

# Selective removal of arsenate from drinking water using a polymeric ligand exchanger

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## Abstract

The new maximum contaminant level (MCL) of 10 µg/L for arsenic in the US drinking water will take effect on January 22, 2006. The compliance cost is estimated to be ~\$ 600 million per year using current treatment technologies. This research aims to develop an innovative ion exchange process that may help water utilities comply with the new MCL in a more cost-effective manner. A polymeric ligand exchanger (PLE) was prepared by loading Cu<sup>2+</sup> to a commercially available chelating ion exchange resin. Results from batch and column experiments indicated that the PLE offered unusually high selectivity for arsenate over other ubiquitous anions such as sulfate, bicarbonate and chloride. The average binary arsenate/sulfate separation factor for the PLE was determined to be 12, which were over two orders of magnitude greater than that (0.1–0.2) for commercial strong-base anion (SBA) exchangers. Because of the enhanced arsenate selectivity, the PLE was able to treat ~10 times more bed volumes (BVs) of water than commonly used SBA resins. The PLE can operate optimally in the neutral pH range (6.0–8.0). The exhausted PLE can be regenerated highly efficiently. More than 95% arsenate capacity can be recovered using ~22 BVs of 4% (w/w) NaCl at pH 9.1, and the regenerated PLE can be reused without any capacity drop. Upon treatment using FeCl<sub>3</sub>, the spent brine was recovered and reused for regeneration, which may cut down the regenerant need and reduces the volume of process waste residuals. The PLE can be used as a highly selective and reusable sorbent for removal of arsenate from drinking water.

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## 1. Introduction

The presence of arsenic (As) in the US waters is widespread. It was estimated that 14% of groundwater sources exceeded 5 µg/L in various regions of the US (Focazio et al., 1999). The US EPA estimates that approximately 2% of the US population receives

drinking water containing >10 µg/L As (Holm, 2002), and the Natural Resources Defense Council estimates that ~56 million people in the US drinking water with As at unsafe levels.

As has been associated with various cancerous and non-cancerous health effects. According to a recent report by the National Academy of Science (NAS) and National Research Council (NRC), even at 3 µg/L of As, the risk of bladder and lung cancer is between 4 and 7 deaths per 10,000 people. At 10 µg/L, the risk increases to between 12 and 23 deaths per 10,000 people (NRC,

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2001). In addition, As can cause high blood pressure and diabetes (NRC, 2001).

Triggered by the risk concern, the US EPA announced its ruling in October 2001 to lower the maximum contaminant level (MCL) from current 50 µg/L (established in 1942) to 10 µg/L with a compliance date of January 22, 2006. This ruling poses tremendous impacts on water utilities. Approximately 4100 water utilities serving ~13 million people will be affected by the law (EPA, 2001b). The compliance cost has been estimated to be ~\$600 million per year using current treatment technologies (Frey et al., 2000). For instance, almost half of the wells in Albuquerque, NM, will require additional treatment to meet the new standard (German, 2001). In the State of Maine, 12% of community water systems will need additional treatment (PR Newswire, 2001).

In general, three types of treatment technologies are commonly cited for As removal, including modified conventional treatment (MCT) (Chwirka et al., 2004; Ghurye et al., 2004; Clifford et al., 2003; Fan et al., 2003; Brandhuber and Amy, 1998; McNeill and Edwards, 1997; Hering and Elimelech, 1996; Scott et al., 1995), sorption using activated alumina (AA) (Wang et al., 2002), standard ion exchange (IX) resins (Clifford, 1999), granular ferric hydroxide (GFH) (Sperlich et al., 2005; Badruzzaman et al., 2004; Driehaus et al., 1998), or granular ferric oxide (GFO) (Westerhoff et al., 2005; Manna et al., 2003), or iron-coated sand (Benjamin et al., 1996), and reverse osmosis (RO) (EPA, 2002). The treatment cost increases in the order of: MCT ≪ AA or IX < RO (Chen et al., 1999). MCT employs various coagulants to enhance As removal in a conventional water treatment process. However, it is extremely difficult to meet the new MCL using MCT alone. Therefore, additional treatment such as microfiltration is often required (Ghurye et al., 2004). Other processes such as IX using strong-base anion (SBA) resins or AA adsorption or RO are less cost-competitive due to lack of selectivity for As, frequent regeneration requirements and production of large volumes of As-laden process residuals (EPA, 2000b). GFH and GFO are relatively cheaper sorbents, and they are often used as 'disposable' sorbents (i.e., no regeneration and reuse are attempted). However, the process may result in large volumes of As-laden sorbents, which will require additional handling and disposal.

To meet the urgent technology needs, a number of other technologies were also explored, including electrocoagulation (Kumar et al., 2004), polymer inclusion membrane process (Ballinas et al., 2004), mesoporous alumina sorption (Kim et al., 2004), activated mud (Genc-Fuhrman et al., 2004) and ferrihydrite crystallization process (Richmond et al., 2004). However, these new techniques are in the developmental stage. Consequently, innovative cost-effective treatment processes are urgently needed (Han et al., 2003).

IX is currently an EPA-identified best available technology (BAT) for removal of As(V) (EPA, 2000a). However, current commercial SBA resins suffer from poor selectivity for As. Due to the strong competition from some ubiquitous anions such as sulfate, the As capacity of SBA resins is prohibitively retarded (Clifford, 1999). For example, the binary arsenate/sulfate separation factor for a typical SBA resin was reported to be ~0.5 (a separation factor of less than one indicates the resin's preference toward the competing ions) (Clifford, 1999). As a result, the As breakthrough occurs before sulfate, and chromatographic peaking of As, i.e., effluent concentration exceeds influent concentration, is often observed (Kim et al., 2003).

Due to the lack of As-selectivity, current IX processes require frequent regeneration. As a result, large amounts of regenerant brine are needed, which in turn results in large volumes of As-laden process residuals (EPA, 2001a; EPA, 2002). The spent regenerant brine and the associated waste residuals contain high levels of As, and often fall into the category of hazardous waste that is subject to stringent disposal and management requirements under the Clean Water Act (CWA) and the Resource Conservation Recovery Act (RCRA).

