MONTANA UNIVERSITY SYSTEM RESEARCH INITIATIVE

Recovery of Metal Contaminants from Industrial Wastewaters with Magnetic Nanocomposites in a Novel Continuous Flow Process System

Quarterly Progress Report

January 1 to March 31, 2016

Submitted to:

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RECOVERY OF METAL CONTAMINANTS FROM INDUSTRIAL WASTEWATERS WITH MAGNETIC NANOCOMPOSITES IN A NOVEL CONTINUOUS FLOW PROCESS SYSTEM

This quarterly progress report covers the project period from January 1, 2016 to March 31, 2016. Data related to the results described in this quarterly progress report are available on request.

PERSONNEL/HIRES

Project staffing was completed in March 2016 with the hiring of Dr. Ryan Latterman. Dr. Latterman received his Ph.D. degree at Montana State University (MSU) in 2016. He will work with Dr. Rosenberg and the University of Montana (UM) Team. The Montana Tech (MTech) team is planning to add an undergraduate student to its portion of the project for summer 2016.

MTECH TEAM; Jerry Downey, PI

- Hsin Huang, Co-PI, Professor, Metallurgical and Materials Engineering

- Alysia Cox, Co-PI, Assistant Professor, Chemistry and Geochemistry

- David Hutchins, Materials Science Ph.D. student at MTech

- Jared Geer, undergraduate student in Metallurgical and Materials Engineering at MTech

- Renee Schmidt, Geochemistry MS student at MTech

UM TEAM; Ed Rosenberg, PI

- Emil DeLuca, Research Associate Lab Manager

- Ryan Latterman, Post-Doctoral Research Associate (arrived March 7, 2016).

EXPENDITURES

The total expenditures to date represent approximately 6% of the overall project budget of $495,127. The rate of expenditures for labor and materials accelerated in the second quarter after the project team rosters were filled. Overall, expenditures to date are below the projected totals, mainly because spending authority was not granted until approximately midway through the first quarter and the subsequent time required to fully staff the project. Rate of expenditure is expected to accelerate substantially in the summer months.

Table 1 – Summary of Project Expenditures through March 24, 2016

Category	Budget	Amt Spent	% Spent	Balance
Personal Services	$ 162,226	$ 4,029	2.5	$ 158,197
Contracted Services				
Subcontracts	$ 188,001	$ 12,935	6.9	$ 175,066
General	$ 50,000		0.0	$ 50,000
Supplies	$ 45,000	$ 5,546	12.3	$ 39,454
Travel	$ 2,500	$ 44	1.7	$ 2,456
Utilities	$ -	$ 82		$ (82)
Waivers & Scholarships	$ 17,400	$ 2,901	16.7	$ 14,499
Capital Equipment	$ 30,000	$ -	0.0	$ 30,000
Total Operating & Capital	**$ 495,127**	**$ 25,538**	**5.2**	**$ 469,589**

MTECH TEAM

- Total Budget: $309,953; total expenditures of $12,603 (4.1%) through March 24.

- Supplies expenditures include various fittings, pipes, pumps, and electrical components purchased in order to complete the reactor.

- Electromagnets, magnet wire, a power source, and other components were purchased in order to construct the magnetic separation module.

- Imminent supply purchases include a pH meter to support the continuous flow reactor; an imminent capital equipment purchase is an integrated electrowinning circuit to demonstrate the ability to recover metal from the ion exchange strip solution.

UM TEAM

- Total Budget: $188,001; total expenditures of $12, 935 (6.9%) through March 25.

- No equipment expenditures in the second quarter.

- All UM invoices forwarded to MTech have been approved for payment.

PROGRESS TOWARD MILESTONES

In the following sections, progress is described according to the specific project objectives.

OBJECTIVE 1: WASTEWATER CHARACTERIZATION

MTECH TEAM; Alysia Cox (Co-PI)

- The Environmental Dynamics in Geobiochemical Engineering (EDGE) Lab has sampled local surface waters (Blacktail and Silver Bow Creeks, 5 sites on two different days) and the flooded underground mine complexes (Anselmo, Kelley, Steward, Ophir, and Travona) in order to provide specific chemical targets and mixtures for treatment in the flow reactor.

