

## Reduction of arsenic in groundwater by coprecipitation with iron

R. Mamtaz and D. H. Bache

### ABSTRACT

This study examines the potential of removing arsenic from water by coprecipitation with naturally occurring iron. It focuses on the conditions found in the groundwater in Bangladesh where there is a need to develop a low-cost method of arsenic removal, which can be implemented at household level. The experimental study examined the sensitivity of removal of arsenic in response to manual mixing and prolonged settlement. It was demonstrated that up to 90% of the arsenic could be removed after 3 days' settlement, this being sufficient to attain the Bangladesh standard of arsenic concentration of  $0.05 \text{ mg l}^{-1}$  provided the Fe/As ratio and pH were favourable. The necessary iron (as  $\text{Fe}^{3+}$ ) to attain the standard was expressed by  $\text{Fe} = 66 \text{ As}^{1.75}$ , where Fe and As are in  $\text{mg l}^{-1}$ . The study also examined the effects of interference and found for typical levels of co-occurring solutes encountered in the groundwater in Bangladesh, that removal was enhanced. It was also apparent that the removal rate was sensitive to the form of the iron. There was evidence that adsorption may be the dominating trapping mechanism when Fe/As weight ratio was  $\geq 10$ .

**Key words** | adsorption, arsenic, arsenite, coprecipitation, iron, low cost

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### INTRODUCTION

Arsenic, a toxic and carcinogenic inorganic contaminant, presents potentially serious environmental problems throughout the world. Recent epidemiological studies of several countries like Taiwan, Bangladesh and India suggested that arsenic exposure might pose a significant health risk. New regulations for the maximum contaminant level (MCL) of arsenic in drinking water have been proposed by USEPA; these aim at a standard in the range of  $2\text{--}20 \mu\text{g l}^{-1}$ . The WHO drinking water standard for arsenic is  $10 \mu\text{g l}^{-1}$ . This is more rigorous than the  $50 \mu\text{g l}^{-1}$ , which is the allowable limit for arsenic in Bangladesh (DOE 1991).

Technologies for removal of arsenic from water already exist (Kartinen and Martin 1995). However, these techniques are not suitable for developing countries such as Bangladesh where the water supply system is not centralised; individual household or small groups are served by their own tube well. Solutions to the problem of arsenic removal from drinking water necessitate the

development of technology that can be implemented at household level at very low cost.

A related problem in the groundwaters of Bangladesh and in some other parts of the world is the presence of iron. While this not a health hazard, it is usually removed because of taste and staining problems. It is well known that iron hydroxide adsorbs arsenic (Ferguson and Gavis 1972). In this study we attempt to exploit the naturally occurring iron as a means of arsenic removal through the development of simple practices based on adsorption-coprecipitation and settlement. This work extends the previous studies reported in Mamtaz and Bache (2000).

### BACKGROUND

#### Groundwater in Bangladesh: arsenic and iron

The presence of arsenic in groundwater in Bangladesh is the most serious health hazard the country has ever faced.

A recent study carried out by BGS and Mott Macdonald (1999) shows many areas within Bangladesh with arsenic concentration greater than  $0.05 \text{ mg l}^{-1}$  implying that millions of people are at serious risk of arsenic poisoning. According to the EGIS (1997) report the concentration of arsenic varies from  $0.02$  to  $0.5 \text{ mg l}^{-1}$ . This aspect was examined in some detail in Mamtaz and Bache (2000). The latter paper also provides detail of the distribution of iron in groundwater in Bangladesh. Groundwater in about 65% of the area of Bangladesh contains dissolved iron in excess of  $2 \text{ mg l}^{-1}$  and in many areas concentration is as high as  $15 \text{ mg l}^{-1}$  (Ahmed *et al.* 1998). While arsenic and iron pose individual problems, their association in groundwater has the potential to provide a simple means of removing arsenic by coprecipitation and adsorption.

### Arsenic chemistry and its removal

Arsenic occurs in waters in several different forms depending on the pH and redox potential  $E_h$ . Arsenate (As(V)) and arsenite (As(III)) are the primary forms of arsenic found in natural waters (Ferguson and Anderson 1974). The thermodynamically stable forms are As(V) in oxygenated surface water and As(III) in reducing groundwater. The latter is of concern in this study. However, both forms can occur together in both environments due to the slow oxidation and reduction kinetics (Edwards 1994).

The review paper by Jekel (1994) indicated that coagulation-precipitation is a very effective and most frequently applied technique in arsenic removal. In this technique, addition of coagulant facilitates the conversion of soluble arsenic species into insoluble products through coprecipitation and adsorption (Shen 1973; Sorg and Logsdon 1978; Dutta and Chaudhuri 1991; Edwards 1994; Cheng *et al.* 1994; Hering *et al.* 1996). Much of the research concerns the removal of As(V). In contrast, relatively little work has been carried out on As(III) removal. Among those published, Sorg and Logsdon (1978) carried out a study with initial As(III) concentration as high as  $0.3 \text{ mg l}^{-1}$ , in the range encountered in a significant part of Bangladesh. Most work has focused on As(III) in the range  $0.015$ – $0.15 \text{ mg l}^{-1}$  (Edwards 1994; Hering *et al.* 1996; McNeill and Edwards 1997). Hering *et al.* (1996)

reported more than 75% removal of As(III) by ferric chloride coagulation ( $20 \text{ mg l}^{-1} \text{ FeCl}_3$ ) when initial As(III) concentration was  $20 \text{ } \mu\text{g l}^{-1}$  at pH 7.0. In the case of Sorg and Logsdon (1978), they found 50–60% removal with initial As(III) concentration of  $0.3 \text{ mg l}^{-1}$  using coagulation with ferric ions of  $0.09 \text{ mmole l}^{-1}$  in the pH range 5–9.

