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
October 1 to December 31, 2015

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 October 1, 2015 to December 31, 2015. Reasonable progress has been achieved with respect to Objectives 1, 2, 3, and 4 even though the Principal Investigators were not granted formal authorization to proceed until November 6, 2015. Data related to the results described in this quarterly progress report are available on request.

HIRINGS

Project staffing is nearly complete. Most of the individuals hired for this project will begin work in January or February, 2016.

MTECH TEAM

- David Hutchins, a Materials Science Ph.D. student at Montana Tech. His work will focus on the design, construction, commissioning, and operation of the magnetic field reactor system. Bachelor of Science in Environmental Engineering (Montana Tech, 2014).
- Jared Geer, an undergraduate student in Metallurgical and Materials Engineering at Montana Tech. Mr. Geer will assist the PI and Mr. Hutchins in system fabrication/construction, sampling and analysis, and execution of experiments.
- Renee Schmidt, a Geochemistry MS student at Montana Tech will contribute to and work on this project. Her undergraduate degree is in chemistry (and art) and her interests keenly align with remediation of contaminated water resources. The focus of her MS thesis is linking the geochemistry of the flooded underground mine shafts in Butte to the identity and activity of microbial communities present.

UM TEAM

- Emil DeLuca, Research Associate Lab Manager-started 10/01/15. B. S. in Chemistry, UM, 2015, research experience at UW.
- Ryan Letterman, Post-Doctoral Research Associate, will start 02/01/16. Currently completing his doctorate at MSU, experience in Nanotechnology.

EXPENDITURES

Expenditures for the quarter were quite modest because authorization to proceed was not received until November 6. The total expenditures and encumbrances to date represent approximately 3% of the overall project budget of $495,127. Rate of expenditures for labor and materials are expected to accelerate in the second quarter after the post-doctoral research assistant (UM), graduate and undergraduate students (MTech) join the project. Subsequent progress reports will include a more detailed tabulation of expeditures, including current quarter and cumulative breakdowns.

MTECH TEAM; Dr. Jerry Downey (PI)

- Total Budget: $309,953

- Total Expenditures & Encumbrances: approximately $2,300 for supplies purchased to begin fabrication of the bench-scale reactor.

UM TEAM; Dr. Ed Rosenberg (PI)

- Total Budget: $188,001

- Total Expenditures & Encumbrances: $6,567

- Equipment Ordered: ultrasonic processor UP400S, Hielscher, USA $6,600.

PROGRESS TOWARD MILESTONES

Progress is described according to the specific project objectives.

OBJECTIVE 1: WASTEWATER CHARACTERIZATION

MTECH TEAM; Dr. Alysia Cox and Dr. H.H. Huang

- Under the direction of Dr. Alysia Cox, the Environmental Dynamics in Geobiochemical Engineering (EDGE) Laboratory has begun to compile local surface water data as well as sample local surface waters in order to provide specific chemical targets and mixtures for treatment in the continuous flow reactor system.

- Dr. H.H. Huang contacted Terrence E. "Ted" Duaime, Associate Research Hydrologist at the Montana Bureau of Mines and Geology (MBMG) regarding acid rock drainage sites in Montana. The Berkeley pit is an obvious choice because it contains the largest volume body of contaminated water, an estimated 45 billions gallons as of January 2015, and multiple pollutants. Mr. Duaime also suggested consideration of the following drainages in Montana:

  1. The abandoned Crystal and Bullion mines near Basin Montana,
  2. Beal mountain gold mine near Fairmont, Montana
  3. Waste rock dumps at the Stillwater Mining Company
  4. Two coal mines located near Great Falls

OBJECTIVE 2: MAGNETIC NANOCOMPOSITE SYNTHESIS

UM TEAM; Dr. Ed Rosenberg (PI)

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

   We have identified three methods of modifying iron magnetic nanoparticles with ligands capable of capturing metal ions of interest for remediation and/or resource recovery.

   Method 1. Using commercially available 30 nm magamite (Fe_2O_3) nanoparticles the surface is first treated with aminopropyltriethoxysilane (APTES) (we used the methyl analog, APTMS) and then reacted with EDTA in pyridine to give a ligand-modified nanoparticle (Y. Huang *Water Research* 80 (2015) 159-168). We performed this protocol three times and obtained nanoparticles that were characterized to be the same as that reported. However, these authors reported very high capacities for Pb and Cd while we obtained much lower capacities; but the values were consistent with the analyzed ligand loading. The authors of this paper did not report ligand-loading values and did their metal ion capture in the presence of phosphate buffer. Pb and Cd phosphates are very insoluble making their reported values suspect. The particles were easy to manipulate with a magnet and dynamic light scattering measurements gave diameters in the range of 1 micron, as the authors reported. Overall, this method is straightforward but the use of pyridine as a solvent is not compatible with a commercial process and the metal capacities were not satisfactory in our hands.

