

# **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**

**April 1 to June 30, 2016**

**Submitted to:**

**Janelle Booth  
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**Submitted: July 1, 2016**

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

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This quarterly progress report covers the project period from April 1, 2016 to June 30, 2016. Significant progress has been made toward completion of the five project objectives. Data related to the results described in this report are available on request.

## **PERSONNEL/HIRES**

The Montana Tech (MTech) team added a second undergraduate student in summer 2016. Auva Speiser has been assigned the task of commissioning and optimizing the electrowinning operation. Each of the students will continue working on the project during the upcoming Academic Year. 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

## **EXPENDITURES**

The total expenditures recorded to date represent approximately 16.3% of the overall project budget of \$495,127. The actual expenditures through the end of June are substantially higher than reported because project labor charges for June and the UM invoice for June have not entered the system yet. The rate of expenditure 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 are within budget.

**Table 1 – Summary of Project Expenditures through June 27, 2016\***

<b>Category</b>	<b>Budget</b>	<b>Amt Spent</b>	<b>% Spent</b>	<b>Balance</b>
Personal Services	\$ 162,226	\$ 19,230	11.9	\$ 142,996
Contracted Services				
Subcontracts	\$ 188,001	\$ 45,217	24.1	\$ 142,784
General	\$ 50,000		0.0	\$ 50,000
Supplies	\$ 45,000	\$ 12,864	28.6	\$ 32,136
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
<b>Total Operating &amp; Capital</b>	<b>\$ 495,127</b>	<b>\$ 80,471</b>	<b>16.3</b>	<b>\$ 414,656</b>

**\*totals do not include some labor charges**

**MTECH TEAM**

- Total Budget: \$309,953; total expenditures of \$35,254 (11.4%) through June 27, 2016. As previously noted, the actual expenditures are considerably higher than shown in Table 1 because the labor charges for June have not entered the system.
- Supplies expenditures include carboys for collecting wastewater; chemicals, various fittings, pipes, pumps, and electrical components.

**UM TEAM**

- Total Budget: \$188,001; total expenditures of \$45,217 (34.7%) through May 31, 2016.
- No equipment expenditures.
- 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.

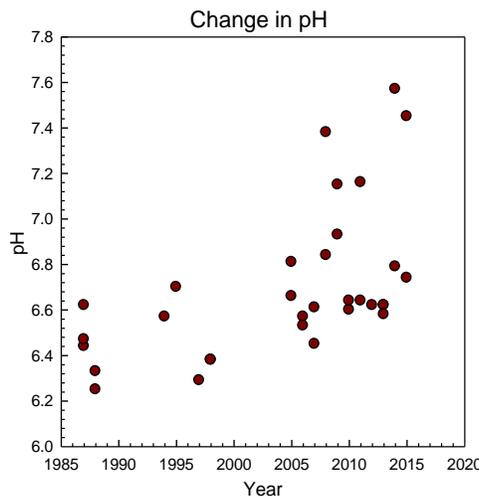
**OBJECTIVE 1: WASTEWATER CHARACTERIZATION**

**MTECH TEAM; Alysia Cox (Co-PI)**

- The Environmental Dynamics in Geobiochemical Engineering (EDGE) Lab sampled local surface waters this quarter (Blacktail and Silver Bow Creeks, 5 sites on one day in May) for a total of 15 sites on three different 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), including four this quarter in order to provide specific chemical targets and mixtures for treatment in the flow reactor. The flooded underground mine samples

collected were representative of three hydrological zones surrounding the Berkeley Pit. A groundwater divide runs in a northwestern direction with the Berkeley Pit located to the east of the divide. The mines sampled to the east of the divide include the Anselmo, Kelley, Steward and Pilot Butte. Those sampled directly west of the divide and on the outer perimeters include the Travona, Emma, Ophir, Orphan Boy, and Orphan Girl. Water samples were collected for cation, anion, ICP-MS, dissolved organic and inorganic carbon, organic acids, and water isotopes.

