Adsorptive Capacity of Orange Peels and Zero Valent Iron Filings for Removal of Uranium and Arsenic Final Design Report

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ABBREVIATIONS

As: Arsenic

DI Water: Deionized Water

EPA: Environmental Protection Agency

MCL: Maximum Contaminant Level

PPE: Personal Protective Equipment

U: Uranium

ZVI: Zero Valent Iron

ACKNOWLEDGEMENTS

1.0 Project Description

1.1 Project Purpose

The purpose of the Adsorptive Capacity of Orange Peels and Zero Valent Iron for Water Treatment project is to find the removal efficiency and rate of removal of orange peels for uranium and zero valent iron for arsenic from water. The goal is to conduct research in order to determine the maximum water volume and chemical concentrations the orange peels and zero valent iron can treat prior to exhaustion. Overall, this project will provide further data that supports this inexpensive and unique method for arsenic and uranium removal from drinking water.

1.2 Existing Conditions

The testing conducted by the previous Low-Cost Water Filtration capstone team included preparing a water sample contaminated with various concentrations of arsenic and uranium and running the water through the selected treatment options. The synthetic water had an average uranium concentration of 84.71 µg/L and an average arsenic concentration of 68.65 µg/L in order to model the average chemical concentrations found at the Navajo Nation site the team was working with. The volumes of water tested included a 1 L, 3 L, 5 L, and 7 L samples of contaminated water. The orange peels removed uranium with a removal efficiency ranging from 99.03% to 99.39%, increasing with increased volume. The orange peels were not as effective at removing arsenic, with a removal efficiency ranging from 27.43% to 62.02%, decreasing with increased volume. The zero valent iron filings had a uranium removal efficiency ranging from 99.82% to 99.87%, and an arsenic removal efficiency ranging from 88.46% to 98.85% [1]. This data supports the uranium and arsenic removal capability of orange peels and zero valent iron filings. Figure 1.0 shows removal data of the original project. The red figures represent final concentrations above the maximum contaminant level (MCL) for the specific contaminant. The green figures represent final concentrations below the MCL.

Comparison of all Materials							
				Filtered Water Volume (L)			
Contaminant	USEPA MCL Standard	Synthetic Water	Filter Media	1	3	5	7
Uranium Concentration (µg/L)	30 (Primary Standard)	84.71	Sand	77.65	77.64	84.13	81.43
			Ion Exchange Resin	0.13	0.09	0.09	0.09
			Orange Peels	0.82	0.52	0.57	0.52
			ZVI Turnings	27.91	49.64	70.92	41.69
			ZVI Filings	0.11	0.15	0.14	0.12
			Rice Husks	0.77	1.38	7.89	67.41
Arsenic Concentration (µg/L)	10 (Primary Standard)	68.65	Sand	38.28	47.12	53.12	55.48
			Ion Exchange Resin	2.27	1.90	1.84	1.86
			Orange Peels	26.07	48.31	46.35	49.82
			ZVI Turnings	6.26	4.76	5.60	6.84
			ZVI Filings	7.92	2.29	1.29	0.79
			Rice Husks	29.63	51.48	56.36	61.02

Figure 1.0: Uranium and Arsenic Removal Data [1]

1.3 Exclusions

Due to time constraints, this project did not include any testing for kinetics, or the rates of reaction, which is needed for final design of a filter. Therefore, the design of a filter is also excluded from the project.

2.0 Background Information

This project is a continuation of the Low-Cost Water Filtration capstone project completed from the previous capstone year [1]. The goal for the original capstone team was to design a water filter for the removal of uranium, arsenic, and bacteria. The water filter needed to be low-cost, electricity free, and needed to have the capability of removing the contaminants below their maximum contaminant limits (MCLs). The team explored several removal methods that included the use of orange peels and zero valent iron. However, the lack of adsorption capacity data of the orange peels and zero valent iron made the team unable to incorporate the materials into a water filter design. At the conclusion of the original capstone project, it was determined that orange peels were capable of removing uranium while zero valent iron was capable of removing both uranium and arsenic (see section 1.2 for removal efficiency data). Therefore, it was necessary to determine the actual capacity of the orange peels and zero valent iron in order to further the science in order to ultimately design a water filter utilizing the materials.

2.1 Adsorption Theory

Adsorption is the process in which molecules of a given substance accumulate on the surface of a separate substance due to Van der Waals interactions. Unlike absorption, which is a chemical process where the molecules enter the bulk phase of the second substance, adsorption is a

physical process that occurs on the surface layer of the second substance. Since adsorption deals with the surface layer of a material, a higher surface area usually yields higher adsorption. The different adsorption processes include liquid (L)-gas (G), L-L, solid (S)-L, and S-G, with S-G and S-L being the most common. The adsorptive capacity of orange peels and ZVI filings for uranium and arsenic removal from water project is dealing with S-L adsorption. The term adsorptive refers to the molecule in bulk liquid phase being adsorbed onto the solid. The term adsorbate refers to the adsorptive molecules on the interfacial layer of the adsorbent, which is the substance causing adsorption. The terms sorptive, sorbent, sorbate, and sorption are used when both adsorption and absorption are taking place, or when the two cannot be distinguished. Figure 1 shows an image of the adsorption system [2].
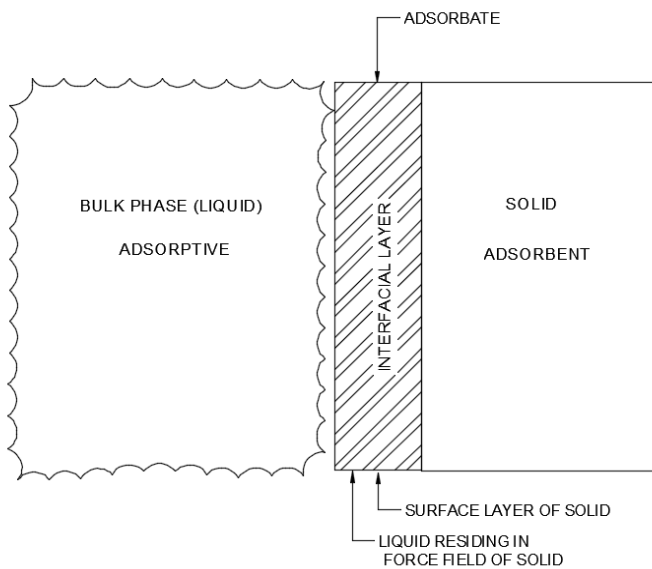
Figure 2.0: Adsorption System

With respect to the project, the adsorptive would be the water, the adsorbate would be either uranium or arsenic, and the adsorbent would be the orange peels or the ZVI filings.

Adsorption is typically described through isotherms. Isotherms show the equilibrium relation between the amount of adsorbed material and the pressure or concentration in the bulk phase at a constant temperature [3]. An example of an isotherm model is the Freundlich isotherm, which is commonly used for drinking water and air treatment applications. The Freundlich isotherm equation is shown below.

$$q = KC_e^{\frac{1}{n}}$$ *Equation 2.1: Freundlich Isotherm Equation*

Where,

q = Mass of adsorbate per unit mass of adsorbent after equilibrium (mg/g)

K = Freundlich isotherm capacity parameter ((mg/g)(L/mg)^(1/n))

C_e = Equilibrium concentration of adsorbate (mg/L)

1/n = Freundlich isotherm intensity parameter (unitless)

The following figure shows a graph with various Freundlich isotherm intensity parameters plotted.
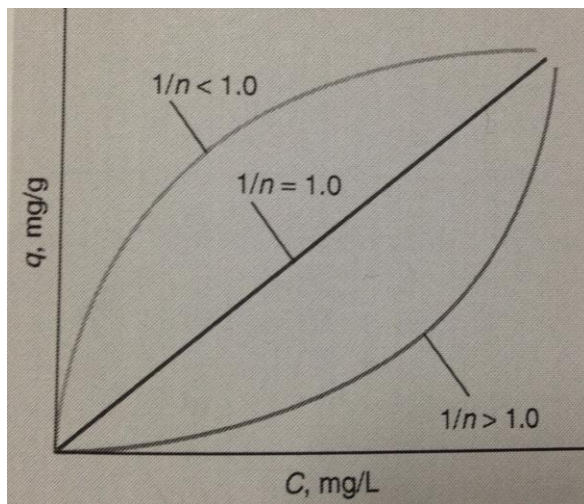
Figure 2.1: Freundlich Isotherm Model [3]

In order to determine the K and 1/n values, a log plot must be created. The equation for the log plot is shown below.

$$\log q = \log K + \frac{1}{n}\log C$$ *Equation 2.2: Freundlich Isotherm Log Equation*

Where,

q = Mass of adsorbate per unit mass of adsorbent after equilibrium (mg/g)

C = Equilibrium concentration of adsorbate (mg/L)

The log values for q and C are then plotted, as shown in Figure 2.3.
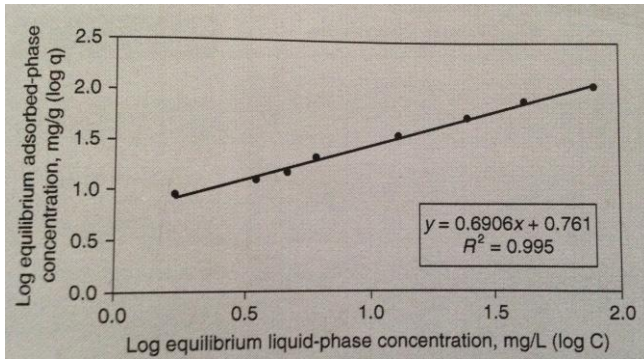
Figure 2.2: Example Freundlich Isotherm Log Plot [3]

A linear regression is used to determine the K and 1/n values, where K is 10 to the power of the y-intercept and 1/n is the slope. For Figure 2.2, the K value would then be 10^0.761, or 5.77 (mg/g)(L/mg)^(1/n), and 1/n would be 0.6906.

For Freundlich isotherm intensity parameters less than one, the isotherm is considered to be favorable for adsorption because lower concentrations of the adsorbate in the aqueous phase yield higher values of adsorption. Conversely, a Freundlich isotherm intensity parameter greater than one is considered to be unfavorable for adsorption. When the 1/n value is equal to one, the isotherm is considered a linear isotherm [3].

Another example of an isotherm model is the Langmuir isotherm model. The equation is shown below.

$$q = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$ *Equation 2.3: Langmuir Isotherm Model*

Where,

q = Mass of adsorbate per unit mass of adsorbent after equilibrium (mg/g)

Q_0 = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg)

C_e = Equilibrium concentration of adsorbate (mg/L)

The linear form of the equation is shown below.

$$\frac{1}{q} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$ *Equation 2.4: Linear Langmuir Isotherm Model*

By graphing 1/q vs 1/ C_e, which are the variables of the experiment, Q_0 and K_L are able to be determined by finding the slope and intercept of the graph. The following figure gives an example of a Langmuir isotherm graph.

