

# Arsenic Removal Using Polymer-Supported Hydrated Iron(III) Oxide Nanoparticles: Role of Donnan Membrane Effect<sup>†</sup>

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The conditions leading to the Donnan membrane equilibrium arise from the inability of ions to diffuse out from one phase in a heterogeneous system. In a polymeric cation exchanger, negatively charged sulfonic acid groups are covalently attached to the polymer chains, and thus, they cannot permeate out of the polymer phase. Conversely, a polymeric anion exchanger contains a high concentration of non-diffusible positively charged quaternary ammonium functional groups. It is well-established that submicron or nanoscale hydrated iron(III) oxide (HFO) particles exhibit high sorption affinity toward both arsenates and arsenites. In this study, commercially available cation and anion exchangers were used as host materials for dispersing HFO nanoparticles within the polymer phase using a technique previously developed. The resulting polymeric/inorganic hybrid sorbent particles were subsequently used for arsenic removal in the laboratory. The most significant finding of the study is that the anion exchanger as a substrate containing dispersed HFO offered substantially higher arsenate removal capacity as compared to the cation exchanger, all other conditions remaining identical. In fact, HFO nanoparticles dispersed within the gel-type cation exchanger were unable to remove arsenic. The Donnan membrane effect resulting from the non-diffusible negatively charged sulfonic acid groups in the cation exchanger did not allow permeation of arsenate into the polymer phase (i.e., arsenate was excluded from the spherical beads dispersed with HFO nanoparticles). On the contrary, anion-exchanger-supported HFO particles or HAIX offered very high arsenic removal capacity; less than 10% of influent arsenic broke through after 10 000 bed vol. HAIX was also amenable to efficient regeneration with 2% NaOH and 3% NaCl and capable of simultaneously removing both perchlorate and arsenic selectively. According to the information in the open literature, HAIX is the first hybrid sorbent that utilizes the Donnan membrane effect of the host material for sorption enhancement. From a generic viewpoint, other metal oxide/metal nanoparticles may also be judiciously embedded in appropriate support materials that would reject or enhance permeation of targeted ionic solutes.

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## Introduction

It is well-recognized that oxides of polyvalent metals, namely, Al(III), Fe(III), Ti(IV), and Zr(IV), exhibit ligand sorption properties through formation of inner-sphere complexes (1–7). Of them, hydrated iron(III) oxide or HFO is innocuous, inexpensive, readily available, and chemically stable over a wide pH range. Many previous studies confirmed that iron(III) oxides have high sorption affinity toward both As(V) or arsenates and As(III) or arsenites, which are Lewis bases (i.e., electron pair donors). Their selective sorption onto HFO particles results from 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) are selectively bound to the oxide surface through coordinate bonding (8). Table 1 shows the major As(V) and As(III) species at slightly above- and below-neutral pH values and also highlights their ligand characteristics (i.e., electron-donating ability). Removal of dissolved arsenic from naturally contaminated groundwater essentially involves selective separation of As(V) and As(III) oxyanions or oxyacids from the background of other electrolytes or competing species. Compared to crystalline forms of iron(III) oxides (namely, goethite, hematite, and magnetite), amorphous iron oxides have highest surface area per unit mass. Since sorption sites reside primarily on the surface, amorphous iron oxides (referred to as hydrated iron(III) oxides or HFO) offer the highest sorption capacity on a mass basis (7, 9).

The sizes of freshly precipitated amorphous HFO particles were found to vary between 20 and 100 nm. Despite high arsenic removal capacity, such fine submicron particles and their aggregates are unusable in fixed beds or any flow-through systems because of excessive pressure drops and poor mechanical strength. To overcome the foregoing problems, we dispersed HFO nanoparticles within a macroporous polymeric cation exchanger in a previous study and used the resulting hybrid material for arsenic removal (10, 11). Alginate has been used as host materials to support HFO nanoparticles; zeolite, activated carbon, and chitosan also qualify as potential host materials (12, 13). All the foregoing support materials including cation exchangers have charged surface functional groups to a varying degree. Also, the charged groups are fixed on the solid phase (i.e., they cannot permeate or diffuse into the aqueous phase). The role of these surface functional groups of the host materials and more specifically, the Donnan membrane effect resulting from them, has not been taken into consideration in previous studies for relative sorption of target solutes. The general objective of the present study is to show how the fixed surface charge of the host material and, more specifically, Donnan co-ion exclusion effect influences the arsenic sorption behaviors of HFO nanoparticles.

**Donnan Membrane Equilibrium and Co-Ion Exclusion Effect.** The Donnan membrane principle is essentially an extension of the second law of thermodynamics, but it deals specifically with completely ionized electrolytes in a heterogeneous system (14, 15). To make the illustration more relevant to the subject of arsenic removal, consider monosodium arsenate ( $\text{NaH}_2\text{AsO}_4$ ), a completely ionized 1–1 electrolyte in water:



