NORTHERN ARIZONA UNIVERSITY

College of Engineering, Informatics, and Applied Sciences

To: Fethiye Ozis, NAU Professor, Capstone Client
From: A-Maize Cob-oration
Date: May 5, 2020
Re: Final Design Report

Dr. Ozis,

This report addresses the final project design of the corn cob biosorbent capstone project. Included are the results for the Cadmium removal test, which was based on the 2019 NAU research, as well as a developed isotherm. Also in this document are the results from the Arsenic testing with XRF and ICP analysis, the corn cob sorption results with XRF analysis, and finally the Total Coliform results and analysis.

The final project cost was determined to be $76,787.

For additional information, please contact eip6@nau.edu.

Sincerely,

A-Maize Cob-oration

Final Design Report: Corn Cob Biosorption

Removal of Cadmium, Arsenic, and Total Coliform

CENE 486C

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Final Version

Table of Contents

List of Tables

List of Figures

List of Abbreviations

Environmental Protection Agency	EPA
Inductively Coupled Plasma-Mass Spectrometry	ICP-MS
Instrument Detection Limits	IDL
Limit of Detection	LOD
Maximum Contaminant Level	MCL
Maximum Contaminant Level Goal	MCLG
Northern Arizona University	NAU
Personal Protective Equipment	PPE
X-Ray Florescence	XRF

Acknowledgements

1.0 Project Introduction

The purpose of this research project is to create an environmentally and economically feasible treatment process for the removal of Cadmium, Arsenic, and Total Coliform in contaminated water for implementation in marginalized communities.

1.1 Project Background

Metal contamination in surface waters from mining efforts has serious effects on human health. The potential health effects from Cadmium and Arsenic exposure range from skin problems to kidney damage [2]. The Environmental Protection Agency (EPA) maximum contaminant level (MCL) for Cadmium and Arsenic are 0.005 and 0.010 mg/L, respectively [2]. For both contaminants, the maximum contaminant level goal (MCLG), respectively, are 0.005 and 0.00 mg/L [2]. While the health effects of Total Coliform are not as severe, it is still beneficial to aim for zero percent for the MCLG, which is slightly lower than the MCL at 5% TT [2]. Total Coliform, while not particularly dangerous, can indicate pathogens contaminating the water. Removal of Total Coliform will ensure removal of pathogens. These concentrations and effects are shown in Table 1-1.

Table 1-1: Drinking water regulations of contaminants of interest [2]

Contaminant	MCLG (mg/L)	MCL (g/L)	Potential Health Effects from Long-Term Exposure Above the MCL	Sources of Contamination in Drinking Water
Arsenic	0	0.010	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Total Coliforms	0	5% of all monthly tests	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and E. coli only come from human and animal fecal waste

In 2017, Arizona released over 130 million pounds of toxic chemicals into the environment, over half of which was disposed of without treatment or recycling [3]. More than half the waste produced was from metal mining [3]. Specifically, the Tohono O'odham Tribal Community located in Southern Arizona, produced over 5 million pounds of toxic waste from metal mining; 100% of which was disposed of without recycling or treatment [2]. Accessible and cost-effective treatment solutions can reduce and mitigate the spread of contamination of heavy metals within the environment.

This biosorbent research is a continuation of the previous year's Senior Design Capstone Project, and the structure will mimic prior corn biosorbent research done at NAU [4]. In 2019, the capstone team worked on testing nitric acid treated corn cob and natural corn cob for the removal of Cadmium, specifically. The results obtained from the previous capstone team proved that treated corn cob had a removal efficiency of 97%, and natural corn cob had a removal efficiency of 77%. Building off the results reported last year, this project aims to further validate the Cadmium removal efficiency results and achieve publication while assessing the removal efficiency of Arsenic and Total Coliform using treated and untreated corn cob.

1.2 Objectives

The objectives of this research project include:
1. Expand Cadmium removal data using corn cob as a biosorbent.
2. Evaluate the efficiency of corn cob as a biosorbent in the removal of Arsenic and Total Coliform.
3. Evaluate the efficiency of corn cob activation using a weak acid.
4. Develop an analytical method for the use of the XRF machine for organic materials and liquids.
5. Present research at various research symposiums.
6. Help publish the research found on the removal of Cadmium using corn cob as a biosorbent.

1.3 Constraints and Limitations

Due to the nature of the project, there were multiple constraints and limitations. All work completed for the project was done in a lab setting under a fume hood. With this, exposure from outside contaminants is exceptionally low, making the project limited to possible contamination as would be found in a real-world implementation. For a field application of this research, the limitations of lab testing would be apparent, as there would be additional external influences and contamination. Another constraint and limitation of the research project was the detection limit of the XRF device, which was used to determine the levels of Arsenic in corn after batch reactions. The detection limits were too high for the concentrations tested in the research project.

1.4 Exclusions

For the corn cob research, the exclusions include field sample testing, such as collecting contaminated water samples from mine spill discharge areas, the creation of a design prototype, and column testing for further verification of the proposed testing methods. Additionally, the project will not identify the physicochemical characteristics of the corn cob biosorbent.

2.0   Testing Methods

The following sub-sections elaborate the testing methods used for corn cob preparation, treatment, and contaminant removal.

2.1   Biosorbent Preparation

The corn cob was broken down and prepared to be used as the biosorbent. A published methodology for preparing corn cobs as a biosorbent was used by the former NAU corn cob capstone team and was replicated for quality assurance purposes [4]. Quality assurance precautions were taken due to the analytical expansion of the Cadmium testing and results (Objective 1). Modifications were made to this methodology for Arsenic and Total Coliform testing (Objective 2).

Once the corn was acquired, the preparation and activation processes began. Approximately 200 corn cobs were purchased at local supermarkets in Flagstaff, Arizona. This procedure began with husking each ear of corn, so only the kernels and cobs remained. The corn was then cut into thirds or quarters, depending on its length and diameter to ensure uniform drying, see Figure 2-1.

Figure 2-1: Cut corn ready for drying

The corn was placed into a drying oven at ~100°C and baked for a minimum of 24 hours until each corn segment was thoroughly dried. Once the corn was done drying, the kernels were stripped off by hand, saved, and presented as animal feed to minimize waste, see Figure 2-2.

Figure 2-2: Dried corn being stripped of kernels

The stripped cob pieces were ground until the particles passed through a 250 μm (No. 60) sieve. The process of breaking down the corn cob alternated between the use of a ring and puck mill (provided by the Geology Department at NAU) and a food processor, see Figures 2-3 and 2-4. After the initial pulverization process in Professor Parnell's geology laboratory, the small particles that were unable to pass the 250 μm sieve were further ground by placing them into the food processor, Figure 2-5, or by using a pestle and mortar, Figure 2-6. With this varying methodology, the team was able to produce 200 grams of dried corn cob.

Figure 2-3: Ring and puck bowl

Figure 2-5: Grinding corn larger than the 250-μm sieve with a mini food processor

Figure 2-4: Ring and puck bowl with corn inside

Figure 2-6: Grinding corn with a mortar and pestle

2.2 Biosorbent Treatment

Past research shows that acid activation increases the efficiency of sorption sites within a biosorbent's matrix [1, 5]. To expand the corn cob biosorbent research for Cadmium removal in drinking water done at NAU in 2019, the same activation process was followed for nitric acid treatment. For the other contaminants, Arsenic and Total Coliform, the biosorbent was activated using three treatment methods. These included using the previously mentioned nitric acid, a weak acid determined from a decision matrix after a literature review, and natural, untreated corn. Weak acid and untreated corn were used to

test more sustainable and feasible options with greater likelihood for implementation as a water treatment technique in marginalized communities.

2.2.1 Nitric Acid Treatment for Cadmium Sorption

Nitric acid treatment was performed using the same methodology created by the previous team during their research. The corn was saturated in 1M nitric acid (HNO_3) and placed on a rotary shaker for 12 hours at 250 rotations per minute (rpm). After the saturation process, Figure 2-7, the corn cob solution was centrifuged for 20 minutes at 3000 rpm.
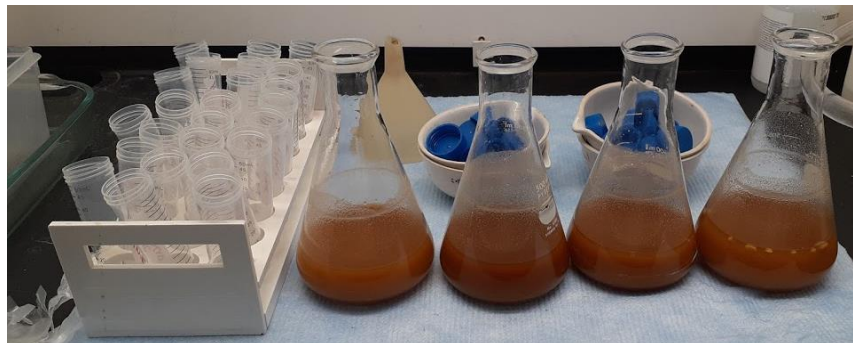
Figure 2-7: Saturated corn cob before centrifuge process

The layer of nitric acid above the surface of the settled corn in each centrifuge tube was drained into the hazardous waste container; then approximately 40 mL of deionized (DI) water was poured in with the settled corn cob and reagitated for saturation purposes. The new corn cob solution was run through the centrifuge using the same parameters, 20 minutes at 3000 rpm, Figure 2-8. The top layer of liquid was again poured off into the hazardous waste container. The corn cob was removed from the centrifuge tubes and placed in evaporation dishes to dry at 80°C for 12 hours, Figure 2-9.

Figure 2-8: Centrifuged corn cob solutions

Figure 2-9: Filtered nitric acid treated corn cob

Once dried, the previous steps were repeated using a 1.0 M sodium hydroxide (NaOH) solution to neutralize the pH of the corn, Figure 2-10. When the NaOH steps were completed, the corn was saturated in DI water and put on the rotary shaker for 12 hours at 250 rpm. The pH was adjusted with hydrochloric acid (HCl) to approximately 6. The corn

cob and DI water solution was separated using a 4.5cm glass fiber filter, Figures 2-11 and 2-12, and dried at 80°C for 12 hours [4].

Figure 2-10: Dried NaOH saturated nitric acid treated corn cob with filtration
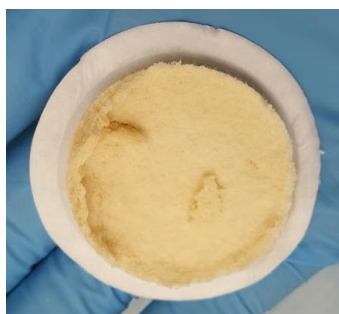
Figure 2-11: Filtered nitric acid treated corn cob before drying

Figure 2-12: Filtering nitric acid treated corn cob solution

This drying process was the final step in activating the biosorbent with nitric acid. The nitric acid activation process takes more than 72 hours to complete from start to finish. It is important to note the final mass of corn is a third to a half of the initial mass using this methodology. Due to the insufficient yield, physical properties, and characteristics of the resulting corn, a different methodology was developed and used for Arsenic and Total Coliform testing.

2.2.2 Nitric Acid Treatment for Arsenic and Total Coliform Sorption

Nitric acid treatment for Arsenic and Total Coliform was determined based on previously published research [1]. Following this methodology, 40 grams of corn cob was mixed with 200 mL of 1.0 M nitric acid (HNO_3) until all the corn was saturated. The evaporation dish was put into the oven at 60°C for 2 hours. The corn cob was taken out of the oven to cool. The cooled solution was filtered, and the corn cob was washed multiple times with DI water until the pH of the corn was stable. The corn then dried at 50°C for 24 hours to complete the activation process. Figure 2-13 shows the new nitric acid treated corn cob after drying and collection.
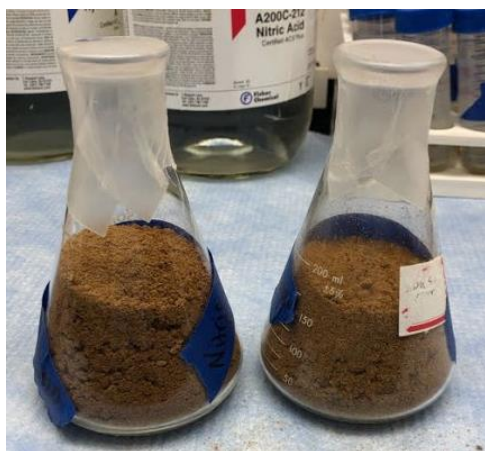
Figure 2-13: Modified methodology nitric acid treated corn

2.2.3 Weak Acid Decision Matrix

Previous studies using weak acids for biosorbent activation were reviewed. The weak acids that were used frequently and successfully were mercaptoacetic [6], citric [7], and tartaric acids [8]; thus, these three acids were compared in a decision matrix. In the published research, mercaptoacetic acid was used to activate orange peel, citric acid was used to activate corn cob, and tartaric acid was used to activate rice husks. The full decision matrix is seen in Table 2-1, where the highlighted box indicates the chosen acid with the lowest final sum. Cost, effectiveness in activating sorption sites on biosorbents, ease of use during the activation process including time constraints, and the level of danger the acid poses to society (human health) and the environment were chosen as the criteria in which the decision matrix would be constructed. Each criterion was weighted equally since the overall purpose of this research is for the biosorbent to be used in marginalized communities, and the chosen categories were based on the most beneficial and efficient uses for that situation.

Table 2-1: Final decision matrix

Acid	Decision Matrix Categories				SUM
	Cost	*Effectiveness*	*Ease of Use*	*Hazardous*	
Mercaptoacetic	2	2	2	3	9
Citric	**1**	**1**	**1**	**1.5**	**4.5**
Tartaric	2	2	3	1.5	8.5

For each criterion, a low number indicates the best fit regarding feasibility and functionality of this research. Scores, between one and three, were determined by reviewing each acid in conjunction with the others, to ensure the categories would represent each criterion impartially. For example, citric and tartaric acids were given a 1.5 for hazardous since each had some form of irritation present during use. Beyond that, mercaptoacetic and tartaric acids had similar costs and effective properties within their

respective research, compared with untreated and strong acid treated biosorbents. With all scores considered, citric acid was chosen as the weak acid for corn cob activation.

