Research Proposal

Alternative Biosorbent Design and Implementation

Corn Corps

CENE 476
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List of Abbreviations

AM (Abandoned Mine)
AMD (Acid Mine Drainage)
EBCT (Empty bed contact time)
EPA (Environmental Protection Agency)
GI (Grading instructor)
GAC (Granular Activated Carbon)
TA (Technical advisor)

1.0 Project Understanding

1.1 Project Purpose

The purpose of this research project is to determine the feasibility of utilizing corn cob as a biosorbent to remove cadmium and lead from contaminated drinking water. Some tests will be performed using corn cobs treated with nitric acid to assess the potential for increasing sorption efficiencies [1]. The removal of these contaminants through low-cost treatment alternatives is desired because traditional treatment technologies tend to be expensive and are not environmentally friendly [2]. Heavy metal contaminants such as lead and cadmium can enter drinking water supplies through a variety of natural and anthropogenic sources, such as the erosion of mineral deposits and via acid mine drainage (AMD). Heavy metals can pose serious threats to human health when ingested due to bioaccumulation and cause various diseases and disorders [3]. Corn cobs have the potential to remove lead and cadmium and provide clean drinking water economically, while simultaneously converting a waste product into a resource.

1.2 Project Background

1.2.1 Heavy Metal Background

Mining is a major industry in the United States. In 2016, the US produced $74.6 billion worth of minerals from 13,089 active mines [4], [5]. After mines have been exhausted, they are referred as abandoned mines (AM), which continue to produce AMD and contaminate the surrounding soil, water, and ecosystem. It is estimated that there are over 200,000 AMs nationwide, and 5,000 to 10,000 miles of streams and rivers that are impacted by AMD [6]. The worldwide cost of treating AMD is estimated in the tens of billions of dollars [7].

Heavy metal treatment technologies such as chemical precipitation, ion exchange, reverse osmosis, and biological treatment have been well developed. While these techniques often achieve high removal efficiencies, they use harsh chemicals, produce high volumes of waste, or require high energy inputs [2]. Biosorption technologies are being increasingly recognized for use in water treatment due to their simplicity, wide availability, and sustainability.

The accumulation of heavy metals in large quantities can pose serious threats to human health. The main health concerns for adults due to lead include but are not limited to joint/muscle pain, difficulties with memory, mood swings, reduced sperm count, and miscarriages/still births [8]. For children, health concerns include but are not limited to developmental delay, reduced IQs, weight loss, and seizures [8]. The health effects of cadmium include kidney, liver, bone, and blood damage [9]. The EPA maximum contaminant level (MCL) is 5 ppb for cadmium and 15 ppb for lead [10].

1.2.2 Corn Biosorbent Research at NAU

Corn is the most widely produced grain in the United States, with an estimated 120 million tons of biomass waste available for potential use [11]. During the 2017-2018 academic school year at NAU, the NASA space grant funded Melissa Jacquez, an environmental engineering undergraduate, to research the validity of corn cobs as a biosorbent for removing cadmium from water. Corn cobs were dried for 24 hours at 100 °C, then pulverized using a food processor, and sifted through a 250 µm sieve. One gram of the corn biosorbent was then added to 300 mL of cadmium solution at three known concentrations displayed in the experimental matrix in Table 1-1.

Table 1.1: Spring 2018 NASA Space Grant experimental matrix

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

By using HACH Method 8017 and a batch time of 90 minutes with three replicates for all testing, the following average removal efficiencies were obtained (Table 1-2). The initial and final concentrations resulting from the cadmium testing are shown below in Table 1-3.

Table 1.2: Removal efficiencies by mass for each tested concentration

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

Table 1.3: Initial and final cadmium concentration

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

* Final concentrations higher than initial concentrations due to analytical error

It was observed that higher initial concentrations of cadmium resulted in greater removal efficiencies. The validity of the isothermal model (Figure 1.1) has limitations because the isotherm model was produced from only three concentrations – a very small sample size – and several tests yielded higher final concentrations than the starting concentrations. There was likely experimental and/or analytical error, possibly due to a lack of familiarity with the HACH 8017 method. However, the research showed cadmium removal potential.

