

# Arsenic removal from drinking water using granular ferric hydroxide

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## Abstract

This paper examines the use of granular ferric hydroxide (GFH) to remove both arsenate [As(V)] and arsenite [As(III)] present in drinking water by conducting batch and column studies. The kinetic studies were conducted as a function of pH, and less than 5 µg/l was achieved from an initial concentration of 100 µg/l for both As(III) and As(V) with GFH at a pH of 7.6, which is in the pH range typically encountered in drinking water supplies. In the isotherm studies, the observed data fitted well with both the Freundlich and the Langmuir models. In continuous column tests (five cycles) with tap water using GFH, consistently less than 5 µg/l of arsenic was achieved in the finished water for 38 to 42 hours of column operation, where the influent had a spiked arsenic concentration of 500 µg/l. High bed volumes (1260 and 1140) up to a breakthrough concentration of 5 µg/l were achieved in the column studies. The adsorptive capacities for GFH estimated from the column studies were higher than that of activated alumina reported in the previous studies. Speciation of a natural water sample with arsenic showed the dominance of As(III) species over As(V). Batch and column studies showed that granular ferric hydroxide (GFH) can be effectively used in small water utilities to achieve less than 5 µg As/l in drinking water.

**Keywords:** adsorption, drinking water, arsenic removal, granular ferric hydroxide, arsenic speciation

## Nomenclature

$C$	equilibrium concentration (µg/l)
$C_e$	effluent adsorbate concentration (µg/l)
$C_o$	influent adsorbate concentration (µg/l)
$k$	Thomas rate constant (ml/min.µg)
$x$	mass of solute adsorbed (µg)
$m$	mass of adsorbent (g)
$b$	a constant related to the energy or net enthalpy of adsorption (l/µg)
$Q^o$	mass of adsorbed solute completely required to saturate a unit mass of adsorbent (µg/g)
$K$	the Freundlich constant indicative of the adsorption capacity of the adsorbent (l/µg)
$k$	rate constant for adsorption (g/h.µg)
$n$	experimental constant indicative of the extent of adsorption of the adsorbent
$Q$	volumetric flow rate (ml/min)
$q_o$	maximum solid phase concentration (µg/g)
$V$	throughput volume (ml)
$R$	separation factor estimated from the Langmuir constant
$r$	regression coefficient.

## Introduction

Arsenic contamination of surface and subsurface waters is reported in many parts of the world and is considered a global issue. As a naturally occurring toxic substance in the earth's crust, arsenic

enters into aquifers and wells through natural processes, and to the water cycle as a result of anthropogenic activities. Arsenic contamination of subsurface waters is believed to be geological. High arsenic concentrations may result from dissolution of, or desorption from iron oxide, and oxidation of arsenic pyrites (Welch et al., 1999). The severity of arsenic pollution of groundwater is reported in Bangladesh, where most of the people rely on tube wells as a source of drinking water. It is estimated that 30 to 70 million people in Bangladesh are at risk due to the exposure of arsenic contaminated water (Chowdhury et al., 1999; Ward, 2000). Until recently, occurrence of arsenic in Bangladesh water supplies was believed to be caused by pyrite oxidation; however, recent studies showed that the causative mechanism of arsenic release to groundwater was reductive dissolution of As-rich Fe oxyhydroxide. The reduction was driven by microbial degradation of organic matter, which was present in concentrations as high as 6% C in water (Nickson et al., 2000; McArthur et al., 2001).

Ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non-cancer effects (NRC, 1999). The acute and chronic toxicity effects of the ingestion of arsenic-contaminated water have been well documented. Population-based studies showed that arsenite [As(III)] and arsenate [As(V)] may adversely affect several organs in the human body (Tseng et al., 1968; Smith et al., 1998; Mazumder et al., 1998; Subramanian and Kosnett, 1998; Ma et al., 1999; Chowdhury et al., 1999; Karim, 2000). Since the majority of the people affected world-wide live in small communities, it makes sense to develop a treatment technology tailored for small communities. Furthermore, a reduction in acceptable consumption levels of arsenic by the regulatory agencies is forcing water utilities to identify and implement cost-effective arsenic removal technologies.

Treatment technologies that have been tested to remove arsenic from drinking water under both laboratory and pilot-scale studies were summarised by Viraraghavan et al. (1994). Iron-based salts

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have been used as coagulants for arsenic removal from drinking water, and were found to be effective in the case of large-scale water utilities (Scott et al., 1995; Cheng et al., 1994; Sancha, 1999). Bench-scale studies were conducted with various iron oxides to remove arsenic from drinking water (Pierce and Moore, 1980; Pierce and Moore, 1982; Hsia et al., 1994; Wilkie and Hering, 1996; Joshi and Chaudhuri, 1996; Raven et al., 1998; Driehaus et al., 1998; Viraraghavan et al., 2000; Thirunavukkarasu et al., 2001). Recent studies (Korte and Fernando, 1991; Chada, 2000) showed that As(III) is more prevalent in groundwater than As(V). An effective technology is sought that would remove both As(III) and As(V) present in drinking water.

