Available online at www.sciencedirect.com
ScienceDirect
Applied Geochemistry 22 (2007) 1039–1051
Applied Geochemistry
www.elsevier.com/locate/apgeochem

# Removal of arsenic from aqueous solution by natural siderite and hematite

Huaming Guo [a,*], Doris Stüben [b], Zolt Berner [b]

[a] Department of Water Resources and Environment, China University of Geosciences, Beijing 100083, PR China
[b] Institute for Mineralogy and Geochemistry, University Karlsruhe (TH), Karlsruhe 76128, Germany

Received 27 July 2006; accepted 22 January 2007
Editorial handling by W.B. Lyons
Available online 6 March 2007

**Abstract**

Batch and column experiments were conducted to examine the capability of naturally formed hematite and siderite to remove As from drinking water. Results show that both minerals were able to remove As from aqueous solutions, but with different efficiencies. In general, each material removed arsenate much more efficiently than As–DMA (dimethylarsinic acid), with the lowest adsorption efficiency for arsenite. The best removal efficiency for As species was obtained using a hematite, with a grain size range between 0.25 and 0.50 mm. The adsorption capacity for inorganic As(V) reached 202 μg/g. The pH generally had a great impact on the arsenate removal by the Fe minerals studied, while arsenite removal was slightly dependent on the initial pH of between 3 and 10. The presence of phosphate always had a negative effect on arsenate adsorption, due to competitive adsorption between them. A column packed with hematite in the upper half and siderite in the lower half with a grain size range of 0.25–0.5 mm proved to be an efficient reactive filter for the removal of all As species, causing a decrease in As concentration from 500 μg/L (including 200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L As(V) as DMA) to less than 10 μg/L after 1055 pore volumes of water were filtered at a flow rate of 0.51 mL/min. After 2340 pore volumes passed through the column filter, the total inorganic As in the effluent was less than 5 μg/L. The total As load in the column filter was estimated to be 0.164 mg/g. Results of μ-synchrotron X-ray fluorescence analysis (μ-XRFA) suggest that coatings of fresh Fe(III) oxides, formed on the surface of the siderite grains after two weeks of operation, greatly increased the adsorption capacity of the filling material towards As.


## 1. Introduction

The contamination of drinking water with As is an increasing environmental issue and has been extensively discussed especially during recent years, because of its occurrence in many parts of the world. High As concentrations (>50 μg/L) in natural groundwater sources, which provide drinking water for millions of people, have been found, for example, in parts of Bangladesh (Nickson et al., 1998; Dhar et al., 1997), West Bengal (Chatterjee et al., 1995; Das et al., 1995; Mandal et al., 1996), Argentina (Farias et al., 2003), China (Chen et al., 1994; Smedley et al., 2001; Guo et al., 2003), Mexico (Del Razo et al., 1990), the upper Midwest and the western United States (Matisoff et al., 1982; Welch

* Corresponding author. Tel.: +86 10 82320679; fax: +86 10 82321081.
*E-mail address:* hm_guo@hotmail.com (H. Guo).

0883-2927/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apgeochem.2007.01.004

et al., 1988; Schlottmann and Breit, 1992; Peters et al., 1999), Chile (Borgono et al., 1977) and Japan (Kondo et al., 1999).

Arsenic is ranked among the top 20 most hazardous, high priority substances by the Agency for Toxic Substances and Disease Registry (ATSDR, 2005). It is of particular concern due to its chronic toxicity even at relatively low concentrations (<100 μg/L), a level that has been widely detected in drinking water. The World Health Organization set a provisional guideline limit of 10 μg/L for As in drinking water (World Health Organization, 1996), which was subsequently adopted by the European Union (European Commission, 1998) and the United States (EPA Office of Groundwater and Drinking Water, 2002). This low As drinking water standard requires the development of simple, cost effective methods for As removal from drinking water. Arsenic occurs in both inorganic and organic forms in natural water (Cheng et al., 2005). Inorganic As compounds are about 100 times more toxic than organic As compounds (Nagy and Korom, 1983; Yamauchi and Fowler, 1994). However, more recent research has shown that methylation of As does not always mean it is non-toxic, and the organic As species may be more toxic than inorganic arsenicals (Zakharyan et al., 1999; Petrick et al., 2000; Styblo et al., 2000). Therefore, technologies for removing both inorganic and organic As species are urgently needed.

Due to their high surface area and positive charge, synthetic Fe(III)-oxides/hydroxides, such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous ferric oxide (ferrihydrite) and goethite (α-FeOOH) are promising adsorptive materials for removing both inorganic As(III) and As(V) from aqueous solutions (Hsia et al., 1994; Wilkie and Hering, 1996; Raven et al., 1998; Sun and Doner, 1998). However, despite their strong affinity for aqueous As species due to their very high specific surface area, most of these materials are available as fine powders, which are difficult to separate from water after adsorption is completed. Compared to these synthetic Fe minerals, natural Fe-oxides, such as hematite, ferrihydrite, goethite and lepidocrocite, are more attractive for such purposes, because they are more cost effective and are readily available in different particle sizes. Though natural Fe-ores are widely used to efficiently remove both metals (including Fe, Co, Ni, Cd, Zn, Hg) and anions (including $SO_4^{2-}$, $HPO_4^{2-}$) (Andrade et al., 1999; Pivovarov, 2001; Jeon et al., 2003; Rabung et al., 1998; Ioannou and Dimirkou, 1997; Horanyi and Joo, 2000), there are comparatively few studies published on the removal of As species by natural Fe minerals.

This study investigates the applicability of selected natural Fe minerals for remediation of As species from contaminated waters. The main objectives are to (i) characterize the proposed natural materials with respect to their chemical and mineralogical compositions; (ii) select the best materials from a set of different natural hematite and siderite samples for removal of As species; and (iii) investigate the potential for using the target natural minerals as packed bed material to remediate drinking water contaminated with As.

## 2. Methodology

### 2.1. Materials and methods

Natural minerals used in this study were taken from the mineral collection centre of Technische Universität Bergakademie Freiberg, Germany, and originated from different deposits (Table 1). The samples were ground and sieved to produce fractions with various particle sizes. Each particle size fraction was washed with deionised water to remove dust adhering on the surface of the grains prior to adsorption experiments.

All the reagents used, including acids, were of analytical grade. Stock As solutions (100 mg/L) were prepared by dissolving sodium arsenite ($NaAsO_2$, Fluka Chemical, Germany), sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$, Fluka Chemical, Germany), and dimethylarsinic acid ($(CH_3)_2As(O)OH$, Sigma, Germany), respectively, in Milli-Q water. All glassware and sample bottles were washed with a detergent solution, rinsed with tap water, soaked in 1% sub-boiled $HNO_3$ for at least 12 h, and finally rinsed with Milli-Q water three times before use.