- Renee Schmidt will present at Techxpo (the Annual Montana Tech Technical Exposition on April 28) with a poster entitled, "Microbial Habitats in Butte, MT Flooded Mine Shafts." EDGE Lab undergraduate Jordan Foster will present a talk at the Montana Academy of Sciences and a poster at Techxpo entitled, "Stormwater in Butte Area One: Implications for the Microbial Community."

- The EDGE Lab will finish processing chemical analyses on already collected water samples. Plans for sampling wastewater outside of the Butte Silver Bow area are being developed and will allow for characterization to be state-wide rather than local. In addition, sufficient quantities (40L) of wastewater will be selected and collected for future testing of reactor efficiency.

OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS

UM TEAM; Ed Rosenberg (PI)

Synthesis and characterization iron-magnetic nanoparticles modified for metal ion capture.

In our first quarterly report, we reported on four approaches to the synthesis of the iron-silica core-shell nanoparticles. These different approaches used 3-amino-propyltrimetoxysilane (APTMS) as the metal capturing reagent. The goal in the second quarter was to use the polyallylamine (PAA) as the metal capturing reagent, as for the previous micro-silica particles that have been commercialized. The work with APTMS allowed us to evaluate different ways to make the iron nanoparticles and the best way to bind the silanes to the iron surface without using the more expensive PAA. Transmission Electron Microscopy (TEM) verified the size of the iron nanoparticles.

Conversion of the iron cores to polymer modified core-shell iron-silica nanoparticles focused on two methods. One of the two best methods we found for this synthetic procedure involves precipitation of silicic acid onto the iron nanoparticles made from sodium silicate after removal of the sodium ions by ion exchange (Figure 1, Scheme 1, Pathway A). This is followed by reaction with a mixture of chloropropyltrimethoxy-

