Removal of Arsenic in Drinking Water by Iron Oxide-Coated Sand and Ferrihydrite — Batch Studies

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Arsenic, a common toxic element is mainly transported in the environment by water. Arsenic in drinking water is of major concern to many of the water utilities in the world. Numerous studies have examined the removal of arsenic from drinking water through treatment processes such as coagulation-precipitation, reverse osmosis and ion exchange. The focus of research has now shifted to solve the problems using suitable adsorbents to achieve low level As in drinking water for communities with high raw water arsenic concentration. The determination of arsenic species is also essential for a better understanding and prediction of the toxic and carcinogenic nature of the species present in natural water systems. It is generally known that As(III) is more toxic than As(V) and inorganic arsenicals are more toxic than organic derivatives. The objective of this study was to study the arsenic adsorption behaviour on iron oxide-coated sand (IOCS) and ferrihydrite (FH). Batch studies were conducted using these adsorbents with natural water containing 325 µg/L arsenic, and the removal of approximately 90% was obtained. The adsorption capacity of the IOCS and FH used in this study for arsenic was estimated as 18.3 and 285 µg/g, respectively. The experimental data fitted well with the well-known isotherms, namely, Freundlich, Langmuir and BET, indicating a favourable adsorption by these adsorbents. Speciation studies were also conducted with natural water containing arsenic. Particulate and soluble arsenic in water were determined, and As(III) in the sample was determined by passing the sample containing arsenic through anion exchange resin (Dowex 1X8-100; acetate form) packed in the column. Speciation studies with natural water showed that the particulate and soluble arsenic contributed 11.4 and 88.6% of the total arsenic present in the natural water, respectively. In the case of soluble arsenic, As(III) and As(V) were 47.3 and 52.7%, respectively.

Key words: arsenic, drinking water, treatment, adsorption, isotherm, speciation

Introduction

Arsenic, a potential carcinogenic element is present in natural water systems as a result of both natural and anthropogenic activities. The natural weathering processes contribute approximately 40,000 tons of arsenic to the global environment annually, while twice this amount is being released by human activities (Paige et al. 1996). In natural waters, arsenic exists predominantly as inorganic forms, mainly as arsenite [As(III)] and

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arsenate [As(V)]. On the other hand, organic forms of arsenic such as monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA) are rarely present at concentrations above 1 µg/L (Anderson and Bruland 1991) and of less interest compared with inorganic forms with respect to drinking water treatment. Over the pH range typically encountered in water treatment, arsenite exits as the uncharged species H$_3$AsO$_3$, while arsenate is distributed between the anionic species H$_2$AsO$_4^-$, HAsO$_4^{2-}$ and AsO$_4^{3-}$ (Ferguson and Gavis 1972).

Elevated levels of arsenic concentration have been reported in many parts of the world (Shen 1973; Cebrian et al. 1983; Meranger and Subramanian 1984; Chatterjee et al. 1995; Choprapawan and Rodcline 1997; Luo et al. 1997; Niu et al. 1997; Boyle et al. 1998; Koch et al. 1999; Burkel and Stoll 1999; Hinkle and Polette 1999; Karim 2000). The results of the study conducted by Meranger and Subramanian (1984) in selected groundwater samples from Halifax County, Nova Scotia, Canada, showed that most of the samples exceeded the current MAC level of 25 µg/L, and the arsenic concentration of samples ranged between 1 and 738 µg/L. In a recent study conducted by Koch et al. (1999), the results showed that the levels of arsenic in water from Meager Creek hot springs, British Columbia, Canada, were found to be tenfold higher than the MAC level of 25 µg/L. Boyle et al. (1998) reported that 50% of groundwater samples from Bowen Island, British Columbia, Canada, exceeded the MAC level for arsenic, and the maximum arsenic concentration was reported to be 580 µg/L in one of the wells studied.

