Corn Cob Biosorption

A-Maize Cob-oration

CENE 486C - Final Presentation

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Figure 2-1: Gold King Mine Spill Before and After
https://www.sudrum.com/news/2018/08/31/three-year-water-quality-study-reveals-no-lasting-impacts-from-gold-king-mine-spill/c

Introduction

Purpose: Test adsorption capability of corn cob with Arsenic contamination, validate the Cadmium isotherm, test for Total Coliforms using corn cobs as a biosorbent

Client: Dr. Ozis

Stakeholders: Dr. Ozis, marginalized communities

Location: Inspired by the Gold King Mine Spill

Background

A–Maize Cob–oration

Figure 3-1: Team logo

Cadmium

- Maximum Contaminant Level (MCL): 5 µg/L (ppb)
- Average drinking level concentration: below 1 µg/L (ppb)
- Highest concentration after mine spill: 100 µg/L (ppb)
- Previous NAU capstone research average removal efficiency: 97%

Arsenic

- Maximum Contaminant Level (MCL): 10 µg/L (ppb)
- Average drinking level concentration: below 1 µg/L (ppb)
- Highest concentration after mine spill: 500 µg/L (ppb)

Total Coliforms

- Maximum Contaminant Level (MCL): Present in ≥5% of monthly tests

Objectives

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 Coliforms,
3. Evaluate the efficiency of corn cob activation using a weak acid,
4. Develop an analytical method for the use of the XRF device for organic materials and liquids

Weak Acid Decision Matrix

Table 5-1: Weak acid 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

- Grade of 1 = most favorable
- Grade of 3 = least favorable

Biosorbent Preparation

- Cut into segments
- Dry @ 100℃
- Strip kernels from cob
- Grind with mortar and pestle
- Sieve through 250 μm

Figure 6-1: Corn cob being cut into uniform segments (Photo by: Kileigh Phillips)

Figure 6-2: Corn cob segments ready to be dried (Photo by: Kileigh Phillips)

Figure 6-3: Dried corn cob segments (Photo by: Kaitlyn Tighe)

Figure 6-4: Mortar and pestle used to break down corn and 250 μm sieve (Photo by: Kaitlyn Tighe)

Figure 6-5: Final diameter of corn cob, ready for use (Photo by: Erin Pflueger)

Biosorbent Treatment

- Nitric acid treatment
- Citric acid treatment

Figure 7-1: Dried citric acid treated corn cob
(Photo by: Kaitlyn Tighe)

Figure 7-2: Corn cob and nitric acid centrifuged
(Photo by: Kileigh Phillips)

Figure 7-3: Corn cob and nitric acid solution being filtered in preparation for drying oven
(Photo by: Kileigh Phillips)

Figure 7-4: Citric acid saturation
(Photo by: Kileigh Phillips)

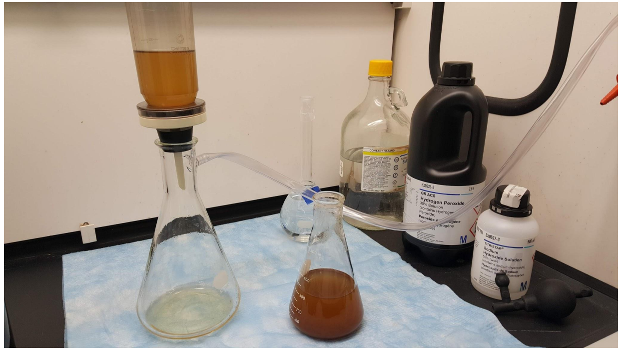

Figure 7-5: Final filtration of nitric acid activation process
(Photo by: Kaitlyn Tighe)

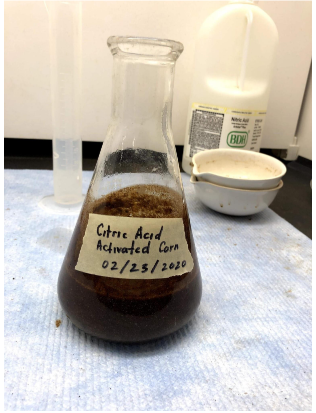

Figure 7-6: Corn cob being activated by citric acid
(Photo by: Kileigh Phillips)

