing with nitric acid and centrifuging



Figure B.14. Third batch of treated corn after titrating with base



Figure B.15. Final mixture of treated corn (right)

Appendix C: HACH 8017 Dithizone Method Step-by-Step Procedure





5. Put the stopper on the funnel. Shake to dissolve.



6. Prepare the DithiVer solution: Add 30 mL of chloroform to a 50-mL mixing cylinder.

7. Add the contents of one

Powder Pillow.



mixing cylinder. Invert the mixing cylinder several times to mix.



9. Add 20 mL of 50% Sodium Hydroxide Solution to the funnel.



10. Add one 0.1-g scoop of potassium cyanide to the . funnel.



11. Put the stopper on the funnel. Shake vigorously for 15 seconds.



12. Remove the stopper. Start the instrument timer. A 1-minute reaction time starts.

Cadmium, Dithizone Method (80.0 µg/L)



13. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel.



17. Close the stopcock and shake the funnel vigorously during the 1-minute time period.



14. Put the stopper on the funnel and invert to mix. Invert the funnel and open the stopcock to vent.



18. Put the funnel in the stand. Do not move the funnel until the timer expires. If there is cadmium in the sample, the bottom (chloroform) layer becomes orange or pink.



open the stopcock to vent.



19. Prepare the sample: Put a cotton plug the size of a pea into the funnel delivery tube. Slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell. Put the stopper on the sample cell. The Cd-dithizone complex is stable for more than 1 hour if the sample cell is closed tightly and kept out of direct sunlight.



16. Start the instrument timer. A 1-minute reaction time starts.



20. Prepare the blank: Put at least 10 mL of chloroform in a dry sample cell. Put the stopper on the sample cell.



21. Clean the blank sample cell



22. Insert the blank into the cell holder.



23. Push ZERO. The display shows 0.0 µg/L Cd.



24. Clean the prepared sample cell.

4





Figure C.1. HACH 8017 Dithizone Method Steps [8]

Appendix D: Light Sensitivity Data

Placed in DR 3900 Immediately, Then Stored in Light					
	5 ug/l	75 ug/l			
Time (min)	Measured Conce	entration (ug/L)		Stored in Da	rk
0	8.8	77 3		5 ug/l	75 ug/l
0.25	8.1	77.5	Time (min)	Measured Con	ncentration (ug/L)
0.23	0.1	77	15	9.8	80.1
0.5	1.1	76.9	15.5	9.1	79.3
0.75	/.6	/6.8	16.5	8.2	78.5
1	7.6	76.8	17	7.8	77.8
1.25	7.6	76.7	17	7.8	77.8
1.5	7.6	76.7	18	7.5	//.4
1.75	7.6	76.6	19	7.2	//.1
2	7.6	76.5	20	7.1	76.9
2.25	7.6	76.5	21	6.9	76.8
2.5	7.6	76.4	22	6.8	76.7
3	7.0	76.1	23	6.6	766
	7.7	76.3	24	6.5	76.5
4	7.8	70.3	25	6.4	76.4
5	7.9	/6.3	26	6.4	76.4
6	7.9	76.2	27	63	76.3
7	8	76.1	27	6.2	76.3
8	8	76.1	20	0.2	70.3
9	8	76	29	6.2	/6.2
10	8	75.9	30	6.1	76.2
11	7.9	75.9	31	6.1	76.2
12	7.9	75.9	32	6.1	76.1
13	7.8	75.8	39	6.9	77.6
14	7.8	75.8	4		
15	7.8	75.8			
34	8.3	77.4	4		
35	8	77.1	4		
36	7.9	76.6	4		
37	7.8	76.4			
38	7.7	76.2			

Table D.1. Light sensitivity test - raw data

sat on table while testing other one

76.2

7.7

39

sat in dark while testing the other one



Figure D.1. The 5 μ g/L light sensitivity test graphical results

Table D.2. ANOVA single factor analysis on light sensitivity data for the 5 ug/L test

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	24	187.9	7.829167	0.069982		
Column 2	19	133.1	7.005263	1.102749		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7.198617	1	7.198617	<mark>13.75379</mark>	0.000618	<mark>4.078546</mark>
Within Groups	21.45906	41	0.523392			
Total	28.65767	42				

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	24	1832.7	76.3625	0.181576		
Column 2	19	1463.8	77.04211	1.272573		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	4.897899	1	4.897899	<mark>7.414876</mark>	0.009458	<mark>4.078546</mark>
Within Groups	27.08257	41	0.66055			
Total	31.98047	42				

Table D.3. ANOVA single factor analysis on light sensitivity data for the 75 ug/L test

Appendix E: Method and Reagent Blank Raw Data The raw data collected for the method and reagent blanks is displayed in Table E.1 below.