The total As concentration of the aqueous solutions was analyzed by graphite furnace atomic absorption spectrometry (GF-AAS 4110ZL, Perkin–Elmer), with a fraction of the analyses being cross-checked with high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Axiom, VG Elemental). The cross check results show that the difference in As concentrations obtained by ICP-MS and AAS was less than 4%, indicating that the graphite furnace method was suitable for As determination. A flow injection

Table 1
Description and XRD results of natural minerals investigated

| Sample | Colour | Structure | Siderite (%) | Ankerite (%) | Calcite (%) | Hematite (%) | Pyrite (%) | Chalcopyrite (%) | Magnetite (%) | Goethite (%) | Cordierite (%) | Muscovite (%) | Quartz (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SIO1 | Light purple | Blocky | 95 | 4 | – | – | – | – | – | – | – | – | 1 |
| SIO2 | Light grey | Blocky | 90 | – | – | – | 5 | 1 | – | – | – | – | 4 |
| SIO3 | Dark grey | Blocky | 78 | – | – | – | – | 1 | – | 19 | – | – | 2 |
| SIO4 | Black | Blocky | 96 | – | Trace | – | – | – | – | 2 | – | – | 2 |
| HIO1 | Aterrimus | Stratified, partially radial | 4 | – | – | 86 | – | – | – | 5 | – | 1 | 4 |
| HIO2 | Magenta | Block with few pores | 1 | – | – | 97 | – | – | – | – | – | – | 2 |
| HIO3 | Magenta | Blocky | 8 | – | – | 55 | 1 | – | 9 | 17 | 1 | – | 9 |
| HIO4 | Red | Blocky | – | – | 4 | 69 | – | – | – | – | – | – | 27 |

hydride generation system (FIAS 200, Perkin–Elmer) coupled with atomic absorption spectrometry (AAS 4001, Perkin–Elmer) was used for As speciation analyses in Sections 3.3 and 3.8. With regard to different As species, hydride generation was carried out in different acid media in the presence of reductant. After filling the sample loop the sample plug was pushed out by the acidic carrier solution and completely mixed with the selected acid in the mixing coil before reduction took place by entraining the potassium tetrahydroborate. The detailed analysis procedure has been described in Rüde and Puchelt (1994) and Rüde (1996).

The trace element composition of the minerals used in the experiments was determined by HR-ICP-MS on dissolved sample materials, using a standard total digestion procedure with $HNO_3$–$HClO_4$–HF. Total C and S contents in the minerals were determined by a Carbon–Sulphur-Analyzer based on non-dispersive infrared spectrometry (CSA 5003, Leybold Heraeus). The mineral composition of the adsorbents was determined by X-ray diffraction analysis (XRD), using a URD-6 powder diffractometer (Co K$\alpha$ radiation, graphite monochromator, $2\theta$ range 5–80°, step 0.03°, counting time 5 s per step). The BET surface area was measured by $N_2$ adsorption using PMI Automated Brunauer–Emmett–Teller (BET) Sorptometer (Autosorb-1-C, Quantachrome).

The distribution of Fe and As in the mineral particles after adsorption of As from the solution was examined at a microscopic resolution by means of μ-synchrotron X-ray fluorescence analysis (μ-XRFA) at the Ångström-Source of the Forschungszentrum Karlsruhe (ANKA), Germany. Before analysis, the particles embedded in epoxy resin were double-side polished to a thickness of 100 μm. The surface morphology of the selected minerals with specific grain size was examined using scanning electron microscopy (SEM).

### 2.2. Batch experiments

Unless specified otherwise, the batch experiments to study the removal of As from solution were carried out by reacting 50 mL of As solution in 100 mL polyethylene bottles with 0.5 g of sample material of known grain size range (mostly the fraction between 0.25 and 0.50 mm). The experiments were conducted at room temperature ($20 \pm 2$ °C) and the bottles were manually shaken every 8 h. After a predetermined contact time, the aqueous samples in

each bottle were decanted and filtered through a 0.45 μm cellulose acetate filter. The supernatant was analyzed for total As and/or As species. To determine whether the filter pore size affected the total concentration of As in solution, duplicate samples were analyzed after filtering through membrane filters with 0.20 and 0.45 μm pore diameter, respectively. The percent difference between the duplicate analyses was less than 3%, indicating that the 0.45 μm cellulose acetate filter efficiently retained As-associated particles. Unless specified otherwise, the concentration of the different As species was expressed as the element (As).

Solution pH was monitored by a WTW pH meter (Model # pH 330) equipped with a SenTix 43-1 pH electrode and adjusted by addition of dilute HCl and NaOH solutions. In order to maintain a relatively constant ionic strength, all As solutions contained 0.01 M NaCl as background electrolyte. Adsorption isotherm studies were conducted by varying the amount of solid material added to the As solution. Because As(V) is the dominant As species in aerobic natural water, and As(III) was less adsorbed at natural pH as neutral species ($H_3AsO_3$), As(V) was used as the adsorbate in the experiments of adsorption isotherms and competing anions.

To determine the effect of other competitive anions on As adsorption, batch tests were performed using solutions of 1000 μg/L As(V) containing 1, 2, 5, and 10 mg/L of P (as $PO_4^{3-}$) or N (as $NO_3^-$). After a 24 h reaction time, the suspension was filtered through a 0.45 μm cellulose acetate filter and analyzed for total As, as described above.

### 2.3. Column experiments

Based on the results from the batch adsorption test, a hematite and a siderite sample were selected for the column experiments. The experiments were carried out using a plexi-glass column of 30 mm inner diameter and 150 mm height, with an empty bed volume of 100 mL. The upper half of the column was packed with hematite (sample HIO1), and the lower half with siderite (sample SIO4). The water flowing through the column contained 500 μg/L of As (composed of 200 μg/L As(V), 200 μg/L As(III) and 100 μg/L As as DMA), in a 0.01 M NaCl matrix in order to maintain a relatively constant ionic strength. The water was pumped from the bottom using a peristaltic pump (Model # 205S, Watson Marlow Company, Germany). The flow rate was kept at 0.51 mL/min, which yielded an empty bed contact time (EBCT) of approximately 200 min. The effluent was sampled at regular time intervals and was analyzed for residual As species.

The US EPA toxicity characteristic leaching procedure (TCLP) was applied to the As-loaded adsorbents used in the column experiment (US EPA, 1999). Following adsorption, the dried filter filling materials were extracted with extraction fluid (5.7 mL glacial $CH_3COOH$ added to 500 mL of Mill-Q water, plus 64.3 mL of 1 N NaOH and diluted to 1 L, pH 4.9), and agitated in a shaker. The solid/liquid ratio was 1:20. The aqueous As was determined after 18 h by GF-AAS. If the As concentration exceeds 5 mg/L, the solid is classified as hazardous waste.

## 3. Results and discussion

### 3.1. Characterization

The results of the XRD analysis (Table 1) show that samples SIO1, SIO2, SIO3 and SIO4 are siderite-dominated materials, with siderite contents of 95%, 90%, 78% and 96%, respectively, while HIO1, HIO2, HIO3 and HIO4 are mainly composed of hematite, with hematite contents of more than 55%. All of the materials contain variable quantities of quartz. Samples SIO3 and HIO3 contain considerable amounts of goethite (19% and 17%, respectively), which according to the X-ray diffractogram was crystalline. Relatively high contents of Mn in SIO1, SIO2, SIO3 and SIO4 indicate that some of the Fe was possibly substituted by Mn in these samples (not shown). HIO1, HIO2 and HIO3 show complex peak shapes, indicating a bimodal distribution of crystallite size, or that the material was possibly affected by micro-strain.