Adsorption of arsenic onto preformed  $\text{Fe}(\text{OH})_3$  has also been shown to be an effective method for removing arsenic. As with coagulation, the removal of As(III) by adsorption is less than that of As(V). Typical adsorption densities for As(V) range from  $0.075$  to  $0.16 \text{ mg As(V) per mg Fe}$  for pH within the range 4–7 (Wilkie and Hering 1996; Driehaus *et al.* 1998). For As(III), the adsorption density varies from  $0.06$  to  $0.07 \text{ mg As(III) per mg Fe}$  at pH 7.0 (Pierce and Moore 1982; Wilkie and Hering 1996). Hering *et al.* (1997) report that arsenic removal during coagulation with  $\text{FeCl}_3$  is more efficient than arsenic adsorption onto preformed hydrous ferric oxide.

Settlement is a well-known mechanism in the context of iron precipitation and iron removal. Depending on the initial iron concentration in the raw water, Ghosh and O'Connor (1966) indicated that a 1-h design period was 'inadequate for complete iron precipitation'. It suggests that where arsenic removal depends on iron precipitation, the settling time must exert a major influence on the removal process. A study carried out by Shen (1973) with just arsenic-containing water, showed that sedimentation could only remove 8.7% arsenic after 24-h settlement. A drawback of the approach used by Ghosh and O'Connor (1966) was the lack of settling time. In the case of Shen (1973), the study was restricted to arsenic and provides no insight into the potential influence of iron on the removal efficiency.

### MATERIALS AND METHODS

Laboratory nano-pure water was used for the preparation of the standard and sample waters. The chemicals employed for the experiments were general purpose grade (GPR) and used without any purification. Solutions of arsenic (As(III)) were prepared from concentrated stock

solution of arsenic trioxide,  $\text{As}_2\text{O}_3$ , ( $1 \text{ mg ml}^{-1}$ ) in  $0.5 \text{ M l}^{-1}$  HCl supplied by BDH, UK, for use in the tests. In common with other studies (Shen 1973; Edwards 1994; Cheng *et al.* 1994) the iron presence was based on  $\text{FeCl}_3$  solution obtained by dissolving solid  $\text{FeCl}_3$  in nano-pure water. This study also examined the influence of the form of iron. For this purpose,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution was used to provide the ferrous form of iron ( $\text{Fe}^{2+}$ ). In general, the iron salt solution was added to the arsenic-containing solution.

All experiments were performed with a constant ionic strength of  $0.01 \text{ M l}^{-1}$   $\text{NaNO}_3$  and  $0.1 \text{ g l}^{-1}$   $\text{NaHCO}_3$  to provide necessary alkalinity. pH was maintained by adding  $0.1 \text{ M NaOH}$ . All glassware was cleaned by soaking in  $10\% \text{ HNO}_3$  and rinsed three times with nano-pure water. Blank tests (without Fe) confirmed that no arsenic was lost through adsorption onto the glassware. Each type of test was carried out in (at least) triplicate.

Total arsenic was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) method. In the ICP-AES method, all samples and standards were acidified according to the *Standard Methods* (1995).

Values of the parameters such as arsenic, pH and iron/arsenic ratios were chosen to be representative of the range found in Bangladesh (EGIS 1997). The As(III) form of arsenic was selected for the experimental investigation, As(III) having been identified as the prevalent form in the most severely affected areas of Bangladesh (BGS 2000). Experiments were carried out with initial As(III) concentration of  $0.2 \text{ mg l}^{-1}$ , Fe dosages of  $4.0 \text{ mg l}^{-1}$  and pH 7.5. The selection of these parameters was justified in Mamtaz (2000).

Additional detail on methods is included in the subsequent text to support specific parts of the experimental programme.

## EXPERIMENTS AND RESULTS

### Mixing, filtration and settlement

Mixing is a necessary stage in order to ensure aeration and to induce flocculation, as well as assuring the dispersion of

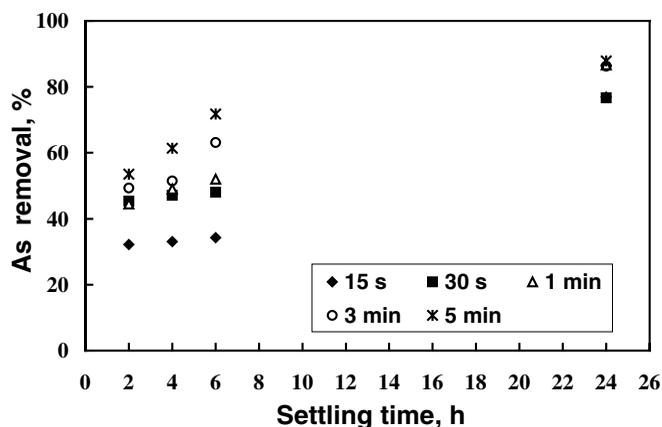
**Table 1** | As removal at different mixing conditions of filtered and unfiltered samples after 2 h settlement (Initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5)

Test condition	Mean As removal (%)	
	Filtered	Unfiltered
Manual mixing:		
15 s manual mixing	63.7	32.2
30 s manual mixing	63.6	45.4
1 min manual mixing	64.3	44.5
3 min manual mixing	64.0	49.3
5 min manual mixing	63.6	53.5
Mechanical mixing	68.5	60.4

chemicals. At village level, shaking is a straightforward means of achieving mixing. This was compared with mechanical mixing, the latter being included for reference purposes. Similarly, filtration was introduced for reference purposes, but the prime focus of the study was to exploit sedimentation as a means of achieving solid–liquid separation following the initial As–Fe interaction.