After a careful review, the United States Environmental Protection Agency (USEPA) suggested ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration, and modified lime softening as best available technologies for As(V) removal. However, the importance of iron-based coagulation-assisted microfiltration, iron oxide-coated sand, and granular ferric hydroxide (GFH) was stressed for arsenic removal. Rigorous testing is necessary to validate these technologies (USEPA, 1999; USEPA, 2000). In addition, it is essential to study the speciation changes to establish the occurrence and toxicity of species present in the drinking water. The objective of the present study was to assess the potential and applicability of granular ferric hydroxide (GFH) for removing both As(III) and As(V) present in drinking water. Batch kinetic and isotherm studies were conducted to study the extent of arsenic adsorption onto GFH. Column studies were conducted at normal filtration rates to study the removal of arsenic species that were added to the tap water. In studies with natural water, a speciation technique was used to observe the speciation changes in the treated water.

## Materials and experimental methods

### Water and standards

Natural water (containing arsenic) from Kelliher Water Treatment Plant, Kelliher, Saskatchewan, Canada and tap water from the City of Regina, Saskatchewan, Canada were used in the batch and column studies. The major physicochemical characteristics of the Regina tap water and Kelliher natural water are listed in Table 1. Distilled (double) deionised water was used in the preparation of standard solutions and for dilution purposes. As(V) stock solution (1000 mg/l) was prepared by dissolving 4.164 g of sodium hydrogen arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ; 99.7% purity; Sigma Chemical, Ontario) in 1 l distilled water and was preserved with 0.5% trace metal grade  $\text{HNO}_3$  (Fisher Scientific, Ontario). Fresh stock solution was prepared once in 30 d. One mg/l of As(V) was prepared by pipetting 1 ml of stock solution into a 1 l volumetric flask, and making up the solution 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; Fisher Scientific, Ontario) into a 1 l volumetric flask, and making up the solution to 1 l with distilled water. In both the cases [As(V) or As(III)] required working standards were prepared daily from the stock solution. All glassware and sample bottles were washed with a detergent solution, rinsed with tap water, soaked with 10% nitric acid for at least 12 h, and finally rinsed with distilled water three times.

### Granular ferric hydroxide (GFH)

Granular ferric hydroxide (GFH) was obtained from the manufacturer Wasserchemie GmbH and Co.KG, Germany. In the manufac-

Parameters	Tap water*	Kelliher water*
pH	7.6	7.4
Iron	0.07	2.1
Manganese	0.02	1.2
Turbidity (NTU)	0.28	Not analysed
Chloride	12	Not analysed
Copper	0.001	0.04
Zinc	<0.005	0.01
Lead	<0.002	0.002
Cadmium	<0.001	<0.001
Barium	0.073	0.011
Chromium	<0.001	0.001
Chlorine (residual)	0.2	Not analysed
TOC	1.6	Not analysed

\* all parameters except pH and turbidity are in mg/l

turing process, GFH was produced from a ferric chloride solution by neutralisation and precipitation with sodium hydroxide. The ferric hydroxide precipitate was centrifuged and granulated by a high-pressure process. The GFH consists of ferric oxihydroxide (approximately 52 to 57% by mass), 43 to 48% by mass moisture content and grain porosity of 72 to 77% (Driehaus et al., 1998). The grain size of the GFH obtained from the manufacturer ranged between 0.32 and 2 mm. The GFH was sieved to a size of 0.8 to 1.2 mm and used in the studies.

### Batch studies

Batch kinetic studies were conducted as a function of pH to study the removal of both As(III) and As(V), spiked to required concentrations in tap water. In the isotherm studies, arsenic [As(III) and As(V)] removal was studied at the normal pH (7.6) of the tap water in Regina. Isotherm studies were also conducted with raw water collected from the Kelliher Water Treatment Plant, Kelliher, Saskatchewan, Canada. The raw water (containing arsenic) was collected using 18.9 l (5 US gallon) low-density polyethylene containers and studies were conducted immediately on receipt of samples in the laboratory. In both kinetic and isotherm studies, 100 ml samples were transferred to 250 ml Erlenmeyer flasks containing GFH and the flasks were sealed with parafilm. The samples were placed on a mechanical shaker and shaken at 175 r/min. All experiments were conducted at the room temperature of  $22 \pm 1^\circ\text{C}$ . A portable bench top platform shaker (New Brunswick Scientific Co. Inc., NJ, USA) was used to conduct the batch studies.

The mass of GFH used was kept at 0.2 g in the kinetic studies. The initial concentration of both As(III) and As(V) in the tap water was 100  $\mu\text{g/l}$ . The effect of solution pH on adsorption of arsenic species on to GFH was studied at the pH levels of 5, 6, 7.6, and 8.5. Isotherm studies were conducted by varying the mass of GFH. The initial concentrations of As(V) and As(III) were same as in kinetic studies. The latter studies were conducted only at pH 7.6. The equilibrium time (6 h) from the kinetic studies was kept as contact time. Samples were collected at regular time intervals and analysed for residual As through graphite furnace atomic absorption spectrometry (GFAAS). In the case of natural water samples, soluble As, As(III) and As(V) in the samples were determined as per speciation protocol.

