

Adsorption Studies with Arsenic onto Ferric Hydroxide Gel in a Non-oxidizing Environment: the Effect of Co-occurring Solutes and Speciation

Bishwajit Nayak, Md. Amir Hossain, Mrinal Kumar Sengupta, Saad Ahamed, Bhaskar Das, Arup Pal and Amitava Mukherjee*

School of Environmental Studies, Jadavpur University, Kolkata-700032, India

Groundwater arsenic contamination has emerged as a major health threat to millions of people around the world. Studying the sorption process of As(III) and As(V) onto ferric hydroxide gel is important to understand the mobilization of arsenic under non-oxidizing conditions. Most of the previous adsorption studies were limited to single element or multi-element equilibrium in synthetic water. To investigate the effect of matrix and speciation in real groundwater systems, adsorption tests with added As(III) and As(V) separately and in mixture were conducted in both double-distilled deionized water (DDDW) and As-safe ($<3 \mu\text{g L}^{-1}$) tubewell water. In DDDW, the As(III)/As(V) ratio in the mixture strongly influenced the sorption behaviour by shifting the adsorption edge and also the efficiency. For As(III) and As(V) mixture in 1:1 proportions in tubewell water, the adsorption of both the species decreased up to pH 8; in the alkaline ranges the adsorption extent was marginally increased in comparison to that in DDDW. When As(III):As(V) was added in 3:1 proportions in tubewell water, the adsorption of both was enhanced in alkaline ranges compared to that in DDDW. When As(V) was predominant [As(V):As(III) = 3:1] in tubewell water, no significant changes were observed for As(V), though adsorption of As(III) was notably retarded. The statistical analysis of the results indicates the concentration ratio of As species in the system has a definite impact on adsorption behaviour onto ferric hydroxide gel.

Key words: arsenic sorption, ferric hydroxide gel, speciation effect, matrix effect

Introduction

Arsenic, a toxic trace element, is a known carcinogen causing multiple adverse health effects (NRC 1999, 2001). Groundwater arsenic contamination in the Bengal delta has been termed the largest mass poisoning in history (Smith et al. 2000). A significant part of the Ganga-Meghna-Brahmaputra (GMB) plain with area 569,749 km² and population 500 million, is at risk of contamination (Chakraborti et al. 2004). Recently, new instances were revealed from different Asian countries, including the eastern Qinghai province, China (Virikutyte and Sillanpää 2006), Nepal (Shrestha et al. 2003), Vietnam (Berg et al. 2001; Agusa et al. 2006), Pakistan (Nickson et al. 2005) and Lower Mekong (Stanger et al. 2005). Arsenic contamination is spread around the globe (Smedley and Kinniburgh 2002).

The WHO provisional guideline value for arsenic in drinking water is set at $10 \mu\text{g L}^{-1}$ (WHO 2004). The U.S. EPA and European Union have also complied with the same standard, though in developing countries like India and Bangladesh the standard remains at $50 \mu\text{g L}^{-1}$.

In natural waters inorganic arsenic occurs mainly in two forms, As(III) and As(V). In circumneutral pH levels the predominant As(V) species are H_2AsO_4^- and divalent HAsO_4^{2-} while the predominant arsenite species is

H_3AsO_3 (Wilkie and Hering 1996). The distribution of different arsenic species depends on redox potential and pH, among other factors. The source and mobility of arsenic species in natural waters and also in different water treatment processes for arsenic removal have received much attention.

One of the possible arsenic mitigation strategies is an arsenic removal plant (ARP). The removal technologies applied in these plants are mostly based on the principles of oxidation, coagulation, precipitation, ion exchange, adsorption, reverse osmosis, etc. Adsorption certainly remains one of the predominant technologies with a variety of sorbents being employed to remove arsenic from water including oxides, oxy hydroxides of iron, manganese and aluminum (Manning and Goldberg 1997; Jain et al. 1999; Chiu and Hering 2000; Gregor 2001; Lin and Wu 2001; Xu et al. 2002).

Hydrated ferric oxide (HFO) seems to be one of the important sorbents both in natural or engineered systems. Sorption of arsenic onto HFO becomes important for dual aspects: for implications in the mobilization processes as well as remedial methods. As shown in Table 1, arsenic sorption behaviour onto HFO was investigated extensively (Pierce and Moore 1982; Dzombak and Morel 1990; Wilkie and Hering 1996; Jain et al. 1999; Raven et al. 1998).

In recent years there have been ongoing experiments on arsenic removal from groundwater using gran-

