

Sensing of Toxic Metals Through pH Changes Using a Hybrid Sorbent Material: Concept and Experimental Validation

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DOI 10.1002/aic.11915

Published online August 11, 2009 in Wiley InterScience (www.interscience.wiley.com).

This article reports a new hybrid sorbent material that is capable of detecting trace concentration of toxic metals, such as zinc, lead, copper, nickel, etc., through pH changes only. The material is essentially a composite granular material synthesized through rapid fusion of a mixture of amorphous hydrated ferric oxide (HFO) and akermanite or calcium magnesium silicate ($\text{Ca}_2\text{MgSi}_2\text{O}_7$). When a water sample is rapidly passed through a mini-column containing this hybrid material, effluent pH at the exit always remains alkaline (≈ 9.0) because of slow hydrolysis of akermanite and steady release of hydroxyl (OH^-) ions. This exit solution turns pink through the addition of a phenolphthalein indicator. Commonly encountered electrolytes containing sodium, calcium, chloride, and sulfate have no impact on the exit pH from the mini-column. However, when trace concentration of a heavy metal (say lead) is present in the sample water, a considerable drop in pH (>2 units) is observed for the exiting solution. At this point, the solution turns colorless through the addition of a phenolphthalein indicator. Moreover, the change in the slope of pH, i.e., $-\text{dpH}/\text{d}BV$, provides a sharp, noticeable peak for each toxic metal where BV is the bed volumes of solution fed. The technique allowed detection of zinc and lead through pH swings in synthesized samples, spiked Bethlehem City water, and also in Lehigh River water in the presence of phosphate and natural organic matter (NOM). Using a simple preconcentration technique, lower than $10 \mu\text{g/l}$ of lead was detected with a significant peak. From a mechanistic viewpoint, high sorption affinity of HFO surface sites toward toxic metal cations, ability of akermanite to maintain near-constant alkaline pH for a prolonged period through slow hydrolysis and labile metal-hydroxy complex formation causing dissipation of OH^- ions from the aqueous phase provide a synergy that allows detection of toxic metals at concentrations well below $100 \mu\text{g/l}$ through pH changes. Nearly all previous investigations pertaining to toxic metals sensing use metal-selective enzymes or organic chromophores. This simple-to-operate technique using an inexpensive hybrid material may find widespread applications in the developing world for rapid detection of toxic metals through pH changes. © 2009 American Institute of Chemical Engineers AICHE J, 55: 2997–3004, 2009

Keywords: toxic metal sensing, lead detection, hybrid inorganic material, ion exchange, hydrated iron oxide, akermanite, hybrid ion exchanger

Additional Supporting Information may be found in the online version of this article.

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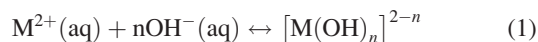
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Introduction

Rapid and operationally simple sensing of trace concentrations of environmentally regulated dissolved toxic metals in water is highly desirable in many diverse applications. Availability of robust and inexpensive sensors will facilitate monitoring of possible contamination of natural bodies of water near industrial outfalls and assessing performance of industrial treatment plants through rapid detection of treated water quality. An accessible, easy-to-use monitoring device will also empower individual households to quickly test for copper, lead, or zinc in water because of rather frequent use of galvanized and copper pipes and soldered lead joints in a water supply network. According to US EPA's drinking water regulations, maximum contaminant level (MCL) for lead, copper, and zinc are 0.015, 1.3, and 5 mg/l, respectively, and they pose health threat at higher concentrations, if ingested.¹ Nearly all the regulated dissolved toxic metals, such as lead, copper, zinc, nickel, cobalt, and cadmium are the transition metal cations can undergo strong metal-ligand or Lewis acid-base interactions. To date, nearly all scientific approaches for heavy metal sensing involve use of enzymes with specific interactions resulting in chemical-electrical signals, use of specific organic molecules as chromophores, fluorescence techniques aided by metal specific ligands.²⁻⁸ Despite the abundant research data, such sensors are often quite delicate with high degrees of sophistication, thus limiting their commercialization and large-scale usage in the public domain. Understandably, a sensing technique that uses pH as a surrogate indicator for toxic metals in water may lead to the development of a relatively inexpensive and user-friendly robust device.

Conceptualized Hybrid Material for Toxic Metal Sensing

Surface hydroxyl or carboxylate groups upon deprotonation at an alkaline pH exhibit high sorption affinity toward all commonly encountered dissolved toxic metal cations, such as copper, nickel, lead, zinc, cobalt, and cadmium. Such selective bindings result from the formation of inner sphere complexes or Lewis acid-base interaction between the oxygen donor atom of the surface functional groups (Lewis base) and toxic metal cations, M^{2+} (Lewis acid). On the contrary, commonly encountered nontoxic alkaline and alkaline-earth metal cations, namely, Na^+ , K^+ , Ca^{2+} , and Mg^{2+} form only outer sphere complexes (electrostatic interaction) and are poorly sorbed.⁹⁻¹² In addition, all toxic metal cations, M^{2+} , form metal-hydroxy complexes rapidly at alkaline pH in accordance with the following reaction:

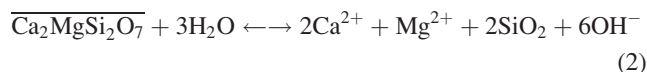


Conceptually, an adsorbent material that contains carboxylate and/or surface hydroxyl functional groups and remains alkaline (say pH around 9.0) in contact with water can serve as a tool to sense the presence of toxic metals through pH changes as described hereunder in conjunction with the illustration in Figure 1. When a typical water sample containing innocuous cations and anions is passed through a short mini-column of this conceptualized material, the exit pH remains

alkaline (Figure 1A). If any dissolved toxic metal (say zinc) is present in the feed solution at trace concentration, Zn^{2+} will selectively bind to its surface while other electrolytes will rapidly pass through. Thus, the exit solution will still remain alkaline as shown in Figure 1B. However, the surface sorption sites will be gradually exhausted with the passage of sample solution. Finally, when Zn^{2+} exits from the bottom of the mini-column, it instantaneously forms complexes with hydroxyl (OH^-) ions resulting in a sharp drop in pH (Figure 1C). Thus, the presence of trace zinc in the influent sample will result in a change in the exit pH signaling the presence of toxic metals in the influent (Figures 1D, E). Once the toxic metals are withdrawn, pH at the exit of the column will again turn alkaline.