## Column studies

In the column studies, all the tests were conducted in the downflow mode and at the normal pH (7.6) of the tap water in Regina, Canada. Both As(III) and As(V) removals were investigated. Water was pumped through the packed column with a peristaltic pump (Model # 7553-70, Cole Parmer Instrument Company, Ontario). The packed volume of GFH in the column (16 mm diameter C 400 mm long) was 43 ml, ensuring enough headspace to allow for expansion of the medium during backwashing. The flow rate was kept constant at 21.5 ml/min (5 m/h or 2 gpm/ft<sup>2</sup>), which yielded an empty bed contact time (EBCT) of 2 min. A column test was also conducted using GFH to remove arsenic from the natural water. In this study, the volume of GFH, EBCT and flow rate were 30.5 ml, 1.42 min and 21.5 ml/min (5 m/h or 2 gpm/ft<sup>2</sup>), respectively.

In the column studies, the initial As(V) and As(III) concentrations were kept at 500 µg/l in the tap water, whilst the experiments were conducted at pH 7.6. Five cycles of downflow column tests were conducted to evaluate the performance of GFH related to As(V) and As(III) removal from the tap water. The first cycle was conducted up to exhaustion for both As(III) and As(V) and for the subsequent cycles the column test was conducted until the effluent arsenic level reached 100 µg/l. Before commencement of each cycle, the column was backwashed with deionised water until the effluent level reached a level that was less than 10 µg/l. Samples from the column tests were collected at regular time intervals and analysed for residual As through GFAAS. In the column test using natural water, the effluent samples were speciated to find soluble As, As(III) and As(V) using the speciation protocol. The speciation protocol used in this study was similar to that of Thirunavukkarasu et al. (2001). The only difference was the use of anion-exchange resin (Dowex 1X8 - 50, Sigma Chemical Co., MO, USA) of 20 to 50 mesh size in the speciation protocol instead of 50 to 100 mesh size.

## Data analysis

The data obtained from the isotherm studies was used to analyse the adsorption isotherms in order to estimate the constants, adsorption density and adsorption maxima. The experimental results were fitted to both the Langmuir and the Freundlich isotherms, which are as follows:

The Langmuir :

$$\frac{x}{m} = \frac{Q^0 b C}{1 + b C} \quad (1)$$

The Freundlich:

$$\frac{x}{m} = K C^{1/n} \quad (2)$$

where:

- $C$  is equilibrium concentration (µg/l);
- $x$  is mass of solute adsorbed (µg);
- $m$  is mass of adsorbent (g);
- $b$  is a constant related to the energy or net enthalpy of adsorption (l/µg);
- $Q^0$  is mass of adsorbed solute completely required to saturate a unit mass of adsorbent (µg/g);
- $K$  is the Freundlich constant indicative of the adsorption capacity of the adsorbent (l/µg); and

$n$  is experimental constant indicative of the adsorption intensity of the adsorbent.

In the adsorption process, fluid flows continuously through a column of adsorbent or a packed bed, where dynamic adsorption of the solute occurs (Faust and Aly, 1987). Fixed bed adsorption columns operated in the downflow mode may perform two functions, namely adsorption and filtration. Breakthrough or exhaustion curves were constructed from the column data by plotting the ratio of  $C_e/C_0$  with the volume of water processed. In the present studies, the Thomas model was used to study the dynamic behaviour of the column. The model is shown below (Reynolds and Richards, 1996):

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp\left[\frac{k}{Q}(q_0 m - C_0 V)\right]} \quad (3)$$

where:

- $C_e$  is effluent adsorbate concentration (µg/l);
- $C_0$  is influent adsorbate concentration (µg/l);
- $k$  is Thomas rate constant (ml/min.µg);
- $Q$  is volumetric flow rate (ml/min);
- $q_0$  is maximum solid phase concentration (µg/g); and
- $V$  is throughput volume (ml).