The chemical composition of the materials (data not shown) is generally consistent with the results of XRD. The calculation of the element concentrations on a molar basis yields the following overall composition formulas: $(Fe_{0.847}Mg_{0.089}Mn_{0.038}Ca_{0.026})CO_3$ for SIO1, $(Fe_{0.842}Mn_{0.103}Mg_{0.045}Ca_{0.010})CO_3$ for SIO2, $(Fe_{0.860}Mn_{0.108}Mg_{0.028}Ca_{0.004})CO_3$ for SIO3, and $(Fe_{0.830}Mn_{0.116}Mg_{0.048}Ca_{0.006})CO_3$ for SIO4. In comparison with siderites, the contents of Fe, Mn, Mg and total C in hematites are much lower, while those of Al, K and P are generally higher. More importantly, As concentrations in these materials are generally low (<35 mg/kg), except for

SIO2, HIO3 and HIO4 which contain 191, 246 and 170 mg/kg As, respectively.

### 3.2. Kinetic considerations

The As(V) adsorption kinetic study was conducted using sample HIO4. Fig. 1 shows that As adsorbed increased with an increase in contact time and the adsorption equilibrium was not reached at the end of the batch experiment (4320 min). This result suggests that diffusion to the micro-pores in the mineral adsorbent may have contributed to the As removal. Adsorption experiments with other materials were conducted for only 1440 min.

The experimental data were analyzed according to the Lagergren (Altundogan et al., 2000) rate equation:

$$\log(Q_e - Q) = \log Q_e - \frac{tK_{ad}}{2.303} \quad (1)$$

where $Q_e$ and $Q$ are the amounts of As adsorbed at pseudo-equilibrium condition and at time $t$, respectively, and $K_{ad}$ is the adsorption rate constant.

A linear relationship with a correlation coefficient of 0.961 was found between $\log(Q_e - Q)$ and contact time (Fig. 1, inset). The rate constant $K_{ad}$ for As(V), as calculated from the slope of the line (Fig. 1, inset) is 0.0012 $min^{-1}$. The linearity of the relationship indicates the first-order nature of the arsenate adsorption.

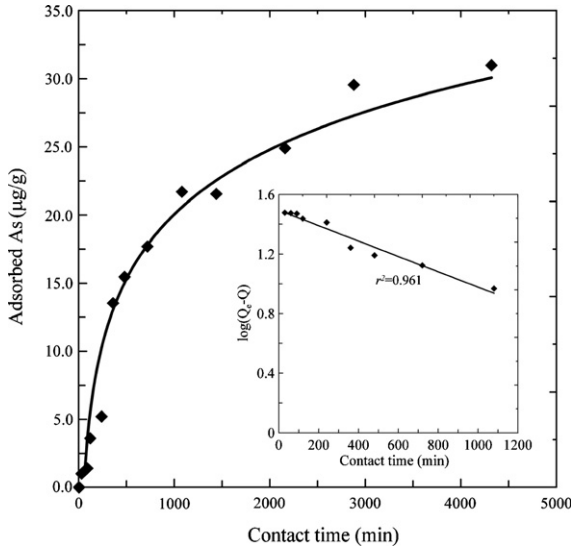


Fig. 1. Effect of contact time on As(V) adsorption on HIO4, with ionic strength of 0.01 M NaCl, initial As of 1000 μg/L, grain size range of 0.25–0.5 mm, and adsorbent dosage of 10 g/L at room temperature. Lower inset shows Lagergren plot of As(V) adsorption on HIO4.

### 3.3. Adsorption of As species on hematite and siderite

The adsorption of different As species (including arsenate, arsenite and DMA) on natural hematite and siderite was investigated in batch experiments for all of the samples. The results (Fig. 2) indicate that HIO1 was the most suitable material to remove the different As species, followed by SIO3 and SIO4. It is noteworthy that except for HIO1, natural siderite proved to remove much more As from water than the hematite samples, despite the well-known fact that synthetic Fe-oxides (including amorphous hydrous ferric oxide, poorly crystalline hydrous ferric oxide and goethite) significantly adsorb As from water (Hsia et al., 1994; Wilkie and Hering, 1996; Raven et al., 1998; Sun and Doner, 1998). Amorphous (or poorly crystalline) Fe-oxides were found to readily transform into well crystalline forms (Ford, 2002), leading to a decrease in specific surface area and hence, sorption site density (Dixit and Hering, 2003). Since most of the hematite in the investigated samples are well crystallized (Table 1), their affinity for As was relatively low, which would possibly limit their application for As removal in practice. In contrast, HIO1 had a very good As adsorption capacity, which was possibly related to the stratified structure with many microfissures. The very good As removal efficiency of the siderite samples was possibly related to their special surface characteristics. Su and Puls (2004) found that the Fe (II, III) hydroxycarbonate (one of the major Fe corrosion product in the

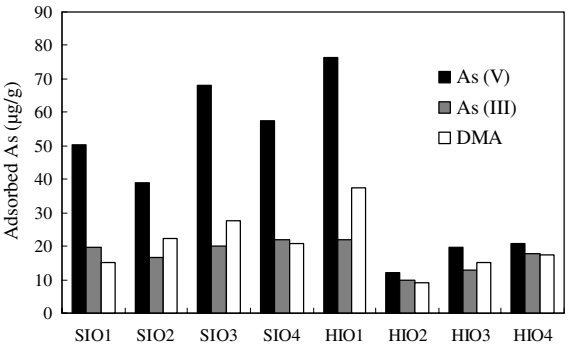


Fig. 2. Removal of As species by different Fe minerals (ionic strength = 0.01 M NaCl; initial As = 1000 μg/L; grain size range = 0.25–0.5 mm, dosage = 10 g/L; contact time = 1440 min; $T = 20 \pm 2$ °C).

$Fe^0$–water–$CO_2$ system), plays an important role in the removal of As from water.

Furthermore, arsenate was removed by the studied Fe-minerals more efficiently than arsenite. This is consistent with the generally recognized relative affinity of the inorganic As species for Fe(III)-oxydroxides (Jain et al., 1999; Goldberg, 2002; Dixit and Hering, 2003). Gu et al. (2005) also found that granular, activated, C-based Fe-bearing adsorbents removed more arsenate from water at pH 7 than arsenite. The removal of DMA from water by the investigated samples was generally more efficient than that of the inorganic As(III) species. However, Cheng et al. (2005) observed that the amount of DMA adsorbed on Fe filings was much less than that of MMA, inorganic As(V) and As(III). They speculated that the two methyl groups of the DMA molecule did not form bidentate inner-sphere complexes with the corrosion products of the Fe-filings, whereas inorganic As(III) and As(V) species, as well as the single methyl group of the MMA molecule, did. The mechanisms of DMA removal by the Fe minerals used in this study were possibly the same as those for inorganic As species. In further batch and column experiments only the mineral samples HIO1, HIO4, SIO3 and SIO4 were used.

### 3.4. Effect of pH on inorganic As removal

The effect of pH on inorganic As adsorption was studied in an initial pH range between 2 and 10, using a contact time of 1440 min for both arsenate and arsenite. Results show that pH had a significant effect on As(V) removal in all of the samples studied (Fig. 3a). On hematites, the adsorption of As(V) decreased with increasing pH, except for HIO1 which adsorbed As(V) in a more constant manner in the pH range between 2 and 8. In contrast, the highest adsorption on siderite samples occurred at an initial pH value of 7. These results clearly show that the hematite sample HIO1 and the siderite samples SIO3 and SIO4 adsorbed As(V) efficiently in a relatively wide pH range, while HIO4 preferentially adsorbed As(V) in an acidic pH range. The adsorption of As(V) on HIO1 occurred optimally within a wide pH range, which is of great advantage in practical application. It was observed that the minerals had a pH buffering effect such that the pH stayed relatively unchanged during the experiments (data not shown). This broad optimum pH was possibly related to the pH buffering effect of the solid samples, which could be explained by the amphoteric nature of the Fe mineral and the density of the acidic functional groups. Ahmed (1966) and Cornell and Schwertmann (1996) also observed the amphoteric nature of the Fe oxides/oxyhydroxides.