Mechanical mixing was applied to  $1 \text{ l}$  of sample water ( $0.01 \text{ M l}^{-1}$   $\text{NaNO}_3$  and  $0.1 \text{ g l}^{-1}$   $\text{NaHCO}_3$ ) containing  $0.2 \text{ mg l}^{-1}$  As(III),  $4.0 \text{ mg l}^{-1}$  Fe at pH 7.5. Samples held in a 2-l conical flask were mixed in an orbital shaker (KL2) at a rapid rate (410 rpm) for 5 min, at a slow rate (100 rpm) for 25 min and allowed to settle. In the series based on manual mixing, samples were shaken vigorously for periods in the range of 15 s to 5 min and then allowed to settle. After 2-h settlement, two sets of supernatant were collected at a depth of 20 mm from the top surface from each type of sample (mechanical and manually mixed samples). One set of samples was analysed for residual As after filtration through a  $0.45 \mu\text{m}$  filter paper and another set was analysed for the same conditions, but without filtration. Table 1 presents the effects of mixing condition and filtration on As removal at different mixing times.

For the filtered samples, shown in Table 1, it is observed that the removal efficiency is insensitive to the



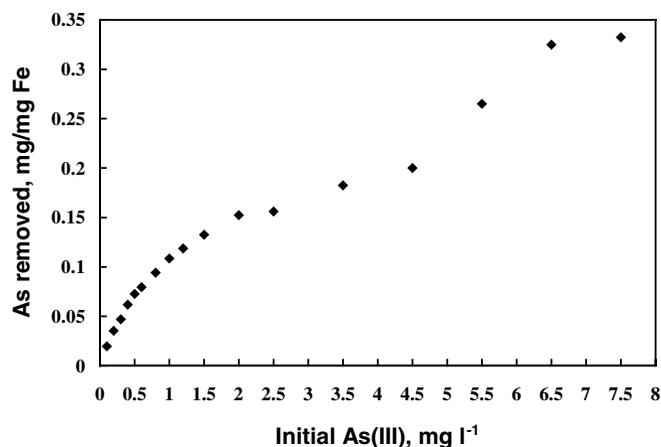
**Figure 1** | Effects of settling time on As removal for manually mixed unfiltered samples at varying mixing time with initial As(III) concentration of  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5.

mixing regime, whereas for the unfiltered samples, removal depends on mixing type and time. In the latter case, the duration of mixing probably enhances flocculation, because it seems likely that the larger removal rates are associated with larger particle sizes. It is seen that 5 min manual mixing is almost as effective as mechanical mixing.

To investigate the effects of settlement on As removal, tests were carried out following the same procedure as the manual mixing method, the samples being allowed to settle for 24 h. Supernatant was collected at specified time intervals, 2, 4, 6 and 24 h and analysed for residual As without filtration. Figure 1 shows the effects of settling time on As removal for manually mixed unfiltered samples at varying mixing times. In Figure 1 it is evident that at shorter settling times, say 2–6 h, removal is fairly sensitive to the mixing time. In contrast, at a longer settling time (24 h) removal is less sensitive to the initial stage of mixing.

### Insight into the removal mechanism

From the experiments described above, it was evident that manual mixing followed by settlement was reasonably effective for reducing the levels of arsenic in the presence of iron. Having gained this experience, additional



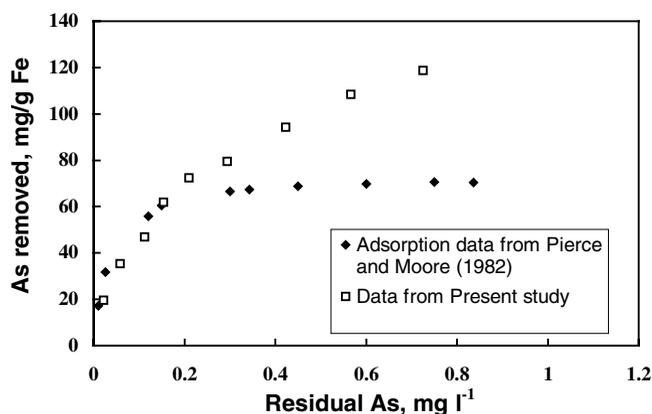
**Figure 2** | Removal density of As using  $\text{FeCl}_3$  with 1 min manual mixing and 24 h settlement with initial As(III) concentration over the range of  $0.1\text{--}7.5 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5.

experiments were conducted to discover more about the interaction between As(III) (as introduced) and Fe(III).

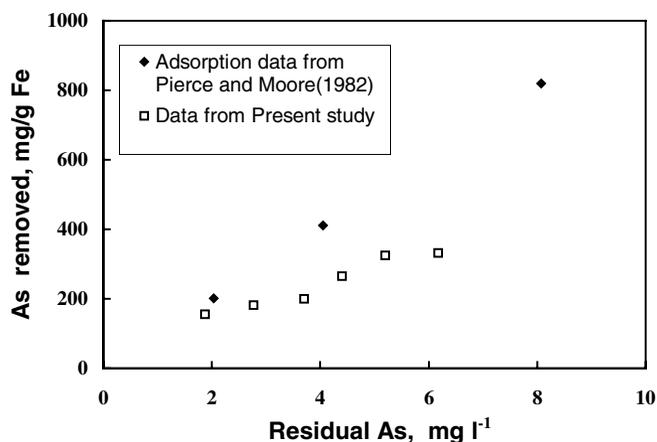
Experiments were carried out with 1 litre of sample water in a 2 litre conical flask at an Fe dosage of  $4.0 \text{ mg l}^{-1}$ , As(III) concentration ranging from  $0.1$  to  $7.5 \text{ mg l}^{-1}$  and pH 7.5. The flask was shaken manually for 1 min and then transferred to a 1.0 l capacity cylinder (432 mm height) to settle for 1 day. After 24 h, the supernatant was collected from the mid depth of the cylinder and the residual arsenic was measured. The removal of As was determined from the difference between As added and the measured residual.

Results of this test are plotted in Figure 2. When the initial As(III) is between 1.6 and 2.8 corresponding to As/Fe ratio (by weight) in the range of 0.4–0.7, it is seen that removal becomes less sensitive to initial arsenic concentration with a removal density  $\sim 0.15 \text{ mg As per mg Fe}$  over this range. However, further increases in the As/Fe ratio lead to higher removals.

