

MONTANA RESEARCH AND ECONOMIC DEVELOPMENT INITIATIVE (MREDI)

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

**Quarterly Progress Report
July 1 to September 30, 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 July 1, 2016 to September 30, 2016. Further significant progress has been made toward completion of the five project objectives. More detailed data related to the results described in this report are available on request.

PERSONNEL/HIRES

The University of Montana (UM) team added two undergraduate students since the progress report dated June 1, 2016 was submitted. The current team rosters:

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 Master of Science student at MTech
- Auva Speiser, undergraduate student in Metallurgical and Materials Engineering at MTech

UM TEAM; Ed Rosenberg, PI

- Emil DeLuca, Research Associate Lab Manager
- Ryan Latterman, Post-Doctoral Research Associate
- Two undergraduate students

EXPENDITURES

Total expenditures of \$187,458 recorded through the end of August, 2016, represent approximately 38% of the overall project budget of \$495,127. The rate of expenditure in the past quarter increased due to the increased level-of-effort for the summer months, mainly summer salary for faculty and longer hours (40 hrs/week) for the students. All phases of the project remain within budget.

Project expenditures are expected to surge in the upcoming quarter. There are two primary reasons for the surge: 1) procurement of equipment necessary to construct the 4th generation reactor at MTech and 2) increased analytical expense as much of the project focus will shift to metal capture and recovery from surrogate and actual wastewater samples.

Table 1 – Summary of Project Expenditures through August 31, 2016*

Category	Budget	Amt Spent	% Spent	Balance
Personal Services	\$ 162,226	\$ 87,872	54.2	\$ 74,354
Contracted Services				
Subcontracts	\$ 188,001	\$ 80,490	42.8	\$ 107,511
General	\$ 50,000		0.0	\$ 50,000
Supplies	\$ 45,000	\$ 15,936	35.4	\$ 29,064
Travel	\$ 2,500	\$ 44	1.7	\$ 2,456
Utilities	\$ -	\$ 202		\$ (202)
Other	\$ -	\$ 13		\$ (13)
Waivers & Scholarships	\$ 17,400	\$ 2,901	16.7	\$ 14,499
Capital Equipment	\$ 30,000	\$ -	0.0	\$ 30,000
Total Operating & Capital	\$ 495,127	\$ 187,458	37.9	\$ 307,669

***totals do not include some charges, such as Fall semester tuition, that had not entered the accounting system as of August 31.**

MTECH TEAM

- Total Budget: \$309,953; total expenditures of \$103,968 (33.5%) through August 31, 2016.
- Expenditures for Supplies and General Contracted Services (specifically analytical support) are anticipated to surge in the next quarter as the focus of the research transitions from reactor design and development to experimental determination of metal removal efficiencies.
- The entire capital equipment budget (\$30,000) is projected to be consumed during the next quarter. Equipment procurement was deferred to this point because the MTech team wanted to confirm the modified reactor design before committing funds to the acquisition of the new equipment.

UM TEAM

- Total Budget: \$188,001; total expenditures of \$80,490 (42.8%) through August 31, 2016.
- 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 Laboratory Exploring Geobiochemical Engineering and Natural Dynamics (LEGEND) sampled local surface waters (5 sites on one day in August). A total of 20 sites have been sampled on four different days since the beginning of the project. Nine flooded underground mine complexes have been sampled for water quality to date (Anselmo, Kelley, Steward, Ophir, Travona, Emma, Pilot Butte, Orphan Boy, and Orphan Girl), in order to provide specific chemical targets and mixtures for treatment in the flow reactor (Figure 1).
- In addition to wastewater collection and characterization, historic data provided by the Groundwater Information Center and Montana Bureau of Mines and Geology were analyzed for the Berkeley Pit, Lexington, Marget Ann, and Granite Mountain mines (Figure 2).
- Renee Schmidt will present a talk at the 2016 Mining and Mineral Symposium Confirmation held at the MBMG on October 21st on campus. Schmidt plans to present the historical trends of the nine mine sample sites with a specific focus on increasing arsenic levels at the American Geophysical Union Fall Meeting in December 2016.