The concept of ligand-exchange-based separation was first introduced by Helfferich (1962). Generally, a polymeric ligand exchanger (PLE) is composed of: (a) a cross-linked hosting resin that can firmly bind with a transition metal such as copper and iron, and (b) metal ions that are immobilized to the functional groups of the hosting resin. While sharing many common features with standard ion exchangers, a ligand exchanger employs transition metal ions as its terminal functional groups. As a result, ligand exchange involves concurrent Lewis acid–base (LAB) interactions (metal–ligand complexation) and electrostatic interactions between the fixed metal ions and target anionic ligands. While conventional anion exchangers' selectivity for various anions is governed by electrostatic interactions, the affinity of a PLE is predominated by both the ligand strength and ionic charge of the ligands.

In his pioneer work, Helfferich (1962) prepared some of the very first PLEs by loading a transition metal (Ni or Cu) onto commercial cation exchange resins. Because the charges of the loaded metal ions are neutralized by the negative charges of the resins' functional groups, the PLEs could only sorb some neutral ligands such as ammonia and diamine (Helfferich, 1962). Later, Chanda et al. (1988) prepared a new PLE for selective removal of As by loading ferric ions onto a weak base chelating resin (known as DOW 3N) with di(2-picolyl)amine groups. They observed that this PLE was able to treat ~140 bed volumes (BVs) of arsenate-laden water and the saturated PLE can be regenerated using 1M of NaOH. However, because of the weak Lewis acid characteristics of ferric ions, the amount of Fe<sup>3+</sup> loaded

was low. As a result, the PLE's capacity for arsenate was very limited. Moreover, the loaded iron was nearly completely stripped off the hosting resin during regeneration and reloading of  $\text{Fe}^{3+}$  was necessary after each cycle of operation. Realizing the critical drawbacks of  $\text{Fe}^{3+}$  ions, Ramana and SenGupta (1992) prepared a PLE by loading  $\text{Cu}^{2+}$  onto a weak base chelating resin (known as DOW 2N) with 2-picolyamine groups. Since  $\text{Cu}^{2+}$  is a much stronger Lewis acid than  $\text{Fe}^{3+}$ , which is in accord with the Irving and Williams order, a much greater metal-loading capacity was observed. The copper loaded DOW 2N showed orders of magnitude greater selectivity for arsenate and selenate in the presence of competing sulfate ions than commercial SBA resins.

To achieve selective removal of phosphate, Zhao and SenGupta (1998) developed and characterized a model PLE, referred to as DOW 3N-Cu, by loading  $\text{Cu}^{2+}$  ions onto the chelating resin DOW 3N resin. Compared to DOW 2N, DOW 3N contains one more (2-picoly)amine group per functional group. As a result, the copper capacity for DOW 3N nearly doubles that for DOW 2N (Henry et al., 2004). DOW 3N-Cu showed unusually high selectivity for phosphate in the presence of high concentrations of sulfate, chloride, nitrate and bicarbonate (Zhao and SenGupta, 1998). Fig. 1 depicts the functional group of such a PLE, where a chelating resin containing nitrogen as electron donor atoms is employed as the metal hosting polymer. Metal ions ( $\text{Cu}^{2+}$ ) are firmly immobilized on the polymer surface by covalently bonding with the N donor atoms. Since the nitrogen atoms are predominately in their free base form at  $\text{pH} > 3$  (Zhao, 1997), the positive charges of loaded  $\text{Cu}^{2+}$  ions remain available to interact with anions in the aqueous phase. Moreover, since only a fraction of the copper's six coordination bonding sites are consumed for binding copper onto the polymer surface, the immobilized  $\text{Cu}^{2+}$  ions remain capable of complexing with target ligands from the aqueous phase. Conse-

quently, the  $\text{Cu}^{2+}$ -loaded PLE can interact with strong anionic ligands such as arsenate in water through concurrent LAB interaction and electrostatic interactions, leading to enhanced selectivity for stronger ligands such as arsenate.

Building upon our prior work on selective phosphate removal and considering the analogous ionic and ligand characteristics between arsenate and phosphate, this present study aims to examine the effectiveness of using DOW 3N-Cu for selective removal of arsenate from drinking water. The specific objectives of this study are to (1) probe the equilibrium sorption capacity of DOW 3N-Cu for arsenate in the presence of high concentrations of competing sulfate; (2) test arsenate breakthrough behaviors in a multi-component system; (3) determine the effect of pH; (4) test the regenerability of the arsenate saturated PLE; and (5) examine the treatability and reusability of spent regenerant brine.

## 2. Materials and methods

### 2.1. Materials

A total of three sorbents were tested in this study, including the copper-loaded PLE (DOW 3N-Cu), and two commercial SBA resins (IRA 900 and IRA 958). DOW 3N-Cu was prepared by loading  $\text{Cu}^{2+}$  ions onto a commercial chelating IX resin (DOW 3N), purchased from Aldrich (Milwaukee, WI, USA). The copper loading procedures used by Zhao and SenGupta (1998) were slightly modified. In brief, DOW 3N was first conditioned through cyclic acid and base washing using 1N HCl and 1N NaOH, respectively. Upon rinsing using DI water, the resin was equilibrated with 0.1% (w/w) copper solution at pH 3.5–4.0 for 2 weeks. Analytical grade  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Aldrich, Milwaukee, WI, USA) was used for preparing the copper solution. The resin-to-solution ratio was approximately 1:200 (w/w). To enhance copper loading, the resin-solution mixture was intermittently heated at  $70^\circ\text{C}$  for  $\sim 4\text{h}$  every other day and then placed back at ambient temperature ( $\sim 21^\circ\text{C}$ ). (Note: Mild heating can cause resin swelling and enhance aging, thereby enhancing the copper loading kinetics and stability). To avoid oxidation of the resin matrix, nitrogen gas was blown in the solution during heating. Upon completion, the copper loaded resin was thoroughly rinsed using DI water and air dried for use.

For comparison, two commonly used conventional SBA resins, known as IRA 900 and IRA 958 were also tested in this study. Table 1 gives important properties of these sorbents. Before use, the resins were conditioned following the same acid-base-washing procedure as described above. All resins were prepared in the chloride form.

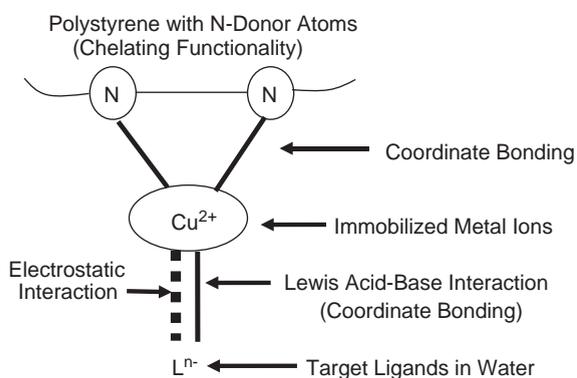
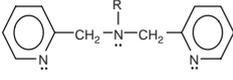
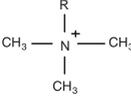
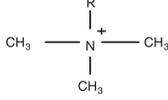
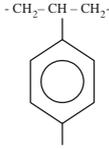
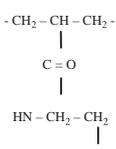


Fig. 1. A conceptualized illustration of the functional group of a PLE.