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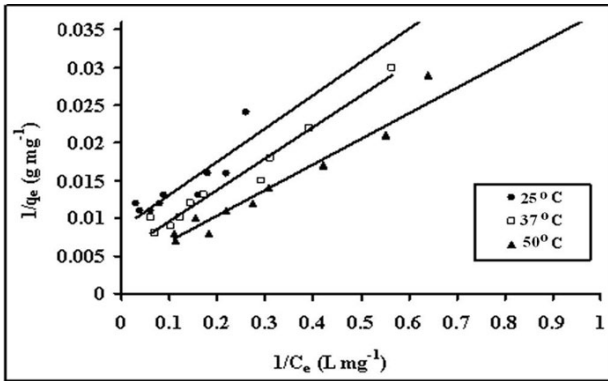
Figure 2.3: Example Langmuir Isotherm Plot [4]

The slope of these lines would be the $1/Q_oK_L$ value and the intercept of the lines would be the $1/Q_o$ value. By solving for Q_o by taking the inverse of the intercept, the K_L term can then be solved for by using the value of the slope. The equilibrium parameter for the Langmuir isotherm, R_L, can be found with the following equation.

$$R_L = \frac{1}{1+(1+K_L C_o)}$$ *Equation 2.5: Langmuir Isotherm Equilibrium Parameter Equation*

Where,

C_o = Initial concentration (mg/L)

An R_L value greater than 1 means the conditions are unfavorable for adsorption, linear if R_L is equal to 1, favorable if R_L is between 0 and 1, and irreversible if R_L is equal to 0 [5]. An irreversible reaction is one that cannot be reversed, making it an absorbtion reaction instead of a reversible adsorption reaction.

3.0 Experimental Design

3.1 Experimental Matrix

An experimental matrix was developed based upon pre-defined data quality needs. Specific parameters were varied throughout the experiment in order to obtain sufficient data for the isotherm models used for determining adsorption capacity. It was expected that significant parameters within each experiment include uranium and arsenic concentration, adsorbent material volume, and adsorbent particle size. Table 3.0 shows which parameters will be held constant and which parameters will be varied for each experiment. The sample identifiers are written in the cells under the replicates section.

Table 3.0: Batch 1 Experimental Matrix

	Constant	Variable	Replicate		
			1	2	3
Batch 1	OP Size 100 mg U/L	0.5 g OP	K 1-1	K 1-2	K 1-3
		0.72 g OP	K 2-1	K 2-2	K 2-3
		0.95 g OP	K 3-1	K 3-2	K 3-3
		1.2 g OP	K 4-1	K 4-2	K 4-3
			1	2	3
	ZVI Filings 10 mg As/L	0.1 g ZVI	K 5-1	K 5-2	K 5-3
		0.25 g ZVI	K 6-1	K 6-2	K 6-3
		0.5 g ZVI	K 7-1	K 7-2	K 7-3
		0.75 g ZVI	K 8-1	K 8-2	K 8-3
		0.9 g ZVI	K 9-1	K 9-2	K 9-3
	ZVI Filings 50 mg As/L	0.65 g ZVI	K 10-1	K 10-2	K 10-3
		1.3 g ZVI	K 11-1	K 11-2	K 11-3
		2.6 g ZVI	K 12-1	K 12-2	K 12-3
		3 g ZVI	K 13-1	K 13-2	K 13-3
		3.3 g ZVI	K 14-1	K 14-2	K 14-3

In order to determine how many variables and replicates would be required to obtain statistically significant data, Dr. Derek Sonderegger from Northern Arizona University's Statistical Consulting Lab was contacted. For adsorption testing, it is necessary to obtain data at removal efficiencies below 100% in order to determine a representative q value, as discussed in section 2.1. The goal for batch 1 is to determine a range of adsorbent masses that will yield data in the desired range. Dr. Sonderegger stated that in order to find this range, a minimum of three masses is required. Estimates of a mass that will yield below 100% removal and two separate masses that will yield 100% removal were the overall goal. Dr. Sonderegger also stated that in order to find the amount of replicates needed for statistically significant data, a variance must be known. Due to the lack of existing data on orange peels and ZVI filings as adsorbent materials, there was no expected variance. For the first batch 3 replicates were run in order to get a better understanding of the variance and then the number of replicates that will be necessary for the second batch of data will be determined. Furthermore, since the first batch was going to be exploratory and the second batch would include the refined values that would be used for the isotherm models, it was advised to dedicate 30% of the samples for the first batch and 70% of the samples for the second batch.

3.2 Safety, Sample Labeling, Shipping Protocols

A lab safety plan was created prior to beginning lab work. This served as a contract that Katharos Engineering had completed the required training to work in the lab, that personal protective equipment (PPE) would be worn when necessary, and that all hazardous materials would be handled and disposed of properly. Furthermore, all of the samples would be labeled properly to avoid confusion and error within the lab. Outlining the

shipping protocols was also included in the lab safety plan to avoid complications throughout the sample shipment process and in turn create errors with the sample analysis. The lab safety plan and the signed contract can be found in Appendix A.

3.3 Experimental Methods

Batch experiments were conducted in order to determine the adsorption capacity. The materials list for the batch experiments can be found below.

- Magnetic stir plate
- Magnetic capsules and stir bars
- 250 mL Erlenmeyer flasks
- 50 mL volumetric pipettes
- Pipette bulbs

The predetermined orange peels and ZVI filings masses were weighed out using an electronic weighing station. The masses of the orange peels and ZVI filings were then placed inside the respective 250 mL Erlenmeyer flasks. Using the 50 mL volumetric pipettes and pipette bulbs, 100 mL of the solution was then poured into the respective 250 mL Erlenmeyer flask. The magnetic capsule was then slid into the 250 mL Erlenmeyer flask and then placed on top of the magnetic stir plate. The magnetic stir plate stayed on 350 rpm for 24 hours, at which point the samples were removed and prepared for shipment.

4.0 Experimentation

4.1 Material Preparation

4.1.1 Orange Peels
Approximately 20 medium navel oranges were purchased from a local grocery store that were to be prepared for the experiment. The orange peels were initially cut to an approximate size of 1 cm × 1 cm and then rinsed in DI water. Three flat sheets of aluminum foil were then prepared and the orange peels were distributed evenly on each sheet and then placed in a drying oven set to 105℃, as shown in Figure 4.0 and Figure 4.1. After a 12 hour period, the orange peels were removed from the drying oven. The peels were then chopped using a blender for approximately 30 minutes, or until there was no longer any visible changes in the size of the peels.

Figure 4.0: Orange Peels Distributed on Foil Trays

Figure 4.1: Foil Trays in Drying Oven

4.1.2 ZVI Filings

The ZVI fillings were purchased through Amazon. The brand was Science Magnets, 12oz. Iron filings. The only material preparation associated with the ZVI filings was saturating the filing with DI water in order to remove any possible dust particles from the surface of the filings.

4.1.3 Particle Size Distribution Analysis

A dry sieve analysis was conducted for both the orange peels and the ZVI filings in order to determine the particle sizes being used throughout the experiment. The USACE EM_1110-2-1906 Appendix V method was used for the sieve analysis procedure, and can be found in Appendix B. Figure 4.2 shows the particle size distribution for the ZVI filings. However, all sizes of the ZVI filings were used in testing. The sieve analysis was conducted solely to determine how the particle sizes were distributed.
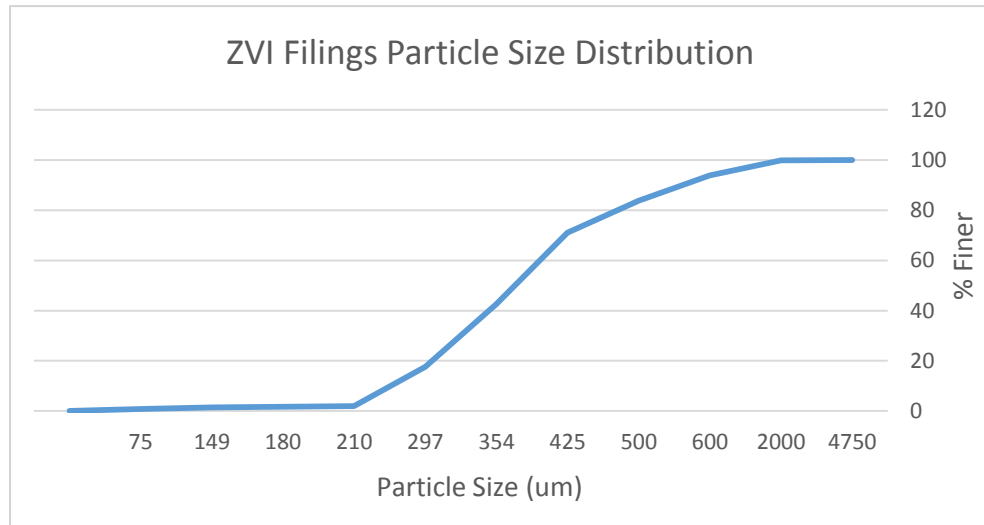
Figure 4.2: ZVI Filings Particle Size Distribution Graph

Figure 4.3 shows the particle size distribution for the orange peels. As shown, the majority of the orange peels were less than 600 um, or no. 30 US Standard Sieve size. Since the orange peels required preparation, the goal was to keep the size practical for an average household to create. As the majority of the orange peels were retained on the no. 30 sieve, this was the selected orange peel size used throughout the testing. This particle size falls under the range for a sand classification. All of the orange peels that were retained on the remaining sieves were not used for any portion of the testing.
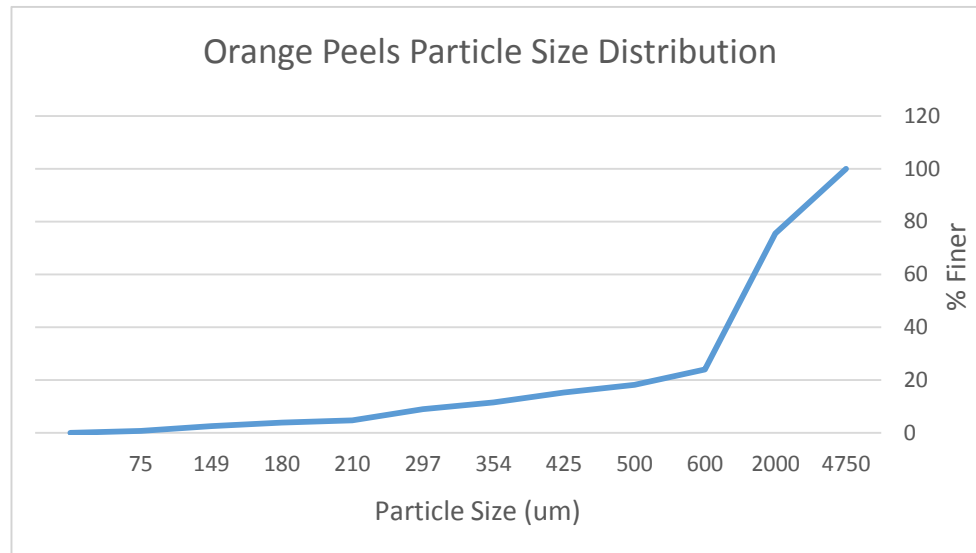
Figure 4.3: Orange Peels Particle Size Distribution Graph

4.2 Sample Water Creation & Analysis

As preferred by the client, the team focused on obtaining a well water source for testing. Dr. Paul Gremillion provided tap water from his home which comes directly from a well water source. Dr. Gremillion also transported the water from his home to the NAU CECMEE Environmental Water Quality Lab. The sample water was created using the dilution equation shown below.

$$C_1V_1 = C_2V_2$$

Where,

C = Concentration of uranium or arsenic (mg/L)

V = Volume (mL)

The materials list used for creating the sample can be found below.