- In addition to wastewater collection and characterization, historic data provided by the Groundwater Information Center and Montana Bureau of Mines and Geology were analyzed. As monitoring of the groundwater began in 1986, the mines showed severe levels of dissolved metals, sulfate, and a lower pH (Figure 1). Due to pumping of the west mines and flooding of the east mines, the waters are slightly, naturally ameliorating (Figure 2). Contributors to acid mine drainage such as dissolved metals and sulfate have decreased and pH has slightly increased (Figure 1). However, the east mines all show an increase in arsenic concentration with time, while arsenic concentrations in the west are depleting (Figure 3; Figure 2). Additionally, the Kelley mine has become more acidic and the temperature of the water has increased overtime (Figure 4). These trends found in the Kelley show a similar behavior to acid mine drainage found in waters above ground in oxic conditions.
- Renee Schmidt presented at Techxpo with a poster entitled, “Microbial Habitats in Butte, MT Flooded Mine Shafts”. 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. EDGE Lab undergraduate Jordan Foster presented a talk at the Montana Academy of Sciences (winning the award for best undergraduate oral presentation) and a poster at Techxpo (winning the award for best poster in the Chemistry and Geochemistry Department). Both were entitled, “Stormwater in Butte Area One: Implications for the Microbial Community”.



**Figure 1: Change in pH in the Orphan Boy mine shaft (graphed after GWIC).**

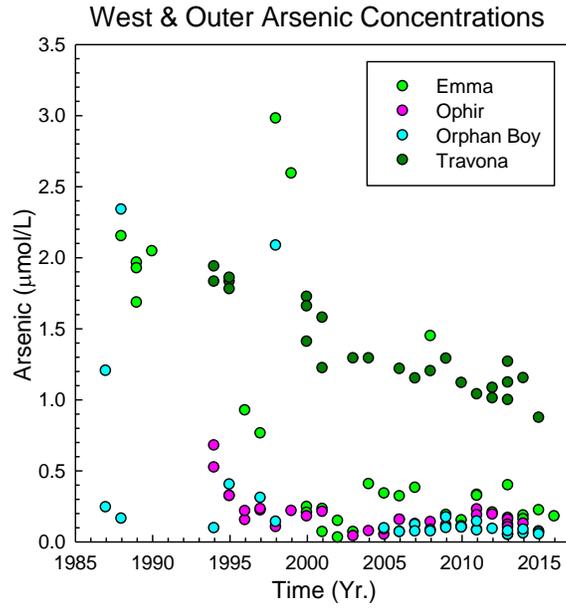


Figure 2: Change in arsenic concentrations in the West and Outer Camp mine shafts (graphed after GWIC).