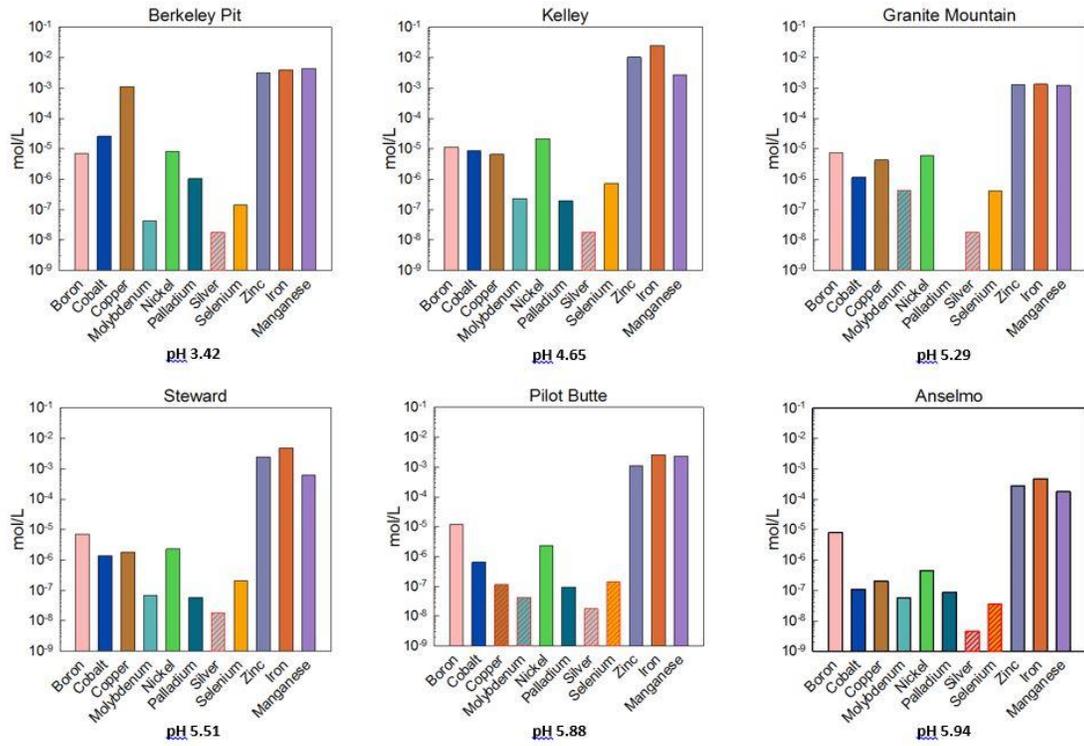


Figure 1. Selected metal concentrations of mine site samples

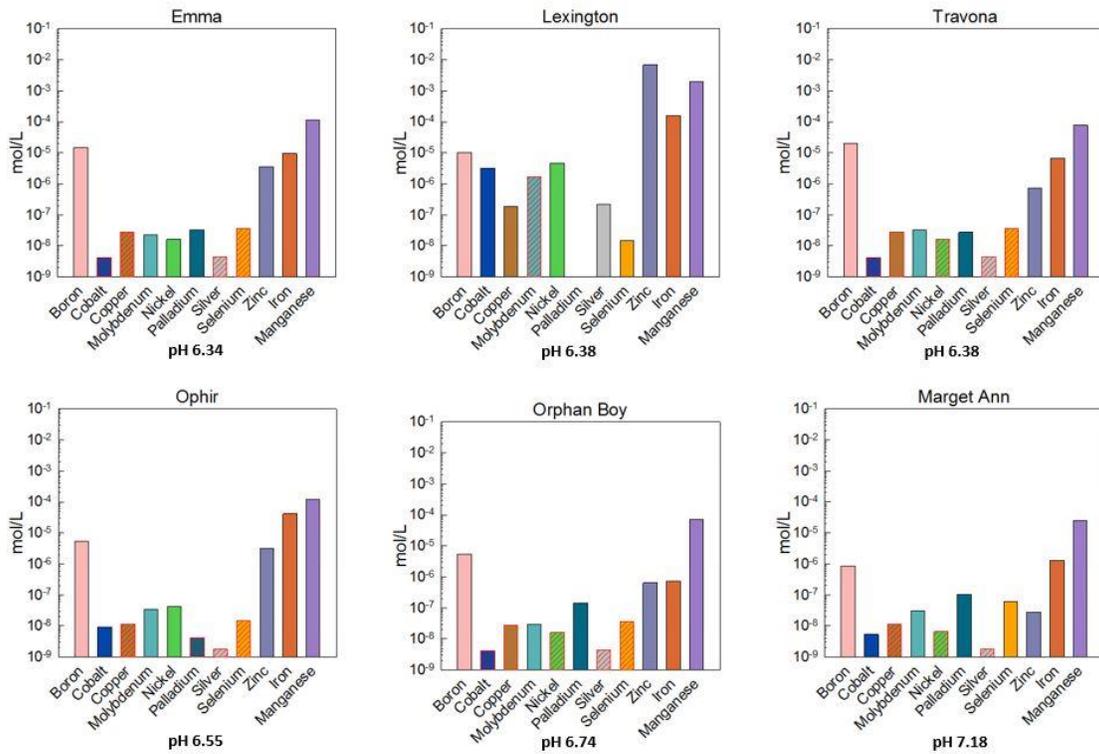


Figure 2. Mine site metal concentrations (historic data from MBMG)

OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS

UM TEAM; Ed Rosenberg (PI)

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

1. Speed of capture of dissolved metal ions.

The rate at which metal ions are captured from water solution by the suspended magnetic nanoparticle composites is probably the most important chemical property of these materials. The rate of capture will determine the residence time in the pipeline reactor for the contaminated stream and will also influence the residence time for the stripping and regeneration steps. To address this issue, we measured the rate of uptake of copper ions onto the PAA modified magnetic nanocomposites at two different concentrations, 1500 ppm and 150 ppm (see Figures 3a and 3b). The vertical axis on these plots shows the amount of copper ion absorbed per gram of composite. In both tests, 100 mg of composite and the amount of copper adsorbed was measured by atomic adsorption of the solution remaining. All measurements were done in triplicate and the volume of solution withdrawn was insignificant compared to the total volume of the solution. The time at which the curve levels off was in good agreement with the batch capacities of the material. It can be seen that the time at which the uptake leveled off is concentration dependent suggesting a second order process is expected.

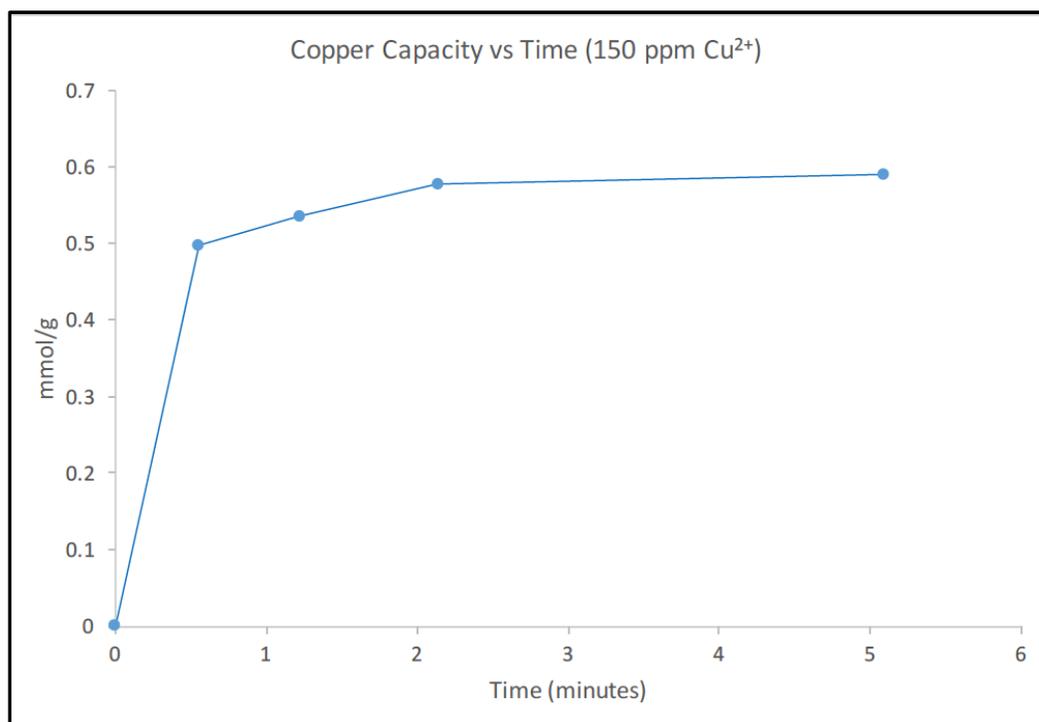


Figure 3a. Rate of capture of copper ions from a 500 ppm solution.