* Corresponding author; amit.mookerjea@gmail.com

TABLE 1. Previous studies on arsenic sorption onto ferric hydroxide gel

<i>Comment/results</i>	<i>Reference</i>
A wide range of data on the adsorption of both cations and anions onto HFO has been presented for the critical compilation of an adsorption constant for a generalized two-layer model. It was observed that the acid-base chemistry of the HFO surface and the adsorption of anions may be adequately described by considering only a single adsorption site.	Dzombak and Morel (1990)
Kinetics and pH dependence of As(V) and As(III) adsorption on HFO (202 m ² /g). Very high As(V) and As(III) loading found (up to 4.4 mol As kg ⁻¹) at the highest concentration.	Raven et al. (1998)
Adsorption isotherm for arsenite and arsenate over free concentration range from 10 ⁻⁷ to 10 ⁻³ M (pH 4–10). Fitted to Langmuir isotherm at low concentration and linear isotherm at higher concentration. Dzombak and Morel (1990) fitted the data to their diffuse double layer model.	Pierce and Moore (1982)
Sorption of As(V) and As(III) on HFO at As concentration of environmental significance and at pH 4 to 9. Compared result with Dzombak and Morel (1990) model predictions, found generally reasonable agreement. Also observed SO ₄ decreased adsorption of As(V) and As(III), especially at low pH, while Ca increased As(V) adsorption at high pH. As(V) or As(III) adsorption was not significantly affected by 1 mM bicarbonate.	Wilkie and Hering (1996)
As(III) and As(V) adsorption and OH ⁻ release/uptake on synthetic two lime ferrihydrite. As(V) at pH 9.2 released up to 1 mole OH ⁻ /mole As sorbed, whereas As(III) released is <0.25 mole As per mole Fe. At pH 4.6 OH ⁻ released was much less for As(V) adsorption and under these conditions there was a net release of H ⁺ by arsenite. These differences show the mechanism of arsenic adsorption and influence the pH dependence of absorption.	Jain et al. (1999)

ular ferric hydroxides (Thirunavukkarasu et al. 2003; Manna et al. 2003; Manna and Ghosh 2005). Through batch and column studies, Lien and Wilkin (2005) showed an arsenic remediation approach by using zero-valent iron. Zhang and Itoh (2005) demonstrated that both As(III) and As(V) can be removed from aqueous systems by loading Fe(III) oxide on municipal solid waste incinerator melted slag.

Results from single-element equilibrium tests, or synthetic multi-element tests as described in most of the prior publications provide useful fundamental information. Still, these results cannot interpret complex multi-component equilibrium often found in real systems where competition occurs between different species for the sorption sites. Secondly results of tests with As(III) and As(V) ions alone (Wilkie and Hering 1996) may not be enough to predict their adsorption behaviour when both are present, which is the case in most real groundwater systems. In an attempt to address these issues, the present study employs typical groundwater composition [As-safe tubewell water (<3 µg L⁻¹ As)] spiked with As(III), As(V) and a mixture of both. This article reports results from a preliminary investigation into effects of co-occurring ions and speciation of As on its adsorption onto HFO as a function of pH.

Experimental

Standards and Reagents

All the chemicals were of reagent grade. All the solutions were prepared with double-distilled deionized water. All

glassware used for experiments was cleaned by soaking in 10% HNO₃ and rinsed four times with deionized water prior to use. The arsenite and arsenate stock solutions were prepared by dissolving appropriate amounts of As₂O₃ (Merck, Germany) and standard arsenic(V) Titrissol (Merck, Germany), respectively. The standard stock solutions thus prepared, were stored in polyethylene bottles and refrigerated at 4°C. Prior to each analysis, standard As(III) and As(V) solutions were diluted with double-distilled deionized water to 1 mg L⁻¹ As from the arsenic stock solution (1000 mg L⁻¹ As). Analytical grade 1.5% (w/v) sodium tetrahydroborate (NaBH₄, Merck, Germany) dissolved in 0.5% (w/v) sodium hydroxide (NaOH, Merck, India Limited) was used for hydride generation. Analytical grade citric acid (0.25 M) (Merck, India Limited) was used as a complexing agent and 2% KBrO₃ for oxidizing As(III) to As(V) in speciation analysis. Grade acetylene (liquid air) and nitrogen (99.999%) were used as the fuel for the atomic absorbance spectrometer furnace and purge gas for the hydride generation unit, respectively.

Arsenic Analysis

Arsenic analysis was conducted using a Perkin-Elmer Model 3100 atomic absorption spectrometer. The details of the instrumentation and analysis have been discussed previously (Chatterjee et al. 1995; Samanta and Chakraborti 1997). The minimum detection limit with a 95% confidence level was 3 µg L⁻¹ of arsenic. The samples not analyzed on the day of the adsorption experiment were acidified to about pH 1 with concentrated

HNO₃ and stored in 10-mL volumetric flasks. All the samples were analyzed within two days of collection.

As speciation. For speciation we divide the sample in two parts.

- (A) In one part the concentration of total inorganic arsenic [As(III) + As(V)] in the water was measured by FI-HG-AAS after potassium bromate oxidation using 6 M HCl and NaBH₄ (1.5%) solutions as mobile phase.
- (B) In another part, As(III) in the water was measured by using FI-HG-AAS in the presence of citric acid (0.25 M) and NaBH₄ (0.25%) solutions as the mobile phase, so that As(V) is not detected.

Finally, As(V) concentration was calculated from total arsenic by subtracting (B) from (A) (Roy 2003).

Quality control measures for arsenic analysis. Validation of speciation method was carried out using mixed standards for As(III) and As(V). First, the U.S. EPA (United States Environmental Protection Agency) standard was analyzed having 18 µg L⁻¹ As(V). Then, a synthetic mixture was prepared mixing the U.S. EPA standard with known concentrations of As(III) and As(V) and analyzed for speciation to confirm the validity of analytical method. Each experiment was done in triplicate. The coefficient of variation of the triplicate results was within 5%. The known concentrations of As(III) and As(V) were prepared from standard stock solutions as described above. The analytical results are given in Table 2.