Removal of Contaminants

- **Cadmium Testing**
- **Arsenic Testing**
- **Corn Cob Sorption Capacity Testing**
- **Total Coliforms Testing**

Figure 8-1: Cadmium batch reaction with nitric acid treated corn cob (Photo by: Thalius Belinti)

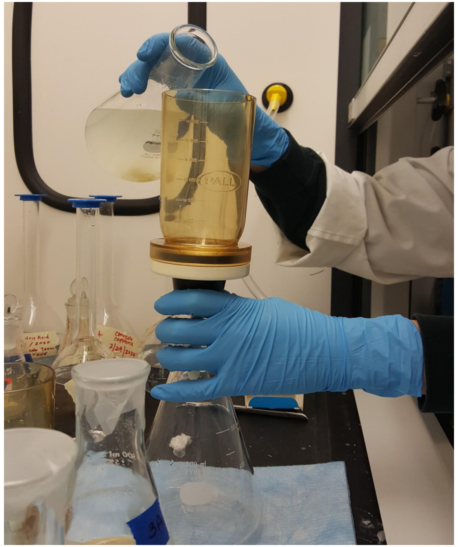

Figure 8-2: Arsenic filtering with nitric acid treated corn cob (Photo by: Kaitlyn Tighe)

Cadmium Testing

- Methodology followed from previous NAU capstone research
- Only nitric acid treated corn cob tested

Table 9-1: Experimental Matrix for Cadmium Testing

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

Corn Cob Sorption Capacity Testing

- Changing variables
  - Mass of biosorbent
  - Contact Time

Table 10-1: Corn Cob Sorption Capacity 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, 4.5 6, 7.5	2
Arsenic	Nitric Acid Citric Acid Untreated	500	3	0.5	3, 4.5 6, 7.5	4
Arsenic	Nitric Acid Citric Acid Untreated	500	3	0.25	3, 4.5 6, 7.5	8

*1.5 hour testing was previously tested and data collected

Arsenic Testing

Table 11-1: 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 As-N2-C2 As-N5-C5 As-N8-C8 As-N3-C3 As-N6-C6 As-N9-C9	Arsenic	Nitric Acid Activated Corn Cob	10 50 125 20 65 250 35 80 500	3	1.0 0.5 0.25
As-C1-C1 As-C4-C4 As-C7-C7 As-C2-C2 As-C5-C5 As-C8-C8 As-C3-C3 As-C6-C6 As-C9-C9	Arsenic	Citric Acid Activated Corn Cob	10 50 125 20 65 250 35 80 500	3	1.0 0.5 0.25
As-U1-C1 As-U4-C4 As-U7-C7 As-U2-C2 As-U5-C5 As-U8-C8 As-U3-C3 As-U6-C6 As-U9-C9	Arsenic	Untreated Corn Cob	10 50 125 20 65 250 35 80 500	3	1.0 0.5 0.25

Total Coliforms Testing

Table 12-1: Total Coliforms 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

Analysis Methods and Results

- **Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**
  - **Cadmium Analysis**
  - **Arsenic Analysis**
- **X-Ray Fluorescence (XRF)**
  - **Arsenic Analysis**
  - **Corn Cob Sorption Capacity Analysis**

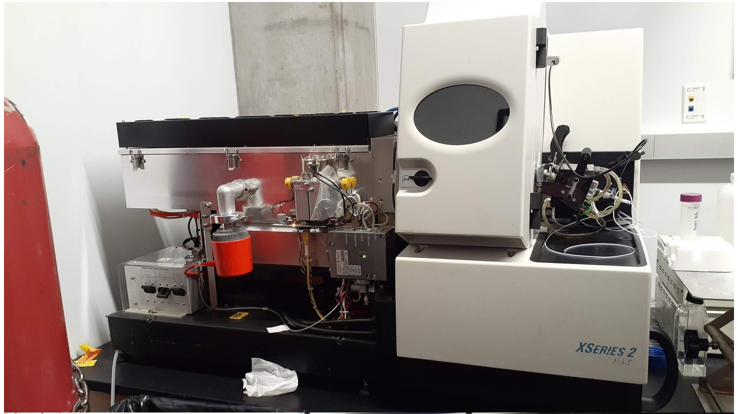

Figure 13-1: ICP-MS instrument (Photo by: Thalius Belinti)