- 1000 mL volumetric flasks
- 1000 mL Erlenmeyer flasks
- 1 mL, 10 mL, 50 mL volumetric pipettes
- Pipette bulbs
- Parafilm

The uranium and arsenic standards used for the lab both have a concentration of 10,000 µg/mL (V_2). The volume of the solutions that were prepared are 1000 mL (V_1). The C_1 concentrations were the predetermined initial uranium and arsenic concentrations. The variable that was solved for, V_2, was the volume of the standard required to create the

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solutions. Using 1000 mL volumetric flasks, the flask was filled with the calculated V_2 value of the standard solution and then filled to the 1000 mL mark with the well water sample. The solution was then transferred to a 1000 mL Erlenmeyer flask, covered in parafilm, and stored in the fume hood. For Batch 1, three stock solutions were created of uranium and arsenic all at 1000 mL. The concentrations were 100 mg U/L, 10 mg As/L, and 50 mg As/L.

Basic water quality parameters were tested for the well water including hardness, alkalinity, and pH. Hardness testing was done using HACH Method 8226, alkalinity testing was done using HACH Method 8221, and pH was determined using a pH meter. The following table shows the average results found after three runs of each test.

Table 4.0: Water Quality Analysis

pH	7.52
Hardness	286.6 mg CaCO3/L
Alkalinity	26.6 mg CaCO3/L

4.3 Data Collection

The data collected for the experiments include the initial and final concentrations of uranium and arsenic. The test samples were shipped to Dr. Michael Ketterer, Chemistry Department Professor and Chair at the Metropolitan State University of Denver. Dr. Ketterer tested the samples for uranium and arsenic using the ICP-MS (Inductively Coupled Plasma Mass Spectrometry) lab technique. Raw data was sent back to Northern Arizona University, where Dr. Gremillion helped in decoding the data into the desired uranium and arsenic concentration values.

5.0 Data Analysis

5.1 Batch Testing Results

At the conclusion of first batch tests, graphs were created in order to determine the range of removal and the variance of the results. The following graphs show the results for the uranium and arsenic removal, as well as the initial concentrations of the chemical.
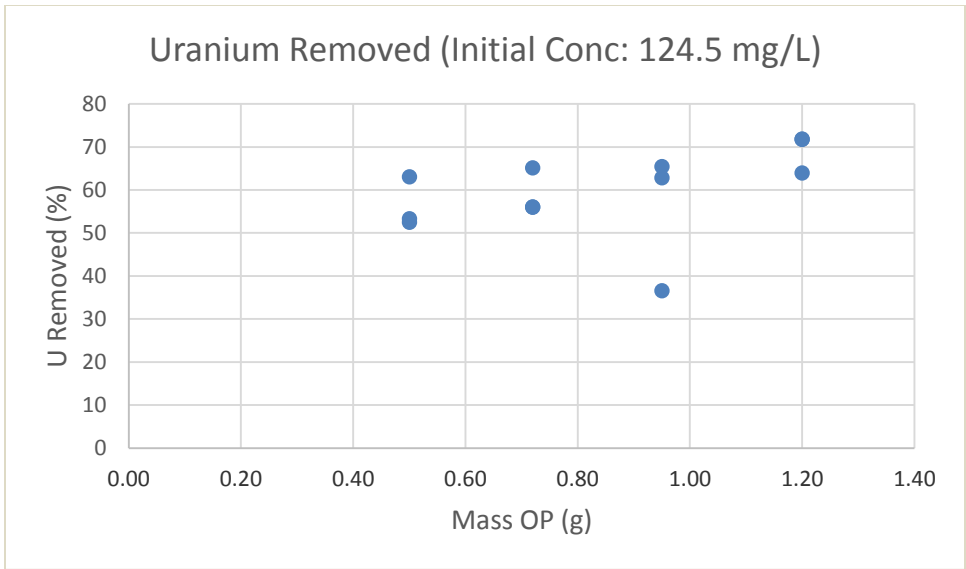
Figure 5.0: Batch 1 Uranium Removal

The results for the uranium removal showed that there was no significant variance between replicates. With at least two of the replicates nearly identical and only one outlier, it was decided that for the second batch of uranium testing there would also be three replicates per sample. With regards to removal efficiencies, there was no removal above 80% and there was also not a large range of removal. It was decided the second batch of uranium tests would need to include a much broader range of masses.
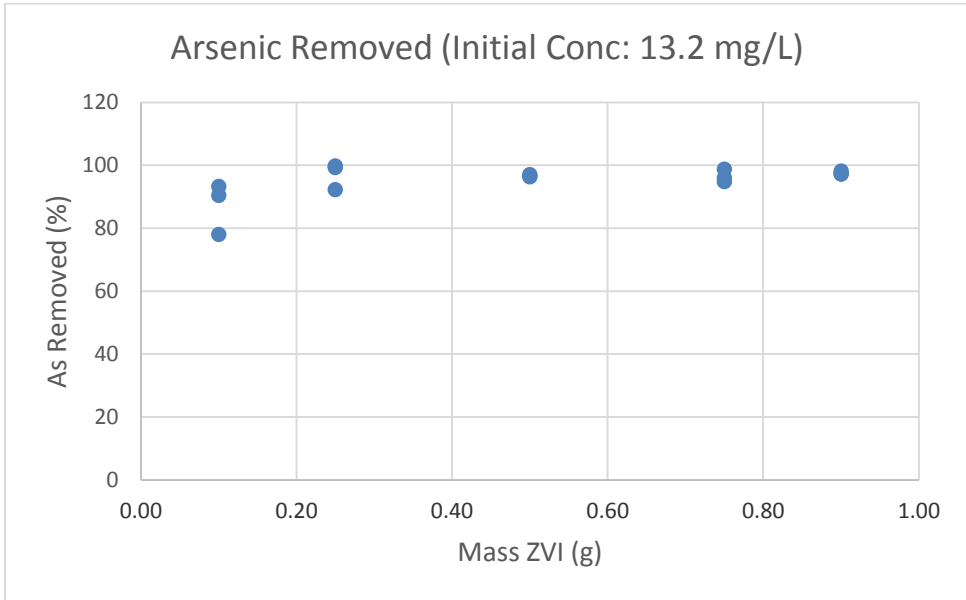
Figure 5.1: Batch 1 Arsenic-1 Removal
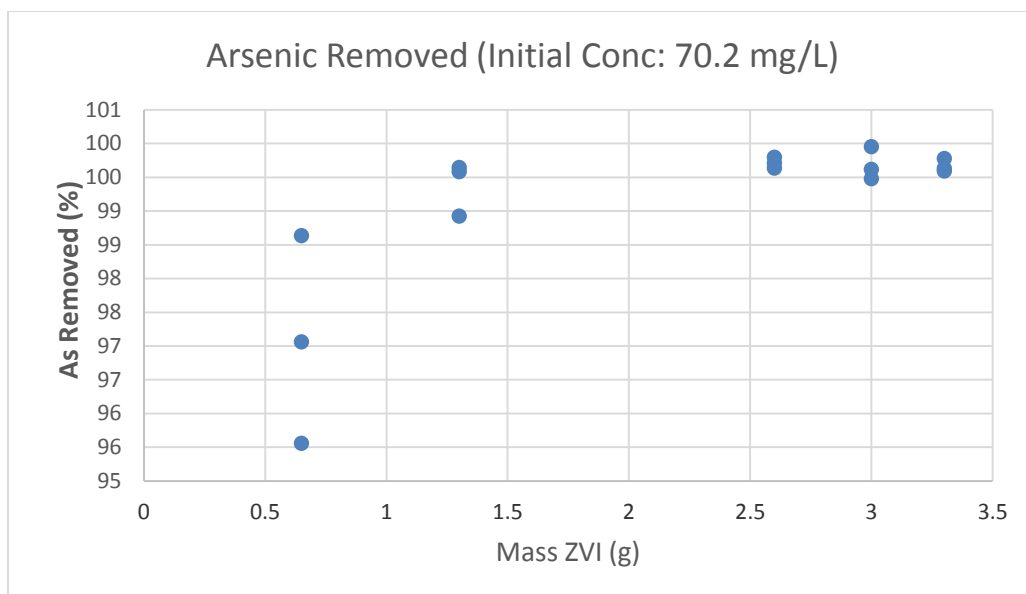
Figure 5.2: Batch 1 Arsenic-2 Removal

On average, the results for the arsenic removal had an even smaller variance than uranium with the exception of the 0.65 g of ZVI filings for the 70.2 mg As/L initial concentration. This mass produced quite a large variance, and it is unsure if this was a lab or machine error. Due to the risk of a larger variance, it was decided that for arsenic there would also be three replicates per sample. The removal efficiencies for both initial concentrations of arsenic were also all near 100%. This indicated that much smaller masses would need to be used for the second batch of tests. Since smaller masses would be used for ZVI filings, it was decided that the smaller initial concentration of arsenic would be used for the second batch in order to keep the mass sizes practical. The following table shows the final experimental matrix for the second batch.

Table 5.0: Batch 2 Experimental Matrix

			1	2	3
Batch 2	OP Size 100 mg U/L	0.05 g OP	K 15-1	K 15-2	K 15-3
		0.1 g OP	K 16-1	K 16-2	K 16-3
		0.15 g OP	K 17-1	K 17-2	K 17-3
		0.25 g OP	K 18-1	K 18-2	K 18-3
		0.35 g OP	K 19-1	K 19-2	K 19-3
		0.4 g OP	K 20-1	K 20-2	K 20-3
		0.45 g OP	K 21-1	K 21-2	K 21-3
		0.5 g OP	K 22-1	K 22-2	K 22-3
		0.6 g OP	K 23-1	K 23-2	K 23-3
		0.75 g OP	K 24-1	K 24-2	K 24-3
		0.9 g OP	K 25-1	K 25-2	K 25-3
		1 g OP	K 26-1	K 26-2	K 26-3
		1.5 g OP	K 27-1	K 27-2	K 27-3
		2 g OP	K 28-1	K 28-2	K 28-3
		3 g OP	K 29-1	K 29-2	K 29-3
			1	2	3
	ZVI Filings 10 mg As/L	0.01 g ZVI	K 30-1	K 30-2	K 30-3
		0.02 g ZVI	K 31-1	K 31-2	K 31-3
		0.03 g ZVI	K 32-1	K 32-2	K 32-3
		0.04 g ZVI	K 33-1	K 33-2	K 33-3
		0.05 g ZVI	K 34-1	K 34-2	K 34-3
		0.06 g ZVI	K 35-1	K 35-2	K 35-3
		0.07 g ZVI	K 36-1	K 36-2	K 36-3
		0.075 g ZVI	K 37-1	K 37-2	K 37-3
		0.08 g ZVI	K 38-1	K 38-2	K 38-3
		0.085 g ZVI	K 39-1	K 39-2	K 39-3
		0.09 g ZVI	K 40-1	K 40-2	K 40-3
		0.095 g ZVI	K 41-1	K 41-2	K 41-3
		0.1 g ZVI	K 42-1	K 42-2	K 42-3
		0.15 g ZVI	K 43-1	K 43-2	K 43-3
		0.2 g ZVI	K 44-1	K 44-2	K 44-3
		0.25 g ZVI	K 45-1	K 45-2	K 45-3
		0.3 g ZVI	K 46-1	K 46-2	K 46-3