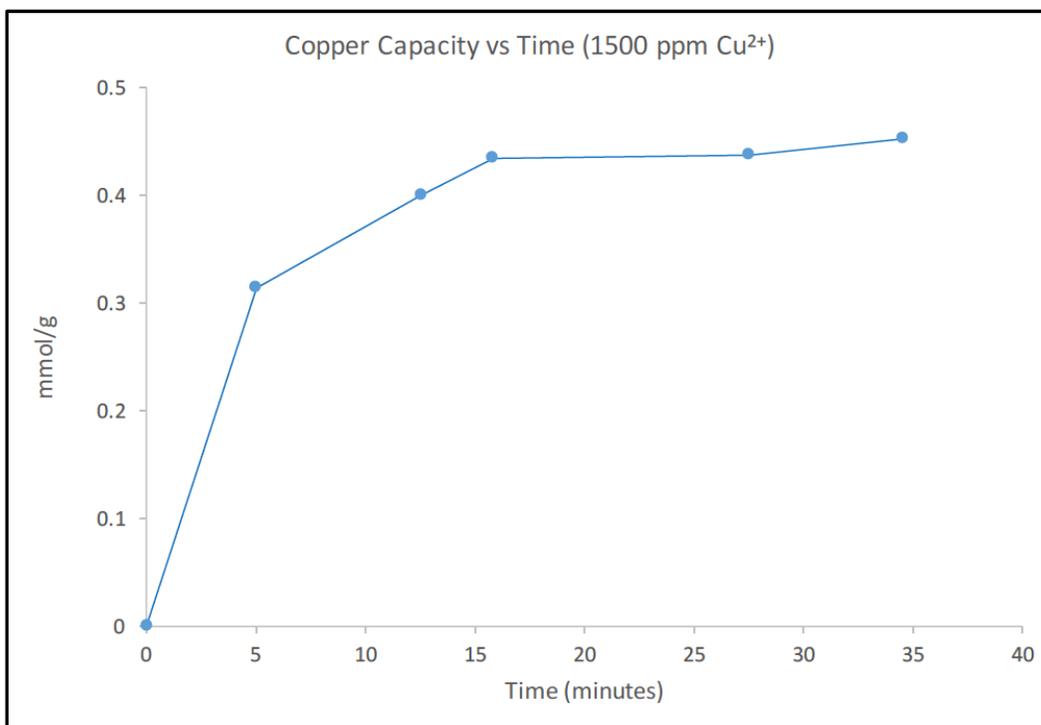


Figure 3b. Rate of capture of copper ions from a 1500 ppm solution.

It can be seen that the composite reaches full capacity in less than one minute (Figure 3a). This concentration of copper is close to that found in many mine waste streams. At 1500 ppm, saturation of the composite was reached at 15 minutes. The micro particles with a similar functionalization took about 150 minutes to reach saturation with the 1500 ppm solution. Thus, the nanoparticles are 10 times faster than the related silica polyamine composites made on the micro scale. These results bode well for the use of the nanoparticles in the pipeline reactor.

2. Commercial magnetite compared with magnetite prepared in the laboratory.

During the last two quarters, we have begun to use commercially available 20-30 nm magnetite made by Sky Spring Nanomaterials. The larger size provides stronger magnetism and these are the same particles used in testing the pipeline reactor. We have been able to make TEOS-PAA, core shell magnetic nanoparticles (CSMN) with copper capacities similar to the CSMN made with the smaller magnetite made by co-precipitation. The particles are easier to handle as they come as a dry powder and provide facile separations after modification. However, they are more difficult to suspend. On scale-up (*vide infra*) copper capacities were significantly lower than the particles made by the co-precipitation method previously used. The CSMN made with the Sky Spring particles appear to aggregate to a greater extent than the CSMN made from magnetite by the in house co-precipitation method (see Figure 4). This does not slow down the rate of capture of the metal ions from solution but may impact other properties such as stripping of the metal ions or the effective usable lifetime. We recently found a method of making magnetite from one-component solution (Ferrous Hydroxide). This worked nicely on a small scale but on scale-

up conversion to magnetite was incomplete. We are working on optimizing this conversion. The best situation would be 30 nm magnetite particles made by co-precipitation that should provide efficient magnetic capture with higher capacity for metal. We hope to have this resolved by the end of the next quarter.