## Analytical methods

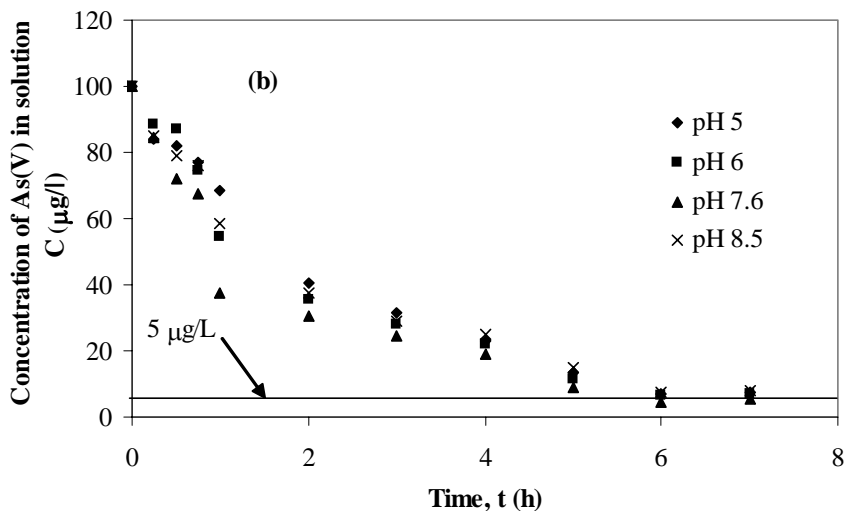
All samples were acidified (pH < 2) with 0.3% HNO<sub>3</sub> (trace metal grade) and analysed for arsenic using a Varian type SpectrAA-600 Zeeman GFAAS equipped with a GTA 100-graphite tube atomiser and programmable sample dispenser (Limit of Detection of the instrument is 2 µg/l). Pyrolytically coated notched partition graphite tubes (Varian Canada Inc., Toronto) were used in the experiments. Argon gas of ultrahigh purity (99.995%; Praxair Products Inc, Ontario) was used to sheath the atomiser and to purge it internally. An arsenic hollow cathode lamp (Varian Canada Inc., Toronto) was used with emitting wavelength of 193.7 nm with a slit width of 0.5 nm. Palladium solution (1500 µg/l) + magnesium nitrate (1 000 µg/l) solution was used as matrix modifier for calibration. Fresh modifier solution was prepared for calibrating the instrument. An external reference standard from the National Water Research Institute (NWRI), Environment Canada, Ontario was used to verify the calibration.

The iron content of the GFH was determined by acid digestion using the procedure described in AWWARF (1993). One gram of GFH was added to 50 ml of 10% HNO<sub>3</sub> in a beaker and the solution was heated on a hot plate to boiling point. After 2 h, the iron oxide in the medium was completely dissolved and the acid solution turned yellow. At this point, digestion was discontinued, the solution was made up to 1 l with distilled deionised water, filtered through 0.45 µm filter, and the iron content determined by a FerroVer method using Hach instrument (model DR/850, Hach Company, Loveland, CO, USA). The BET surface area of the GFH was determined using Flowsorb 2300 (Micromeritics Instrument Corporation, Georgia, USA). Single point surface area measurements were employed to determine the surface area of the samples.

## Results and discussion

### Batch kinetic studies

Figure 1 shows that arsenic (both As(III) and As(V)) was successfully removed from the solution with time. More than 80% arsenic



**Figure 1**  
Arsenic concentration remaining with time using GFH a) arsenite and b) arsenate

removal was achieved after 3 h of contact time with less than 5 µg/l achieved at pH levels of 6 and 7.6 for both As(III) and As(V) at an equilibrium time of six hours. The most efficient As(III) adsorption on to GFH occurred at a pH of 7.6, with 68% of As(III) removed within 1 h and 97% removed at the equilibrium time of 6 h. The kinetic study data were fitted to Ho pseudo second-order reaction rate model (1996) to describe the adsorption kinetics. Non-linear regression was performed with Statistica for Windows (release 5.1) software (Statsoft Inc., 1997) using Quasi-Newton method (start values were 0.1 for all parameters; initial step size for all parameters was 0.5; maximum number of iterations was 50). The rate constant for adsorption 'k' for both As(III) and As(V) was estimated as 0.003 and 0.002 g GFH/h.µg As, respectively.

Arsenite adsorption was similar to results reported in previous studies (Pierce and Moore, 1980; Wilkie and Hering, 1996) where the adsorption of As(III) on to amorphous ferric hydroxide increased as the pH increased, with maximum adsorption occurring at a pH of 7. A maximum removal (96%) of As(V) occurred at a pH of 7.6 at an equilibrium time of 6 h. More than 90% removal of As(V) was observed at all the pH levels studied. These results were similar to the results of earlier studies (Hsia et al., 1994; Wilkie and Hering, 1996). In studies with hydrous ferric hydroxide (HFO), close to 100% As(V) removal was observed in the pH range of 4 to 8 by Hsia et al. (1994) and Wilkie and Hering (1996).

### Batch isotherm studies

Results of the isotherm studies were fitted into both the Freundlich and the Langmuir isotherms. Non linear regression was performed with Statistica for Windows (Release 5.1) software (Statsoft Inc., 1997) using the Quasi-Newton method (start values, initial step size and number of iterations were as before). The estimated adsorption densities by the Langmuir and the Freundlich models with the concentrations of As(III) and As(V) remaining in solution are shown in Fig. 2. All the isotherms were convex curves.

