ENVIRONMENTAL ENGINEERING PROGRAM

Luis Cumbal Flores

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Research Title:

Polymer-Supported Hydrated Fe(III) oxide Nanoparticles: A Robust Arsenic-Selective Sorbent

Research Objectives:

The primary objectives of this research were to investigate the properties of a new hybrid material which will remove Arsenic from contaminated water. This hybrid material was synthesized and tested at Lehigh University. Currently, the material is being produced for commercial applications and further field tests.

It is well recognized that a fixed-bed sorption process is operationally simple, requires virtually no start-up time and is forgiving toward fluctuations in feed compositions. However, in order for the fixed-bed process to be viable and economically competitive, the sorbent: i) must exhibit high selectivity toward the target contaminant, ii) be durable and iii) amenable to efficient regeneration and reuse. Ideally, the removal of the target contaminant should not cause major changes in pH or in the composition of the influent water. In this regard, both amorphous and crystalline Hydrated Fe Oxide (HFO) show strong sorption affinity toward both As(III) and As(V) oxyacids and oxyanions through ligand exchange in the coordination spheres of structural Fe atoms. Recent investigations using extended X-ray absorption fine structure (EXAFS) spectroscopy confirmed that As(III) and As(V) species are selectively bound to the oxide surface through formation of inner-sphere complexes. HFO particles also exhibit high sorption affinities toward phosphate, natural organic matters, selenite and other anionic ligands. **Figure 1** shows an illustration of the binding of various solutes onto hydrated Fe(III) oxides or HFO. Note that, ligands such as arsenite, monovalent arsenate, divalent arsenate, and phosphate are sorbed strongly through Lewis acid-base interaction or formation of inner-sphere complexes. On the contrary, commonly encountered competing anions, such as chloride or sulfate can be sorbed only through Coulombic interaction or formation of outer-sphere complexes. Therefore, they exhibit poor sorption affinity toward HFO particles.

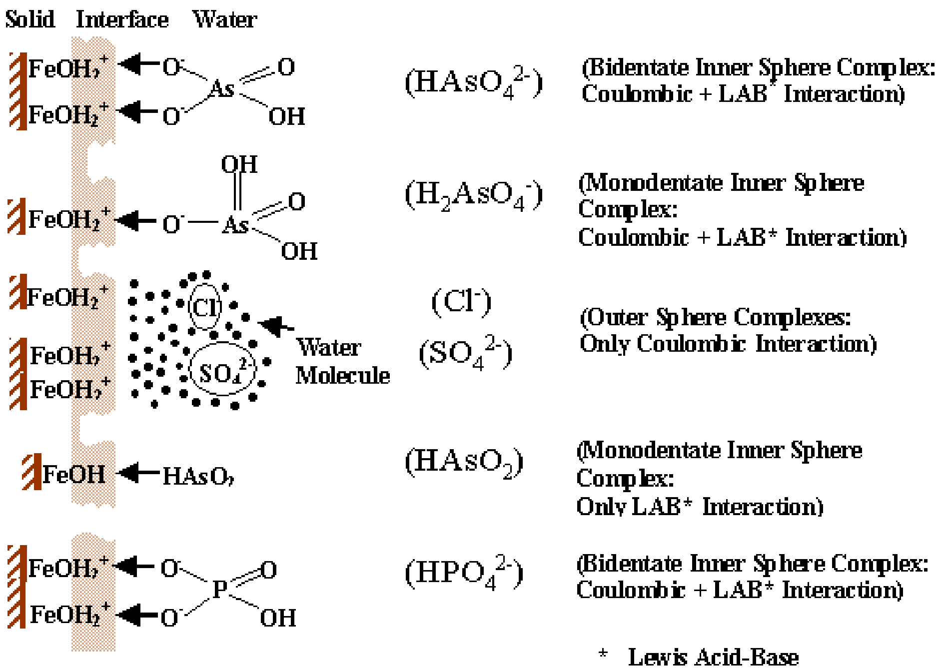

Figure 1 An illustration of the binding of various solutes onto hydrated Fe(III) oxides (HFO)

The process of preparation, although straightforward, produces only very fine submicron HFO particles which are unusable in fixed beds, permeable reactive barriers or any flow-through systems because of excessive pressure drops, poor mechanical strength and unacceptable durability. In order to overcome the referred shortcomings of the iron oxide nanoscale particles, it would be desirable to encapsulate the HFO particles within a robust polymeric support which can confer excellent mechanical strength, durability, and favorable hydraulic properties.