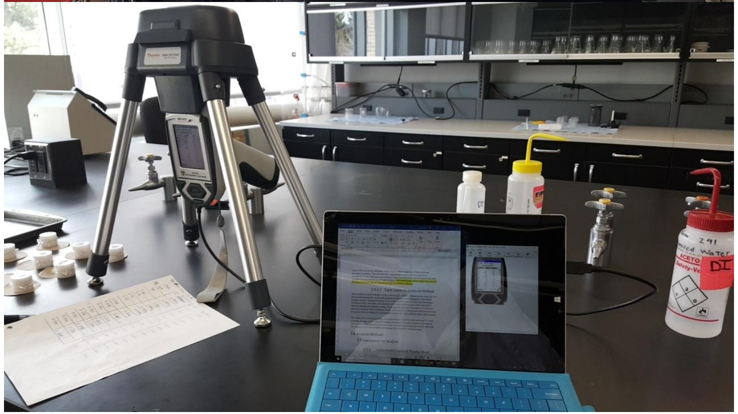

Figure 13-2: XRF device running final analysis of corn cob after 500 ppb Arsenic testing with citric acid and untreated corn (Photo by: Kaitlyn Tighe)

Total Coliforms Analysis

- **HACH Method 8074**

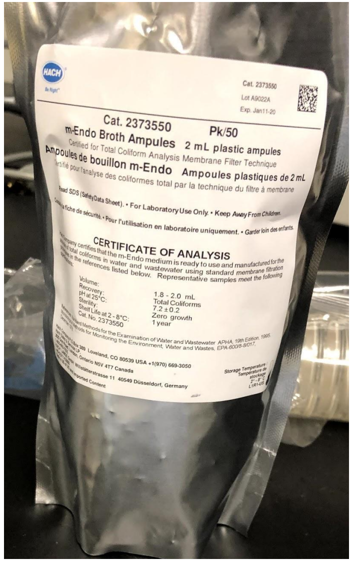

Figure 14-1: m-Endo broth
(Photo by: Kileigh Phillips)

Figure 14-2: Serial dilution process
(Photo by: Kileigh Phillips)

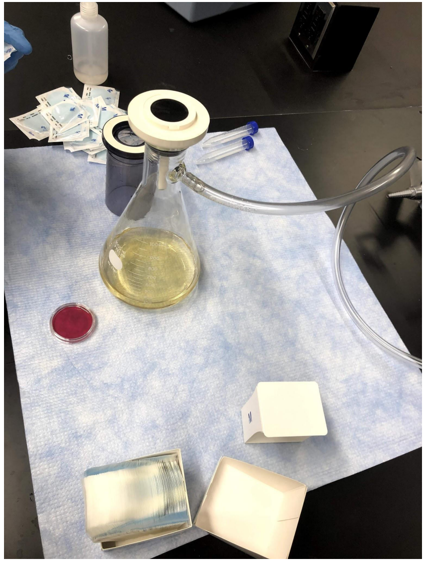

Figure 14-3: Final filtration of each dilution before incubation
(Photo by: Kaitlyn Tighe)