The separation factor 'R' (Hall et al., 1996) estimated from the Langmuir constant for As(V) and As(III) was 0.33 and 0.14 ( $0 < R < 1$ ), respectively. This suggested that arsenic adsorption can be modelled by the Langmuir isotherm. The 'K' parameters estimated from the Freundlich isotherm for As(V) and As(III) were 10.3 and 18 (L/µg), respectively. High levels of K suggested that adsorption capacity of the adsorbent is

**Figure 2**  
Isotherm plot for arsenic adsorption onto GFH a) the Langmuir and b) the Freundlich



high (AlDuri, 1996). Low  $1/n$  values ( $<1$ ) from the Freundlich isotherm suggested that any large change in the equilibrium concentration of arsenic would not result in a marked change in the amount of arsenic sorbed by GFH. The correlation coefficient ( $r$ ) for all the isotherms ranged between 0.97 and 0.99, representing an excellent fit of the observed data. The t-test values showed that the coefficients were significant at the 95% confidence level for all the model equations.

In the case of As(V) removal, the adsorption maximum and the adsorption density at a residual concentration of  $5 \mu\text{g As/l}$  were estimated through the Langmuir model and were 159 and  $32 \mu\text{g As/g GFH}$ , respectively. Acid digestion results showed that 1 g GFH contained 269 mg Fe. By expressing the mass of GFH in terms of Fe content and the concentration of As(V) in  $\mu\text{mol/l}$ , the adsorption maximum was estimated at  $17.6 \mu\text{mol As/g Fe}$  ( $1 \text{ mmol As/mol Fe}$ ). The adsorption density was  $3.4 \mu\text{mol/g Fe}$  ( $0.2 \text{ mmol As/mol Fe}$ ). The estimated adsorption density was lower than the value reported by Driehaus et al. (1998) and Fuller et al. (1993). The difference could be attributed to different experimental conditions discussed below. In the batch studies for As(V) removal from the synthetic solution at pH 7, Driehaus et al. (1998) reported that at a residual As(V) concentration of  $10 \mu\text{g/l}$ , the adsorption density on GFH was  $1 \text{ mmol As/g Fe}$ , at high initial As(V) concentration. They also reported that arsenate adsorption on freshly prepared ferric hydroxide was higher than the adsorption on GFH. It is expected that at a high initial As concentration or at a high As/Fe ratio, the adsorption maximum and the adsorption density will be also high. High adsorption density was reported by Fuller et al. (1993) in their adsorption studies, where the initial As/Fe ratio was 0.12. In the present studies the initial As/Fe ratio was maintained between 0.025 and 0.0025. Further, the surface area of GFH ( $112 \text{ m}^2/\text{g}$ ) estimated in this study was smaller than the value reported by Fuller et al. (1993).

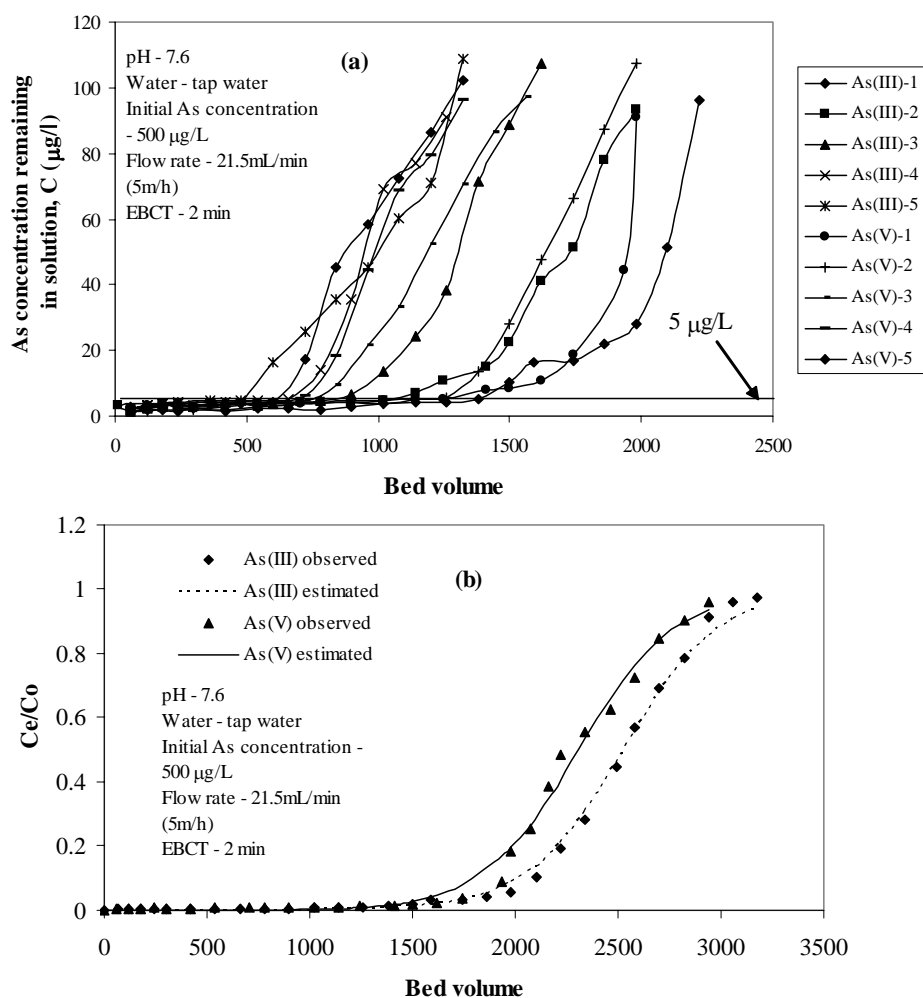
In the studies on As(III) removal, the adsorption maximum and the adsorption density at  $5 \mu\text{g/l}$  were estimated at 112 and  $31 \mu\text{g As/g GFH}$ , respectively from the Langmuir model. In terms of available Fe content in GFH, the adsorption maximum and adsorption density at  $5 \mu\text{g/l}$  were  $11 \mu\text{mol As/g Fe}$  ( $0.7 \text{ mmol As/mol Fe}$ ) and  $1.7 \mu\text{mol/g Fe}$  ( $0.1 \text{ mmol As/mol Fe}$ ), respectively. The estimated adsorption density was smaller compared to the value reported by Wilkie and Hering (1996). However, the percent of As(III) removal observed in the present studies was higher than the value reported by Wilkie and Hering (1996). The initial As/Fe ratio maintained in their studies was high compared to the present studies.