Other Analysis Methods

In all the experiments pH was measured with a Systronics digital pH meter (model 335). The pH electrode was calibrated with two buffers (pH 4.0 and 7.0). For tubewell water, Cl⁻ ions were measured by argentometric titration method, SO₄²⁻ was measured by turbidimetric method (using Systronics NEPHALO-TURBIDITY METER 131), total hardness and Ca²⁺ by EDTA Titrimetric Method, and Mg²⁺ by difference between hardness and calcium as CaCO₃. Total alkalinity was measured by titrimetric method to pH 4.5 by using methyl orange indicator (APHA, AWWA, WPCF 1985).

The 1,10-phenanthroline method with UV-visible spectrophotometer was used for iron analysis in water samples (Fries and Getrost 1975).

Conditions and Apparatus for Adsorption Experiments

The ferric hydroxide gel was prepared immediately prior to each adsorption experiment using the following procedure (Wilkie and Hering 1996): a solution of 1 M NaOH was added drop-wise with stirring to 50 mL of 0.05 M Fe (NO₃)₃ in a 250-mL beaker at 25°C. The final pH was kept at 8.5. The pH was allowed to stabilize to ensure the complete precipitation of iron. After precipitation, equal portions of HFO stock suspension was transferred to four polycarbonate centrifuge tubes. The solid was washed four times with deionized water (water-solid separation by centrifugation). The solution was pre-adjusted to the same pH and composition as selected for the adsorption experiments.

In all the experiments ferric hydroxide gel preparation and subsequent adsorption experiments were performed without excluding CO₂. During preparation and adsorption experiments the suspension was continuously purged with 99.99% nitrogen gas. The stock solutions were also purged with nitrogen gas before adding to the adsorption reaction vessel.

The adsorption experiments were run in duplicate for the desired experimental conditions. The coefficient of variation of the results was within 5%. The reaction vessel 600-mL glass beakers (Borosil) were filled with 120 mL of double-distilled deionized water (DDDW) or tubewell water (containing arsenic <3 µg L⁻¹) as per the experimental requirements. The solution was then spiked with arsenic stock solution [1000 mg L⁻¹; in the form of either As(III) or As(V) or a mixture of As(III) and As(V) in different proportions] and then ferric hydroxide gel stock solution, which measured 18 g L⁻¹ Fe (0.25 mL suspension was added to 120 mL volume), was added to obtain the desired concentration in the working solution. Before addition of HFO and arsenic stock solution, pH of the DDDW was in the range of 5.5 to 6.0, and in the case of tubewell water, pH was 6.5 to 7.0. The iron concentration in the working solution was calculated at 37.5 mg L⁻¹. Since the centrifuge tubes used for preparing

TABLE 2. Analytical validation of speciation method with mixed standard samples

Serial no.	Details of sample spiked	Measured total As conc. (µg/L)	Measured As(III) conc. (µg/L)	Calculated As(V) conc. (µg/L)
1	EPA (18 µg/L)	19	—	19
2	EPA (18 µg/L) + As(III) 20 µg/L	40	22	18
3	EPA (18 µg/L) + As(III) 30 µg/L	50	31	19
4	EPA (18 µg/L) + As(V) 40 µg/L	60	—	60
5	EPA (18 µg/L) + As(V) 30 µg/L	48	—	48

the gel suspension had volume markings, we could take the required volume. The pH of the arsenic solution was adjusted to initial experimental pH before addition to the experimental vessel. The suspension was continuously mixed with the help of a magnetic stirrer at 150 rpm for 30 min at 25°C. At the end of the reaction period the final pH was measured and the suspension was filtered through a 0.45- μm (Millipore) filter. The final pH value was not the same as the initial one. The final pH is being reported here as adsorption pH. In the results and discussion section the adsorption pH values are reported. The initial measured experimental pH (before starting the adsorption test) and final measured pH was not the same in all cases; the difference varied on a case to case basis. The absence of detectable iron in filtrates from adsorption studies conducted at pH 4 and 5 demonstrated the suitability of the filter for removal of ferric hydroxide gel colloids. The filtered solution was either immediately analyzed for arsenic or acidified and stored. Dilution due to acid addition to stored samples was accounted for in the calculation for arsenic concentrations. Blank losses (i.e., to the reaction vessels and filters) were evaluated over a range of initial arsenic concentration and pH values consistent with the adsorption experiments. The losses for both As(III) and As(V) were low (below 3%) and negligible filter losses were observed.

Adsorption tests were performed under the following experimental conditions:

- Adsorption of As(III) and As(V) onto ferric hydroxide gel in the pH range 4 to 10 in low As tubewell water, spiked with As.
- Adsorption of a mixture of As(III) and As(V) (proportions 1:1, 1:3 and 3:1) onto ferric hydroxide gel in double-distilled deionized water media and low-As tubewell water, both spiked with As.

Statistical Analysis

The data from adsorption experiments under different conditions were analyzed and interpreted using standard statistical tools such as the independent sample t-test, Duncan multiple comparison test, analysis of variance (F-test) and multiple regression analysis with categorical independent variable applying dummy variable approach. All these analyses were performed using the statistical package SPSS version 11.5.