The masses highlighted in yellow represent the minimum mass used for the first batch and the masses highlighted in orange show the maximum mass used in the first batch. For the orange peels, reaching a removal efficiency higher than 80% was attempted by increasing the mass amounts. However, the lack of range did result in using much smaller mass amounts as well. For the ZVI filings, the maximum mass that was used in the first batch was not considered in the second batch. Instead, the minimum mass for the first batch was taken to be the near maximum for the second batch and the remaining masses were decreased. The following graphs show the removal efficiencies for the second batch of tests.
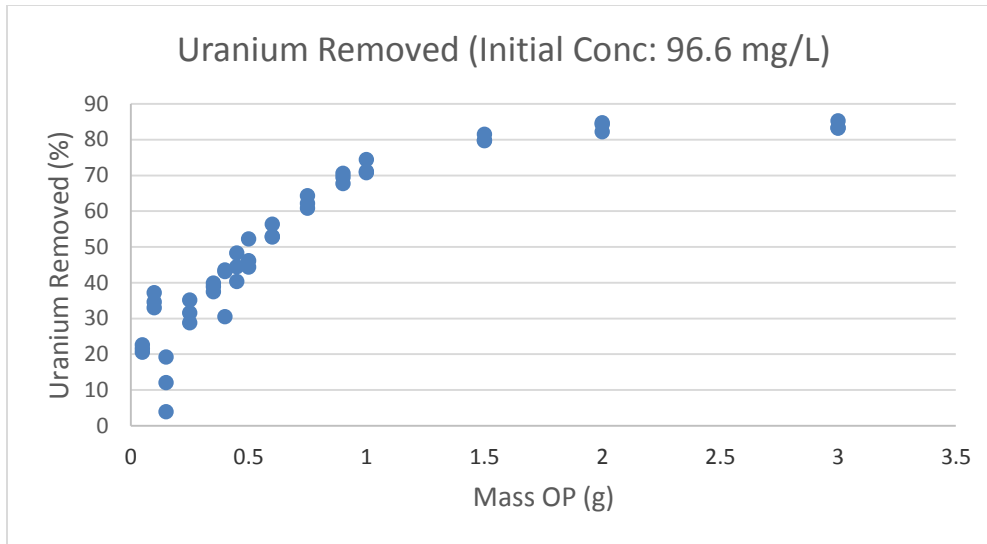
Figure 5.3: Batch 2 Uranium Removal
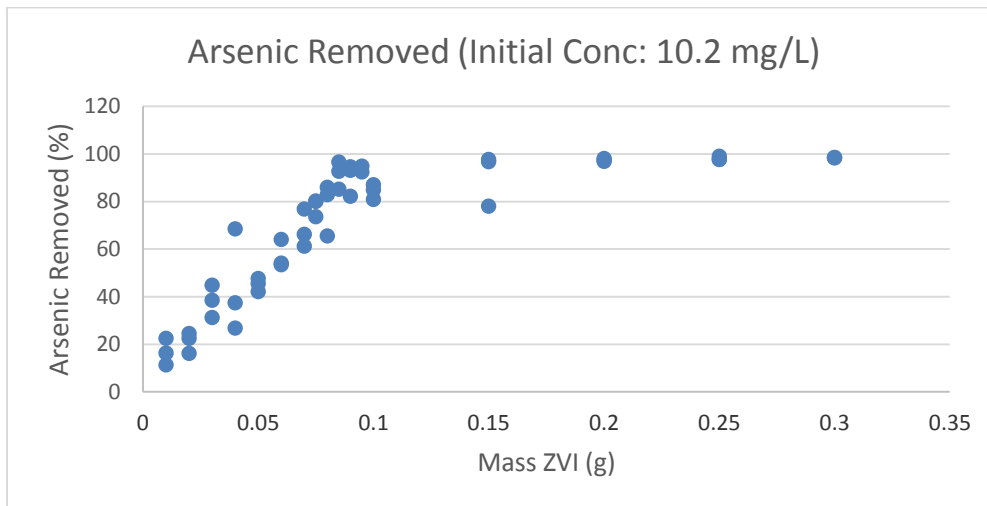
Figure 5.4: Batch 2 Arsenic Removal

The results for the second batch had the desired broad range of removal. At the conclusion of the second batch, the isotherm models were created.

5.2 Isotherm Models

The orange peel data was fit into the Freundlich and Langmuir Isotherm Models using Equations 2.2 and 2.4, respectively. The following graphs show the final isotherm models for the orange peels.
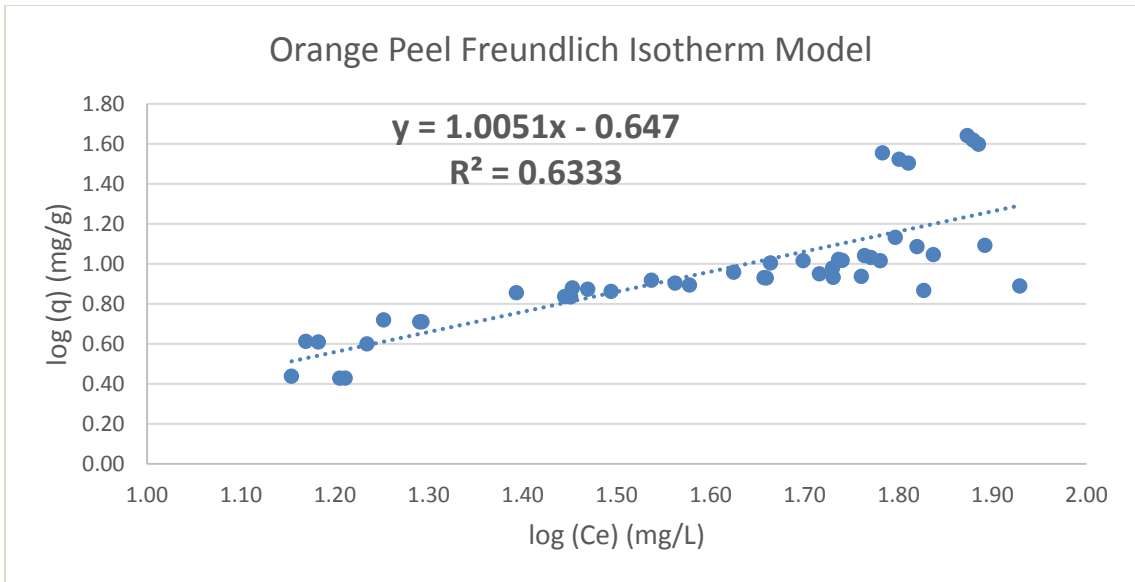
Figure 5.5: Orange Peel Freundlich Isotherm Model
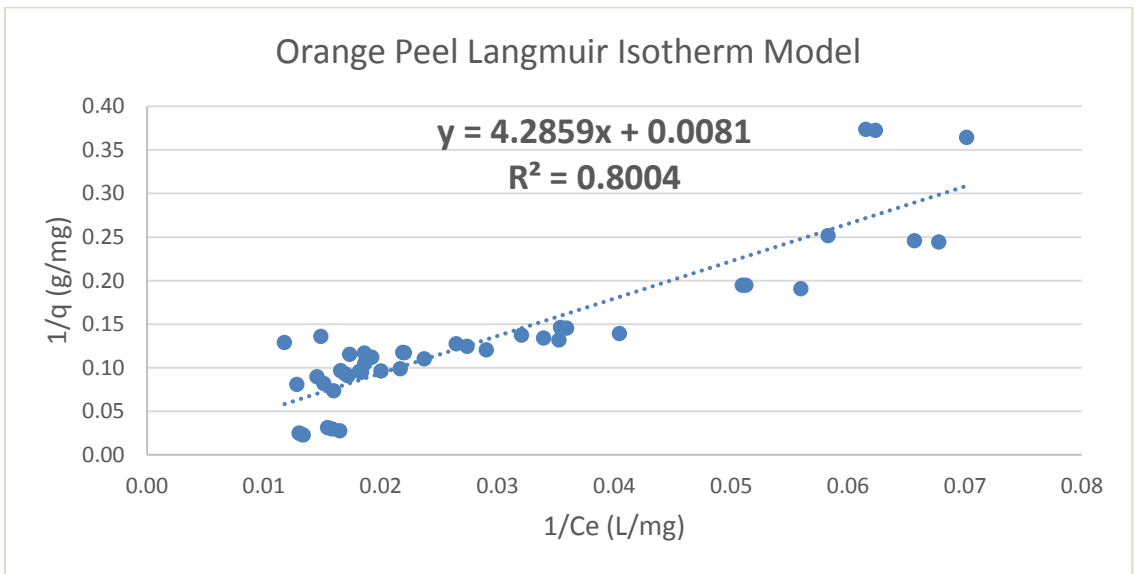
Figure 5.6: Orange Peel Langmuir Isotherm Model