Premise of the Study

The primary challenge in realizing the earlier 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. In previous studies at Lehigh University,^{13,14} a hybrid inorganic material (HIM) was synthesized that exhibited high metal sorption affinity while maintaining alkaline pH for a prolonged period of time. Every HIM particle is essentially hydrated Fe(III) oxide (HFO) along with a silicate phase, akermanite, in close proximity to each other. Akermanite is sparingly soluble calcium magnesium silicate ($Ca_2MgSi_2O_7$) that slowly hydrolyzes with release of OH^- ions in accordance with the following reaction:



The over bar indicates solid phase.

Consequently, pH within HIM always remains slightly alkaline (i.e., in the vicinity of 9.0), thus greatly enhancing the metal affinity of the surface hydroxyl groups in HIM. Because of the close proximity of Fe(III) oxide and akermanite, HIM embodies the attributes of the conceptualized sorbent illustrated in Figure 1.

The primary objectives of the article are to: first, present convincing experimental evidence to validate the concept of using pH as a parameter for toxic metal sensing through use of an engineered sorbent material; and second, demonstrate how the interference caused by the presence of phosphate, natural organic matter (NOM), etc., in water can be overcome through minor modification of HIM. The future challenges for wider application of the technique are also discussed. According to the information in the open literature, no technique currently exists to sense the presence of toxic metals using pH as the sole surrogate parameter.

Materials and Methods

Synthesis of HIM

HIM was synthesized in the laboratory using an operationally simple chemical-thermal technique. Freshly prepared precipitates of ferric hydroxide were mixed with ground