Ingestion of arsenic-contaminated water can cause deleterious effects on the human body, and these effects are well documented (Chakraborti et al. 1998; Smith et al. 1998; Mazumder et al. 1998; Subramanian and Kosnett 1998; Karim 2000). The increased worldwide concern for the health effects of arsenic ingestion has compelled the respective regulatory agencies to consider lowering the maximum contaminant level (MCL) for arsenic to less than 25 µg/L. The World Health Organization standard for arsenic stands at 10 µg/L. The current maximum contaminant level for arsenic in drinking water is 50 µg/L in the U.S., whereas the maximum acceptable concentration for arsenic is 25 µg/L in Canada. The U.S. Environmental Protection Agency has proposed to reduce the maximum contaminant level of arsenic to 5 µg/L; this proposal is under review (U.S. EPA 2000). The German drinking water standard for arsenic had been reduced to 10 µg/L, and the commission of the European Community is aiming at a standard in the range of 2 to 20 µg/L (Driehaus et al. 1998).

Various treatment processes such as coagulation-precipitation, adsorption onto activated alumina, reverse osmosis and ion exchange have been reported in the literature to remove arsenic from drinking water (Viraraghavan et al. 1992). Technologies for arsenic removal in drinking water have been summarized by Viraraghavan et al. (1994). In the earlier studies conducted at the University of Regina, manganese greensand and ion exchange resins were used to remove arsenic from drinking water (Subramanian et al. 1997; Viraraghavan et al. 1999). Iron addition was found to be necessary to achieve an effluent arsenic level of
25 µg/L in the manganese greensand filtration system. In order to achieve a lower level of arsenic (<25 µg/L) in drinking water supplies, further studies were conducted using iron based materials. Iron oxides, oxyhydroxides and hydroxides (all are called as “iron oxides”) consist of Fe, O and/or OH. They differ in composition, in the valence of Fe, and in crystal structure. The basic structural unit of all Fe oxides is an octahedran, in which each Fe atom is surrounded either by six O or by both O and OH ions (Scwertmann and Cornel 1991).

Based on experimental results, Gulledge and O’Connor (1973) reported that As(V) adsorption on ferric hydroxide exceeded the adsorption on aluminium hydroxide, and an increased coagulant dosage resulted in an increase in arsenic removal. In the pH range 5 to 7, more than 90% removal of As(V) was achieved with 30 mg/L dose of ferric sulfate. Cheng et al. (1994) concluded that for the source waters tested, enhanced coagulation was effective for arsenic removal, and less ferric chloride than alum, on a weight basis, was needed to achieve the same removal. Scott et al. (1995) reported that arsenic removal of 81 to 96% was achieved when source water was treated with 3 to 10 mg/L of ferric chloride, and concluded that ferric chloride was more effective than alum in removing arsenic.

Edwards (1994) reported that As(III) removal by coagulation was primarily controlled by coagulant dose and relatively unaffected by pH solution. He also added that ferric coagulants were effective in the removal of As(V) at pH less than 7.5, and iron was more effective than alum in removing both As(V) and As(III) at pH >7.5. Pierce and Moore (1980) showed that adsorption of As(III) onto amorphous ferric hydroxide increased with pH up to a maximum pH of 7. Pierce and Moore (1982) found that the rate of adsorption of As(V) onto amorphous ferric hydroxide was much faster than of As(III) in the initial phase (1 h) of contact with the adsorbent. They also recommended that for maximum arsenic removal, pH 7 was optimum for As(III), and pH 4 was optimum for As(V). Driehaus et al. (1998) reported that the results obtained from the fixed adsorber tests with granular ferric hydroxide (GFH) for arsenic removal were encouraging, and nearly 30,000 bed volumes were treated, keeping the effluent As concentration at 10 µg/L. The results of the studies conducted by Raven et al. (1998) showed that both arsenite and arsenate had strong affinities for ferrihydrite, and arsenite could be retained in much larger amounts than arsenate at high pH (approximately >7.5) or at high As concentrations in solution.