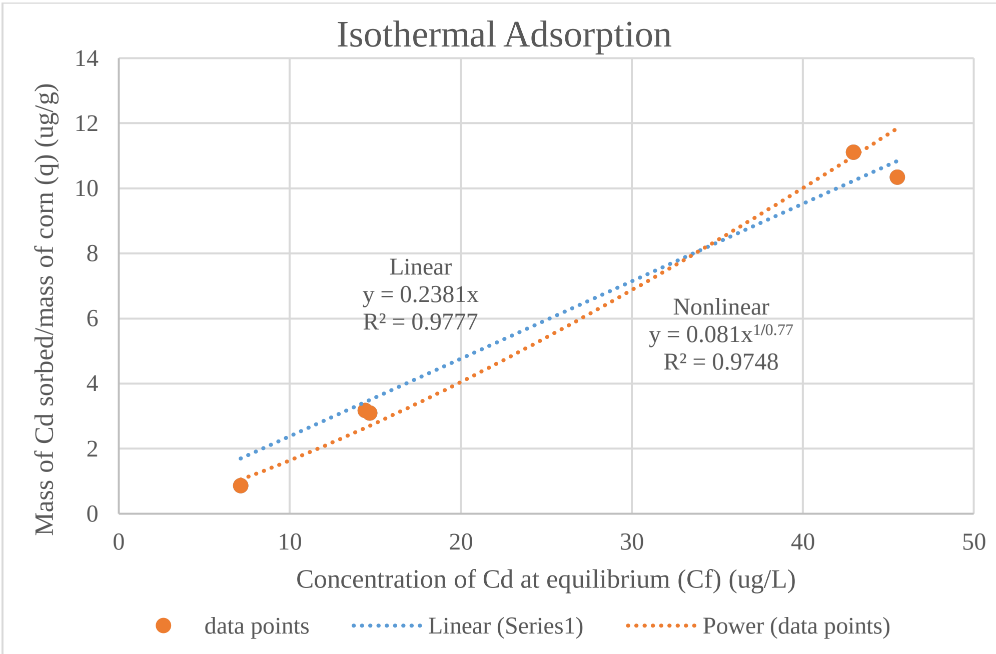

Figure 1.1: Preliminary adsorption isotherm of Spring 2018 research

1.3 Technical Considerations

Technical aspects of this project include experimentally determining the removal efficiencies of cadmium and lead by corn cobs following HACH Method 8017 and 8033. A bench-scale prototype will be constructed to model contaminant removal by corn cobs in real scenarios, such as the treatment of mine effluent. The parameters and results of the prototype will be scaled up to predict the effectiveness of a full-size design.

1.4 Potential Challenges

Potential challenges for this project include availability of lab space and equipment and limited funding. To ensure that testing can take place in the lab when there are no classes present, flexible schedules will be maintained until each member is comfortable with testing methods. Lab work can be rotated between two people at a time to work with available lab times. The number of tests conducted will be constrained by funding availability.

1.5 Major Stakeholders

Major stakeholders in this project are rural communities such as the Navajo Nation that depend on surface water, especially those located near current or AM operations which are at high risk for heavy metal contamination [12]. These types of communities could benefit from this research because it has the potential to increase drinking water quality and protect against heavy metal contamination for a relatively low cost.

In addition, local ecosystems and wildlife have a stake in this project due to the detrimental effects of lead and cadmium contamination. Both aquatic organisms and land animals have been shown to be adversely affected by heavy metal contamination. This depreciates the intrinsic value of wilderness and can also potentially diminish tourism rates in areas containing surface waters at risk of heavy metal pollution, which includes many rivers in the southwestern United States.

2.0 Research Plan

2.1 Health and Safety Considerations

2.1.1 Environmental Impacts

This project will involve working with toxic heavy metals, and therefore proper disposal is critical. All hazardous material, including cadmium, lead, and hazardous byproducts of testing such as chloroform will be disposed of as hazardous waste. Disposal will be coordinated with NAU’s Environmental Health and Safety, Office of Regulatory Compliance.

2.1.2 Health Impacts

The project would create direct health impacts in the event of accidental ingestion or inhalation of lead, cadmium, or toxic testing materials. This will be mitigated with safe lab practices, such as wearing the proper personal protective equipment (PPE), in accordance to the standard methods discussed in Task 2.

2.2 Task 1.0 Experimental Methods

2.2.1 Task 1.1 Corn Biosorbent Preparation

Enough corn will be prepared to satisfy testing and prototype needs. Heads of corn will initially be dried, first by removing the husks and then cutting the corn into 2-inch sections (kernels are still present at this point). The corn must be dried for at least 24 hours at 180 ˚C in a drying oven. The dried corn is de-kernelled, and the remaining dried cobs are pulverized and sieved through #60 sieve (250 μm).