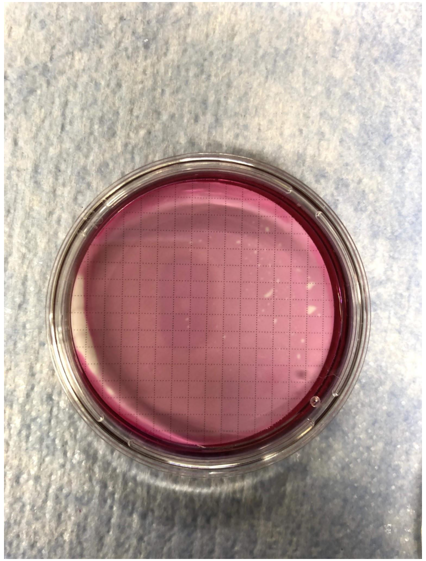

Figure 14-4: Sample in Petri dish with m-Endo broth, ready for incubation
(Photo by: Kileigh Phillips)

Cadmium Analysis

- ICP-MS analysis method
- Final concentration of Cadmium
- Efficiency of nitric acid treated corn cob
- Average efficiency for each concentration

Table 15-1: ICP-MS Cadmium Analysis

Sample #	Std Conc (ppb)	C_i (µg/L)	$C_{f,ave}$ (µg/L)	Ave % Removal, η_{ave}
7A_Cd	100	112.91	15.43	86.33
7B_Cd	100	112.91		
7C_Cd	100	112.91		
6A_Cd	75	84.21	11.30	86.59
6B_Cd	75	84.21		
6C_Cd	75	84.21		
5A_Cd	60	68.01	8.88	86.94
5B_Cd	60	68.01		
5C_Cd	60	68.01		
4A_Cd	40	46.90	6.59	85.95
4B_Cd	40	46.90		
4C_Cd	40	46.90		
3A_Cd	20	27.88	4.75	82.98
3B_Cd	20	27.88		
3C_Cd	20	27.88		
2A_Cd	10	14.08	3.29	76.66
2B_Cd	10	14.08		
2C_Cd	10	14.08		
1B_Cd	5	7.33	2.39	67.34
1C_Cd	5	7.33		

Cadmium Analysis (cont.)

