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ORIGINAL ARTICLE

Utilization of anion exchange resin Spectra/Gel for separation of arsenic from water

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Abstract Arsenic in drinking water is one of the most challenging health hazards facing mankind today. Arsenic is a naturally occurring carcinogen and creates epidemiological problems through chronic ingestion from drinking water. Arsenic is present in water primarily as As(III) or As(V). Removal of both As(III) and As(V) from water by adsorption on strong base anion-chloride has been studied. Arsenic concentration was measured by Inductively Coupled Argon Plasma (ICP) analysis. The resin was regenerated and the adsorbed arsenic fractions were eluted by using 2 M NaCl. The effect of different parameters that influence adsorption process, such as relative arsenic and resin concentrations, retention time, and pH, were investigated. Results obtained revealed that As(III) was poorly adsorbed, whereas As(V) was successfully retained on the resin. The adsorption process was optimized by using 1 g resin for 16 ppm As(V) at pH 9 for 30 min. The removal efficiency of As(V) was 99.2%.

1. Introduction

Arsenic contamination of drinking water has been an environmental issue that requires serious attention in many parts of world. Although in certain situations it might be possible to switch the water supply source in the affected areas to a safer and easily available one, this solution is temporary at best and may only be possible during the part of the year when alternate water supplies are available. It may also be prohibitively expensive. Arsenic removal may be a more prudent option. In January 2001, EPA published a revised maximum contaminated level (MCL) for arsenic in drinking water that requires public water suppliers to lower the arsenic concentrations standard from 50 μg/L (part-per-billion, or

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ppb) to 10 ppb in 2006 (US EPA, 2000, 2001). The revised standards may affect arsenic cleanup goals for groundwater. Based on information from EPA's CERCLIS 3 database (Comprehensive Environmental Response, Compensation, and Liability Information System) through fiscal year (FY) 1999 (US EPA Office of Water, 2001), arsenic is the second most common contaminant of concern (COC) cited in Records of Decision (RODs) for sites on the Superfund National Priorities List (NPL). Mining activities are responsible for arsenic poisoning in Thailand, while natural sources cause or have caused poisoning of populations, as has happened in Bangladesh, where nearly 30 million people were affected (Smedley and Kinniburgh, 2002). Because arsenic readily changes valence state and reacts to form species with varying toxicity and mobility, effective treatment of arsenic could be challenging. As(III) salts are generally more toxic to humans and 4–10 times more soluble in water than As(V) salts (US Occupational Safety and Health Administration, 2001). Most arsenic removal technologies are effective in removing the pentavalent form of arsenic. The trivalent form (arsenite) is predominantly non-charged below pH 9.2. Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Various processes dealing with arsenic in hydrometallurgical treatments include; coagulation and filtration (Cheng et al., 1994; Kang et al., 2003), sorption onto metal oxides such as activated alumina (Clifford, 1999), etc. Granular ferric hydroxides were also used with high removal efficiency and capacity (Christopher, 2004; Pawel and Bartlomiej, 2004). Adsorption is one of the most commonly reported techniques for removal of As(V). This process regulates the fate and mobility of As in soil, and it is mainly linked to different environmental factors such as pH, redox potential, reaction time, oxidation state of arsenic, and adsorbent type. Synthetic ion exchange resins developed for removal of anions such as sulfate and nitrate have proven to be reasonably effective at removing arsenic from water (Clifford, 1999). Anion exchange resins (AER) offer an economical alternative to other As separation methods. The use of AER minimizes the adverse effects that sample preservatives can have on As species in environmental samples as the separation can be performed instantly (Christopher, 2004). Pawel and Bartlomiej(2004) used ion exchange column chromatography to speciate arsenic in solution. Different AER have been previously tested and evaluated for pentavalent arsenic removal (Thomas et al., 1996; Clifford and Ghurye, 2002; Pawel and Bartlomiej, 2004). Clifford et al. (2003) and Iesan et al. (2004) used a conventional sulfate-selective type 2 polystyrene strong-base-anion resin at pH of 7.5–8.0. Bissen et al. (2000) used Amberlite IRA-93, while Dominguez et al. (2003) synthesized anion exchange fibers from a vinylbenzyl chloride precursor. Kim et al. (2003) and Kim and Benjamin (2004) described an approach for operating an ion exchange process for separating As(V) selectively from sulfate or nitrate.

