

ENVIRONMENTAL ENGINEERING PROGRAM



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Research Title:

Sensing of environmentally regulated heavy metals using novel sorption based processes

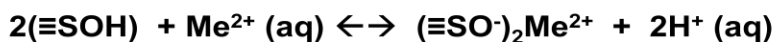
1) Rapid sensing of toxic heavy metals using pH as surrogate parameter

Research Objectives:

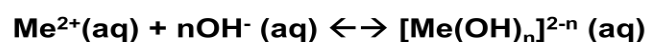
The primary objectives of this research were to investigate rapid and operationally simple sensing of environmentally toxic heavy metals in water using a sorption based process. A specially synthesized hybrid sorbent material forms the heart of the process which detects the presence of trace heavy metals simply through change of pH. Laboratory investigation validates detection of trace concentration (in $\mu\text{g/L}$) of lead and zinc and can avoid interference caused by phosphate and natural organic matter (NOM). According to information in open literature no technique currently exists that detects the presence of toxic heavy metals in water using pH as sole surrogate parameter.

Key concept:

Hydrated oxides of polyvalent metals namely Fe(III) and Zr(IV) exhibit high sorption affinity for dissolved toxic metals such as zinc, copper, lead, nickel and cadmium at alkaline pH. Surface hydroxyl groups ($\equiv\text{SOH}$) upon deprotonation selectively pick up Zn^{2+} , Cu^{2+} , Pb^{2+} etc in preference to common cations (Na^+ , K^+ , Ca^{2+} etc) through Lewis acid base interaction according to the following reaction:



In addition all these toxic metal cations, Me^{2+} form rapidly metal-hydroxy complexes at alkaline pH as per the reaction below.



Conceptually, an adsorbent that contains surface hydroxyl groups and remains alkaline (pH ~ 9) in contact with water can serve as a tool to sense the presence of toxic metals through pH swing.

Material Synthesis:

The primary challenge in realizing the above-mentioned concept lies in synthesizing/preparing a material that contains selective metal exchange sites with oxygen donor atoms and simultaneously maintains a near-constant alkaline pH in contact with an aqueous solution. Based on previous researches at Lehigh University on heavy metal separation by inorganic sorbent, a hybrid inorganic material (HIM) with selective metal binding sites while maintain alkaline pH for a long time has been synthesized. Every HIM particle comprises hydrated ferric oxide (HFO) and a silicate phase ($\text{Ca}_2\text{MgSi}_2\text{O}_7$ or akermanite) synthesized through simple thermal-chemical technique (illustrated in figure 1).

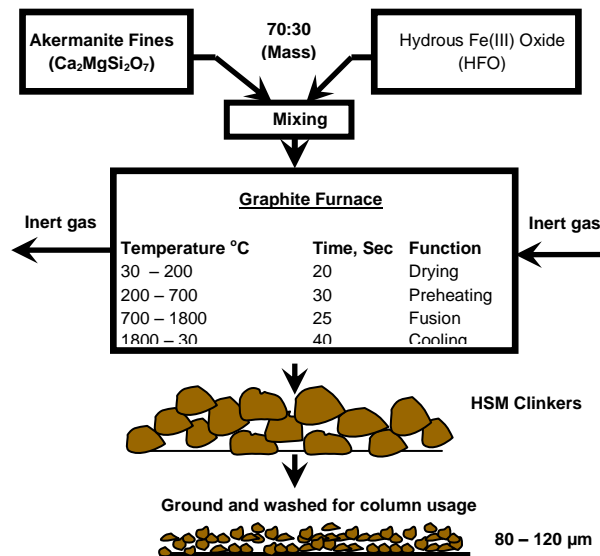


Figure 1 Schematic illustration of synthesis of hybrid inorganic material (HIM)

Calcium magnesium silicate or akermanite releases hydroxyl ions through slow hydrolysis, maintains a near-constant alkaline pH for a prolonged time according to the following reaction:



(The over bar represents solid phase.) As a result of alkaline pH (around 9.0) around the micro-environment of HIM particles, metal affinity towards the binding sites of HFO particles (surface hydroxyl groups) are greatly enhanced.