silane (CPTMS) and methyltrimethoxysilane (MTMOS) (Scheme 1). Use of this mixture is based on our prior work with silica nanoparticles. We have studied three ratios 1:7, 1:4 and 1:2 CPTMS:MTMOS. We found that 1:7 worked best based on the copper capacity of the material after reaction with polyallylamine (PAA, Scheme1), the final step in the synthesis. Dynamic Light Scattering (DLS) measurements gave a Z averaged diameter (ZAD, Scheme 1) of 243 nm. The copper capacity was 0.74 mmole/g for the 1:7 ratio, falling off to 0.58 and 0.4 mmole/g with the 1:4 and 1:2 ratios respectively (Figure 2). The 1:7 ratio is the same optimal ratio that we obtained with the previously reported silica nanoparticles, but the capacity is somewhat lower (~1mmol/g for the silica). SEM and TEM images of these core-shell nanoparticles showed particle aggregates of about 200 nm, almost the same as that obtained in solution from the DLS measurements but individual 10-12 nm core-shell nanoparticles could be clearly identified and iron core was clearly differentiated from the silica shell (Figure 3). Energy dispersive X-ray measurements (EDX) gave a percent by iron of 80-81 % and a 10 % Si, consistent with a thin layer of silica. Most importantly, we were able to successfully scale-up the synthesis from 1 to 5 grams and obtained identical copper capacities and particle size distributions. The nanoparticles from the scale-up have been given to Professor Downey's group at Montana Tech. Emil Deluca and I visited there on March 24.
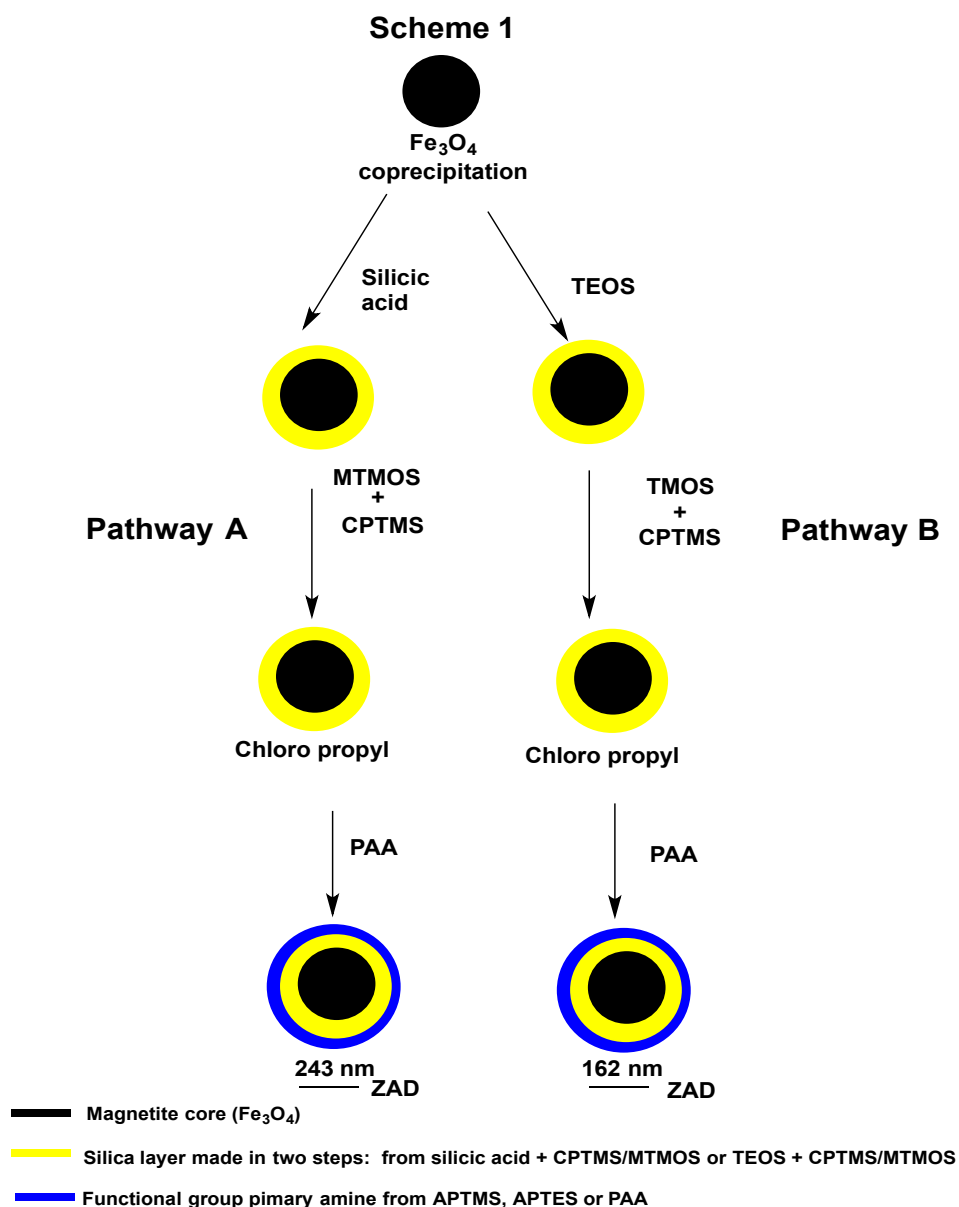
The other method utilized to synthesize the core-shell nanoparticles using PAA as the metal capturing ligand starts with the hydrolysis of tetraethyoxysilane (TEOS) (Scheme 1, Pathway B). This method is reported in the literature to give a silica coating on iron nanoparticles. This is followed by reaction with a mixture of CPTMS and MTMOS (Scheme 1). As for Pathway A we have studied three ratios 1:7, 1:4 and 1:2. Here again, we found that 1:7 worked best based on the copper capacity of the material after reaction with PAA (Scheme1) the final step in the synthesis. Dynamic Light Scattering (DLS) measurements gave a Z averaged diameter (ZAD, Scheme 1) of 162 nm. The copper capacity was 0.48 mmole/g for the 1:7 ratio, falling off to 0.38 mmole/g for the 1:4 and 1:2 ratios (Figure 4). Thus, so far this method does not provide copper capacities as good as Pathway A. SEM and TEM images are being made at the time of this writing for the products of Pathway B.