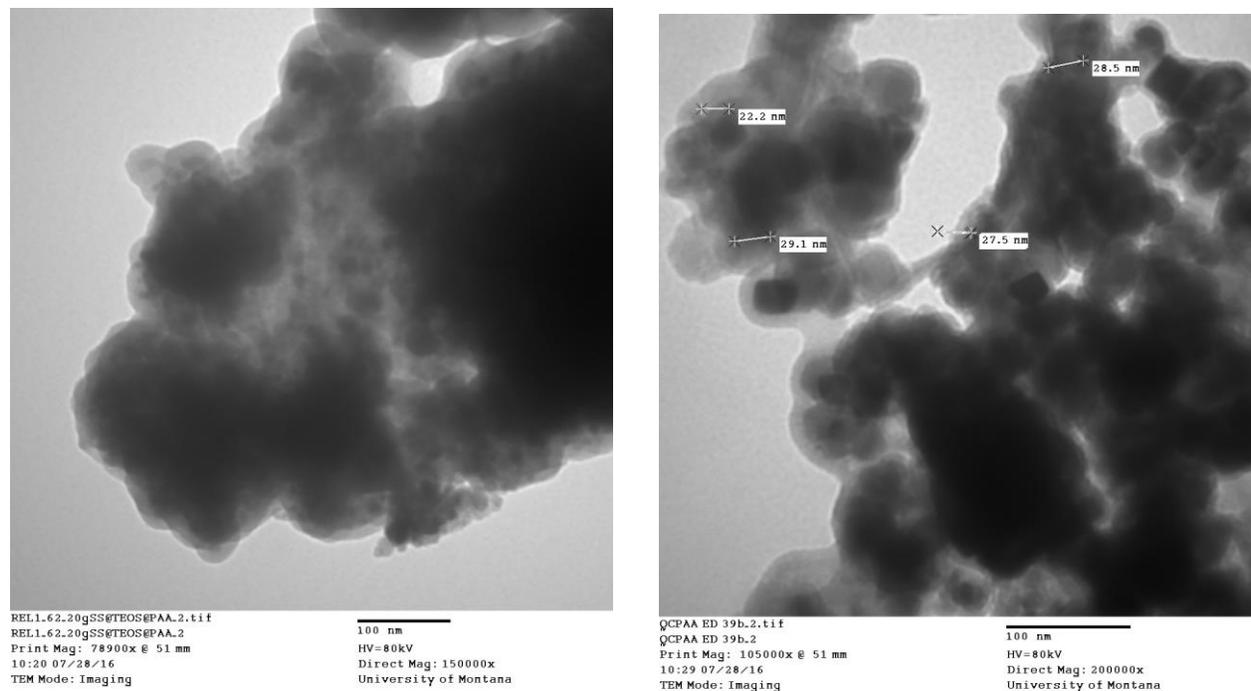


Figure 4. TEM image of magnetic nanoparticle composite materials: particles made from commercial magnetite (at left) and magnetic nanoparticle composite made from ferrous hydroxide (at right).

3. Scale-up of the core shell magnetic nanoparticles.

Our initial investigations revolved around defining the synthetic process and were performed on a 5 g reaction scale. David Hutchins, the designer and builder of the pipeline reactor at Montana Tech, said he needed at least 20 grams of CSMN to test in the reactor. In the last quarter, we have been making 20-25 gram batches starting with the Sky Spring magnetite and using the same TEOS-silane linker-PAA reaction sequence used on the smaller scale reactions. The procedure worked reasonably well but capacity for copper was about 25% lower than the small scale reactions. However, this lower capacity is still competitive with existing technologies and the results are reproducible. There are some reaction parameters that have still not been optimized such as reaction times and solvent volumes and these are currently being addressed. However, it should be noted that the behavior of the particles is identical to that observed for the particles made on a smaller scale. Figure 5 shows the apparatus used for the large-scale reaction. The picture shows the step where the excess TEOS reagent is being removed by suction and where the particles are efficiently gathered at the bottom.