Half of the pulverized cob will be treated with nitric acid in order to determine whether acid treatment increases sorption potential. The treated corn will be soaked with 1.0 M nitric acid (HNO_3) solution for 12 hours, then washed with distilled water. The washed corn sample will be oven dried at 100˚C for 12 hours. The corn sample will then be soaked with 1.0 M sodium hydroxide (NaOH) for 12 hours and rewashed with de-ionized water. Finally, the corn sample is oven dried again at 100˚C for 12 hours.

2.2.2 Task 1.2 Cadmium Testing

A standard cadmium solution will be prepared and then diluted to 10 μg/L, 20 μg/L, 35 μg/L, 50 μg/L, and 75 μg/L concentrations. This range of concentrations was selected because it is within the 80 μg/L testing limit of HACH Method 8017. Each of these concentrations will be tested three times. One gram of corn will be added to 300 mL of each of the known cadmium concentrations, then put on a rotary shaker table for 90 min at 250 rpm. The corn will be separated from the solution using a vacuum apparatus and

VWR® Fiber Filter 1.6 µm. The filtrate will be tested for remaining cadmium in accordance to HACH Cadmium Dithizone Method 8017.

Table 2.1: Cadmium experimental matrix

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

2.2.3 Task 1.3 Lead Testing

A standard lead solution will be prepared and then diluted to 10 µg/L, 50 µg/L, 100 µg/L, 175 µg/L, 225 µg/L, and 300 µg/L concentrations. Each of these concentrations will be tested three times. One gram of corn will be added to 300 mL of known lead concentrations, and then put on a rotary shaker table for 90 minutes at 250 rpm. The corn will be separated from the solution using a vacuum apparatus and VWR® Fiber Filter 1.6 µm. The filtrate will be tested for remaining lead in accordance to HACH Lead Dithizone Method 8033.

Table 2.2: Lead experimental matrix

Lead Experimental Matrix			
Experiment	Ci (µg/L)	Treated	Number of Replicates
Pb-1	10	No	3
Pb-2	50	No	3
Pb-3	100	No	3
Pb-4	175	No	3
Pb-5	225	No	3
Pb-6	300	No	3
Pb-7	10	Yes	3
Pb-8	50	Yes	3
Pb-9	100	Yes	3
Pb-10	175	Yes	3
Pb-11	225	Yes	3
Pb-12	300	Yes	3

2.3 Task 2.0 Isotherm Development

After all laboratory research has been completed and all samples have been analyzed for residual metal contamination, a Freundlich adsorption isotherm model will be developed. To ensure only valid results are utilized in the model, a geometric mean will be calculated for each concentration triplicate. Any outliers within each triplicate will be determined using Dixon's Q test, and the outlying concentration will not be used for the geometric mean calculation. Using the difference in initial and final metal concentration in the sample, the mass of metal removed from the water can be calculated. Sample analysis results will be plotted in Microsoft Excel to create the isotherm model. By graphing the mass of metal adsorbed per unit mass of corn cob (q) against the final equilibrium metal concentration in the sample (C_e), a best-fit line for both a linear and power model can be determined by maximizing the coefficient of determination (r^2) [13]. The model that has the higher r^2 value will be accepted as the adsorption isotherm and will be used for prototype development.

2.4 Task 3.0 Prototype Development

2.4.1 Task 3.1 Design Calculations

Based on the ideal ratio of mass of metal adsorbed per unit mass of corn cob and an empty bed contact time (EBCT) specified by the existing literature and practice, prototype dimensions (column volume and bed depth) and surface loading rate will be calculated. The EBCT refers to the time required for the contaminants to be adsorbed onto the biosorbent for adequate removal, and the surface loading rate refers to the flow rate through a given area of the filter bed [14].

2.4.2 Task 3.2 Prototype Construction

Construction drawings for the adsorption tower will be developed using SolidWorks. The final prototype will be manufactured by the NAU Machine Lab using acrylic plexiglass pipe.

2.5 Task 4.0 Pilot Testing and Scale-Up

Pilot tests will be conducted for both lead and cadmium removal using the constructed prototype. The results will be used to develop a breakthrough curve and generate scale up factors for full-scale design [14]. During the pilot test, one contaminant will be tested at a time, and the most effective corn cob (either treated with nitric acid or untreated) will be packed into the tower. Contaminated water will be passed through the column and the effluent concentration will be measured periodically until it reaches 95% of the influent concentration [14]. The volume of water treated will be calculated from a timed flow rate and the column dimensions [14]. Then, the effluent concentration will be plotted against the volume of water treated to develop the breakthrough curve and verify the breakthrough point (the point where the effluent adsorbate concentration reaches its maximum allowable concentration and the biosorbent must be replaced) [14]. This allows for the biosorbent usage rate to be determined. The breakthrough curve and biosorbent usage rate will be used to scale up the prototype to a theoretical full-scale design.