In this type of test, the removal depends on a series of mechanisms; i.e. contact between Fe and As (influenced by molecular diffusion), floc formation (influenced by shaking) and solid–liquid separation by sedimentation. In order to gain insight into the data corresponding to removal at 24 h, the results were plotted in the same form as an adsorption isotherm (Figures 3 and 4). Here it is



**Figure 3** | A comparison of As removal density as a function of residual As concentration by adsorption–coprecipitation and sedimentation with  $\text{FeCl}_3$  at pH 7.5 and adsorption onto preformed  $\text{Fe}(\text{OH})_3$  at pH 7.0 for initial As(III) concentration of 0.05–1.0  $\text{mg l}^{-1}$  and a 24 h contact time.



**Figure 4** | A comparison of As removal density as a function of residual As concentration by adsorption–coprecipitation and sedimentation with  $\text{FeCl}_3$  at pH 7.5 and adsorption onto preformed  $\text{Fe}(\text{OH})_3$  at pH 7.0 for initial As(III) concentration of 2.5–10  $\text{mg l}^{-1}$  and contact time 24 h.

recognised that the resultant trend refers to the combination of processes rather than being restricted to just adsorption. This form of plot has the benefit of identifying the removal ratio ( $\text{mg}(\text{As})/\text{g}(\text{Fe})$ ) corresponding to the residual level of arsenic, the latter needing to comply with target water quality standards. Figures 3 and 4 also show adsorption data from the Pierce and Moore (1982) study. Pierce and Moore (1982) investigated the behaviour of As(III) removal by just adsorption onto pre-prepared amorphous  $\text{Fe}(\text{OH})_3$ . They found that for a certain range

of initial As(III) concentrations (0.05–1.0  $\text{mg l}^{-1}$ ), the adsorption reaches saturation. At higher initial As(III) concentrations (2.5–50  $\text{mg l}^{-1}$ ), the adsorption of As(III) per unit mass of adsorbent increased linearly with increasing equilibrium concentration.

Before commenting on the behavioural features shown in Figures 3 and 4, it is necessary to provide some of the background behind adsorption plots. The Pierce and Moore (1982) data refer to adsorption at pH 7.0 whereas the pH in the current study was 7.5. The differences between the separate studies were not considered to be significant as it is known that around neutral pH range, As(III) removal by coagulation is largely unaffected by pH (Edwards 1994). The adsorption tests reported by Pierce and Moore (1982) were carried out for 24 h continuous mixing by magnetic stirrers and then supernatants were centrifuged and analysed for arsenic concentration. The present work was also carried out for 24 h settlement, the supernatant being analysed for residual arsenic concentration without filtration.

In Figure 3, there is a remarkable similarity between the trends (removal/adsorbed) in the domain As(mg) per g Fe < 60. This may be a coincidence, or alternatively, may point to the role of adsorption as the dominating removal mechanism when the Fe/As weight ratio is  $\geq 10$ . In the case of the adsorption–centrifugation combination (Pierce and Moore 1982), saturation occurs at an adsorption density of around 70 mg As(III) per g Fe, whereas higher levels of removal (about 130 mg As(III) per g Fe) are achieved by the coprecipitation–sedimentation technique for the stated range of initial As(III) concentration (Figure 3).

Figure 4 shows the comparison at higher initial As(III) concentration and displays a very different form of behaviour. In contrast to Figure 3, the removal density obtained in the adsorption study (Pierce and Moore 1982) is higher than those obtained in the present study for the stated range of initial As(III) concentration (Figure 4). The different nature of the removal density of the present study might be due to the differences in experimental procedure. Pierce's work was carried out by introducing preformed ferric hydroxide to the solution and not by neutralising an acid solution that contains both Fe and As, whereas the latter procedure was adopted in the present study. Further,

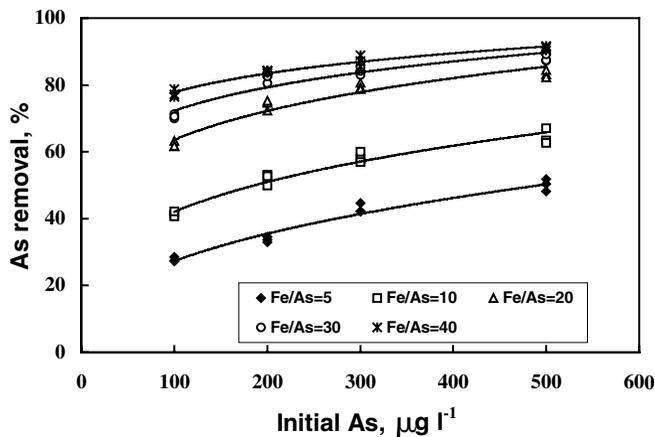


Figure 5 | Effects of As removal at different Fe/As weight ratios and initial As(III) concentration at pH 7.5 after 3 day settlement.

at higher initial dosage of As(III) ( $\geq 2.5 \text{ mg l}^{-1}$ ), a large amount of 0.1 M NaOH was required to maintain pH 7.5 constant. Here, it is conceivable that the NaOH might change or reorder the internal properties of adsorption surface sites.

### Implication of iron concentration for reducing the level of arsenic

A series of tests was conducted with varying As(III) concentration ranging from  $0.1 \text{ mg l}^{-1}$  to  $0.5 \text{ mg l}^{-1}$  and Fe/As ratios (by weight) ranging from 5 to 40 at pH 7.5. The sample was mixed for 1.0 min manually and transferred to a measuring glass cylinder (432 mm height) to settle for 3 days. After 3 days' settlement, the supernatant was collected and the residual arsenic was measured.