Key findings:

Fixed bed column experiment with HIM:

- Exit pH of column remains alkaline for feed with common cations (Na^+ , Ca^{2+} etc). When a heavy metal (say $\text{Zn}=0.5$ mg/L) is present with other common cations in the feed, pH sharply drops after certain time with simultaneous breakthrough of zinc in exit solution and change over to feed solution without zinc pH rises to alkaline domain (figure 2 A).

- Visual color change with phenolphthalein indicator signals the presence of toxic heavy metal. Initially Zn is not detectable (ND) at the column exit, indicator shows a pink color and as color goes off Zn breaks through. Again, following withdrawal of Zn from feed solution, pH swings back to alkaline domain and pink color reappears (figure 2 B).
- Plot of the negative slope of pH curve ($-dpH/dBV$) shown in figure 2 A vs. bed volume (BV) produces a distinctive peak which is a characteristic to type of metal and its concentration (figure 3 A)
- This technique allows to sense the presence of lead even at $< 100 \mu\text{g/L}$ in the feed. Plot of $(-dpH/dBV)$ vs. BV shows distinctive peaks for 53 and 74 $\mu\text{g/L}$ lead in the feed solution (figure 3 B) for the experiment performed under identical physical and hydrodynamic conditions.

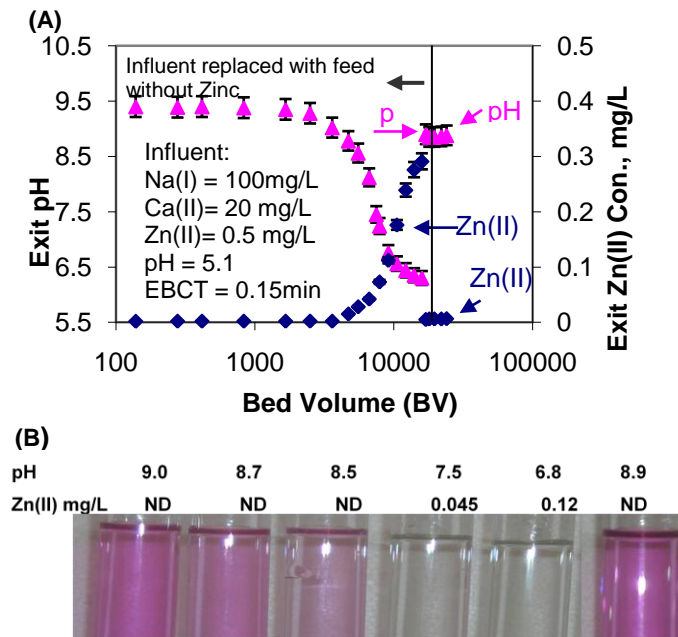


Figure 2. (A) Exit pH profile and zinc breakthrough for column run with HIM. (B) Visual change in color with phenolphthalein indicator from pink to colorless with zinc breakthrough and again pink following withdrawal of zinc

Challenge:

The presence of any buffering solute (e.g carbonate, phosphate or other weak acid anions) along with toxic metals in the sample is likely to interfere with the change of pH and detection technique. The buffering effect of carbonate was avoided by stripping of carbonates from the aqueous phase as carbon dioxide through adjustment of sample pH to 4.5 – 5. However, phosphate is non-volatile and often added as a corrosion inhibitor in municipal and industrial water systems. Also, NOM which essentially comprises weak aliphatic and aromatic anionic ligands (e.g fulvate) is also present in rivers, lakes and surface water supplies. So, a different strategy is adopted to overcome influence of phosphate and NOM.

- Hybrid anion exchange resin (HAIX), a ligand-selective exchanger is placed ahead of HIM. Dispersed HFO nano-particles within resin phase of HAIX selectively uptakes

phosphate or other ligand but rejects all cations according to Donnan co-ion exclusion principle

- After HAIX sample is free from interfering phosphate and NOM but contains toxic heavy metal and subsequently passing through HIM significant pH drop is expected. Figure 4 validates the strategy, shows a distinctive peak for zinc in presence of phosphate while passing through HAIX and HIM combined bed as opposed to very diffused and flat peak when passed through HIM alone.