The regression coefficient, or R^2 value, was much closer to 1 for the Langmuir Isotherm model meaning this was the better fit isotherm. Similarly, the ZVI filings data was fit into the two different isotherm models.
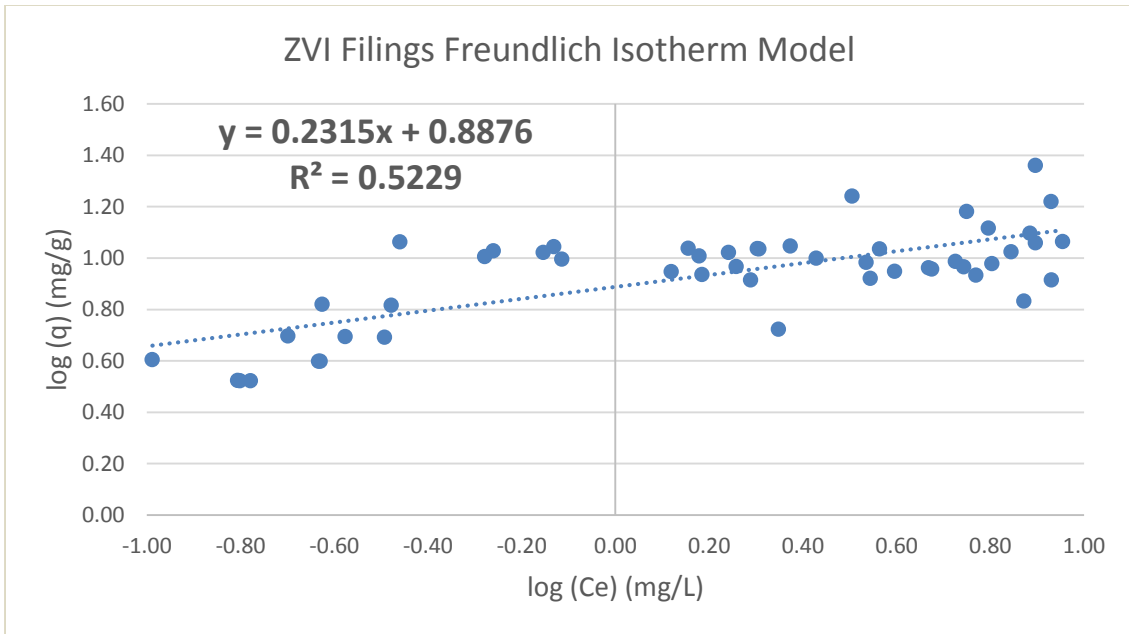
Figure 5.7: ZVI Filings Freundlich Isotherm Model
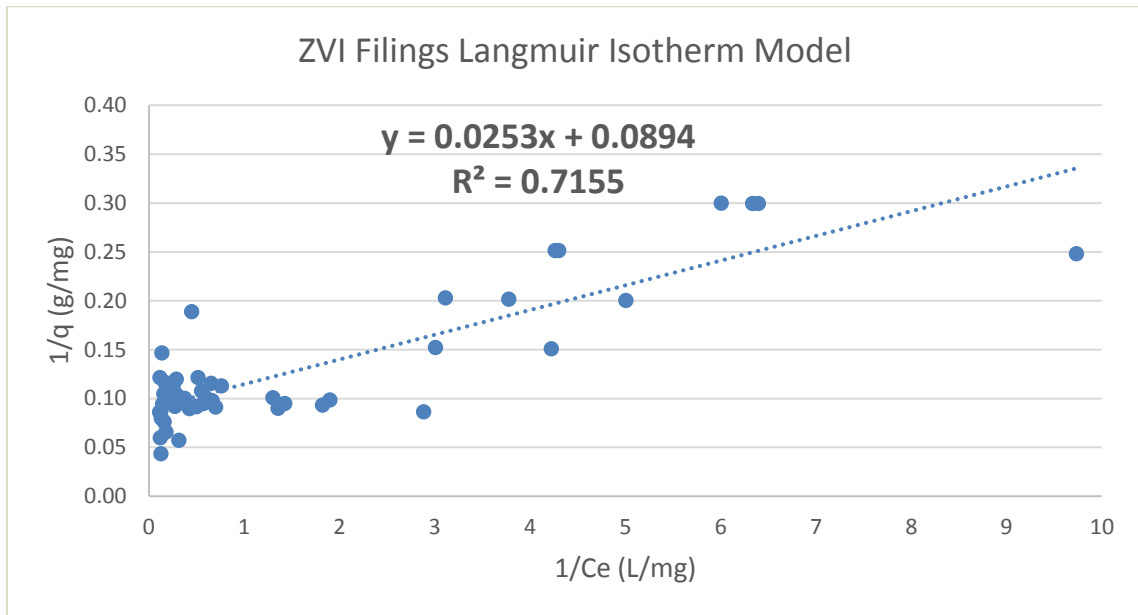
Figure 5.8: ZVI Filings Langmuir Isotherm Model

The ZVI filings data also had a regression coefficient closer to 1 for the Langmuir Isotherm model, indicating it was the better fit. The raw data used for the isotherm models can be found in Appendix C. The remaining analysis was conducted using the Langmuir Isotherm parameters, shown in the table below.

Table 5.1: Langmuir Isotherm Parameters

	Orange Peels	ZVI Filings
Q_O (mg/g)	123.47	11.19
K_L (L/mg)	3.53	1.89E-3
R_L (unitless)	0.458	0.03

The maximum adsorption capacity, Q_O, shows how much the material is capable of adsorbing. The Langmuir isotherm constant, K_L, is used to calculate the Langmuir Isotherm Equilibrium Parameter, R_L, which indicates the favorability of adsorption. An R_L value in the range from 0 to 1 indicates the material is favorable for adsorption. The orange peels and the ZVI filings were both determined to be favorable for adsorption.

6.0 Conclusions & Recommendations

At the conclusion of the data analysis, it was established that orange peels and ZVI filings are favorable for adsorption of uranium and arsenic, respectively. Two example scenarios were created in order to show the required mass of material to remove a specific amount of uranium or arsenic. The table below outlines the two separate scenarios.

Table 6.0: Example Scenarios

	Scenario #1 – Orange Peel	Scenario #2 – ZVI Filings
Initial Chemical Concentration	90 µg Uranium/L	70 µg Arsenic/L
Desired Final Chemical Concentration	30 µg Uranium/L	10 µg Arsenic/L
Adsorption Capacity (q)	0.007 mg U/g OP	0.38 mg As/g ZVI filings
Required Mass of Material for 10L of Contaminated Water	85.71 g OP	1.58 g ZVI filings

The initial concentrations were based off of the average chemical concentrations found at the Navajo Nation site from the previous year's team. The desired final concentrations are the EPA MCL's for uranium and arsenic. The adsorption value, q, was calculated based off of the isotherm models. The required mass of material to treat 10L of contaminated water calculated in order to give a representation of the removal efficiency of the material. It is recommended that the materials are tested for kinetics before being incorporated into water filter design.

7.0 Project Impacts

Uranium and arsenic are naturally occurring metals in the environment, and are often found at unhealthy levels on sites that have been impacted by activities such as mining. Levels of uranium and arsenic that exceed the EPA MCL's have negative human and ecological health effects. Conducting research on potential treatment materials for the chemicals can help eliminate these negative effects. Often times the public is not aware of the conditions at these contaminated sites, even if they live nearby. A project that is focusing on finding treatment methods for metal contamination can be a source of awareness to the public on these contaminated sites and the need for remediation. Similarly, this research has the potential to promote the findings of other sustainable water treatment methods. This is crucial for rural areas and developing countries that are also suffering from drinking water contamination, as it gives them a more accessible form of water treatment.

8.0 Summary of Project Costs

The original Gantt chart can be found in Figure 8.0 below. Although there were no changes to the task list, the dates of some of the tasks changed considerably. The final Gantt chart can be found in Figure 8.1.
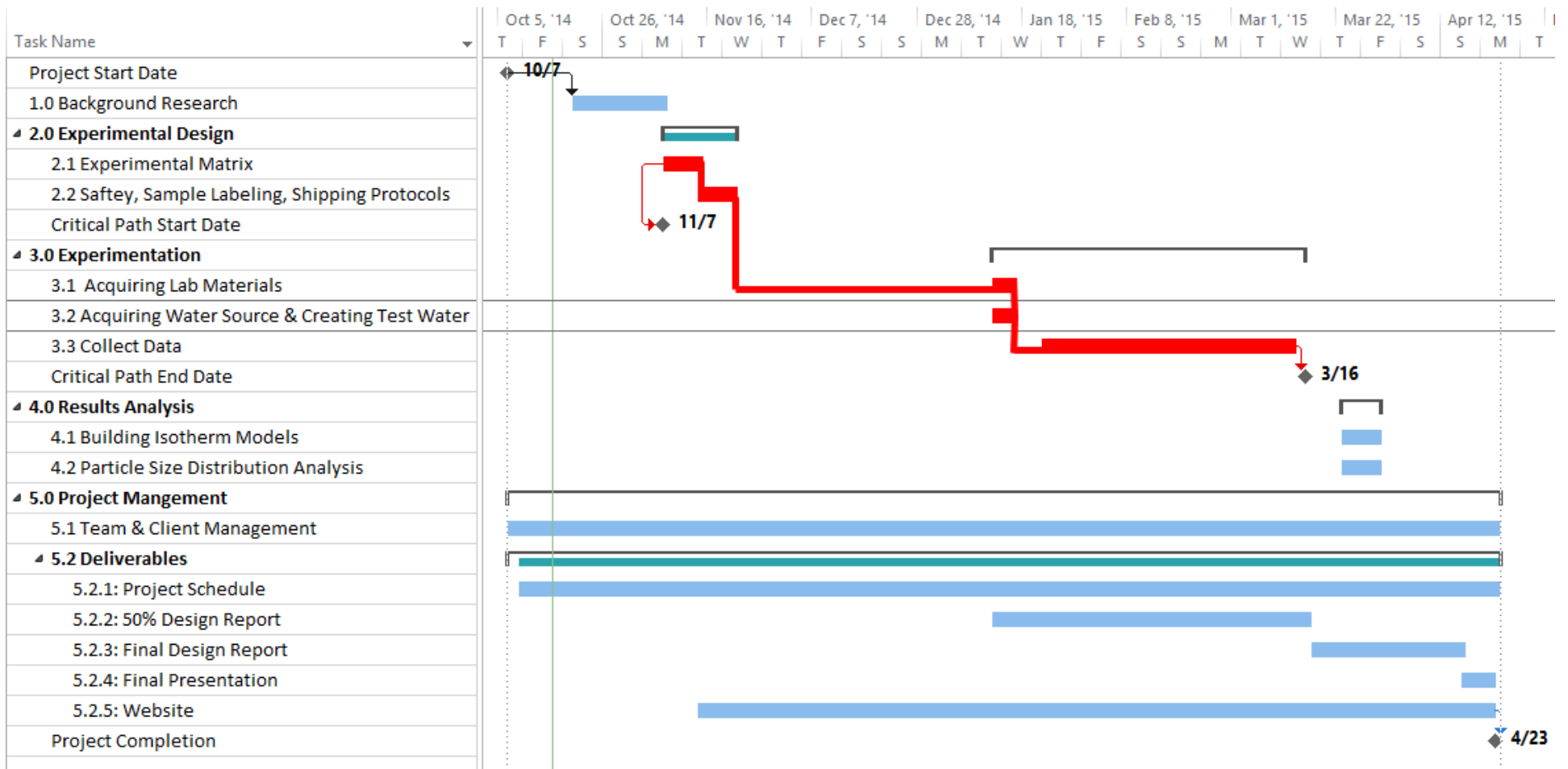
Figure 8.0: Original Gantt Chart [6]
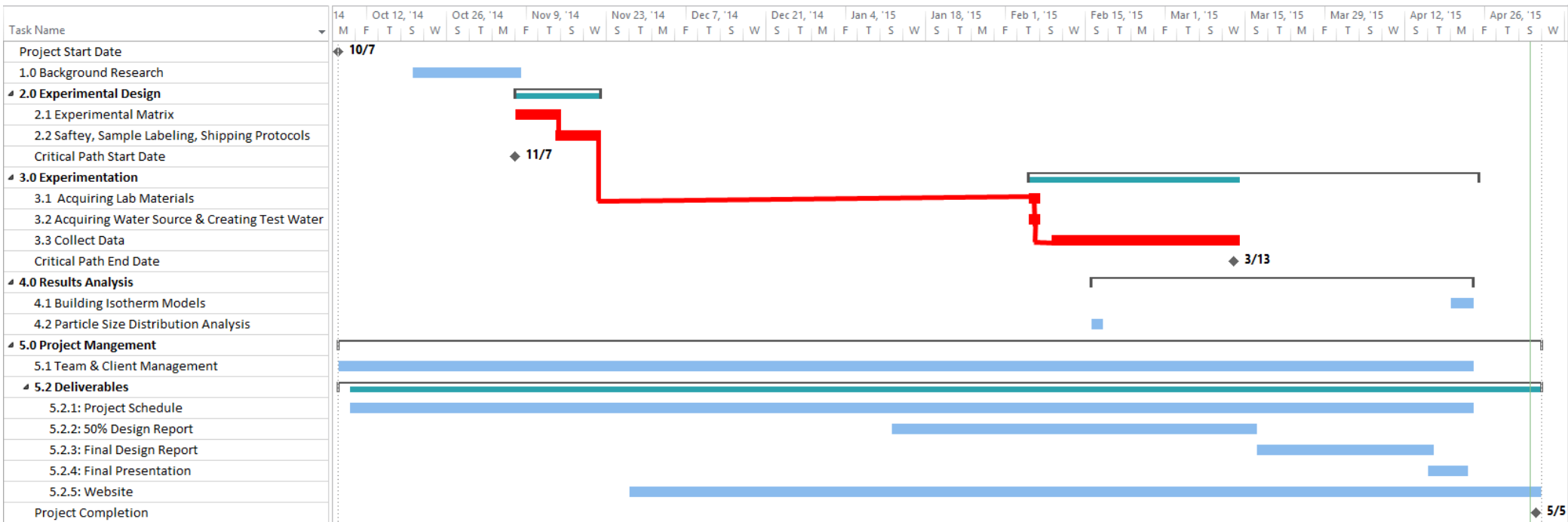
Figure 8.1: Final Gantt Chart

There were some issues in beginning the lab work, as coordinating the required meetings to begin working in the lab proved to be more difficult than anticipated. Further issues arose when the results for the second batch took much longer to arrive than the original two week time period that was given. Fortunately, all of the data arrived with time to complete all of the analysis for the project in order to still meet the project deadline as shown in the final Gantt chart.