Time (minutes)	Method Blank 1	Method Blank 2	Reagent Blank
	(µg/L)	(µg/L)	(µg/L)
0	5.8	13.8	3.6
1	4.4	9.8	3.4
2	3.8	7.5	3.4
3	3.6	6.2	3.4
4	3.3	5.5	3.4
5	3.1	5.1	3.4
6	2.9	4.9	3.5
7	2.8	4.8	3.4
8	2.7	4.7	3.4
9	2.6	4.6	3.4
10	2.5	4.5	3.5
11	2.5	4.4	3.5
12	2.4	4.4	3.5
13	2.3	4.2	
14	2.3	3.7	
15	2.2	3.8	
16	2.2	3.7	
17	2.1	3.6	
18	2.1	3.6	
19	2.1	3.5	
20	2.0	3.5	
21	2.0	3.4	
22	2.0	3.4	
23	1.9	3.4	
24	1.9	3.3	
25	1.9	3.3	
26	1.9	3.3	
27	1.8	3.3	
28	1.8	3.3	
29	1.8	3.3	
30	1.8	3.2	
31	1.8	3.2	
32		3.2	
33		3.2	
34		3.2	

Table E.1. Method and reagent blank raw data

Blank Type	Stabilized Concentration (µg/L)
Method	2.5
Reagent	3.4

The stabilized method blank concentration was determined by taking the average of the two method blank tests' final readings. The above results mean that the reagents cause readings to be $3.4 \,\mu$ g/L than the true value and the corn cob residual causes readings to be $2.5 \,\mu$ g/L higher than the true value.

Appendix F: Untreated Corn Raw Data

Untreated	1/24/19, JG MS				1/25/19	, KD MJ		
Time (minutes)	Standard	10 ug/L A	10 ug/L B	10 ug/L C	Standard	20 ug/L A	20 ug/L B	20 ug/L C
0	12.5	6.7	No data	12.2	22.7	11.7	13.7	18
1	12.1	6.8	Accidentally	8.0	23	10.2	12	Redid
2	12.1	6.7	dumped before	6.7	22.9	9.9	11.4	Blank
3	12	6.7	running in	6.1	22.8	9.6	10.9	
4	12	6.5	spectropho.	5.7	22.8	9.2	10.9	
5	11.9	6.4		5.5	22.8	9	10.7	
6	11.9	6.4		5.3	22.7	8.8	10.5	11.7
7	11.9	6.3		5.2	22.7	8.5	10.4	11.6
8	11.9	6.3		5.1	22.6	8.4	10.1	11.2
9	11.8	6.2		5.0	22.6	8.1	10	10.7
10	11.8	6.2		4.9	22.6	7.9	9.8	10.4
11	11.8	6.1		4.9	22.5	7.7	9.4	10
12	11.8	6.1		4.8	22.4	7.6	9.3	9.8
13	11.7	6.0		4.8	22.3	7.4	9.1	9.5
14	11.7	6.0		4.7	22.3	7.3	8.9	
15	11.7	5.9		4.7	22.2	7.2	8.7	9.2
16	11.7	5.9		4.7	22.1	7.1	8.2	9.1
17	11.7	5.9		4.7	22	7	8.1	8.9
18		5.8		4.6	22	6.8	7.8	8.8
19		5.8		4.6	22	6.7	7.7	8.7
20		5.8		4.6	22	6.6	7.6	8.6
21		5.8		4.6	22	6.5	7.5	8.5
22		5.8		4.6		6.5	7.4	8.4
23		5.8				6.4	7.3	8.3
24						6.3	7.2	8.2
25						6.2	7.1	8.2
26						6.2	7	8.1
27						6.1	6.9	8.1
28						6	6.9	8
29						6	6.8	8
30						5.9	6.7	7.9
31						6		
32						5.8		
33						5.8		
34								

Table F.1. Untreated corn raw data

	2/2/19,	KD MJ		1/29/19, JG MS				1/31/19	JG MS		
Standard	35 ug/L A	35 ug/L B	35 ug/L C	Standard	50 ug/L A	50 ug/L B	50 ug/L C	Standard	75 ug/L A	75 ug/L B	75 ug/L C
41.6	22	30.3	29.8	48.5	22.7	16.6	17.5	70.5	47.3	29	26.7
41.6	17.3	22.9	24.7	48.3	22.1	15	16.1	70	44.5	25.7	23.4
41.6	16.6	20.8	21.4	48.7	22.2	14.6	15.4	70.1	42.6	23.9	22.4
41.6	15.8	19.9	19.2	48.9	21.8	14.1	15.1	70.3	41.3	23	21.8
41.5	15.6	18.6	17.9	49	21.4	13.8	14.7	70.3	40.4	22.5	21.4
41.7	15.3	17.6	17.2	49.3	21.3	13.5	14.6	70.2	39.6	22.1	21
41.7	14.8	17.1	16.6	49.5	21.2	13.4	14.5	70.2	38.8	21.7	20.8
41.6	14.6	16.7	16.1	49.5	21.1	13.2	14.4	70.1	38	21.4	20.5
41.6	14.4	16.3	15.8	49.5	21	13.1	14.3	70	37.2	21.1	20.4
41.5	14.2	15.8	15.4	49.5	21.1	13	14.3	70	36.4	20.9	20.3
41.5	14	15.6	15	49.3	21.1	12.9	14.2		35.6	20.8	20.2
41.5	13.8	15.3	14.8	49.5	21	12.8	14.1		35	20.6	20.2
41.5	13.7	14.9	14.7	49.4	21.1	12.8	14.1		34.3	20.5	20.2
41.4	13.6	14.8	14.4	49.5	21.1	12.7	14.1		33.5	20.3	20.1
41.3	13.5	14.6	14.2	49.3	21.1	12.7	14		32.8	20.2	20
41.2	13.5	14.4	14	49.2	21.1	12.7	14		32.1	20.2	20
41.1	13.4	14.3	14	49		12.7			31.7		
41.1	13.4	14.3	13.9	49		12.6			31.2		
41	13.3	14.3	13.8	49		12.6			30.9		
41	13.2	14.1	13.7			12.5			30.4		
40.9	13.1	14	13.8			12.5			29.9		
40.8	13.1	14	13.7	48.6					29.6		
40.8	13	14.1	13.7						29		
40.7	13	14	13.7						28.7		
40.6	12.9	14	13.7						28.5		
40.6	12.9	14	13.7						28.3		
									27.9		
									27.5		
									27.3		
									27		
									26.8		
									26.5		