In comparing the two methods it is important to note that $NaSiO_3$ is much cheaper than TEOS but to convert it to silicic acid the sodium must be removed by ion exchange. This adds some cost and can be tedious on a large scale. So far the silicic acid approach (Pathway A) gives better capacity 0.74 vs 0.48 mmole/g.
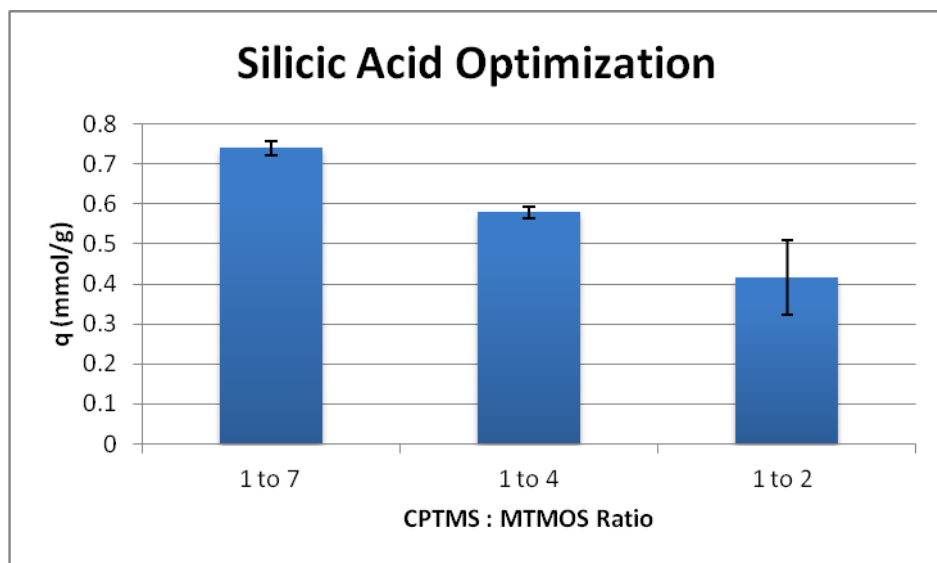
Summary and Next Steps:

- Although we have optimized the ratio of CPTMS: MTMOS for both Pathways, there are other reaction parameters such as reagent concentrations, times and temperatures as well sonication of the reactions during synthesis. These parameters will be optimized in the next quarter.

- We will extend the synthesis to the branched polymer polyethylene imine (PEI). This polymer is cheaper than PAA and has some certain advantages for recovery of specific metals.
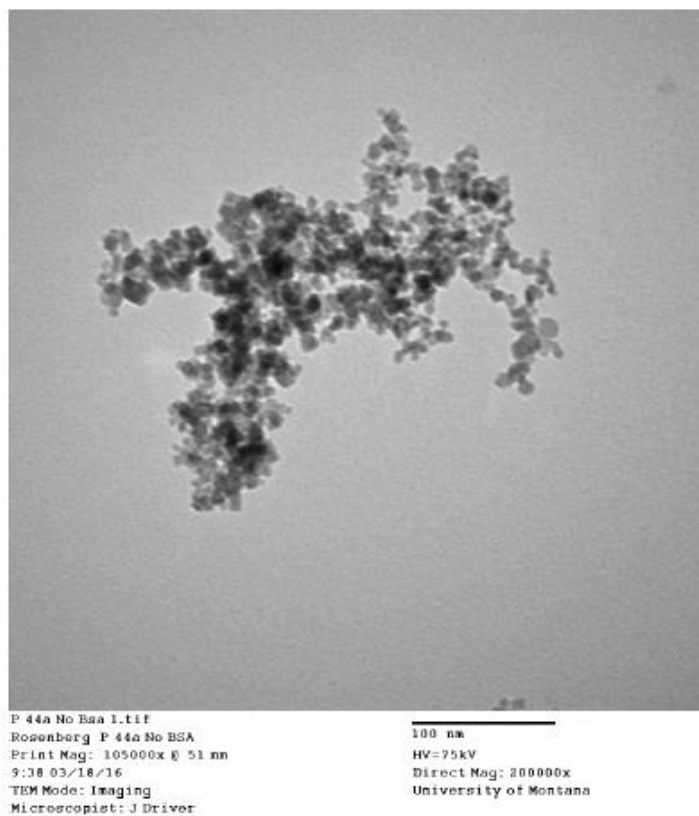
- We will begin to graft metal specific ligand onto the surface of the PAA-Fe-Si-core-shell nanoparticle.