Table 1  
Important properties of the ion exchange resins used in this study

Sorbent	DOW 3N	IRA 900	IRA 958
Manufacturer	DOW Chemical, Midland, MI, USA	Rohm and Haas, Philadelphia, PA, USA	Rohm and Haas, Philadelphia, PA, USA
Functional group			
Matrix (R or R')	 Polystyrene, Macroporous	 Polystyrene, Macroporous	 Polyacrylic, Macroporous
Capacity (meq/g)	2.98 <sup>a</sup>	3.6 <sup>a</sup>	3.4 <sup>a</sup>
BET surface area (m <sup>2</sup> /g)	139 <sup>a</sup>	N/A	N/A

<sup>a</sup>From Henry et al. (2004).

The following chemicals (all in analytical grades) were purchased from Fisher Scientific (Pittsburgh, PA, USA): FeCl<sub>3</sub>, NaOH, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and NaCl. Reagent grade of sodium hydrogen arsenate (Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O) was purchased from (Aldrich, Milwaukee, WI, USA).

## 2.2. Equilibrium sorption tests

Batch isotherm tests were carried out for the three resins in 60 mL glass vials with Teflon-lined screw caps. The tests were initiated by adding known masses (0.004–0.15 g) of a resin to 50 mL of a solution containing an initial concentration of 10 mg/L as As and 100 mg/L sulfate. The mixture was then shaken on a rotating tumbler for 7 days, which were sufficient to reach equilibrium as confirmed through separate kinetic tests. The initial pH of the solution was ~7.5, and pH during equilibration was maintained in the range of 7.0–7.5 through intermittent adjusting using dilute NaOH or HCl until final equilibrium was reached. At equilibrium, water samples were taken from each vial and analyzed for As and sulfate remaining in water. As or sulfate uptake was then calculated based on the mass balance equation,

$$q_e = \frac{V(C_o - C_e)}{M}, \quad (1)$$

where  $q_e$  is the equilibrium mass uptake of As by a sorbent (mg/g),  $V$  is the solution volume (L),  $C_o$  and  $C_e$  are the initial and final concentration of As or sulfate in solution, respectively (mg/L), and  $M$  is the mass of a

sorbent added (g). All tests were carried out at room temperature (~21 °C).

## 2.3. Fixed-bed column tests

The breakthrough behaviors of arsenate as well as various competing anions were tested for DOW 3N–Cu and IRA 900 in a fixed-bed configuration. The experimental setup included a Plexiglass column (11 mm in diameter and 25 cm in length), an Accuflow Series II high-pressure liquid chromatography stainless steel pump, and an Eldex automatic fraction collector. Approximately 5 mL of a resin was used in each run. Simulated contaminated water was introduced in the resin bed in a down-flow mode. The major compositions in the influent water were as follows: for IRA 900, As = 75 µg/L, SO<sub>4</sub><sup>2-</sup> = 1.9 meq/L, Cl<sup>-</sup> = 2.4 meq/L, and pH = 8.3; for DOW 3N–Cu: As = 94 µg/L, SO<sub>4</sub><sup>2-</sup> = 1.0 meq/L, HCO<sub>3</sub><sup>-</sup> = 0.50 meq/L, Cl<sup>-</sup> = 1.3 meq/L, and pH = 8.6. A constant flowrate of 1.2 mL/min was maintained, which translates to an empty bed contact time (EBCT) of 4.1 min, and a superficial liquid velocity (SLV) of 3.0 m/h.

## 2.4. pH effect

The pH effect on equilibrium uptake of arsenate was tested for DOW 3N–Cu in a similar fashion to that in the isotherm tests. However, the final solution pH was adjusted to span from 2.8 to 11 (each vial had a different pH). Each testing vial contained 50 mL solution with an initial As of 8.3 mg/L and SO<sub>4</sub><sup>2-</sup> of 86 mg/L. The

sorption was initiated upon the addition of  $\sim 0.020$  g of air-dried DOW 3N–Cu to each vial.

### 2.5. Kinetic tests

Batch kinetic test was conducted to test the As sorption rate and determine the effective intraparticle diffusivity for DOW 3N–Cu. The experiment was initiated by adding 0.95 g of the sorbent into 2 L of a solution containing 0.92 mg/L As and 100 mg/L sulfate and at an initial pH of 8.0. The solution pH was adjusted intermittently by adding small amounts of dilute NaOH to keep the solution pH within 7.0–7.5, where pH effect on the PLE's uptake was minimal (see Section 3.3). During the experiment, the resin–solution mixture was intensively agitated on a shaker to eliminate the possible film diffusion limitation on the mass transfer process. At predetermined time intervals, water samples ( $\sim 2$  mL/each) were taken and analyzed for As. The As uptake at various times was then determined through mass balance calculations.

### 2.6. Resin regeneration, reuse of regenerated resin, and regenerant treatment and reuse

Regeneration of As loaded DOW 3N–Cu was carried out in the same fixed-bed column configuration and in the down-flow mode. In search for an optimal regenerant recipe, a 4% (w/w) NaCl solution at pH 4.1, 7.0, and 9.1 was tested in separate column runs. The operating hydrodynamic conditions were maintained identical for all cases, including an EBCT of 22 min and a SLV of 14 m/h.

Sorption capacity of DOW 3N–Cu that was subjected to up to eight saturation-regeneration cycles was compared to that of the virgin DOW 3N–Cu. The best regenerant (i.e., 4% NaCl at pH = 9.1) was employed to regenerate the resin repeatedly. Equilibrium sorption of As was in a similar manner as described in Section 2.2, with the following conditions: initial As =  $\sim 10$  mg/L, initial  $\text{SO}_4^{2-}$  = 100 mg/L, resin weight = 0.01 g, solution volume = 50 mL, final pH = 7.0–7.5.