In recent years, there has been an overwhelming research effort to develop an innovative technology to achieve a low level of arsenic in drinking water supplies. Chemical precipitation-coagulation is a simple method in which chemicals are added to water to form precipitates or flocs containing arsenic that are removed by subsequent sedimentation process. The disadvantage of chemical methods is that they produce large amounts of sludge containing arsenic (hazardous in nature) that will pose serious problems for safe disposal. Adsorption/filtration appears to be a promising technology that is applicable to small community water supplies. Speciation of arsenic and concentration of individual arsenic species
are required to predict (i) As behavior in water treatment processes, and (ii) to assess health effects, cost of regulatory compliance and treatment options. The presence of As (III) and As (V) in different proportion in water supplies may produce different toxic effects. Often, it is documented in the literature that measurement of total arsenic concentration is insufficient to assess the risk of As exposure in human populations. A recent study by Edwards et al. (1998) established an arsenic speciation protocol that can be applied to a water treatment plant in situ. It is necessary to test the arsenic speciation protocol of Edwards et al. (1998) with a suitable sample preservation technique. In the present study, batch isotherm studies were conducted using iron oxide-coated sand (IOCS) and ferrihydrite (FH) to study the removal of arsenic from the natural water. Speciation studies were conducted to speciate As(III) and As(V) from the natural water containing arsenic.

Materials And Methods

Water

Natural water from the Kelliher Water Treatment Facility, Kelliher, Saskatchewan, was used in the batch and speciation studies. The major physicochemical characteristics of the raw water were pH, 7.4; iron, 2.1 mg/L; manganese, 1.2 mg/L; nitrate, 2.9 mg/L; sulfate, 518 mg/L; copper, 0.04 mg/L; zinc, 0.01 mg/L; lead, 0.002 mg/L; selenium, <0.001 mg/L; aluminium, <0.005 mg/L; barium, 0.011 mg/L; cadmium, <0.001 mg/L; and chromium, <0.001 mg/L. Distilled (double) deionized water was used in the speciation recovery studies. A portable pH meter (Hanna Cheker 1, Sigma Chemical, Ontario) was used to measure the pH of the water. The accuracy of the pH meter was ±0.2 pH unit.

Reagents

As(V) stock solution (1000 mg/L) was prepared by dissolving 4.164 g of sodium arsenate (Na2HAsO4. 7H2O, Sigma Chemical) in 1L distilled water and was preserved with 0.5% HNO3 (trace metal grade). 1 mg/L of As (V) was prepared by pipetting 1 mL of stock solution into 1-L volumetric flask, and then the solution was made up to 1 L with distilled water. One mg/L of As(III) stock solution was prepared by pipetting 1 mL of arsenic oxide (1000 mg/L reference solution from Fisher Scientific, Ontario) into 1-L volumetric flask, and then the solution was made up to 1 L with distilled water. In both cases, As (V) or As (III) required working standards were prepared from the stock solution.

Preparation of Iron Oxide-Coated Sand (IOCS)

The red flint filter sand used in the preparation of iron oxide-coated (IOCS) was purchased from Watergroup Canada Ltd., Regina. The sand was sieved to a geometric mean size of 0.6 mm to 0.8 mm, acid washed (pH 1; 24 h), rinsed with distilled water three times and dried at 100°C for
20 h before use. The preparation of IOCS was done according to the procedure mentioned by Edwards and Benjamin (1989). In the preparation of coated sand, 200 gram of dried red flint filter sand, 20 gram of Fe(NO₃)₃.9H₂O (BDH Inc., Toronto) and enough distilled water to cover the sand were placed in a beaker (wide mouth), and after 3 min of gentle agitation, the open beaker was placed in an oven (110°C) for 20 h. The oven-dried coated sand was washed with distilled water four times until the run off was clear. The sand was then dried at 110°C for 12 h and kept in capped bottles.