2.2.4 Citric Acid Treatment

To activate the corn cob using citric acid, the first step was washing 40 grams of corn cob with DI water, Figure 2-14, and placing it in the drying oven for 24 hours at 70°C. The dried corn was transferred to an Erlenmeyer flask with 200 mL of 1.0 M citric acid and heated at 60°C for 2 hours. The mixture was filtered and placed into evaporation dishes and dried for 24 hours at 60°C. After 24 hours, the temperature was increased to 120°C for an additional 3 hours. Once cooled, the corn cob was washed multiple times with DI water, Figures 2-15 and 2-16, with a goal of reaching pH 6. After a stable pH was measured, the corn cob was dried for 24 hours at 50°C to complete the citric acid activation process, Figure 2-17 [1].
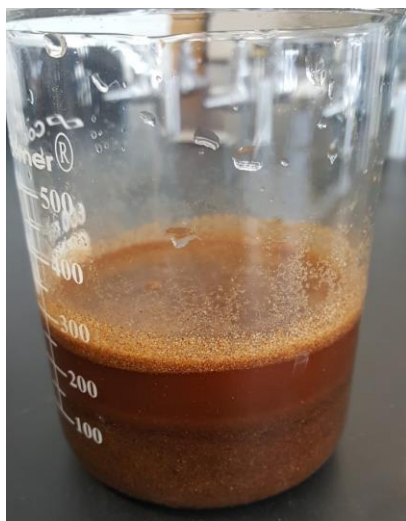
Figure 2-14: DI saturated corn cob

Figure 2-16: DI rinsed evaporation dishes, citric acid treated corn cob
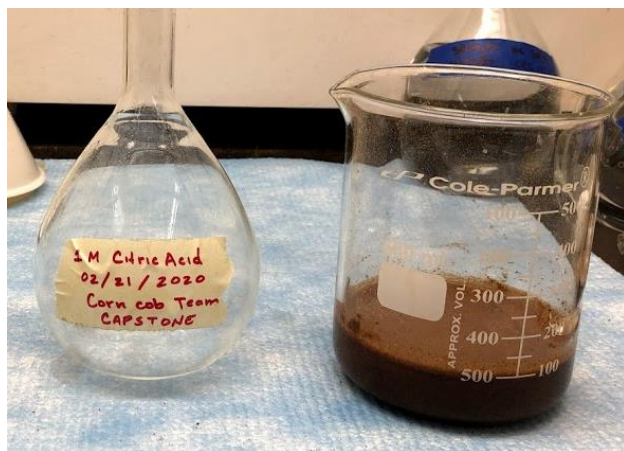
Figure 2-15: DI washed citric acid treated corn cob

Figure 2-17: Citric acid treated corn cob

2.3 Removal of Contaminants

For each contaminate being removed (Cadmium, Arsenic, and Total Coliform), various methodologies were necessary.

2.3.1 Cadmium Testing

The following sections discuss the process and methodologies used during Cadmium testing.

2.3.1.1 Cadmium Sample Preparation

A range of seven concentrations were selected for testing; the minimum concentration being tested, 5 µg/L, is the Maximum Contaminant Level (MCL) for Cadmium as defined by the EPA [2]. The maximum concentration, 100 µg/L, is the maximum recorded concentration found in the environment as reported by the World Health Organization (WHO) [9]. The other five concentrations being tested were chosen based upon the original points used in the previous NAU study to construct an isotherm for Cadmium removal efficiency, three of which are exact replicates shown in yellow in Table 2-2. All concentrations were triplicated for quality assurance purposes. A HACH Cadmium solution of 100 mg/L was used to create all concentrations for the Cadmium trials and the volume of the standard delivered to each sample is provided in Table 2-2. Equation 2-1 represents the formula used to determine the concentrations of Cadmium standard needed for the selected concentrations.

Equation 2-1: Cadmium dilution correlation

$$C_1 V_1 = C_2 V_2$$

Where:

C_1 = concentration of experimental Cadmium (µg/L),
V_1 = volume of experimental solution (L),
C_2 = concentration of Cadmium standard (mg/L), and
V_2 = volume of Cadmium standard solution (mL).

Table 2-2: Tested concentrations of Cadmium

Samples	Cadmium (µg/L)	Vol. DI Water (mL)	Standard (mg/L)	Vol. Solution (mL)
1	5	300	10	0.0015
2	10	300	10	0.003
3	20	300	10	0.006
4	40	300	100	0.012
5	60	300	100	0.018
6	75	300	100	0.0225
7	100	300	100	0.03

An additional dilution, to 10 mg/L, was performed for the lower concentrations (5, 10, 20 µg/L) to ensure accurate displacement of the standard volume for the required concentration. Along with these seven concentrations, two blanks were ran for additional quality assurance. These blanks went through the same "treatment" process; however, they were not contaminated with Cadmium and were purely DI water.

2.3.1.2 Cadmium Removal Method

In order to complete Objective 1, expand on Cadmium removal data using corn cob as a biosorbent, an expansion of the previous Cadmium research was performed using EPA Method 6020B Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) [10].

The seven concentrations were prepared using the 100 mg/L Cadmium standard and DI water in 500 mL Erlenmeyer flasks. One gram of nitric acid activated corn cob was deposited into each sample and placed on the rotary shaker for 90 minutes at 250 rpm. After the 90 minutes elapsed, the samples were filtered using the proper methodology provided by the NAU Chemistry Department in preparation for ICP-MS analysis.

Per the Chemistry Department, samples were required to be filtered and acid preserved prior to ICP-MS analysis. Each sample was filtered twice, the first time using a 4.5 cm glass fiber filter and the second time using a 47 mm glass fiber filter. Once filtered, the samples were acid-preserved at a pH of 2 or below using 1M nitric acid.

All samples were further diluted to ensure uniform concentrations within the water matrix for proper, more accurate analysis. Two dilution factors were used to do this; these can be found in Table 2-3. A base element, Ruthenium, having a similar molecular weight to Cadmium, was added to the ICP-MS-diluted samples to create a constant elemental concentration to determine the concentration of Cadmium present within the samples for analysis. ICP-MS analysis commenced, and final Cadmium concentrations were calculated.

A summary of the tests is shown in Table 2-3. Three replicates of each sample were performed. A full version with all replicates can be found in Appendix A.

Table 2-3: Cadmium testing experimental matrix

Sample Name	Type of Contaminant	Type of Corn cob Biosorbent	Concentrations (µg/L)	Replicates	Corn Cob Mass (g)	Total Number of Blanks
1-Cd-NA 2-Cd-NA 3-Cd-NA 4-Cd-NA 5-Cd-NA 6-Cd-NA 7-Cd-NA	Cadmium	Nitric Acid Activated Corn Cob	5 10 20 40 60 75 100	3	1.0	2

The three highlighted Cadmium concentrations denote the replicated 2019 NAU data points. The other concentrations were assessed for the expansion of the Cadmium analysis. NA in the sample name refers to nitric acid, which was the corn cob type used for all Cadmium testing.

2.3.2 Arsenic Testing

The following sections discuss the parameters and methods used for Arsenic testing.

2.3.2.1 Arsenic Sample Preparation

Nine concentrations of Arsenic were selected to be tested. The minimum concentration, 10 µg/L, is what the EPA defines as the Maximum Contaminant Level (MCL) for Arsenic [2]. The maximum concentration, 500 µg/L, is the mean contamination level in groundwater according to the World Health Organization (WHO) [11] The other seven concentrations were chosen between the maximum and minimum concentrations, focusing on lower concentrations more commonly found in drinking water sources. Sodium Arsenite (NaAsO$_2$) was used to create a 30 mg/L Arsenic stock solution for the test concentrations. The testing concentrations can be found in Table 2-4 below.

Table 2-4: Concentrations of Arsenic to be tested with the biosorbent

Samples	Arsenic (µg/L)	Solution Vol. (mL)	Standard (mg/L)	Vol. Standard (mL)
1	10	300	30.015	0.100
2	20	300	30.015	0.200
3	35	300	30.015	0.350
4	50	300	30.015	0.500
5	65	300	30.015	0.650
6	80	300	30.015	0.800
7	125	300	30.015	1.249
8	250	300	30.015	2.499
9	500	300	30.015	4.997

The standard in Table 2-4 refers to the stock solution made by the team using Sodium Arsenite, which resulted in a 30.015 mg/L standard. To obtain the testing concentrations for Arsenic, a volume of standard for each concentration was needed, as seen in the right most column of Table 2-4.

2.3.2.2 Arsenic Removal Method

For the completion of Objectives 2 and 4, an X-ray fluorescence (XRF) device was used to determine Arsenic concentrations. XRF devices read concentrations in the mg/L range, which introduced a challenge as to whether the concentrations being tested would be picked up by the device. Another challenge posed by the XRF was that solid matrices are

analyzed more successfully than liquid matrices. The liquid solutions and the corn cob solid matrix were analyzed for quality control and mass balance purposes to verify the concentrations read from the corn cob.

The XRF device requires a large mass of solid for proper analysis (5 grams is recommended [12]), but due to the low density of the corn cob, the maximum mass of corn that can fit into an XRF cup is 2 grams. Three masses of corn cob were used for the batch reactions: 1 gram, 0.5 grams, and 0.25 grams. These masses were used to attempt to concentrate the amount of Arsenic adsorbed to the corn cob. The math regarding this Arsenic concentrating effect can be found in Appendix B, with the general equation used to perform these calculations in Equation 2-2. For each mass, a total of about 2 grams of corn cob was used. This means that 2 samples with 1 gram of biosorbent, 4 samples with 0.5 grams of biosorbent, and 8 samples with 0.25 grams of biosorbent were tested for each Arsenic concentration and biosorbent preparation method (nitric acid activated, citric acid activated, and untreated). After the adsorption process, each respective biosorbent mass was air dried to prevent volatilization and combined in one XRF cup for analysis.

Equation 2-2: Equation used to calculate contaminate adsorbed to corn cob

$$VC_{L,i} + mC_{s,i} = VC_{L,f} + mC_{s,f}$$

Where:

V = total volume of the liquid solution (L),
$C_{L,i}$ = initial As concentration of the liquid solution (μg/L),
m = mass of corn cob (g),
$C_{s,i}$ = initial As concentration in the corn as read by the XRF (μg/g),
$C_{L,f}$ = final As concentration of the liquid solution (μg/L), and
$C_{s,f}$ = final XRF As concentration in the corn reading (μg/g).

Any changes in corn mass between initial and final XRF readings were assumed to be negligible regarding the final XRF reading in the corn cob.

The Arsenic adsorption methodology was like that of Cadmium. The indicated volume of Arsenic stock solution was delivered to a 500 mL Erlenmeyer flask and the necessary volume of DI water was put into the flask until the solution was 300 mL. One of the three masses of biosorbent was deposited into each flask, and the samples were put onto a rotary shaker for 90 minutes at 250 rpm. Once completed, each sample was filtered twice through glass fiber filters, the first through 4.5 cm and the second through 47 mm. The corn cob was placed in an evaporation dish to air dry with all the corn cob added at the same mass to the Arsenic solutions. The liquid was poured into XRF cups for XRF analysis and storage tubes for ICP-MS analysis. The corn cob was packed in XRF cups once the matrix was completely dried.

Liquid samples were also sent to ICP-MS to confirm the data values the XRF was able to gather from the solid corn cob samples. In addition, these ICP-MS results were gathered to construct an isotherm for Arsenic removal using a corn cob biosorbent. The Arsenic samples sent to ICP-MS followed the same sample preparation methodology for the Cadmium samples regarding filtering and acid preservation.

A summary of the Arsenic tests can be found in Table 2-5; it indicates the type of corn cob, the tested Arsenic concentrations, and the varied corn cob mass for each test. The full matrix including triplicates, corn masses, and standard solution information with the collected XRF data can be found in Appendix C.

Table 2-5: Arsenic testing experimental matrix

Sample Name			Type of Contaminant	Type of Corn Cob Biosorbent	Concentrations (µg/L)			Replicates	Corn Cob Mass (g)
As-N1-C1	As-N4-C4	As-N7-C7	Arsenic	Nitric Acid Activated Corn Cob	10	50	125	3	1.0
As-N2-C2	As-N5-C5	As-N8-C8			20	65	250		0.5
As-N3-C3	As-N6-C6	As-N9-C9			35	80	500		0.25
As-C1-C1	As-C4-C4	As-C7-C7	Arsenic	Citric Acid Activated Corn Cob	10	50	125	3	1.0
As-C2-C2	As-C5-C5	As-C8-C8			20	65	250		0.5
As-C3-C3	As-C6-C6	As-C9-C9			35	80	500		0.25
As-U1-C1	As-U4-C4	As-U7-C7	Arsenic	Untreated Corn Cob	10	50	125	3	1.0
As-U2-C2	As-U5-C5	As-U8-C8			20	65	250		0.5
As-U3-C3	As-U6-C6	As-U9-C9			35	80	500		0.25

As seen in the table above, nine concentrations were initially chosen for Arsenic testing, each concentration being tested with the three corn cob mass variations. Blanks were tested with each experiment, along with a raw of each concentration, consisting of the Arsenic concentration in DI water.

2.3.2.3 XRF Sorption Capacity Testing

The team was tasked to determine the amount of time it took for the corn cob to saturate with Arsenic. To do this, the team used an Arsenic concentration of 500 ppb and tested various masses of corn cob for each batch reaction, focusing on 0.5 and 0.25 grams of corn per flask. Each mass variation had an overall mass of 2 grams of corn for XRF analysis in the sample cups. With the three corn types, each mass was tested at 90 minutes, 3 hours, 4.5 hours, 6 hours, and 7.5 hours for sorption capacity.

The methodology determined by the team was based on the Cadmium and Arsenic analysis procedures. First, 2-gram samples of one corn cob type were weighed out and transferred into XRF analysis cups. The corn was analyzed with the XRF device, to determine how much

Arsenic was present before testing. The corn was then removed and weighed out according to mass discrepancy, 0.5 grams and 0.25 grams; there were four batch reactions containing 0.5 grams of corn cob and eight batch reactions with 0.25 grams of corn cob. Once the corn was weighed out, a 500 µg/L Arsenic solution was made for each Erlenmeyer flask. This was done with Sodium Arsenite, with the same methodology mentioned in the Arsenic Removal Method section. This Arsenic concentration was made in a 500 mL Erlenmeyer flask with a total volume of 300 mL. The flasks were then placed on the rotary shaker for the allotted time at 250 rpm. The flasks were taken off the shaker and filtered through a 45-µm glass fiber filter to separate the corn and liquid. Once the samples were filtered, the mass variations were combined (0.5- and 0.25-gram samples), dried overnight, placed in XRF cups, and scanned by the XRF machine to determine the final concentration of Arsenic after sorption. This was done for all corn variations at each time interval previously mentioned to determine the optimal reaction time to adsorb the maximum level of contaminant.

A summary of the experimental matrix can be found in Table 2-6. The full matrix including triplicates, corn masses, and standard solution information with the collected XRF data can be found in Appendix D.

Table 2-6: Sorption testing experimental matrix

Type of Contaminant	Type of Corncob Biosorbent	Initial Concentration (µg/L)	Replicates	Corn Cob Mass (g)	Contact Time (hr)		Samples per Test
Arsenic	Nitric Acid Citric Acid Untreated	500	3	1.0	3 6	4.5 7.5	2
Arsenic	Nitric Acid Citric Acid Untreated	500	3	0.5	3 6	4.5 7.5	4
Arsenic	Nitric Acid Citric Acid Untreated	500	3	0.25	3 6	4.5 7.5	8

*samples with a contact time of 1.5 hour testing were taken from the Arsenic testing

As seen in the experimental matrix, only 3-, 4.5-, 6-, and 7-hour time intervals were tested during the corn cob sorption tests since the 1.5-hour testing was completed during initial Arsenic testing. It should be noted again that this sorption test was only using Arsenic as a contaminant, and there was a set concentration of 500 µg/L.

The preliminary XRF readings of the corn cob were used as blanks to document the contaminant level in the corn before it was exposed to the samples. Liquid blanks were not applicable for XRF testing but were provided for ICP-MS with DI water solutions. Internal

14

standards were also created using the same standard solution volume to provide an initial concentration.

2.3.3 Total Coliforms Testing

The following sections describe the methodology used to test for Total Coliforms.

2.3.3.1 Total Coliforms Sample Preparation

Because quantifying Total Coliforms (*E. coli*) is more difficult than heavy metal contaminants in drinking water, the EPA regulates it differently and has determined the MCL as 5% of samples taken in a month can be contaminated. For this research, one wastewater sample was used to deliver Total Coliform to each trial. It was assumed the wastewater was homogenous, indicating equal volumes would deliver the same number of Colony Forming Units (CFU) to each sample. This did not allow for an exact number of initial CFU to be known; however, it did create a uniform dispersal of Total Coliform amongst all samples. This allowed for a quantifiable analysis between the three treatments of corn cob (nitric acid activated, citric acid activated, and untreated) and their separate removal efficiencies of Total Coliform. This wastewater was acquired from Rio de Flag Water Reclamation Plant as a primary effluent through Jim Huchel. It was advised by Huchel to dilute the effluent due to its high concentration of Total Coliform, so the sample was diluted (1:1) before any testing was conducted.