The following tables show the estimated project costs and the actual project costs. The classifications are as follows: senior engineer (SENG), engineer (ENG), lab technician (LAB), intern (INT), administrative assistant (AA).

Table 8.0: Estimated Project Costs [6]

Item	Classification	Hours	Rate $/hr	Cost
1.0 Personnel	SENG	112	146	$16,336
	ENG	320	81	$25,907
	LAB	72	48	$3,450
	INT	152	22	$3,371
	AA	96	50	$4,847
	Total Personnel	752		$53,911
2.0 Subcontract	Analytical			
	150 samples + 2 shipments			$300
3.0 Total				**$54,211**

Table 8.1: Actual Project Costs

Item	Classification	Hours	Rate $/hr	Cost
1.0 Personnel	SENG	46	146	$6,716
	ENG	213	81	$17,253
	LAB	45	48	$2,160
	INT	12	22	$264
	AA	61	50	$3,050
	Total Personnel	377		$29,443
2.0 Subcontract	Analytical			
	150 samples + 2 shipments			$300
3.0 Materials	Orange Peels & ZVI Filings			$60
			Total Cost	**$29,803**

The assigned hours were greatly overestimated, as the final total project hours was 377 instead of the anticipated 752. This was largely due to the overestimation of hours worked in the lab. The batch testing procedures performed did not require as much man-hours as originally anticipated. The cost of materials was also not calculated into the estimated project cost, although it was in the actual project costs. This left the actual project costs at a total of $29,803 versus the estimated $54,211.

8.0 References

[1] D. Cummings, C. Dilks, Y. Sun, & T. Weir, "Final Design Report: Water Filter for Uranium, Arsenic and Bacteria Removal," Northern Arizona University, Flagstaff, Arizona. May 1st, 2014.

[2] A. Dabrowski, "Adsorption – from theory to practice", Faculty of Chemistry, M. Curie-Skodowska University., Lublin, Poland., 2001.

[3] J.R. Mihelcic and J.B. Zimmerman, "Chemistry," in Environmental Engineering: Fundamentals, Sustainability, Design, 1st ed. Hoboken, NJ: John Wiley & Sons, Inc., 2010, ch. 3, sec. 10, pp. 76-89.

[4] S. K. Bajpai and A. Jain, "Equilibrium and Thermodynamic Studies for Adsorption of Crystal Violet onto Spent Tea Leaves (STL)," Water Journal., Nov 2012. Doi: 10.14294/WATER.2012.5

[5] A.O. Dada, A.P. Olalekan, A.M. Olatunya, "Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk," IOSR Journal of Applied Chemistry vol. 3 issue 1., Nov-Dec 2012.

[6] H. Alkandari, A. Alsaraf, M. Beltran, & J. Zhang, "Adsorptive Capacity of Orange Peels and Zero Valent Iron Filings for the Removal of Uranium and Arsenic," Northern Arizona University, Flagstaff, Arizona. December, 2014.

9.0 Appendices

Appendix A: Lab Safety Plan

KATHAROS
ENGINEERING

Northern Arizona University

Adsorptive Capacity of Orange Peels and Zero Valent Iron Filings Project Lab Safety Plan

February 3rd, 2015

Table of Contents

1.0 Overview

The goal of the lab safety plan is to promote safety throughout the project. The lab work will be conducted in the Northern Arizona University (NAU) Environmental Engineering Lab (Building 69, Room 245). This lab safety plan will include the facilities the lab offers for safety purposes. The lab safety plan will also review chemical hygiene information. This includes proper chemical handling, the personal protective equipment that must be worn, proper sample labeling, accidents response, the necessary lab training that must be completed to work in the lab, and the proper waste disposal methods. Each individual team member will be required to review the lab safety plan and sign a contract stating they have read and agree with all of the lab work requirements. This contract can be found in Appendix A.

2.0 Laboratory Facilities

2.1 Shower & Eye Wash Station

There are two shower and eye wash stations located in room 245, one on the north section and one in the south section of the lab. Instructions on how to use the shower and eye wash station are shown in the figures below. If eye contact occurs with the chemical, the eyes must be flushed with water at the eye wash station for at least 15 minutes.

Figure 6: Shower & Eye Wash Station Room 245, North Side

Figure 7: Shower & Eye Wash Station Room 245, South Side

Figure 8: Shower & Eye Wash Station, Shower Instructions

Figure 9: Shower & Eye Wash Station, Eye Wash Instructions

As shown in Figure 3, in order to use the shower station the individual must stand underneath the shower head and pull on the triangular handle. As shown in Figure 4, in order to use the eye wash station the individual must stand over the station with eyes lined up with the respective water outlets and push on the paddle to the right of the station.

2.2 Fume Hoods

There is one fume hood located in room 245, as shown in the figure below. The fume hood provides the ventilation required for the use of chemicals. All of the arsenic and uranium solutions will be stored in the fume hood for the duration of the tests.

Figure 10: Fume Hood Room 245

3.0 Chemical Hygiene

3.1 Chemical Handling

When handling uranium and arsenic chemicals, personal protective equipment must be worn at all times and any contact with skin, eyes, and clothing must be avoided. All arsenic and uranium solutions must be sealed and stored under a fume hood. Inhalation and ingestion must also be avoided.

3.2 Personal Protective Equipment

The personal protective equipment that must be worn while conducting lab work includes lab coats and gloves for hand and body protection, and goggles for eye protection. If the student already wears eye glasses for vision correction, there are eye goggles meant to be worn over prescription glasses available in the lab. Additionally, closed toed shoes must be worn at all times and individuals with long hair must tie their hair back.

3.3 Labeling

All solutions must be clearly labeled with the concentration of the chemical, the date the solution was created, and the name of the team. All of the samples that will be used throughout the adsorption testing must be clearly labeled with the concentrations of the chemical, the adsorbate, mass of adsorbate, particle size of adsorbate, and the name of the team.

3.4 Accidents

Should a spill of any uranium or arsenic solution occur, it should be absorbed with a liquid-binding material. The material should then be disposed of by the methods set by the Northern Arizona University's Environmental Health and Safety program (see section 3.6).

If eye contact with any uranium or arsenic occurs, rinse opened eyes at the eye wash station for at least 15 minutes. If skin contact with any uranium or arsenic occurs, wash skin with plenty of soap and water, rinsing thoroughly, for at least 15 minutes. If inhalation of any uranium or arsenic occurs, the individual should move to fresh air immediately. If there is difficulty breathing, do not conduct mouth-to-mouth resuscitation, instead seek immediate medical attention. If ingestion of any uranium or arsenic occurs, do not induce vomiting and seek immediate medical attention.

3.5 Laboratory Training

There is required laboratory training that must be completed prior to working in the lab. In order to be able to work in the lab, each individual must have completed the Chemical Hygiene and Field Safety Training setup through Northern Arizona University's Environmental Health and Safety program. Certifications of training completion for each team member can be found in Appendix B.

3.6 Waste Disposal

The waste disposal methods are dependent on the Northern Arizona University's Environmental Health and Safety program. Decisions on how to properly dispose of the wastewater will be based upon the concentrations and volumes of uranium and arsenic that will be used throughout the lab.

4.0 Material Safety Data Sheets

The Material Safety Data Sheets (MSDS) for the arsenic and uranium standards can be found in the MSDS binders at the Right-To-Know station located in the north section of Room 245.

5.0 Appendices

5.1 Appendix A: Contract

KATHAROS
ENGINEERING

By signing this document I am confirming that I have read the Adsorptive Capacity of Orange Peels and Zero Valent Iron Filings Project Lab Safety Plan and I agree to comply with all of the lab work requirements outlined in the document.

X _____
Hussain Alkandari

X _____
Abdulaziz Alsaraf

X _____
Makenzi Beltran

X _____
Jiahao Zhang

5.2 Appendix B: Lab Training Certifications

Hussain Alkandari:

Completed tutorials for : Hussain Alkandari

Tutorial	Completed
Online Chemical Hygiene Training Part 3/3	Monday, September 01, 2014
Online Chemical Hygiene Training Part 2/3	Monday, September 01, 2014
Online Chemical Hygiene Training Part 1/3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 5	Monday, September 01, 2014
Field Safety Training- Module 1: Section 4	Monday, September 01, 2014
Field Safety Training- Module 1: Section 3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 2	Monday, September 01, 2014
Field Safety Training Module 1: Section 1	Monday, September 01, 2014

Abdulaziz Alsaraf:

Completed tutorials for : Abdulaziz Alsaraf

Tutorial	Completed
Online Chemical Hygiene Training Part 2/3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 5	Monday, September 01, 2014
Field Safety Training- Module 1: Section 4	Monday, September 01, 2014
Online Chemical Hygiene Training Part 3/3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 2	Monday, September 01, 2014
Field Safety Training Module 1: Section 1	Monday, September 01, 2014
Online Chemical Hygiene Training Part 1/3	Monday, September 01, 2014

Makenzi Beltran:

Completed tutorials for : Makenzi Beltran

Tutorial	Completed
Field Safety Training- Module 1: Section 5	Sunday, August 31, 2014
Field Safety Training- Module 1: Section 4	Sunday, August 31, 2014
Field Safety Training- Module 1: Section 3	Friday, August 29, 2014
Field Safety Training- Module 1: Section 2	Friday, August 29, 2014
Field Safety Training Module 1: Section 1	Friday, August 29, 2014
Online Chemical Hygiene Training Part 3/3	Friday, February 28, 2014
Online Chemical Hygiene Training Part 2/3	Friday, February 28, 2014
Online Chemical Hygiene Training Part 1/3	Friday, February 28, 2014

Jiahao Zhang:

Completed tutorials for : Jiahao Zhang

Tutorial	Completed
Field Safety Training- Module 1: Section 5	Monday, September 01, 2014
Field Safety Training- Module 1: Section 4	Monday, September 01, 2014
Field Safety Training- Module 1: Section 3	Monday, September 01, 2014
Field Safety Training- Module 1: Section 2	Sunday, August 31, 2014
Field Safety Training Module 1: Section 1	Sunday, August 31, 2014
Online Chemical Hygiene Training Part 3/3	Sunday, August 31, 2014
Online Chemical Hygiene Training Part 2/3	Sunday, August 31, 2014
Online Chemical Hygiene Training Part 1/3	Sunday, August 31, 2014

Appendix B: Dry Sieve Analysis Method

APPENDIX V:

GRAIN-SIZE ANALYSIS

1. DEFINITION. Grain-size analysis is a process in which the proportion of material of each grain size present in a given soil (grain-size distribution) is determined. The grain- size distribution of coarse -grained soils is determined directly by sieve analysis, while that of fine-grained soils is determined indirectly by hydrometer analysis. The grain-size distribution of mixed soils is determined by combined sieve and hydrometer analyses, Detailed procedures for determining the grain-size distribution of soils by sieve, hydrometer, and combined analyses are given below.