For a membrane that is completely permeable to both  $\text{Na}^+$

**TABLE 1. Oxyacids and Conjugate Anions of As(V) and As(III)**

Parent Oxyacids	pK <sub>a</sub> Values	Predominant Dissolved Species at pH 6.0	Predominant Dissolved Species at pH 8.0	Sorption Interaction
As(V): H <sub>3</sub> AsO <sub>4</sub>	pK <sub>a1</sub> = 2.2 pK <sub>a2</sub> = 6.98 pK <sub>a3</sub> = 11.6			As(V) species or arsenates can undergo Coulombic (ion exchange) as well as Lewis acid-base interaction
As(III): HAsO <sub>2</sub>	pK <sub>a1</sub> = 9.2			As(III) species or arsenites can undergo only Lewis acid-base interaction

and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, the Donnan membrane principle provides the following equality at equilibrium considering ideality:

$$[Na^+]_L [H_2AsO_4^-]_L = [Na^+]_R [H_2AsO_4^-]_R \quad (1)$$

where subscripts “L” and “R” refer to the solution at the left-hand and right-hand side of the membrane, respectively, and [ ] represents molar concentration or activity under ideal condition. If sodium arsenate is the only electrolyte present in the solution phase and the volume on either side of the membrane is the same (say 1.0 L), the constraint from electroneutrality requires that

$$[Na^+]_L = [H_2AsO_4^-]_L \quad (2)$$

$$[Na^+]_R = [H_2AsO_4^-]_R \quad (3)$$

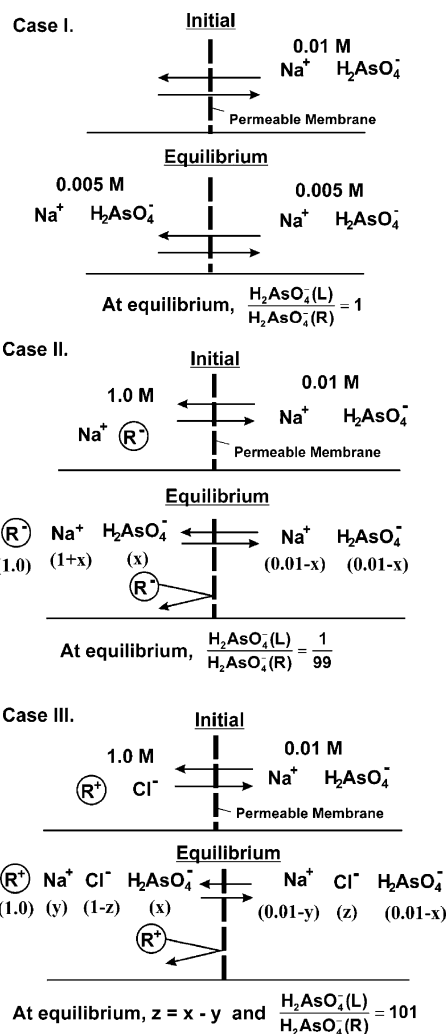
Thus,

$$\frac{[H_2AsO_4^-]_L}{[H_2AsO_4^-]_R} = \frac{[Na^+]_R}{[Na^+]_L} = 1$$

The above equality is understandably trivial, as shown in Figure 1 (case I). The distribution of H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> on both sides of the membrane is however greatly altered in the presence of an impermeable cation or anion. Consider the illustration in case II where the salt NaR is initially present on the left-hand side of the membrane at 1.0 M concentration. The resulting anion (R<sup>-</sup>) cannot however permeate through the membrane. All other conditions are essentially the same as in case I (i.e., the membrane is completely permeable to both Na<sup>+</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and the initial concentration of NaH<sub>2</sub>AsO<sub>4</sub> on the right-hand side is 0.01 M. At equilibrium, the equality stated in eq 1 will hold even in the presence of non-permeating R<sup>-</sup>. Hence, Na<sup>+</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> will redistribute to arrive at the following equilibrium condition:

$$\frac{[Na^+]_R}{[Na^+]_L} = \frac{[H_2AsO_4^-]_L}{[H_2AsO_4^-]_R} = \frac{1}{99} \quad (4)$$

Note that the monovalent arsenate concentration on the left-hand side of the membrane, [H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>]<sub>L</sub>, is nearly 2 orders of magnitude lower than [H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>]<sub>R</sub>. Although the membrane is permeable to Na<sup>+</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, the presence of electrolytically dissociated NaR at high concentration suppresses the permeability of H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> in one direction. This phenomenon is known as Donnan co-ion exclusion effect and does not result from Coulombic or electrostatic interaction. The derivation of eq 4 (and also eq 5 later) can be readily followed by consulting the recently published English translation of



**FIGURE 1. Depiction of three specific cases presenting the Donnan distribution of arsenate (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>) when the membrane is permeable to (case I) all the ions; (case II) all the ions except R<sup>-</sup>; and (case III) all the ions except R<sup>+</sup>.**

Donnan’s original paper (14, 15). It is assumed that the volume on each side of the membrane is not altered by osmosis. Should HFO particles be now added to the solutions on both sides of the membrane at equilibrium, arsenic sorption capacity in the left-hand side would be relatively low due to significantly lower aqueous-phase arsenic concentration caused by the presence of non-permeating R<sup>-</sup>.

The illustration in case III (Figure 1) is, in principle, similar to case II except that the non-permeating ion (R<sup>+</sup>) is a cation.