2.3.3.2 Total Coliforms Removal Method

Batch reaction sorption tests were conducted to treat the wastewater of Total Coliform using corn cob as a biosorbent. Triplicates of each biosorbent (nitric acid activated, citric acid activated, and untreated) were tested. One (1) gram of biosorbent was added to a 60 mL glass reaction vial and the 1:1 wastewater dilution was added to the vial. It was crucial to do this carefully to not lose any biosorbent mass and to ensure the vials were sealed with no air. Once the vials were prepared, they were placed on a rotary shaker for 90 minutes at 250 rpm. The solutions were filtered, and the wastewater was ready for serial dilution.

Because of the high Total Coliform concentration advisory, 6 dilutions were done for each sample (2x; 20x; 200x; 2,000x; 20,000x; 200,000x). An additional dilution was done for the raw wastewater sample (2,000,000x). Blanks with DI water and 1 gram of biosorbent were tested to analyze the corn's independent coliform concentration.

HACH 8074 (Coliforms, Total, Fecal and *E. coli*), a membrane filtration technique with m-Endo Broth Ampules, was used to quantify the removal of Total Coliform from contaminated water sources using a corn biosorbent 13].

A summary of the experimental matrix can be found in Table 2-7. This includes the dilution factor, the type of corn cob, and the corn cob mass.

Table 2-7: Total Coliforms testing experimental matrix

Sample Name *#=Dilution Factor	Type of Contaminant	Type of Corn Cob Biosorbent	Corn Cob Mass (g)	Analytical Method	Dilution Factor	Replicates
NA-S1-# NA-S3-# NA-S2-# NA-BLANK	Total Coliforms	Nitric Acid Activated Corn Cob	1.0	HACH 8074	2x 200x 20000x 20x 2000x 200000x	3
CA-S1-# CA-S3-# CA-S2-# CA-BLANK	Total Coliforms	Citric Acid Activated Corn Cob	1.0	HACH 8074	2x 200x 20000x 20x 2000x 200000x	3
UT-S1-# UT-S3-# UT-S2-# UT-BLANK	Total Coliforms	Untreated Corn Cob	1.0	HACH 8074	2x 200x 20x 2000x	3
RAW-#	Total Coliforms	--	--	HACH 8074	2x 200x 20000x 20x 2000x 200000x 2000000x	1

It should be noted that untreated corn only had four dilution factors, ranging from 2 to 2,000. Since untreated corn cob had a high removal efficiency, further testing was not required after the 2,000x dilution factor.

3.0   Analysis Methods

The following sub-sections discuss the various equipment and methods used to analyze Cadmium, Arsenic, and Total Coliforms samples.

3.1   Equipment for Analysis

The following sections describe the analytical equipment being used to quantify the final concentrations of Cadmium and Arsenic.

3.1.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS nebulizes solutions into an element's respective atomic ions using inductively coupled plasma for detection and measurement. ICP-MS analyzes Cadmium as Cadmium 111 and Cadmium 114; the instrumental detection levels for these isotopes are 0.5 ppb and 0.2 ppb, respectively. The instrumental detection level for Arsenic 75 is 0.5 ppb [14]. The ability to detect such low levels of these contaminants allowed for realistic drinking water contamination levels to be tested with very little, if any, instrumental uncertainty. Sub-contracting was done through the NAU Chemistry Department. Grant Hettleman conducted the ICP-MS assessment and educated the team on the operation of the instrument and data

utilization for further analysis. Cadmium and Arsenic samples were analyzed via ICP-MS with a base element of Ruthenium for both.

3.1.2 X-Ray Fluorescence (XRF)

Methods for scanning the corn cob and liquid used in Arsenic removal were created after reviewing the XRF user manual. The XRF device scans between 60 and 300 seconds at the user's discretion. After discussing the time intervals with an NAU graduate student well versed in the instrument, the team decided 180 seconds was enough to meticulously analyze each sample. This time duration was used for solid and liquid sample analysis.

Each sample, solid and liquid, was placed in an XRF sample cup using XRF thin-film sample supports. This vessel reduced the chances of contaminating the samples, as well as human error that can occur when using plastic bags, another form of XRF sample testing, and reduced the necessary amount of each sample. The latter was the most pivotal because preparing and activating the corn cob biosorbent is expensive both in labor and money, decreasing the feasibility of this project. The limit of detection (LOD) of Arsenic for the XRF machine is recommended at 10 ppm, which was higher than the concentrations the project was working with; however, the XRF was set to record Arsenic concentrations at 2 ppm [12]. With this, there was a high level of uncertainty, as the XRF machine is not confident in any detection of Arsenic below 10 ppm.

The data collected by the XRF device was exported to a PC for further analysis. Further results of analysis and detection of Arsenic in the corn cob samples is discussed below.

3.2 Cadmium Analysis Method

The sorbed mass of Cadmium to the corn cob was calculated using Equation 3-1.

Equation 3-1: Mass of Cadmium sorbed to corn cob

$$q = \frac{(C_i - C_f) * V}{m}$$

Where:

q = mass sorbed,
C_i = initial Cadmium concentration, and
C_f = final Cadmium concentration.

Removal efficiencies were calculated using Equation 3-2.

Equation 3-2: Removal efficiency

$$Removal\ Efficiency\ (\%) = \frac{C_i - C_f}{C_i} * 100\%$$

The data relationship is represented by the Freundlich isotherm, as seen in Equation 3-3.

Equation 3-3: Freundlich isotherm, empirical model

$$q = KC_f$$

Where:

q = mass sorbed,
K = empirical constant, and
C_f = final Cadmium concentration.

The Freundlich Isotherm model was chosen for the data analysis since the previous NAU research analyzed the data using the Freundlich Isotherm model; to ensure consistent results, the team used the same analysis method. The relationship in Equation 3-3 is based off Equation 3-1, where q is the mass of contaminant adsorbed, C_f is the final concentration, and K is the slope in the trendline function.

3.3 Arsenic Analysis Method

The Arsenic analysis was completed using the XRF collection device, by scanning the corn cob once batch reactions were completed for Arsenic sorbed to the corn cob. Once the data was obtained from the XRF machine, the final concentration was used in the mass balance, Equation 3-4, which can be found below.

Equation 3-4: Equation used to calculate contaminate adsorbed to corn cob

$$VC_{L,i} + mC_{s,i} = VC_{L,f} + mC_{s,f}$$

Where:

V = total volume of the liquid solution (L),
$C_{L,i}$ = initial As concentration of the liquid solution (µg/L),
m = mass of corn cob (g),
$C_{s,i}$ = initial As concentration in the corn as read by the XRF (µg/g),
$C_{L,f}$ = final As concentration of the liquid solution (µg/L), and
$C_{s,f}$ = final XRF As concentration in the corn reading (µg/g).

Using Equation 3-4, the contaminant sorbed to the biosorbent was determined, as well as the percent removal for each test.

3.4 XRF Sorption Capacity Analysis Method

The concentration of Arsenic in the liquid samples after testing was determined by taking the final reading of the XRF machine and completing a mass balance based on Equation 3-4,

seen in the previous section. From this, the contaminant sorbed to the biosorbent was determined, as well as the percent removal for each time interval and corn cob type.

3.5   Total Coliforms Analysis Method

After each sample had incubated, the colony forming units (CFUs) could be counted. Each petri dish was placed under a magnifying glass and the CFUs were counted, seen in Figure 3-1. In samples that had a high CFU count, one quarter of petri dish was counted, and that number was multiplied by a factor of 4 to give an estimate of the CFU count for the entire petri dish. If the CFU count could not be quantified, as seen in Figure 3-2, it was defined as Too Numerous to Count, or TNTC.
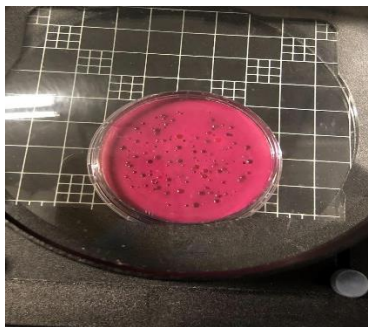
Figure 3-1: Coliform colonies under a magnifying glass

Figure 3-2: Sample that was defined as TNTC

4.0   Results of Analysis

The following sub-sections discuss the analysis of the results of the Cadmium, Arsenic, Sorption Capacity and Total Coliforms testing.

4.1   Cadmium Results

Using the method described in the previous section, the Cadmium analysis was done using the ICP-MS machine and followed the previous NAU research analysis methods. The results from Cadmium testing can be found in the table below, Table 4-1.

Table 4-1: ICP Cadmium data and analysis

Sample #	Std Conc (ppb)	ICP Reading, C_i (ppb)	q (µg/g)	C_f (µg/L)	$C_{f,ave}$ (µg/L)	Efficiency, η (%)	Ave Efficiency, $η_{ave}$ (%)
1B_Cd	5	7.33	2.20	2.61	2.39	64.45	67.34
1C_Cd	5	7.33	2.20	2.18		70.23	
2A_Cd	10	14.08	4.22	3.47	3.29	75.34	76.66
2B_Cd	10	14.08	4.22	3.24		76.97	
2C_Cd	10	14.08	4.22	3.14		77.68	
3A_Cd	20	27.88	8.36	4.97	4.75	82.18	82.98
3B_Cd	20	27.88	8.36	4.79		82.81	
3C_Cd	20	27.88	8.36	4.47		83.95	
4A_Cd	40	46.90	14.07	6.30	6.59	86.56	85.95
4B_Cd	40	46.90	14.07	6.82		85.46	
4C_Cd	40	46.90	14.07	6.64		85.84	
5A_Cd	60	68.01	20.40	9.15	8.88	86.55	86.94
5B_Cd	60	68.01	20.40	8.93		86.87	
5C_Cd	60	68.01	20.40	8.57		87.40	
6A_Cd	75	84.21	25.26	12.63	11.30	85.00	86.59
6B_Cd	75	84.21	25.26	11.31		86.57	
6C_Cd	75	84.21	25.26	9.95		88.19	
7A_Cd	100	112.91	33.87	14.75	15.43	86.94	86.33
7B_Cd	100	112.91	33.87	15.78		86.02	
7C_Cd	100	112.91	33.87	15.76		86.04	

Sample 1, listed in the first two rows, is the only sample concentration without triplicated data. This is due to the fact sample 1A was determined to be an outlier in the data, so it was disregarded for the analysis and results. As seen in Table 4-1, the average removal efficiencies can be found for all tests in the right column. There was a determined average removal efficiency of 81.33%.

The results determined for Cadmium removal using nitric acid treated corn cob from the previous NAU research team can be found in Table 4-2 below.

Table 4-2: 2019 ICP Cadmium data and analysis

Standard Conc (ppb)	ICP Reading, C_i (ppb)	Mass Cd Sorbed to Corn ($\mu g/g$)	C_f ($\mu g/L$)	$C_{f,ave}$ ($\mu g/L$)
10	8.47	2.541	N/A	N/A
20	25.60	7.68	1.05	1.05
35	35.40	10.62	1.35	1.32
35	35.40	10.62	1.28	
50	48.40	14.52	1.92	1.68
50	48.40	14.52	1.43	
75	70.60	21.18	2.20	2.16
75	70.60	21.18	2.11	

The results obtained by the 2019 research received an average removal efficiency of 97%. The replicates of the prior NAU corn cob capstone's Cadmium concentrations were samples 2, 3, and 6, at 10, 20, and 75 ppb, respectively, represented by color correlations.

A comparison of the isotherm developed from the 2019 analysis and the 2020 analysis can be found below, in Figure 4-1. A linear Freundlich Isotherm model was used.
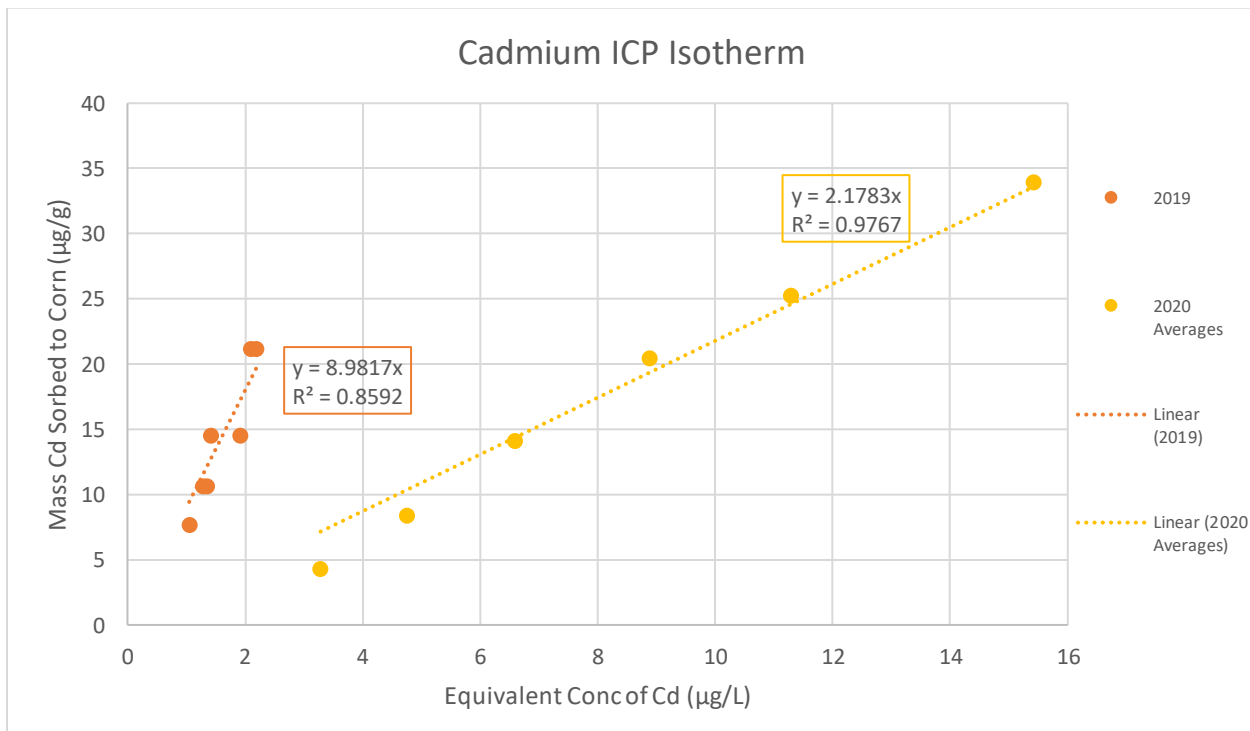
Figure 4-1: ICP Cadmium data and analysis, 2019 vs 2020 data

As seen in the figure above, the analysis from the 2019 research shows an R^2 value of 0.8592, while the 2020 research shows an R^2 value of 0.9715. Both analyses used a linear Freundlich Isotherm model for the correlation.

4.2 Arsenic Results

The following sections discuss the Arsenic results as analyzed by XRF and ICP-MS.

4.2.1 XRF Results

Analysis was performed using the XRF on the highest Arsenic concentration, 500 ppb, for citric acid treated (CA), nitric acid treated (NA), and untreated (UT) corn cob. Table 4-3 shows the contaminant levels found with the XRF for initial and final corn cob samples. The results presented in the table were the only Arsenic readings even though 82 XRF runs were completed.