The aim of this work is to study the effectiveness of the anion-exchange (Spectra/Gel IE 1 × 8) resin for removal of the arsenic species {As(III) and As(V)} from aqueous solution (with As concentration close to that of the untreated drinking water). Different parameters affecting the adsorption process, such as solution pH, metal adsorption capacity and time are investigated.

2. Experimental

2.1. Materials

Strong base anion exchange resin Spectra/Gel IE 1 × 8 (type 1) with bead size of 75–150 μm was used and evaluated for separation of As(III) and As(V) species. Spectra/Gel resins are supplied in chloride form, and use a trimethylbenylammonium group as the exchange site. Sodium arsenite ($NaAsO_2$) 0.1 N standardized solution (Alfa Aesar) was used as precursors of As(III). Sodium hydrogen arsenate ($Na_2HAsO_4{\cdot}7H_2O$), ACS, 98.0–102.0% (Alfa Aesar) were used as precursors of As(V). All chemicals used were of technically analytical grade.

2.2. Batch adsorption experiments

Batch adsorption experiments were conducted in a Pyrex glass flask, with 500 mL capacity. A magnetic rod was used for stirring. The selected range of arsenic concentration in the study was close to that in the untreated drinking water. For each flask, 500 mL of a solution containing a specific amount of the resin was transferred. The adsorption capability of As(III) and As(V) on the Spectra/Gel resin was investigated over a wide pH range. The pH values of the solutions were adjusted from 1 to 11 with 0.5 M NaOH and 0.5 M $HClO_4$ and measured with an Orion Model 801A pH meter. The pH was kept at a specific value during experiments using a pH controller (New Brunswick Scientific, Edison, NJ). The experiments were carried out for 180 min. A 10-mL sample was drawn every 15 min during the first hour, and then after every 30 min during the rest. The liquid samples were filtered for analysis through 0.2 μm syringe filters (Gelman Acrodisc syringe filter with 25 mm diameter, and Nylon membrane of 0.2 μm pore size, PN4436T, Pall Gelman Laboratory, Ann Arbor, Michigan). The adsorbed arsenic fractions were eluted from the resin using 2 M NaCl. Finally, the resin was washed with bi-distilled water for reusing. Arsenic concentrations in solutions were analyzed by Inductively Coupled Argon Plasma (ICP), Optical

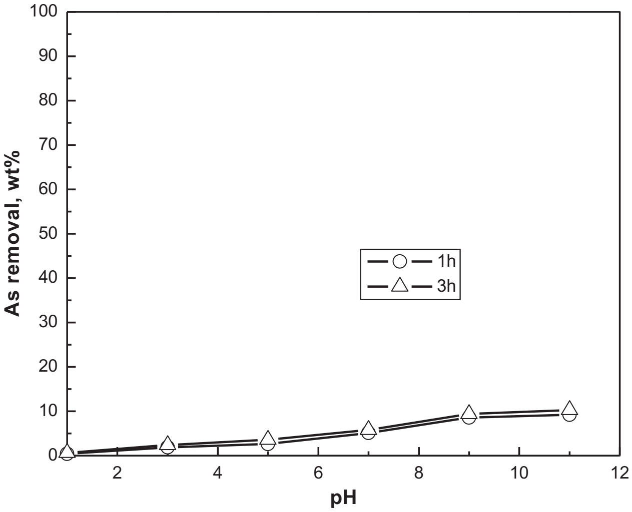

Figure 1 Adsorption behavior of As(III) on Spectra/Gel IE 1 × 8 at different pH values. As(III) conc. 20 ppm, resin conc. 1 g/L.

Emission Spectrometer (model Optima 5300 DV PerkinElmer).