To study the treatability of spent regenerant brine,  $\sim 2$  L of a simulated spent brine solution was prepared based on the analysis of the spent brine collected from prior fixed-bed regeneration tests. The primary compositions of the spent brine were: As = 300 mg/L,  $\text{SO}_4^{2-}$  = 600 mg/L,  $\text{HCO}_3^-$  = 305 mg/L, and NaCl = 4% (w/w) (or 24 g/L as  $\text{Cl}^-$ ). The solution was dispensed to a number of Nalgene HPDE sample bottles at 100 mL/bottle. Ferric chloride was then added to the bottles at Fe:As molar ratios of 5, 10, 15, 20, 25, 30, and 40, respectively. The mixture was then mixed on a gang mixer for  $\sim 2$  h, with pH being adjusted intermittently to a desired value, and then allowed the precipitates to settle for  $\sim 1$  h. When the ferric precipitates were fully

settled, approximately 5 mL of supernatant was sampled from each bottle, centrifuged and analyzed for As remaining in water. To study the pH effect on As removal, the experiments were carried out in three separate sets with a final pH of 6.0, 7.0, and 9.0, respectively. The solution pH was maintained by adding known quantities of NaOH in the solution.

To test the reusability of the brine, the treated brine supernatant was separated from the precipitates, adjusted to pH  $\sim 10$ , and then tested for regenerating an As-laden DOW 3N–Cu bed under the same conditions as in the above regeneration test using the fresh brine.

### 2.7. Chemical analyses

As and copper were analyzed using a Perkin Elmer Atomic Adsorption Spectrophotometer, which has a detection limit of 3  $\mu\text{g/L}$  as As. Solution pH was measured using an Orion pH meter (model 520A). Sulfate and chloride ions were analyzed using a Dionex Ion Chromatograph (Model DX-120). Bicarbonate was analyzed with a UV- Persulfate TOC Analyzer (Phoenix 8000).

## 3. Results and discussion

### 3.1. Equilibrium isotherms and nature of arsenate sorption

As mentioned before, one of the critical limitations for current SBA resins is its low selectivity and sorption capacity for arsenate especially in the presence of some omnipresent anions such as sulfate. To probe the PLE's sorption capacity, arsenate sorption isotherms were constructed for DOW 3N–Cu in the presence of 100 mg/L sulfate as competing anions. For comparison, As isotherms were also measured for the two commercial SBA resins (IRA 900 and IRA 958) under otherwise identical conditions. The equilibrium pH was maintained at 7.0–7.5 in all cases to minimize the pH effect on the uptake (see Section 3.3). Fig. 2 shows the observed (symbols) and simulated (lines) isotherms for the three sorbents. The classical Langmuir model was employed for fitting the experimental data (Zhao et al., 1995),

$$q_e = \frac{bQC_e}{1 + bC_e}, \quad (2)$$

where  $q_e$  is the equilibrium As uptake (mg/g),  $C_e$  is the equilibrium concentration of As in water (mg/L), and  $b$  and  $Q$  are the Langmuir affinity and capacity coefficients, respectively. The non-linear fitting was performed using the SigmaPlot8.0. Table 2 lists the model-fitted  $b$  and  $Q$  values.

The binary separation factor has been commonly used to compare the relative affinity of a sorbent for various

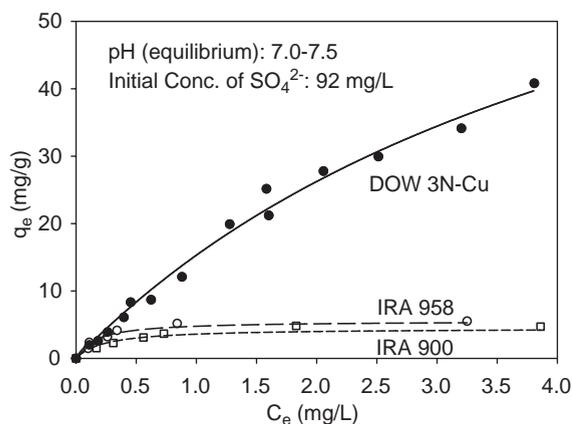


Fig. 2. Arsenate sorption isotherms for DOW 3N-Cu and two conventional SBA resins (IRA 900 and IRA 958) in the presence of competing sulfate ions. (Symbols: Observed data; lines: Langmuir model fits).

Table 2

The values of model-fitted Langmuir parameters ( $Q$ ,  $b$ ) and the mean arsenate/sulfate separation factor ( $\alpha_{As/S}$ )

Resin	$Q$ (Standard error) (mg/g)	$b$ (Standard error) (L/mg)	$\alpha_{As/S}$ (Standard deviation)
DOW 3N-Cu	92 (8.2)	0.20 (0.028)	12 (0.73)
IRA 958	5.5 (0.36)	6.1 (1.5)	0.10 (0.026)
IRA 900	4.5 (0.51)	4.1 (2.1)	0.20 (0.057)

competing sorbates. In a binary system, the As/sulfate separation factor ( $\alpha_{As/S}$ ) is defined as

$$\alpha_{As/S} = \frac{q_{As} C_S}{C_{As} q_S}, \quad (3)$$

where  $q$  and  $C$  represent the concentration of As in the polymer phase and in the aqueous phase, respectively; As and S in the subscripts denote As and sulfate, respectively. In general, a value of  $\alpha_{As/S}$  of greater than unity indicates the resin's preference toward As over sulfate, whereas the opposite is true if  $\alpha_{As/S}$  is less than unity. The greater the  $\alpha_{As/S}$  value, the more selective is the resin for arsenate. Based on the experimental equilibrium sorption data in Fig. 2, the average separation factor was calculated for the three resins and is given in Table 2. The mean  $\alpha_{As/S}$  value of DOW 3N-Cu is  $\sim 12$ , which clearly indicates the resin's preference toward arsenate over sulfate. In contrast, the  $\alpha_{As/S}$  value for the commercial resins was 0.1 for IRA 900, and 0.2 for IRA 958, which is consistent with the literature that these resins are more favorable for sulfate.