Table 4-3: XRF results for Arsenic testing

SAMPLE	Ave XRF Reading (ppm)	Ave Liq Conc, $C_{f,ave}$ (ppb)	Std Deviation	ΔC	Ave % Removal, η_{ave}
UT_0.25g(2)i	2.41	515.82		-15.82	-3.21
UT_1g(1)	4.07	472.99		27.01	5.43
UT_0.5g(1)	3.06	479.55		20.45	4.08
UT_0.25g(1)	2.48	483.32		16.68	3.31
CA_1g(1)	3.15	479.08	0.523	20.92	4.19
CA_1g(2)		+	0.486		
CA_1g(3)		-	0.554		
CA_0.5g(1)	2.86	481.00	0.919	19.00	3.80
CA_0.5g(2)		+	1.052		
CA_0.5g(3)		-	0.651		
CA_0.25g(1)	3.21	478.72	1.250	21.28	4.26
CA_0.25g(2)		+	1.44		
CA_0.25g(3)		-	0.76		
NA_0.5g(1)	2.85	478.29		21.71	3.82
NA_0.25g(1)	3.85	472.84		27.16	5.15
UT_0.25g(1)L	1.49	489.92		10.08	-198

The value seen in parenthesis shows the replicate number from each test with provided data. The i and L after some of the values represent initial and liquid concentrations, respectively. For example, the first sample, UT_0.25g(2)i, was from testing performed prior to Arsenic sorption with untreated corn. The next nine samples are results from citric acid treated corn cob after Arsenic adsorption where the three masses and replicates all delivered data for analysis. The two nitric acid treated corn cob results were performed during sorption analysis since nitric acid adsorption was performed independently.

Furthermore, one of the liquid samples, L, from untreated corn cob recorded results below the detection range of 2ppm, but the error factor from the instrument, see raw data in Appendix E, was just high enough for it to be recorded.

4.2.2 ICP-MS Results

On the other hand, the ICP-MS results from Arsenic testing presented completely different final concentrations and removal efficiencies, most ending with more Arsenic than the initial concentration.

Table 4-4: ICP-MS results from Arsenic testing

As Sample #	Std Conc (ppb)	C_i (μg/L)	C_f (μg/L)	Efficiency (%)	Ave % Removal, η_{ave}
1B_As	10	10.51	33.44	-218.346	
1C_As	10	10.51	29.56	-181.383	-205.70
1D_As	10	10.51	33.34	-217.362	
2B_As	20	18.27	38.55	-111.006	
2C_As	20	18.27	42.08	-130.310	-123.02
2D_As	20	18.27	41.61	-127.742	
3B_As	35	30.48	54.91	-80.170	
3C_As	35	30.48	54.43	-78.602	-79.66
3D_As	35	30.48	54.93	-80.221	
4B_As	50	43.50	86.91	-99.797	
4C_As	50	43.50	91.95	-111.380	-106.35
4D_As	50	43.50	90.43	-107.877	
5B_As	65	53.03	105.95	-99.786	
5C_As	65	53.03	104.07	-96.243	-99.25
5D_As	65	53.03	106.97	-101.718	
6B_As	80	64.70	112.92	-74.516	
6C_As	80	64.70	111.80	-72.781	-62.20
6D_As	80	64.70	90.13	-39.298	
7B_As	125	102.73	176.97	-72.272	
7C_As	125	102.73	179.03	-74.278	-72.11
7D_As	125	102.73	174.40	-69.767	
8B_As_100X	250	189.43	292.17	-54.236	
8C_As_100X	250	189.43	281.20	-48.446	-51.48
8D_As_100X	250	189.43	287.44	-51.744	
9B_As_100X	500	374.89	370.42	1.193	1.19
9C_As_100X	500	374.89	367.11	2.076	2.08

The results from the ICP-MS analysis of the Arsenic testing show a negative removal efficiency for 8 of the 9 concentrations tested for the experiment. From this analysis, it is determined that there was a higher concentration of Arsenic in the liquid solution after the experiment occurred than the initial concentration of Arsenic.

4.3 XRF Sorption Capacity Testing Results

Table 4-5 presents recorded and determined data for Arsenic analysis at 500 ppb, from a total of 52 XRF readings, for an exact corn mass of 2 grams in each XRF sample cup. All raw data and complete analysis can be seen in Appendix D.

Table 4-5: XRF Arsenic data and analysis for 500 ppb at 2 grams of corn cob

SAMPLE	Ave XRF Reading (ppm)	Ave Liq Conc, $C_{f,ave}$ (ppb)	ΔC	Ave % Removal, η_{ave}
CA_0.5g_3hr	2.10	480.68	19.32	2.83
CA_0.25g_4.5hr	1.93	483.88	16.12	2.59
NA_0.5g_7.5hr	3.22	475.40	24.60	4.32
NA_0.5g_3hr	1.95	482.61	17.39	2.62
NA_0.25g_7.5hr	2.40	484.00	16.00	3.20
NA_0.25g_3hr	3.01	478.34	21.66	4.03
UT_0.5g_7.5hr	3.56	474.95	25.05	4.76
UT_0.5g_6hr	4.45	467.75	32.25	5.96
UT_0.5g_4.5hr	3.94	470.97	29.03	5.28
UT_0.5g_3hr	5.74	455.19	44.81	7.75
UT_0.25g_7.5hr	4.66	467.07	32.93	6.24
UT_0.25g_6hr	4.40	468.53	31.47	5.89
UT_0.25g_4.5hr	3.14	476.83	23.17	4.21
UT_0.25g_3hr	8.51	433.32	66.68	11.58

UT stands for untreated corn cob, CA is for citric acid treated corn cob, and NA represents nitric acid treated corn cob. Experiments performed for the sorption capacity test are recorded with time intervals. Figure 4-2 is a graph of the final concentration of Arsenic for untreated corn cob related to the time interval tested at a 2-gram correlation for corn mass, as untreated corn cob had the best removal results of all three types of corn cob used.
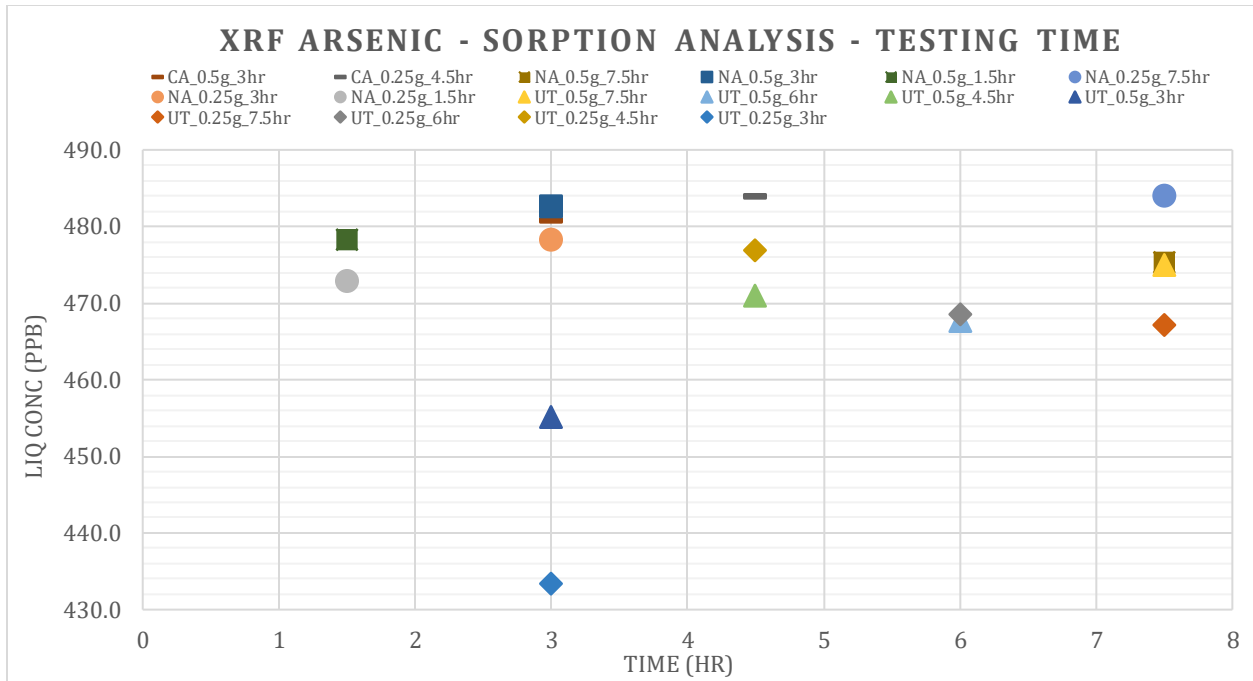
Figure 4-2: XRF Arsenic sorption analysis for 500 ppb at 2 grams of corn cob

The graph depicts final liquid concentrations of Arsenic against the time interval tested. As shown in the figure, as well as in Table 4-5, untreated corn cob tested at a 3-hour interval proved to have the best removal results for Arsenic contamination. Data for individual corn cob type results can be found in Appendix D.

4.4 Total Coliform Testing Results

The data and corresponding analysis for the testing of Total Coliform removal from water can be found in Table 4-6 through Table 4-8. All corn cob biosorbent types, nitric acid treated, citric acid treated, and untreated were tested. The average removal efficiencies for each corn type were calculated, nitric acid treated corn was 80.65%, 89.20% for citric acid treated corn, and the best removal efficiency of 98.69% was calculated for the untreated corn. For the graphical representation of this analysis, please see Appendix F for Figure F-1 through Figure F-3. The raw data is also presented in Appendix F.

Table 4-6: Results of Total Coliform removal with nitric acid treated corn cob

Nitric Acid Corn					
Sample ID	Corn Mass (g)	Dilution Factor	CFU Count	Removal Efficiency (%)	Average Removal Efficiency (%)
1	1.0011	2	TNTC	N/A	91.86
1		20	TNTC	N/A	
1		200	496	95.06	
1		2000	134	86.65	
1	1.0156	20000	0	100.00	
1		200000	1	85.71	
2	0.99	2	TNTC	N/A	73.65
2		20	TNTC	N/A	
2		200	896	91.08	
2		2000	420	58.17	
2	1.0097	20000	6	73.91	
2		200000	2	71.43	
3	0.99	2	TNTC	N/A	76.45
3		20	TNTC	N/A	
3		200	624	93.78	
3		2000	478	52.39	
3	1.0116	20000	6	73.91	
3		200000	1	85.71	
BLANK	1.0078	2	7		80.65
BLANK		20	1		
BLANK		200	1		
BLANK		2000	2		
BLANK		20000	0		

Table 4-7: Results of Total Coliform removal with citric acid treated corn cob

Sample ID	Corn Mass (g)	Dilution Factor	CFU Count	Removal Efficiency (%)	Average Removal Efficiency (%)
Citric Acid Corn					
1	1	2	TNTC	N/A	94.40
1		20	896	99.11	
1		200	283	97.18	
1		2000	57	94.32	
1	1.0093	20000	1	95.65	
1		200000	1	85.71	
2	1	2	TNTC	N/A	88.47
2		20	916	99.09	
2		200	224	97.77	
2		2000	42	95.82	
2	1.011	20000	5	78.26	
2		200000	2	71.43	
3	1	2	TNTC	N/A	83.60
3		20	TNTC	N/A	
3		200	410	95.92	
3		2000	100	90.04	
3	1.0098	20000	2	91.30	
3		200000	3	57.14	
BLANK	1	2	6		89.20
BLANK		20	4		
BLANK		200	4		
BLANK		2000	2		

Table 4-8: Results of Total Coliform removal with untreated corn cob

Untreated Corn					
Sample ID	Corn Mass (g)	Dilution Factor	CFU Count	Removal Efficiency (%)	Average Removal Efficiency (%)
1	1	2	580	99.94	99.83
1		20	136	99.86	
1		200	29	99.71	
1		2000	2	99.80	
2	1	2	588	99.94	99.92
2		20	98	99.90	
2		200	16	99.84	
2		2000	0	100.00	
3	1	2	TNTC	N/A	93.96
3		20	TNTC	N/A	
3		200	323	96.78	
3		2000	89	91.14	
BLANK	1.01	2	0		98.69
BLANK		20	0		
BLANK		200	0		
BLANK		2000	0		

With the results presented in Tables 4-6 through 4-8, the results show that untreated corn cob had the best removal efficiency across a smaller range of dilution factors. The triplicates were treated with 1 gram of corn cob. A removal efficiency for each dilution factor was determined to calculate the average removal efficiency for each triplicate. From there, the overall removal efficiency was calculated.

5.0 Discussion

The following sub-sections expand on and discuss the results of analysis of the Cadmium, Arsenic, Sorption Capacity and Total Coliform testing.

5.1 Cadmium Discussion

Data from 1A, in Table 4-1, had been removed since the removal efficiency was calculated to be 44.92%. Since the final concentration was significantly greater than 1B and C, 1A was not factored into the results, leaving two samples to be averaged. All dilution factors were 10 for ICP-MS testing and presented data within the set parameters from 0 to 20 ppb. Additionally, samples 1 and 2, at 5 and 10 ppb, respectively, had lower removal efficiencies compared to the other concentrations. This is assumed to be the effect of further diluting the Cadmium standard to more accurately disperse the initial volume. This also presents a justification for sample 3 being slightly lower as well.

Looking at Table 4-2, only sample 1C, from Table 4-1, had a final concentration able to be correlated with the data. Based on the results in Table 4-2, sample 1 should have had the lowest concentration. No results were available for their 10 ppb experiments, but the rest of the data represents a decrease in concentration for each standard. Figure 4-1 shows the data from both year's Cadmium ICP-MS sorption tests.

As seen in Figure 4-1, and discussed above, the points for the 2019 data and the 2020 data do not relate. However, the individual years have good, relative data, as presented by their respective linear R^2 values of 0.8592 and 0.9767, when the y-axis is set at zero. These differences were mentioned previously since both data sets provide adequate results, just not between each data set. This has been attributed to several plausible variables. These variables have been narrowed down to the following: different personnel taking over the research a year after the initial research was conducted, the time difference leading to different corn harvests may have yielded corn with different properties, and the lack of information in the previously published nitric acid activation methodology, discovered after consultations with the previous research's team.

5.2 Arsenic Discussion

From these results, the team has determined untreated corn cob to be an unfeasible treatment technique for use with the XRF. Citric acid activated corn cob provided the most consistent results, but the LOD range was nominal and significantly below the recommended range for the XRF. Nitric acid treated corn cob also presented decent results, but the insufficient range of data below 10 ppm makes it impossible to determine whether the results are accurate or instrument flaws.

As displayed in Table 4-4, ICP-MS samples 1 through 7 were diluted 10 times, but samples 8 and 9 required a dilution factor of 100. It should also be noted that the initial concentration was read as the 'A' category for each sample. As seen for all concentrations except sample 9, the 500-ppb standard, the final concentrations are greater than initial ones, leading to a negative removal efficiency. Sample 9B was also tested using the XRF machine, the sample sent to ICP-MS being the liquid matrix, from a 0.5-gram nitric acid treated corn cob mass determinant. A 0.25-gram mass was used similarly for sample 9C. While there was minimal positive removal recorded with the ICP-MS device, there were no results for these masses at a 1.5-hour time interval documented with the XRF machine, leaving the results to be indeterminant. Additional research may provide different results, but the team decided corn cob was not a viable treatment method for the removal of Arsenic in water sources. It would also be beneficial to check the calculations used to transfer the stock solution at the desired concentration since the initial concentration of sample 9 was significantly smaller than 500 ppb, potentially contributing to the insufficient XRF data.