2.6 Task 5.0 Cost-Benefit Analysis

2.6.1 Task 5.1 Feasibility Assessment

Once scaled up, the prototype will be compared to common metal-removing technology, such as granular activated carbon (GAC), to determine if the corn biosorbent design is feasible for implementation. Removal efficiencies and cost will be the primary criteria for consideration.

2.6.2 Task 5.2 Assessment of Potential Impacts

An assessment of potential impacts for implementing a full-scale corn biosorbent design will be completed. The three primary criteria for assessment include environmental benefits, social benefits, and economic benefits.

2.7 Task 6.0 Project Management

2.7.1 Task 6.1 Meetings Management

Meetings with the client, the technical advisor (TA), the grading instructor (GI), and the team will be arranged throughout the project. Team meetings will be held as needed but will occur at minimum on a weekly basis. Upcoming project tasks and deliverables will be discussed, and every meeting will include an assessment of progress regarding the work schedule. If the team is behind schedule, ways to get back on schedule must be discussed. Team meetings will also be arranged to review and finalize deliverables prior to submittal. All team members are required to attend, except in the event of extenuating circumstances.

The client and TA, Dr. Fethiye Ozis, will be consulted biweekly. These meetings will cover what the team has accomplished since the previous meeting and what is expected by the next meeting. Dr. Ozis will be the contact who will vet all project ideas and provide suggestions. All team members are required to attend, except in the event of extenuating circumstances.

Meetings with the GI, Dr. Bridget Bero, will be held as needed to discuss upcoming deliverable expectations and address any questions or concerns regarding comments made on the previous deliverable. Dr. Bero may occasionally be contacted to provide further valuable technical advice from the perspective of a chemical engineer during the design phase of the project. All team members are required to attend, except in the event of extenuating circumstances.

All meetings require that an agenda be prepared and sent out via email to all attendants a minimum of 48 hours in advance. A meeting leader will be selected to lead the conversation according to the agenda and a secretary will take meeting minutes. The agendas and meeting minutes will be recorded in a Google Drive document so that all team members have full access.

2.7.2 Task 6.2 Project Deliverables

2.7.2.1 Task 6.2.1 30% Report

One third of the way into the project timeline, a progress report detailing the work completed thus far will be generated and submitted to the technical advisor, client, and grader.

2.7.2.2 Task 6.2.2 60% Report

Two thirds of the way into the project timeline, a progress report detailing the work completed thus far will be generated and submitted to the technical advisor, client, and grader.

2.7.2.3 Task 6.2.2 Final Report

Once the project is completed, a final design report will be developed and submitted to the technical advisor, client, and grader. The final report will include the project description, technical work and results, and the final design.

2.7.2.4 Task 6.2.2 Website

Once the final design report has been completed, a website will be developed to showcase the entire research project. The website will consist of multiple webpages, including but not limited to a home page, project information page, and a documents page. Pictures during various stages of project development will also be uploaded. The website will be easy to navigate, minimizing the amount of links.

2.7.2.5 Task 6.2.2 Presentation

To conclude the research project, a presentation will be created with Microsoft PowerPoint and will summarize the final design report. The presentation will include important information and pictures from the project. The presentation will introduce the project, explain the motivation for the research, describe the major tasks performed to complete the research project, and provide a summary of staffing and expenses.

2.8 Project Limitations

2.8.1 Challenges

Challenges will be present throughout the project, including during lab analysis and prototype development. The primary challenge that will be faced is maintaining uniformity among team members for all laboratory techniques so that the results are comparable. Another challenge will be the availability of corn during the off-season, as enough corn must be prepared in the fall to complete two breakthrough curves. This will be mitigated by ensuring that enough corn is prepared before corn becomes difficult to find in local grocery stores.

The primary challenge for prototyping will include adjusting the EBCT for the adsorption tower to ensure a residual effluent metal concentration exists. In addition, a major challenge will be designing a system to deliver a highly concentrated metal solution to a water line and allow for proper mixing to ensure a uniformly mixed influent metal concentration.

2.8.2 Exclusions

Several exclusions apply to this project due to time constraints. Lab analysis is limited to cadmium and lead removal, so no other contaminants will be assessed for sorption to corn. The concentrations that will be used in testing are limited to those within the detectable range specified by HACH. Additionally, only corn cobs will be analyzed as a sorbent, excluding the sorption to kernels, stalks, and husks of corn. In the design phase, exclusions apply to scale. Only a bench-scale will be developed, not a full-scale design due to time constraints.