**TABLE 2. Polymeric Ion Exchangers as Host Materials**

Anion and Cation Resin	Purolite A-400 and IRA-900	Purolite C-100
Structure (Repeating Unit)		
Functional Group	Quaternary ammonium	Sulfonic acid
Matrix	Polystyrene	Polystyrene
Capacity (meq/g resin)	3.6	4.0 (Dry) 2.5 (Wet)
Manufacturer	Purolite Inc. and Rohm and Haas Co., Philadelphia	Purolite Inc., Philadelphia

The relative distribution of  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{AsO}_4^-$  in both sides of the membrane, after necessary calculations, stands as follows at equilibrium:

$$\frac{[\text{Na}^+]_R}{[\text{Na}^+]_L} = \frac{[\text{Cl}^-]_L}{[\text{Cl}^-]_R} = \frac{[\text{H}_2\text{AsO}_4^-]_L}{[\text{H}_2\text{AsO}_4^-]_R} = \frac{101}{1} \quad (5)$$

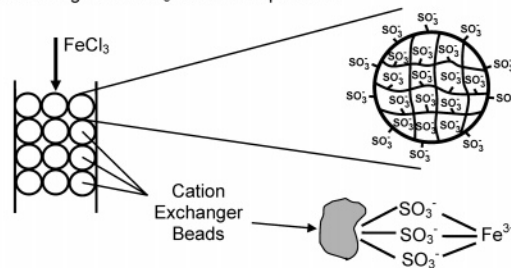
Note that contrary to case II, arsenic concentration in the left-hand side,  $[\text{H}_2\text{AsO}_4^-]_L$ , is nearly 2 orders of magnitude greater than  $[\text{H}_2\text{AsO}_4^-]_R$ . The addition of HFO particles in the LHS of the membrane will therefore offer very high sorption capacity due to an enhanced arsenic concentration at equilibrium. The chloride concentration is also enhanced in the left-hand side of the membrane, but HFO particles have negligible sorption affinity for chloride anions. It is noteworthy that the conditions leading to the Donnan membrane equilibrium do not arise from the physical existence of a semipermeable membrane but from the inability of an ion to diffuse out from one phase in a heterogeneous system. In comparison, the osmotic membrane equilibrium results from the presence of a membrane permeable only to the solvent separating two solutions.

Conceptually, eqs 4 and 5 provide meaningful guidelines toward formulating hybrid sorbents based on the Donnan membrane principle. If HFO particles are dispersed within a solid phase containing a high concentration of fixed (non-diffusing)  $\text{R}^+$  groups, HFO will offer high arsenic(V) removal capacity. On the contrary, arsenic removal capacity of HFO particles will be greatly suppressed when dispersed within a solid phase with fixed  $\text{R}^-$  groups. In principle, a strong-base polymeric anion exchanger is essentially a solid phase containing positively charged fixed quaternary ammonium functional groups while a strong-acid polymeric cation exchanger is a solid phase with negatively charged sulfonic acid functional groups. The specific objective of the proposed study is to experimentally validate that a hybrid anion exchanger (HAIX) dispersed with HFO nanoparticles offers significantly greater arsenic removal capacity than a hybrid cation exchanger (HCIX), all other conditions remaining identical. Also, experimental data pertaining to regenerability and removal of other contaminants by HAIX will be presented.

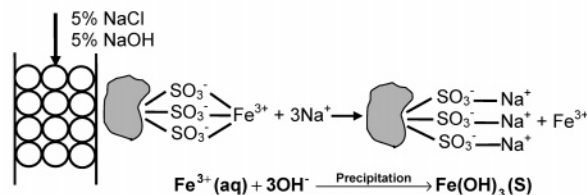
### Experimental Section

**Preparation of Hybrid Ion Exchangers.** Table 2 includes the salient properties of the commercially available cation

Step 1. Loading with  $\text{FeCl}_3$  Solution at  $\text{pH} < 2.0$



Step 2. Desorption and simultaneous hydroxide precipitation in the gel phase and pore surface



Step 3. Alcohol wash and mild thermal treatment



**FIGURE 2. Illustration of the three-step procedure to disperse HFO nanoparticles inside spherical cation exchanger beads.**

exchanger and anion exchanger used for preparation of the hybrid sorbent materials. However, no endorsement is implied; similar exchangers are also available from other manufacturers. The preparation of the hybrid cation exchanger or HCIX consisted of the following three steps: first, loading of  $\text{Fe(III)}$  onto the sulfonic acid sites of the cation exchanger by passing 4%  $\text{FeCl}_3$  solution at an approximate  $\text{pH}$  of 2.0; second, desorption of  $\text{Fe(III)}$  and simultaneous precipitation of iron(III) hydroxides within the gel phase of the exchanger through passage of a solution containing both  $\text{NaCl}$  and  $\text{NaOH}$ , each at 5% w/v concentration; and third, rinsing and washing with a 50/50 ethanol-water solution followed by a mild thermal treatment ( $50\text{--}60^\circ\text{C}$ ) for 60 min.

Figure 2 depicts the major steps of the process. Additional information is available elsewhere (10). Hybrid anion exchangers were prepared through a slightly modified proprietary technique (16). Total iron contents of the hybrid exchangers were determined following 24-h digestion in two successive steps with 10% sulfuric acid.