The substantially improved As selectivity of DOW 3N-Cu is attributable to the concurrent LAB interaction and electrostatic interactions between arsenate and the immobilized  $\text{Cu}^{2+}$  ions at the sorbent-sorbate interface. Under the experimental conditions, mono-hydrogen arsenate ( $\text{HAsO}_4^{2-}$ ) is considered the predominant arsenate species (see Section 3.3 for details).  $\text{HAsO}_4^{2-}$  is a divalently charged, bidentate ligand, and a strong Lewis base (donor of electron lone pairs). The competing sulfate is also a divalently charged ligand, but it is a much weaker Lewis base. Consequently, interactions between arsenate and the immobilized  $\text{Cu}^{2+}$  ions involve both LAB interaction (or inner-sphere complexation) and ion pairing (or electrostatic interactions), while interactions between sulfate and the  $\text{Cu}^{2+}$  ions is predominantly ion pairing. It is noteworthy that LAB interaction also enhances the electrostatic interactions between arsenate and the loaded  $\text{Cu}^{2+}$  ions. This is because the inner-sphere complexation occurs over a much shorter distance than outer-sphere complexation, and the electrostatic interactions within the much shortened distance are much stronger in accord with the Coulomb's law. Consequently, DOW 3N-Cu offered much greater affinity for arsenate over sulfate. For the commercial SBA resins, the quaternary amine functionalities ( $\text{RN}^+(\text{CH}_3)_3$ ) take up anions predominately through electrostatic interactions, i.e., the ligand strength of an anion does not play a role in sorption affinity. Therefore, SBA resins are not selective for arsenate.

The underlying mechanism for the enhanced arsenate sorption by DOW 3N-Cu can also be revealed by inspecting the fundamental thermodynamic driving forces, i.e., the overall standard free energy change ( $\Delta G_o^\circ$ ). For arsenate sorption by DOW 3N-Cu,  $\Delta G_o^\circ$  is composed of two synergistic terms as shown in Eq. (4):

$$\Delta G_o^\circ = \Delta G_{\text{EL}}^\circ + \Delta G_{\text{LAB}}^\circ, \quad (4)$$

where  $\Delta G_{\text{EL}}^\circ$  is due to electrostatic interactions and  $\Delta G_{\text{LAB}}^\circ$  is to the LAB interaction (i.e., metal-ligand complexation). Compared to arsenate, other anions such as sulfate, nitrate and chloride are much weaker ligands, namely, only  $\Delta G_{\text{EL}}^\circ$  in Eq. (4) is operative, thus the resultant driving force ( $\Delta G_o^\circ$ ) for these anions is much smaller than that for arsenate. Commercial SBA resins interact with anions through only electrostatic interactions (i.e.,  $\Delta G_{\text{LAB}}^\circ \approx 0$ ). Therefore, DOW 3N-Cu is able to take advantage of the strong ligand characteristics of arsenate over other competing anions and to achieve highly selective removal of arsenate.

### 3.2. Breakthrough behaviors

Figs. 3 and 4 show the breakthrough histories of arsenate and other competing anions during the fixed-bed column experiments using IRA 900 and DOW

3N–Cu, respectively. Fig. 3 shows that for IRA 900, the sulfate breakthrough occurred ~100 BVs) later than the arsenate breakthrough, confirming the resin’s greater affinity for sulfate over arsenate. Fig. 3 also reveals a sharp chromatographic peaking of the arsenate breakthrough curve, which again indicates that this commercial SAB resin favors sulfate much more than arsenate. Due to the strong competition from sulfate, IRA 900 can treat only ~600 BVs of contaminated water per operation cycle (a cycle = saturation run + regeneration run). The breakthrough sequence of the anions reveals the following selectivity order for IRA 900:



Field data from Albuquerque, NM, USA, showed that As breakthrough took place typically within ~450 BVs using SBA commercial resins (Clifford, 1999).

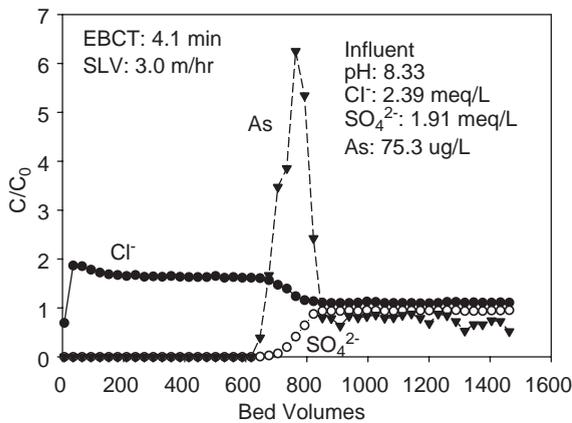


Fig. 3. Breakthrough histories of arsenate and competing anions in a multi-component system using a standard SBA resin, IRA 900.

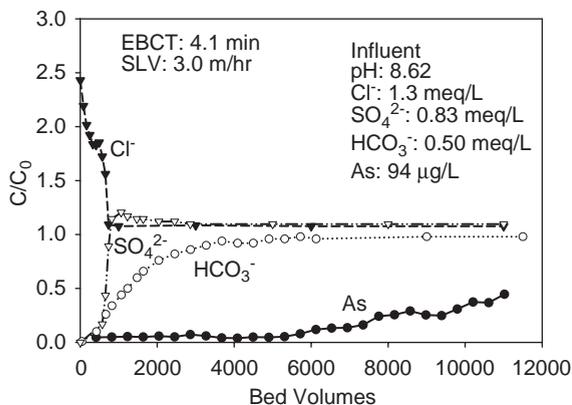
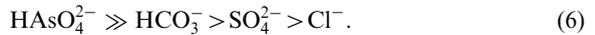


Fig. 4. Breakthrough histories of arsenate and competing anions in a multi-component system using a polymeric ligand exchanger, DOW 3N–Cu.

In contrast, a completely different breakthrough behavior was observed when DOW 3N–Cu was used. Fig. 4 shows that all three competing anions broke through before 500 BVs. Based on the new MCL value of 10 µg/L for As, arsenate breakthrough did not occur until after 6000 BVs, i.e., the PLE can treat over 10 times more water than IRA 900 in each run. A minor chromatographic peaking of sulfate was observed. The breakthrough sequence indicates the following selectivity sequence:



It is noteworthy that the monovalent bicarbonate displayed slightly greater affinity over the divalent sulfate, which is not surprising given that bicarbonate is a stronger ligand than sulfate.

### 3.3. Effect of pH

As in any ion exchange process, the PLE’s selectivity for various competing ligands can be strongly impacted by solution pH. Solution pH can affect the PLE’s As uptake in two different aspects. First, solution pH governs the speciation of arsenate, resulting in arsenate species ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ ) of different ionic charges and ligand strength. Second, the hydroxyl anions become aggressively formidable competitors for the ligand exchange sites as solution pH goes up.