Table F.2. Stabilized readings used for untreated corn isotherm calculations

Prepared Initial Concentration (ug/L)	Initial Concentration Reading (ug/L)	Final Concentration Sample A (ug/L)	Final Concentration Sample B (ug/L)	Final Concentration Sample C (ug/L)
10	11.7	5.8	Х	4.6
20	22.1	5.8	6.7	7.9
35	41.1	12.9	14.0	13.7
50	49.0*	21.1	12.5	14.0
75	70.0	26.3	20.2	20.0

Appendix G: Treated Corn HACH Method Raw Data as of 2/10/19

Treated Corn		2/9/19, JG MJ				2/10/19, KD MS			
Time (minutes)	Standard	10 ug/L A	10 ug/L B	10 ug/L C	Standard	10 ug/L A	10 ug/L B	10 ug/L C	
0	11.4	30.8	18.1	30.7	39.7	45.8	38.1	35.6	
1	10.9	28.1	10.2	25.7	39	40.7	34	28.5	
2	10.9	26.7	10	23.5	38.4	38	31	21.4	
3	10.9	25.4	9.5	23	38.2	36.7	29.2	18.6	
4	11	24.1	9	22	37.9	36.1	28	15.9	
5	11.1	23.3	8.5	21.1	36.5	35.1	26.8	14.4	
6	11	21.5	8.3	20.3	35.1	33.7	25.7	13	
7	11.1	20.6	8	19.4	33	32	24.7	11.9	
8	10.9	19.8	7.4	18.2	32.5	31.2	24	11.1	
9	11.1	18.9	7.7	17.7	31.7	30.2	23.2	10.1	
10	11	18.6	7.6	17	30.8	29.3	22.8	9.6	
11	10.9	17.9	7.4	16.6	30.1	28.2	22.2	9.2	
12	10.9	17,3	7.3	16.1	29.4	27.5	21.6	8.7	
13	10.9	16.8	7.2	15.5	28.6	26.4	21.2	8.3	
14	10.9	16.3	7.2	15.2	27.9	25.3	21.1	8.1	
15	10.9	15.9	7	14.8	27.2	24.8	20.8	7.8	
16		15.7	7	14.6	26.2	23.9	20.5	7.5	
17		15.3	6.9	14.4	25.3	23.1	20.3	7.4	
18		15.1	6.8	14.1	24.6	22.7	19.6	7.2	
19		14.8	6.8	13.8	23.9	21.7	19.5	7.1	
20		14.6	6.7	13.6	22.9	21.5	18.8	6.9	
21		14.4	6.7	13.2	22.4	21	19.5	6.8	
22		14.1	6.7	13.1	21.8	20.5	19.4	6.7	
23		14	6.7	13	21.2	19.9	19	6.6	
24		13.7	6.6	12.8	20.7	19.6	18.9	6.5	
25		13.6	6.6		20.1	19.2	18.7	6.5	
26		13.4			19.7	18.7	18.5	6.4	
27		13.3			19.3	18.4	18	6.3	
28		13.2			18.9	18.1	18.4	6.2	
29		13.1			18.5	17.8	17.9	6.2	
30		13				17.4	18.3	6.2	
31						17.1	18.2		
32						16.9			
33						16.6			
34						16.4			
35						16.1			
36						16			
37						15.8			
38						15.6			
39						15.5			
40						15.4			
41						15.1			

Table G.1. Treated corn raw data

Appendix H: Treated Corn Lab Results and Chain of Custody Forms



ANALYTICAL REPORT

Nortest

Sample Delivery Group: Samples Received: Project Number: Description:

Report To:

L1074024 02/28/2019

Lisa Marie Macario 2400 E. Huntington Dr. Flagstaff, AZ 86004

Entire Report Reviewed By: Napline & Richards

Daphne Richards Project Manager

Results relate only to the items tested or calibrated and are reported as rounded values. This test report shall not be reproduced, except in full, without written approval of the laboratory. Where applicable, sampling conducted by Pace National is performed per guidance provided in laboratory standard operating procedures: 060202, 060202, and 060204.