- Continue characterization using TGA, XPS and porosymmetry.

- Further SEM and TEM using different sample preparations to see if the aggregates can be broken up. If the aggregates are broken up it is likely that they would do so in solution.

Scheme 1

Fe_3O_4
coprecipitation

Silicic acid

TEOS

MTMOS + CPTMS

TMOS + CPTMS

Pathway A

Pathway B

Chloro propyl

Chloro propyl

PAA

PAA

243 nm

162 nm

ZAD

ZAD

Magnetite core (Fe_3O_4)

Silica layer made in two steps: from silicic acid + CPTMS/MTMOS or TEOS + CPTMS/MTMOS

Functional group pimary amine from APTMS, APTES or PAA

Figure 2.1. Schematic diagram of scheme 1 illustrating two pathways to conversion of the iron cores to polymer modified core-shell iron-silica nanoparticles.

Figure 2.2. Copper capacity as a function CPTMS : MTMOS

P 44a No Bsa 1.tif
Rosenberg P 44a No BSA
Print Mag: 105000x @ 51 mm
9:38 03/18/16
TEM Mode: Imaging
Microscopist: J Driver

100 nm

HV=75kV
Direct Mag: 200000x
University of Montana

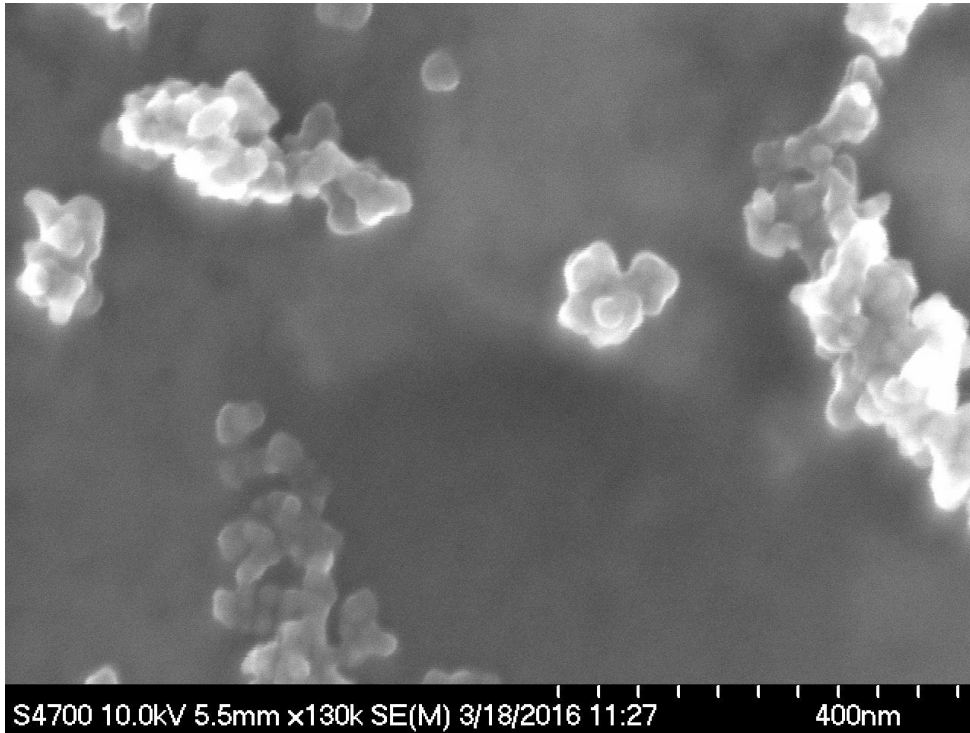**Figure 2.3a. TEM of Fe-Si-PAA core-shell nanoparticle made by Pathway A**