This study includes the preparation and environmental applications of a new class of arsenic-selective hybrid ion exchanger using both cation and anion exchangers as the host materials. First, strong-acid cation exchangers were doped/dispersed with HFO particles for removal of arsenic. Although cation-exchanger-loaded hydrated Fe(III) oxide particles are capable of removing arsenates, the removal capacity is reduced due to the following reason: the gel phase of the cation exchanger is negatively charged due to the presence of the sulfonic acid groups. Thus arsenates or As(V) oxyanions are rejected because of the Donnan co-ion exclusion effect and dispersed HFO particles in the gel phase are not accessible to dissolved As(V) anionic species for selective sorption. When macroporous cation exchangers were used as the host materials, arsenic removal capacity was not high but quite reasonable. When gel-type cation exchanger was used for dispersing HFO particles, the Donnan effect was much stronger, thus the resulting material was ineffective in removing As(V) oxyanions. This observation provided significant evidence that HFO particles when encapsulated within cation exchange sites are not accessible to arsenates or other anionic ligands for selective sorption as illustrated in **Figure 2**.

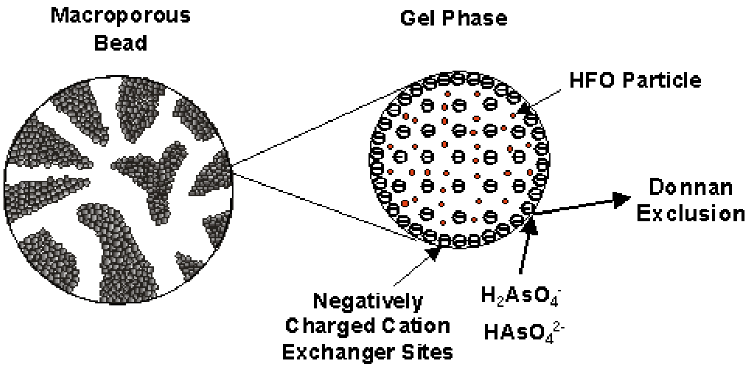

Figure 2 Illustration of the mechanism explaining why HFO-doped cation exchange resin shows reduced sorption capacity for arsenic

Nevertheless, dispersing HFO particles within a cation exchanger material is a relatively simple process and the same has been carried out previously by several researchers including our group and consists of the following three steps: i) loading of Fe^{3+} onto the sulfonic acid sites of the cation exchanger by passing 4% $FeCl_3$ solution at approximate pH of 2.0, ii) desorption of Fe^{3+} and simultaneous precipitation of Fe^{3+} hydroxides within the gel and pore phase of the exchanger through the passage of a solution containing both NaCl and NaOH, each at 6% (w/v) concentration, and iii) rinsing and washing with 50/50 ethanol-water solution followed by a mild thermal treatment at 50-60^{o}C for 12 hours.

Since the functional groups of the cation exchange resin played a significant role in the removal of arsenates, anion exchange resins were used as supports of HFO. Unlike, cation-exchanger-loaded HFO particles, HFO loaded-anion exchangers have positively charged functional groups. Therefore, As(V) oxyanions can easily permeate in and out of the gel phase without encountering Donnan co-ion exclusion effect and subsequently can be sorbed into the HFO particles located inside the gel phase. **Figure 3** shows the parent Anion Exchangerand the hybrid anion exchanger beads (HAIX-M).

Figure 3 Parent Anion Exchange Resin (left) and hybrid anion exchanger (right) beads.

Performance of Hybrid Anion Exchanger

Figure 4 shows the breakthrough of As(V) during two separate column runs with freshly prepared HAIX-M and the parent Anion Exchanger, under otherwise similar experimental conditions. The results indicate that As(V) is removed very efficiently using the hybrid anion exchangers. Over 12,000 bed volumes of water are treated before arsenic reaching its MCL value (10 mg As/L). In contrast, for the column run with the parent anion exchanger, As(V) elutes during the first 200 bed volumes and undergoes chromatographic elution with a peak concentration of approximately three times higher than the influent.

In addition, the performance HAIX-M particles also compared with the commercially available sorbent, named as granular ferric hydroxide (GFH) for the removal of arsenic. **Figure 5** shows the effluent histories of arsenic for both sorbents. HAIX-M removes arsenic more efficiently compared to GFH. This high arsenic affinity can be attributed to the large surface area provided by the tiny HFO particles dispersed within the hybrid sorbent.