**Preparation of Ferrihydrite**

Ferrihydrite (FH) was prepared as per Scwertmann and Cornell (1991), with little modifications. Forty grams of Fe(NO)₃.9H₂O was dissolved in 500 mL of distilled water and 330 mL of 1M KOH was added slowly at a rate of 75 mL/min, during vigorous stirring with magnetic stirrer. The final 30 mL of 1M KOH was added carefully to bring the pH of the suspension to 7.3. The suspension was allowed to stand for 3 h and the supernatant was decanted. The red brown precipitate obtained in the above titration was washed with distilled water and centrifuged (IEC Centra-8R Centrifuge, International Equipment Company, Massachusetts) at 5200 RPM. Washing and centrifugation was done three more times. Finally, after decanting the supernatant, the precipitate was oven dried at 40°C for 72 h, and air dried for 6 days. After drying, the precipitate was crushed to small particles and freeze dried.

The surface area of IOCS and FH was determined using Flowsorb 2300 manufactured by Micromeritics Instrument Corporation, Georgia. Single-point surface area measurements were employed to determine the surface area of the samples. In the test, a gas mixture of 29% nitrogen and 71% helium was used and, prior to surface area measurements, the samples were degassed at 150°C for 20 min and then cooled with liquid nitrogen.

**Batch Isotherm Studies**

Batch isotherm studies were conducted using IOCS and FH to study the removal of arsenic in the natural water collected from the Kelliher Water Treatment Facility. At present, water from wells 1 and 3 are mixed and, after treatment with manganese greensand filtration system, the treated water is supplied to the people of Kelliher. The raw water from well 1 has a low arsenic concentration, whereas well 3 has a high arsenic concentration. The raw water was collected from well 3 using 2-L low-density polyethylene containers, and upon arrival in the laboratory, isotherm studies were conducted using the adsorbents. The containers used for the sample collection were thoroughly washed with a detergent, rinsed with 1N nitric acid and dried before use. In the experiments, the adsorbent (IOCS, 0.5 to 1.2 g; FH, 0.02 to 0.09 g) was transferred to 250-mL Erlenmeyer flasks containing 100 mL of raw water. The Erlenmeyer flasks were sealed with parafilm and the samples were shaken at 125 rpm for a
contact time of 5 h using Labline Orbit Shaker manufactured by Labline Instruments Inc., Melrose Park, Illinois. After completion of the contact time, the samples from each flask were decanted and analyzed for residual arsenic by graphite furnace atomic absorption spectrometry (GFAAS). Experiments were conducted in duplicate and average values were used in the analysis.

**Speciation Studies**

The speciation protocol used in the present study is similar to that of Edwards et al. (1998), except that acidification of samples was done using nitric acid (trace metal grade [Fisher Scientific, Ontario]) instead of sulfuric acid. The speciation protocol adopted in this study is shown in Fig. 1. Total arsenic of the natural water was determined by GFAAS after diges-

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**Fig. 1.** Arsenic speciation protocol as per Edwards et al. (1998) — modification in acid preservation samples.
tion of samples in 5% HNO\textsubscript{3} as described in APHA (1998). Initially 30-mL sample was filtered with 0.45 µm polycarbonate filter (MSI, Westboro, Maine). The filtered sample was acidified with 0.05% nitric acid (trace metal grade) and measured as soluble As; the acid was pipetted with model 8100 syringes (Nichiryo Oxford, Tokyo). The difference between total and soluble As was measured as particulate As. The filtered, acidified sample was speciated using anion exchange resin (Dowex 1X8-100; mesh size 50–100) and As(III) was determined. As(V) was calculated as the difference between soluble As and As(III). A liquid chromatography column (Sigma Chemical, Ontario) of size 1.5 × 10 cm was used in the speciation studies.

Before packing the resin in the column, the resin was converted into acetate form as follows. Thirty grams of resin was placed in a 500-mL beaker. Thirty milliliters of 1N NaOH (diluted from 6N NaOH-VWR Scientific Products, West Chester, Pennsylvania) was added to the above resin and stirred for 1 h in magnetic stirrer. After draining the NaOH, another 30 mL of 1N NaOH was added and stirred for 1 h and the NaOH rinse was repeated one more time. The resin was then rinsed with 30 mL of distilled water twice. Thirty milliliter of 1N reagent grade acetic acid was then added, stirred for 5 min, and drained; the acid rinse was repeated twice. The resin was rinsed with 30 mL of distilled water three times.