5.3 XRF Sorption Capacity Discussion

Based on the results seen in Table 4-5 and Figure 4-2, untreated corn cob has the most consistent results with higher XRF readings. The range between 0.5 grams and 0.25 grams does not appear to follow the expected results, with some of the 0.25-gram tests having higher removal efficiencies but not all. Citric acid treated corn cob did not have good results with only two tests providing final concentrations at different masses and times. These results are on the borderline for the LOD with the XRF making them even less accurate. Nitric acid treated corn also had satisfactory results, however there were none for the 6-hour time interval and the final concentrations were less accurate with values closer to 2 ppm.

5.4 Total Coliforms Discussion

The higher removal efficiency by the untreated corn cob, as seen in Table 4-8, has been attributed to the possible organic properties and nutrients that are stripped of the corn in the acid treatment process. The biological properties of Total Coliform may be more susceptible to adsorbing to these organic properties and nutrients and rather than the chemical properties that the treated corn cob biosorbents possess.

It is noteworthy to state the blank samples for nitric acid and citric acid treated corn cob with just DI water solution, had traces of Total Coliforms in them. This is believed to be from a stripping of nutrients in the corn cob during the acid treatment process, leaving more sorption sites for contaminants in the air.

6.0 Impacts

This research project can benefit and impact marginalized communities immensely, as well as the environment surrounding these communities. The Triple Bottom Line (social, economic, and environmental) has been addressed regarding this alternative water treatment process.

6.1 Social Impacts

With the potential implementation of a water treatment system utilizing corn as a biosorbent for the removal of Cadmium, Arsenic and *E. coli*, changes will be made to the surrounding communities and areas of impact. The main priority of any water treatment facility is to improve the overall health of the community. Secondary effects include the creation of jobs focused around the treatment process and an increase in recreational use of local surface water bodies. Most of the outlined social impacts relates to the health impacts on the personnel working with the treatment process but also on the community members themselves. In order to protect the health of all facility personnel, there are strict standards and safety procedures in place to ensure work is as smooth as possible. Additionally, with the overall purpose being the increased health of the public, efforts to

treat contaminated waters that often have severe health effects on humans will have beneficial effects on other systems. In marginalized communities like the Navajo Nation, there are often not enough medical workers to placate the needs of the community. In the event of any of these contaminates entering the water supply, the medical system would be overwhelmed with the volume of people affected. In these situations, having a treatment process in place would put less strain on the health service system by reducing the number of people getting sick from the contaminate.

6.2   Economic Impacts

The economic impacts of potentially implementing this water treatment system would combine both the environmental and social impacts to the local communities' economy. For instance, there would be economic stimulation from the creation of jobs within the community. The cleaner waters would give more opportunities for the community to economically expand in areas like tourism, population sustainability, increase recreational activities, and agricultural activities. Additionally, it would be beneficial to investigate implementing this treatment method in areas where agriculture and livestock-related activities commonly occur. In these rural areas, there could be an influx of *E. coli* events throughout the year.

6.3   Environmental Impacts

With the removal of Cadmium, Arsenic, and *E. coli* from contaminated waters, using strong acids and bases for various steps of the process will likely result in environmental impacts of varying degrees during the treatment process as well as during the implementation of a full-scale system. The impacts have yet to be fully defined and assessed but will be based on the testing and research already completed for the project. The most evident environmental impact is the hazardous health effects of these substances after introduced into the environment. Both nitric and citric acid are used during the activation process and are byproducts carried throughout the entire treatment process, eventually meeting their fate as waste products sorbed into the corn cob biosorbent. At the final stage of the system, the genuine disposal of the hazardous waste would need to be evaluated based on the site location and the available resources. There are various disposal methods available such as incineration, the use of an autoclave from the introduction of biological material in the *E. coli* testing, general disposal at a landfill, disposal through another third-party entity, or even the possibility of extracting the heavy metals from the biosorbent after removal. Another promising route that can be further researched is using the corncob waste as burning fuel for heat sources. This potential method would fall under the incineration disposal method.

7.0 Recommendations

It is recommended to further research and test the removal efficiency of a weak acid treated biosorbent with Cadmium. It has already been proven that nitric acid treated corn can remove Cadmium at a high removal efficiency, so it would be more reasonable and less hazardous for marginalized communities to use citric acid to activate the biosorbent. The removal may be even better with a weak acid than the strong acid, as found in some published research [1].

If further XRF testing of the sorption of Arsenic using a corn cob biosorbent is conducted, higher initial concentrations of Arsenic are recommended. If this is done, use caution because of the hazards present when working with Arsenic. It may be helpful and provide better analyses if the final mass of the corn cob is measured after the sorption test and before the XRF reading. This value would have allowed for more accurate mass balance calculations.

Other methodologies for quantifying Total Coliform removal by a corn cob biosorbent should be used to confirm the results and analysis done using HACH 8074. Additional published methodologies can be used to quantify Total Coliform including: Standard Method 9222 J Total Coliform and *E. coli* by Dual Chromogen Membrane Filter Procedure, EPA Method 1604 Total Coliforms and *Escherichia coli* in Water by Membrane Filtration Using a Simultaneous Detection Technique (MI Medium), and HACH Method 10029 Coliforms, Total and *E. coli*.

Since this research project did not include a prototype, the team was unable to accurately and effectively calculate a scale-up factor to be used in the design of a full-scale treatment process. Based on the cost analysis of implementing a full-scale system in marginalized communities, it was determined supplementary research and testing must be performed to decrease the personnel and O&M costs. It would also be beneficial to calculate the amount of corn cobs needed beyond what may be used within a marginalized community. However, this would depend greatly on the growing season and harvest year-to-year. Cadmium would be removed significantly in this system, but further testing is required to determine other contaminant removal efficiencies. Other recommendations include supplementary quantification of Total Coliforms using additional methodologies.

8.0 Statistical Analysis

A t-test analysis for the data collected in both the Total Coliforms analysis and Cadmium analysis were conducted for statistical analysis purposes. T-testing is used in hypothesis testing when deciding if the null hypothesis should be supported or rejected [15]. The Total Coliforms and Cadmium analysis were chosen due to the amount of data gathered, as well as having valid triplicates, and there being multiple sample populations. This analytical method would not work for the sorption capacity test because each time interval resulted

in only one initial and final reading. The same limitations are present for the XRF analysis completed for Arsenic testing.

The type of t-tests used depends on the sample populations being evaluated which affects their corresponding parameters and conditions. Generally for the sample populations of interest, there is an assumption of independence (i.e. when there are two independent, categorical groups), an assumption of normality (i.e. when a dependent variable is approximately normally distributed), and an assumption of homogeneity of variance (i.e. when the variance among the sample set is equal) [15][16]. In most cases, it cannot be confirmed if the variances are equal or not unless explicitly stated within the context of the situation, so the team decided to use the two-sample unequal variances t-test. Additionally, the team opted to use two-tailed metrics to determine the statistical significance of the sample set. This approach is highly encouraged by various sources [15][16].

For the two-sample approach, it is important to note that the team only compared each acid-treated types of corn cob to the untreated corn cob. The purpose of this analysis was to see if any conclusions could be made regarding the relationship between the different types of acid-treated corn cob and the standard, untreated corn cob. The p-value, or probability value, used in the analysis was 5%, which is standard when conducting t-tests. The null hypothesis for all t-tests conducted is as followed: the means of both sample sets are equal and there is no difference between the values. These parameters were applied to the entire analysis and the following tables outline the results of the Total Coliforms analysis:

Table 8-1: Nitric acid vs. untreated corn cob information and initial conditions

NA Removal Efficiencies (%)	UT Removal Efficiencies (%)	Null Hypothesis:
91.86	99.83	Means are the same
73.65	99.92	p = 0.05
76.45	93.96	

Table 8-2: Results of t-test for nitric acid vs. untreated corn cob

t-Test: Two-Sample Assuming Unequal Variances		
Sample Set	*Nitric Acid Corn Cob*	*Untreated Corn Cob*
Mean	80.65	97.90
Variance	96.14	11.67
Observations	3	3
Hypothesized Mean Difference	0	
df	2	
T-Stat	-2.88	
P-value (two-tail)	0.10	
T-Critical Value (two-tail)	4.30	

Table 8-3: Citric acid vs. untreated corn cob information and initial conditions

CA Removal Efficiencies (%)	UT Removal Efficiencies (%)	Null Hypothesis:
94.40	99.83	Means are the same
88.47	99.92	p = 0.05
83.60	93.96	

Table 8-4: Results of t-test for citric acid vs. untreated corn cob

t-Test: Two-Sample Assuming Unequal Variances		
Sample Set	*Citric Acid Corn Cob*	*Untreated Corn Cob*
Mean	88.82	97.90
Variance	29.22	11.67
Observations	3	3
Hypothesized Mean Difference	0	
df	2	
T-Stat	-2.46	
P-value (two-tail)	0.09	
T-Critical Value (two-tail)	4.30	

The following tables outline the results of the Cadmium analysis between the 2019 and 2020 experimental process.

Table 8-5: 2019 Cadmium data vs. 2020 Cadmium data information and initial conditions

2019 Cadmium Removal Efficiencies (%)	2020 Cadmium Removal Efficiencies (%)	Null Hypothesis:
96	67.34	Means are the same
96	76.66	p = 0.05
97	82.98	
97	85.95	
	86.94	
	86.59	
	86.33	

Table 8-6: Results of t-test for 2019 Cadmium data vs 2020 Cadmium data

t-Test: Two-Sample Assuming Unequal Variances		
Sample Set	*2019 Cadmium Data*	*2020 Cadmium Data*
Mean	96.50	81.83
Variance	0.33	54.00
Observations	4	7
Hypothesized Mean Difference	0	
df	6	
T-Stat	5.25	
P-value (two-tail)	0.00	
T-Critical Value (two-tail)	2.45	

The results of this analysis allowed for the team to make conclusions regarding the data sets and their relation to one another. The major takeaways from the t-test revolve around the calculated p-values, experimental t-values (t-stat), and t-critical values. For the null hypotheses, there was an initial condition of making p=0.05; this p-value directly relates to the t-critical values which are outlined in a standardized t-table [17]. A summary of the results is seen in the following table:

Table 8-7: Results of t-test for all analyses

Results of Two Sample T-Test with Unequal Variances			
Sample Set	*NA vs. UT*	*CA vs. UT*	*2019 vs 2020*
Null	0.05	0.05	0.05
T-Stat	-2.88	-2.46	5.25
P-value (two-tail)	0.10	0.09	0.002
T-Critical Value (two-tail)	4.30	4.30	2.45
P-value vs. Null	P > Null	P > Null	P < Null
T-Crit vs T-Stat	T-Crit > T-Stat	T-Crit > T-Stat	T-Crit < T-Stat
Null Hypothesis	Not Rejected	Not Rejected	Rejected

The t-test shows the significant difference between sample sets and whether the differences could have been up to chance. The t-value is a ratio between the difference of two sets of data compared to the difference within the set itself. So, a larger t-value shows that the sample sets are different while a smaller t-value shows that the sample sets are similar. In other words, the larger the t-value, the more likely it is that the results are repeatable [15]. Additionally, having lower p-values is better for the analysis because it indicates that the data did not occur by chance. The negative t-stat values indicate a reverse direction within the distribution and do not affect the overall statistical significance of the data set. To account for this occurrence, the analysis compares the absolute values of t-stat to the t-critical values.

In conclusion, the absolute values of t-stat are less than the t-critical values for the Total Coliforms analysis. The opposite case is seen in the Cadmium analysis. In the Total Coliform analysis case, the results suggest that the means of the two groups are not statistically significant (i.e. the null hypothesis is not rejected). In the Cadmium analysis case, the results indicate that the means of the two groups are statistically significant (i.e. the null hypothesis is rejected). By rejecting the null hypothesis, there seems to be a definite, consequential relationship between the two sample sets. By not rejecting the null hypothesis, there does not seem to be an identifiable, consequential relationship between the two sets of data. Further statistical analysis is needed to further expand the results of this analysis.

9.0 Summary of Engineering Work

Due to a three-week, unexpected delay at the beginning of the project, the research was put behind schedule. As shown in the original Gantt chart in Appendix G, lab work, starting with the activation processes, was set to be completed by January 11; however, we did not get lab access until February 20. This set back was addressed by completing all lab work in 5 weeks, a cumulative 506 hours by the Lab Assistant. Regarding the original Gantt chart: lab work was supposed to be completed on March 20, but the real completion date was April 1, 1.5 weeks behind schedule. Rather than waiting to analyze the data when all research was completed, analysis was completed as the data was gathered. This made up for the 3 weeks of lost time at the beginning of the project. The continual data collection and data analysis combined with continual corn activation allowed for sorption tests to be continuously conducted. Eliminating wait time between the activation processes and the sorption testing, allowed for a more effective use of time. The time allotted between February 20 and April 1 was valuable because of the ever-changing testing required due to the requested data. From these schedule changes, with delay in the start date and the abrupt closure of the Environmental Lab and the need to finish all lab work in a condensed amount of time, an updated Gantt chart can be found in Appendix G.

Table 9-1: Original table for task hours

Task	SENG hrs	ENG hrs	LAB hrs	INT hrs	AA hrs
1.1 Corn Preparation	4	0	250	80	0
1.1.1 Biosorbent Preparation	2	--	150	40	--
1.1.2 Activated Biosorbent Prep	2	--	100	40	--
2.1 Cadmium Testing	--	25	40	10	--
2.2 Arsenic Testing	--	30	60	10	--
2.3 Total Coliform Testing	--	25	35	10	--
3.1 Cadmium Analysis	15	30	--	5	5
4.0 Project Impacts	6	10	--	--	2
5.0 Project Deliverables	20	20	--	--	30
6.0 Project Management	30	10	15	5	15
Subtotal	95	210	400	120	52
Total Hours	877				

Table 9-2: Actual table for task hours

Task	SENG hrs	ENG hrs	LAB hrs	INT hrs	AA hrs
1.0 Weak Acid Decision Matrix	2	3	0	0	0
1.1 Weak Acid Determination	--	--	--	--	--
1.1.1 Weak Acid Decision Matrix	--	3	--	--	--
1.1.2 Decision Matrix	2	--	--	--	--
2.0 XRF Method Development	4	4	10	0	0
2.1 XRF Corn Cob Testing Method	2	2	5	--	--
2.2 XRF Solution Cob Testing Method	2	2	5	--	--
3.0 Biosorbent Preparation	0	0	209.5	51	0
3.1 Corn Preparation	0	0	209.5	51	0
3.1.1 Biosorbent	--	--	77.5	36	--
3.1.2 Activated Biosorbent	--	--	132	15	--
4.0 Testing of Contaminants	5	7	286.5	6.5	0
4.1 Sample Preparation	5	7	1	0	0
4.1.1 Cadmium Sample Preparation	2	2	--	--	--
4.1.2 Arsenic Sample Preparation	3	5	--	--	--
4.1.3 Total Coliform Sample Prep	--	--	1	--	--
4.2 Cadmium Testing	--	--	48	--	--
4.3 Arsenic Testing	--	--	211.5	6.5	--
4.3.1 Chemistry Department Planning	3	--	--	--	--
4.4 Total Coliform Testing	--	--	26	--	--
5.0 Analysis	0	15	0	0	0
5.1 Cadmium Analysis	--	7.5	--	--	--
5.2 Arsenic Analysis	--	6.5	--	--	--
5.3 Total Coliform Analysis	--	1	--	--	--
6.0 Project Impacts	3	0	0	12	0
6.1 Environmental Impacts	1	--	--	1	--
6.2 Social Impacts	1	--	--	1	--
6.3 Economic Impacts	1	--	--	10	--
7.0 Project Deliverables	19.5	32	0	2	14
7.1 CENE 486C	18.5	32	0	0	12
7.1.1 30% Deliverables	7.5	--	--	--	5
7.1.2 60% Deliverables	2	13.5	--	--	4
7.1.3 90% Deliverables	4	18.5	--	--	1
7.1.4 Final Deliverables	5	--	--	--	2
7.2 UGRADS	1	--	--	2	2
8.0 Project Management	57	26	0	0	0
8.1 Meetings	26	26	0	0	0
8.1.1 Clients/TA Meetings	14	14	--	--	--
8.1.2 GI Meetings	8	8	--	--	--
8.1.3 General Meeting Requirements	4	4	--	--	--
8.2 Project Schedule	3	--	--	--	--
8.3 Resource Management	28	--	--	--	--
Subtotal	90.5	87	506	71.5	14
Total Hours	769				

With the information from Table 9-1 and 9-2, the predicted total hours of the project was 877, while the actual total hours of the project was 769. This discrepancy is attributed to a

lower number of actual hours by the Senior Engineer working on the project, as well as a shortened methodology for nitric acid activation.