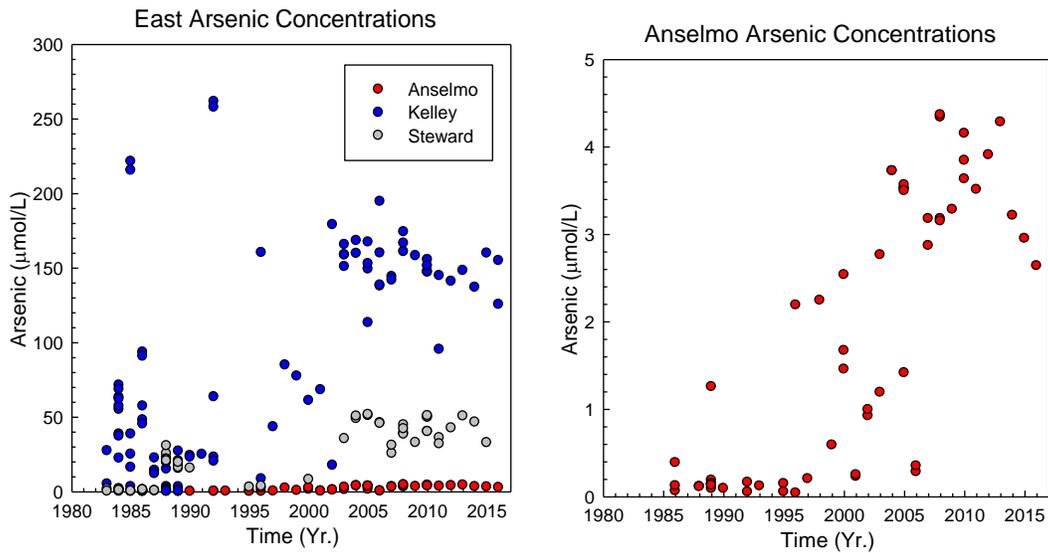
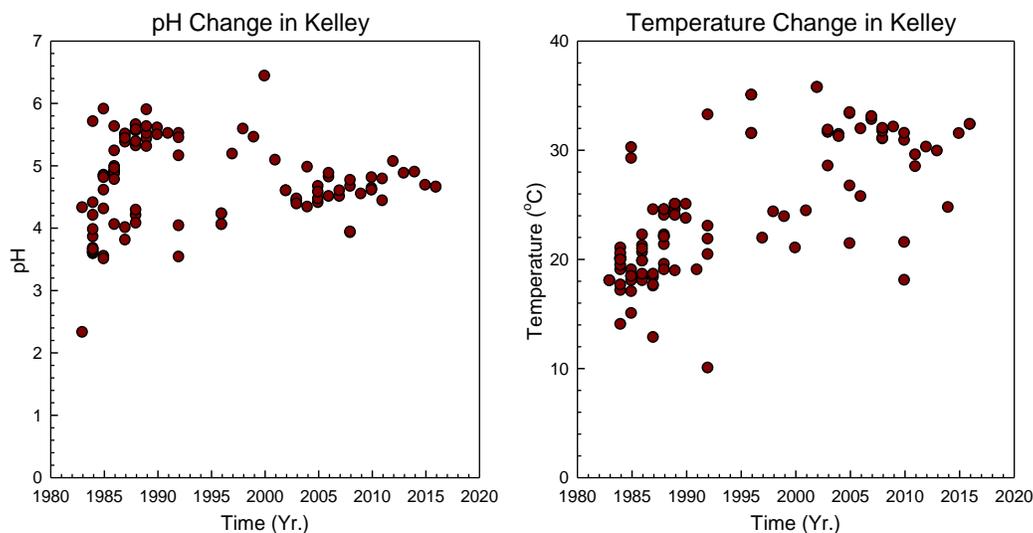


Figure 3: Change in arsenic concentrations in the East Camp mine shafts (graphed after GWIC).



**Figure 4: Change pH (left) and temperature (right) in the Kelley mine shaft (graphed after GWIC).**

## **OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS**

**UM TEAM; Ed Rosenberg (PI)**

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

### **1. Method of choice for nanoparticle synthesis.**

In the last quarterly report, we outlined two methods for synthesizing the core-shell magnetic nanoparticles (CSMN): a) the silicic acid method where silicic acid made by removal of sodium from sodium silicate is reacted directly with the iron nanoparticles at elevated temperature; b) hydrolysis of tetraethoxysilane (TEOS) at ambient temperature in the presence of base. Initially it appeared that the silicic acid gave better metal capacities but more recent studies showed that the capacities for the TEOS method gave similar copper capacities ( $\sim 1.2 \text{ mmol/g}$ ). Both methods benefitted from sonication during reaction. TEM micrographs show that the TEOS method gives a thicker silica coating. This is evidenced by EDX measurements that show a higher silica content for the particles when made by the TEOS method (38-42%) than when made by the silicic acid method (12-32%). Based on these recent results, we plan to focus on the TEOS method based on the simplicity of the process and the promise of a more robust material. Of course, a final decision must await an evaluation of how the particles behave in the pipeline reactor and a detailed economic analysis.

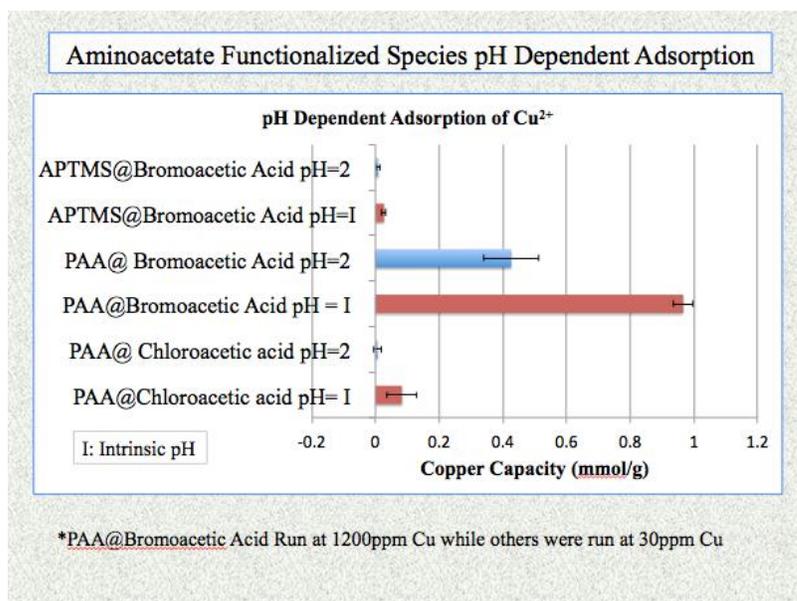
### **2. Use of the polyamine versus direct modification with pre-functionalized silanes.**