Figure 3A shows gel-type HAIX particles; note that the spherical geometry is retained after processing. Figure 3B,C shows the scanning electron microphotographs (SEMs) of sliced parent anion exchanger bead and the hybrid material after HFO dispersion. Since gel-type exchangers do not possess any separate pore structure, no distinction can be made between these two particles even at high magnification. However, the hybrid particles develop a deep brown color due to the presence of HFO.

Fixed-bed column runs were carried out using glass columns (11 mm in diameter), constant-flow stainless steel pumps, and an ISCO fraction collector. The ratio of column diameter to exchanger bead diameter was approximately 20:1; earlier work on chromate and phosphate removals with similar setups showed no premature leakage due to wall effects under identical conditions (17, 18). The superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were recorded for each column run. For  $\text{As(III)}$  column runs, nitrogen gas was continuously sparged to guarantee that no  $\text{As(III)}$  was oxidized to  $\text{As(V)}$ . Independent analyses of feed samples at various stages of the column run confirmed the same.

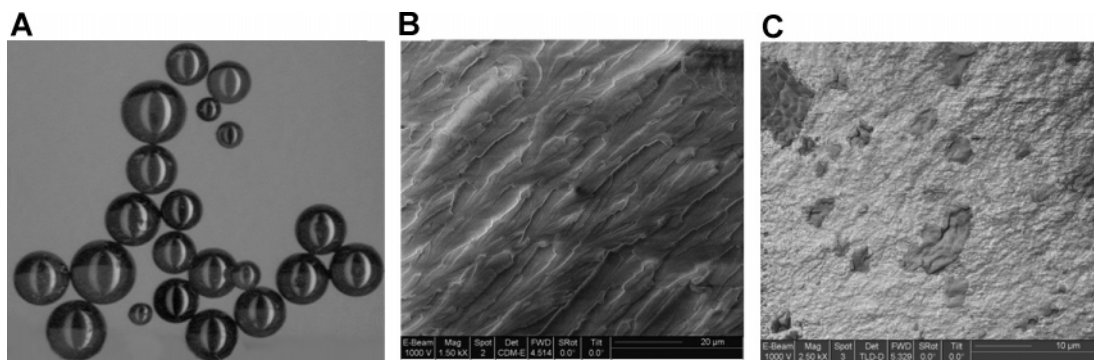


FIGURE 3. (A) Photographs of HAIX-G beads (20 $\times$ ), scanning electron microphotograph (SEM) of a sliced (B) parent anion exchanger-gel bead (20,000 $\times$ ), and (C) HAIX-G bead (20,000 $\times$ ).

TABLE 3. Ion Exchanger Supported HFO Particles

designation	type of ion exchanger	pore structure	functional group	matrix	source	Fe loading (mg of Fe/g)
HCIX-G	cation	gel	sulfonate (SO <sub>3</sub> <sup>-</sup> )	styrene-divinylbenzene	Purolite C-100, Philadelphia	70
HAIX-G	anion	gel	quaternary ammonium (R <sub>4</sub> N) <sup>+</sup>	styrene-divinylbenzene	Purolite A-400, Philadelphia	60

Exhausted HAIX beads following lengthy column runs were regenerated using 2% NaOH and 3% NaCl solution. Following regeneration, the bed was rinsed with carbon dioxide sparged water for about 10–15 bed vol.

**Chemical Analyses.** Chloride and sulfate were analyzed using a Dionex ion chromatograph (model DX-120 IC). Bicarbonate or inorganic carbon was determined using a Shimadzu carbon analyzer (model 5050A). Particle size analysis of the HIX beads was carried out using a Beckman/Coulter LS 100Q particle counter with a binocular optical system.

Total dissolved arsenic analyses of samples were carried out using a Perkin-Elmer atomic absorption spectrophotometer (AAS) with graphite furnace accessories (model SIMAA 6000) and an electrodeless discharge lamp (EDL). Filtration of samples through 0.4- $\mu$ m filters and subsequent analyses confirmed that arsenic during fixed-bed column run was present only in the dissolved state.

For analyses of As(V) and As(III), they were first separated at pH near 4.0 using a strong-base anion exchange resin in accordance with the technique developed by Ficklin (19) and Clifford et al. (20). Total arsenic was determined from the original sample, As(III) was determined from the sample collected at the exit of the anion exchange column, and As(V) was determined by the difference. The technique was validated by using samples of known As(III) and As(V) concentrations.

## Experimental Results

**Hybrid Ion Exchangers: Cation versus Anion.** Two separate column runs were carried out with similar influent solutions and under identical hydrodynamic conditions. In both cases, As(V) or arsenate was a trace species as compared to other competing electrolytes (namely, sulfate, chloride, and bicarbonate anions). Gel-type hybrid cation exchanger (HCIX-G) and gel-type hybrid anion exchanger (HAIX-G) were the sorbents used for the fixed-bed column runs. Their general characteristics are summarized in Table 3.