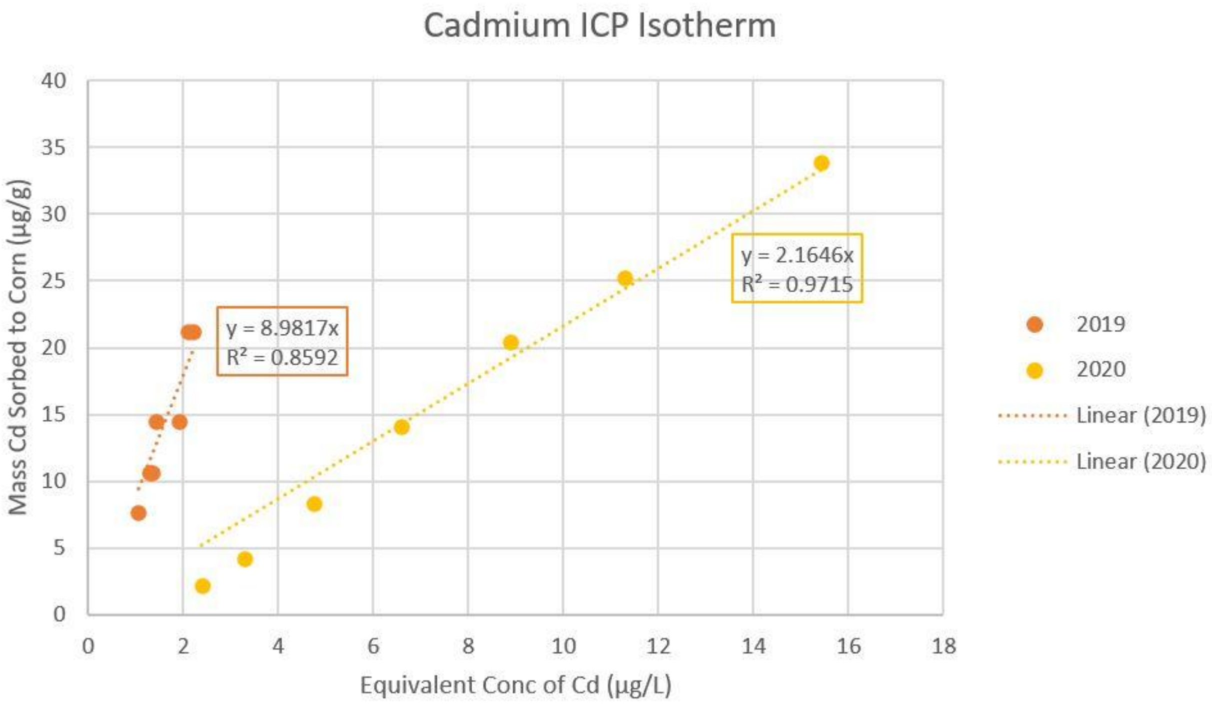

Figure 16-1: ICP-MS Cadmium analysis

Equation 16-1: Linear Freundlich isotherm model

$$q = KC_f$$

Where:

q = mass sorbed,

K = empirical constant, and

C_f = final Cadmium concentration.

Arsenic Analysis

Equation 17-1: Mass balance

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

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).

Table 17-1: XRF Arsenic Results

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

KEY
i = preliminary XRF corn cob reading
UT = untreated corn cob
CA = citric acid treated corn cob
NA = nitric acid treated corn cob
L = XRF liquid reading

Arsenic Analysis (cont.)

- ICP analysis results
- Nitric acid treated corn cob

Figure 18-1: Untreated corn cob after Arsenic testing (From left: 1g, 0.5g, 0.25g) (Photo by: Kileigh Phillips)

Table 18-1: ICP-MS Arsenic Results

As Sample #	Std Conc (ppb)	C_i (μg/L)	$C_{f,ave}$ (μg/L)	Ave % Removal, η_{ave}
9B_As_100X	500	374.89	370.42	1.19
9C_As_100X	500	374.89	367.11	2.08
8B_As_100X	250	189.43	286.94	-51.48
8C_As_100X	250	189.43		
8D_As_100X	250	189.43		
7B_As	125	102.73	176.80	-72.11
7C_As	125	102.73		
7D_As	125	102.73		
6B_As	80	64.70	104.95	-62.20
6C_As	80	64.70		
6D_As	80	64.70		
5B_As	65	53.03	105.66	-99.25
5C_As	65	53.03		
5D_As	65	53.03		
4B_As	50	43.50	89.76	-106.35
4C_As	50	43.50		
4D_As	50	43.50		
3B_As	35	30.48	54.76	-79.66
3C_As	35	30.48		
3D_As	35	30.48		
2B_As	20	18.27	40.75	-123.02
2C_As	20	18.27		
2D_As	20	18.27		
1B_As	10	10.51	32.11	-205.70
1C_As	10	10.51		
1D_As	10	10.51		