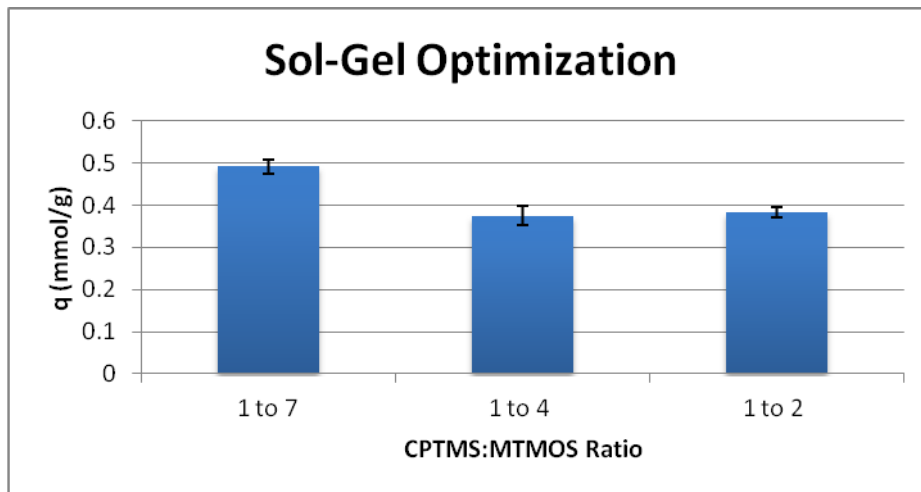**Figure 2.3b SEM of Fe-Si-PAA core-shell nanoparticle made by Pathway A**

Figure 2.4. Copper capacity as a function CPTMS : MTMOS

OBJECTIVE 3: SECURE FUNDAMENTAL AQUEOUS PROCESSING DATA AND GENERATE PROCESS MODELS

MTECH TEAM; H.H. Huang (Co-PI)

Dr. Huang initiated fundamental modeling of the Ion Exchange Column (or Packed Bed) reaction and equation. Much of the derivation of the ion exchange reaction in a column is predicated on the concept described by Helfferich[1].
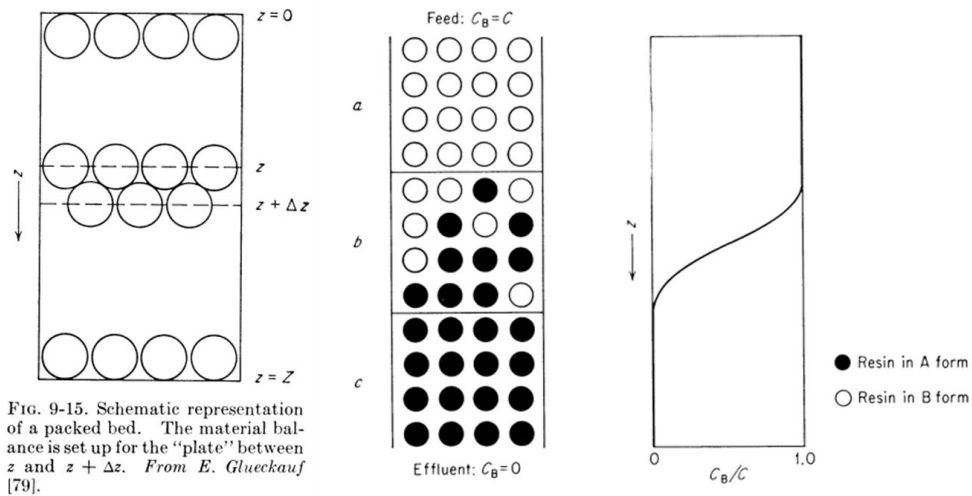

Figure 3.1 – Ion exchange in a packed bed column (Helfferich, 1962)

The overall rate of extraction for species B can be established from the mass balance in the solution and the mass transfer between the solution and the exchanger.