Fig. 5 shows the observed arsenate uptake data as a function of the equilibrium solution pH. Note that sulfate at an initial concentration of 86 mg/L was present for all points tested. Also superimposed in Fig. 5 is the speciation curve of the  $\text{HAsO}_4^{2-}$  species as a function of solution pH calculated based on the reported  $\text{pK}_a$  values. Fig. 5 indicates that the optimal arsenate uptake occurs in the pH range of ~6.0–~8.0, with the peak uptake being at pH~7.0. At pH<4.0 or pH>11, there

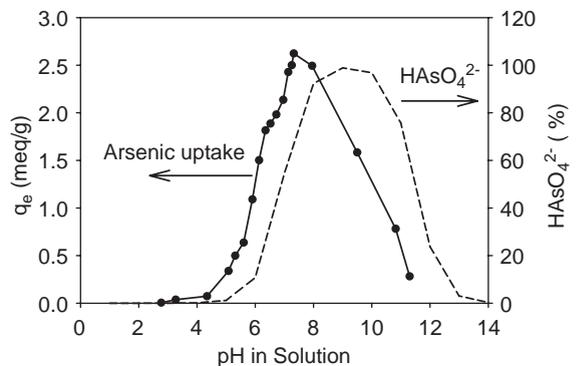


Fig. 5. Arsenic uptake by DOW 3N–Cu as a function of solution pH. The dashed line shows calculated speciation curve of  $\text{HAsO}_4^{2-}$ .

was virtually no uptake of arsenate observed. It is also interesting that As uptake started increasing at pH~4.0 almost in proportion to the increasing formation of the bidentate hydrogen arsenate species ( $\text{HAsO}_4^{2-}$ ). However, the As uptake drops sharply as pH exceeds ~8.0.

The acid dissociation constants ( $\text{p}K_a$ ) for arsenate are:  $\text{p}K_{a1} = 2.2$ ,  $\text{p}K_{a2} = 6.9$ , and  $\text{p}K_{a3} = 12$  (Dean, 1979). Based on both ligand strength and ionic charge, the adsorbability of various arsenate species follows the sequence of  $\text{H}_3\text{AsO}_4 < \text{H}_2\text{AsO}_4^- < \text{HAsO}_4^{2-} < \text{AsO}_4^{3-}$ . At pH < 4.0, the much less adsorbable  $\text{H}_2\text{AsO}_4^-$  or  $\text{H}_3\text{AsO}_4$  is the predominant arsenate species, which cannot stand the competition of divalently charged sulfate anions. As a result, no As uptake is likely in the low pH range as observed in Fig. 5. The fact that the As uptake appears to be in proportion to the formation of  $\text{HAsO}_4^{2-}$  in the pH range of 4.0–7.0 agrees with the notion that to overcome the competition from sulfate, arsenate must be converted to the more adsorbable  $\text{HAsO}_4^{2-}$  species. However, comparing the As uptake and  $\text{HAsO}_4^{2-}$  speciation curves, it appears counter-intuitive in the sense that formation of  $\text{HAsO}_4^{2-}$  and its uptake did not really take place concomitantly, i.e., there appears to be a pH shift (~1 pH unit) between the uptake curve and the  $\text{HAsO}_4^{2-}$  formation curve.

The observed pH shift reveals that the pH at the ligand exchange sites is actually higher than that in the bulk solution phase. This is in accord with the Donnan co-ion exclusion principle (Kunin and Meyers, 1950). The immobilized  $\text{Cu}^{2+}$  ions in DOW 3N-Cu tend to attract counter-ions including  $\text{OH}^-$  to the close vicinity of the resin surface, and simultaneously exclude co-ions including  $\text{H}^+$  away from the surface. As a result, an excess of  $\text{OH}^-$  at the resin-solution interface is built up, which promotes the conversion of the  $\text{H}_2\text{AsO}_4^-$  from the bulk solution to  $\text{HAsO}_4^{2-}$  at the resin surface. This interfacial pH shift was also observed by Zhao and SenGupta (2000) in their study on phosphate uptake by DOW 3N-Cu. At pH above 8.0, although the more adsorbable  $\text{HAsO}_4^{2-}$  ions are the predominant species, the competition from  $\text{OH}^-$  ions becomes increasingly fierce, resulting in the increasing reduction in As uptake as pH goes up.

From a practical viewpoint, the optimal pH range of 6.0–8.0 is quite novel. Since the pH value for most natural waters falls in this range (Sawyer, 1978), there is no need to adjust source water pH to achieve the PLE's maximal sorption capacity.

### 3.4. Kinetic test

In a prior study on phosphate sorption, Zhao and SenGupta (2000) identified that intraparticle diffusion is the rate-limiting step during sorption of phosphate to DOW 3N-Cu. They also determined the effective intraparticle diffusivity for phosphate to be

$1.0 \times 10^{-8} \text{ cm}^2/\text{s}$ . Given the molecular analog between phosphate and arsenate, the intraparticle diffusivity is determined in a similar manner. Fig. 6 presents the change in As concentration in solution during the transient sorption of As by DOW 3N-Cu in a continuously stirred batch reactor.

For intraparticle-diffusion-controlled process, sorption rates are often modeled based on the Fick's second law. For spherical sorbents, the governing equation is (Crank, 1975)

$$\frac{\partial q}{\partial t} = D \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right), \quad (7)$$

where  $r$  is the radial coordinate and  $q(t, r)$  is the solid-phase As concentration at time  $t$ . Under the experimental conditions, the following initial and boundary conditions apply:

$$q(0) = 0 \text{ at } 0 \leq r \leq a, \quad (8)$$

$$\partial q / \partial r = 0 \text{ at } r = 0, \quad (9)$$

$$(\partial q / \partial r)(3DM/a) = -V(\partial C / \partial t) \text{ at } r = a, \quad (10)$$

where  $a$  is the mean radius of the resin beads, which was determined to be ~0.22 mm,  $M$  is the mass of the resin added, and  $V$  is the solution volume, which is considered constant during the course of the experiment.