12065 Lebanon Rd Mount Juliet, TN 37122 615-758-5858 800-767-5859 www.pacenational.com

	SAMPLE S	SUMN		ONE LAB. NATIONWIDE		
190087-01 L1074024-01 WW			Collected by	Collected date/time 02/26/19 19:44	Received da 02/28/19 08	te/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 18:29	LD	Mt. Juliet, TN
190087-02 L1074024-02 WW			Collected by	Collected date/time 02/26/19 19:45	Received da 02/28/19 08	te/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:25	LD	Mt. Juliet, TN
190087-03 L1074024-03 WW			Collected by	Collected date/time 02/26/19 16:50	Received da 02/28/19 08	te/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:30	LD	Mt. Juliet, TN
190087-04 L1074024-04 WW			Collected by	Collected date/time 02/26/19 19:48	Received da 02/28/19 08	te/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:34	LD	Mt. Juliet, TN
190087-05 L1074024-05 WW			Collected by	Collected date/time 02/26/19 19:50	Received date/time 02/28/19 08:45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:39	LD	Mt. Juliet, TN
190087-06 L1074024-06 WW			Collected by	Collected date/time 02/26/19 17:12	Received date/time 02/28/19 08:45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:44	LD	Mt. Juliet, TN
190087-07 L1074024-07 WW			Collected by	Collected date/time 02/26/19 19:53	Received date/time 02/28/19 08:45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:48	LD	Mt. Juliet, TN
190087-08 L1074024-08 WW			Collected by	Collected date/time 02/26/19 19:55	Received da 02/28/19 08	te/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1243660	1	03/01/19 12:57	03/04/19 19:53	LD	Mt. Juliet, TN

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ACCOUNT:	PROJECT:	SDG:	DATE/TIME:	PAGE:
Nortest		L1074024	03/07/19 09:22	3 of 30

	SAMPLE S	SUMN	/IARY		ONEL	AB NATIONWID
190087-09 L1074024-09 WW			Collected by	Collected date/time 02/26/19 17:30	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:12	LD	Mt. Juliet, TN
190087-10 L1074024-10 WW			Collected by	Collected date/time 02/26/19 19:57	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:16	LD	Mt. Juliet, TN
190087-11 L1074024-11 WW			Collected by	Collected date/time 02/26/19 19:59	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:21	LD	Mt. Juliet, TN
190087-12 L1074024-12 WW			Collected by	Collected date/time 02/26/19 17:40	Received da 02/28/19 08	ite/time .45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:25	LD	Mt. Juliet, TN
190087-13 L1074024-13 WW			Collected by	Collected date/time 02/26/19 20:01	Received da 02/28/19 08	ite/time .45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:30	LD	Mt. Juliet, TN
190087-14 L1074024-14 WW			Collected by	Collected date/time 02/26/19 20:03	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:50	LD	Mt. Juliet, TN
190087-15 L1074024-15 WW			Collected by	Collected date/time 02/26/19 17:46	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:54	LD	Mt. Juliet, TN
190087-16 L1074024-16 WW			Collected by	Collected date/time 02/26/19 19:39	Received da 02/28/19 08	ite/time :45
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location
Metals (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/06/19 23:59	LD	Mt. Juliet, TN

ACCOUNT:	PROJECT:	SDG:	DATE/TIME:	PAGE:
Nortest		L1074024	03/07/19 09:22	4 of 30

	SAMPLE S	SUMN	MARY		ONEL	AB. NATIONWIDE.	*
190087-17 L1074024-17 WW			Collected by	Collected date/time 02/26/19 19:41	Received da 02/28/19 08	te/time 45	Ср
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	² Tc
Metais (ICPMS) by Method 200.8	WG1245386	1	03/05/19 15:11	03/07/19 00:04	LD	Mt. Juliet, TN	3



ACCOUNT:	PROJECT:	SDG:	DATE/TIME:	PAGE:								
Nortest		L1074024	03/07/19 09:22	5 of 30								
E 11.1.7			DATE/TIME: PAGE: 03/07/19 09:22 5 of 30									