Though the pH dependency of the adsorption behaviour of hematite and siderite were found to be different (Fig. 3a), the effects of pH on As(V) removal are generally related to the point of zero charge (PZC) of pure Fe oxides, which is typically in the pH range of 7.4–8.7 (Parks and De Bruyn, 1962; Lumsdon and Evans, 1994; Cornell and Schwertmann, 1996; Manning and Goldberg, 1996; Dzombak and Morel, 1990). Above these $pH_{PZC}$

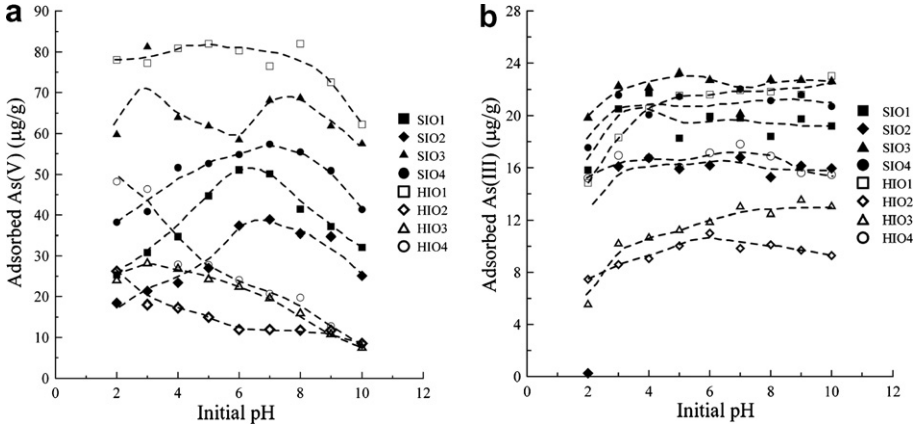


Fig. 3. Effect of pH on As(V) (a) and As(III) (b) adsorption on natural Fe minerals (ionic strength = 0.01 M NaCl; initial As = 1000 μg/L; dosage = 10 g/L; grain size range = 0.25–0.5 mm; contact time = 1440 min; $T = 20 \pm 2$ °C).

values, Fe-oxides are in monomeric anionic forms, and consequently have no affinity for As-oxyanions.

The pH dependence of arsenite removal by the different mineral samples is shown in Fig. 3b. Results indicate that adsorption of arsenite on both siderite and hematite was largely independent of the initial pH in the range between 3 and 10. Its removal efficiency was lower than that for arsenate due to the lack of electrostatic attraction between the adsorbent and arsenite being a neutral species at $pH < 9$. It is assumed that arsenite was mainly removed by means of specific adsorption, which was relatively independent of initial pH. A significant decrease in the arsenite removal, particularly in sample SIO2, was observed only at a pH below 3. It is evident from Fig. 3a and b that the siderite samples SIO3 and SIO4 and hematite samples HIO1 and HIO4 selected for the further investigations have a wide working pH range within which they all strongly adsorb both inorganic As(III) and As(V).

### 3.5. Effect of grain size on As(V) removal

The effect of grain size on arsenate removal from aqueous solution was tested using samples SIO3, SIO4, HIO1 and HIO4 in size ranges of 1.50–2.00, 1.00–1.50, 0.5–1.00, 0.25–0.50, <0.25 mm. In these experiments, an adsorbent dosage of 40 g/L was used.

The experimental results show significant variations in As(V) removal efficiency with grain size (Fig. 4). In general, As removal increased with the decrease of grain size of the selected minerals. For example, the removal efficiency of SIO4 at the grain size of 1.50–2.00 mm was 43.0%, whereas for the fraction <0.25 mm the removal efficiency increased to 99.6%. A BET surface area of two representative size fractions: <0.25 and 0.25–0.50 mm, was obtained. The fine size fraction was found to possess a little greater surface area per gram of the solid than the coarse fraction (36.0–27.3 $m^2/g$ for SIO3, 8.5–6.8 $m^2/g$ for SIO4, 5.5–4.4 $m^2/g$ for HIO1, and 4.3–3.7 $m^2/g$ for HIO4). This possibly suggests that both internal porosity and outer surface area were the major determinants of surface area. Therefore, the higher removal efficiency of the fine size fraction probably indicates that solute adsorption generally depended on the surface area of the porous adsorbent (Stumm, 1992).

It was observed that removal efficiency drastically decreased when the particle size increased from

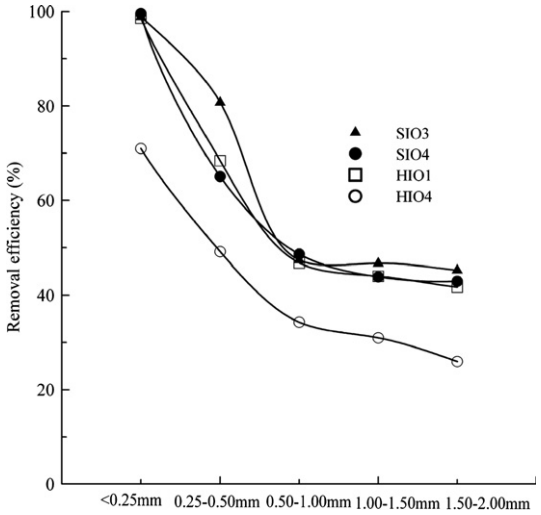


Fig. 4. Effect of the grain size on As(V) removal by SIO3, SIO4, HIO1 and HIO4 (ionic strength = 0.01 M NaCl; initial As = 1000 μg/L; dosage = 40 g/L; contact time = 1440 min; $T = 20 \pm 2$ °C).

<0.25 mm to 0.50–1.00 mm, and remained nearly constant at coarser fractions for all of the investigated samples. Though the removal efficiency was highest with the finest grain size faction, this is not suitable for column application, because of the significant hydraulic obstruction and possible clogging when water flows through the column. Therefore, in all of the further column experiments the mineral fraction of 0.25–0.50 mm was used.

### 3.6. Adsorption isotherms for As(V)

Adsorption isotherms for arsenate were investigated at an initial As(V) concentration of 1000 μg/L and an adsorbent dosage between 2 and 40 g/L. The adsorption capacity varied in the ranges of 23.3–67.5, 22.2–36.8, 30.9–202 and 7.71–17.3 μg/g for SIO3, SIO4, HIO1 and HIO4, respectively. The experimental data obtained under these conditions were applied to linearized forms of Langmuir, Freundlich and Temkin isotherms (Eqs. (2)–(4), respectively):

$$C_e/Q_e = (1/bQ^0) + C_e/Q^0 \quad (2)$$

$$\ln Q_e = \ln b + n \ln C_e \quad (3)$$

$$Q_e = n \ln b + n \ln C_e \quad (4)$$

where $C_e$ (μg/L) is the pseudo-equilibrium concentration in the solution, $Q_e$ (μg/g) is the amount adsorbed on the adsorbent at pseudo-equilibrium, $Q^0$, $n$ and $b$ are isotherm constants. The value of $Q^0$ (the

Langmuir constant) is related to adsorption capacity or adsorption maxima, whereas the definitions of $n$ and $b$ are different for the various models.