2. SIEVE ANALYSIS. a. Description. A sieve analysis consists of passing a sample through a set of sieves and weighing the amount of material retained on each sieve, Sieves are constructed of wire screens with square openings of standard sizes. The sieve analysis is performed on material retained on a U. S. Standard No. 200 sieve. The sieve analysis, in itself, is applicable to soils containing smali amounts of material passing the No. 200 sieve provided the grain-size distribution of that portion of the sample passing the No. 200 sieve is not of interest.

b. Apparatus. The apparatus should consist of the following:

(1) A series of U. S. standard sieves with openings ranging from 3 in. to 0.074 mm (No. 200), including a cover plate and bottom pan, conforming to ASTM Designation: E ii, Standard Specifications for Sieves for Testing Purposes.* The number and sizes of sieves used for testing a given soil will depend on the range of soil sizes in the material, and the intended use of the gradation curve.

(2) Sieve shaker, a mechanical unit which can produce on duplicate samples the same consistent results as those obtained by the circular and tapping motion used in hand sieving. Typical commercially available mechanical shakers are the Tyler "Ro-Tap" and the Combs and

* See page V-26 for U. S. Standard Sieve Sizes or numbers and sieve openings in inches and millimeters.

Syntron machines; there appears to be no significant differences in the resultsobtained among these machines.†

    (3)   Balances, sensitive to 0.1 g for samples weighing less than 500 g, and to 1.0 g for samples weighing over 500 g.

    (4)   Paintbrush, 1 in., or soft wire brush, for cleaning sieves.

    (5)   Sample splitter or riffle for dividing samples.

    (6)   Mortar and rubber-covered pestle, for breaking up aggregations of soil particles.

    (7)   Oven, similar to that described in Appendix I, WATER CONTENT - GENERAL.

    c.   <u>Preparation of Sample.</u>‡ The material to be treated is first air-dried, after which the aggregations present in the sample are thoroughly broken up with the fingers or with the mortar and pestle. A representative sample is then obtained by dividing, using the sample splitter or riffle. The size of the sample to be used will depend on the maximum particle size in the sample and the requirement that the sample be representative of the material to be tested. The sample should be limited .in weight so that no sieve in the series will be overloaded. Overloading of a sieve will result in incomplete separation with errors in the test. The following tabulation will be used as a guide in obtaining a minimum-weight sample:

*

Maximum Particle Size	Minimum Weight of Sample, g
3 in.	64,000 g
2 in.	19,000 g
1-1/2 in.	8,000 g
1 in.	2,400 g
3/4 in.	1,000 g
1/2 in.	300 g
3/8 in.	150 g
No. 4	50 g

*

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† U.S. Army Engineer Waterways Experiment Station, CE, <u>Sieve Analyses of Granular Soils by Division Laboratories,</u> Engineering Study 516 (Vicksburg, Miss., October 1963).

‡ Clay shale materials require special preparation. See paragraph 5.

If the sample contains more than about 10% of sizes larger than the No. 4 sieve, it is generally advisable to separate the material on the No. 4 sieve, retaining both fractions for independent sieve analysis as subsequently described. If the sample contains plastic fines which tend to form hard lumps or to coat the coarser particles during air-drying, the entire sample should be placed in a pan filled with water and allowed to soak until all the soil lumps or the coatings have disintegrated, before it is separated on the No. 4 sieve. The coarser fraction and the fraction passing the No. 4 sieve including the fines and water should be retained for independent sieve analysis as subsequently described.

d. **Procedure.** (1) Material predominantly finer than the No. 4 sieve. The procedure for samples predominantly finer than the No. 4 sieve consists of the following steps:

(a)   Record all identifying information for the sample, such as project, boring number, or other pertinent data, on a data sheet (see Plate V-1 for suggested form).

(b)   Oven-dry the sample at 110 ± 5 C, allow to cool, and weigh. If the sample weighs less than 500 g, weigh it to the nearest 0.1 g; if the sample weighs over 500 g, weigh to the nearest 1 g. Record the dry weight of the sample on the data sheet.

(c)   If the sample consists of clean sands or gravels, proceed with step (f).† If the sample contains plastic fines which tend to form hard lumps or to coat the coarser particles during oven-drying, place the oven-dry sample in a pan filled with enough water to cover all the material and allow it to soak until all the soil lumps or coatings have disintegrated. The length of time required for soaking will vary from about 2 to 24 hr, depending in general on the amount and plasticity of the fines.

(d)   Transfer the sample and water from the pan to a No. 200 sieve, or if the sample contains an appreciable amount of coarse

---

† If there is any doubt concerning the cleanness of a sand or gravel, i.e. whether or not the particles may be coated with fines, or if the test is performed to determine whether or not a material complies with specifications, then the sample should be treated as subsequently described in steps (c) through (e).

particles, to a combined set of No. 4 and No. 200 sieves. Care should be taken not to overload the No. 200 sieve; if necessary, transfer the sample in increments. Wash the sample thoroughly through the sieves, discarding the material passing the No. 200 sieve. Larger particles in the sample may be individually washed and removed from the sieves.

(e) Oven-dry the combined material retained on the No. 4 and the No. 200 sieves and, after the sample has cooled, weigh. Record on the data sheet in the "Weight Retained in grams" column the difference between the original oven-dry weight and the oven-dry weight after washing. Use the washed sample for the remainder of the analysis.

(f) Select a nest of sieves suitable to the soil being tested. The choice of sieves usually depends on experience and judgment, and the use for which the grain-size curve is intended. Select as the top sieve. one with openings slightly larger than the diameter of the largest particle in the sample. Arrange the nest of sieves according to size as shown in Figure 1, with decreasing openings from top to bottom. Attach the bottom pan

Figure 1. Arrangement of sieves for grain-size analysis

to the bottom of the smallest sieve used. Place the sample on the top sieve of the nest as shown in Figure 2 and put the cover plate over the top sieve.

(g) Place the nest of sieves in the shaking machine as shown in Figure 3 and shake them for 10 min, more or less, or until additional shaking does not produce appreciable changes in the amounts of material on each sieve. If a shaking machine is not available, the nest of sieves may be shaken by hand. In the hand operation, shake the nest of

sieves with a lateral and vertical motion, accompanied by jarring, to keep the material moving continuously over the surfaces of the sieves. Jarring is accomplished by occasionally dropping the nest lightly on several thicknesses of magazines. The nest should not be broken to rearrange particles or to

Figure 2. Placing soil on sieves

manipulate them through a sieve by hand. Hand-shaking should be continued for at least 15 min.

(h)   Remove the nest of sieves from the mechanical shaker, if used. Beginning with the top sieve, transfer the contents of the sieve to a piece of heavy paper approximately 1 ft square. Carefully invert the sieve on the paper and gently brush the bottom of the sieve, as shown in Figure 4, to remove all the sample. Transfer the sample from the paper to the balance and weigh in accordance with requirements in
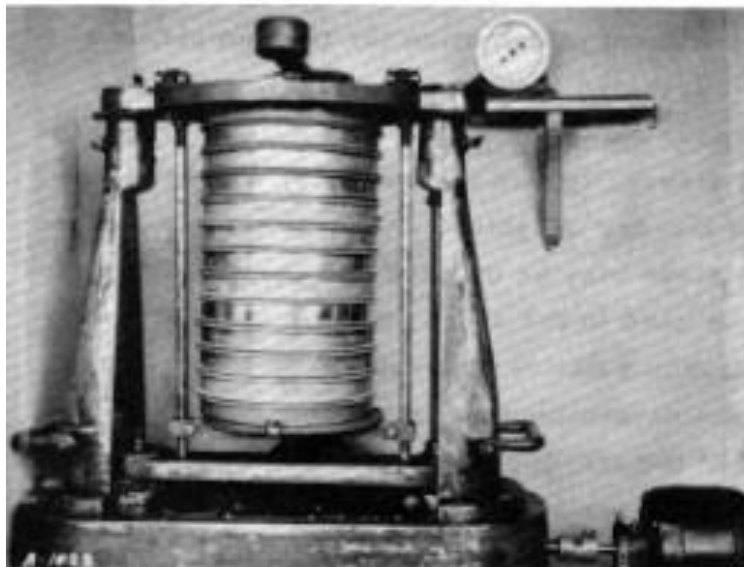
Figure 3.   Nest of sieves placed in typical machine for shaking

'Figure 4. Removing soil from sieves

step (b). Care should be exercised that no loss of material occurs during the transfer. Coarser fractions may be transferred more readily from the sieves directly onto the balance pan. Record the weight of material retained on each sieve on the data sheet.

(i) Repeat step (h) for each sieve. The sum of the weights retained on each sieve and pan should equal the initial total weight of the sample within 1 percent. If the difference is greater than 1 percent, the sieving should be repeated.

(2) Material split on No. 4 sieve. The procedure for samples which have been split on the No. 4 sieve consists of the following steps:

(a) Record pertinent information for the sample on a data sheet (see Plate V-i for suggested form).

(b) Oven-dry the sample, allow it to cool, and weigh the fraction retained on the No. 4 sieve. Record the oven-dry weight on the data sheet. Alternatively, the air-dry weights of the total sample and the fraction retained on the No. 4 sieve may be utilized and the air-dry material retained on the No. 4 sieve used in the sieve analysis as in step (c) below. In the latter procedure, the relative percentages of materials greater than the No. 4 sieve are determined on an air-dry basis. This method is satisfactory provided the air-dry water contents of the plus and minus No. 4 portions of the sample are approximately equal.

(c) Proceed as in paragraphs 2$\underline{d}$(1)(f) through 2$\underline{d}$(1)(i). In general, it is advisable to use large sieves and a Ty-Lab or Gilson shaker for the coarse fraction.