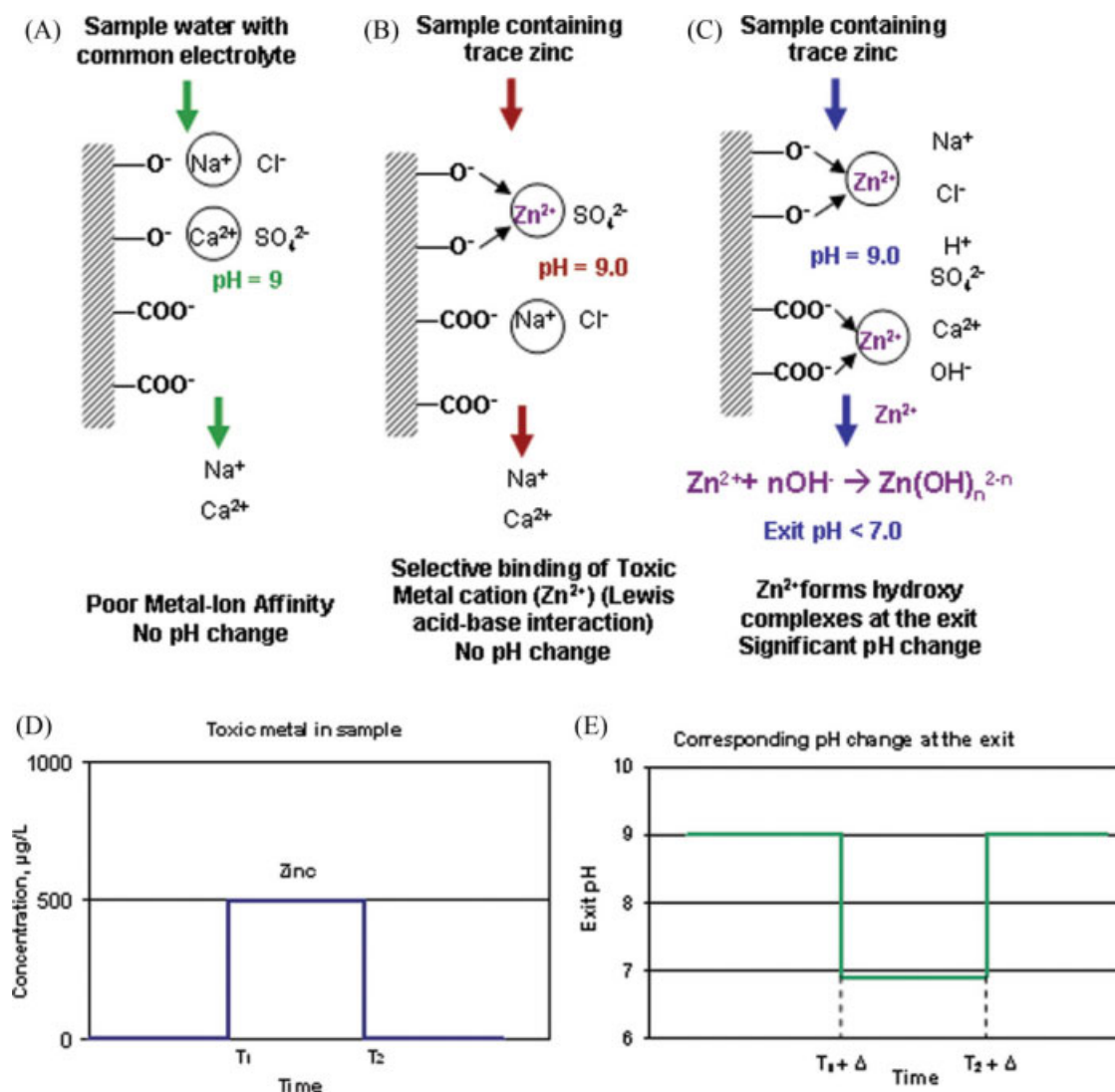


Figure 1. (A–E) Illustration of sensing of toxic metal based on conceptualized approach using pH as surrogate indicator.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amorphous akermanite (calcium magnesium silicate, $\text{Ca}_2\text{Mg-Si}_2\text{O}_7$) purchased from Ward Earth Science (Rochester, NY). The mixture was rapidly heated to 1800°C in a graphite furnace (Perkin Elmer A-500) leading to fusion and formation of clinkers. The mass ratio of HFO and akermanite was varied for different batches. Figure 2A shows a schematic illustrating the steps of the chemical-thermal technique to synthesize HIM using HFO and akermanite. The clinkers were subsequently ground and rinsed with deionized water prior to use in the mini-column study. Figure 2B shows the scanning electron microscopy (SEM) photograph ($3000\times$) of a HIM particle used in the study. A series of SEM photographs suggested that each particle is an aggregate of micro particles containing large macropores of sizes in the order of 50–500 nm; the average BET surface area of HIM is $\sim 10\text{ m}^2/\text{g}$.

Mini-column runs

Less than 1 g of HIM and an empty bed contact time (EBCT) of about 10 s in the column were adequate to bring

about the needed pH change signaling the presence of toxic metals. One glass column of 5-mm diameter, one constant-flow pump (Fluid Metering) and an ISCO fraction collector were used for the study. Average HIM particle size was $100 \pm 20\text{ }\mu\text{m}$. Other characteristics of the column runs were similar to those described earlier^{15,16} and the pH of the sample solution was adjusted to around 4.5–5.0 before being fed to the mini-column. For runs that included phosphate and NOM in the feed sample, a specially prepared hybrid anion exchanger (HAIX) was placed in the mini-column above the HIM. Details of the preparation of hybrid ion exchangers and their ability to preferentially reject cations and anions are available elsewhere.^{17–20} For every run, toxic metals were present in the dissolved state, i.e., their concentrations were well below the solubility limit.

Analyzes

Dissolved zinc, lead, and copper were analyzed using a Perkin Elmer atomic absorption spectrophotometer (AAS)

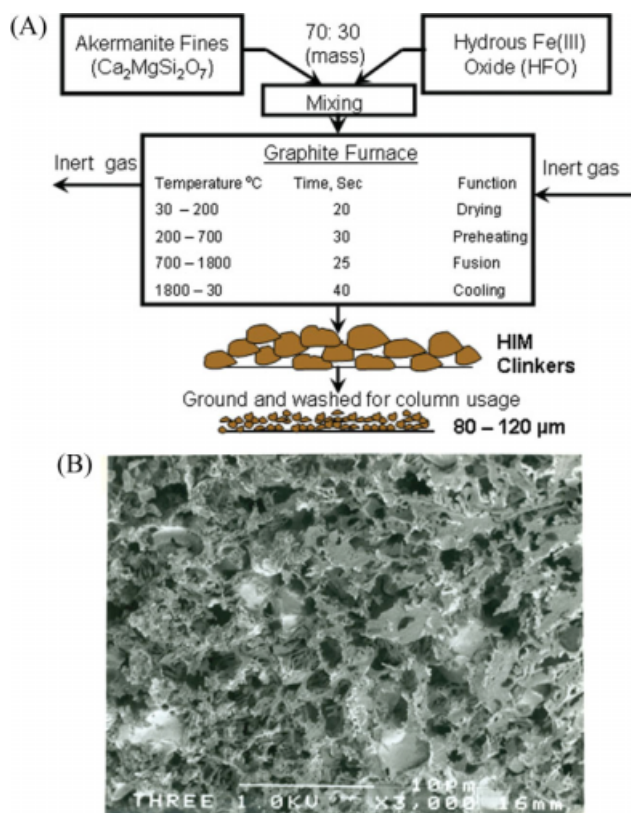


Figure 2. (A) Schematic illustration of synthesis of HIM using akermanite and HFO. (B) Scanning electron microphotograph (3000 \times) of a HIM particle.

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with graphite furnace accessories (Model SIMAA 6000). Filtration of samples through 0.4 micron filters and subsequent analyzes confirmed that toxic metals were present in the dissolved state only. Calcium was analyzed using an AAS with flame attachment (Perkin Elmer AAnalyst 200). Sodium, chloride, and sulfate were analyzed using Dionex Ion Chromatograph (model DX-120 IC); pH was determined using Accumet meter (model XL15). Inorganic carbon, dissolved organic carbon (DOC) was analyzed using SHIMADZU carbon analyzer. Phosphate was analyzed using Perkin Elmer's UV/VIS Spectrometer Lambda-2 according to colorimetric Stannous Chloride protocol of 4500-P.²¹

Results

Mini-column runs and pH changes

An aqueous solution containing commonly encountered ions (e.g., Na^+ , Ca^{2+} , Cl^- , and SO_4^{2-}) but with no toxic metal was passed through an HIM mini-column with an EBCT of 0.15 min. Figure 3A shows the plot of exit pH vs. bed volumes (BVs) of solution fed to the mini-column. At the exit of the mini-column, the solution always stayed slightly alkaline (pH around 9.0) due to the hydrolysis of akermanite and its color turned pink by the addition of a drop of phenolphthalein indicator. Fluctuations in the con-

centration of alkaline and alkaline-earth metal cations (e.g., Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) had no noticeable effect on the exit pH. For comparison, influent solution was replaced by deionized water. Note that the changeover showed practically no significant fluctuation at the exit pH (Figure 3A).