1. The mass balance of species B in the solution phase can be derived from:

   Rate of input – rate of output = rate of adsorption by the resin

2. Mass transfer of species B adsorbed by the resin can be controlled by one of the following steps in sequence as:

   Step 1 – mass transfer from the solution to the solution/resin interface

   Step 2 – mass transfer from the solution/resin interface to the resin surface

   Step 3 – diffusion of species B inside the resin

Cifuentes[2] showed two combined differential equations when Step 1 becomes the rate controlling step:

A. Mass balance in the liquid phase:

$$(C_{LB} - C^*_{LB}) = \partial C_{LB}/\partial t$$

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B. Mass balance in the solid phase

$$\partial C_{SB}/\partial t = k_{LB} \times A_L/(1 - \varepsilon) \times (C_{LB} - C^*_{LB})$$

where

C_{SB} and C_{LB} represent the solute concentrations in resin and in liquid, respectively

k_{LB} is the mass transfer coefficient per unit time unit interfacial (solution/resin) area

A_L is the interfacial area between solution and resin per unit volume of empty column

ε is the void fraction (volume solution space/volume of bed)

$1-\varepsilon$ represents the resin volume/volume of bed

C_{LB}^* is the solute concentration at solution/resin interface

U_f is the linear or superficial velocity (velocity of solution in empty bed)

By analysis of an experimentally determined breakthrough curve, the saturated concentration on the interface surface, C_{LB}^*, the mass transfer coefficient, K_{LB}, can be statistically estimated from the equations. Although our research project differs from Cifuentes' hypothesis both in physics and chemistry the method of derivation provides a useful guideline by identifying the important parameters to be collected throughout our research.

OBJECTIVE 4: CONTINUOUS FLOW REACTOR DESIGN, CONSTRUCTION, COMMISSIONING, AND OPERATION.

### MTECH TEAM; Jerry Downey (PI), David Hutchins, Jared Geer

- The literature review and patent search have been initiated and are ongoing. Findings to date confirm the novel nature of the continuous flow ion-exchange process.

- On January 14, David Hutchins delivered a presentation on the project to the Montana Legislature Education and Local Government interim committee in Helena.

- Construction and commissioning of the continuous flow reactor is nearing completion, and a control panel was installed. The integrity of the new pipeline reactor design has been established and liquid flow parameters have been defined. A system for slurry injection of the magnetic nano-composite particles has been designed, constructed and tested. Particle velocity and residence time data have been collected utilizing a surrogate ion-exchange resin. A Coriolis flow meter (donated by Emerson Process Management in Billings, MT) will be installed in the next quarter.

- Scoping tests involving multiple electromagnet configurations were conducted. A novel and potentially patentable in-flow electromagnet (Figure 4.2) was modeled, designed, tested, and installed. Experiments are planned to evaluate magnetic particle collection efficiency and to optimize the electromagnet design.

- Scoping experiments are in progress to define the analytical methods required to support process development.

- A computational model for the electromagnet design was developed and confirmed. A computational model for the collection of the ion-exchange particles via a high-gradient magnetic field was initiated. This model will be integrated into the greater model of the system.

- An electrowinning circuit that is compatible with the continuous flow reactor system has been identified and procurement is in progress; the circuit will be constructed and commissioned are planned during the next quarter.