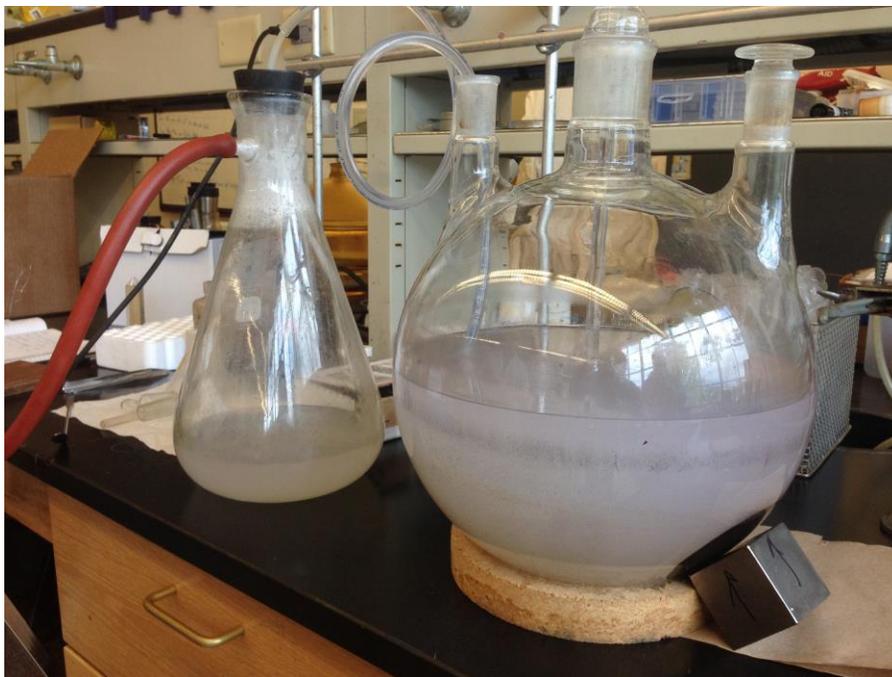


Figure 5. Large scale reaction vessel (12L) after the TEOS step showing the gathering of the particles with a permanent magnet at lower right hand corner

4. Summary of Progress

- Synthesized pilot scale quantities of functional nanoparticles with metal capacities competitive with current technologies.
- Demonstrated efficient capture by electromagnet.
- Demonstrated rapid capture of ions (10 x faster than current technologies).
- Demonstrated efficient recovery and regeneration with copper and cadmium ions.

5. Next Steps

- Further scale-up tailored to size of identified contaminated streams by MTech group.
- Optimize metal recovery and reuse parameters
- Modify particles to target toxic metals (cadmium, mercury, lead) and valuable metals (gold, palladium).
- Design and construction of cycle testing apparatus to determine usable lifetime.
- Economic evaluation of the manufacturing process

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

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

Fundamental study: Adsorption reaction for ion exchanger made from fine silica gel particles

Research performed by one of the co-PIs, Professor Rosenberg, indicated that the ion exchange reaction using nanoporous silica gel seems to be controlled by adsorption reaction. Results follow the Langmuir monolayer adsorption model. The following analysis used data presented by Professor Rosenberg entitled, “Characterization of Surface-Bond Zr(IV) and Its Application to Removal of As(V) and As(III) from Aqueous System Using Phosphonic Acid Modified Nanoporous Silica Polyamine Composites,” published by *Ind. Eng. Chem. Res.*, **2009**, 48(8), pp 3991-4001. Briefly, the experiment used immobilized Zr(IV) on BPAP (phosphonic acid modified silica polyamine composite) resin to exchange As(V) from the aqueous solution.

Adsorption reaction, Equilibrium Constant and adsorption isotherm

Symbol $S\equiv$ represents surface site that is capable of adsorbing species A from the solution to form $S\equiv A$ on the surface. The general adsorption reaction is shown in Reaction 1:



and the equilibrium constant, K, is given in Reaction 2:

$$K = [S\equiv A]/([S\equiv] \times [A]) \quad [2]$$

where the symbols $[S\equiv]$ and $[S\equiv A]$ denote the surface concentration of empty site and site occupied by adsorbate A, respectively. The symbol $[A]$ represents the concentration of adsorbate in the solution phase.

Adsorption isotherms are commonly employed to represent the equilibrium relationship between $[S\equiv A]$ and $[A]$. Using As(V) as an example, the amount of As(V) adsorbed, $[S\equiv As(V)]$, was determined by measuring equilibrium concentration of $[As(V)]$ in the solution at pH 6 (Figure 8).

Monolayer and Langmuir adsorption

The adsorption curve in Figure 8 indicates that adsorption approaches maximum at a high equilibrium As(V) concentration. This example provides a typical indication of monolayer adsorption, and is commonly explained by the Langmuir adsorption model. From the equation given above for the equilibrium constant, K, $[S\equiv]$ can be replaced by $[S\equiv T] - [S\equiv A]$, where the new symbol $[S\equiv T]$ represents the maximum coverage by the species A. By rearrange the equilibrium equation,

$$[S\equiv A] = [S\equiv T] \times \frac{K[A]}{1+K[A]} \quad [3]$$

$$\frac{[A]}{[S\equiv A]} = \frac{1}{K[S\equiv T]} + \frac{[A]}{[S\equiv T]} \quad [4]$$

Replacing [A] with C_e , [S≡A] with Q_c , [S≡T] with Q_m , and K with K_{ads} , a straight line equation based on Langmuir model between C_e/Q_c and C_e can be obtained, presented by Professor Rosenberg,

$$\frac{C_e}{Q_c} = \frac{1}{K_{ads}Q_m} + \frac{1}{Q_m}C_e$$

[5]

Figure 9 is the Langmuir linear plot for As(V) adsorption by Zr-BPAP at pH 6. The excellent fit of the model can be observed from experimental results. Constants Q_m and K_{ads} can be computed from the slope and intercept of the straight line equation.