Results and Discussion

Arsenic adsorption experiments were undertaken at different pH values from 4 to 10, with 1 mg L⁻¹ (13.42 μM) As and 37.5 mg L⁻¹ (671 μM) total Fe with As:Fe molar ratio at 1:50. Since no external buffering agent was applied to adjust pH, there was a difference between initial and final pH. The final equilibrium pH is reported

here as adsorption pH. All the tests were performed under continuous nitrogen purging to maintain a non-oxidizing atmosphere.

To observe the effect of co-occurring solutes on the adsorption behaviour of As(III), As(V) and their synthetic combination sorption experiments were conducted with tubewell water having total As <3 $\mu\text{g L}^{-1}$.

The analysis of tubewell water was: As <3 $\mu\text{g L}^{-1}$, Fe 2.095 mg L⁻¹, Cl⁻ 226 mg L⁻¹, total hardness 300 mg L⁻¹ CaCO₃, Ca²⁺ 81 mg L⁻¹, Mg²⁺ 219 mg L⁻¹, SO₄²⁻ 169 mg L⁻¹, and total alkalinity 817 mg L⁻¹ CaCO₃.

Adsorption of As(III) onto Ferric Hydroxide Gel in Presence Co-occurring Solutes

No clear trend in adsorption with pH could be observed in either tubewell water media or control (deionized distilled water) (Fig. 1). In comparison to control, decreased adsorption in tubewell water was noted over a range from pH 4 to 9. This effect is slightly more pronounced at lower pH values, and decreases with increas-

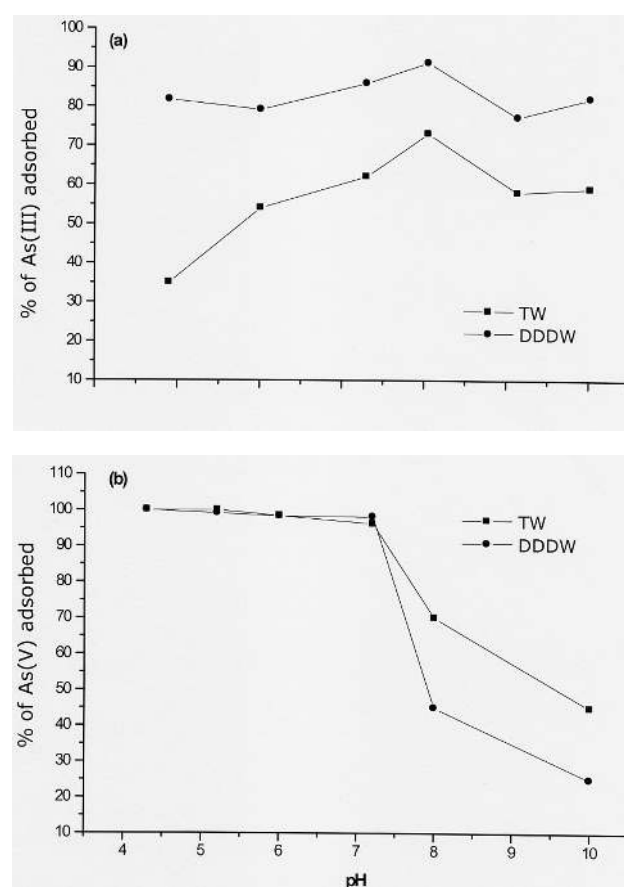


Fig. 1. Adsorption of arsenic onto HFO in presence of cations (a) As(III) (b) As(V) [TW is tubewell water (composition mentioned in the text); DDDWW is double-distilled deionized water]. Here pH is defined as measured pH after the adsorption experiment.

ing pH. The tubewell water represents a typical multi-adsorbate system. Previous studies of competitive adsorption of anions on various iron oxides (Balistrieri and Murray 1987; Mesuere and Fish 1992a,b) suggested that effects of surface heterogeneity on adsorption may be more pronounced in multi-adsorbate than in single adsorbate systems. In particular, when the concentrations of competing adsorbates are vastly dissimilar the preferential adsorption of the minor component at a strong binding site could dramatically increase its apparent competitiveness with respect to the major component. This may have caused decreased adsorption of As(III) in tubewell water.

Adsorption of As(V) onto Ferric Hydroxide Gel in Presence of Co-occurring Solutes

Comparisons between Fig. 1A and 1B indicate that in the pH range 4 to 7, As(V) is more strongly adsorbed than As(III) irrespective of the matrix used. This behaviour is well supported from previously published literature (Pierce and Moore 1982; Wilkie and Hering 1996). But at higher pH values, the adsorption decreased drastically with 20% adsorption in DDDW at pH 9. Another group (BGS-DPHE 2001) also observed a decrease of adsorption above pH 7 and noted that the desorption edge depends strongly on the solid/solution ratio and these pH values are not fixed; the higher the solid-solution ratio the smaller the desorption at a given pH and the sorption edge shifts to a higher pH. The implication of this observation is that as the iron concentration (a few mg L⁻¹) typically prevalent in Bangladesh groundwater (BGS-DPHE 2001) and used in arsenic removal plants As(V) sorption decreases after pH 7, a pH shift may result in desorption of As(V) from ferric hydroxide gel and concomitant increase in dissolved arsenic in solution in a closed system.