   Method 2. The co-precipitation of ferrous and ferric salts provides magnetite (Fe_3O_4) nanoparticles with reported diameters of ~10 nm (M. Ma *Colloids and Surfaces A: Physicochem. Eng. Aspects* 212 (2003) 219-226). The magnetite nanoparticles are then treated with silicic acid and then finally with APTES to give functionalized magnetic nanoparticles. These authors made these particles for medical applications but we have tested the APTES modified particles for copper adsorption and obtained reasonable loading of 33 mg/g. We have measured the size of these particles by dynamic light scattering (DLS) and they are much larger than that reported in the paper (~200 nm). The authors used SEM and we need to check that. If the DLS measurements are correct the difference may be due to the rate of addition of reagents, which was difficult to control on a small scale in this protocol. We are now going on to modify the surface with EDTA to test for Pb and Cd capacities. We will use a method developed in our lab that does not use pyridine and is the method that is used industrially starting with EDTA anhydride

   Method 3. This method uses a mixture of tetraethoxysilane (TEOS) and APTES in a 4:1 ratio to coat magnetite particles made by co-precipitation or by using the commercially available Ferrofluid, a liquid containing magnetite nanoparticles (Y. Xia et. al. *Nano Letters* (2002) 2, 183-186). To date we have only used the co-precipitated magnetite, but have ordered the Ferrofluid. We have done this reaction twice and measured the resulting nanoparticles ability to adsorb copper ions. Capacities were slightly higher than in method 2 being 38 mg/g. Next step will be modification with EDTA as for Method 2. The sol-gel approach described here is very similar to the approach used in our prior work on the micro composite particles. A further development in this approach is the use of sonication during the sol-gel procedure (S. I. Nikitenko et. al. *ACS Nano* 2 (2008) 847-856). We will be trying this modification later this week.

2. **Summary and Next Steps:** 01/01/2016- 03/31/2016

   To date we have been able to make magnetite core-shell silica nanoparticles that have the ability to adsorb metal ions. In the next weeks we will be modifying these APTES modified particles with EDTA and testing their performance with regard to Pb and Cd capture. The next step will be to use the sol-gel approach with chloropropyltriethoxysilane, which will provide the needed anchor points for grafting the polyamines to the surface. It is anticipated, based on our prior work that this will dramatically improve metal ion capacities and we will follow up with modifying the polymer surface with metal selective ligands and then testing them on actual waste streams in our lab and in the pilot pipeline reactor.

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

MTECH TEAM; Dr. H.H. Huang

Using data obtained from the Montana Bureau of Mines and Geology, Dr. H.H. Huang (MTech) prepared a preliminary database of Berkeley Pit water parameters, including dissolved metal concentrations. The Excel spreadsheet is designed to facilitate access by and utilization within Dr. Huang's (StabCal) software, which will be used to generate aqueous processing models throughout the life of this project. Data generated by these models will serve both to guide design of experiments and as an aid in the interpretation of experimental results.

To conduct a meaningful wastewater treatment study, it is essential to characterize the chemical composition, including pH and oxidation-reduction potential (ORP). Thermodynamically based contaminant speciation analyses are crucial to understand reactions among dissolved species and evaluate the degree of saturations related to the solids. To initiate these studies, recent Berkeley Pit and Bullion drainage water analyses have been investigated. The findings are highlighted below:

1. Based on MBMG data dated June 14, 2012, the composition of the Berkeley pit water 790 ft below the surface at 6.0° C registered pH 2.60 and ORP 680 mV. A total of 45 components include major, minor, rare earth and trace metals are reported. Sulfate is the predominant anion 7850 ppm, and five cations have concentrations above 200 ppm (aluminum, calcium, iron, magnesium, manganese, and zinc). Speciation calculations performed using Berkeley Pit data indicate 25% of total sulfate complexes with metal ions, and 30% of all metals complex with sulfate ions. The calculations also showed that the saturated and near saturated solids are hematite (Fe_2O_3), magnetite (Fe_3O_4), $FeSO_4$, silica (SiO_2), anhydrite ($CaSO_4$), jarosite ($KFe(SO_4)_2(OH)_6$), and schwertmannite, ($Fe_{16}O_{16}(OH)_{12}(SO_4)_2$).

2. Based on Focused Remedial Investigation data reported by CH2M Hill in 2013, Bullion mine drainage sampled on September 23, 2010 from Adit Intercept Boring Well (MW5) at well depth 80.50 feet at 5.8° C registered pH 5.16 and ORP 240 mV and contains 12 components. Speciation calculations revealed only 10% of total sulfate complexes with metal ions, and only 0.2% of all metals complex with sulfate. Saturated and near saturated solids are Fe_2O_3, Fe_3O_4, iron hydroxides and aluminum hydroxides.

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

MTECH TEAM; PI Dr. Jerry Downey (PI) and Mr. David Hutchins

- Literature review was initiated and is ongoing. Findings to date confirm the novel nature of the continuous flow ion-exchange process.

- Design, procurement, and construction of the bench-scale continuous flow reactor system is underway. A basis for bench-scale operations was identified based on candidate wastewater streams at various Montana sites. The reactor cross-sectional area will be scaled up from the previous prototype by a factor of 4.

- Scoping experiments are planned to define the analytical methods necessary to support process development.

- The next prototype continuous flow reactor will be commissioned in the next quarter. Research will focus on maximizing capture efficiency of nanoscale magnetic particles in the pipeline reactor system.

OBJECTIVE 5: DATA CONSOLIDATION AND REPORTING

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

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