10.0 Summary of Engineering Costs

To calculate the total cost for the engineering services provided by this research project, personnel hours, supply expenses, and subcontracting costs were evaluated. Personnel hourly rates were determined from prior information provided by practicing professionals that are familiar with the present hourly rates in the industry. These hourly rates are for a Senior Engineer (SENG), Project Engineer (ENG), Laboratory Assistant (LAB), Intern (INT), and Administrative Assistant (AA). The original estimate for personnel costs was $79,276, seen in the first section of Table 10-1.

Table 10-1: Original staffing and cost table

Cost Table					
	Classification	Hours	Rate, $/hr	Cost	
1.0 Personnel	SENG	95	194	$	18,430
	ENG	210	117	$	24,570
	LAB	400	82	$	32,800
	INT	120	19	$	2,280
	AA	52	23	$	1,196
	Total Personnel			**$**	**79,276**
	Item	Quantity	Cost	Total	
2.0 Supplies	Corn cob	100	0.75	$	75
	Total Coliform Testing Kit, 50 Bottles	1	218	$	218
	Total Coliform Testing Kit, 15 Brilliant Green Tubes	2	32.15	$	64
	0.45 μm filters, 100 units	1	3.79	$	4
	Citric Acid, 100g	1	36.10	$	36
	Environmental Lab Access, per day	45	100	$	4,500
	Geotechnical Lab Access, per day	10	100	$	1,000
	Total Supplies			**$**	**5,897**
	Item	Quantity	Cost	Total	
3.0 Subcontract	NAU Chemistry Dept, ICP Testing	54	30	**$**	**1,620**
4.0 Total				**$**	**86,793**

Table 10-2 shows the updated, actual staffing and supply cost summary.

Table 10-2: Actual staffing and cost table

Cost Table					
	Classification	Hours	Rate, $/hr	Cost	
1.0 Personnel	SENG	90.5	194	$	17,557
	ENG	87	117	$	10,179
	LAB	506	82	$	41,492
	INT	71.5	19	$	1,359
	AA	14	23	$	322
	Total Personnel			**$**	**70,909**
	Item	Quantity	Cost	Total	
2.0 Supplies	Corn cob	230	0.75	$	173
	Sodium Hydroxide	1 L	65	$	65
	Nitric Acid	2.5 L	242.81	$	243
	Citric Acid, Ball	7.5 oz	6	$	6
	Sodium Arsenite	1 g	20.9678	$	21
	Cadmium HACH Standard (100 mg/L)	100 mL	27.95	$	28
	HACH m -Endo Broth, 50 ampules/pack	2 packs	84.45	$	169
	HACH dish w/pad, 50 dishes/pack	2 packs	79.35	$	159
	0.45 µm filters, 100 units/pack	1 pack	3.79	$	4
	Geotechnical Lab Access, per day	19	100	$	1,900
	Environmental Lab Access, per day	26	100	$	2,600
	Total Supplies			**$**	**5,367**
	Item	Quantity	Cost	Total	
3.0 Subcontract	NAU Chemistry Dept, ICP Testing	50 tests	500	**$**	**500**
4.0 Total				**$**	**76,787**

After the completion of the project, the exact cost for personnel labor was $70,909, seen in the top section of Table 10-2, above. There was a decrease of $8,387 attributed to the number of hours put in by the Laboratory Assistant, offset by a large reduction in the hours put in by the Project Engineer as estimated prior to beginning the research. There was also a reduction in supplies used.

The middle section of Tables 10-1 and 10-2 break down the supplies and equipment that were thought to be required and the supplies and equipment used. There was a change in

HACH method used for the Total Coliform testing that required a different agar than the previously decided HACH method, 10029. In HACH method 8074, m-Endo Broth was used instead of m-ColiBlue24 as prescribed by the methodology initially ascertained (HACH 10029). In addition, several other chemicals were purchased for the research procedures and price changes were made to represent the actual price spent for the consumed chemicals. A few chemicals were overlooked in the original cost estimate such as the contaminant standards and acids and bases. There was significantly more corn needed to complete this research, increasing the quantity of corn cobs, leading to an overall cost increase. This increase may have been evened out by the decrease in days spent in each of the laboratories, Geotechnical and Environmental. The original estimate for supplies and laboratory rental expenses was $5,897, seen in the middle section of Table 10-1. The true cost for supplies and rental expenses was $5,367, seen in the middle section of Table 10-2. The difference in the estimated and the real costs is attributed to additional chemicals purchased throughout the testing process, a decrease in the amount of days spent in each of the two labs, and the increase in the amount of samples and testing that was actually conducted that required more corn, chemicals, and equipment. The difference between the proposed and the actual cost of supplies was $570.

The last expense of this research project was the subcontracted work done by the Chemistry Department to run ICP-MS analysis. There were many samples that needed to be analyzed, about 50 was the original estimate. The Chemistry Department agreed to analyze all the samples for $500. This cost was much less than the original estimate of $900, the value estimated at the bottom of Table 10-1. The difference of $400 saved this project a large sum of money.

The overall actual cost of the engineering services provided by this research project was $76,787, the final number in Table 10-2. The estimated cost of the engineering services provided by this research project was $86,793, found in Table 10-1. The difference between the estimated and the actual cost of this project was $10,006.

11.0 Conclusion

For the corn cob biosorbent capstone research project, various conclusions were made about the effectiveness of the biosorbent, the treatment of the biosorbent, and the contaminants that were used for the research. A correlation between Cadmium removal and corn cob as a biosorbent was expanded on, proving that nitric acid treated corn maintained a high percent removal consistent with previous research. Research on the effectiveness of corn cob used for the removal of Arsenic was studied, and it was determined that corn cob was not effective at removing Arsenic. Corn cob was also tested as a biosorbent for the removal of Total Coliforms from contaminated water and had great removal success.

With all the data collected throughout the capstone project, conclusions and correlations were developed in accordance with the objectives of the project. The list of objectives is provided below.

1. Expand Cadmium removal data using corn cob as a biosorbent.
2. Evaluate the efficiency of corn cob as a biosorbent in the removal of Arsenic and Total Coliform.
3. Evaluate the efficiency of corn cob activation using a weak acid.
4. Develop an analytical method for the use of the XRF machine for organic materials and liquids.
5. Present research at various research symposiums.
6. Help publish the research found on the removal of Cadmium using corn cob as a biosorbent.

In addressing Objective 1, the Cadmium data collected and analyzed this semester was unable to expand on the data results from the NAU 2019 capstone team, as it was adequate for separate publication. Objective 2 was met, as it was evaluated from the analysis that corn cob did not effectively remove Arsenic, but it did effectively remove Total Coliforms in contaminated waters. Objective 3 was also addressed in Arsenic and Total Coliform testing. Citric acid was the selected weak acid for the project treatment and proved to be the best treatment for Total Coliform removal. Due to the conclusion that corn cob was an ineffective biosorbent in the removal of Arsenic, citric acid could not be thoroughly analyzed as an effective acid activation treatment of corn cob for Arsenic removal. Objective 4 was partially addressed, as a methodology was created for the analysis of organic material but not for liquids. Corn cob was extensively tested using the XRF machine, but the LOD was too high for the concentrations dealt with in this project and leading to unreliable results. Objective 5 was not completed for this project. The team participated in one symposium, the Northern Arizona University Undergraduate Symposium, but did not participate in any other presentations or symposiums during the length of the project. The last objective, Objective 6, has not yet been addressed, but will be addressed after the project is completed and the team has graduated per the client's request. The data collected for Cadmium testing will be further analyzed and polished, allowing for the team to compose and complete a research article that has the potential to be published.

The corn cob biosorbent capstone research project has completed 5 of the 6 listed and described objectives of the project throughout the Spring 2020 semester.

12.0 Works Cited

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Appendices

Appendix A – Cadmium Experimental Matrix

Table A-1: Complete Cadmium testing experimental matrix

Date of Test	Sample ID	Standard (µg/L)	Final Volume (mL)	Volume Std Delivered (mL)	µL	Corn Mass (g)	ICP-MS Dilution
	Blank	0	0	0	0	0	10
	1A	5	300	0.15	150	1.00000	2
	1B	5	300	0.15	150	0.99950	2
	1C	5	300	0.15	150	0.99920	2
	1D	5	300	0.15	150	0.00000	10
	2A	10	300	0.3	300	0.99960	2
	2B	10	300	0.3	300	0.99992	2
	2C	10	300	0.3	300	0.99910	2
	2D	10	300	0.3	300	0.00000	10
	3A	20	300	0.6	600	0.99993	2
	3B	20	300	0.6	600	0.99991	2
	3C	20	300	0.6	600	1.00000	2
2020/02/28	3D	20	300	0.6	600	0.00000	10
	4A	40	300	0.12	120	1.00005	2
	4B	40	300	0.12	120	0.99985	2
	4C	40	300	0.12	120	0.99994	2
	4D	40	300	0.12	120	0.00000	10
	5A	60	300	0.18	180	1.00260	2
	5B	60	300	0.18	180	1.00060	2
	5C	60	300	0.18	180	0.99993	2
	5D	60	300	0.18	180	0.00000	10
	6A	75	300	0.225	225	1.00012	2
	6B	75	300	0.225	225	1.00007	2
	6C	75	300	0.225	225	1.00017	2
	6D	75	300	0.225	225	0.00000	10
	7A	100	300	0.3	300	1.00100	2
2020/03/02	7B	100	300	0.3	300	1.00010	2
	7C	100	300	0.3	300	1.00005	2
	7D	100	300	0.3	300	0.00000	10
2020/02/28	OG 1	0	300	0	0	0.99991	2
2020/03/02	OG 2	0	300	0	0	1.00030	2
2020/03/02	SRM1						10
	SRM2						10
			TOTAL	**7.5**	**7500**	**23.00185**	

Appendix B – Arsenic Mass Justification

02/21/2020
9:45am (Kaitlyn and Kileigh)

XRF Testing Methodology
- XRF Detection Level for Arsenic: 10 ppm
- Last year's Cadmium removal efficiency
  - Nitric Acid: 97%
  - Untreated: 77%
  - Citric Acid: N/A
- < 1000 μg/g (ppm), XRF will not read Arsenic in corn cob
- 1 g corn: $\left(\frac{1\,g}{10^6\,\mu g}\right)\left(\frac{1\,L}{1000\,mL}\right)\left(\frac{10\,\mu g}{1\,L}\right)\left(\frac{300\,mL}{1\,g\,Corn}\right) = 3ppm$ As @ 100% Removal Efficiency
  - 3 ppm As in 1 g of corn after batch reaction of 10 ppm initial concentration
  - 2.25 ppm @ 75% Removal Efficiency
- 0.5 g corn: $\left(\frac{1\,g}{10^6\,\mu g}\right)\left(\frac{1\,L}{1000\,mL}\right)\left(\frac{10\,\mu g}{1\,L}\right)\left(\frac{300\,mL}{0.5\,g\,Corn}\right) = 6ppm$ As @ 100% Removal Efficiency
  - 4.5 ppm @ 75% Removal Efficiency
- 0.25 g corn: $\left(\frac{1\,g}{10^6\,\mu g}\right)\left(\frac{1\,L}{1000\,mL}\right)\left(\frac{10\,\mu g}{1\,L}\right)\left(\frac{300\,mL}{0.25\,g\,Corn}\right) = 12ppm$ As @ 100% Removal Efficiency
  - 9 ppm @ 75% Removal Efficiency
- BATCH REACTION TESTING:
  - Corn masses added to each sample for batch reaction (g)
    - 1.00, 0.50, 0.25
  - Test highest concentration because of XRF detection limit (ppb)
    - 500
  - 3 replicated for each scenario (3 scenarios for concentration)
    - Repeat for each corn type
    - Do each scenario with enough samples so the corn adds up to 2 g
  - Test each of these at the following time intervals (hours)
    - 1.5, 3, 4.5, 6, 7.5, 9
      - This is to figure sorption optimization for the corn biosorbent

Figure B-1: Typed initial XRF methodology plans

Appendix C – Arsenic Experimental Matrix

Table C-1: Complete Arsenic testing experimental matrix

Conc As (µg/L)	Mass Corn (g)	# Experiments	Trials	Total Trials	Corn Types (NA, CA, UT)	Total Corn (g)	Total Standard (mL)
10	1.00	2	3	6	3	18	1.80
	0.50	4	3	12	3	18	3.60
	0.25	8	3	24	3	18	7.20
20	1.00	2	3	6	3	18	3.60
	0.50	4	3	12	3	18	7.20
	0.25	8	3	24	3	18	14.39
35	1.00	2	3	6	3	18	6.30
	0.50	4	3	12	3	18	12.59
	0.25	8	3	24	3	18	25.19
50	1.00	2	3	6	3	18	9.00
	0.50	4	3	12	3	18	17.99
	0.25	8	3	24	3	18	36.0
65	1.00	2	3	6	3	18	11.69
	0.50	4	3	12	3	18	23.39
	0.25	8	3	24	3	18	46.8
80	1.00	2	3	6	3	18	14.39
	0.50	4	3	12	3	18	28.79
	0.25	8	3	24	3	18	57.6
125	1.00	2	3	6	3	18	22.49
	0.50	4	3	12	3	18	45.0
	0.25	8	3	24	3	18	90.0
250	1.00	2	3	6	3	18	45.0
	0.50	4	3	12	3	18	90.0
	0.25	8	3	24	3	18	179.9
500	1.00	2	3	6	3	18	90.0
	0.50	4	3	12	3	18	179.9
	0.25	8	3	24	3	18	360
					Total	486	1429.4
					Per Corn Type	162	