**Figure 3**  
*Arsenic removal from Kellihier water using GFH a) As species remaining in solution and b) isotherm plot*

In the isotherm studies with natural water, the initial total As, soluble As, and particulate As in the raw water were determined as 177.3, 169.8, and  $7.5 \mu\text{g/l}$ , respectively. At the end of isotherm studies, samples were collected and speciated to find soluble As, As(III) and As(V). The speciation of raw water showed the dominance of As(III) species over As(V). The As(V)/As(III) ratio in the raw water was 0.45. The results showed that the minimum concentrations of soluble As, As(III) and As(V) achieved were 4.8, 3.3, and  $1.6 \mu\text{g/l}$ , respectively. A plot of the concentration of As remaining in solution vs. the mass of GFH is shown in Fig. 3 (a). The results were fitted into the Freundlich and the Langmuir models. The model curves are shown in Fig. 3 (b). As before, the isotherm had convex curves. The estimation of isotherm parameters such as 'K' value (18.5) and  $1/n$  value (0.6) confirmed that the adsorption capacity of GFH was high. A statistical t-test confirmed that the coefficients were significant at the 95% confidence level. The adsorption density at a residual concentration of  $5 \mu\text{g As/l}$  was estimated at  $24 \mu\text{g As/g GFH}$  ( $2.6 \mu\text{mol As/g Fe}$  or  $0.15 \text{ mmol As/}$

Isotherm parameters		Arsenic species		
		As(III)	As(V)	Soluble As
Adsorption maxima, $\mu\text{g As/g GFH}$ (mmol As/mol Fe)		112 (0.67)	159 (1)	141 (0.8)
Adsorption density, $\mu\text{g As/g GFH}$ (mmol As/mol Fe)		31 (0.1)	32 (0.2)	24 (0.15)
The Freundlich isotherm	Regression coefficient, $r$	0.99*	0.97*	0.97*
	' $K$ ' value	18	10.3	18.5
	' $n$ ' value	2.3	1.5	1.65
The Langmuir isotherm	Regression coefficient, $r$	0.97*	0.98*	0.95*
	Separation factor, $R$	0.14	0.33	0.22

\* coefficients are significant at the 95% confidence level.



**Figure 4**

Arsenic removal from tap water in column studies a) As concentration remaining in solution with throughput volume and b) estimated values of  $C_e/C_0$  by the Thomas model

mol Fe) from the Langmuir model. The results of the batch studies are summarised in Table 2.

### Column studies

Figure 4 (a) shows the concentration of arsenic remaining in solution vs. the bed volumes achieved for all the cycles up to an effluent arsenic level of 100  $\mu\text{g/l}$ . In the first cycle of column tests for As(V) removal, the column continued to remove As(V) to a level of less than 5  $\mu\text{g/l}$  for a contact time of 38 h. The bed volumes achieved up to 5  $\mu\text{g/l}$  were 1 140. Similarly, the bed volumes achieved for As(III) removal in the first cycle were 1 260. The bed volumes achieved in the remaining cycles decreased. This could be ascribed to the observed loss of GFH along with the effluent during the back-wash operations. The bed volumes achieved for both As(V) and As(III) up to 10  $\mu\text{g/l}$  were 3 240 and 3 000, respectively. The bed volumes achieved for As(V) removal in the present study were high compared to the values reported in the studies using ion-exchange resin (Clifford et al., 1999), and lower than the values reported by Driehaus et al. (1998). In the laboratory studies using an ion-exchange resin, Clifford et al. (1999) achieved bed volumes of 400 to 800 up to a breakthrough arsenic concentration of 2  $\mu\text{g/l}$ , where the influent