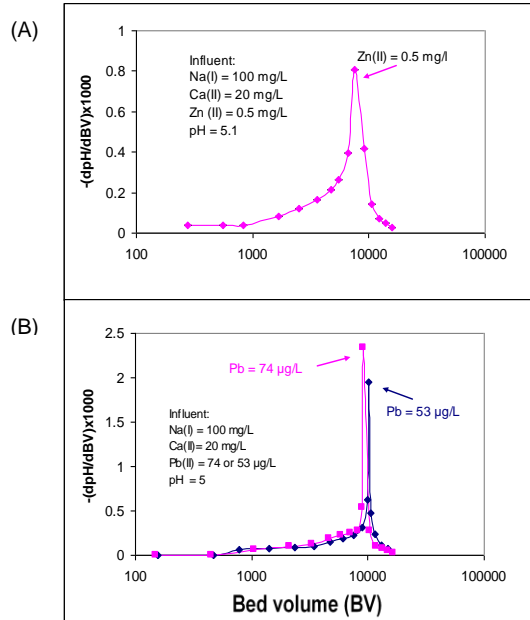


Figure 3. Plot of $(-dpH/dBV)$ vs. bed volume (BV). (A) For feed with 0.5 mg/L zinc and (B) feed solution containing 74 and 53 $\mu\text{g/L}$ respectively.

Sensing mechanism:

Slow dissolution of sparingly soluble akermanite maintains a near-constant alkaline pH (about 9.0) for a long time. At this alkaline pH HFO offers deprotonated binding sites (FeO^-). Common alkaline metal cations (Na^+ , Ca^{2+}) have poor affinity for binding sites (FeO^-). In contrast toxic metal cation (e.g. Zn^{2+}) shows strong affinity towards the binding sites and is selectively picked up by FeO^- through Lewis acid base interaction. Upon saturation of binding sites, Zn^{2+} breaks through and forms labile metal-hydroxy complex resulting into depletion of OH^- ions and consequent decline in pH. Almost all of these heavy metals from strong metal hydroxyl complexes which is confirmed by their high value of stability constants available in open literature. Figure 4 illustrates underlying sensing mechanism for heavy metals using pH as surrogate parameter.

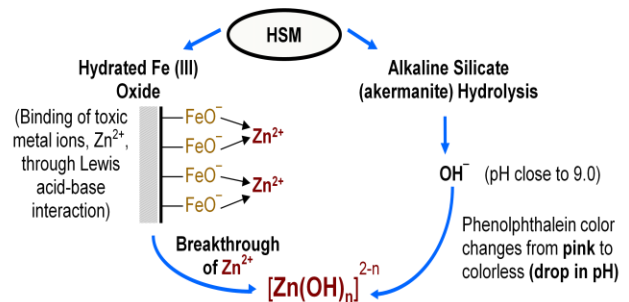


Figure 4. Illustration of sensing mechanism for toxic heavy metals

2) Interference free detection of trace copper using chelating polymer

Research objectives:

The primary objectives were to detect trace copper in water avoiding interference of strong chelating agents and other heavy metals. Copper laden waste water is commonly accompanied with EDTA (a strong chelating agent) and/or other competing metals such as lead, nickel and zinc. The present research investigates detection of trace copper through a simple colorimetric technique using polymeric sorbent, not interfered by the presence of EDTA or other competing metals.

Background:

Copper has unique regulatory standards. Being an essential micro-nutrient, the limit in drinking water is 1.3 mg/L according to US EPA. In contrast, limit of copper in wastewater is several folds lower than drinking water because even trace copper is toxic to fish and many other aquatic living species. Laboratory studies of 96 hours LC50s for fishes are reported to be as low as 30µg/L for some juveniles. Copper containing wastes from industrial sources (e.g. semi-conductor, plating industry) are commonly accompanied with EDTA and other heavy metal which interfere with copper detection unless an advanced instruments like AA spectrometer or ICP- MS is employed. Simple, in-situ detection of trace copper overcoming interferences is a challenge.