The influence of Fe/As ratio on As removal is presented in Figure 5. The trend in Figure 5 shows that the effectiveness of As removal is strongly influenced by the Fe/As ratio and is also sensitive to initial As concentration. The trends are reasonably similar for the different values of the Fe/As ratios. In Mamtaz and Bache (2000), it was shown that the data were adequately represented by the empirical equation:

$$\text{As removal (\%)} = 3.98(\text{Initial As(III)})^{0.22}(\text{Fe/As(III)})^{0.39}(\text{pH})^{0.24} \quad (1)$$

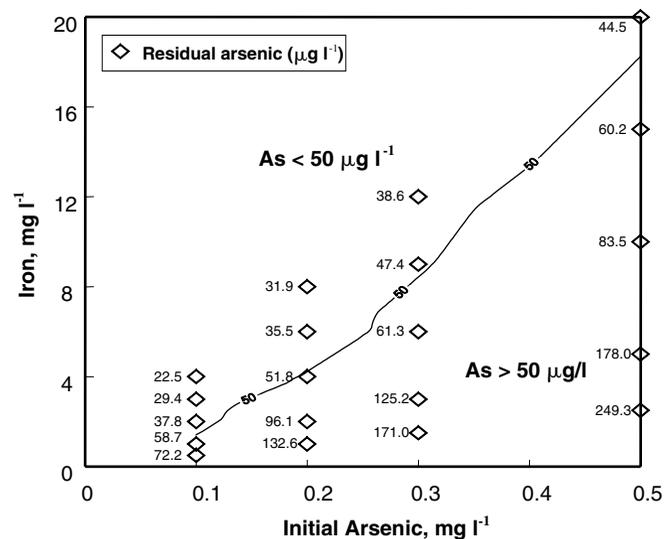


Figure 6 | Contour line showing the boundary of the zone complying with Bangladesh standard ( $50 \mu\text{g l}^{-1}$ ) for residual arsenic concentration at pH 7.5 after 3 day settlement.

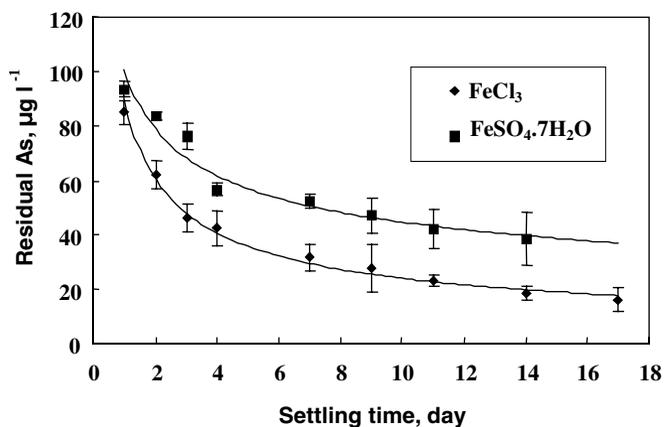
where As(III) is expressed in  $\mu\text{g l}^{-1}$ . This equation is valid for As(III) concentrations of  $0.1\text{--}0.5 \text{ mg l}^{-1}$ , Fe/As ratio (by weight) 5–40 and pH 5–8 and a settling time of 3 days.

The present paper focuses on a different aspect of the data shown in Figure 5. From the experimental results of Fe/As ratio (by weight) tests at different initial As(III) concentrations at pH 7.5 and 3 day settling (Figure 5), it is possible to calculate the minimum amount of Fe required for reducing the arsenic level to the Bangladesh standard ( $0.05 \text{ mg l}^{-1}$ ) for a given As(III) concentration. A contour analysis allows one to identify the  $50 \mu\text{g l}^{-1}$  isoconcentration line of residual arsenic for the data shown in Figure 6. This was well represented by the empirical relationship as follows:

$$\text{Fe} = 66 \text{ As}^{1.75} \text{ Fe} > 1 \text{ mg l}^{-1} \quad (2)$$

where Fe and As concentrations are in  $\text{mg l}^{-1}$ .

In essence, Equation (2) shows the necessary iron concentration to allow reduction of the arsenic to achieve the Bangladesh standard ( $50 \mu\text{g l}^{-1}$ ) for a given level of arsenic. For example, when the arsenic level is  $0.10 \text{ mg l}^{-1}$ , the minimum amount of iron requirement is



**Figure 7** | Dependence of residual As concentration on time and form of iron with As(III) 0.2 mg l<sup>-1</sup>, Fe 4.0 mg l<sup>-1</sup> and pH 7.5. Error bars refer to standard deviations.

1.2 mg l<sup>-1</sup> at pH 7.5 with 3 day settlement to attain the Bangladesh limit (0.05 mg l<sup>-1</sup>). It is noted that Figure 6 and Equation 2 are tied to 3 days settlement. Had a different time scale been used, the trends would have been different because of the dependence of the removal rate on the settling time.

### Effects of forms of Fe

Tests were performed to study the relative capacity of two different forms of iron, Fe<sup>2+</sup> and Fe<sup>3+</sup>, because naturally occurring iron often exists as a soluble ferrous form. FeCl<sub>3</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O solutions were used to provide Fe<sup>3+</sup> and Fe<sup>2+</sup> respectively. Samples were prepared by 1-min manual shaking followed by up to 17 days' settlement in 1 litre measuring cylinders (432 mm height). Supernatant was collected at different times and the residual As was measured.

Figure 7 shows a comparison between the residual As concentration obtained by FeCl<sub>3</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O. It is evident that greater As removal is obtained when using FeCl<sub>3</sub>. It demonstrates that the particular form of Fe affects the removal process. Similar removal efficiencies can be obtained provided that the settlement time is adjusted.