A fundamental question that must be answered with regard to synthesis of the CSMN is the necessity of using a polyamine grafted to a surface bound chloropropyl-group versus the use of commercially available pre-functionalized trimethoxy-silanes. Initial

experiments used 3-aminopropyltrimethoxysilane (APTMS) on both silicic acid and TEOS surfaces. Reasonable copper capacities (0.9 and 0.7 mmol/g) were obtained but attempts to further modify the amino group with halo-acetic acids lead to almost complete loss of copper capacity; a process that worked well on polymer modified surfaces (*vide infra*). Our prior work with silica nanoparticles and micro-particles showed that APTMS does not provide a robust material for metal sequestration. Following a literature preparation, a commercially available trimethoxysilylpropyl-ethylenediaminetetraacetic acid ligand was reacted with a TEOS surface. The results were comparable to the literature values where we used cadmium solutions while the literature focused on neodymium. The values of 0.15 mmol/g are quite low but could be useful for very valuable metals. In an attempt to improve on the EDTA loading we have reacted trimethoxysilylethylenediamine with the TEOS surface and obtained reasonable copper capacities (0.6 mmol/g). This material will be reacted with bromoacetic acid to give an analog of the EDTA ligand. We are concerned that this material will be subject to decomposition upon attempted modification as observed for APTMS on TEOS. We also have plans to modify polyamine surfaces with EDTA anhydride to get a surface bound EDTA type ligand; a method that has worked well with the commercialized micro-particle technology. The EDTA ligand system is a top priority for the development of the proposed technology.

### 3. Modification of the surface bound polyamine with pro-ligands.

The amino acetate and aminodiacetic acid ligands are two of the most widely used chelator ligands employed in the ion exchange industry. They also proved to be the most widely used systems employed industrially in previously developed SPC technology. This last quarter we modified the silicic-PAA and the TEOS-PAA surfaces with bromoacetic acid. This modification provides better copper capacity at lower pH values (<3) for transition metals. Figure 5 shows the results of the copper capacities before and after modification with bromoacetic acid.