**Arsenic Measurement**

The instrument used in this study was Varian type SpectrAA–600 Zeeman GFAAS equipped with GTA 100–graphite tube atomizer and PSD–00 programmable sample dispenser. All operations of the GFAAS were controlled by spectra 600-series version 1.23 software package. Pyrolytically coated notched partition graphite tubes (part number 63-100023-00, batch Number VI/43/34301) purchased from Varian Canada Inc., Toronto, were used for the experiments. Argon gas of ultrahigh purity (99.99 5%) (Praxair Products Inc., Ontario) was used to sheath the atomizer and to purge internally. Arsenic hollow cathode lamp (Part No. 56101003-00; Varian Canada Inc., Toronto) was used at a wavelength of 193.7 nm with a slit width of 0.5 nm. Palladium solution+magnesium nitrate solution was used as matrix modifiers for calibration. An external reference standard from the National Water Research Institute, Environment Canada, was used to verify the calibration.

**Results and Discussion**

**Batch Studies**

**Iron oxide-coated sand (IOCS)**

The batch isotherm study was conducted by varying the mass of iron oxide-coated sand to remove arsenic in the natural water. The total arsenic concentration of the natural water at Kelliher was determined as 325 µg/L. The well-known isotherms Langmuir, Freundlich and BET were used to describe the adsorption. The basic assumptions (Faust and
Aly 1987) underlying the Langmuir model are (i) that the molecules are adsorbed on definite sites on the surface of the adsorbent; (ii) each site can accommodate only one molecule (monolayer), and the area of each site is a fixed quantity determined by the geometry of the surface; and (iii) the adsorption energy is the same at all sites. The BET model is based on the assumption that each molecule in the first adsorbed layer serves as a site for the adsorption of a molecule into the second (multilayer), and so on. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. The isotherm equations are as follows.

**Freundlich:**

\[
\frac{X}{M} = KC_e^{1/n}
\]  

(1)

**Langmuir:**

\[
\frac{X}{M} = \frac{abC_e}{1 + aC_e}
\]  

(2)

**BET:**

\[
\frac{X}{M} = \frac{AX_e C_e}{(C_e - C_s)(1 + A - 1)}
\]  

(3)

where \(X\) is the mass of solute adsorbed (µg); \(M\) is the mass of adsorbent (g); \(b\) is the mass of adsorbed solute required to completely saturate a unit mass of adsorbent (µg/g); \(a\) is a constant related to the energy or net enthalpy between the adsorbed solute molecule and the adsorbent (L/µg); \(C_e\) is the equilibrium concentration (µg/L); \(K\) is an experimental constant indicative of the adsorption capacity of the adsorbent (L/µg); \(n\) is an experimental constant indicative of the adsorption intensity of the adsorbent; \(C_s\) is the saturation (initial) concentration of the solute (µg/L); \(A\) is a constant related to the energy of interaction between the solute and the adsorbent surface; and \(X_m\) is a constant related to the amount of solute adsorbed in forming a complete monolayer (µg/L).

The data was subjected to non-linear estimation on “Statistica for Windows” (release 5.1, 97 edition), and the simplex method was used to solve the equations. The predicted values of the model were plotted with arsenic concentration remaining in solution, as shown in Fig. 2. The isotherm models appeared to fit the data better in the linear portion, but the data points for higher equilibrium concentrations were quite removed from the models. The Freundlich constants, \(k\) and \(n\), were estimated to be 1.36 L/µg and 1.26, respectively. High \(k\) value in the Freundlich isotherm indicated that the adsorption capacity of the IOCS was very high. Low \(1/n\) value (0.79) suggested that any large change in the equilibrium concentration of arsenic would not result in a change in the amount of arsenic taken by the IOCS. The separation factor, \(R\) of 0.55 (0<R<1), estimated from the Langmuir constant indicated a favorable arsenic adsorption by the Langmuir isotherm. The high correlation coefficient, “r” of 0.92 for both the Freundlich and the BET isotherms showed that arsenic adsorp-
Removal of Arsenic in Drinking Water

Adsorption can be best described by these isotherms. The adsorption capacity of IOCS used for arsenic removal in the natural water was estimated at 18.3 µg/g from the Freundlich isotherm. The results showed that a maximum arsenic removal of 92% (26 µg/L) was obtained in the isotherm studies and the mass of the IOCS corresponding to this removal was 1.2 g. Increase in mass of the IOCS beyond 1.2 g might have reduced the arsenic concentration to less than 10 µg/L.