Subsequently, a second feed solution was passed through the mini-column; every experimental condition was identical to the previous one excepting that 0.5 mg/l of dissolved zinc was present in the influent along with other electrolytes. Figure 3B shows how the exit pH from the mini-column dropped (from 9.2 to 6.5) after ~ 6000 BVs. The drop in pH, as it is noted, coincided with the zinc breakthrough from the mini-column. After a prolonged time, the influent was

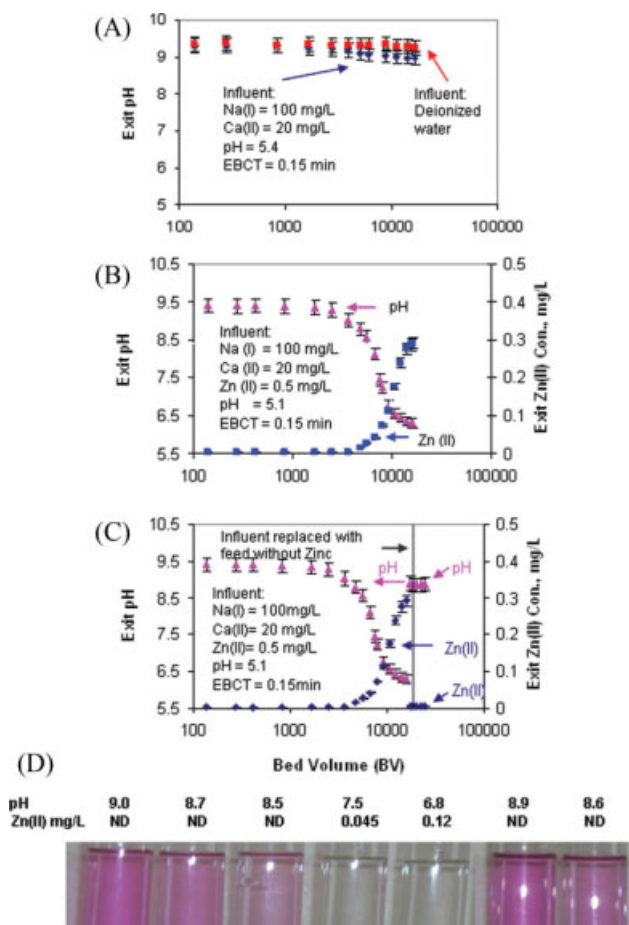


Figure 3. (A) Plot of exit pH vs. bed volume for HIM mini-column runs using two different feed solutions in the absence of toxic metals. (B) Plot of exit pH and zinc concentration vs. bed volume for HIM mini-column run with a feed solution containing 0.5 mg/l Zn(II) . (C) Rise of pH with replacement of zinc in feed solution. (D) Visual change in the color of phenolphthalein indicator from pink to colorless with zinc breakthrough and again pink due to withdrawal of zinc from feed as in Figure 3C. ND, not detectable.

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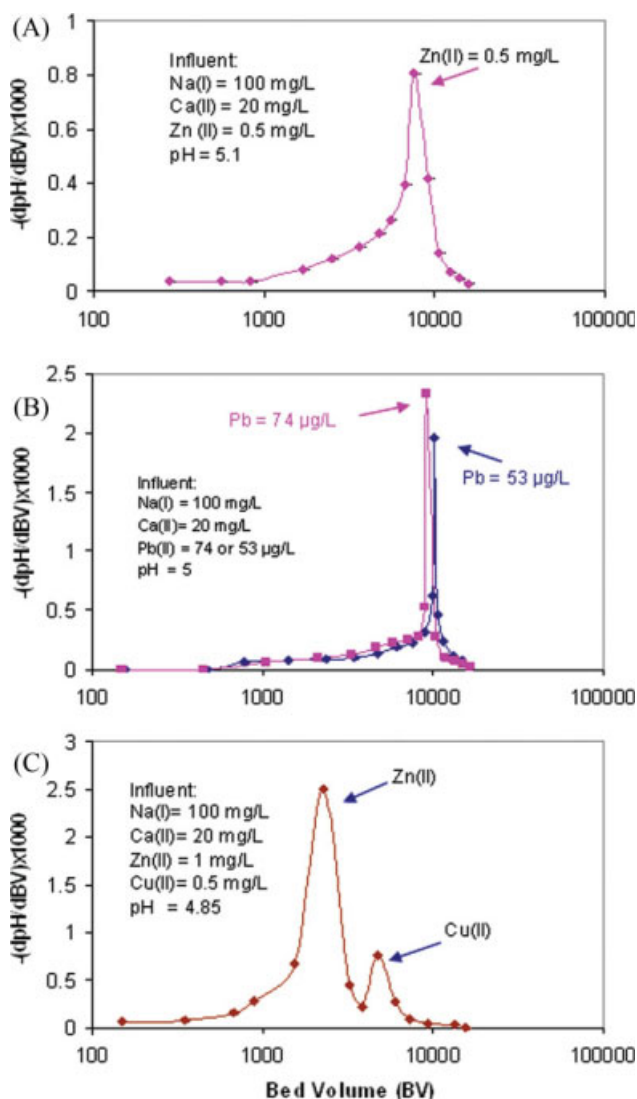


Figure 4. (A) Plot of $-\text{dpH}/\text{d}BV$ vs. bed volume (BV) for zinc based on data presented in Figure 3B. (B) Plot of $-\text{dpH}/\text{d}BV$ vs. BV for two trace concentrations of lead. (C) Plot of $-\text{dpH}/\text{d}BV$ vs. BV for zinc and copper present simultaneously.