Premise of study:

The coordination properties of Cu(II) emerged from electronic configuration of its 3d shell; demonstrates a very favorable affinity towards numerous organic and inorganic ligands such as imminodiacetic acids, ethylenediamine and ammonia. Cu(II)-ligand complexes often exhibit spectacular color; such colors arise out of electronic transitions by the absorption of light. Copper Immino-di-acetic acid (IDA) complex exhibit characteristic blue color as revealed in Figure 1(a) when 1 ppm copper solution of 200 mL pass through chelating fiber with IDA functionality. The color is specific identification of copper on IDA. Unfortunately, in the presence of EDTA no such color is developed (shown in figure 1b) and also, this colorimetric approach is interfered by other competing metals. Herein, we demonstrate a rapid, simple sorption-based interference-free colorimetric identification of trace copper using chelating polymers. Ion-exchanging Chelating polymer with 3 nitrogen (3 N) donor atoms commonly known as bis-picolylamine functionality exhibits extra-ordinary sorption affinity towards copper even at very low pH and higher ionic strength in preference to common alkaline earth metals (Ca^{2+} , Mg^{2+}) or other transition group of metals. Copper sorbed onto 3N chelating exchanger is efficiently eluted using 2-10% NH_3 solution as eluent.

Exploiting the advantage of unique sorption and desorption of copper in relation to 3N chelating exchanger, a novel colorimetric detection of trace copper is speculated. Selective sorption of copper onto 3N polymer at $\text{pH} < 2$, followed by desorption using 4% NH_3 solution, followed by further arrest of copper onto IDA chelating fiber according to scheme in figure 2 will essentially produce distinctive copper specific color avoiding interference

Key Findings:

Figure 5 demonstrates color development of trace copper on to IDA fiber for different copper concentration in feed solution in the presence of EDTA and other competing heavy metals following the scheme described in figure 2. 3-N chelating polymers with its extra-ordinary copper sorption at ultra-low pH, forms the heart of the system. The process exhibits sub-micromolar sensitivity, free from interferences of other competing toxic metals, strong chelator like EDTA and dissolved organic matter.

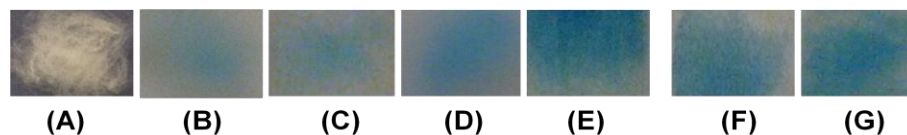


Figure 5 Comparison of color on IDA-fiber for different feed sample. (A) parent fiber (B), (C), (D), (E) Feed with copper and other common electrolytes (Na^+ , Ca^{2+} , Cl^- etc) with Cu $25\mu\text{g/L}$, $50\mu\text{g/L}$, $100\mu\text{g/L}$ and $250\mu\text{g/L}$ respectively. (F) Cu and other competing metals all at $200\mu\text{g/L}$ (G) Cu $200\mu\text{g/L}$, EDTA and other competing metals.

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Publications/ Conference presentation/ Patent:

1. Chatterjee, P. and SenGupta, A.K. "Sensing of Toxic Metals Through pH Changes: Concept and Experimental Validation." *AIChE Jour.* (2009). Vol.55, 11, 2997-3004.
2. Rapid sensing of toxic heavy metals in water using a hybrid inorganic material, AIChE centennial meeting, November 2008, Philadelphia, U.S.A
3. SenGupta, A.K. and Chatterjee, P. US Patent Application No. 60/941, 769, JUNE 4, 2007, Title of Invention: Rapid Sensing of Toxic Metals With A New Hybrid Material Through pH Changes.