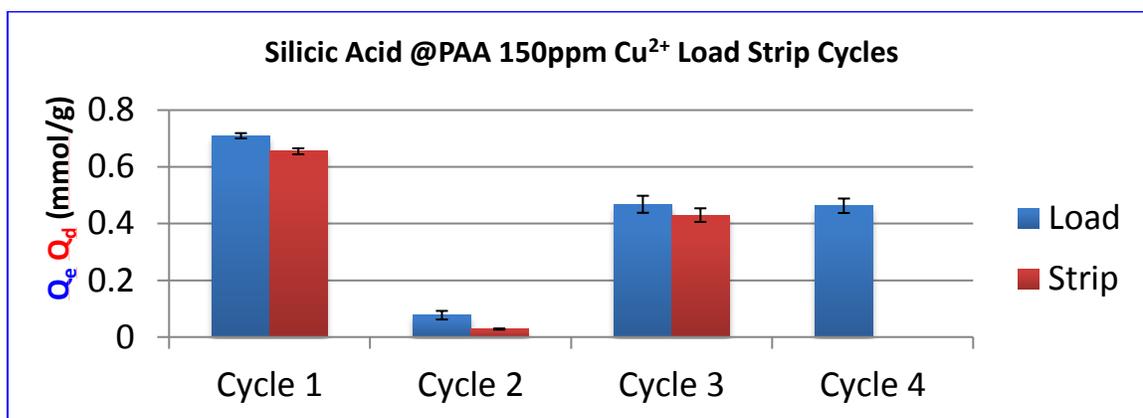


**Figure 5. Copper capacities of aminoacetate modified CSMN**

As can be seen in Figure 5, the PAA modified surface showed good capacity at both pH = 2 and at intrinsic pH (4-5). Note that the APTMS analog decomposed under the reaction conditions. The use of chloroacetic that requires elevated temperatures (>80C) and more basic conditions also resulted in apparent decomposition. This is good information that will guide us in the future. As stated above EDTA is the next target for modification, followed aminophosphonic acid and then thiolate derivatives. These four, including the amino acetate cover a broad range of metals in terms of their binding constants.

#### **4. Stripping, regeneration and general behavior of the nanoparticles during the metal sequestration process.**

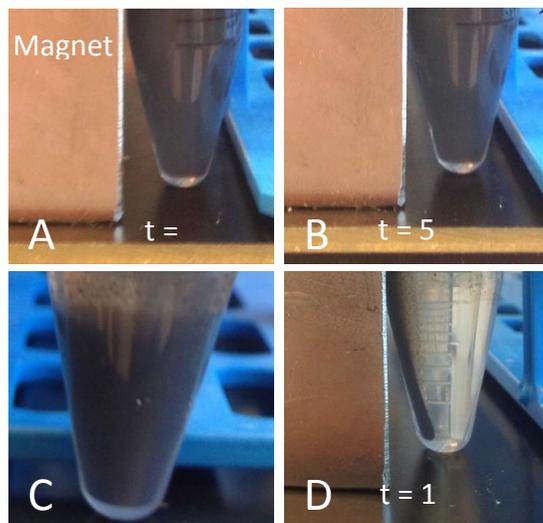
One of the most important aspects of the CSMN technology is the ability to load, strip and regenerate the particles multiple times. We have just begun these studies and they will be a focus of the work in the next quarter. The results of our initial studies with copper adsorbed onto silicic acid PAA are shown in Figure 6.



**Figure 6. Load–rinse Strip cycling for CSMN with PAA (Note capacities of 1.12 mmol per gram are observed with 1500 ppm solutions and have been at this value in tests done after these experiments were done).**

Cycle 1 shows that the material strips very well using 0.1 M citric acid with about 90% of the copper adsorbed. Cycle 2 shows attempted regeneration with water; clearly this did not work. Cycle 3 shows the results after regeneration with 1M base and Cycle 4 shows that the copper capacity is not reduced after the base regeneration. These are promising results and further cycle testing is underway. Very similar results are obtained with the TEOS-PAA system and data for that will be included in the next report. An interesting but, as yet, poorly understood change in the CSMN is observed on metal coordination of copper and zinc. On coordination we observe aggregation to larger particles. These particles are much easier to separate and persist after stripping of the metal. Capacity in subsequent cycles is not affected (Figure 6). This phenomenon does not take place with Cd which has a lower capacity (0.3 mmol/g) relative to copper (0.7-1.2 mmol/g) and zinc (0.5 mmol/g). The aggregation is also not observed with the TEOS-PEI system (*vide infra*).

The difference in aggregation before and after metal loading is clearly seen in Figure 7.



**Figure 7. CSMNs (Silicic acid/PAA): (A) Before zinc binding, (B) 5 minutes near a permanent magnet, (C) after zinc binding zinc binding, (D)1 second near a permanent magnet.**

The bigger aggregates in C and D in Figure 3 separate spontaneously and are attracted much more strongly to the permanent magnet and are therefore more readily collected. This could be a clear advantage in the pipeline reactor as long as suspension can be maintained using the baffles to create turbulence. We will be investigating the origin of this phenomenon using SEM, TEM and TGA. Other spectroscopic investigations are also planned including IR, XPS and NMR on diamagnetic surrogates.