The presence of co-occurring solutes (tubewell water) enhanced As(V) adsorption at pH values greater than 7.0. The adsorption of a particular adsorbate is sometimes enhanced rather than inhibited in a multi-adsorbate system (cooperative effect). In an adsorption experiment with As(V) at pH 9 with a total As(V) concentration of 0.47 μM and a total iron concentration of 50 μM, addition of 3.0 μM calcium was observed to increase As(V) adsorption (Wilkie and Hering 1996). The adsorption of As(V) onto HFO is mostly attributed to the formation of highly charged negative species as mentioned in detail in section 2.5. Above p*H*_{PZC} of HFO (pH 8.1), due to change in the electrostatic characteristics of the HFO surface, the adsorption of anionic species is retarded. Therefore we observed a drop in adsorption above pH 8 when co-ions are absent. However, the presence of cations like Ca²⁺ (81 mg L⁻¹ in tubewell water) in much higher concentrations than the arsenate ions, can maintain the positive charge characteristic of the HFO surface even at pH 9. This may have caused enhanced adsorption of arsenate at alkaline pH ranges.

Adsorption from Synthetic Mixture of As(III) and As(V) onto Ferric Hydroxide Gel in Double-Distilled Deionized Water

Redox conditions are important triggers which control behaviour of many major and minor species in the natural waters, and arsenic is no exception. Equilibrium thermodynamic calculations predict that As(V) concentrations should be greater than As(III) concentrations in all but strongly reducing conditions. Cherry et al. (1979) suggested that As(V)/As(III) ratios in natural waters may serve as an indicator of ambient redox conditions as redox conditions are sufficiently rapid to occur over periods of years. Arsenic speciation studies in West Bengal and Bangladesh have revealed a large range in the dissolved concentrations of arsenite and arsenate present in the groundwater (Das et al. 1995). The modal proportion of arsenite appears to be between 50 to 60% of the total arsenic (BGS-DPHE 2001).

The adsorption studies were carried out with synthetic mixtures of As(V) and As(III) in different proportions [1:1, 1:3, 3:1] in deionized distilled water under nitrogen atmosphere to observe the effect of variable species ratios. Total As concentration was fixed at 13.42 μM and iron concentration at 671 μM with an applied As:Fe ratio of 1:50.

The adsorption behaviour in the mixture [As(III):As(V) = 1:1] is shown in Fig. 2A. The maximum adsorption of As(III) in the presence of As(V) occurred at pH 7 to 7.5 and thereafter decreased in the alkaline range (up to 49% at pH 9.4). When present with As(III) the As(V) adsorption was enhanced, with around 70% adsorption at pH 9.4. This result contradicts the general trend of drastic decrease in adsorption of As(V) in alkaline pH levels.

The adsorption behaviour in the mixture [As(III):As(V) = 3:1] is shown in Fig. 2B. Here the maximum adsorption of both As(III) and As(V) occurred at around pH 6.5. As(III) adsorption decreased after around pH 8, up to 54% at pH 9. These results indicate that desorption of As(III) is favoured to that of As(V), when As(III) is present in equal proportions or in excess in alkaline pH levels.

The adsorption behaviour in the mixture [As(III):As(V) = 1:3] in DDDW is shown in Fig. 2C. In this case, adsorption of both As(III) and As(V) follow a similar trend. After pH 7 the adsorption of both the ions drops. This indicates that in pH values generally found in groundwater, desorption of both As(III) and As(V) is favoured when As(V) is present in excess.

From these results (Fig. 2A to 2C), it can be seen that the ratio of As(III)/As(V) in the mixture strongly influences the sorption behaviour onto ferric hydroxide gel by shifting the adsorption edge as well as the desorption extent. The effect is more prevalent in highly alkaline pH ranges, which is more relevant to the mobilization process in groundwater and remedial processes.

Adsorption of Mixture of As(III) and As(V) onto Ferric Hydroxide Gel in Presence of Co-occurring Solutes

Adsorption tests were performed after spiking a synthetic mixture of As(III) and As(V) in different proportions [1:1, 1:3, 3:1] in tubewell water media. Total As concentration was fixed at $13.42 \mu\text{M}$ (1 mg L^{-1}) and total Fe at $671 \mu\text{M}$ (37.5 mg L^{-1}) keeping the As:Fe

molar ratio at 1:50. The comparison between adsorption behaviour in presence (tubewell water) and absence (DDD W) of co-ions is discussed below.

As seen in Fig. 2A and 3A, in the presence of co-occurring solutes when As(III) and As(V) are present in equal proportions in the synthetic mixture, the adsorption of both As(V) and As(III) decreased till pH 8. In the alkaline ranges the adsorption extent was marginally increased in comparison to that in distilled deionized water.