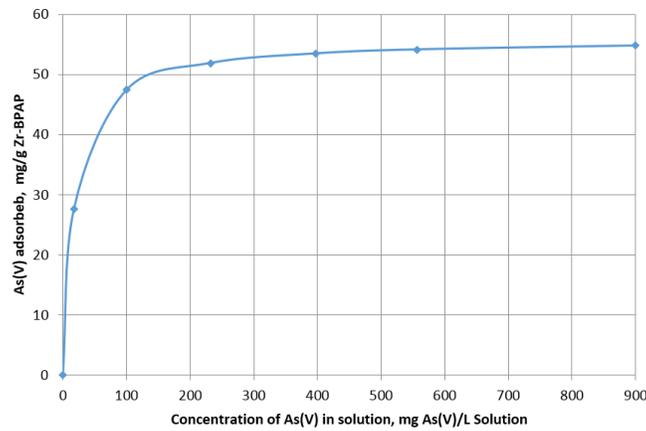


Figure 6. Adsorption isotherm of As(V) by Zr-BPAP at pH 6 replotted from data (from Rosenberg, 2009)

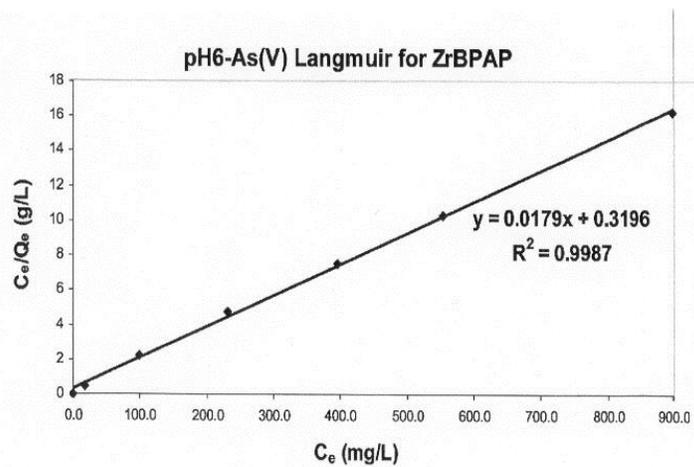


Figure 7. Linear plot based on Langmuir model for As(V) adsorption by Zr-BPAP (from Rosenberg, 2009)

Langmuir adsorption for competitive ions

As presented in the previous report and the preceding paragraphs, adsorption depends strongly with the equilibrium between the concentration of the ions in the aqueous phase and the amount adsorbed. The hypothesis of Langmuir adsorption model assumes the surface sites are limited only to a monolayer. The equilibrium equation is:

$$[S\equiv A] = [S\equiv T] \times \frac{K[A]}{1 + K[A]} \quad \text{or} \quad \Gamma_A = \Gamma_{\max} \frac{K[A]}{1 + K[A]}$$

Where K is the equilibrium constant, [A] is the concentration in the solution and [S≡A] is surface site occupied by species A having the unit such as moles adsorbed /m² of surface. It turns out that the new variable Γ_A (moles adsorbed / mass of adsorbent) would be easier to understand and determine.

When several different ions are present in the solution, they have to compete the only surface sites available from the adsorbent. According to W. Stumm (Chemistry of the Solid-Water Interface – A Wiley-Interscience Publication, New York – 1992). Assume Species B is competing with Species A, the amount of A adsorbed will become

$$\Gamma_A = \Gamma_{\max} \frac{K_A[A]}{1 + K_A[A] + K_B[B]}$$

Where K_A and K_B are the equilibrium constants for species A and species B, respectively. Those equilibrium constant can be independently measured from the experiment. The formula can be expanded for more competitive ions.

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

MTECH TEAM; Jerry Downey (PI), David Hutchins

Development and optimization of the continuous flow reactor is ongoing. In this quarter, an improved electromagnet was constructed with tighter windings and a more efficient core. These improvements provide a higher magnetic flux and higher particle collection efficiencies. With these improvements incorporated, two more coils were commissioned with a resin coating expected to provide longevity in harsh environments. A Coriolis meter was installed in order to capture fluid flow data in the continuous flow reactor.

The majority of the research continues in two areas: magnetic collection of particles and electrowinning.