3. Results and discussion

The adsorption results of As(III) are shown in Fig. 1, As(III) concentration of 20 ppm was used with a resin concentration of 1 g/L, for adsorption times of 1 and 3 h. It can be seen that As(III) was poorly adsorbed, in general, the adsorption capability increases slowly with the increase of solution pH reaching a maximum As(III) removal of about 10 wt%. Increasing the adsorption time from 1 to 3 h did not greatly affect the removal efficiency. The adsorption behavior of As(V) on the Spectra/Gel resin and the effect of solution pH at different adsorption times are shown in Fig. 2. The pH of the solution has a strong effect on the adsorption and removal processes of As(V) from solution. Better arsenic removal efficiencies were achieved with As(V) as compared with that of As(III). Removal efficiency of As(V) was not measured to be significant at low pH values but increased rapidly with increasing pH, attaining a maximum value of 97.8% at pH of 7 after an adsorption time of 90 min. The removal % attained a maximum value of 99.2% at pH 9 after treatment for 30 min only. Further increase in pH, beyond 9, showed only a small increase in the removal efficiency. Fig. 3 shows the effect of adsorption time on the removal of As(V) by the Spectra/Gel resin at different pH values. A fast removal of As(V) was achieved in a short time. About 93.2% and 99.2% of As(V) was removed after 30 min of treatment at pH values of 7 and 9, respectively. However, increasing the time beyond 30 min did not affect the As(V) removal at lower pH in which case the removal efficiency values were about 51% and 85% at pH values of 3 and 5, respectively.

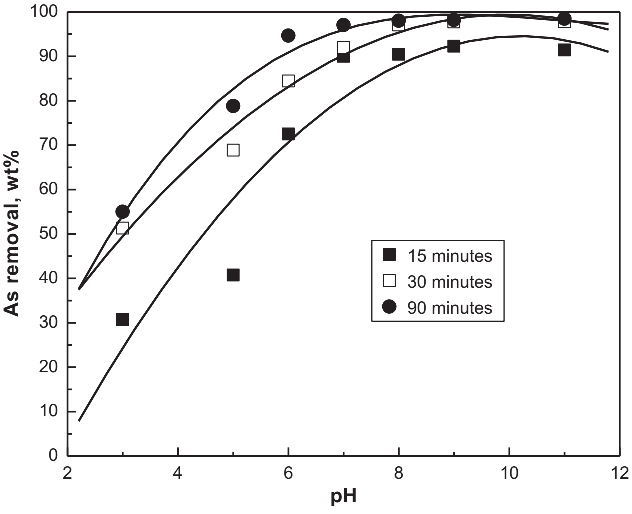

Figure 2 Adsorption behavior of As(V) on Spectra/Gel IE 1 × 8 at different pH values. As(V) conc. 16 ppm, resin conc. 1 g/L.

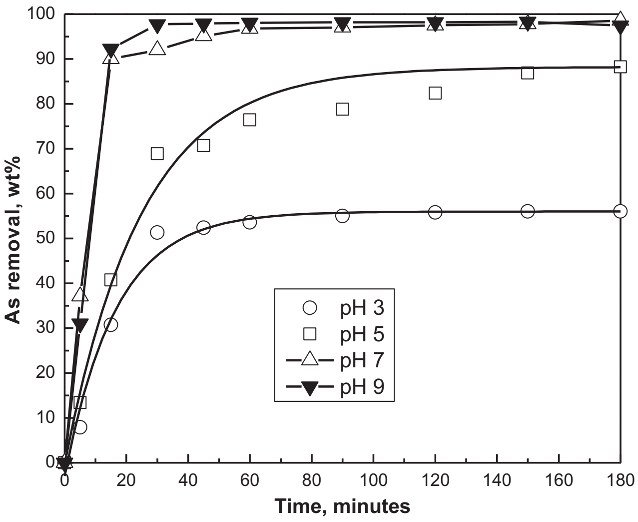

Figure 3 Adsorption behavior of As(V) on Spectra/Gel IE 1 × 8 at different pH values. As(V) conc. 16 ppm, resin conc. 1 g/L.