**Ferrihydrite (FH)**

In the isotherm studies with ferrihydrite (FH), the convex nature of the Langmuir isotherm (Fig. 3) and the separation factor R of 0.99 esti-
mated from the Langmuir constant suggested a favorable arsenic adsorption by FH. The Freundlich constant, \( k \), was estimated to be 0.47 L/µg, and a high correlation coefficient, \( r \), of 0.97 for the Freundlich isotherm suggested that arsenic adsorption can be adequately described by the Freundlich isotherm at the range studied. The adsorption capacity of FH used for arsenic removal in the natural water was estimated at 285 µg/g, using the Langmuir isotherm; a maximum arsenic removal of 87% (42.2 µg/L) was obtained in the isotherm studies and the mass of FH corresponding to this removal was 0.09 g. Raven et al. (1998) used a suspension containing a known amount of ferrihydrite to study the removal of As(III) and As(V) in the synthetic water. In their study, adsorption maxima of approximately 0.6 and 0.25 mol\(_{\text{As}}\)/mol\(_{\text{Fe}}\) was achieved for As(III) and As(V), respectively, at pH 4.6.

The model equations for all the isotherms for arsenic adsorption onto IOCS and FH are shown in Tables 1 and 2, respectively. The results of batch studies are summarized in Table 3. The surface areas of iron oxide-coated sand and ferrihydrite were 5.1 and 141 m\(^2\)/g, respectively. The large difference in surface area of the materials might be the reason that the adsorption capacity of FH (285 µg/g) was high compared to the adsorption capacity of IOCS (18.3 µg/g). The results showed that the percent of arsenic removal with iron oxide-coated sand was higher compared to the percent of arsenic removal with ferrihydrite. The reason for this difference could be due to the use of higher mass of IOCS in the batch studies compared to the mass of FH used.

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<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Correlation coefficient (r)</th>
</tr>
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<tbody>
<tr>
<td>Freundlich</td>
<td>( \frac{X}{M} = 1.3 \times \frac{C^{1.12}}{1.2} )</td>
<td>0.92</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( \frac{X}{M} = \frac{0.01 \times 265.8 \times C}{1 + 0.01 \times C} )</td>
<td>0.91</td>
</tr>
<tr>
<td>BET</td>
<td>( \frac{X}{M} = \frac{4.5 \times 56.3 \times C}{(325 - C) \times (1 + (4.5 - 1) \times (C/325))} )</td>
<td>0.92</td>
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<tr>
<th>Isotherm</th>
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</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>( \frac{X}{M} = 0.46 \times \frac{C^{1.63}}{1.63} )</td>
<td>0.97</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( \frac{X}{M} = \frac{8.1 \times 10^{-7} \times 8331554 \times C}{1 + 8.1 \times 10^{-7} \times C} )</td>
<td>0.93</td>
</tr>
<tr>
<td>BET</td>
<td>( \frac{X}{M} = \frac{0.18 \times 6572 \times C}{(325 - C) \times (1 + (0.18 - 1) \times (C/325))} )</td>
<td>0.96</td>
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Speciation Studies

Initially, the liquid chromatography column used in the studies was filled with 19.5 g (wet weight) of resin in acetate form. The packed depth of the resin in the column was 9.5 cm. To find out the breakthrough volume, 360 mL of distilled water spiked with 50 µg/L of As(V) was allowed to pass through the column. The sample was filled in 60-mL syringes and then injected into the column at a flow rate of 15 mL/min. The pH of the influent to the column was adjusted to 2.2 with nitric acid (trace metal grade). The influent pH was within the optimum operating pH range (1.8 to 5), as mentioned by Edwards et al. (1998). The effluent from the column was collected at regular intervals and analyzed for residual As(V). The results showed that the column was effective in 100% removal of As(V), thereby ensuring the effectiveness of the column to treat the sample up to a volume of 360 mL.