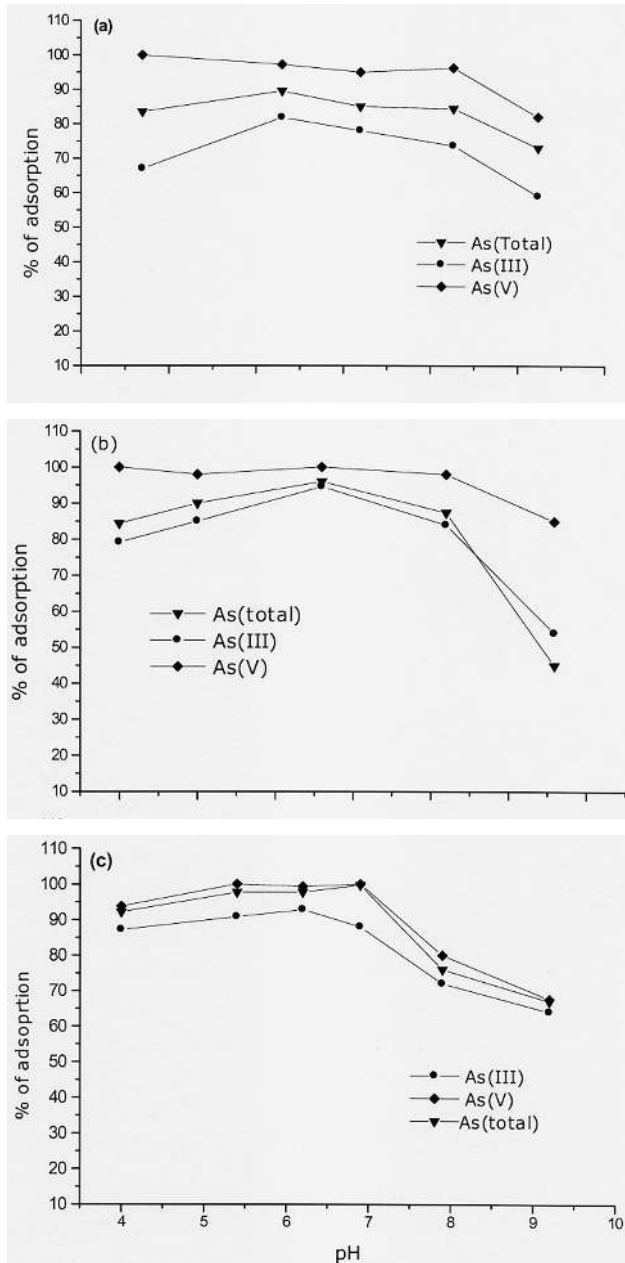


Fig. 2. Adsorption from synthetic mixture of As(III) and As(V) onto HFO in DDD W media (a) As(III):As(V) = 1:1, (b) As(III):As(V) = 3:1, (c) As(III):As(V) = 1:3. Here pH is defined as measured pH after the adsorption experiment.

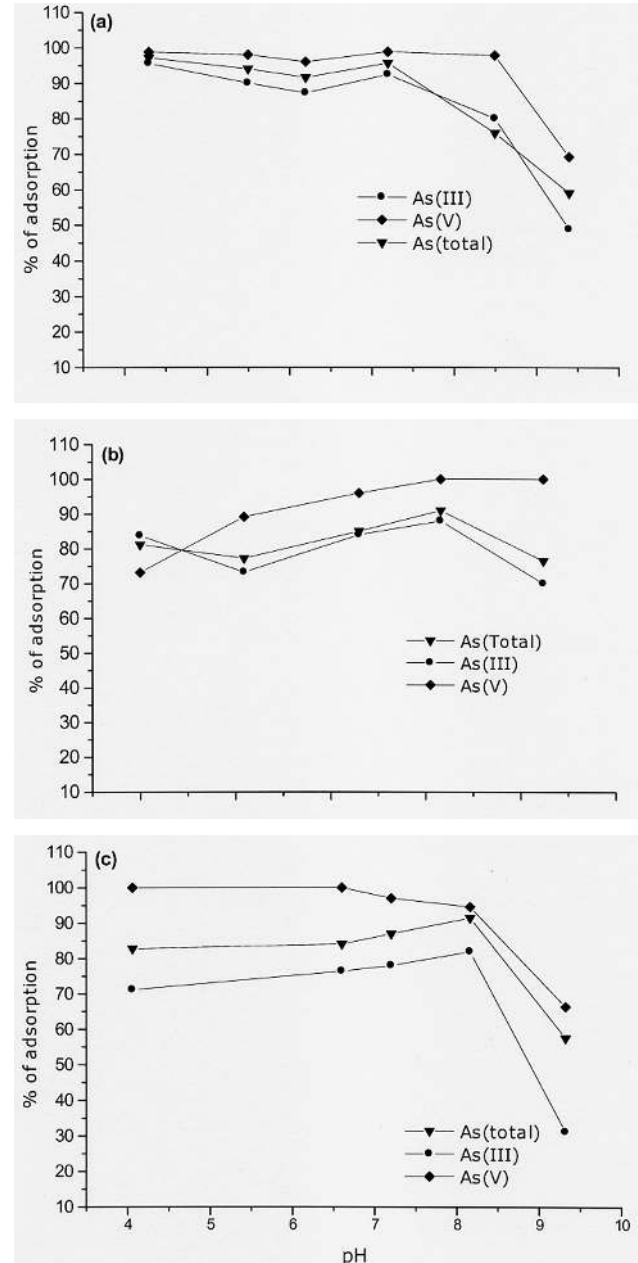


Fig. 3. Adsorption from synthetic mixture of As(III) and As(V) onto HFO in presence of co-ions (a) As(III):As(V) = 1:1, (b) As(III):As(V) = 3:1, (c) As(III):As(V) = 1:3. Here pH is defined as measured pH after the adsorption experiment.