Corn Cob Sorption Capacity Analysis

- **XRF testing method development**
  - **Organic matter**

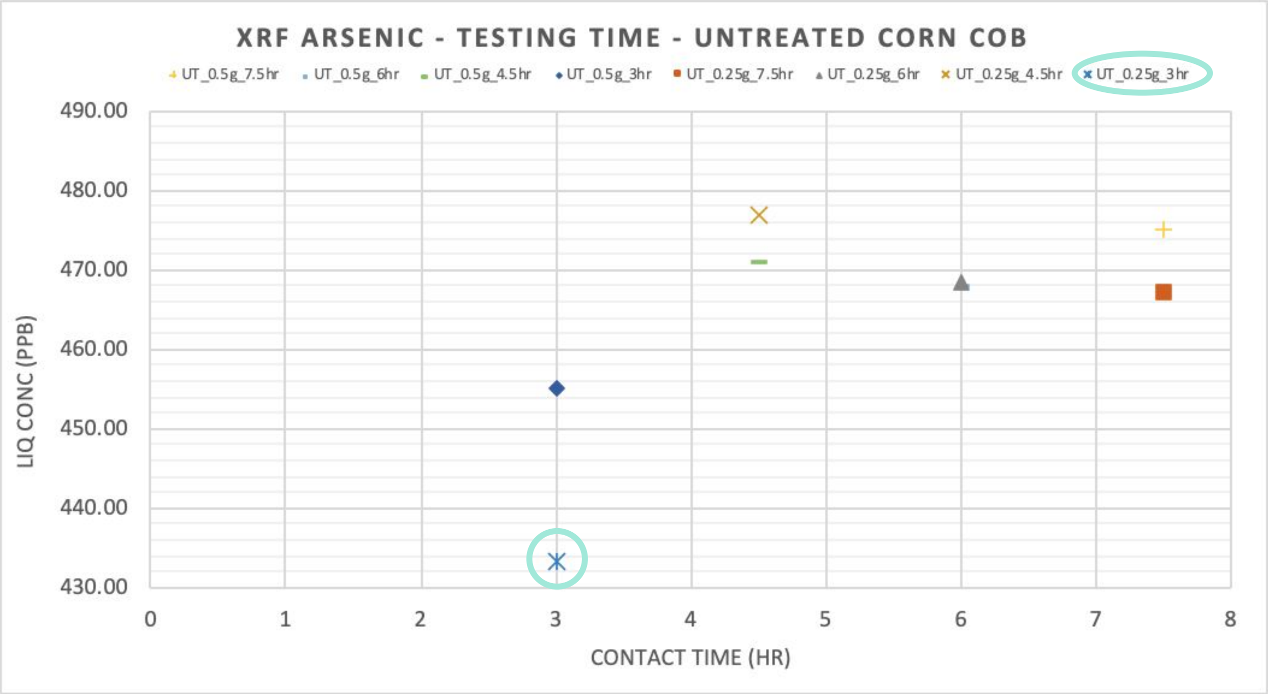

Figure 19-1: Untreated corn cob XRF As sorption results

Total Coliforms Analysis

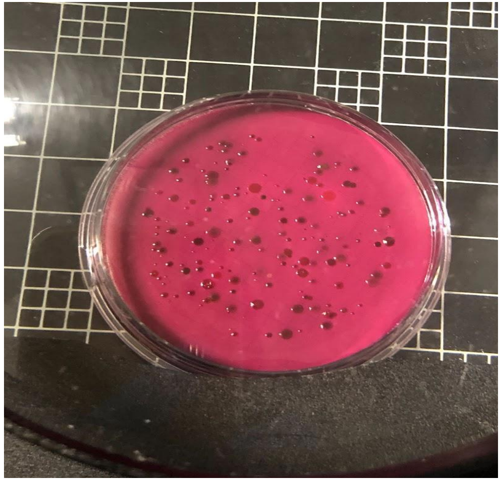

Figure 20-1: Coliform colonies under a magnifying glass
(Photo by: Kileigh Phillips)