Figure 4 shows comparison of As(V) effluent histories between the two column runs; the marked difference in the performance of the two sorbents is quite apparent. Note that despite greater HFO content, HCIX-G was essentially unable to remove As(V), which broke through almost immediately after the start of the column run. On the contrary, HAIX-G

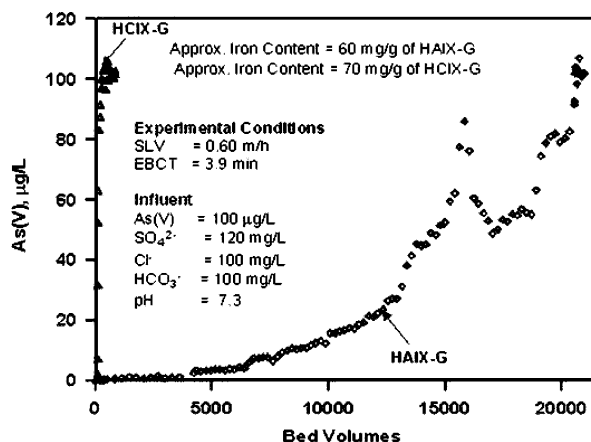


FIGURE 4. Comparison of As(V) effluent histories between HCIX and HAIX for two separate column runs under otherwise identical conditions.

with HFO nanoparticles dispersed within an anion exchanger showed excellent arsenic removal capacity. Only 10% of arsenic breakthrough occurred after nearly 10 000 bed vol.

It is worth noting that after 16 000 bed vol, As(V) concentration in the effluent first dropped rapidly and then rose again. The column run was deliberately interrupted for 48 h slightly after 16 000 bed vol of influent were fed. The sharp decrease in arsenic concentration in the effluent occurred immediately after the re-start of the column run. Such a significant drop in arsenic concentration after the interruption suggests that the sorption of arsenic is controlled by intraparticle diffusion within the hybrid particle (17, 18). However, any elaborate discussion on sorption kinetics is avoided in this paper.

**Parent Anion Exchanger versus HAIX.** At near-neutral pH, arsenate or As(V) exists in the aqueous phase as a mono- or divalent anion. Previous studies and field trials used macroporous anion exchangers for removal of As(V) (21). However, arsenic removal capacity is greatly reduced in the presence of competing anions, especially by divalent sulfate ions. Figure 5 shows As(V) effluent histories for two separate column runs using two different sorbent materials, namely, a commercially available anion exchanger (IRA-900, Rohm and Haas Co., Philadelphia, PA) and the hybrid anion

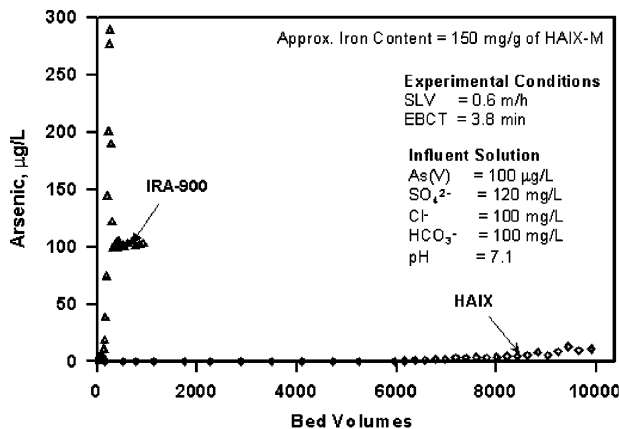


FIGURE 5. Comparison of As(V) effluent histories between a strong-base anion exchanger (IRA-900) and HAIX under identical conditions.

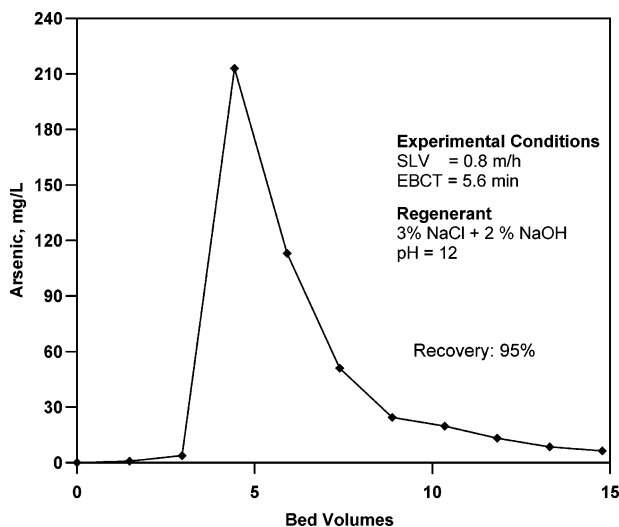


FIGURE 6. Dissolved arsenic concentration profile during desorption of HAIX using 2% NaOH and 3% NaCl as the regenerant.

exchanger (HAIX-M) after dispersing HFO within the anion exchanger. It can be readily inferred that the arsenic removal capacity of the parent anion exchanger is greatly enhanced after the dispersion of the HFO nanoparticles.

Note that for the IRA-900 column run, arsenic concentration in the treated water exceeded its influent concentration after breakthrough. This resulted from the chromatographic elution effect caused by higher sulfate selectivity for IRA-900 over arsenate.

**Efficiency of Regeneration and Reusability.** Following several trials, a mixture of brine and sodium hydroxide was found to be an efficient regenerant for HAIX sorbed with arsenate. Figure 6 shows the concentration profile of arsenic during desorption with 2% NaOH and 3% NaCl. Note that 95% arsenic recovery is achieved in 15 bed vol.

It is recognized that any significant loss of HFO nanoparticles from the hybrid ion exchanger during lengthy column runs would adversely affect the reusability of the material. Figure 7 shows total iron concentration at the exit of the fixed-bed column for nearly 15 000 bed vol. Although there is no specific trend, total iron concentration in the treated water never exceeded 5 µg/L.