Figure H.1. Treated corn isotherm lab results from Nortest Analytical

RECEIVING ORDER & CHAIN OF CUSTODY RECORD	PNGE OF 2	AUTHORIZED SIGNATURE DATE RELEASE TO ADEQ	An 1001/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/	SAMPLE I COOLER	///////	I I I I I ABORATORY IDENTIFICATION	19-10-130061	190037-02 62	190087-03 63	190087-04 01	190037-05 %	1, 0,0 - 1300,91	p ro - rsoup1	190057 - 08 64	190087 - 09 09	1 01 - 420061	190087 - 11	VI C1 - 7800 PI	COMMENTS		PAD SCREEN: -O 5 mBAr	1.5-1-1,21	D FAX RESULTS SPECIAL DETECTION LIMITS / RECURREMENTS	COMPLET PROCESS TO PREATON DIME:	ALL WORK SUBJECT TO STANDARD TERMS AND
au edu	15606 Stiva	61110	REQUESTED	ANAL	LON	8	X	X	X	X	X	X	X	X	×	X	X	X	DATE / TIME	KO11 6 62	2/28/19:0845				- Client
(ad 429@n	BLOON POBON	1001 1001 1001 10	CONTAINERS LAB USE ONLY	OFD	H 7(H E SSESE	HCI H ^S 2C HRO HRO													PRINT NAME	Lisa Mucario 2	Eric Struck				Yeltow Work File; Pink
K N	S Huffer Istaff AZ	micday		Z I AINERS TYPE		NO. ON MOD MOD	I XA	II X A	I XA	II XA	I KA	II XA	I XA	1 MA	AX I	AA II	T X A	11 14 14	LASTGNATURE)		4				e Laboratory;
tington Drive ona 86004-8934 • fax 774-646	NDRESS 2112 FLOG	CONTEST QUOTE V	YPE CODES	F FIELD BLANK		OCATION	A	B	10	A	B	20	SA	SB	35	0 Å	08	50	RECEIVED	A	VEro				White
2400 East Hun Flagstaff, Ariz (928) 774-2312	ns Slayton 8) \$23-1393	20	SAMPLE T A WATER B SOIL	D DRINKING WATER	SPECIFY:	TIME SAMPLEL	1:4 110	1:45 T 10	50 50	4:48 T 21	:50 720	:12 SD	:53 7 39	:55 7.3	7:30 SD	151 TS	51 FS:	1:40 SD	PRINT NAME	Dykstra					16384
vtical vtical ^{ality} People	BEYU * (Stall/Sing) 9-1538/192			RA	Stol 15	DATE	2/26/19/1	2/26/19 1	2/26/19 4	2/26/19/1	2/26/19 19	2/26/195	2/26/19/19	2/26/19/19	2/26/19 13	2/26/19 19	2/26/19 19	2/26/19/19	TURE)	- Kylie					4510 155
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Figure H.2. Treated corn isotherm Chain of Custody Form

Appendix I: Breakthrough Lab Results and Chain of Custody Forms



ANALYTICAL REPORT

Nortest

Sample Delivery Group: Samples Received: Project Number: Description:

Report To:

03/30/2019

L1084004

Lisa Marie Macario 2400 E. Huntington Dr. Flagstaff, AZ 86004

Entire Report Reviewed By:

Daphne R Richards

Daphne Richards Project Manager

<text>

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190127-01 L1084004-01 DW			Collected by	Collected date/time 03/29/19 11:45	Received da 03/30/19 08	ite/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 02:51	LAT	Mt. Juliet, TN	
190127-02 L1084004-02 DW			Collected by	Collected date/time 03/29/19 11:51	Received da 03/30/19 08	ite/time :45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 02:55	LAT	Mt. Juliet, TN	
190127-03 L1084004-03 DW			Collected by	Collected date/time 03/29/19 11:54	Received da 03/30/19 08	ite/time :45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:00	LAT	Mt. Juliet, TN	
190127-04 L1084004-04 DW			Collected by	Collected date/time 03/29/19 11:57	Received da 03/30/19 08	ite/time :45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:04	LAT	Mt. Juliet, TN	
190127-05 L1084004-05 DW			Collected by	Collected date/time 03/29/19 12:00	Received da 03/30/19 08	ite/time .45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:09	LAT	Mt. Juliet, TN	
190127-06 L1084004-06 DW			Collected by	Collected date/time 03/29/19 12:03	Received da 03/30/19 08	ite/time :45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:13	LAT	Mt. Juliet, TN	
190127-07 L1084004-07 DW			Collected by	Collected date/time 03/29/19 12:05	Received da 03/30/19 08	ite/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:27	LAT	Mt. Juliet, TN	
190127-08 L1084004-08 DW			Collected by	Collected date/time 03/29/19 12:08	Received da 03/30/19 08	ite/time :45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:32	LAT	Mt. Juliet, TN	