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deliberately replaced with the feed solution containing no zinc. Note that pH promptly rose to alkaline condition (Figure 3C). Figure 3D shows how the color of phenolphthalein indicator solution turned from pink to colorless as zinc gradually appeared at the column's exit with concurrent reduction in pH. Subsequently, the phenolphthalein color turned pink again following the withdrawal of zinc from the feed solution.

Development of distinctive peaks ($-\text{dpH}/\text{d}BV$ plots)

Results in Figures 3A–C demonstrated that the pH changes at the exit of the mini-column were strongly correlated to the presence of zinc in the feed sample. This phe-

nomenon can be easily transformed into meaningful peaks as commonly observed in chromatographic analytical instruments. Quantitatively, the slope of the pH breakthrough curve (i.e., $-\text{dpH}/\text{d}BV$) exhibits a distinctive peak; such a peak occurs because the negative slope of the pH breakthrough curve (i.e., $-\text{dpH}/\text{d}BV$) gradually increases, goes through a maximum and then drops. Figure 4A shows the plot of $-\text{dpH}/\text{d}BV$ vs. BV for the data presented earlier in Figure 3B for 0.5 mg/l of zinc in the feed. Figure 4B shows the peaks for lead concentrations of 53 $\mu\text{g/l}$ and 74 $\mu\text{g/l}$ for two separate runs under identical bed parameters and hydrodynamic conditions. Figure 4C shows the peaks of zinc and copper when they are simultaneously present in the feed sample.

Determination of ultra-low lead concentration

For a very low target metal concentration, the sensitivity of the technique can be greatly enhanced through an operationally simple preconcentration step. A typical synthesized fresh water sample was spiked with less than 10 $\mu\text{g/l}$ of lead or Pb(II) . The preconcentration technique involved passing 1000 ml of sample through a mini-column containing chelating ion exchange resin or fiber and subsequently regenerating the ion exchanger with 1% sulfuric acid with complete recovery of sorbed lead. Similar evidences of sorption-desorption with chelating ion exchangers are available in the open literature.^{22,23} The preconcentrated spent regenerant, after necessary pH adjustment, is ready to be fed into the HIM column for metal sensing with a greater sensitivity.

Figure 5 shows the results of $-\text{dpH}/\text{d}BV$ plots for both the parent and preconcentrated (10 \times) sample using Chelex 100 (Biorad). Note that the preconcentrated sample offers a very distinctive sharp peak. The lead concentrations in both samples were also determined independently using an AAS (SIMAA 6000, Perkin Elmer). The observation that the lead concentration (78 $\mu\text{g/l}$) was practically 10 times greater than that in the parent sample (8 $\mu\text{g/l}$) confirms the precision of the preconcentration technique used.

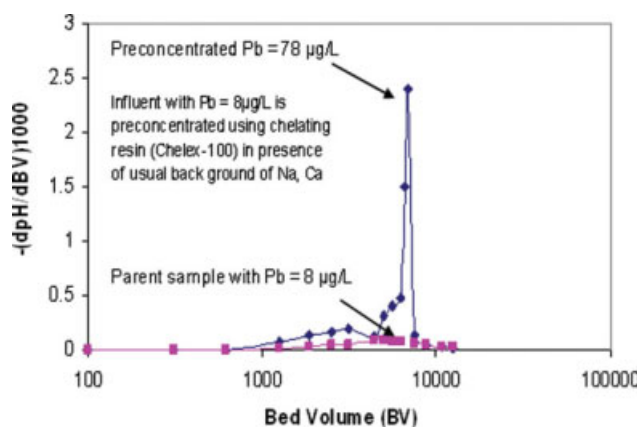


Figure 5. Plot of $-\text{dpH}/\text{d}BV$ vs. bed volume for demonstration of detection of ultra-low concentration of lead (8 $\mu\text{g/l}$) by preconcentration technique through HIM bed.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

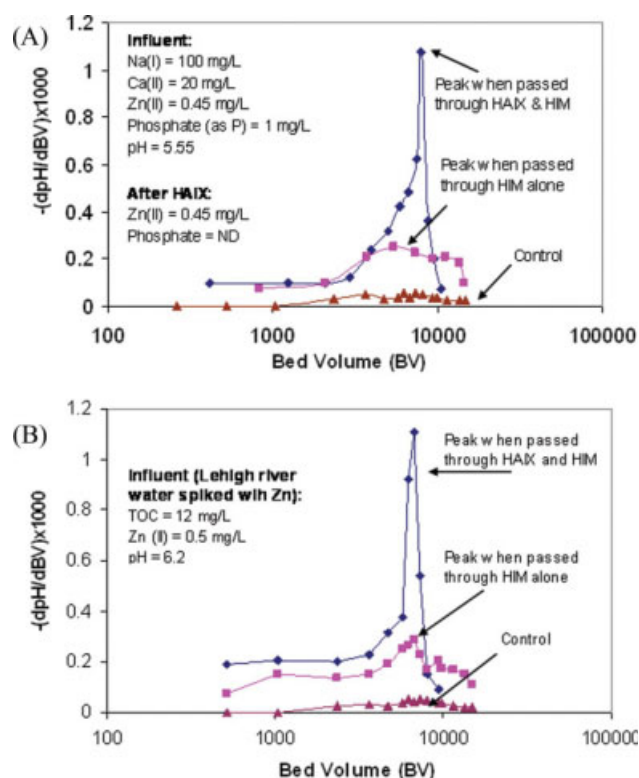


Figure 6. (A) Plot of $(-\text{dpH}/\text{dBV})$ vs. bed volume for demonstration of interference of phosphate and subsequent peak with modification of bed in mini-column run. (B) Plot of $(-\text{dpH}/\text{dBV})$ vs. bed volume for demonstration of interference of NOM and subsequent peak with modification of bed in mini-column run. ND, not detectable.