With aging and changes in environmental condition, amorphous HFO nanoparticles may get transformed into crystalline forms, namely, goethite, hematite, or magnetite. However, X-ray diffractograms (XRDs) for sliced HAIX beads after prolonged usage did not show any noticeable increase in the crystalline forms of iron oxide particles.

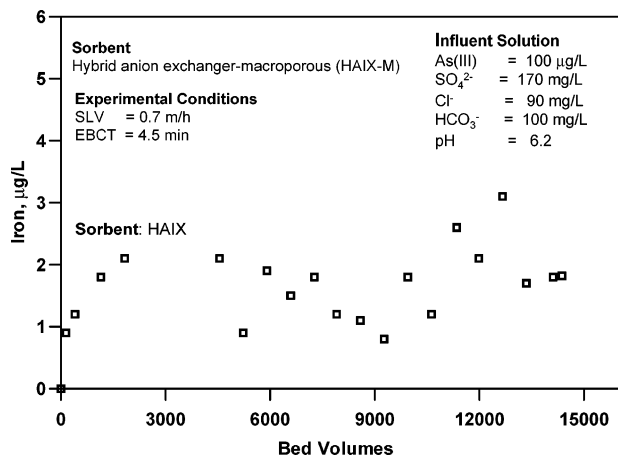


FIGURE 7. Dissolved iron leakage during a lengthy column run in the absence of oxygen in the feed.

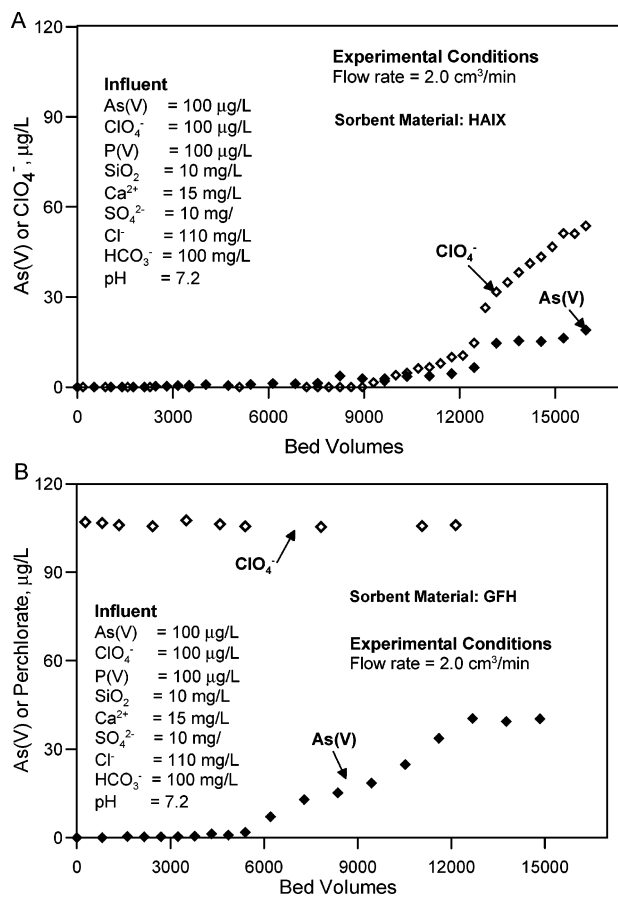
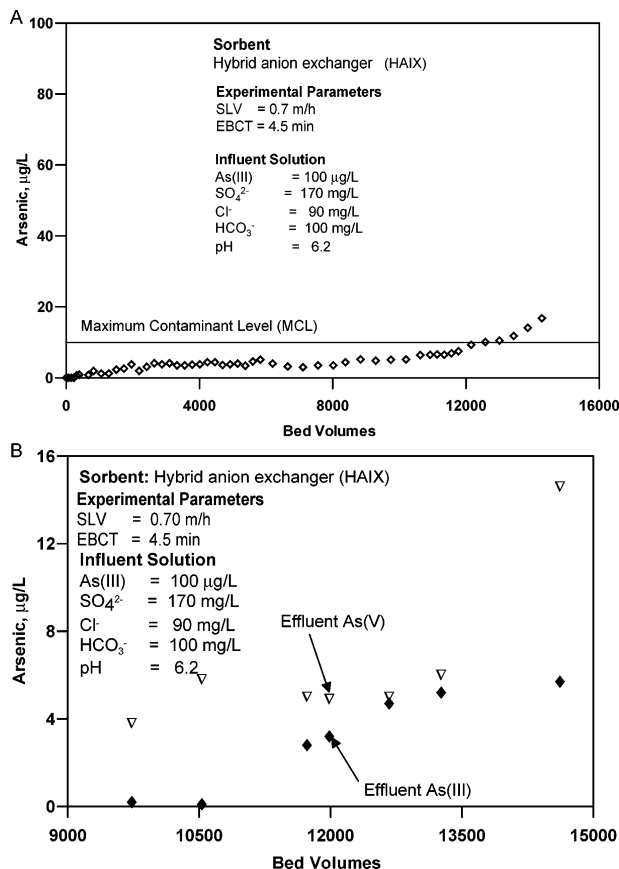


FIGURE 8. (A) Effluent histories of arsenic and perchlorate during fixed-bed column run with HAIX. (B) Effluent histories of arsenic and perchlorate during a fixed-bed column run using granulated ferric hydroxide (GFH) sorbent.