**TABLE 3**  
**Summary of the results from column studies using GFH**

Water	Tap water					Kellihier water
	As(V)					
Arsenic species	As(III)					Soluble As
Column cycles	1	2	3	4	5	1
Initial As concentration (µg/l)	500	500	500	500	500	169.3
Flow rate (ml/min)	21.5	21.5	21.5	21.5	21.5	21.5
Mass of GFH (g)	60	60	60	60	60	40
Volume of the media (ml)	43	43	43	43	43	30.5
EBCT (min)	2	2	2	2	2	1.4
Total Throughput volume (l)	137	85	70	54	57	93
Maximum solid phase concentration, 'q <sub>0</sub> ' (mg/g) from the Thomas model	0.88					0.3
'q <sub>0</sub> ', mmol As/g Fe (mmol As/ mol Fe)	0.04					0.03
'k' value from the Thomas model (ml/min·µg)	(2.2)					(1.7)
Regression coefficient, r	0.22					0.05
Bed volumes achieved up to 5 µg/l of As	0.93*	1020	780	540	480	0.91*
Arsenic removal capacity of the media to 5 µg/l (mg/cm <sup>3</sup> )	0.63	0.51	0.39	0.27	0.24	1523
						0.15

\* coefficients are significant at the 95% confidence level.

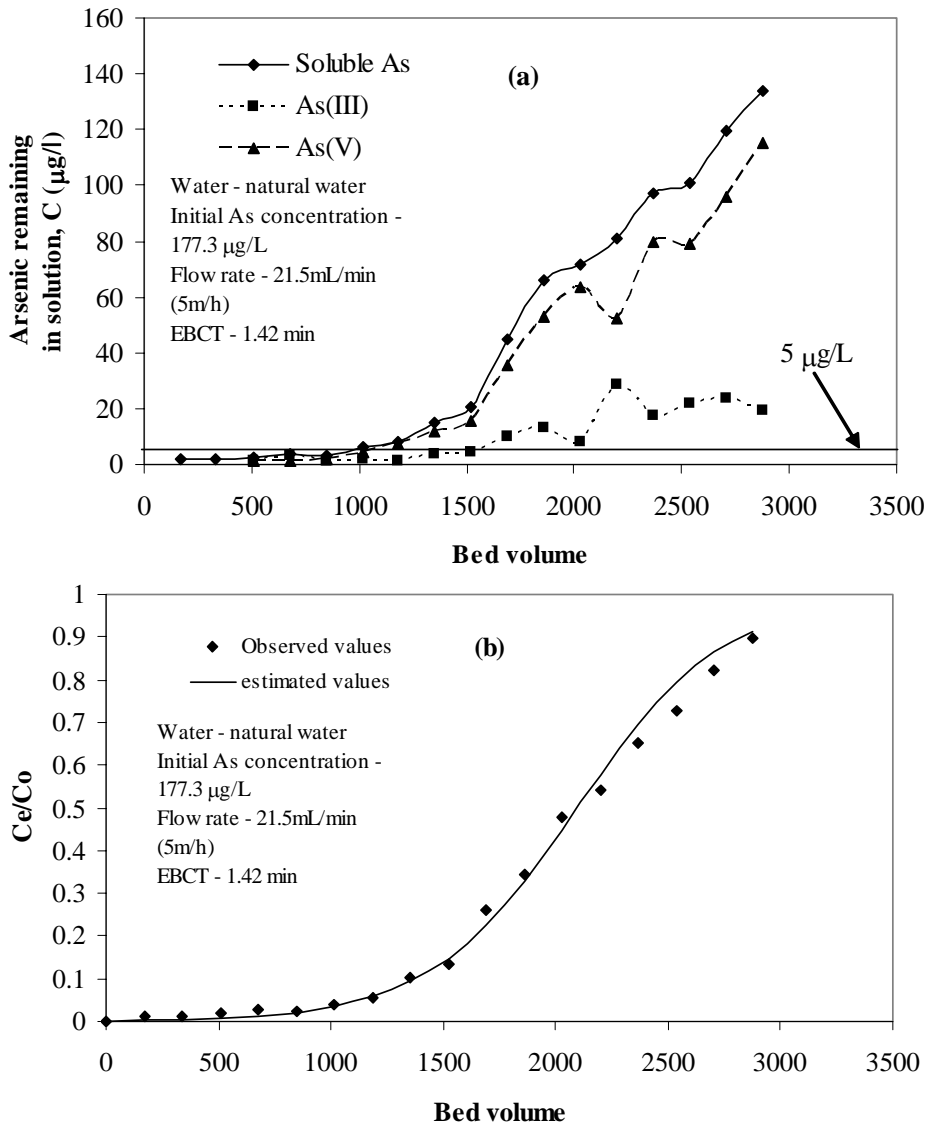
formed with Statistica for Windows (release 5.1) software (Statsoft Inc., 1997) using the Hooke-Jeeves method (start values were 0.1 for all parameters; an initial step size of 2 for all parameters; maximum number of iterations at 50). The model values of  $C_0/C_0$  are shown in Fig. 4 (b). The adsorptive capacity or maximum solid phase concentration ' $q_0$ ' estimated from the Thomas model for As(III) and As(V) was 0.88 and 0.82 mg/g GFH, respectively. In terms of Fe content ' $q_0$ ' for As(III) and As(V) was estimated at 0.04 mmol As/g Fe (2.2 mmol As/mol Fe) and 0.09 mmol As/g Fe (5 mmol As/mol Fe), respectively. The As(V) adsorptive capacity of GFH (0.82 mg/g) estimated in the present study was similar to the value (0.8 g/kg GFH) achieved by Driehaus et al., (1998) in one of the pilot facilities (W) located in Germany.