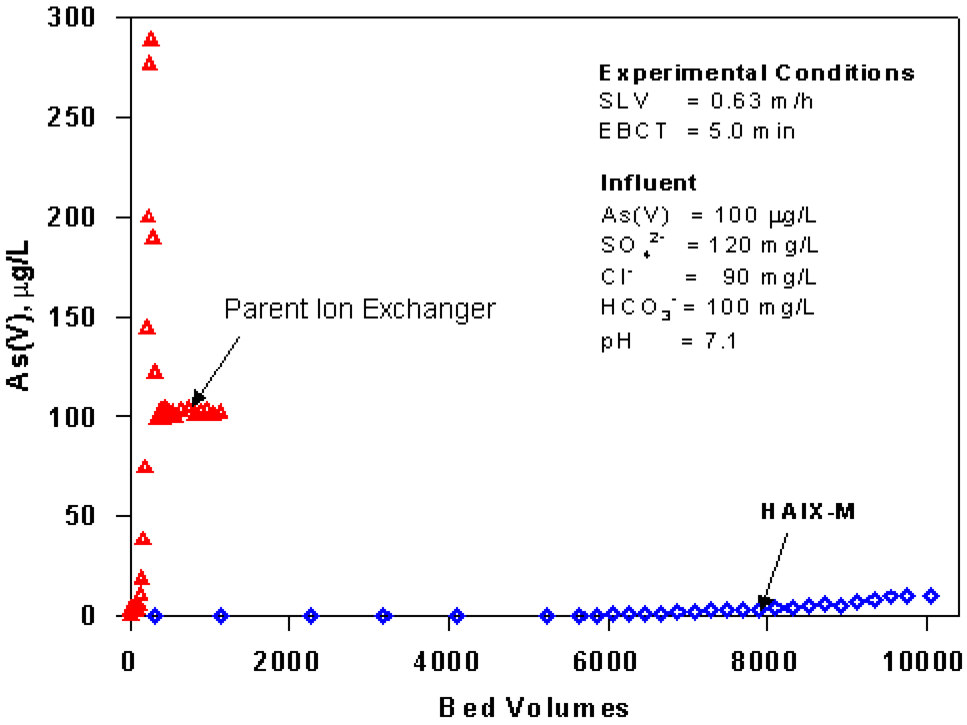

Figure 4 Effluent history of arsenic during two separate column runs using freshly prepared HAIX-M and parent Anion Exchanger

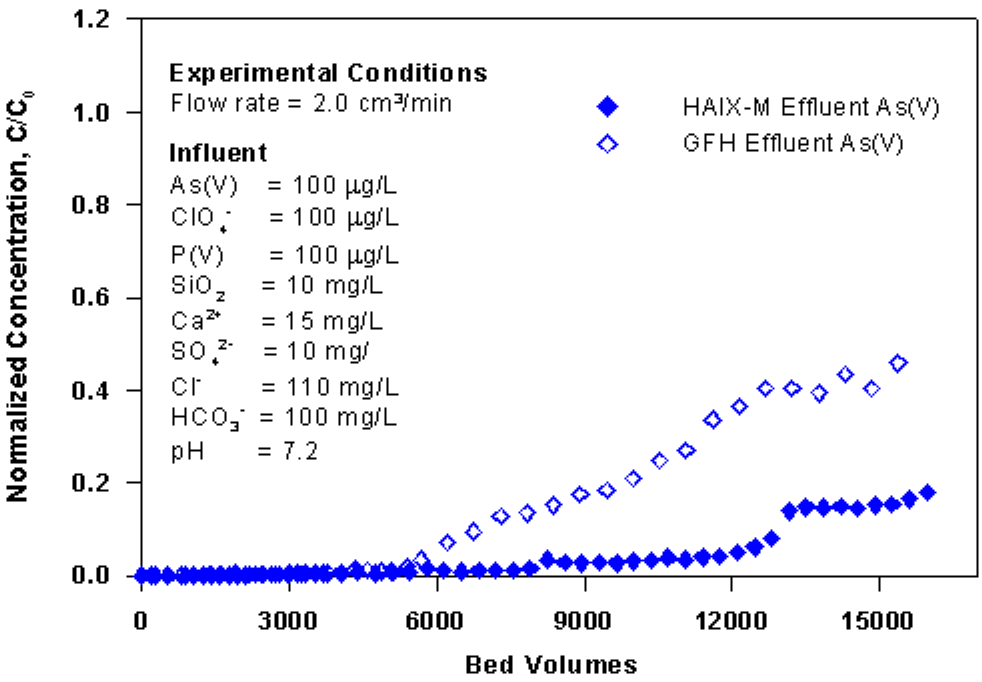

Figure 5 Breakthroughs of arsenic for two separate column tests using freshly prepared HAIX-M and GFH.

Publications

1. DeMarco, M. J.; SenGupta, A. K.; and Greenleaf, J. E., (2003) “Arsenic Removal Using a Polymeric/Inorganic Hybrid Sorbent”, *Water Research*, 37, 164-176.

2. Cumbal, L.; Greenleaf, J.; Leun, D.; and Sengupta, A. K. (2003) “Polymer Supported Inorganic Nanoparticles: Characterization and Environmental Applications”, *Reactive&Functional Polymers*, 54, 167-180.

3. Cumbal, L.H. and SenGupta, A.K. "Preparation and characterization of magnetically active dual-zone sorbent" *Ind. Eng. Chem. Res.,* (2005), 44, 600-605.

4. Cumbal, L., SenGupta, A.K. "Arsenic Removal Using Polymer-Supported Hydrated Iron (III) Oxide Nanoparticles: Role of Donnan Membrane Effect." *Environ. Sci. Technol.*, (2005), 39, 6508-6515.