**Simultaneous Removal of Perchlorate and Arsenate.** Both perchlorate ( $\text{ClO}_4^-$ ) and arsenate ( $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ) exist as anions in the aqueous phase; however, their chemical characteristics are very different. While perchlorate is a hydrophobic anion with poor ligand characteristic, arsenate is a fairly strong ligand. Several groundwater sources in the western states of the United States are contaminated with trace concentrations of both arsenic and perchlorate. Figure 8A shows the effluent histories of both perchlorate and arsenic for an HAIX column run using simulated groundwater. For nearly 10 000 bed vol, both arsenic and perchlorate were completely removed. The parent strong-base anion exchange



**FIGURE 9. (A) Arsenic effluent history during a fixed-bed column run with an influent containing only As(III) or arsenite. (B) As(III) and As(V) concentrations in the treated water for the column run in Figure 10A beyond 9000 bed vol.**

resin was unable to remove arsenic as already demonstrated in Figure 5. For comparison, simultaneous removal of perchlorate and arsenic was also examined independently for one commercially available iron oxide based sorbent media (namely, granular ferric hydroxide or GFH) purchased from US Filter Co. Figure 8B presents effluent concentration profiles of perchlorate and arsenic through a GFH column. Note that GFH was unable to remove perchlorate. However, arsenic removal was quite satisfactory with GFH.

**As(III) in the Feed.** Figure 9A provides As(III) effluent history for an HAIX column run with 100 µg/L As(III) in the feed; the complete influent composition is also provided in the same figure. Nitrogen was continuously sparged in the influent storage tank to eliminate any possible As(III) oxidation to As(V). At near-neutral pH, As(III) is non-ionized (i.e., it exists as HAsO<sub>2</sub>). Previous studies (22, 23) demonstrated that, during fixed-bed column runs with plug flow configuration, HFO particles can partially oxidize As(III) to As(V) at neutral pH. Figure 9B shows both As(V) and As(III) concentrations from 9000 bed vol onward for the same column run after arsenic has broken through. The results confirm that As(V) is partially produced within the column. Anion exchanger as a support material for HFO nanoparticles is thus beneficial because it enhances permeation of arsenate into the polymer phase as demonstrated earlier.

## Discussion

Donnan membrane processes, also referred to as Donnan dialysis, have been successfully applied in many chemical processes including selective separation of toxic ions (24–26). Recently, alum and Fe(III) coagulant have been recovered in high purity from water treatment plant residuals using

DuPont's Nafion cation exchange membrane with no signs of noticeable membrane fouling (27–29). However, according to the information in the open literature, preparation and development of a highly selective hybrid sorbent based on the Donnan membrane principle has not been reported to date. Results of Figures 4 and 5 clearly demonstrate how the Donnan effect resulting from the polymer support materials can greatly influence the sorption behaviors of HFO particles and enhance the arsenic removal performance.

To elucidate the lack of arsenic removal capacity of the hybrid cation exchanger or HCIX, let us consider a typical cation exchanger bead of 0.5 mm or 500 µm diameter ( $d_p$ ).

Considering a bead density ( $\rho_b$ ) of 1100 kg/m<sup>3</sup>, the mass ( $m$ ) of a single bead is

$$m = \frac{\pi d_p^3}{6} \rho_b = 7.2 \times 10^{-5} \text{ g}$$

The estimated capacity of C-100 cation-exchange resin is  $q = 4.0$  equiv/kg. Then, the number of fixed negative charges ( $N_e$ ) in a single bead is

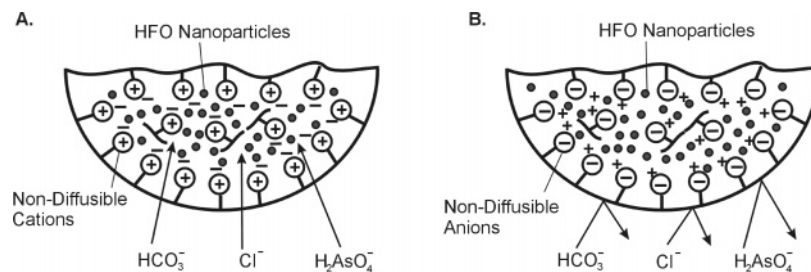
$$N_e = \frac{qm}{1000} \times 6.02 \times 10^{23} = 1.73 \times 10^{17} \text{ charges}$$

where  $6.02 \times 10^{23}$  is the Avogadro's number.