The arsenic removal capacities to achieve levels of less than 5 µg/l by GFH in the first cycle of column tests for As(III) and As(V) were 0.63 (0.39) and 0.56 mg/cm<sup>3</sup> GFH (0.35 mg/g GFH), respectively. The arsenic removal capacity was calculated by the difference between the applied arsenic loading and the amount removed by GFH, divided by the volume of GFH used in the column tests. These values were higher than the values reported by Simms and Azizian (1997) using activated alumina. In a pilot plant study for arsenic removal from natural water using activated alumina (AA) at a pH of 7.5, they reported that the arsenic removal capacity of AA to 10 µg/l varied between 0.19 and 0.35 g As/kg AA at different empty bed contact times. The results of the present column studies are summarised in Table 3. Data pertaining to arsenic recovery through backwash operations at the end of column operations are shown in Table 4. The average As(V) recovery efficiency (82.5%) for the first four cycles was slightly higher than the recovery efficiency (81.5%) for As(III).

In the column studies with Kellihier water using GFH, the results (Fig. 5 (a)) showed the dominance of As(V) species after 24 h of column operation because of oxidation of As(III) to As(V). Similar to the column studies with Regina tap water, high bed volumes (1 523) were achieved up to 5 µg/l of soluble As. The column data were fitted to the Thomas model. The model (Fig. 5 (b)) fitted well with the observed data. The ' $q_0$ ' value was estimated at 0.28 mg/g GFH (0.03 mmol As/g Fe or 1.7 mmol As/mol Fe).

### Application to practice

Despite the fact that several technologies have been proven to be successful in the removal of arsenic from drinking water at laboratory and pilot-scale studies, the practical applicability of a number of such systems to small communities has not been fully tested and exploited. In addition to a high arsenic removal efficiency, the system should be simple, economically viable and acceptable to the community. Although coagulation-assisted microfiltration and ion-exchange systems may be suitable for large communities, systems based on adsorption/filtration processes are appropriate and advantageous to small communities, especially in



**Figure 5**  
Plot showing a) the arsenic concentration remaining in Kelliher water in the column studies using GFH and b) the estimated values of  $C_e/C_o$  by the Thomas model

developing countries such as Bangladesh. This is due to factors such as simplicity, ease of construction, operation and maintenance. Currently, simple household purification systems such as bucket filtration systems containing sand and iron filings are used in a number of arsenic-affected areas in Bangladesh as short-term measures. However, a permanent solution has to be developed to provide appropriate treatment facilities to supply the drinking water needs of people in small communities. GFH based filtration systems offer a competitive choice amongst the treatment systems available for arsenic removal in small water facilities.

## Conclusions

The following conclusions were made based on this study:

- GFH is effective in reducing both As(III) and As(V) to a level less than 5 µg/l in drinking water.
- The kinetic study showed that less than 5 µg/l of As could be achieved at the pH levels of 6 and 7.6, with highest arsenic removal observed at pH 7.6 (the normal pH of the Regina tap water). The equilibrium time was found to be 6 h.
- In the isotherm studies, the observed data fitted well with both the Freundlich and the Langmuir models and the model equa-

tions were found to be statistically significant at the 95% confidence level. In the studies with Regina tap water the adsorption densities estimated from the Langmuir model for both As(V) and As(III) at a residual concentration of 5 µg/l were 3.4 (0.2) and 1.7 µmol As/g Fe (0.1 mmol As/mol Fe), respectively.

- The speciation of natural water containing arsenic showed that the As(V)/As(III) ratio in the raw water was 0.45. However, conversion of As(III) to As(V) species was observed in the column studies.
- The results of five cycles of column tests with Regina tap water showed that the bed volumes and arsenic removal capacity were high, which suggested that GFH-based filtration systems could be effectively used in small water utilities.

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**TABLE 4**  
**Arsenic recovered from the column studies after backwash operations using GFH**

Adsorbent	As species	Column test cycles	Total As load to the column (mg)	As removed in the column tests (mg)	As recovered by regeneration and back wash (mg)	As recovery efficiency (%)
GFH	As(III)	1	68	66	50	75
		2	43	42	35	82
		3	35	34	30	87
		4	27	26	22	82
	As(V)	1	63	61	51	84
		2	43	42	35	82
		3	34	33	27	81
		4	27	26	22	83

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