### Effects of interference

A preliminary investigation was carried out to examine the potential influence of co-occurring solutes (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>,

**Table 2** | Concentrations of different parameters in synthetic water

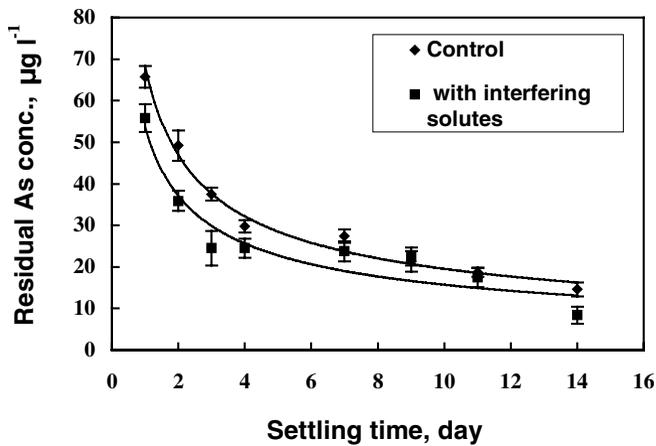
Parameter	Value	Chemical
As(III)	0.2 mg l <sup>-1</sup>	As <sub>2</sub> O <sub>3</sub> solution
Fe	4.0 mg l <sup>-1</sup>	FeCl <sub>3</sub> solution
Turbidity	8.5 NTU	Kaolin
Alkalinity	190 mg l <sup>-1</sup> as CaCO <sub>3</sub>	NaHCO <sub>3</sub>
Nitrate, NO <sub>3</sub>	4.0 mg l <sup>-1</sup>	NaNO <sub>3</sub>
Sulphate, SO <sub>4</sub> <sup>2-</sup>	5.0 mg l <sup>-1</sup>	Na <sub>2</sub> SO <sub>4</sub>
pH	7.5	0.1 M NaOH
Temperature	18.9°C	

turbidity and alkalinity) present in natural water on arsenic removal. The purpose was to gain an insight into the behaviour of a representative group of factors as well as those of individuals.

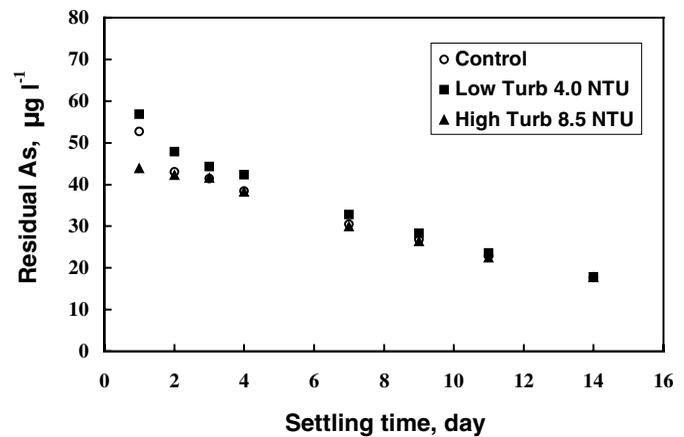
The concentrations of these solutes were in keeping with the values found in the groundwaters of Bangladesh; this aspect was examined in Mamtaz (2000). Synthetic sample water was prepared by adding the required amount of solutes in nano-pure water to simulate the conditions likely to be encountered in the groundwater of Bangladesh. Table 2 provides a summary of the concentration of different parameters used in this phase of tests.

One-litre samples of water containing the parameters described in Table 2 were mixed by manual shaking for 1.0 min and then allowed to settle in a measuring cylinder for up to 14 days. A control (i.e. without the interference additives) was also prepared in the same way. Samples of supernatant were obtained from the synthetic water and the control at different times from the mid-depth of the cylinder. Residual As was measured without filtration; data are shown in Figure 8.

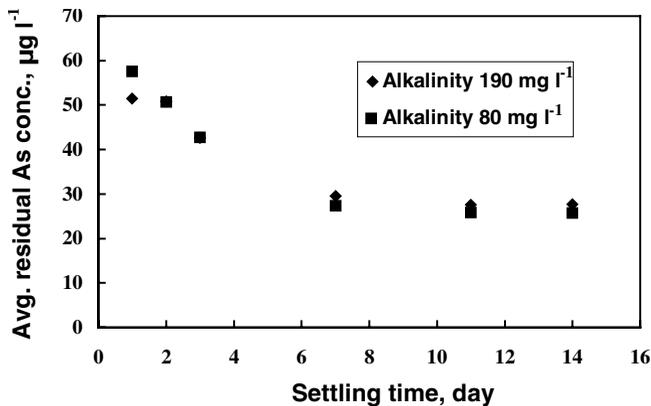
Figure 8 shows that higher residual As concentration is obtained in the control than in the synthetic water. Residual As concentration reduced to 8.4 µg l<sup>-1</sup> after 14 days' settling for samples containing co-occurring



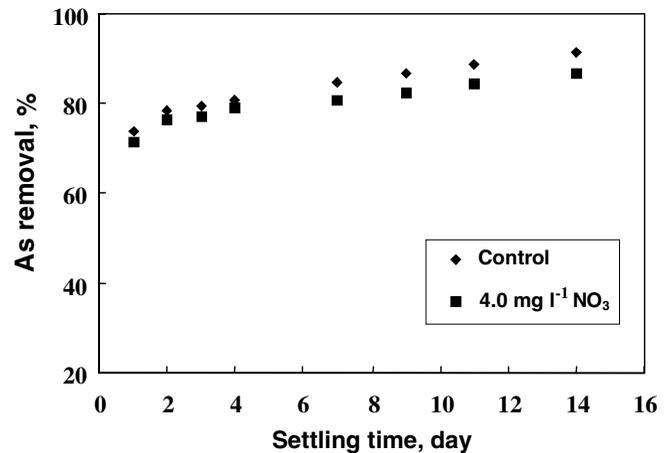
**Figure 8** | Response of residual As to the presence of interference and time with initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5. Error bars denote standard deviations.



**Figure 10** | Response of residual As to turbidity and with initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5.