Appendix D – XRF Sorption Data

Table D-1: Raw and initial XRF data for Arsenic sorption tests at 500 ppb

SAMPLE	Time (hr)	Mass Corn (g)	As	Units	XRF Uncertainty
CA_0.5g	3	2.0215	2.10	ppm	1.2
CA_0.25g	4.5	2.0131	1.93	ppm	1.22
NA_0.5g	7.5	2.0126	3.22	ppm	1.23
NA_0.5g	3	2.0177	1.95	ppm	1.23
NA_0.25g	7.5	2	2.40	ppm	1.25
NA_0.25g	3	2.0064	3.01	ppm	1.22
UT_0.5g	7.5	2.0053	3.56	ppm	1.62
UT_0.5g	6	2.0104	4.45	ppm	1.62
UT_0.5g	4.5	2.0111	3.94	ppm	1.68
UT_0.5g	3	2.0265	5.74	ppm	1.68
UT_0.25g	7.5	2.0075	4.66	ppm	1.57
UT_0.25g	6	2.0086	4.40	ppm	1.56
UT_0.25g	4.5	2.009	3.14	ppm	1.67
UT_0.25g	3	2.0406	8.51	ppm	2.91
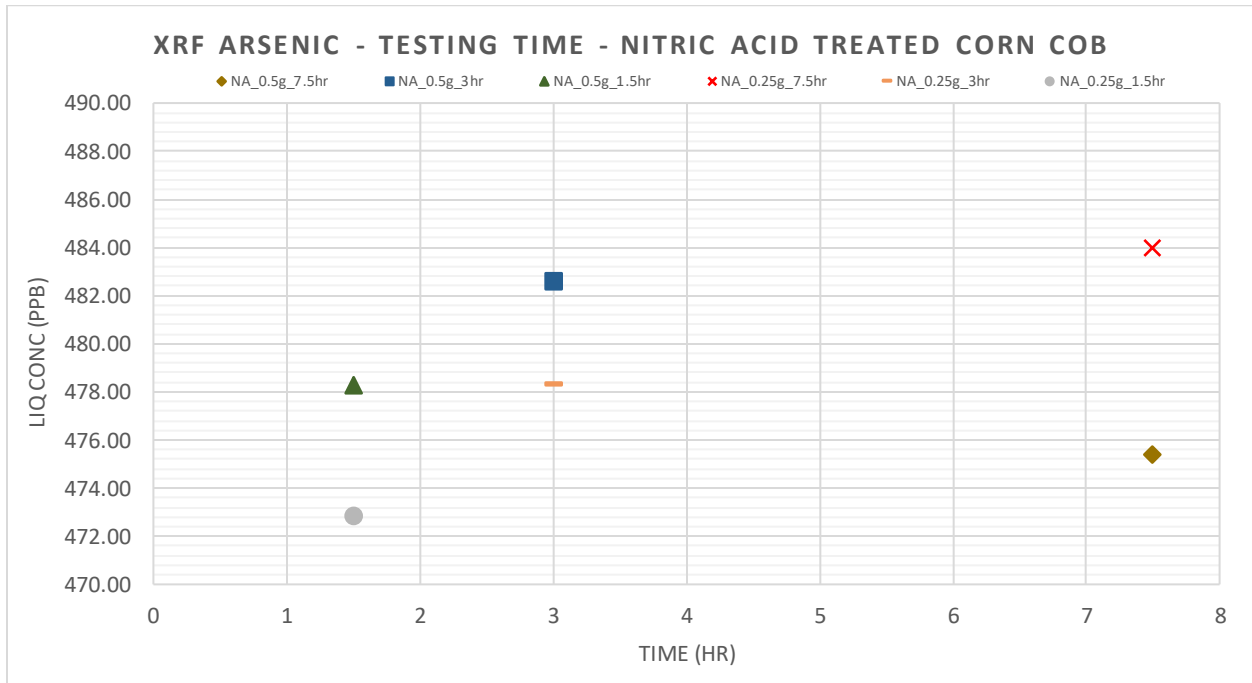
Figure D-1: XRF Arsenic sorption analysis for 500 ppb at 2 grams of nitric acid treated corn cob
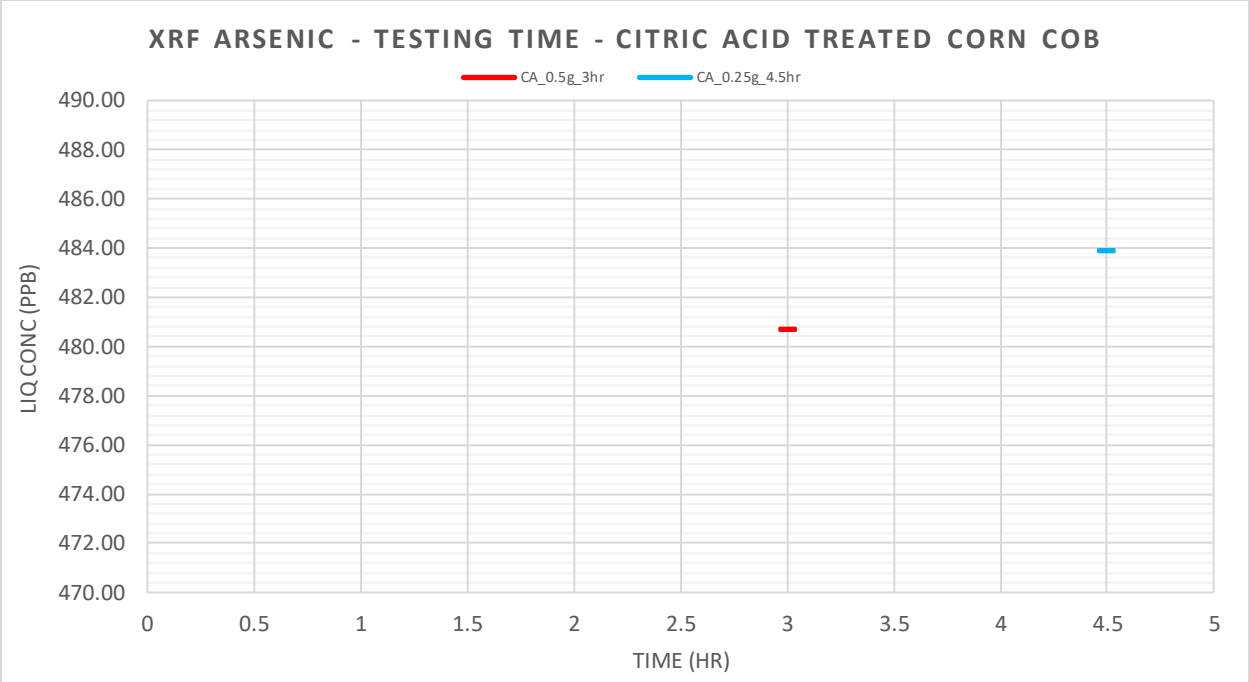
Figure D-2: XRF Arsenic sorption analysis for 500 ppb at 2 grams of citric acid treated corn cob
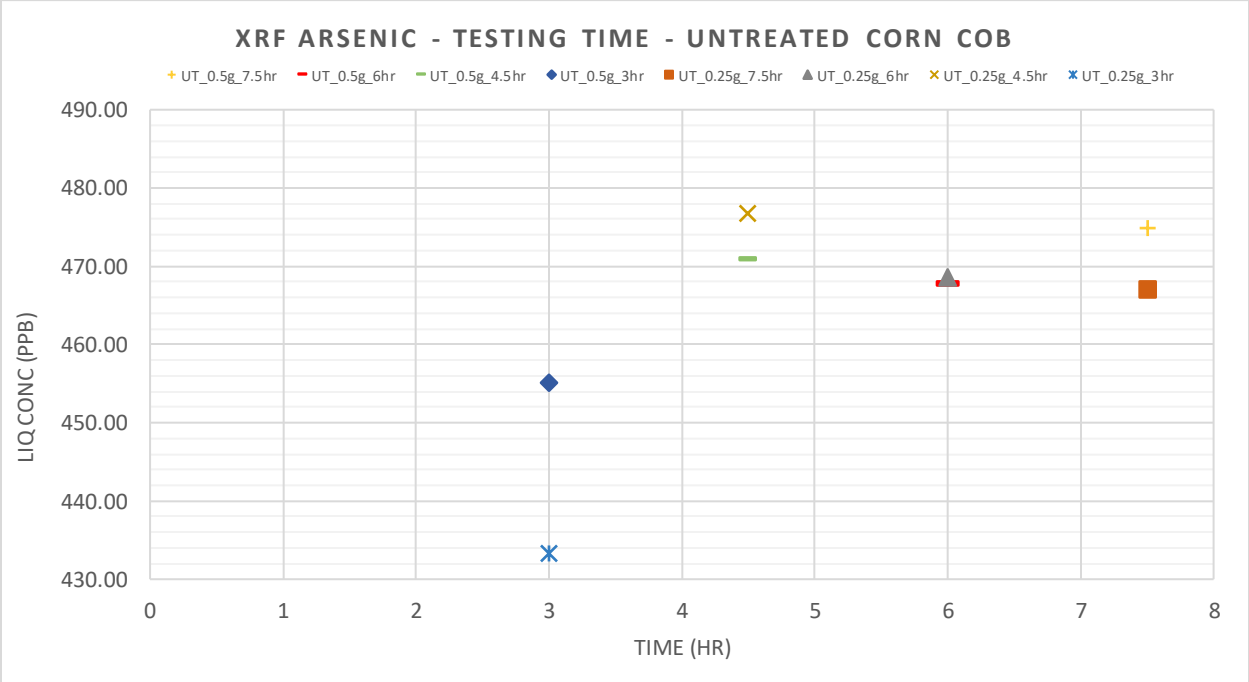
Figure D-3: XRF Arsenic sorption analysis for 500 ppb at 2 grams of untreated corn cob

49

Appendix E – XRF Arsenic Raw Data

Table E-1: Raw and initial XRF data for Arsenic tests at 500 ppb

SAMPLE	Time (hr)	Mass Corn (g)	As	Units	XRF Uncertainty
UT_0.25g(2)i	1.5	2.001	2.41	ppm	1.48
UT_1g(1)	1.5	1.9995	4.07	ppm	1.62
UT_0.5g(1)	1.5	2.0002	3.06	ppm	1.68
UT_0.25g(1)	1.5	2.0006	2.48	ppm	1.56
CA_1g(1)	1.5	1.9985	3.22	ppm	1.48
CA_1g(2)	1.5	2.0003	3.64	ppm	1.53
CA_1g(3)	1.5	2.0001	2.60	ppm	1.5
CA_0.5g(1)	1.5	1.9988	3.91	ppm	1.44
CA_0.5g(2)	1.5	2	2.21	ppm	1.44
CA_0.5g(3)	1.5	2.0005	2.46	ppm	1.47
CA_0.25g(1)	1.5	1.9986	2.52	ppm	1.48
CA_0.25g(2)	1.5	2.0002	2.45	ppm	1.47
CA_0.25g(3)	1.5	2.0002	4.65	ppm	1.52
NA_0.5g(1)	1.5	2.0109	2.85	ppm	1.18
NA_0.25g(1)	1.5	2.006	3.85	ppm	1.21
UT_0.25g(1)L	1.5	2.0006	1.49	ppm	0.92

Appendix F – Total Coliform Data

Table F-1: Results of Total Coliform in the raw sample

Raw (C_0)		
Corn Mass (g)	Dilution Factor	CFU Count
	2	1004000
	20	100400
	200	10040
0	2000	1004
	20000	23
	200000	7
	2000000	1