## **5. Extension of the process to the branched poly(ethyleneimine).**

The SPC based on the branched polymer poly(ethyleneimine) (PEI) has been shown to have significantly metal coordinating properties than the PAA analogs. It has found commercial applications in Pd recovery where the PAA analog does not work and its amino acetate modified version has been used in many industrial applications mainly because it is cheaper than PAA. The polymer also has the advantage for being available in a wide range of molecular weights. We began our studies on CSMN with PAA because of its simpler and more uniform structure but now that we have shown that the polyamine chemistry is compatible with CSMN we turned our attention to PEI. PEI with a 23,000 molecular weight was successfully grafted to the TEOS surface and gave a copper capacity of 0.61 mmol/g. Lower capacities relative to the PAA SPC were also seen with the silica micro- and nanoparticles. As mentioned above the aggregation phenomenon observed with PAA is not observed with the PEI analog, suggesting that polymer structure is important the behavior of CSMN under working conditions. In the next funding periods the differences in CSMN made with these two different polymers will be thoroughly investigated.

## 6. Commercial nanoparticles versus co-precipitation.

During this last quarter we have begun to use commercially available 20-30 nm magnetite made by Skyspring 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 CSMN with copper capacities (0.8 mmol/g) similar to the CSMN made with the smaller ones made by co-precipitation. The particles are easier to handle as they come as a dry powder and provide facile separations after modification. They also demonstrate persistent aggregation after metal coordination. Ultimately cost will determine whether these particles will completely replace the in-house version.

### Summary of Progress

This last quarter has seen significant progress towards a commercially viable CFMN metal sequestering product:

1. The best method of synthesis for the basic silica-coated CSMN has been determined (TEOS over silicic acid).
2. The superior performance using polyamines rather than pre-functionalized silanes has been demonstrated.
3. The ability to modify the polyamine with more specialized pro-ligands has been demonstrated.
4. The polyamine modified CSMN can be regenerated and reused after metal recovery.
5. The technology can be extended to the branched polyamine, PEI, providing a wider range of products for development.
6. Commercially available iron nanoparticles serve as well as the in-house versions in the experiments done to date.

As with all new projects there are always surprises and the aggregation observed with the PAA CSMN fall into this category. So far this looks good but we must first understand the phenomenon and the factors that control it. This will be a primary focus of the research in the next quarters.

## 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,

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

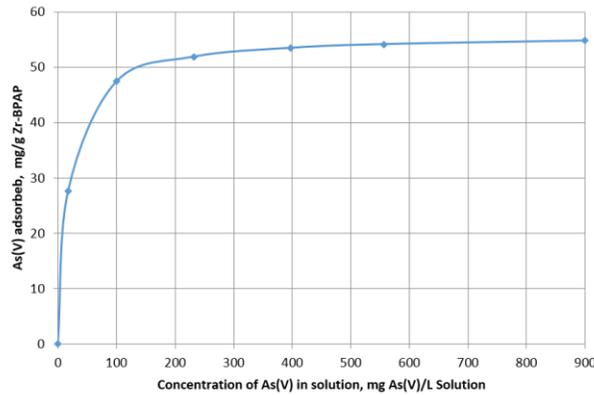
$$\frac{[A]}{[S\equiv A]} = \frac{1}{K[S\equiv T]} + \frac{[A]}{[S\equiv T]} \quad [4]$$

Replacing  $[A]$  with  $C_e$ ,  $[S\equiv A]$  with  $Q_c$ ,  $[S\equiv T]$  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,

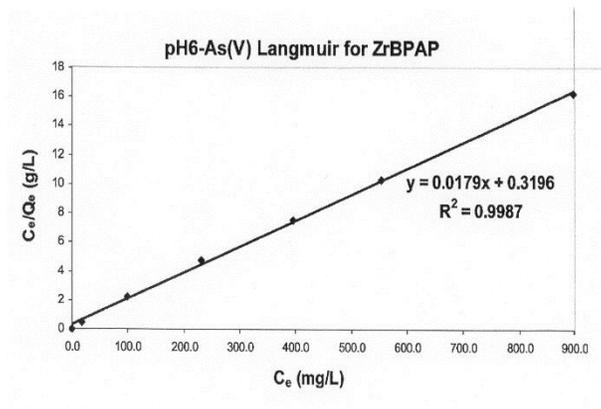
$$\frac{C_e}{Q_c} = \frac{1}{K_{ads}Q_m} + \frac{1}{Q_m}C_e$$