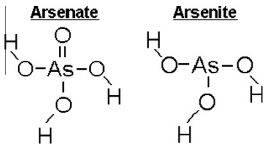

Figure 4 Differences in the molecular configuration of arsenate and arsenite in water.

The difference in the adsorption capability of both As(III) and As(V) may be attributed to the difference in molecular structure between arsenite and arsenate, as shown in Fig. 4 (Pauling, 1970). The double bond oxygen in the arsenate molecule influences its ability to become ionized through the loss of hydrogen ions, the process is termed dissociation. A negative charge develops on the molecule when dissociation occurs. The double bond oxygen increases the capacity to delocalize that charge, easing the loss of hydrogen ions. The propensity for ionization is expressed by pK_a the constant of dissociation. For arsenate and arsenite pK_a values are as follows (Pauling, 1970):

$$\text{Arsenate }(H_3AsO_4):\ pK_1 = 2.19,\ \ pK_2 = 6.94,\ \ pK_3 = 11.5 \quad (1)$$

$$\text{Arsenite }(H_3AsO_3):\ pK_1 = 9.20,\ \ pK_2 = 14.22,\ \ pK_3 = 19.22 \quad (2)$$

where pK_1 is 1st ionization constant, pK_2 is 2nd ionization constant, pK_3 is 3rd ionization constant. The pH at which these

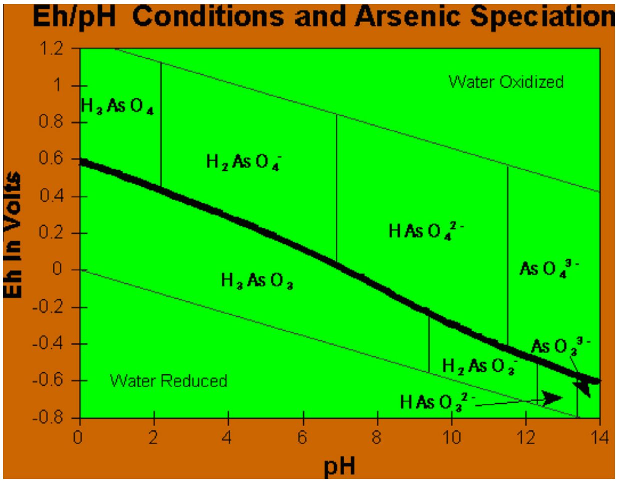

Figure 5 Control of arsenic speciation by Eh and pH conditions.

ionization steps occur is significantly different between arsenate and arsenite, as illustrated in Fig. 5 (Robins, 1985; Welch et al., 1988). This Eh/pH relationship is the key to understand arsenic mobility in water and the effectiveness of arsenic water treatment systems. The most commonly recognized adsorption reactions are based on ion exchange between charged adsorption sites and charged soluble ions. Arsenic immobilization through ionic adsorption can be controlled within normal oxidizing Eh/pH conditions. The boundary between the stability fields for As(III) and As(V) slopes over the Eh–pH ranges of interest in most water systems. For example, the conversion between As(V) and As(III) would occur at an Eh of 0.02 volts at a pH of 7 and at an Eh of 0.29 volts at a pH of 4. As a result, As(III) can be converted to As(V) at constant Eh if the pH increases (forward *X*-direction in Fig. 5), just as it can be converted by increasing the Eh at constant pH (up *Y*-direction in Fig. 5). Depending upon the position of a solution's starting point in the As(III) stability field, the arsenic may be converted to As(V). This is the type of evolution that might be expected in the system.

Fig. 6 shows the effect of the resin dosage on the As(V) removal. The removal efficiency is increased by increasing the resin concentration. The As(V) removal reached a maximum value of 99.2% with resin dosage of 1 g/L after 90 min. Although further increase in the resin dosage only slightly increased the removal efficiency, it facilitated the As(V) removal by decreasing the treatment time. About 99.2% of the As(V) was removed after 30 min of treatment with 2 g resin, but it took only 20 min with 3 g resin to reach the same 99.2% removal efficiency.