When As(III):As(V) mixture was present in 3:1 proportions in tubewell water, the adsorption of both As(III) and As(V) was enhanced in alkaline ranges with adsorption minima raised for both As(III) as well as As(V) (Fig. 2B and 3B).

When As(V) was predominant [As(V):As(III) = 3:1] in tubewell water, no significant changes were observed in adsorption of As(V) though adsorption of As(III) was notably retarded (Fig. 2C and 3C).

The implications of these results (Fig. 3A to 3C) are far reaching especially to understand the mobilization aspect and designing proper sorbents for arsenic removal from groundwater. In natural water systems we are likely to encounter the presence of both As(III) and As(V) with other co-ions. The co-ions, depending on their characteristics and the prevailing redox conditions and pH, may have retarding, associative or neutral effects on As sorption on ferric hydroxide gel. The results demonstrate the cumulative effect of these factors. It can also be observed from these results that in a multi-adsorbate system replicating typical groundwater composition, arsenic adsorption behaviour onto ferric hydroxide gel is definitely influenced by speciation of arsenic.

Comparison among Different Varying Conditions of the Adsorption by Statistical Analysis

The results of ANOVA (analysis of variance) show no significant difference between adsorption behaviour of As(III) and As(V) species irrespective of pH level. However, the Duncan multiple range test showed a significant difference between adsorption behaviour of As(III) alone and As(III) in the 1:3 mixture. The results of an independent sample t-test also support the fact. Multiple regression analysis implies As(III) adsorption in 1:3 mixtures is more than As(III) alone. Therefore statistical analysis corroborates the fact that the presence of both As(III) and As(V) influences the adsorption behaviour.

Conclusions

The salient points from our observations are noted below:

1. In the absence of co-ions, the ratio of As(III)/As(V) in the mixture strongly influences the sorption behaviour onto ferric hydroxide gel by shifting the adsorption edge as well as desorption extent. The effect is more prevalent in highly alkaline pH ranges.
2. Comparing the adsorption results between DDDW and tubewell water systems:
 - i. For As(III):As(V) mixture in 1:1 proportions in the tubewell water, the adsorption of both As(V) and As(III) decreased till pH 8; in the alkaline ranges the adsorption extent was marginally increased.

- ii. When As(III) was predominant [As(V):As(III) = 1:3] in the tubewell water, the adsorption of both As(III) and As(V) was enhanced in alkaline ranges with adsorption minima raised for both.
- iii. When As(V) was predominant [As(V):As(III) = 3:1] in tubewell water, no significant changes were observed in adsorption of As(V) though adsorption of As(III) was notably retarded.

Acknowledgements

This work is part of a project sponsored by the Department of Science & Technology (DST), Government of India. We are grateful to Dipankar Chakraborti, Director and Head, School of Environmental Studies, for encouragement, critical discussion and useful advice.

References

- Agusa T, Kunito T, Fuzihara J, Kubota R, Minh TB, Trang PTK, Iwata H, Subramanian A, Viet PH, Tanabe S. 2006. Contamination by arsenic and other trace elements in tube well water and its risk assessment in Hanoi, Vietnam. *Environ. Pollut.* 139:95–106.
- APHA, AWWA, WPCF. 1985. Standard methods for the examination of water and wastewater. 16th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation.
- Balistreri LS, Murray JW. 1987. Influence of major ions of seawater on the adsorption of simple organic acids by goethite. *Geochim. Cosmochim. Acta.* 51:1151–1160.
- Berg M, Tran HC, Nguyen TC, Pham MV, Schertenleib R, Giger W. 2001. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environ. Sci. Tech.* 35:2621–2626.
- BGS-DPHE. 2001. Arsenic contamination in groundwater of Bangladesh. In Kinniburgh DG, Smedley PL (ed.), British Geological Survey, Technical Report WC/00/19, 4 volumes. British Geological Survey, Keyworth.
- Chakraborti D, Sengupta MK, Rahman MM, Ahamed S, Chowdhury UK, Hossain MA, Mukherjee SC, Pati S, Saha KC, Dutta RN, Quamruzzaman Q. 2004. Groundwater arsenic contamination and its health effects in the Ganga-Meghna-Brahmaputra plain. *J. Environ. Monitor.* 6:74N–83N.
- Chatterjee A, Das D, Mandal BK, Chowdhury TR, Samanta G, Chakraborti D. 1995. Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 1. Arsenic species in drinking water and urine of the affected people. *Analyst* 120:643–650.
- Cherry JA, Shaikh AU, Tallman DE, Nicholson RV. 1979. Arsenic species as an indicator of redox conditions in groundwater. *J. Hydrol.* 43:373–392.
- Chiu VQ, Hering JG. 2000. Arsenic adsorption and oxida-