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Interferences from phosphate and NOM

As pH is the surrogate indicator for the presence of toxic metals, any buffering solute (e.g., weak-acid anions) is likely to interfere with the detection technique. The interfering effect of commonly encountered carbonate species can be easily overcome by adjusting the sample pH at 4.5–5.5 and stripping off carbonates from the aqueous phase as carbon dioxide. However, phosphate is nonvolatile and often added as a corrosion inhibitor in municipal and industrial water systems. In a similar vein, NOM, which essentially comprises weak aliphatic and aromatic anionic ligands is also present in rivers, lakes, and surface water supplies. The interference of phosphate, NOM or other ligands can be overcome by letting the sample solution first pass through a ligand-selective exchanger prior to HIM. Earlier studies have shown that such ligand-selective sorbents exhibit high sorption affinities toward phosphate, oxalate, phthalate, arsenate, and similar other anions.^{24–28}

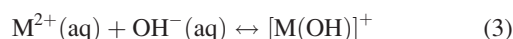
Figure 6A shows the peaks of the mini-column runs when phosphate is present in the sample along with trace concentration of zinc. Note that the mini-column containing the ligand-selective HAIX above HIM gave a larger and more

distinctive peak in comparison with HIM alone. The third peak is nearly flat (control) when zinc is absent in the influent, all other conditions remaining identical. In a similar vein, Figure 6B shows that a sample of the Lehigh River water spiked with 0.5 mg/l zinc gives a very sharp peak for the combined HAIX-HIM mini-column. The DOC in Lehigh River was 12 mg/l. The peak with HIM alone is shorter and more diffuse in the presence of NOM. Again, in the absence of zinc in the influent, Figure 6B did not show any peak (control) with HAIX-HIM mini column confirming the scientific premise that the pH fluctuation was caused solely by the presence of zinc.

Discussion

Concept validation

The experimental results in Figures 3A–C and Figures 4A–C demonstrated that toxic metals when present in water at concentration well below 1.0 mg/l can be detected through pH changes occurring at the exit during an HIM mini-column run. More significantly, the slope of the exit pH curve (i.e., $-\text{dpH}/\text{dBV}$) provides distinguishable peaks confirming the presence of toxic metals, namely, zinc and lead. The akermanite is responsible for maintaining a near-constant alkaline pH through hydrolysis for a very prolonged period of time in accordance with reaction (2); this property was independently confirmed through dissolution tests (Refer Supporting Information Figures S1A–C and Table S1). Besides, the rise of pH to the alkaline domain following withdrawal of zinc from the feed confirms HIM's ability to respond to fluctuations in toxic metal concentrations in the influent sample. When present as the only toxic metal, the peak for lead appeared after zinc. When both zinc and copper were present, the zinc peak preceded the copper peak (Figure 4C) in accordance with the already established affinity sequence of metals onto iron oxide binding sites at an alkaline pH.^{10–12} Also, the stability or association constant for metal-hydroxy complex formation is different for different metals.



For reaction 3, the first association constant, K_{a1} , for three metals of interest are as follows²⁹:

$$\text{Zn(II)} : K_{a1} = 10^{+5.0}$$

$$\text{Pb(II)} : K_{a1} = 10^{+6.3}$$

$$\text{Cu(II)} : K_{a1} = 10^{+6.5}$$

At well below micro-molar concentration, these metals may cause very significant pH reduction by forming hydroxyl complexes. Breakthrough of toxic metal coinciding with pH drop shown in Figures 3B, C suggests depletion of OH^{-} ions upon metal breakthrough.

Figures 6A, B demonstrated that the interferences caused by phosphate and NOM can be overcome by putting a HAIX ahead of HIM in the mini-column. The underlying mechanism with an appropriate sequence of steps leading to the pH changes at the end of the mini-column can be presented as follows: The HAIX contains very high

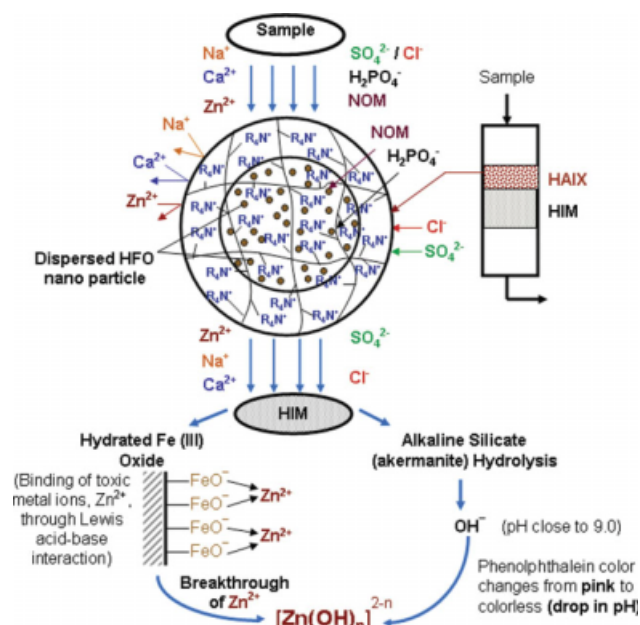


Figure 7. Schematic illustration of toxic metal sensing mechanism with modified bed of HAIX and HIM for avoiding interference of buffers like phosphate, NOM, and similar anionic ligand.