The effect of varying As(V) concentration on its removal rate is shown in Fig. 7. The lower the As(V) concentration, the higher the efficiency of it's removal. The limitation of surface sites for the reaction may control the As(V) adsorption. At a concentration of 8 ppm, As(V) can be totally adsorbed (complete removal) within 30 min. The As(V) removal decreased with increasing concentration and the reaction was time independent. The removal attained its maximum after 90 min of treatment at any As(V) concentration. Maximum removal efficiency values of 99.2%, 96%, 78.8%, and 68.5% were achieved for As(V) concentration values of 16, 32, 48, and 64 ppm, respectively. The results clearly demonstrate that the As(V) adsorption process is promising at low concentrations of the pollutant. This is also typical for heterogeneous catalytic systems where the reaction occurs at the interface between two phases.

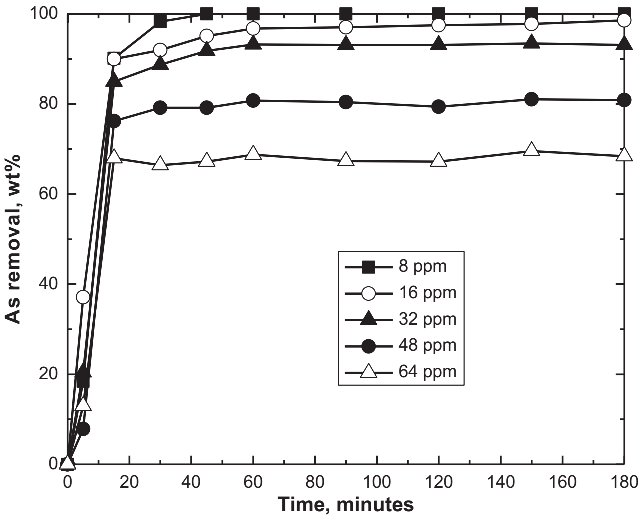

Figure 7 Adsorption behavior of different concentrations of As(V) on Spectra/Gel IE 1 × 8. pH 9, resin conc. 1 g/L.

The removal of As(V) by Spectra/Gel anion exchange resin can be explained as follows; the water containing As(V) passes through a bed of the chloride form resin (designated by RCl), during which the chloride arsenate ion exchange reaction (Eq. (3)) takes place to yield resin in the arsenate form (R_2HAsO_4). When the column capacity for arsenic is exhausted, the reaction is easily reversed and regeneration returns the resin to the chloride form according to Eq. (4) (Clifford, 1999).

$$2RCl + HAsO_4^{-2} = R_2HAsO_4 + 2Cl^- \tag{3}$$

$$R_2HAsO_4 + 2NaCl = 2RCl + Na_2HAsO_4 \tag{4}$$

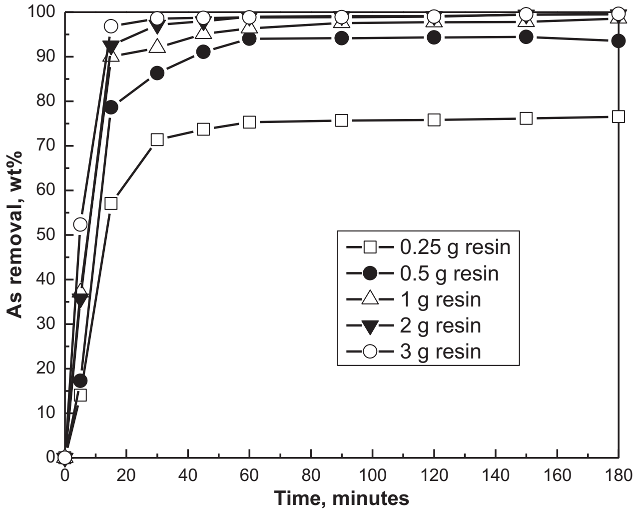

Figure 6 Adsorption behavior of As(V) on Spectra/Gel IE 1 × 8 as affected by resin concentration. As(V) conc. 16 ppm, pH 9.