The above system conforms to the scenario where diffusion takes place in a well-stirred solution of limited volume (Crank, 1975). The solution given by Crank (1975) as the fractional attainment of equilibrium ( $F$ ),

$$F = \frac{q(t)}{q_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1) \exp(-Dq_n^2 t/a^2)}{9+9\alpha+q_n^2 \alpha^2}, \quad (11)$$

where  $q_\infty$  is the arsenate uptake by DOW 3N-Cu at infinite time (i.e., at equilibrium), the parameter  $\alpha$  is expressed in terms of the final fractional uptake of

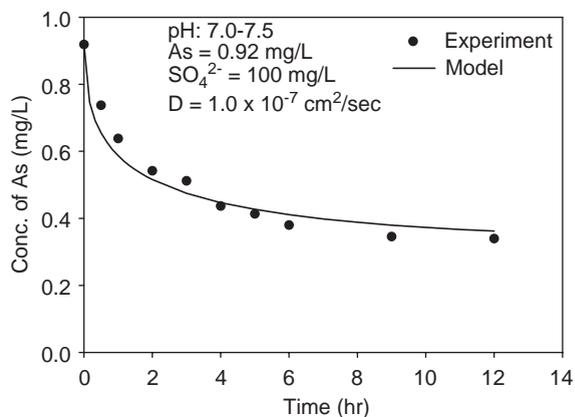


Fig. 6. Experimental and model-simulated arsenate sorption kinetics of DOW 3N-Cu. (Symbols: observed data; Line: model simulation).

arsenate as

$$\frac{Mq_{\infty}}{V_o C_o} = \frac{1}{1 + \alpha}, \tag{12}$$

where  $V_o$  and  $C_o$  are initial solution volume and initial arsenate concentration in solution, respectively. The  $q_n$ 's are the non-zero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}. \tag{13}$$

The form of Eq. (13) is convenient in bracketing the roots in well-defined intervals as determined by the tan function, which allows for simple root finding using the method of bisection.

The aqueous phase concentration at time  $t$ ,  $C(t)$ , was determined using the following mass-balance equation:

$$Mq(t) = V[C_o - C(t)]. \tag{14}$$

The best fit of the model to the experimental kinetic data in Fig. 6 was achieved by adjusting the diffusivity value ( $D$ ) until the sum of the squared error is minimized, which yields a diffusivity value of  $1.0 \times 10^{-7} \text{ cm}^2/\text{s}$ . This value is comparable in the order of magnitude to that for commonly used standard macro-porous SBA resins.

### 3.5. Resin regeneration, reuse of regenerated PLE, and reuse of treated spent regenerant

Form the standpoints of both cost-effectiveness and environmental friendliness; it is highly desirable that an IX resin be amenable to efficient regeneration using cheapest possible regenerant. Furthermore, it is even more beneficial if the spent regenerant can be recycled and reused. Multiple reuses of regenerant brine can further reduce the brine needs and cut down the volume of process waste residuals. Minimizing process waste residuals is currently gaining increasing attention in the US due to the much tightened regulations on the waste discharge.

Regeneration of arsenate-saturated DOW 3N–Cu was tested in the same fixed-bed configuration. Fig. 7 compares arsenate elution profile and recovery during regeneration using 4% (w/w) NaCl at pH 4.1, 7.0, and 9.1, respectively. As expected from the results in Fig. 4, greater regeneration efficiency was observed at either acidic or alkaline pH than at neutral pH. At pH 9.1, more than 96% of sorbed arsenate was recovered within 22 BVs of the regenerant. For comparison, regeneration of As-saturated IRA 900 was also tested using 4% NaCl at pH 9.1 (data not shown), and the results showed that under the same conditions, it took ~15 BVs of the regenerant to achieve a 95% of arsenate recovery.

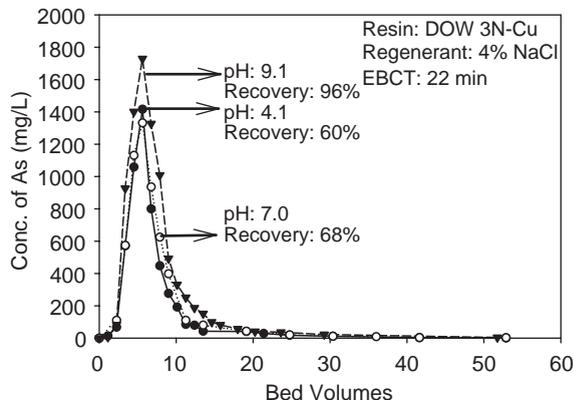
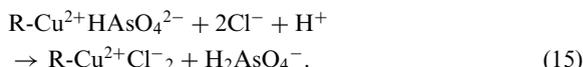


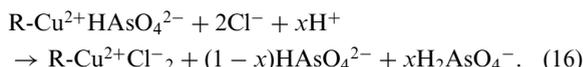
Fig. 7. Arsenic elution profile during regeneration of saturated DOW 3N–Cu using 4% NaCl (w/w) at pH 4.1, 7.0, and 9.1, respectively.

Eqs. (15)–(17) illustrate the regeneration reaction stoichiometry at the specified pH:

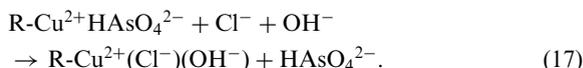
At pH 4.1



At pH 7.0



At pH 9.1



Evidently, the participation of  $\text{OH}^-$  in the ligand exchange reaction at alkaline pH greatly enhanced the regeneration efficiency.

For practical viability, the PLE should be amenable to multiple cycles of operation without significant capacity drop. Fig. 8 compares the equilibrium uptake of As of virgin DOW 3N–Cu and when it was subjected to up to eight consecutive operating cycles. Evidently, the regenerated DOW 3N–Cu did not show any significant capacity drop compared to its fresh form. The fact that the As capacity of the PLE was essentially unchanged over multiple cycles indicated that the copper leakage was minimal during both saturation and regeneration runs. Indeed, direct measurement of copper eluted showed that the copper leakage per operation cycle (saturation and regeneration) was less than 0.01% of total copper loaded.

The spent regenerant was repeatedly used for regeneration for seven times with only pH adjustment (pH 9.2–10), and more than 95% of recovery was consistently observed. After the regenerant was used for eight times, the recovery was dropped to less than 50%. Earlier, Clifford et al. (2003) reported that 5.5 BVs of 2.0 M brine

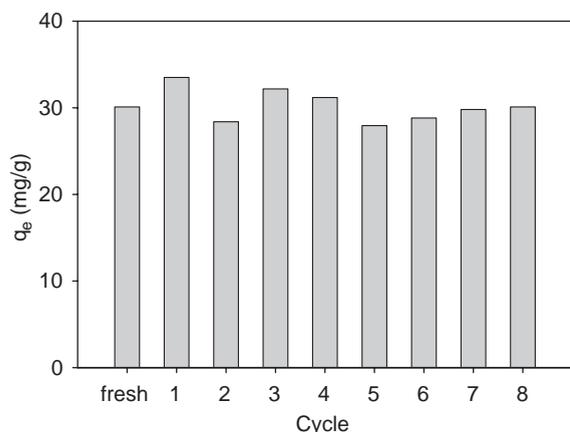


Fig. 8. Comparing the equilibrium arsenate sorption ( $q_e$ ) of fresh and regenerated DOW 3N-Cu under otherwise identical conditions. (Note: (a) One cycle consists of one saturation run and subsequent regeneration run; (b) each point represents mean of duplicates, the maximum standard deviation was 1.60).

solution can be reused for six times without chloride makeup for regeneration of a commercial SBA resin.