All these isotherms were fitted to the obtained adsorption data. Correlation coefficients for the isotherms were calculated by using linear regression, and the Langmuir isotherm was found to yield the best fits to the experimental data, except for sample HIO4 which more closely followed the Freundlich isotherm. Langmuir plots for the adsorption of arsenate on SIO3, SIO4 and HIO1 are shown in Fig. 5. The values of the Langmuir constants are shown in Table 2.

These results were consistent with previously published data, where the adsorption of As(III) and As(V) on different substrates (e.g., activated carbon and clinoptilolite: Payne and Abdel-Fattah, 2005; red mud: Altundogan et al., 2000; Fe-oxide coated sand: Thirunavukkarasu et al., 2003; amorphous Fe-hydroxide: Harper and Kingham, 1992; hydrous ferric oxide: Wilkie and Hering, 1996; titanium dioxide adsorbent: Bang et al., 2005) also followed Langmuir isotherms. This indicates that the coverage of the adsorption sites was in the form of a monolayer (Singh et al., 1988) and all surface sites had nearly the same adsorption energies.

### 3.7. Effect of competing anions on As removal

Table 3 shows the effect of different anions ($NO_3^-$ and $PO_4^{3-}$) on arsenate adsorption on samples SIO3, SIO4, HIO1 and HIO4. The $NO_3^-$ ion up to 10 mg N/L had no significant effect on As(V) uptake by the selected materials. For example, at a $NO_3^-$ concentration of 10 mg N/L, As(V) adsorption decreased from 54% to 52% on sample SIO4. The presence of phosphate (10 mg/L in terms of P), on the other hand, reduced the uptake of As(V) by SIO4 from 54% to 28% and by HIO1 from 69% to 36%, as a consequence of the competitive adsorption between them (Roy et al., 1986; Manning and Goldberg, 1996; Su and Puls, 2001). The phosphate affected arsenate adsorption in the order of HIO1 > SIO4 > SIO3 > HIO4.

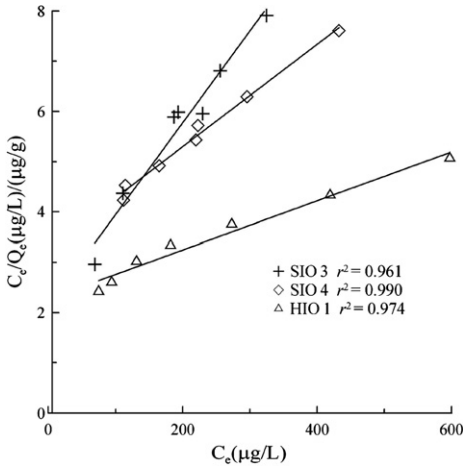


Fig. 5. Langmuir plots for As(V) adsorption on SIO3, SIO4 and HIO1 (ionic strength = 0.01 M NaCl; initial As = 1000 μg/L; dosage = 10–40 g/L; grain size range = 0.25–0.5 mm; contact time = 1440 min; $T = 20 \pm 2$ °C).

Table 2
Calculated Langmuir constants for inorganic As(V) adsorption on SIO3, SIO4 and HIO1

| Adsorbent | $T$ (°C) | $Q^0$ (μg/g) | $b$ (L/μg) | $r$ |
|---|---|---|---|---|
| SIO3 | $20 \pm 2$ | 54.6 | 0.0086 | 0.104 |
| SIO4 | $20 \pm 2$ | 98.0 | 0.0031 | 0.244 |
| HIO1 | $20 \pm 2$ | 204 | 0.0022 | 0.313 |

Ionic strength = 0.01 M NaCl; initial As = 1000 μg/L; dosage = 10–40 g/L; contact time = 1440 min; grain size range = 0.25–0.5 mm.

### 3.8. Column experiment

A column experiment was conducted to assess the feasibility of natural hematite and siderite as filling material for the removal of As from contaminated waters. Total As concentration in the influent was 500 μg/L (200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L of As as DMA). Fig. 6 shows that after 1055 pore volumes, total As concentrations in the effluent were still below 10 μg/L, which is the concentration limit of the European Drinking Water Standard. The pH of filtered water ranged between 6.70 and 7.16. Even after As solution corresponding to 2340 pore volumes passed through the column filter, total As in the effluent was still lower than 50 μg/L, which is the current drinking water standard in China, India and other developing countries.

Concerning the speciation of As in the effluent, it was found that more than 90% of total As was in the form of organic As (DMA). After 2340 pore volumes, the effluent contained organic As (DMA) of 41.5 μg/L and total As of 45.8 μg/L. Results also show that the major inorganic As species in the effluent was As(III), the concentration of which

Table 3
Percentage of As(V) removal in the presence of competitive anions[a]

| Anion[b] (mg/L) | % Uptake of As(V) in presence of anion | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $NO_3^-$ | | | | $PO_4^{3-}$ | | | |
| | SIO3 | SIO4 | HIO1 | HIO4 | SIO3 | SIO4 | HIO1 | HIO4 |
| 0 | 64 | 54 | 69 | 20 | 64 | 54 | 69 | 20 |
| 1 | 61 | 53 | 59 | 19 | 59 | 42 | 52 | 9.0 |
| 2 | 60 | 54 | 65 | 15 | 57.3 | 37 | 47 | 6.0 |
| 5 | 64 | 48 | 58 | 13 | 55.2 | 32 | 37 | 5.0 |
| 10 | 67 | 52 | 62 | 8.2 | 48.0 | 28 | 36 | 4.0 |

[a] Initial As(V): 1000 μg/L; size range: 0.25–0.50 mm; contact time: 1440 min; dosage: 10 g/L in 0.01 M NaCl; pH 7 at 20 ± 2 °C.
[b] The concentrations of nitrate and phosphate were expressed in terms of N and P, respectively.

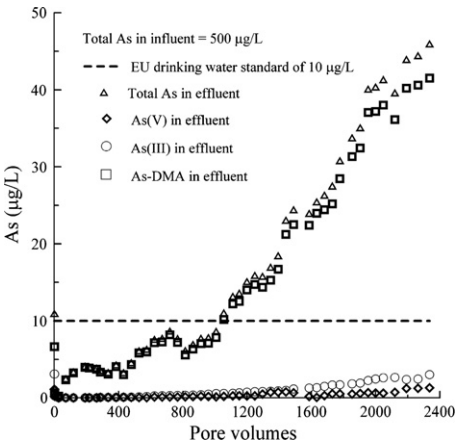


Fig. 6. As removal from aqueous solution using a column filter packed with SIO4 in the lower half and HIO1 in the upper part with a grain size range of 0.25–0.5 mm (flow rate = 0.51 mL/min; EBCT = 200 min; As in influent including 200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L As as DMA).

was 2–4 times higher than that of As(V). Though As(III) was the dominant inorganic As species in the effluent, concentration of total inorganic As was always lower than 5 μg/L during the entire experiment. This indicates that the selected minerals are promising materials to be used for the removal of As, especially for inorganic species. Since organic As occurs at relatively low concentrations in natural waters, the comparatively low adsorption affinity of the column filter for DMA does not appear to limit its applicability for remediation of drinking water with high inorganic As concentrations.