**Figure 9** | Response of residual As to alkalinity condition and with initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5.



**Figure 11** | Mean As removal at different settling time of control sample and samples containing  $4.0 \text{ mg l}^{-1} \text{ NO}_3^-$  with initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5.

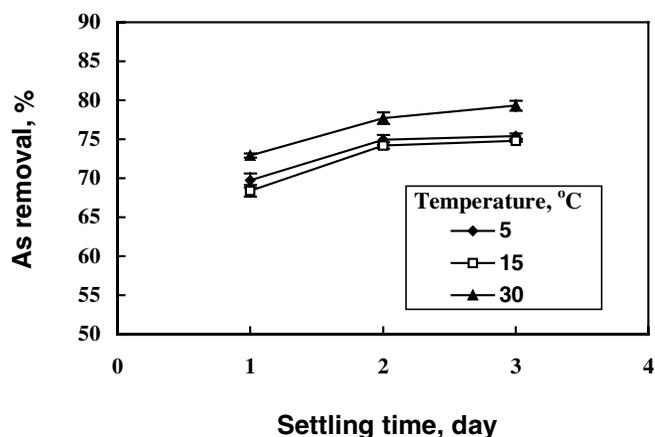
solute whereas for the control samples the mean residual As concentration was around  $14.6 \text{ µg l}^{-1}$  after 14 days.

Tests were also conducted to study the individual effects of each solute such as turbidity, alkalinity and  $\text{NO}_3^-$ . In the case of alkalinity, it was observed that it had no significant effect on As removal as shown in Figure 9. The residual As concentration for low alkalinity ( $80 \text{ mg l}^{-1}$  as  $\text{CaCO}_3$ ) was almost same as with high alkalinity ( $190 \text{ mg l}^{-1}$  as  $\text{CaCO}_3$ ). Similarly, the presence of turbidity showed relatively little effect on As removal (Figure 10) whereas Hering *et al.* (1996) found reduced As(III) removal when using kaolin ( $5 \text{ mg l}^{-1}$ ).

The presence of  $\text{NO}_3^-$  had little influence on removal when samples were allowed to settle for a long time (7–14 days) (Figure 11).

### Effects of temperature

The effects of temperature were studied to allow for the range of temperature encountered during the study and of the typical summer temperature likely to be encountered in Bangladesh. Experiments were conducted at temperatures of 5, 15 and  $30^\circ\text{C}$ . As previously, 1-l samples of water



**Figure 12** | As removal at different temperatures with initial As(III)  $0.2 \text{ mg l}^{-1}$ , Fe  $4.0 \text{ mg l}^{-1}$  and pH 7.5. Error bars represent standard deviations.

containing iron and arsenic were shaken manually for 1 min and allowed to settle in 432 mm high measuring cylinders held in a water bath at the controlled temperature.

Samples of supernatant were taken from each set of temperatures at time intervals of 1, 2 and 3 days and analysed for remaining As concentration without filtration. Figure 12 presents the As removal efficiency at different temperatures for different settling times. After 3 days' settling, arsenic removal efficiency is 79% at 30°C and 75% at 5°C. The change in temperature does not appear to have a major effect on the removal. This is a little surprising when it is considered that diffusion, the kinetics of the Fe–As reaction and viscosity might well have influenced the removal in the temperature range 5–30°C.

## DISCUSSION

The principal achievement in this study has been the demonstration that adsorption and coprecipitation with iron followed by settlement can remove significant amounts of arsenic provided that there is sufficient iron and a sufficient settling time ( $\geq 3$  days). As such, the method has considerable promise as a low-cost technique, because of the total absence of added chemicals.

A surprising aspect of the study (see Table 1 and Figure 1) was that manual mixing and sedimentation was capable of achieving higher rates of removal than mechanical mixing and filtration through a  $0.45 \mu\text{m}$  filter paper. The reasons for this are not clear and require further investigation. At settling times ( $< 6$  h) manual shaking was shown to influence the separation process, presumably arising from the enhancement of the size of the microflocs which were just visible to the naked eye. Simple increases in size are not necessarily responsible for increased settling because experience shows that flocs are fractal structures; larger sizes have lower effective densities (Gregory 1989). A puzzling feature is the influence of temperature. An increase in temperature from 5 to 30°C almost halves the kinematic viscosity of water. This ought to have a major influence on the removal rate (of small particles). However, such behaviour was not apparent in Figure 12.

When comparing the removal mechanisms with other studies, one limitation is that preparation techniques such as manual shaking and settlement have no direct equivalents.

It is also recognised that some interpretations (e.g. Figure 3; 24 h duration) assume the existence of As as As(III), arising from the low rate of conversion of As(III) to As(V). The assumption is based on comments in previous studies, for example Edwards (1994) and Pierce and Moore (1982), together with their approach to the design of experiments and measurement. For example, Pierce and Moore (1982) state that the conversion 'takes weeks (in basic solution) before measurable oxidation occurs. Thus errors due to the presence of arsenate [at 24 h equilibration] did not become a factor in this investigation'. In the case of the long duration experiments (Figures 7–9; 17 days) it is accepted that some oxidation may occur. However, this poses no interpretative problems provided it is recognised that the trends refer to total arsenic reduction. An additional complication is the time-dependence of the removal process.

In Figure 2, it was evident that the removal density did not reach a saturation point of the range of As(III) concentrations tested ( $0.1\text{--}7.5 \text{ mg l}^{-1}$ ). Ferguson and Anderson (1974) also reported that arsenite adsorption did

not reach a state of saturation; they observed a maximum adsorption density at 0.4 mole As per mole Fe. Pierce and Moore (1982) suggested that a multisite adsorption occurred in arsenic adsorption onto  $\text{Fe}(\text{OH})_3$  at higher initial arsenic concentration; i.e. arsenic can penetrate into the oxide surface which is theoretically possible for an open permeable structure of amorphous  $\text{Fe}(\text{OH})_3$ .