The high regeneration efficiency enables arsenate to be concentrated in a small volume (<1% of water treated) of spent regenerant. This affords the spent regenerant to be further treated using simple physical-chemical methods. It is highly desired to form a stable solid waste and to reuse the spent regenerant brine. To test the concept, ferric chloride was added to a batch of spent regenerant brine at various Fe:As molar ratios and at a fixed equilibrium pH of 6.0, 7.0, and 9.0, respectively. The primary compositions of the untreated spent brine were: As = 300 mg/L as As,  $\text{SO}_4^{2-}$  = 600 mg/L,  $\text{HCO}_3^-$  = 305 mg/L, and NaCl = 4% w/w (or  $\text{Cl}^-$  = 24 g/L). Fig. 9 shows the removal of the concentrated As from the spent regenerant as a function of the Fe:As ratio and the final pH. It is evident that more than 99.7% of As in the spent brine was removed at a Fe:As molar ratio of  $\geq 10$  and at pH 9.0. When pH was lowered to 6.0 or 7.0, over 99.9% As was removed at a Fe:As molar ratio of 5 or greater. Earlier, Clifford et al. (2003) demonstrated that at pH 5.6 and a Fe:As molar ratio of 20, As in a spent brine was reduced from 11,300 to 36.9  $\mu\text{g/L}$ , and the resultant sludge can easily pass the current TCLP test. Upon removal of the As-laden precipitates, pH of the supernatant was adjusted to 10 and then reused for another regeneration run. Fig. 10 shows nearly all As capacity was recovered using  $\sim 22$  BVs of the treated spent brine. The compositions of the treated brine were: As =  $\sim 50 \mu\text{g/L}$ , and  $\text{Cl}^-$  = 30 g/L, with sulfate and bicarbonate being about the same before and after the treatment. Note that due to addition of  $\text{FeCl}_3$ , chloride was increased by  $\sim 25\%$ , which favors the subsequent regeneration efficiency.

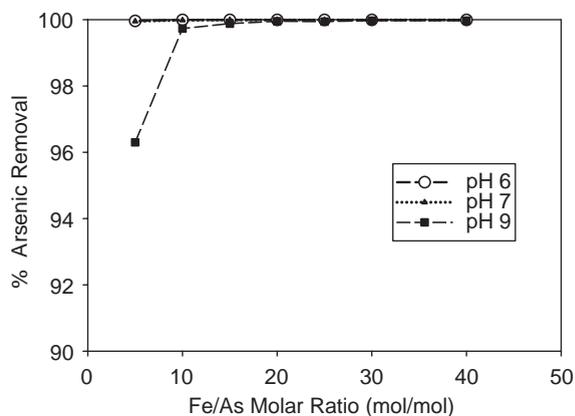


Fig. 9. Arsenic removal from spent regenerant brine using  $\text{FeCl}_3$  as a function of the Fe:As molar ratio and at a fixed pH of 6.0, 7.0 and 9.0, respectively. (Note: Data for pH 7 nearly overlap those for pH 6).

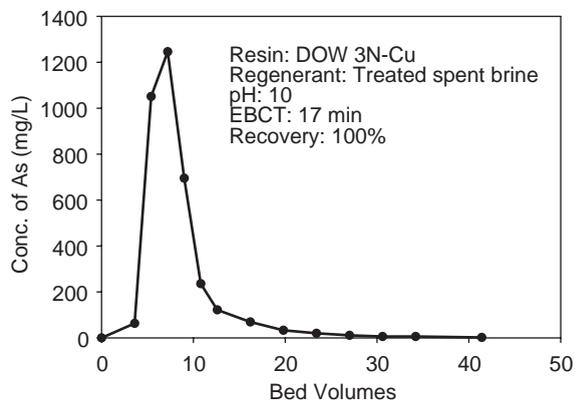


Fig. 10. Regeneration of arsenate-saturated DOW 3N-Cu treated spent brine at pH 10.

#### 4. Conclusions

As concluded in a recent review (Dambies, 2004), metal-loaded resins hold the most promise for selective removal of arsenate. This study reveals that polymeric ligand exchangers (PLE) may serve as a class of novel exchange resins for highly selective removal of arsenate from drinking water. Major findings of this research are summarized as follows:

The copper-loaded PLE, DOW 3N-Cu, showed unusually high selectivity for arsenate even in the presence of high concentrations of sulfate. Compared to conventional SBA resins, the arsenic (As) selectivity of DOW 3N-Cu is 60–120 times greater based on the binary arsenate/sulfate separation factor.

Fixed-bed column tests indicate that DOW 3N-Cu can treat 10 times more water per operation cycle than

the conventional SBA resins, which can potentially cut down the regenerant needs and the amount of process waste residuals by 90%.

DOW 3N–Cu can perform optimally in the pH range 6.0–8.0. Namely, there is no need to adjust pH to achieve the optimal As capacity of the resin. The experimental results indicated a pH shift between the sorption sites and the bulk solution, i.e., pH at the ligand exchange sites was  $\sim 1$  pH unit higher than pH in the bulk water. This pH difference promotes conversion of the less adsorbable  $\text{H}_2\text{AsO}_4^-$  to the more adsorbable  $\text{HAsO}_4^{2-}$  species even at a pH below the  $\text{p}K_{a2}$  value of arsenate (6.9).

The diffusivity of arsenate in DOW 3N–Cu is comparable to that for typical conventional macroporous sorbents.

DOW 3N–Cu can be highly efficiently regenerated using 4% NaCl at pH $\sim$ 9.1, and can be used in multiple cycles of operation without loss in capacity.

As in the spent regenerant can be effectively removed using  $\text{FeCl}_3$  at a Fe:As ratio of 5.0–10 and a pH range of 6.0–9.0. The treated brine showed equally high regeneration efficiency, which further cuts down the regenerant needs.

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