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190127-09 L1084004-09 DW			Collected by	Collected date/time 03/29/19 12:11	Received da 03/30/19 08	te/time 45	ľ
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	2.
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:36	LAT	Mt. Juliet, TN	
190127-10 L1084004-10 DW			Collected by	Collected date/time 03/29/19 12:14	Received da 03/30/19 08:	te/time 45	4
Method	Batch	Dilution	Preparation	Analysis	Analyst	Location	- [
Metals (ICPMS) by Method 200.8	WG1262649	5	04/08/19 14:52	04/09/19 03:41	LAT	Mt. Juliet, TN	5
190127-11 L1084004-11 DW			Collected by	Collected date/time 03/29/19 12:17	Received da 03/30/19 08:	te/time 45	6
Method	Batch	Dilution	Preparation dato/time	Analysis dato/timo	Analyst	Location	7
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:31	LAT	Mt. Juliet, TN	8
190127-12 L1084004-12 DW			Collected by	Collected date/time 03/29/19 12:20	Received da 03/30/19 08:	te/time 45	9
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:36	LAT	Mt. Juliet, TN	_
190127-13 L1084004-13 DW			Collected by	Collected date/time 03/29/19 12:23	Received da 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:41	LAT	Mt. Juliet, TN	
190127-14 L1084004-14 DW			Collected by	Collected date/time 03/29/19 12:26	Received da 03/30/19 08	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	_
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:45	LAT	Mt. Juliet, TN	
190127-15 L1084004-15 DW			Collected by	Collected date/time 03/29/19 12:29	Received da 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	_
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:50	LAT	Mt. Juliet, TN	
190127-16 L1084004-16 DW			Collected by	Collected date/time 03/29/19 12:32	Received da 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	_
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 04:54	LAT	Mt. Juliet, TN	
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Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	-
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 03:46	LAT	Mt. Juliet, TN	
190127-18 L1084004-18 DW			Collected by	Collected date/time 03/29/19 12:37	Received dat 03/30/19 08:	te/time 45	² S
Method	Batch	Dilution	Preparation	Analysis	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 03:50	LAT	Mt. Juliet, TN	5,
190127-19 1084004-19 DW			Collected by	Collected date/time 03/29/19 12:40	Received dat 03/30/19 08:	te/time 45	6
Method	Batch	Dilution	Preparation	Analysis	Analyst	Location	7
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 03:55	LAT	Mt. Juliet, TN	8
190127-20 L1084004-20 DW			Collected by	Collected date/time 03/29/19 12:43	Received dat 03/30/19 08:	te/time 45	9
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1262652	5	04/08/19 14:56	04/09/19 03:59	LAT	Mt. Juliet, TN	_
190127-21 L1084004-21 DW			Collected by	Collected date/time 03/29/19 12:46	Received dat 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1259079	1	04/02/19 07:38	04/02/19 19:08	LD	Mt. Juliet, TN	
190127-22 L1084004-22 DW			Collected by	Collected date/time 03/29/19 12:49	Received dat 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	
Metals (ICPMS) by Method 200.8	WG1259079	1	04/02/19 07:38	04/02/19 17:08	LD	Mt. Juliet, TN	_
190127-23 L1084004-23 DW			Collected by	Collected date/time 03/29/19 12:52	Received dat 03/30/19 08	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	-
Metals (ICPMS) by Method 200.8	WG1259079	1	04/02/19 07:38	04/02/19 17:13	LD	Mt. Juliet, TN	
190127-24 L1084004-24 DW			Collected by	Collected date/time 03/29/19 12:58	Received dat 03/30/19 08:	te/time 45	
Method	Batch	Dilution	Preparation date/time	Analysis date/time	Analyst	Location	_
Metals (ICPMS) by Method 200.8	WG1259079	1	04/02/19 07:38	04/02/19 17:18	LD	Mt. Juliet, TN	
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Figure I.1. Breakthrough testing lab results from Nortest Analytical

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Figure I.2. Breakthrough testing Chain of Custody Form

Appendix J: Additional Bohart-Adams Calculations

The values of a and b are further defined by the Bohart-Adams model in Equations J.1 and J.2 [9]. Obtaining a and b from the BDST curves allows for additional information to be obtained about the column. Equation J.1 can be solved to obtain the value of N, which gives the adsorptive capacity of the biosorbent, and Equation J.2 can be solved to determine the K constant, which is a rate constant required to move an adsorption zone through a critical bed depth [9].

$$a = \frac{F_1 N}{C_{in} V} \tag{J.1}$$

Where:

a= 54.68 m/h (from BDST curve and Table 5.2)

 F_1 = conversion factor for units, 10³ for metric units

N= adsorptive capacity of corn (mass of contaminant removed per volume of corn in the column, kg/m^3)

 C_{in} = 0.0822 mg/L (influent contaminant concentration in mg/L) V= 3.84 m/h (superficial velocity through the column, O/A)

= 3.84 m/n (superficial velocity through the column, Q/A)

$$b = \left(\frac{F_2}{KC_{in}}\right) * \ln\left[\left(\frac{C_{in}}{C_{out}}\right) - 1\right]$$
(J.2)

Where:

b= -0.938 h (from BDST curve and Table 5.2) F₂= conversion factor for units, 10^3 for metric units

K= adsorption rate constant required to move an adsorption zone through critical depth (m^3 of liquid treated per kg of impurity fed per hour, $m^3/(kg*h)$)

 $\begin{array}{l} C_{in} = 0.0822 \ mg/L \ (influent \ contaminant \ concentration \ in \ mg/L) \\ C_{out} = 0.005 \ mg/L \ (contaminant \ concentration \ at \ breakthrough \ in \ mg/L) \end{array}$

The Bohart-Adams parameter values, including the N and K value resulting from solving Equations J.1 and J.2, are shown in Table J.1 below.