- tion at magnetite surfaces, 1. Method for simultaneous determination of adsorbed and dissolved arsenic species. *Environ. Sci. Tech.* **34**:2029–2034.
- Das D, Chatterjee A, Mandal BK, Samanta G, Chanda B, Chakraborti D.** 1995. Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nails, urine, skin - scale and liver tissue (biopsy) of the affected people. *Analyst* **120**:917–924.
- Dzombak DA, Morel FMM.** 1990. Surface-complexation modeling - ferric hydroxide. John Wiley, New York.
- Fries J, Getrost H.** 1975. Organic reagents for trace analysis. Merck, Darmstadt, Germany.
- Gregor J.** 2001. Arsenic removal during conventional aluminium-based drinking-water treatment. *Water Res.* **35**:1659–1664.
- Jain A, Raven KP, Loeppert RH.** 1999. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH⁻ charge stoichiometry. *Environ. Sci. Tech.* **33**:1179–1184.
- Lien H, Wilkin RT.** 2005. High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **59**:377–386.
- Lin TF, Wu JK.** 2001. Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Res.* **35**:2049–2057.
- Manna BR, Dey S, Debnath S, Ghosh UC.** 2003. Removal of arsenic from groundwater using crystalline hydrous ferric oxide (CHFO). *Water Qual. Res. J. Canada* **38**:193–210.
- Manna BR, Ghosh UC.** 2005. Pilot-scale performance of iron and arsenic removal from contaminated groundwater. *Water Qual. Res. J. Canada* **40**:82–90.
- Manning BA, Goldberg S.** 1997. Adsorption and stability of As (III) at the clay-mineral water interface. *Environ. Sci. Tech.* **31**:2005–2011.
- Mesuere K, Fish W.** 1992a. Chromate and oxalate adsorption on goethite. 1. Calibration of surface complexation models. *Environ. Sci. Tech.* **26**:2357–2365.
- Mesuere K, Fish W.** 1992b. Chromate and oxalate adsorption on goethite. 2. Surface complexation modeling of competitive adsorption. *Environ. Sci. Tech.* **26**:2365–2370.
- Nickson RT, McArthur JM, Shrestha B, Kyaw-Myint TO, Lowry D.** 2005. Arsenic and other drinking water quality issues, Muzaffargarh district, Pakistan. *Appl. Geochem.* **20**:56–68.
- NRC.** 1999. Arsenic in drinking water. National Academy Press, Washington DC.
- NRC.** 2001. Arsenic in drinking water, 2001 update. National Academy Press, Washington DC.
- Pierce ML, Moore CB.** 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**:1247–1253.
- Raven KP, Jain A, Loeppert RH.** 1998. Arsenite and arsenate adsorption ferrihydrite: kinetics, equilibrium and adsorption envelopes. *Environ. Sci. Tech.* **32**:344–349.
- Roy N.** 2003. Flow injection hydride generation atomic absorption spectrometry, a fast, reliable and sensitive method for determination of total arsenic in hand tubewell water. M.Sc. thesis, Jadavpur University, Kolkata, India.
- Samanta G, Chakraborti D.** 1997. Flow injection atomic absorption spectrometry for the standardization of arsenic, lead and mercury in environmental and biological standard reference materials. *Fresenius J. Anal. Chem.* **357**:827–832.
- Shrestha RR, Surestha MP, Upadhyay NP, Pradhan R, Maskey A, Maharjan M, Tuladhar S, Dahal BM, Shrestha K.** 2003. Groundwater arsenic contamination, its health impact and mitigation program in Nepal. *J. Environ. Sci. Health A* **38**:185–200.
- Smedley PL, Kinniburgh DG.** 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**:517–568.
- Smith AH, Lingas EO, Rahman M.** 2000. Contamination of drinking water of arsenic in Bangladesh. A public health emergency. *Bull. World Health Org.* **78**:1093–1103.
- Stanger G, Troung TV, Ngoc KSLTM, Luyen TV, Tuyen TT.** 2005. Arsenic in groundwaters of the Lower Mekong. *Environ. Geochem. Health* **27**:341–357.
- Thirunavukkarasu OS, Viraraghavan T, Subramanian KS.** 2003. Arsenic removal from drinking water using granular ferric hydroxide. *Water SA* **29**:161–170.
- Virkutyte J, Sillanpää M.** 2006. Chemical evaluation of potable water in Eastern Qinghai Province, China: human health aspects. *Environ. Int.* **32**:80–86.
- WHO.** 2004. Guidelines for drinking-water quality. Third ed., Vol. 1, Recommendations, World Health Organization, Geneva.
- Wilkie JA, Hering JG.** 1996. Adsorption of arsenic onto ferric hydroxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloid. Surf. A* **107**:97–110.
- Xu YH, Nakajima T, Okhi A.** 2002. Adsorption and removal of arsenic by aluminium loaded Shirasuzelite. *J. Hazard. Mat. B* **92**:275–287.
- Yan X-P, Kerrich R, Hendry MJ.** 2000. Distribution of arsenic (III), arsenic (V), and total inorganic arsenic in pore-waters from a thick till and clay rich aquitard sequence, Saskatchewan, Canada. *Geochim. Cosmochim. Acta.* **64**:2637–2648.
- Zhang F-S, Itoh H.** 2005. Iron oxide-coated slag for arsenic removal from aqueous system. *Chemosphere* **60**:319–325.

Received: May 1, 2006; accepted: June 20, 2006.