Figure 4.1 – Photograph of the continuous flow reactor system (28-Mar-16). A slurry of magnetic nanocomposite ion exchange (IX) particles is introduced to the wastewater stream at the top of the platform. Functional groups impregnated on the surfaces of the ion exchange particles bond with metal ions as the particle-laden stream is pumped through the reactor. The in-line electromagnet (see white arrow in the photograph) captures and retains the magnetic nanoparticles without impeding the wastewater flow. Periodically, the valve positions are changed to divert flow (through a parallel magnetic module) in order to strip the ions from the captured particles; after stripping, the electromagnet is de-energized to release the particles, which are filtered, reconditioned, and returned to service.
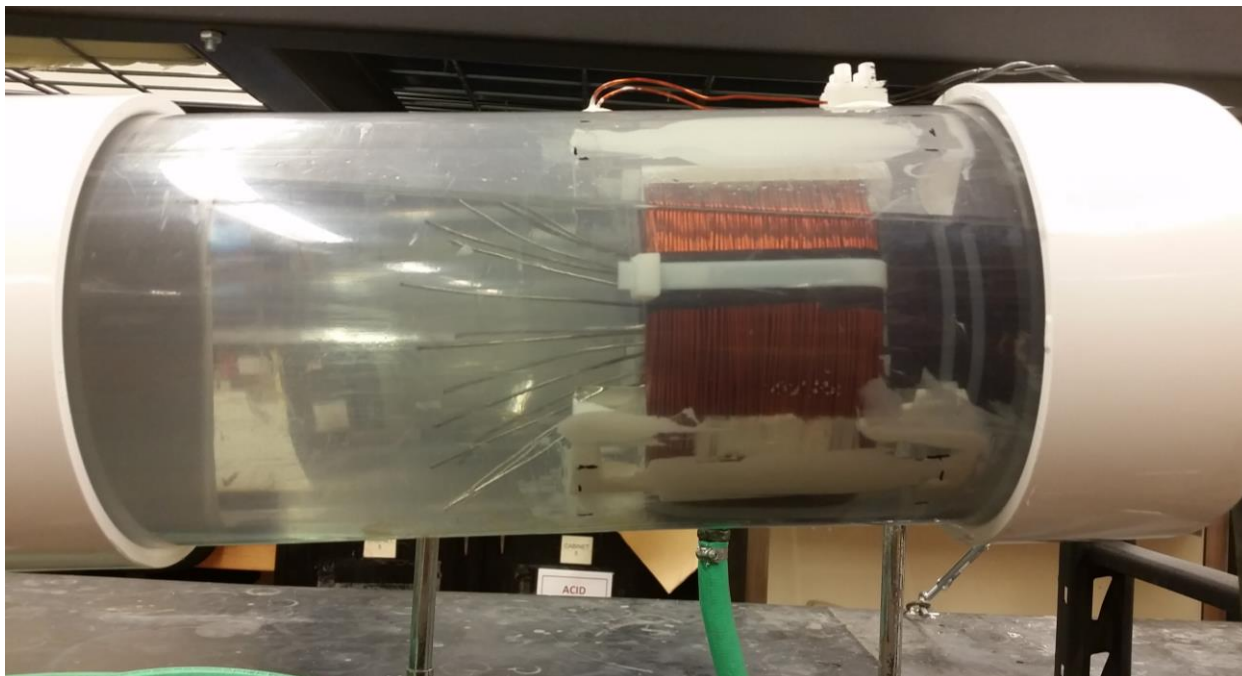
Figure 4.2 – Photograph of the first prototype in-line electromagnet module (28-Mar-16). Situating the electromagnet in the waterway is expected to improve magnetic nanocomposite IX particle capture efficiency and eliminate the need to cool the magnet's coil.

OBJECTIVE 5: DATA CONSOLIDATION AND REPORTING

- Documentation protocols, including laboratory notebook, file naming and sharing procedures, have been established and are in effect.

- Project metadata accumulation, consolidation, and security measures have been established and are in effect.

REFERENCES

Helfferich, F., Ion Exchange, McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Company, New York, 1962.

G. Cifuentes, Model and Simulation of an Ion Exchange Process for Extraction of Antimony," Collected Proceedings of the 140th Annual Meeting & Exhibition, TMS, 2011.