A mass balance calculation based on the amount of water treated, and the influent and effluent As concentrations indicates that the total As load in the column filter was 0.164 mg/g. The high As load on the packed bed materials was possibly due to long contact time and Fe-oxide coatings, which gradually developed on the particles as the As solution flowed through the column. As mentioned above, both internal porosity and outer surface area were the major determinants of surface area, the packed materials would be regarded as a dual porous medium. The diffusion of the solution to the micro-pores is time-dependent, and long time contact would favour the adsorption of micro-pores which are mostly available in the internal porosity. On the other hand, these freshly formed Fe-oxides have a very high affinity for As (Munoz et al., 2002; Gu et al., 2005). The colour of the siderite (SIO4) which turned from black to red after the column was operated for two weeks, was a first indication to support this assumption.

More direct evidence was provided by the results of the μ-synchrotron XRFA which indicate the presence of Fe(III)-oxide coatings on the surface of siderite grains (sample SIO4) taken from the bottom of the column (Fig. 7). The line scans were carried out near the surface of the particles from the batch and the column experiment with a resolution of 4 and 5 μm, respectively. Due to the lack of appropriate standards, only relative intensities are presented, which however are proportional to the actual As contents in the grains. The peak of As intensities means that the high content of adsorbed As was presented on the grain surface. Fig. 7 shows that the width of the reaction rim in which the As adsorption occurred was much broader and the intensity of the As signal was considerably higher for particles taken from the column as compared to those from the batch experiment. This indicates that the development of fresh Fe(III)-oxide coatings on the surface of siderite grains with high adsorption capacity for As was much more intensive in the relatively well aerated flow-through column, in comparison with in the tightly closed bottles of the batch experiments. The coating was possibly due to the oxidation of $FeCO_3$(s).

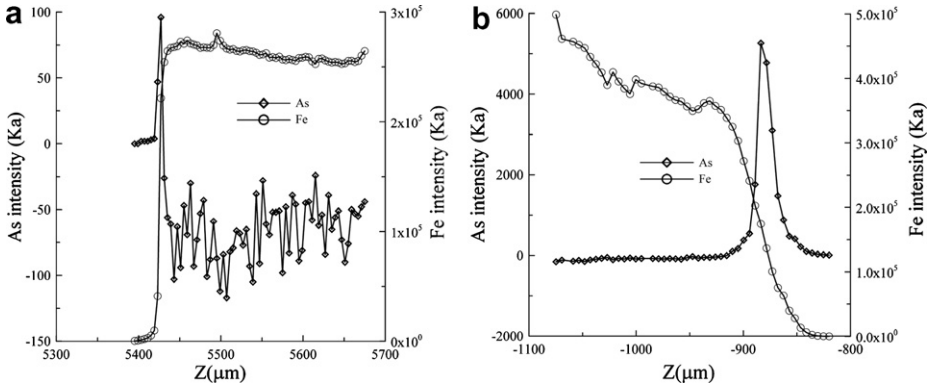


Fig. 7. The results of the μ-synchrotron XRFA in terms of line scanning near the surface of SIO4 particle from the batch (a) and the column (b). SIO4 particle in a was taken from the batch experiments with contact time of 1440 min (initial total As: 500 μg/L (including 200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L As as DMA); dosage: 10 g/L in 0.01 M NaCl; pH 7 at 20 ± 2 °C), while that in b is from the bottom of the column after an As solution containing 200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L As as DMA had been filtered for about 720 h at the flow rate of 0.51 mL/min.

The TCLP results show that the As released was below 250 μg/L, which did not exceed the EPA regulatory limit of 5 mg/L. This suggests that the spent adsorbents were not hazardous, and suitable for discharge in landfill deposits.

### 3.9. Possible mechanisms of the As removal

In order to verify if precipitation was one of the main mechanisms for As removal, equilibrium speciation calculations were carried out using PHREEQC (Parkhurst and Appelo, 1999). In the calculation, Fe concentrations from both batch and column experiments were found to be very low (<63.5 μg/L). The calculated saturation indices (SI) for the As/Fe components, including claudetite ($As_4O_6$), arsenolite ($As_4O_6$), and scorodite ($FeAsO_4 \cdot 2H_2O$) (data not shown here), indicate that the solutions from both batch and flow-through experiments were under-saturated with respect to these minerals, suggesting that precipitation had not contributed to the As removal from aqueous solution.

Based on the available data, the mechanism of As removal by the investigated natural hematite and siderite could not be explained in full detail, though it is evident that it involves electrostatic attraction and surface complexation processes between the As species in solution and Fe(II) and/or Fe(III)-hydroxides in the solid materials. This assumption was supported by the distribution of As in a 450 × 500 μm size SIO4 grain (Fig. 8), which was investigated with a spatial resolution of 50 × 5 μm

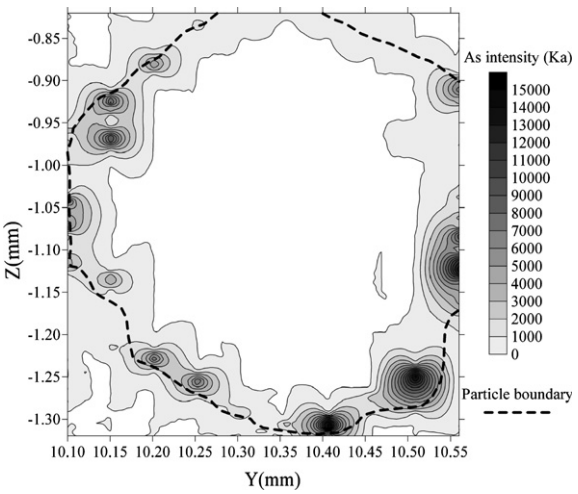


Fig. 8. The results of the μ-synchrotron XRFA in terms of area scanning in a thin section of SIO4 particle from the bottom of the column after an aqueous solution containing 200 μg/L As(V) as arsenate, 200 μg/L As(III) as arsenite and 100 μg/L As as DMA had been filtered for about 720 h at the flow rate of 0.51 mL/min.

by means of the μ-synchrotron XRFA. The particle was taken from the bottom of the column after a solution containing 200 μg/L of As(III) as arsenite, 200 μg/L of As(V) as arsenate and 100 μg/L of As as DMA was filtered through the column for about 720 h at a flow rate of 0.51 mL/min. The data show that the scavenged As was located on the surface of the grain, though on some parts no As could be detected. A hematite grain from sample HIO1 showed a similar As distribution pattern. The freshly formed coatings of Fe-oxides on the surface of the siderite grains in the column filter strongly

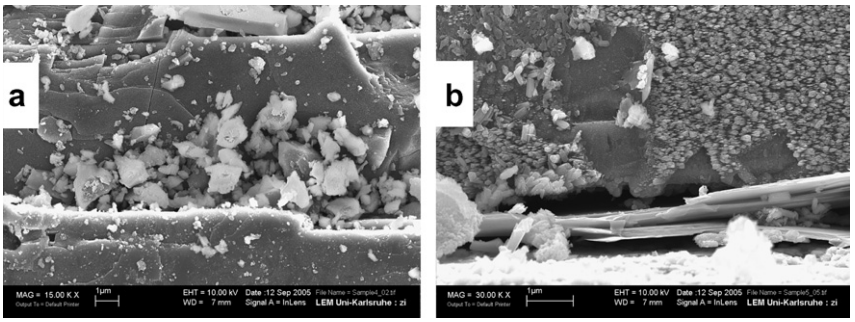


Fig. 9. SEM images of pristine $SIO_4$ (a) and HIO1 (b) with a grain size range of 0.25–0.5 mm.

promoted the removal of As by the filter filling material.