(d)   If the sample has not been washed during the preliminary treatment, process the material passing the No. 4 sieve according to paragraphs 2d(1)(b) through 2d(1)(i). If the material has been washed as part of the preliminary treatment, proceed with paragraphs 2d(1)(d) through 2d(1)(i), except that the material passing the No. 200 sieve in paragraph 2d(1)(d) should be oven-dried and weighed. This weight is added to the oven-dry weight of the plus No. 200 material to obtain the total weight of sample.

e.   <u>Computations.</u>   The percentage of material by weight retained on the various sieves is computed as follows:

$$\text{Percent retained} = \frac{\text{weight in g retained on a sieve}}{\text{total weight in g of oven-dry sample}} \times 100$$

If the sample has been split on the No. 4 sieve during preliminary treatment and the air-dried coarser fraction sieved independently, the percent retained for the coarser fraction is computed as follows:

$$\text{Percent retained} = \frac{\text{air-dry weight in g retained on a sieve}}{\text{air-dry weight in g of total sample}} \times 100$$

Similarly, for the finer fraction when oven-dry weights are used:

$$\text{Percent retained} = \frac{\text{weight in g retained on a sieve}}{\text{oven-dry weight in g of sample passing No. 4 sieve}} \times \text{percent passing No. 4}$$

where the percentage passing No. 4 sieve is computed on an air-dry basis. The values of percent retained based on the above formulas refer to the total weight of sample. Computation of a partial percent retained as indicated in Plate V-i is necessary only when the sample is initially separated on the No. 200 sieve for purposes of a combined analysis, as subsequently described. The cumulative percent finer by weight than an individual sieve size (percent finer) is calculated by subtracting the percent retained

on the individual sieve from the cumulative percent finer than the next larger sieve.

      f.   <u>Presentation of Results.</u>   The results of the sieve analysis are presented in the form of a grain-size distribution curve on a semi-logarithmic chart as shown in Plate V-2. The grain-size distribution curve is obtained by plotting particle diameter (sieve opening) on the abscissa (logarithmic scale) and the percent finer by weight on the ordinate (arithmetic scale).

Appendix C: Isotherm Model Data

Material	Mass	Ce	Co	Co-Ce	q	1/q	1/Ce	log q	log Ce
	g	mg/L	mg/L	mg/L	mg/g	g/mg	L/mg	mg/g	mg/L
OP	0.05	75.78	96.58	20.80	41.60	0.024	0.0132	1.62	1.88
OP	0.05	74.70	96.58	21.88	43.76	0.023	0.0134	1.64	1.87
OP	0.05	76.75	96.58	19.83	39.66	0.025	0.0130	1.60	1.89
OP	0.1	63.18	96.58	33.40	33.40	0.030	0.0158	1.52	1.80
OP	0.1	60.66	96.58	35.92	35.92	0.028	0.0165	1.56	1.78
OP	0.1	64.67	96.58	31.91	31.91	0.031	0.0155	1.50	1.81
OP	0.15	92.84	96.58	3.74	2.50	■	■	■	■
OP	0.15	84.97	96.58	11.61	7.74	0.129	0.0118	0.89	1.93
OP	0.15	78.01	96.58	18.57	12.38	0.081	0.0128	1.09	1.89
OP	0.25	68.75	96.58	27.83	11.13	0.090	0.0145	1.05	1.84
OP	0.25	66.05	96.58	30.53	12.21	0.082	0.0151	1.09	1.82
OP	0.25	62.62	96.58	33.96	13.59	0.074	0.0160	1.13	1.80
OP	0.35	58.97	96.58	37.61	10.75	0.093	0.0170	1.03	1.77
OP	0.35	58.08	96.58	38.50	11.00	0.091	0.0172	1.04	1.76
OP	0.35	60.35	96.58	36.23	10.35	0.097	0.0166	1.02	1.78
OP	0.4	67.15	96.58	29.43	7.36	0.136	0.0149	0.87	1.83
OP	0.4	54.96	96.58	41.62	10.41	0.096	0.0182	1.02	1.74
OP	0.4	54.49	96.58	42.09	10.52	0.095	0.0184	1.02	1.74
OP	0.45	53.68	96.58	42.90	9.53	0.105	0.0186	0.98	1.73
OP	0.45	57.63	96.58	38.95	8.66	0.116	0.0174	0.94	1.76
OP	0.45	49.95	96.58	46.63	10.36	0.097	0.0200	1.02	1.70
OP	0.5	51.98	96.58	44.60	8.92	0.112	0.0192	0.95	1.72
OP	0.5	46.11	96.58	50.47	10.09	0.099	0.0217	1.00	1.66
OP	0.5	53.76	96.58	42.82	8.56	0.117	0.0186	0.93	1.73
OP	0.6	45.65	96.58	50.93	8.49	0.118	0.0219	0.93	1.66
OP	0.6	45.40	96.58	51.18	8.53	0.117	0.0220	0.93	1.66
OP	0.6	42.12	96.58	54.46	9.08	0.110	0.0237	0.96	1.62
OP	0.75	34.43	96.58	62.15	8.29	0.121	0.0290	0.92	1.54
OP	0.75	36.50	96.58	60.08	8.01	0.125	0.0274	0.90	1.56
OP	0.75	37.80	96.58	58.78	7.84	0.128	0.0265	0.89	1.58
OP	0.9	29.46	96.58	67.12	7.46	0.134	0.0339	0.87	1.47
OP	0.9	31.19	96.58	65.39	7.27	0.138	0.0321	0.86	1.49
OP	0.9	28.37	96.58	68.21	7.58	0.132	0.0352	0.88	1.45
OP	1	28.25	96.58	68.33	6.83	0.146	0.0354	0.83	1.45
OP	1	27.85	96.58	68.73	6.87	0.146	0.0359	0.84	1.44
OP	1	24.73	96.58	71.85	7.19	0.139	0.0404	0.86	1.39
OP	1.5	17.87	96.58	78.71	5.25	0.191	0.0560	0.72	1.25
OP	1.5	19.51	96.58	77.07	5.14	0.195	0.0512	0.71	1.29
OP	1.5	19.63	96.58	76.95	5.13	0.195	0.0509	0.71	1.29

OP	2	15.22	96.58	81.36	4.07	0.246	0.0657	0.61	1.18
OP	2	17.15	96.58	79.43	3.97	0.252	0.0583	0.60	1.23
OP	2	14.76	96.58	81.82	4.09	0.244	0.0678	0.61	1.17
OP	3	16.25	96.58	80.33	2.68	0.373	0.0615	0.43	1.21
OP	3	14.25	96.58	82.33	2.74	0.364	0.0702	0.44	1.15
OP	3	16.04	96.58	80.54	2.68	0.373	0.0623	0.43	1.21
ZVI Filings	0.01	9.01	10.172	1.16	11.60	0.086	0.111	1.06	0.955
ZVI Filings	0.01	8.51	10.172	1.66	16.63	0.060	0.118	1.22	0.930
ZVI Filings	0.01	7.88	10.172	2.30	22.97	0.044	0.127	1.36	0.896
ZVI Filings	0.02	7.67	10.172	2.50	12.50	0.080	0.130	1.10	0.885
ZVI Filings	0.02	7.88	10.172	2.29	11.46	0.087	0.127	1.06	0.897
ZVI Filings	0.02	8.53	10.172	1.65	8.23	0.122	0.117	0.92	0.931
ZVI Filings	0.03	6.99	10.172	3.18	10.59	0.094	0.143	1.02	0.845
ZVI Filings	0.03	6.25	10.172	3.92	13.08	0.076	0.160	1.12	0.796
ZVI Filings	0.03	5.62	10.172	4.56	15.19	0.066	0.178	1.18	0.749
ZVI Filings	0.04	3.20	10.172	6.97	17.43	0.057	0.313	1.24	0.505
ZVI Filings	0.04	6.36	10.172	3.81	9.53	0.105	0.157	0.98	0.803
ZVI Filings	0.04	7.45	10.172	2.72	6.81	0.147	0.134	0.83	0.872
ZVI Filings	0.05	5.32	10.172	4.85	9.70	0.103	0.188	0.99	0.726
ZVI Filings	0.05	5.88	10.172	4.29	8.58	0.117	0.170	0.93	0.770
ZVI Filings	0.05	5.54	10.172	4.63	9.26	0.108	0.180	0.97	0.744
ZVI Filings	0.06	3.66	10.172	6.51	10.85	0.092	0.273	1.04	0.564
ZVI Filings	0.06	4.66	10.172	5.51	9.19	0.109	0.215	0.96	0.668
ZVI Filings	0.06	4.73	10.172	5.44	9.07	0.110	0.211	0.96	0.675
ZVI Filings	0.07	3.43	10.172	6.74	9.63	0.104	0.292	0.98	0.535
ZVI Filings	0.07	3.94	10.172	6.23	8.90	0.112	0.254	0.95	0.596

ZVI Filings	0.07	2.36	10.172	7.81	11.16	0.090	0.424	1.05	0.373
ZVI Filings	0.075	2.68	10.172	7.49	9.99	0.100	0.373	1.00	0.429
ZVI Filings	0.075	2.02	10.172	8.15	10.86	0.092	0.494	1.04	0.306
ZVI Filings	0.075	2.01	10.172	8.16	10.89	0.092	0.498	1.04	0.303
ZVI Filings	0.08	1.43	10.172	8.74	10.93	0.092	0.699	1.04	0.155
ZVI Filings	0.08	3.50	10.172	6.67	8.34	0.120	0.286	0.92	0.544
ZVI Filings	0.08	1.74	10.172	8.43	10.54	0.095	0.574	1.02	0.241
ZVI Filings	0.085	0.35	10.172	9.83	11.56	0.087	2.884	1.06	-0.460
ZVI Filings	0.085	0.74	10.172	9.43	11.10	0.090	1.353	1.05	-0.131
ZVI Filings	0.085	1.51	10.172	8.66	10.19	0.098	0.663	1.01	0.178
ZVI Filings	0.09	0.70	10.172	9.47	10.52	0.095	1.426	1.02	-0.154
ZVI Filings	0.09	1.81	10.172	8.36	9.29	0.108	0.552	0.97	0.258
ZVI Filings	0.09	0.55	10.172	9.62	10.69	0.094	1.821	1.03	-0.260
ZVI Filings	0.095	0.53	10.172	9.65	10.15	0.098	1.900	1.01	-0.279
ZVI Filings	0.095	0.77	10.172	9.40	9.90	0.101	1.301	1.00	-0.114
ZVI Filings	0.1	1.32	10.172	8.86	8.86	0.113	0.759	0.95	0.120
ZVI Filings	0.1	1.94	10.172	8.23	8.23	0.122	0.514	0.92	0.289
ZVI Filings	0.1	1.53	10.172	8.64	8.64	0.116	0.653	0.94	0.185
ZVI Filings	0.15	0.24	10.172	9.94	6.62	0.151	4.223	0.82	-0.626
ZVI Filings	0.15	2.23	10.172	7.94	5.30	0.189	0.449	0.72	0.348
ZVI Filings	0.15	0.33	10.172	9.84	6.56	0.152	3.007	0.82	-0.478
ZVI Filings	0.2	0.26	10.172	9.91	4.95	0.202	3.776	0.69	-0.577
ZVI Filings	0.2	0.32	10.172	9.85	4.93	0.203	3.112	0.69	-0.493

ZVI Filings	0.2	0.20	10.172	9.97	4.99	0.201	5.004	0.70	-0.699
ZVI Filings	0.25	0.23	10.172	9.94	3.97	0.252	4.263	0.60	-0.630
ZVI Filings	0.25	0.10	10.172	10.07	4.03	0.248	9.734	0.61	-0.988
ZVI Filings	0.25	0.23	10.172	9.94	3.98	0.252	4.301	0.60	-0.634
ZVI Filings	0.3	0.17	10.172	10.01	3.34	0.300	6.006	0.52	-0.779
ZVI Filings	0.3	0.16	10.172	10.02	3.34	0.300	6.397	0.52	-0.806
ZVI Filings	0.3	0.16	10.172	10.01	3.34	0.300	6.334	0.52	-0.802