Bohart-Adams Parameter Values							
F ₁ (conversion factor)	1000	unitless					
F ₂ (conversion factor)	1000	unitless					
V (superficial velocity)	3.84	m/h					
K (adsorption rate constant)	-33860	$m^3/(kg*hr)$					
N (adsorptive capacity)	0.02	kg/m ³					

Table J.1. Additional Bohart-Adams parameters

Equation J.3 [9] calculates the critical bed depth, or minimum depth required to obtain satisfactory effluent at time zero. In other words, the critical bed depth is the theoretical depth of adsorbent required to ensure that the outlet of the adsorbate concentration does not exceed the breakthrough concentration of 5 μ g/L at t=0. The lower the critical bed depth, the better the adsorbent because it takes a smaller depth of the material to adsorb a certain amount of chemical [25].

$$X(0) = \left(\frac{F_2}{F_1}\right) * \left(\frac{V}{NK}\right) * \ln\left[\left(\frac{C_{in}}{C_{out}}\right) - 1\right]$$
(J.3)

Where:

X(0) = critical bed depth (m)

Using the values from Table J.1 in Equation J.3 results in a critical bed depth of -0.018 m, or -1.8 cm. Because the critical bed depth is a theoretical value calculated from experimental data, it is not unusual to obtain a negative number (Examples of other studies which obtain negative critical bed depth values include *Packed Bed Column for Adsorption of Aqueous Phenols on Cement Kiln Dust* [25] and *Breakthrough Curve Analysis of Enteromorpha prolifera Packed Fixed-Bed Column for the Biosorption* [26]). This simply means that a relatively low amount of corn is required for adequate removal at the outset of the column test. Because such a low critical bed depth value was obtained, the design criteria of having a bed depth greater than the critical bed depth was automatically met, and therefore was not a major design constraint in this case. This critical bed depth value should be further verified with additional column testing.

Appendix K: Scale-Up Hand Calculations



Scale Up for 50,000 gal/day

$$Az = 0.017 \text{ m} \qquad \text{column length} \\
n = (0.017 \text{ m} / (0.9 \text{ in } \times 254 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}})) + 1 = 1.74 \\
\text{We are of lab column'.} \\
Area of lab column'. \\
A = $\frac{\pi d^2}{4} = \frac{\pi}{(1 \text{ in } \times 254 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ m}})} = 0.0005 \text{ m}^2 \\
\text{Loading rate in lab columns'.} \\
V = (0.54 \text{ cm}^3 \times \frac{\text{m}^3}{10^6 \text{ cm}^3} \times \frac{100}{\text{ mn}}) = 0.0648 \text{ m}^3/(\text{m}^2,\text{m}^2) \\
\text{Using same loading rate for full scale:} \\
A = \frac{Q}{V} = (\frac{50.000 \frac{Q}{232} \times \frac{5785L}{1 \text{ gal}} \times \frac{\text{m}^2}{1 \text{ gal}} \times \frac{1 \text{ day}}{1 \text{ gal}}) = 2.028 \text{ m}^3 \\
(0.0048 \text{ m}^3/(\text{m}^2,\text{mm})) \\
A = \pi \frac{1}{4} \longrightarrow d = \sqrt{\frac{14A}{\pi}} = \sqrt{\frac{14(2005 \text{ m})}{\pi}} = 1.6009 \text{ m} \\
\text{Cob utilization = A \times \frac{1}{4} \times \frac{1001}{4} = (2028 \text{ m}^3) \times (\frac{0.018 \text{ m}}{100}) \times (\frac{234100 \text{ gal}}{1003}) \\
= 8991.8 \text{ g/hr} \\
= 215.78 \text{ kg/day}$$$

Figure K..2. Scale up calculations

Dimension Adjustments
* Based on US Army Carps. Adsorption Design
Guide
Off-the-shelf Contactors: 70 - 9100 Kg
Load limit for having: 9100 Kg
Adsorption Column Volume:

$$V = (CCUR \times COP)$$
 S.F.
P
CCUR = Corn cob utilization rate
COP = Change out period
S.F. = safety factor for backwash, typ. 1.2
P = bulk density of corn
Using Change out period of 30 days,
 $V = (\frac{(21b000 \text{ g}/day \times 30 \text{ days})(1.2)}{(0.23919 \text{ g} - \text{cm}^2 \times \frac{10^{\circ} \text{ cm}^2}{\text{m}^3})}$
Height: 4 m
Area = 21 m³/5.5 m = 6.8 m²
Diameter = $((6.8 \text{ m}^3)(4))^{0.5} = 3 \text{ m}$
Loading Rate = $(0.131 \text{ m}^3/\text{min}) \times (50 \text{ min}) = 1.2 \text{ m/hr}$

Figure K.3. Dimension adjustments



Critical Bed Depth Calculations
From Bohart - Adams:

$$a = \frac{F_{1} N}{C_{10} V}$$
Fi = Conversion factor, 10° for metric
Cin = 82.2 Mg/L = 0.0822 mg/L
V = Superficial velocity of column = $\frac{a}{A} = \frac{0.0000 324 \text{ m}^{3}}{0.005067015 \text{ m}^{3}}$
0.063942 m x 60 min = 3.84 m/hr
 \Rightarrow solve for N
Superficial velocity of column = $A = 0.002 \text{ kg/m}^{3}$
 $0.063942 \text{ m} \times \frac{60 \text{ min}}{1 \text{ hr}} = 3.84 \text{ m/hr}$
 \Rightarrow solve for N
Superficial velocity (3.84 m/hr)
 $b = (F_2/KC_{10}) \ln [(Cn/Caut) - 1]$
 $F_{2} = \text{Conversion factor, 10^{3} for metric
Cout = 5 Mg/L = 0.005 mg/L
 \Rightarrow solve for K
 $-0.983 \text{ hr} = (10^{3}/\text{K}(0.0822 \text{ mg/L})) \ln [(0.0822/0.005) - 1]$
 $K = -33860.7 \text{ m}^{3}/(\text{kg.hr})$
 $X(0) = (F_{2}/F_{1})*(V/NK) * \ln [(Cn/Cout) - 1]$
 $X(0) = -0.013 \text{ m}$
Figure K5. Critical bod depth calculations$