As seen in Fig. 8, at the upper part of the section across a mineral grain, only a limited amount of As was deposited, while at the lower right part the As concentration was very high. This suggests that the amount of As adsorbed on the surface of a grain possibly depended on the micro-morphology of the particle surface, which exerted some control on both the distribution of electrostatic charge and the development of the fresh Fe(III)-oxide coating. Besides, in the packed materials of dual porosity nature the micro-morphology affected the diffusion of the solute to the micro-pores where most of adsorption sites were located. The heterogeneous micro-morphology of individual siderite and hematite particles was observed on SEM images of grains from the fraction 0.25–0.5 mm (Fig. 9). In SIO4 (Fig. 9a), between the flat, coarse structure of the siderite matrix, small randomly distributed, possibly amorphous particles ($\leqslant$1 μm) were present. In the upper part of the HIO1 particle, many small crystallites (50–100 nm) occurred, while in the lower part crystalline aggregates apparently deposited along a micro-fissure (Fig. 9b).

## 4. Conclusions

The selected Fe minerals (natural siderites and hematites) effectively removed As species (including arsenate, arsenite and dimethylarsinic acid) from water, with the highest adsorption efficiency for arsenate. In general, the natural siderites eliminated As from water more efficiently than the natural hematites. The pH generally had a great impact on arsenate removal by both the siderites and the hematites, while arsenite removal was slightly dependent on the initial pH between 3 and 10. The presence of nitrate had no significant effect on the uptake of arsenate by the selected materials. In contrast, phosphate greatly impeded the adsorption of arsenate, so that at a concentration of 10 mg P/L the arsenate adsorption was reduced by about 50%. The removal efficiency of the selected Fe-minerals increased parallel to the decrease of grain size.

A column packed with SIO4 and HIO1 with the grain size fraction of 0.25–0.50 mm proved to be an efficient reactive filter for removal of As species, especially inorganic As (arsenate and arsenite). The results of the μ-synchrotron XRFA suggest that coatings of Fe(III)-oxides freshly formed on the surface of the siderite particles during the filter operation contributed considerably to the high adsorption capacity of the packed-bed materials. Morphologic heterogeneities of siderite/hematite grains possibly gave rise to the uneven distribution of adsorbed As on the mineral surface.

## Acknowledgements

H.M.G. is grateful to the Alexander von Humboldt Foundation, Germany, for providing a research fellowship to carry out this research and Prof. B. Merkel for his valuable suggestion on initiation of the research. Funding for this research has also been provided by the Natural Science Foundation of China (No. 40572145). The authors would like to express their gratitude for analytical support from their colleagues U. Kramar (ED-XRF, μ-SXRF), V. Zibat (SEM), C. Moessner (HR-ICP-MS), B. Oetzel (XRD, CSA), R. Kleeberg (XRD), T. Neumann (FI-AAS), G. Preuss (GF-AAS), C. Haug (mineral digestion), and K. Nikoloski (thin section preparation for the μ-SXRF). Special thanks are extended to the synchrotron radiation facility ANKA of the Forschungszentrum Karlsruhe, Germany and its staff (R. Simon) for allowing us to perform the μ-synchrotron XRF analyses. Helpful

comments by Dr. Lai Gui, University of Waterloo, are also acknowledged.

## References


Agency for Toxic Substances and Disease Registry (ATSDR), 2005. Top 20 Hazardous Substances: ATSDR/EPA Priority List for 2005. <http://www.atsdr.cdc.gov/cxcx3.html>.

Ahmed, S.M., 1966. Studies of the dissociation of oxide surface at the liquid–solid interface. Can. J. Chem. 44, 1663–1670.

Altundogan, H.S., Altundogan, S., Tuemen, F., Bildik, M., 2000. Arsenic removal from aqueous solutions by adsorption on red mud. Waste Manage. 20, 761–767.

Andrade, E.M., Molina, F.V., Posadas, D., 1999. Adhesion of colloidal hematite onto mercury in water–ethanol media. J. Colloid Interf. Sci. 215, 370–380.

Bang, S., Patel, M., Lippincott, L., Meng, X., 2005. Removal of arsenic from groundwater by granular titanium dioxide adsorbent. Chemosphere 60, 389–397.

Borgono, J.M., Vincent, P., Venturino, H., Infante, A., 1977. Arsenic in the drinking water of the city of Antofagasta: epidemiological and clinical study before and after installation of a treatment plant. Environ. Health Perspect. 19, 103–105.

Chatterjee, A., Das, D., Mandal, B.K., Chowdhury, T.R., 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.

Chen, S.L., Dzeng, S.R., Yang, M.H., Chiu, K.H., Shieh, G.M., Wai, C.M., 1994. Arsenic species in ground waters of the blackfoot disease area, Taiwan. Environ. Sci. Technol. 28, 877–881.

Cheng, Z.Q., Green, A.V., Louis, R., 2005. Removal of methylated arsenic in groundwater with Fe filings. Environ. Sci. Technol. 39, 7662–7666.

Cornell, R.M., Schwertmann, U., 1996. The Fe Oxides – Structure, Properties, Reactions, Occurrence and Uses. VCH Verlagsgesellschaft, VCH Publishers, New York.

Das, D., Chatterjee, A., Mandal, B., 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.

Del Razo, L.M., Arellano, M.A., Cebrian, M.E., 1990. The oxidation states of arsenic in well water from a chronic arsenicism area of northern Mexico. Environ. Pollut. 64, 143–153.

Dhar, R.K., Biswas, B.K., Samanta, G., Mandal, B.K., Chakraborti, D., Roy, S., Jafar, A., Islam, A., Ara, G., Kabir, S., Khan, A.W., Ahmed, S.A., Hadi, S.A., 1997. Groundwater arsenic calamity in Bangladesh. Cur. Sci. 73, 48–58.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto Fe oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182–4189.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling Hydrous Ferric Oxide. Wiley, New York.

EPA Office of Groundwater and Drinking Water, 2002. Implementation guidance for the arsenic rule. EPA Report-816-D-02-005, Cincinnati, USA.

European Commission, 1998. Directive related with drinking water quality intended for human consumption, Brussels, Belgium, 98/83/EC.

Farias, S.S., Casa, V.A., Vazquez, C., Ferpozz, L., Pucci, G.N., Cohen, I.M., 2003. Natural contamination with arsenic and other trace elements in ground waters of Argentine Pampean Plain. Sci. Total Environ. 309, 187–199.

Ford, R.G., 2002. Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. Environ. Sci. Technol. 11, 2459–2463.

Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Sci. Soc. Am. 66, 413–421.

Gu, Z.M., Fang, J., Deng, B.L., 2005. Preparation and evaluation of GAC-based Fe-containing adsorbents for arsenic removal. Environ. Sci. Technol. 39, 3833–3843.

Guo, H.M., Wang, Y.X., Shpeizer, G.M., Yan, S., 2003. Natural occurrence of arsenic in shallow groundwater, Shanyin, Datong Basin, China. J. Environ. Sci. Health A 38, 2565–2580.

Harper, T.R., Kingham, N.W., 1992. Removal of arsenic from wastewater using chemical precipitation methods. Water Environ. Res. 64, 200–203.

Horanyi, G., Joo, P., 2000. In situ study of the specific adsorption of $HSO_4^-/SO_4^{2-}$ ions on hematite by radiotracer technique. J. Colloid Interf. Sci. 227, 206–211.