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concentration of positively charged quaternary ammonium functional groups (R_4N^+) and HFO nanoparticles are dispersed within the core of the anion exchanger.^{27,28} Because of the Donnan co-ion exclusion effect, Zn^{2+} and other cations are completely rejected by the HAIX. On the contrary, an anionic ligand (e.g., phosphate or fulvate in NOM) permeates preferably into the gel phase of the HAIX and gets selectively bound onto the sorption sites of HFO in preference to other commonly occurring anions, namely, sulfate and chloride. Supporting Information (Figure S2) provides confirmatory experimental evidence in this regard. Now, as zinc comes in contact with HIM, pH turns alkaline (≈ 9.0) due to the hydrolysis of akermanite. At this point zinc is very selectively bound onto HFO binding sites within HIM and the pH at the exit of the column still remains alkaline. Once the sorption sites of HIM are all occupied, zinc breaks through from the exit of the column and rapidly forms metal-hydroxy complex, thus resulting in depletion of OH^- ions and consequent decline in pH. Figure 7 illustrates the sequence of steps leading to a sharp decline in pH. In principle, Donnan co-ion exclusion effect of HAIX, hydrolysis of akermanite leading to slow release of OH^- for a very prolonged period and the specific binding sites of HFO together create a synergy that allows pH to act as a surrogate indicator to sense toxic metals.

Shortcomings and challenges

The adsorption based technique to sense the presence of toxic metals through pH changes, as presented in this investigation, is robust and likely to be inexpensive. Nevertheless,

a few critical impediments need to be overcome before the technique is ready for broader applications to rapidly detect trace toxic metals in water. Nearly one liter of sample water is currently needed to cause the desired pH change at the exit of the mini-column. The volume requirement needs to be significantly reduced. Further development of a hybrid material with reduced ion exchange capacity may address the problem. Also, if the metal binding capacity resides near the outer surface of the particles, sorption/desorption kinetics will be relatively fast leading to an even sharper change in pH. For simultaneous detection of two toxic metals, different elution times may be useful with a large difference in affinity for the sorption sites (e.g., zinc and copper). However, for detection of multiple toxic metals with near-equal sorption affinity present in a sample, further research is needed to achieve prepreparation of the metals prior to feeding in the mini-column.^{30–32} The presence of common cations (Na^+ and Ca^{2+}) in the sample at much higher concentration compared with trace toxic metals does not interfere with the detection technique. Calcium, though a divalent cation, has a poor affinity for the HFO binding sites and also forms a weak metal-hydroxy complex. The present technique is viable even at high concentration of calcium in sample water. For typical surface water sources and municipal water systems, the technique appears to be quite robust to detect toxic metals at concentrations about $50 \mu\text{g/l}$ even in the presence of buffers and NOMs, as demonstrated. However, the technique may not respond well for industrial wastewaters with high concentration of chelating agents. It is likely that doped activated carbons, chitosons, and other hybrid sorbents^{33,34} may also be tailored for detecting toxic metals through pH changes in accordance with the scientific guidelines presented in this study.

Conclusions

To date, nearly all scientific approaches for heavy metal sensing involve specific enzymes, biosensors, and organic chromophores. This investigation presents a new approach for detecting toxic heavy metals solely through pH changes. An environmentally benign, inexpensive HIM forms the heart of the process. As pH meter and/or indicator solutions are universally available, the sensing technique is particularly attractive for developing countries and may find forensic applications as well. Primary conclusions that resulted from the study can be summarized as follows.

- Unique sorption and dissolution behavior of HIM allow sharp change in pH in the presence of toxic heavy metals at concentrations well below $100 \mu\text{g/l}$.
- The interfering effect of phosphate and NOM can be easily overcome by using a HAIX ahead of HIM.
- The sensitivity of the technique for detection of ultra-low concentration of lead or other metals (less than $10 \mu\text{g/l}$) can be easily enhanced using an operationally simple preconcentration method.

Literature Cited

1. National primary drinking water regulations—list of drinking water contaminants and their MCLs. U.S. Environmental Protection Agency, 2003.