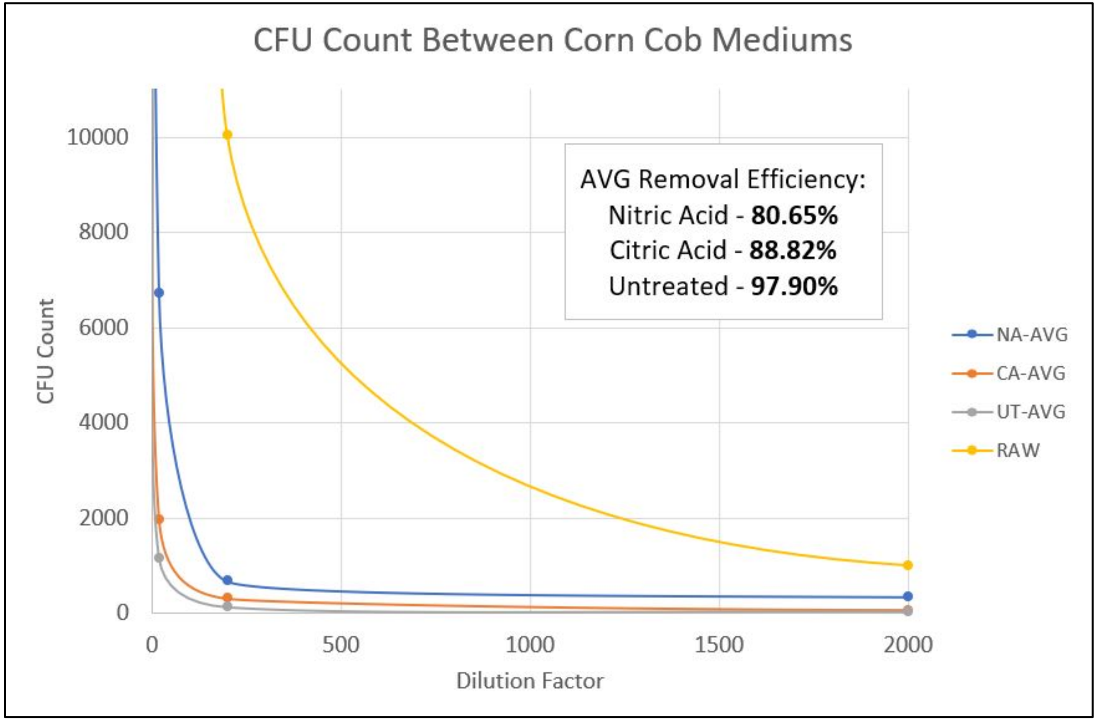

Figure 20-2: Total Coliforms Removal Efficiency

Total Coliforms Analysis (cont.)

Table 21-1: Total Coliforms Analysis, Primary Effluent

Primary Effluent			
Sample ID	Corn Mass (g)	Dilution Factor	CFU Count
RAW	0	2	1004000
RAW		20	100400
RAW		200	10040
RAW		2000	1004
RAW		20000	23
RAW		200000	7
RAW		2000000	1

Table 21-2: Total Coliforms Analysis, Untreated Corn Cob

Untreated Corn					
Sample ID	Corn Mass (g)	Dilution Factor	CFU Count	Removal Efficiency	AVG 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		97.90
BLANK		20	0		
BLANK		200	0		
BLANK		2000	0		

Conclusions

1. Created new set of Cadmium removal data
2. Developed analytic method for XRF device with organic matter
3. Evaluated removal efficiency of corn cob for Arsenic and Total Coliforms
   a. Results from corn cob with weak acid

Recommendations

1. Weak acid treatment with Cadmium
2. Further XRF Arsenic testing
   a. Higher concentrations
   b. Different contaminants
3. Additional Total Coliforms methodologies
   a. EPA Method 1604, HACH Method 10029, Standard Method 9222 J

Impacts

- **Social Impacts**
  - Improving overall health of community
  - Creation of jobs
  - Less strain on health service system
- **Economic Impacts**
  - Economic stimulation from the creation of jobs
  - Cleaner waters = more opportunities for economic expansion (i.e. tourism, population sustainability, etc.)
  - Implementing treatment method in rural areas for agricultural and livestock-related activities
- **Environmental Impacts**
  - Hazardous effects of chemicals used throughout process (e.g. the use of nitric and citric acid during activation process which carries throughout the entire treatment process)
  - Possible disposal methods: incineration, autoclaving, landfill disposal, etc.
  - Further research on extracting heavy metals from corn cob waste
  - Using corn cob waste as burning fuel for heat

Acknowledgements

Department of Engineering at Northern Arizona University for providing us with this opportunity and resources necessary to conduct this research.
Dr. Fethiye Ozis for being our client, technical advisor, and greatest source of support and inspiration.
Dr. Jeffrey Heiderscheidt for being our grading instructor and providing us with the criticism and compliments that have prepared us for our work that will extend past our careers at NAU.
Adam Bringhurst and Dr. Terry Baxter for allowing us access into the labs of the Department of Engineering in order to conduct our research.
Melissa Jacquez and the rest of her capstone team for laying the foundation for this research and being a helpful resource to us throughout this project.
Jean Schuler Mini-Grant Research Foundation for giving us financial support to complete testing and move forward with our project.

Thank you!