Figure F-1: Results of Total Coliform removal with nitric acid treated corn cob

Figure F-2: Results of Total Coliform removal with citric acid treated corn cob

Figure F-3: Results of Total Coliform removal with untreated corn cob

Appendix G – Gantt Chart

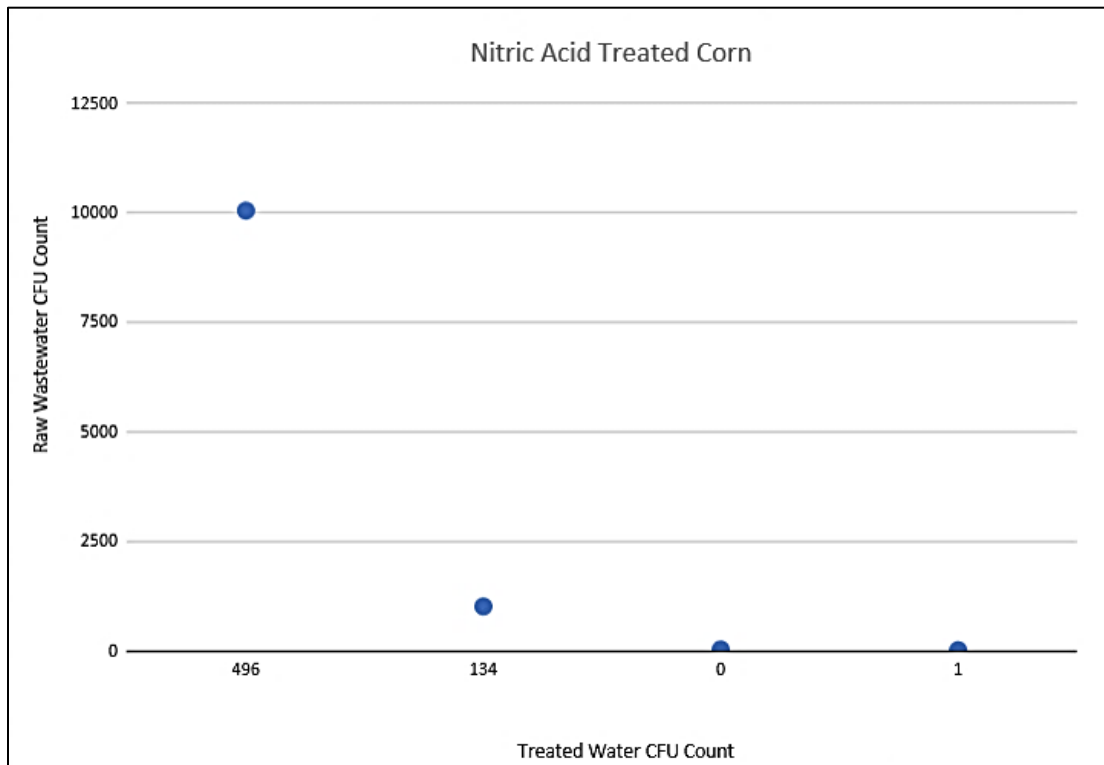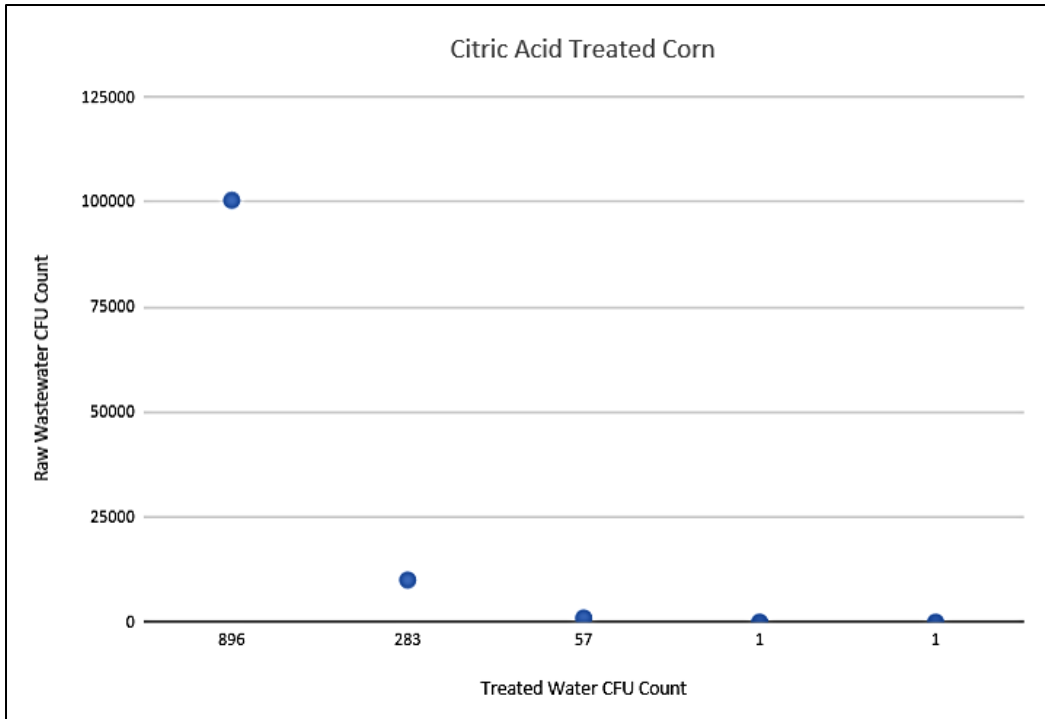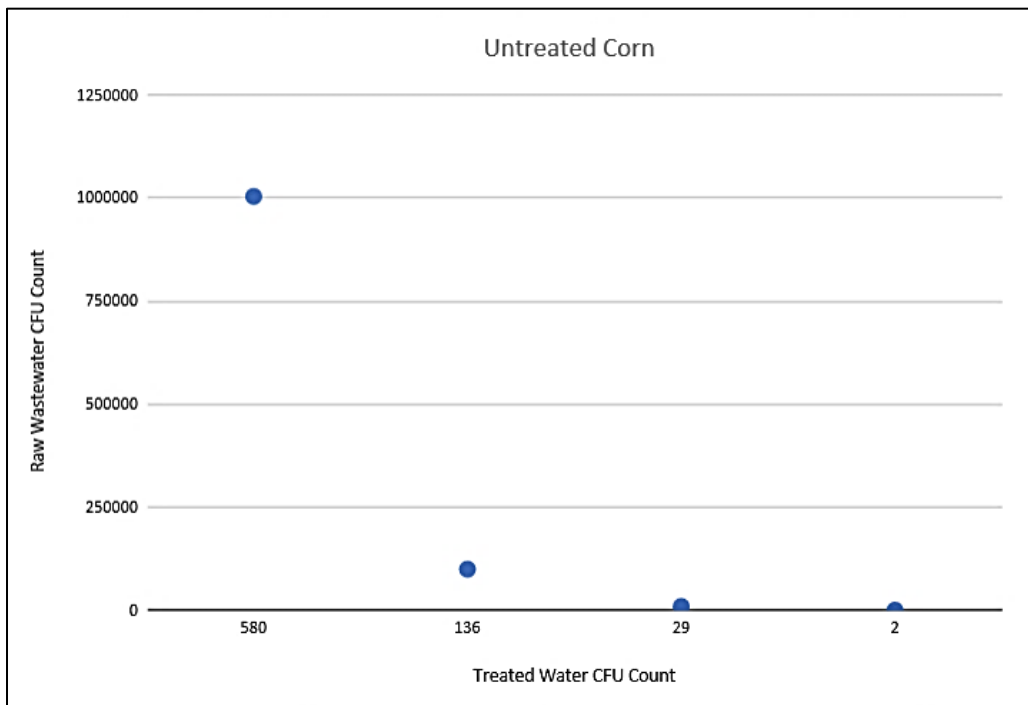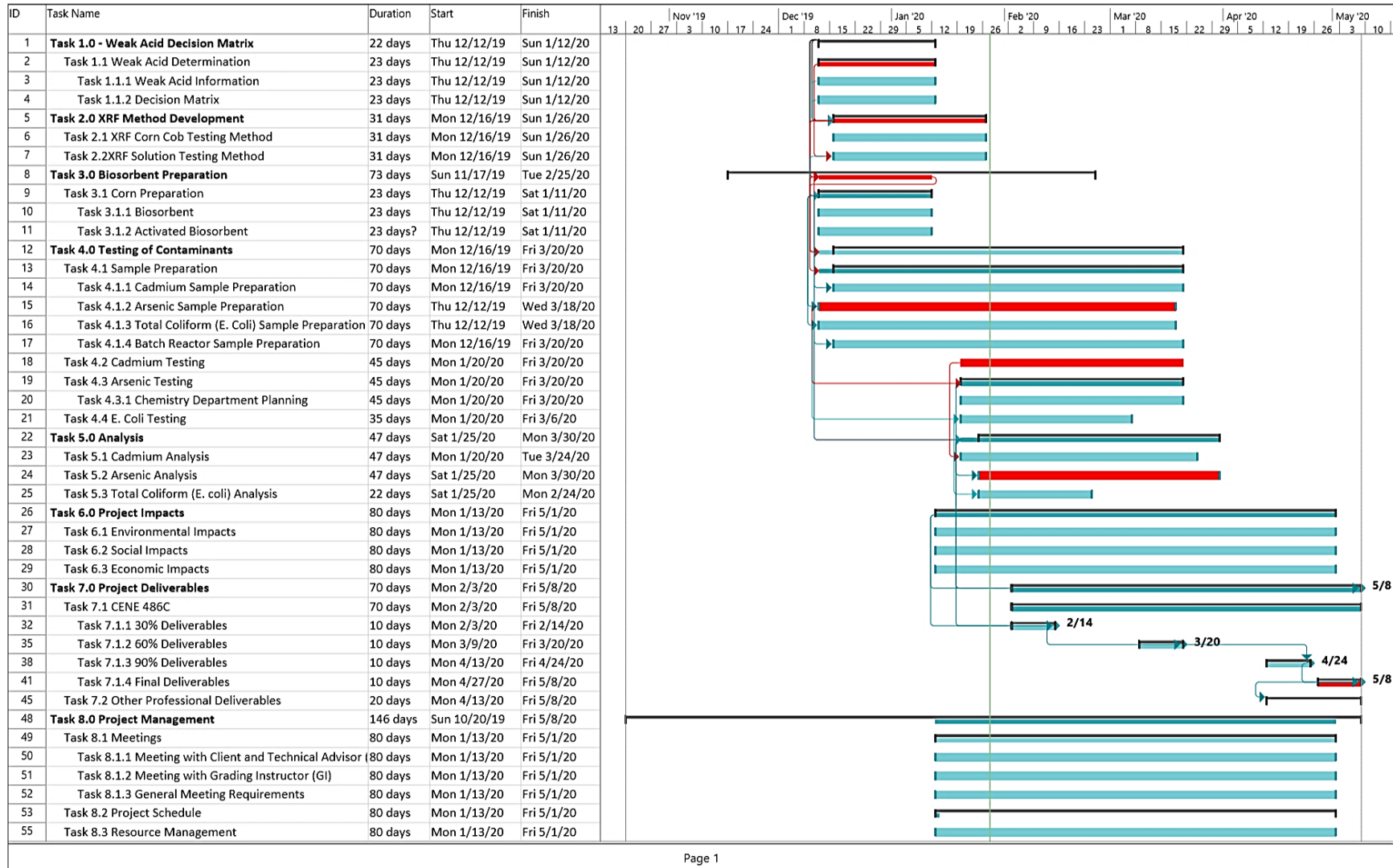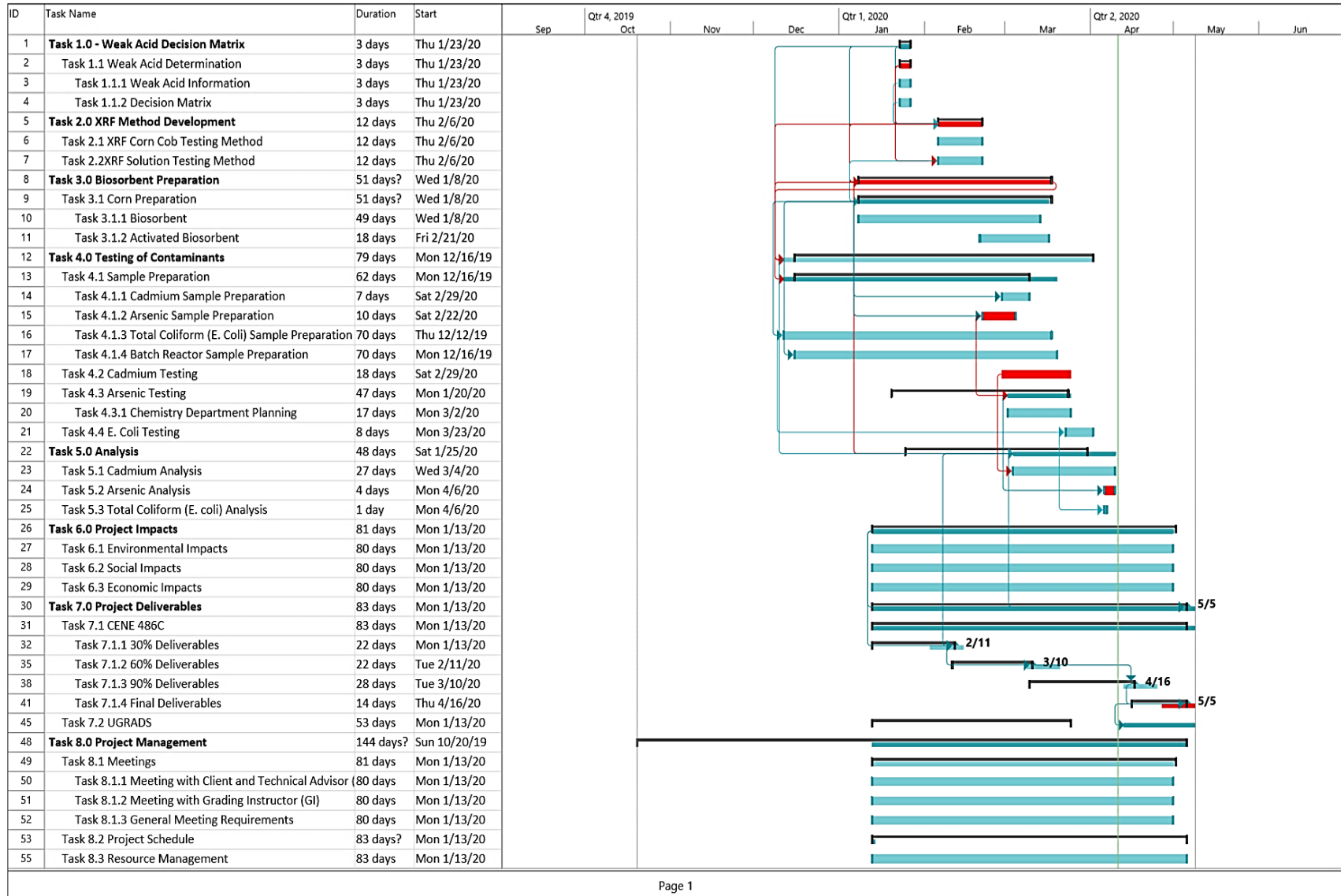| ID	Task Name	Duration	Start	Finish
1	**Task 1.0 - Weak Acid Decision Matrix**	22 days	Thu 12/12/19	Sun 1/12/20
2	Task 1.1 Weak Acid Determination	23 days	Thu 12/12/19	Sun 1/12/20
3	Task 1.1.1 Weak Acid Information	23 days	Thu 12/12/19	Sun 1/12/20
4	Task 1.1.2 Decision Matrix	23 days	Thu 12/12/19	Sun 1/12/20
5	**Task 2.0 XRF Method Development**	31 days	Mon 12/16/19	Sun 1/26/20
6	Task 2.1 XRF Corn Cob Testing Method	31 days	Mon 12/16/19	Sun 1/26/20
7	Task 2.2 XRF Solution Testing Method	31 days	Mon 12/16/19	Sun 1/26/20
8	**Task 3.0 Biosorbent Preparation**	73 days	Sun 11/17/19	Tue 2/25/20
9	Task 3.1 Corn Preparation	23 days	Thu 12/12/19	Sat 1/11/20
10	Task 3.1.1 Biosorbent	23 days	Thu 12/12/19	Sat 1/11/20
11	Task 3.1.2 Activated Biosorbent	23 days?	Thu 12/12/19	Sat 1/11/20
12	**Task 4.0 Testing of Contaminants**	70 days	Mon 12/16/19	Fri 3/20/20
13	Task 4.1 Sample Preparation	70 days	Mon 12/16/19	Fri 3/20/20
14	Task 4.1.1 Cadmium Sample Preparation	70 days	Mon 12/16/19	Fri 3/20/20
15	Task 4.1.2 Arsenic Sample Preparation	70 days	Thu 12/12/19	Wed 3/18/20
16	Task 4.1.3 Total Coliform (E. Coli) Sample Preparation	70 days	Thu 12/12/19	Wed 3/18/20
17	Task 4.1.4 Batch Reactor Sample Preparation	70 days	Mon 12/16/19	Fri 3/20/20
18	Task 4.2 Cadmium Testing	45 days	Mon 1/20/20	Fri 3/20/20
19	Task 4.3 Arsenic Testing	45 days	Mon 1/20/20	Fri 3/20/20
20	Task 4.3.1 Chemistry Department Planning	45 days	Mon 1/20/20	Fri 3/20/20
21	Task 4.4 E. Coli Testing	35 days	Mon 1/20/20	Fri 3/6/20
22	**Task 5.0 Analysis**	47 days	Sat 1/25/20	Mon 3/30/20
23	Task 5.1 Cadmium Analysis	47 days	Mon 1/20/20	Tue 3/24/20
24	Task 5.2 Arsenic Analysis	47 days	Sat 1/25/20	Mon 3/30/20
25	Task 5.3 Total Coliform (E. coli) Analysis	22 days	Sat 1/25/20	Mon 2/24/20
26	**Task 6.0 Project Impacts**	80 days	Mon 1/13/20	Fri 5/1/20
27	Task 6.1 Environmental Impacts	80 days	Mon 1/13/20	Fri 5/1/20
28	Task 6.2 Social Impacts	80 days	Mon 1/13/20	Fri 5/1/20
29	Task 6.3 Economic Impacts	80 days	Mon 1/13/20	Fri 5/1/20
30	**Task 7.0 Project Deliverables**	70 days	Mon 2/3/20	Fri 5/8/20
31	Task 7.1 CENE 486C	70 days	Mon 2/3/20	Fri 5/8/20
32	Task 7.1.1 30% Deliverables	10 days	Mon 2/3/20	Fri 2/14/20
35	Task 7.1.2 60% Deliverables	10 days	Mon 3/9/20	Fri 3/20/20
38	Task 7.1.3 90% Deliverables	10 days	Mon 4/13/20	Fri 4/24/20
41	Task 7.1.4 Final Deliverables	10 days	Mon 4/27/20	Fri 5/8/20
45	Task 7.2 Other Professional Deliverables	20 days	Mon 4/13/20	Fri 5/8/20
48	**Task 8.0 Project Management**	146 days	Sun 10/20/19	Fri 5/8/20
49	Task 8.1 Meetings	80 days	Mon 1/13/20	Fri 5/1/20
50	Task 8.1.1 Meeting with Client and Technical Advisor (	80 days	Mon 1/13/20	Fri 5/1/20
51	Task 8.1.2 Meeting with Grading Instructor (GI)	80 days	Mon 1/13/20	Fri 5/1/20
52	Task 8.1.3 General Meeting Requirements	80 days	Mon 1/13/20	Fri 5/1/20
53	Task 8.2 Project Schedule	80 days	Mon 1/13/20	Fri 5/1/20
55	Task 8.3 Resource Management	80 days	Mon 1/13/20	Fri 5/1/20

Page 1

Figure G-1: Proposed Gantt chart

Figure G-2: Actual Gantt chart