Appendix L: Corn Cob Biosorbent Cost Calculations

Treatment Calculation						
				Liters of		
	Liter		Price	1N	price/ml	
Nitric Acid from Fisher Scientific						
(15.8M)	15	\$	462.92	237	\$ 0.0020	
Sodium Hydroxide Fisher Scientific	20	\$	334.00	N/A	\$ 0.0167	

Table L.1. Cost of nitric acid and sodium hydroxide

Table L.2. The amount of nitric acid and sodium hydroxide required per gram of corn

			mL chemical
Chemical	Grams of corn	mL of corn	per kg corn
Nitric Acid	30	150	6666.67
Sodium Hydroxide	30	2	133.3

Table L.3. Energy demand for grinding per gram of corn

Energy demand for grinding corn [15]						
		Capacity				
Model	Power KW	(kg/h)	kWh/kg			
M6FFC-800	55	5000	0.011			

Table L.4. Energy demand to dry corn after treatment

Drying energy demand [14]							
		Pan					
Model	KW	Capacity	Time (hr)				
Lab Drying/Sterilizing Ovens	1.5	3	12				

Table L.5. Calculating the dry density of corn biosorbent

Corn Characteristics							
volume (ml) mass (g) density (g/ml)							
20	4.7838	0.23919					

Theoretical Pan						
	in	m		ml		
Width	13	0.33	02			
length	21	0.5334				
depth	4	0.10	16			
volume	1092	0.017894674		17	894.674	
mass corn	an	42	280.2			

Table L.6. Pan dimensions used to estimate the mass of corn that can be dried in any given drying oven

 Table L.7. Average cost per g of corn cob waste [13]

Corn Waste [13]								
sample	amount (kg)	cost	cost per kg					
1	907.185	\$140	0.154323539					
2	907.185	\$400	0.440924398					
3	907.185	\$125	0.137788874					
4	907.185	\$140	0.154323539					
average		\$201.25/ton	0.221840088					

Appendix M: Average Cost of GAC calculations [27] [28] [29]

GAC								
Source	Unit mass (lb)	Unit Cost	Mass (g)	Cost per gram				
WaterFilteronline.com	8.5	\$60.00	3855.5	\$0.016				
WaterFilteronline.com	17	\$689.99	7711.1	\$0.089				
WaterFilteronline.com	34	\$57.00	15422.1	\$ 0.004				
Delta Adsorbents	1	\$ 19.98	453.6	\$ 0.044				
Delta Adsorbents	10	\$39.98	4535.9	\$ 0.009				
Delta Adsorbents	75	\$214.98	34019.4	\$0.006				
Alibaba	2000	\$1,000.00	907184.0	\$ 0.001				
Average				\$ 0.024				

Table M.1. Granular activated carbon cost, based on the average cost for available sources

Appendix N: Calculations for the Treatment of 1 Gallon Water Contaminated by 75ug/l

GAC			Co	rn Cob (unt	reated)	Corn Cob (treated)			
Kf	12								
n	1.84		slope	0.6589		slope	8.6817		
C0	5	ug/l	C0	5	ug/l	C0	5	ug/l	
Ce	75	ug/l	Ce	75	ug/l	Ce	75	ug/l	
v	3.78541	L	v	3.78541	L	v	3.78541	L	
		cd ug/			cd ug/			cd ug/	
q	28.77771	GAC g	q	5.4775	corn g	q	43.4085	corn g	
m	9.207775	g	m	48.37585	g	m	6.104304	g	

Table N.1. Isotherm parameters for GAC and treated/untreated corn

Appendix O: Lifecycle Analysis Calculation Methods

Finally, use the following equation to calculate the surface area of either a horizontal or vertical vessel:

$$S = \pi D(L + D/2)$$
 (1.24)

Similar equations can be developed for other vessel shapes, configurations, etc.

Based on vendor data, we developed a correlation between adsorber vessel cost and surface area: [10]

$$C_{v} = 271 \times F_{m} \times S^{0.778} \tag{1.25}$$

where

 C_v = vessel cost (fall 1999 \$), F.O.B. vender⁷ F_m = adjustment factor for fabrication material (from Table 1.3) S = surface area of the vessels (ft²)

Table 1.3: Adjustment Factors to Obtain Costs for Fabricated Material

Material	F _m Factor	Reference(s)
Stainless steel, 304	1.0	[10]
Stainless steel, 316	1.3	[9,10,11]
Carpenter 20 CB-3	1.9	[11]
Monel-400	2.3	[9,11]
Nickel-200	3.2	[11]
Titanium	4.5	[11]

Figure O-1. Method for Calculating Vessel Cost [12]