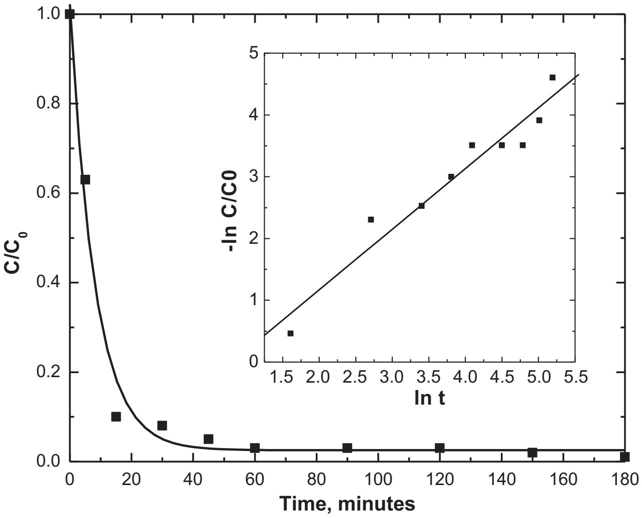

Figure 8 kinetics of As(V) adsorption on Spectra/Gel IE 1 × 8. As(V) conc. 16 ppm, resin conc. 1 g/L, pH 9.

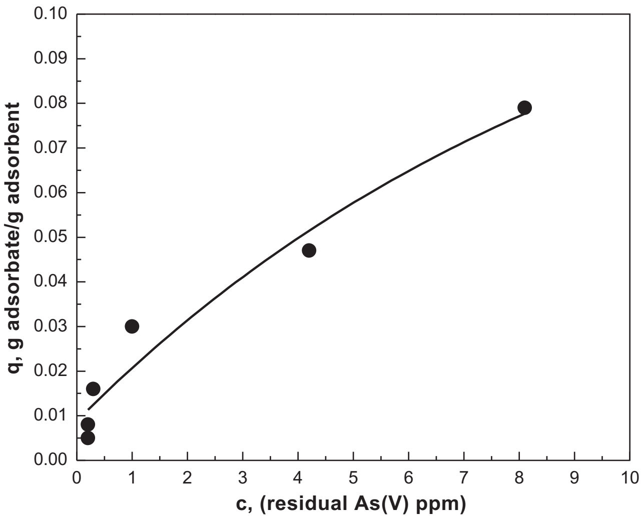

Figure 9 As(V) equilibrium isotherms for Spectra/Gel IE 1 × 8. As(V) initial conc. 16 ppm, pH 9.

The rate equation of the reaction was calculated by plotting ln C/C_0, for As(V) concentration of 16 ppm with 1 g resin at pH of 9, as a function of ln time, as shown in Fig. 8. Here C_0 and C are the initial and remaining As(V) concentrations in the solution, respectively. The plot gave a straight line which confirmed that the adsorption process follows a pseudo-first order reaction. Fig. 9 shows the As(V) equilibrium isotherm for the resin at the same experimental conditions of Fig. 8. In the lower concentration regime, the resin exhibits a higher exchange capacity, followed by a crossover. Although the resin is classified as strongly basic anionic, these systems may posses a combination of strong and weak groups due to side reactions that occur during resin synthesis (Dominguez et al., 2003). It is possible that as the concentration increases, these weaker groups begin to exert exchange capacity thus resulting in a crossover point.

4. Conclusion

Strong base anion exchange resin Spectra/Gel IE 1 × 8 (type 1) with bead size of 75–150 μm was used and evaluated for removal of As(III) and As(V) species from water. As(III) was poorly adsorbed, whereas As(V) was retained on the resin. The adsorption process was optimized by using 1 g resin for 16 ppm As(V) at pH 9 for 30 min. The maximum removal efficiency of As(V) was 99.2%. The adsorption process follows a pseudo-first order reaction. The resin was regenerated and the adsorbed arsenic fractions were eluted by using 2 M NaCl.

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