3.0 Schedule

A schedule for this research project has been developed to ensure that the team accomplishes all tasks in a timely manner. The project has been scheduled to start August 7, 2018 and scheduled to finish April 26, 2018. The total duration of the project is 189 days. The critical path follows finish to start of Task 1.1 to Task 1.2, finish to start of Task 1.2 to Task 2.0, finish to start of Task 2.0 to Task 3.1, finish to start of Task 3.1 to Task 3.2, and then finish to start of Task 3.2 to Task 6.2.3. Task 6.2.3 (the final report) is finish to start of Task 6.2.5 (the final presentation) and project management will be conducted for the full length of the project. Because of the sequential nature of the project, the critical path length is equal to the project duration, which is 189 days. The yellow highlighted tasks are the major tasks that make up the critical path. For a Gantt chart with all tasks identified and highlighted critical path, please see Figure 3.1 (attached).

4.0 Staffing Plan and Cost of Engineering Services

4.1 Staff Titles

Three staff members will be working on this project, including a Senior Engineer (SENG), Engineer (ENG), and Lab Technician (LAB). The Senior Engineer will be leading the project and ensuring that all the requirements specified by the client are met by reviewing all milestone products. It will be the SENG's responsibility to develop and communicate goals and expectations for the project by providing guidance and feedback. Finally, they are responsible for making sure that the project is finished within budget and within deadlines.

The Engineer will perform all data analyses and design elements of the project. They will be developing the isothermal model, calculations, and construction drawing for the prototype. The engineer will be conducting the pilot testing. They will also be responsible for the preparing the cost benefit analysis. Lastly, they will be preparing all the deliverables which will be overseen by the Senior Engineer.

The Lab Technician will be conducting all lab experiments, including corn biosorbent preparation and collection of isothermal data. They will also be conducting cadmium and lead testing during prototype analysis.

4.2 Summary of Qualifications

All staff have acquired various experiences throughout their involvement in the environmental engineering program, however the following qualifications are overarching:

1. Passed the Environmental FE exam licensed through NCEES
2. Handled water samples and conducted water quality analysis using Northern Arizona University's environmental lab
3. Produced isotherms using equipment in Northern Arizona University's environmental lab including the DR 3900 spectrophotometer
4. Completed chemical hygiene training through Northern Arizona University
5. Gained proficiency in writing technical reports that summarize results clearly and rationally.

Melissa Jacquez was funded by NASA space to test the viability of corn cobs as a biosorbent and presented findings at the Arizona NASA Space Consortium, Water Symposium, 2018 AISES National Conference, and NAU Undergraduate Symposium. She established the method for creating a corn biosorbent dried for 24 hours, pulverized, and sieved 250 μm. She conducted the HACH 8017 method for 22 tests using the DR 3900 spectrophotometer and created isothermal adsorption model for the data collected.

Madeleine Stoll has 1.5 years of experience working as a water quality lab assistant in the Environmental Engineering Lab. Her time as an assistant has resulted in great familiarity with the laboratory itself, as well as experimental methods for analyzing water parameters. Madeleine also spent a summer as an intern with the Arizona Hydrological Society analyzing water quality field parameters in the Grand Canyon and Great Basin National Park.

Kylie Dykstra has a minor in chemistry and completed a 10 week internship at an industrial wastewater treatment plant, so she is familiar with large-scale water treatment operations that will be useful for scale up design considerations, pumping and instrumentation diagrams, and water quality testing.

Joel Gilbert gained experience producing isotherms from adsorption batch reactions using equipment in Northern Arizona University's environmental lab including the DR 3900 spectrophotometer. Additionally, he used Microsoft Excel to produce a Freundlich isotherm from the data collected from the batch experiment.

4.3 Task Matrix

Table 4.1 displays the number of hours that will devoted by each staff member specific tasks throughout the project.

Table 4.1: Task Matrix, including number of hours by dedicated by staff

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

These anticipated hours were utilized to determine staffing costs for the project.

5.0 Cost of Engineering Services

Table 5.1 displays the billing rates for each staff member. These rates include overhead.

Table 5.1: Billing rates for each staff member

Classification	Billing Rate, $/hr
SENG	120
ENG	90
LAB	55

Table 5.2 displays the total projected cost of engineering services.

Table 5.2: Total projected cost

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

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