- Experimentation has focused on securing data needed to model the magnetic nanoparticle collection efficiency of the electromagnet as a function of solution flow rate, the concentration of particles in solution, and magnetic flux. In the initial experiments magnetite nano-particles were utilized as a surrogate for coated particles, as well as Dr. Rosenberg's silica coated particles. Extremely high magnetic nanoparticle collection efficiencies continue to be observed (Figure 8), and the limits of the collection efficiency have been established for solution flow rate and mass (i.e. the flow rates and particle mass per unit of solution volume where substantial breakthrough occurs have been identified). Experimentation will continue in order to establish the correlation between magnetic flux and collection efficiency.
- Electrowinning experiments are underway to continue to establish the optimal set of operating parameters for efficient copper and zinc recovery. To date, these experiments have utilized surrogate copper sulfate and zinc sulfate solutions. Thus far, current efficiencies exceeding 94% have been achieved with both copper and zinc. Further experiments with copper and zinc are planned as well as with mixed-metal surrogate solutions. An electrolytic cell for manganese electrowinning will be designed and constructed in the upcoming quarter.
- Metal adsorption tests were conducted on raw magnetite particles, conditioned magnetite particles, and silica-coated functionalized particles. Results showed similar loading for both conditioned and unconditioned magnetite, and nearly 2.5 times the loading with the silica-coated particles.
- A team of electrical engineering students is designing and constructing an automation and data logging system for the continuous flow reactor. Their progress to date includes a process flow diagram and the initial coding of the processor. The data logging portion is expected to be completed in October with the automation system to follow in November.

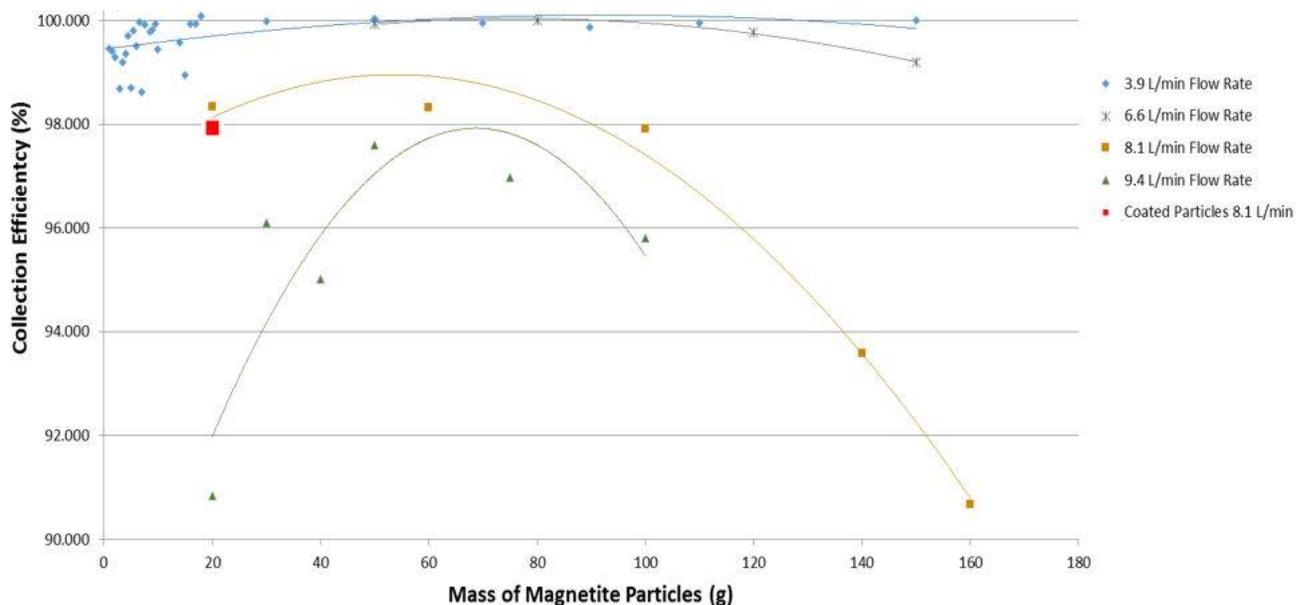


Figure 8. Magnetic nanoparticle collection efficiencies as a function of the total mass of particles charged to the reactor and solution flow rate. The red square indicates the response of particles prepared in Dr. Rosenberg’s laboratory.

OBJECTIVE 5: DATA CONSOLIDATION AND REPORTING

- Documentation protocols, including laboratory notebook, file naming and sharing procedures, have been established and are in effect.
- The established project metadata accumulation, consolidation, and security measures remain in effect.

REFERENCES

Rosenberg, E, Characterization of Surface-Bond Zr(IV) and Its Application to Removal of As(V) and As(III) from Aqueous System Using Phosphonic Acid Modified Nanoporous Silica Polyamine Composites, *Ind. Eng. Chem. Res.*, **2009**, 48(8), pp 3991-4001.