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



**Figure 9. Linear plot based on Langmuir model for As(V) adsorption by Zr-BPAP (from Rosenberg, 2009)**

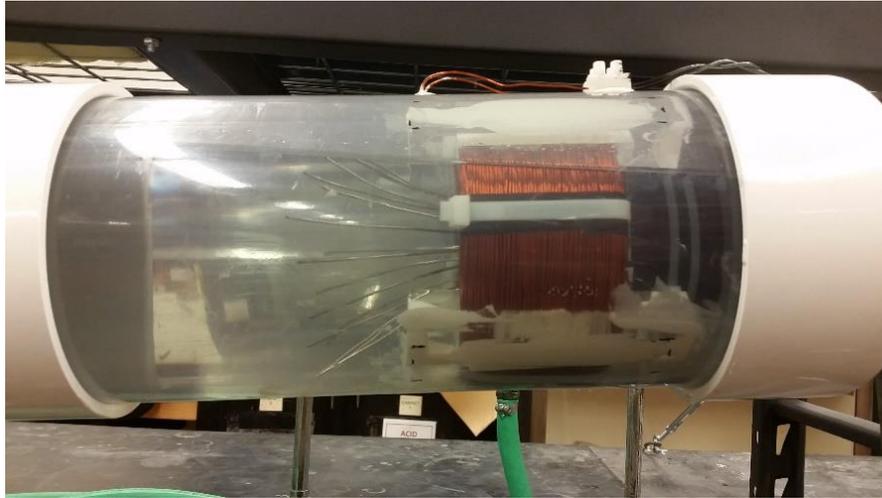
**OBJECTIVE 4: CONTINUOUS FLOW REACTOR DESIGN, CONSTRUCTION, COMMISSIONING, AND OPERATION.**

**MTECH TEAM; Jerry Downey (PI), David Hutchins**

Work on the design, construction, commissioning, and operation of the continuous flow reactor is ongoing. In the past quarter, the majority of the research focused on two areas: magnetic collection of particles and electrowinning.

1. In an effort to model the electromagnet collection efficiency and determine the maximum magnetic particle loading for a given wastewater flowrate, multiple experiments were conducted with the electromagnet positioned within the transport reactor tube as shown in Figure 10. Magnetite ( $Fe_3O_4$ ) nanoparticles with a nominal 20 nanometer diameter were utilized as a surrogate for silica coated particles that are being produced by Dr. Rosenberg's

team. All tests thus far show a collection efficiency of greater than 90%. Future tests with higher flow and loading are expected to show greater breakthrough, data that are required to elucidate the maximum loading and further defining the operating parameters for the entire system.



**Figure 10. Electromagnet positioned inside of the transport reactor tube. This configuration consistently produces magnetic particle capture efficiencies well in excess of 90%.**

2. The electrowinning cell shown in Figure 11 was commissioned, and initial experiments in copper recovery were conducted. A surrogate copper sulfate solution was utilized, and the key parameters were varied in order to optimize the system. Thus far, 74% of the theoretical maximum recovery have been achieved. Under near optimal conditions, the copper is reduced on a stainless steel cathode to produce a coherent copper sheet, as shown in Figure 12. Further experiments are planned with copper, followed by zinc and mixed solutions of copper and zinc.
3. A series of preliminary metal ion adsorption tests were conducted using raw magnetite particles, conditioned magnetite particles, and silica-coated functionalized particles to remove copper from solution in the transport reactor system. Solution samples will be analyzed to determine metal removal efficiencies. The results will help to define adsorption densities and further define parameters for the greater system.
4. Two Montana Tech electrical engineering students were enlisted to begin designing an automation and data logging system. The students will complete the project in fulfillment of their senior capstone requirement.
5. In addition to ongoing experiments, an effort to submit a Nation Science Foundation Small business Technology Transfer (NSF-STTR) proposal has been initiated. A local engineering firm with a proven STTR track record has expressed interest in partnering on the project. A path forward has been developed with proposal submission targeted for December of 2016.



**Figure 11. Laboratory electrowinning circuit. Electrowinning is a means of recovering metals from solution by reducing the ions and plating high-purity metal on a cathode. In this circuit, the actual electrowinning occurs in the cylindrical column at center.**



**Figure 12. Copper sheet electrowon from a surrogate cupric sulfate solution. The sheet was deposited on a stainless steel cathode, which was positioned along the inner periphery of the cylinder in Figure 11.**

## **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.