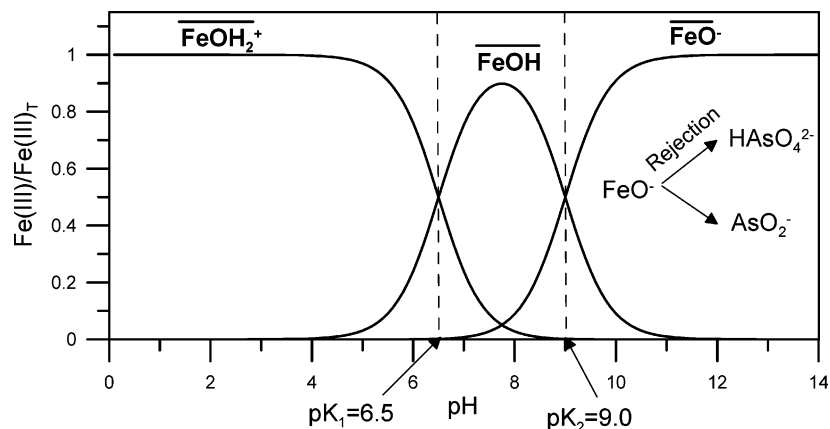
Thus, inside a tiny 500 µm cation exchange bead, there remain  $1.73 \times 10^{17}$  number of covalently attached sulfonic acid groups with negative charges that cannot permeate from the exchanger phase to the aqueous phase. Comparing this situation with case II scenario of Figure 1, it may be readily inferred that monovalent and divalent arsenate will be completely rejected from permeating into the polymer phase due to the Donnan exclusion effect. HFO nanoparticles dispersed inside the cation exchanger are thus inaccessible to arsenate. That is why HCIX did not show any arsenic removal capacity for the column run presented in Figure 4. It is worth mentioning that activated carbon, zeolite, alginate, etc. also contain significant concentration of negatively charged functional groups, namely, carboxylate and aluminosilicate. These substrates may be easily dispersed with HFO nanoparticles, but arsenic removal capacity will not be fully attained due to Donnan exclusion effect. In a previous study, alginate loaded with HFO showed poor arsenic removal capacity during fixed-bed column runs (13).

On the other hand, polymeric anion exchanger is an excellent substrate because it allows enhanced permeation of anions within the polymer phase due to its high concentrations of fixed positive charges. Figure 10 provides a schematic illustrating the difference between cation and anion exchanger as substrate materials. Note that both cation and anion exchanger beads are electrically neutral. Electrostatic repulsion/attraction is not the underlying reason for the difference in permeation of arsenate into the polymer phase. The presence of high concentration of non-diffusing fixed charges ( $R^+$  or  $R^-$ ) in the polymer phase acts as a highly permeable or impermeable interface for arsenate, thus influencing its sorption onto HFO particles embedded in the polymer phase.

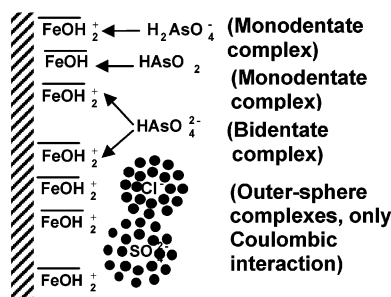
HAIX has two distinctly different binding sites within the polymer phase: first, covalently attached quaternary ammonium functional groups with high affinity toward hydrophobic anions such as perchlorate and second, surface hydroxyl groups of HFO with high affinity toward ligands such as arsenites and arsenates. These two classes of sorption sites are also independent of each other. During the column run in Figure 8, quaternary ammonium groups were responsible for selective sorption of perchlorate ions while HFO surface groups led to the binding of arsenate through formation of inner-sphere complexes. Also, the HFO nano-



**FIGURE 10.** Schematic illustrating (A) enhanced permeation of anions into the hybrid sorbent in the presence of non-diffusible cations (anion exchanger) and (B) exclusion of anions from the hybrid sorbent in the presence of non-diffusible anions (cation exchanger).

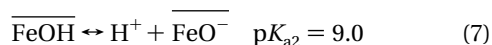
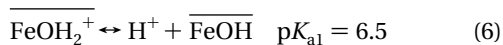


$4.0 \leq \text{pH} \leq 9.0$  (Binding of target solutes)



**FIGURE 11.** Distribution of surface functional groups of HFO particles (symbols with overbars) with pH and predominant sorption/desorption mechanisms for arsenites and arsenates at different pH values.

particles are considered to be a weak diprotic acid with the following two dissociation constants (30):



where the overbar represents the solid phase.

Figure 11 illustrates the distribution of the three surface functional groups of HFO (e.g.,  $\text{FeOH}_2^+$ ,  $\text{FeOH}$ , and  $\text{FeO}^-$ ) with respect to pH. Note that in the pH range of 4.0–9.0, ligands (i.e., Lewis bases such as arsenates and arsenites) get selectively sorbed through the formation of inner-sphere complexes (31). Other ions present in the solution (e.g., chloride, sulfate, bicarbonate) form only outer-sphere complexes through electrostatic interactions and yield poor sorption affinities. At pH greater than 11.0, negatively charged

$\text{FeO}^-$  is the predominant surface functional group, thus rejecting all anions including arsenites and arsenates. That is why arsenic desorption with caustic soda and brine solution is very efficient as demonstrated in the results of Figure 6. Selective arsenic binding through Lewis acid–base interac-

tions onto other transition metals (namely, ion exchanger supported Cu(II)) is also possible and has been reported earlier (32). Last but not least, polymer or zeolite supported metal oxide/metal nanoparticles are finding wider applications in catalysis, bioseparation, drug delivery, and environmental remediation (33–35). Donnan membrane effect caused by the host materials may play a significant role in determining the effectiveness of the hybrid materials for intended applications.

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