The coincidence of the trends plotted in Figure 3 is intriguing. At first sight, it suggests that adsorption is responsible for the removal of arsenic up to the initial arsenic concentration of  $0.4 \text{ mg l}^{-1}$  (corresponding residual concentration is  $\sim 0.15 \text{ mg l}^{-1}$ ). However, without further scrutiny to examine the time-dependence (in our study), this interpretation must remain speculative. Nevertheless, it should be pointed out that just as our own data are linked to a time-dependent process, this aspect is also true of Pierce and Moore's (1982) study wherein centrifugation was used as the separation technique after 24 h adsorption.

In groundwater, iron often exists as  $\text{Fe}^{2+}$  but other forms are present. Because  $\text{FeCO}_3$  is very insoluble in pure water,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was used to provide the  $\text{Fe}^{2+}$  form. It is observed that the As removal capacity using the ferrous form of iron is lower than that from the ferric form of iron (as  $\text{FeCl}_3$ ). Similar findings were reported in Shen (1973). This is probably because the rate of oxidation of  $\text{Fe}^{2+}$  is rather low and less  $\text{Fe}(\text{OH})_3$  is formed than with  $\text{Fe}^{3+}$ . Therefore, the successful transformation of the ferrous form into ferric form by aeration should be the first and principal step in the removal process of arsenic using the naturally occurring iron, provided the pH and alkalinity of the water are in the appropriate range (Robinson and Dixon 1968; Ahmed 1987).

When tests were conducted with co-occurring solutes, they gave higher levels of removal than those obtained in samples without these solutes (control sample) (Figure 8). Tests with individual solutes did not show any marked influence on As removal (Figures 9, 10 and 11). One would guess that that when all the solutes are present in water, they interact and enhance the formation of precipitates and the subsequent settlement. Previous research showed that the presence of  $\text{SO}_4^{2-}$  ( $40\text{--}250 \text{ mg l}^{-1}$ ) (Papassiopi *et al.* 1996; Hering *et al.* 1997) and  $\text{PO}_4^{3-}$  ( $2.5 \text{ g l}^{-1}$ ) (Peng and Di 1994) had a decreasing effect in the

removal of arsenic. Peng and Di (1994) found that  $\text{NO}_3^-$  ( $2.5 \text{ g l}^{-1}$ ) had no effect in the removal. This was also the experience in the current study. In drawing attention to the role of interference, we recognise that this aspect deserves greater scrutiny, particularly at field level. The findings presented in this study provide a useful datum against which to assess the potential influence of interference.

The prime objective of this work has been to ascertain whether the As/Fe interaction offers sufficient promise for arsenic removal (a practical system is described in the Appendix). Although there is still a lack of understanding of the underlying mechanisms, the method appears to have considerable value as a low-cost technique in Bangladesh. According to analysis in Mamtaz and Bache (2000), it was estimated that an additional 7 million people could be free from arsenic contamination (according to the Bangladesh standard) if the removal efficiencies attained in this study can be realised in practice. A necessary condition is the sufficiency of iron. Relationships of the type shown by Equation 2 are useful for discerning the minimum iron concentration.

## CONCLUSIONS

Manual flocculation followed by sedimentation appears to be a promising method for removing arsenic from groundwater containing naturally occurring iron. Over periods of settlement exceeding 24 h, removal of up to 88% can be achieved (Figure 1). Provided the iron levels are sufficiently high (say  $\geq 1.2 \text{ mg l}^{-1}$ ), it has been demonstrated that manual shaking followed by 3 days' settlement can reduce the concentration of arsenic from  $0.10 \text{ mg l}^{-1}$  to the Bangladesh standard ( $0.05 \text{ mg l}^{-1}$ ).

Evidence (Figure 3) suggests that adsorption may be the primary mechanism controlling the As(III) removal by the techniques employed in this study and when the Fe/As weight ratio is  $\geq 10$ . However this aspect requires further scrutiny.

The form of iron has been demonstrated to exert an influence on arsenic removal; higher removals are associated with the  $\text{Fe}^{3+}$  rather than  $\text{Fe}^{2+}$  over the time

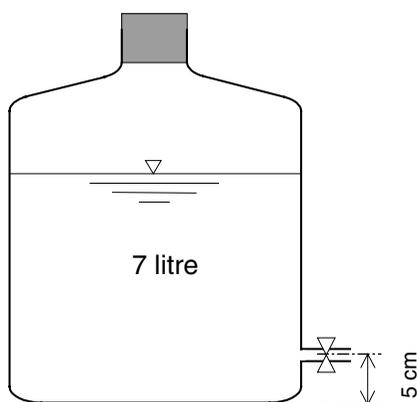


Figure 13 | Type of container used in the investigation.

scales examined. The presence of co-occurring solutes in the water at concentrations typical of those encountered in Bangladesh were observed to enhance arsenic removal, but did not exhibit any marked effect when studied in isolation from each other.

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## APPENDIX

### Arsenic removal at village level

A simple and practical method that can be adopted at village level for reducing the level of arsenic in contaminated groundwater in Bangladesh is described below. The method applies to water in which there is sufficient iron to form iron–arsenic precipitates.

For iron concentrations between 1.0 and 20.0 mg l<sup>-1</sup> and arsenic concentrations between 0.1 and 0.5 mg l<sup>-1</sup>, there is a reasonable expectation (with suitable water chemistry) that after following the procedure described

below, the water will comply with the Bangladesh Water Quality Standard for arsenic (0.05 mg l<sup>-1</sup>).

Procedure:

- Fill a clean container of 10 l capacity (Figure 13) with about 7 l water to be treated, leaving an air space
- Shake the container for 1 minute
- Allow settlement for 3 days
- Take out treated water through tap at a flow not exceeding 0.5 l min<sup>-1</sup> (Mamtaz and Bache 2000).

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