2. Bontidean I, Ahlqvist J, Mulchandani A, Chen W, Weon BW, Mehra RK, Mortari A, Csöregi E. Novel synthetic phytochelatin-based capacitive biosensor for heavy metal ion detection. *Biosens Bioelectron.* 2003;18:547–553.
3. Arduini M, Mancin F, Tecilla P, Tonellato U. Self-organized fluorescent nanosensors for ratiometric Pb^{2+} detection. *Langmuir.* 2007;23:8632–8636.
4. Shimada T, Ookubo K, Komuro N, Shimizu T, Uehara N. Blue-to-red chromatic sensors composed of gold nanoparticles conjugated with thermoresponsive copolymer for thiol sensing. *Langmuir.* 2007;23:11225–11232.
5. Gao HW, Chen F, Chen L, Zeng T, Pan L, Li JH, Luo HF. A novel detection approach based on chromophore-decolorizing with free radical and application to photometric determination of copper with acid chrome dark blue. *Anal Chim Acta.* 2007;587:52–59.
6. Sumner JP, Westerberg NM, Stoddard AK, Hurst TK, Cramer M, Thompson RB, Fierke CA, Kopelman R. DsRed as a highly sensitive, selective, and reversible fluorescence-based biosensor for both Cu^+ and Cu^{2+} ions. *Biosens Bioelectron.* 2006;21:1302–1308.
7. Schöning MJ, Hüllenkremmer B, Glück O, Lüth H, Emons H. Voltammetry—a novel sensing principle for heavy metal determination in aqueous solutions. *Sens Actuators B Chem.* 2001;76:275–280.
8. Xiao Y, Rowe AA, Plaxco KW. Electrochemical detection of parts per billion lead via an electrode-bound DNAzyme assembly. *J Am Chem Soc.* 2007;129:262–263.
9. Kosmulski M, Maczka E. Dilatometric study of the adsorption of heavy-metals cations on goethite. *Langmuir.* 2004;20:2320–2323.
10. Dzombak DA, Morel FMM. *Surface Complexation Modeling: Hydrous Ferric Oxides.* New York: Wiley, 1990.
11. Benjamin MM, Leckie JO. Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. *J Colloid Interface Sci.* 1981;79:209–221.
12. Bargar JR, Trainor TP, Fitts JP, Chambers SA, Brown GE Jr. In situ grazing-incidence extended x-ray adsorption fine structure study of Pb(II) chemisorption on hematite (0001) and 1–102) surfaces. *Langmuir.* 2004;20:1667–1673.
13. Gao Y, SenGupta AK, Simpson DA. New hybrid inorganic sorbent for heavy metals removal. *Water Res.* 1995;29:2195–2205.
14. Kney AD, SenGupta AK. *Synthesis and characterization of a new class of hybrid inorganic sorbents for heavy metals removal.* In: SenGupta AK, Marcus Y, editors. *Ion Exchange and Solvent Extraction: A Series of Advances*, Vol. 14. New York: Marcel Dekker, 2001:295–352.
15. SenGupta AK, Lim L. Modeling chromate ion-exchange processes. *AIChE J.* 1988;34:2019–2029.
16. SenGupta AK, Zhu Y, Hauze D. Metal(II) ion binding onto chelating exchangers with multiple nitrogen donor atoms: some new observations and related implications. *Environ Sci Technol.* 1991;25:481–488.
17. Cumbal L, Greenleaf J, Leun D, SenGupta AK. Polymer supported inorganic nanoparticles: characterization and environmental applications. *React Funct Polym.* 2003;54:167–180.
18. DeMarco MJ, SenGupta AK, Greenleaf JE. Arsenic removal using a polymeric/hybrid inorganic hybrid sorbent. *Water Res.* 2003;37:164–176.
19. SenGupta AK, Cumbal LH. Hybrid anion exchanger for selective removal of contaminating ligands from fluids and method of manufacture thereof. U.S. Patent No. 7,291,578. November 6, 2007.
20. Puttamaraaju P, SenGupta AK. Evidence of tunable on-off sorption behaviors of metal oxide nanoparticles: role of ion exchanger support. *Ind Eng Chem Res.* 2006;45:7737–7742.
21. APHA, AWWA, WEF. *Standard Methods for the Examination of Water and Wastewater*, 18th ed. Washington, DC: American Public Health Association, 1992.
22. Jyo A, Kugara J, Trobradovic H, Yamabe K, Sugo T, Tamada M, Kume T. Fibrous iminodiacetic acid chelating cation exchangers with a rapid adsorption rate. *Ind Eng Chem Res.* 2004;43:1599–1607.
23. Yamabe K, Ihara T, Jyo A. Metal ion selectivity of macroreticular chelating cation exchange resins with phosphoric acid groups attached to phenyl groups of a styrene-divinylbenzene copolymer matrix. *Sep Sci Technol.* 2001;36:3511–3528.
24. Zhao D, SenGupta AK. Ultimate removal of phosphate using a new class of anion exchangers. *Water Res.* 1998;32:1613–1625.
25. Zhu Y, SenGupta AK. Sorption enhancement of some hydrophilic organic solutes through polymeric ligand exchange. *Environ Sci Technol.* 1992;26:1990–1998.
26. Ramana A, SenGupta AK. A new class of selective sorbents for arsenic and selenium oxyanions. *J Environ Eng Div ASCE.* 1992;118:755–775.
27. Cumbal L, SenGupta AK. Arsenic removal using polymer-supported hydrated iron(III) oxide nano particles: role of donan membrane effect. *Environ Sci Technol.* 2005;39:6508–6515.
28. Blaney LM, Chinar S, SenGupta AK. Hybrid anion exchanger for trace phosphate removal from water and waste water. *Water Res.* 2007;41:1603–1613.
29. Morel FMM. *Principles of Aquatic Chemistry.* New York: Wiley, 1983.
30. Ritchie SM, Bachas LG, Olin T, Sikdar S, Bhattacharyya D. Surface modification of silica and cellulose based micro-filtration membranes with functional polyamino acids for heavy metal sorption. *Langmuir.* 1999;15:6346–6357.
31. Clifford D, Subramonian S, Sorg TJ. Removing dissolved inorganic contaminants from water. *Environ Sci Technol.* 1986;20:1072–1080.
32. Deorkar NV, Tavlarides LL. Zinc, cadmium and lead separation from aqueous streams using solid-phase extractants. *Ind Eng Chem Res.* 1997;36:399–406.
33. Huang CP, Vane LM. Enhancing As(V) removal by Fe(II)-treated activated carbon. *J Water Pollut Control Fed.* 1989;61:1596–1603.
34. Guibal E, Chassary P, Vincent T. Metal ion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use. *React Funct Polym.* 2004;60:137–145.

Manuscript received Nov. 14, 2008, and revision received Mar. 17, 2009.