Hsia, T.H., Lo, S.L., Lin, C.F., 1994. Characterization of arsenate adsorption on hydrous Fe oxide using chemical and physical methods. Colloids Surf. A: Physicochem. Eng. Aspects 5, 1–7.

Ioannou, A., Dimirkou, A., 1997. Phosphate adsorption on hematite, kaolinite, and kaolinite–hematite (k–h) systems as described by a constant capacitance model. J. Colloid Interf. Sci. 192, 119–128.

Jain, A., Raven, K.P., Loeppert, R.H., 1999. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net $OH^-$ release stoichiometry. Environ. Sci. Technol. 33, 1179–1184.

Jeon, B.H., Dempsey, B.A., Burgos, W.D., Royer, R.A., 2003. Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto hematite. Water Res. 37, 4135–4142.

Kondo, H., Ishiguro, Y., Ohno, K., Nagase, M., Toba, M., Takagi, M., 1999. Naturally occurring arsenic in the groundwaters in the southern region of Fukuoka prefecture, Japan. Water Res. 33, 1967–1972.

Lumsdon, D.O., Evans, L.J., 1994. Surface complexation model parameters for goethite (a-FeOOH). J. Colloid Interf. Sci. 164, 119–125.

Mandal, B.K., Chowdhury, T.R., Samanta, G., Basu, G.K., Chowdhury, P.P., Chanda, C.R., Lodh, D., Karan, N.K., Dhar, R.K., Tamili, D.K., Das, D., Saha, K.C., Chakraborti, D., 1996. Arsenic in ground water in seven districts of West Bengal, India-the biggest arsenic calamity in the world. Cur. Sci. 70, 976–986.

Manning, B.A., Goldberg, S., 1996. Modelling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Sci. Am. 60, 121–131.

Matisoff, G., Khourey, C.J., Hall, J.F., Varnes, A.W., Strain, W.H., 1982. The nature and source of arsenic in northeastern Ohio ground water. Ground Water 20, 446–455.

Munoz, J.A., Gonzalo, A., Valiente, M., 2002. Arsenic adsorption by Fe(III)-loaded open-celled cellulose sponge: thermo-

dynamic and selectivity aspects. Environ. Sci. Technol. 36, 3405–3411.

Nagy, G., Korom, I., 1983. Spale hautsymptome der arsenvergifturg aut grund der arsenendemic in bugac-alsomonostor. Z. Hautkr. 58, 961–964.

Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. Nature 395, 338.

Parkhurst, D., Appelo, C., 1999. User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey, Water-Resource Investigation Report 99-4259.

Parks, G.A., De Bruyn, P.L., 1962. The zero point of charge of oxides. J. Phys. Chem. 66, 967–973.

Payne, K.B., Abdel-Fattah, T.M., 2005. Adsorption of arsenate and arsenite by Fe-treated activated carbon and zeolites: effects of pH, temperature, and ionic strength. J. Environ. Sci. Health A 40, 723–749.

Peters, S.C., Blum, J.D., Klaue, B., Karagas, M.R., 1999. Arsenic occurrence in New Hampshire drinking water. Environ. Sci. Technol. 33, 1328–1333.

Petrick, J.S., Ayala-Fierro, F., Cullen, W.R., Carter, D.E., Aposhian, H.V., 2000. Monomethylarsonous acid ($MMA^{III}$) is more toxic than arsenite in changing human hepatocytes. Toxicol. Appl. Pharm. 163, 203–207.

Pivovarov, S., 2001. Adsorption of cadmium onto hematite: temperature dependence. J. Colloid Interf. Sci. 234, 1–8.

Rabung, T., Geckeis, H., Kim, J., Beck, H.P., 1998. Sorption of Eu(III) on a natural hematite: application of a surface complexation model. J. Colloid Interf. Sci. 208, 153–161.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32, 344–349.

Roy, W.R., Hassett, J.J., Griffin, R.A., 1986. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Sci. 142, 203–210.

Rüde, T.R., 1996. Beitraege zur geochemie des arsens. Karlsruher Geochem. PhD thesis, Institute for Mineralogy and Geochemistry, Univ. Karlsruhe.

Rüde, T.R., Puchelt, H., 1994. Development of an automated technique for the speciation of arsenic using flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS). Fresenius J. Anal. Chem. 350, 44–48.

Schlottmann, J.L., Breit, G.N., 1992. Mobilization of As and U in the central Oklahoma aquifer, USA. In: Kharaka, Y.K., Maest, A.S. (Eds.), Water–Rock Interaction. Balkema, Rotterdam, pp. 835–838.

Singh, D.B., Prasad, G., Rupainwar, D.C., Singh, V.N., 1988. As(III) removal from aqueous solution by adsorption. Water Air Soil Pollut. 42, 373.

Smedley, P.L., Zhang, M., Zhang, G.Y., Luo, Z.D., 2001. Arsenic and other redox-sensitive elements in groundwater from the Huhhot Basin, Inner Mongolia. In: Cidu, R. (Ed.), Water–Rock Interaction, vol. 1. Swets & Zeitlinger, Lisse, pp. 581–584.

Stumm, W., 1992. Chemistry of the Solid–Water Interface Processes at the Mineral–Water and Particle–Water Interface in Natural Systems. John Wiley & Sons, New York.

Styblo, M., Del Razo, L.M., Vega, L., Germolec, D.R., LeCluyse, E.L., Hamilton, G.A., Reed, W., Wang, C., Cullen, W.R., Thomas, D.J., 2000. Comparative toxicity of trivalent and pentavalent inorganic and methylated arsenicals in rat and human cells. Arch. Toxicol. 74, 289–299.

Su, C., Puls, R.W., 2001. Arsenate and arsenite removal by zerovalent Fe: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environ. Sci. Technol. 35, 4562–4568.

Su, C.M., Puls, R.W., 2004. Significance of Fe(II, III) hydroxycarbonate green rust in arsenic remediation using zero valent Fe in laboratory column tests. Environ. Sci. Technol. 38, 5224–5231.

Sun, X., Doner, H.E., 1998. Adsorption and oxidation of arsenite on goethite. Soil Sci. 163, 278–287.

Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., 2003. Arsenic removal from drinking water using Fe oxide-coated sand. Water Air Soil Pollut. 142, 95–111.

US EPA, 1999. Toxicity characteristics leaching procedure. US Environmental Protection Agency, Fed. Reg. 55, 11798–11877.

Welch, A.H., Lico, M.S., Hughes, J.L., 1988. Arsenic in ground water of the western United States. Ground Water 26, 333–347.

Wilkie, J.A., Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloids Surf. A 107, 97–110.

World Health Organization, 1996. Guidelines for Drinking-water Quality, Health Criteria and Other Supporting Information, second ed., vol. 2. WHO, Geneva, Switzerland, pp. 940–949.

Yamauchi, H., Fowler, B.A., 1994. Toxicity and metabolism of inorganic and methylated arsenicals. In: Nriagu, J.O. (Ed.), Arsenic in the Environment, Part II: Human Health and Ecosystem Effects. John Wiley & Sons, New York, pp. 35–53.

Zakharyan, R.A., Ayala-Fierro, F., Cullen, W.R., Carter, D.M., Aposhian, H.V., 1999. Enzymatic methylation of arsenic compounds, VII. Monomethylarsonous acid ($MMA^{III}$) is the substrate for MMA methyltransferase of rabbit liver and human hepatocytes. Toxicol. Appl. Pharm. 158, 9–15.