Speciation recovery studies were conducted with distilled water containing mixtures of As(III) and As(V). In these studies two sets of samples were used — one set of samples was preserved with sulfuric acid (as per Edwards et al. 1998) and the other was preserved with nitric acid (trace metal grade). In all the samples, initial As(III) concentration was kept at 10 µg/L, whereas the initial concentration of As(V) varied from 10 to 35 µg/L. The pH of the samples preserved with sulfuric acid was in the range of 1.9 to 2.6, whereas the pH of the samples preserved with nitric acid was in the range of 2 to 3.2. Two liquid chromatography columns filled with resin in acetate form were used in the studies. A quantity of 30 mL of sample was passed through the column; first 10 mL was discarded and the remaining sample was collected and analyzed for As(III).
Results of the speciation recovery studies are shown in Fig. 4; As(III)-sulfuric and As(III)-nitric in Fig. 4 represent arsenite concentrations in the effluent samples preserved with sulfuric and nitric (trace metal grade) acid, respectively. The recoveries of As(III) in the samples preserved with sulfuric acid ranged from 76.3 to 121.7%. There was the possibility of leakage of As(V) through the column, which might appear falsely as As(III) in the samples. Removal of As(III) in the column might also be possible, thereby appearing falsely as As(V) in the analysis of samples. In the case of samples preserved with nitric acid (trace metal grade), the recoveries of As(III) were in the range of 81.2 to 105.2%. In the preservation of samples with sulfuric acid, some difficulty was experienced in dispensing the acid because it stuck to the pipette.

The water from wells 1 and 3 of the Kelliher Water Treatment Facility were collected, mixed, and speciation studies were conducted in situ. Samples were collected at five different times on the same day and studies were conducted. The samples were speciated as per the speciation protocol, and nitric acid (trace metal grade) was used in the preservation of samples. After acid preservation, the pH of the samples ranged between 2.8 and 3.8. The total arsenic concentration of the sample was measured as 59.7 µg/L. The results (average of five samples) of the study are shown in Fig. 5. The mean, standard deviation and standard error of the values obtained in the speciation studies with natural water, using the box and whisker model, are shown in Fig. 6. It can be seen that particulate arsenic was 6.8 µg/L and contributed 11.4% of the total arsenic. Soluble arsenic contributed a substantial portion (88.6%) of the total arsenic. The results showed that both arsenite and arsenate equally dominated in the Kelliher water. For the validation of the speciation protocol, it is necessary to speciate more samples; however, because of its simplicity and ease of operation, the speciation protocol using nitric acid preservation can be adopted in the field.

![Fig. 4. Arsenic remaining in the solution after speciation recovery studies.](image-url)
Conclusions

The following conclusions are drawn from this study.

- Batch study results showed that both iron oxide-coated sand (IOCS) and ferrihydrite (FH) can be effectively used to achieve a low level of arsenic in drinking water supplies for small communities.
- The isotherm plots for IOCS and FH suggested that the arsenic adsorption can be best described by the Freundlich isotherm at the range studied.

Fig. 5. Arsenic fractions in Kelliher water.

Fig. 6. Box and whisker plot for the results of speciation studies.
The arsenic adsorption capacities of IOCS and FH were estimated at 18.3 and 285 µg/g, respectively. The large difference in surface area could be the reason that the adsorption capacity of FH was higher compared to the adsorption capacity of IOCS.

The results of the speciation studies with natural water containing arsenic were encouraging and showed that the speciation protocol adopted in this study, using nitric acid preservation, can be adopted in the field. Speciation studies with natural water showed that the particulate and soluble arsenic contributed 11.4 and 88.6%, respectively, of the total arsenic present in the natural water. As(III) and As(V) contributed 47.3 and 52.7% of soluble arsenic.

Acknowledgments

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References


