

Adsorption of arsenic species from water using activated siderite–hematite column filters

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Abstract

Arsenic is present at relatively high concentrations in surface water and groundwater as a result of both natural impacts and anthropogenic discharge, which requires proper treatment before use. The present study describes As adsorption on a siderite–hematite filter as a function of activating condition, empty bed contact time, and As species. Hydrogen peroxide activating increased As adsorption on siderite by 16.2 $\mu\text{g/g}$, and on hematite by 13.0 $\mu\text{g/g}$. The H_2O_2 conditioning enhanced adsorption efficiency of activated siderite–hematite filters up to throughput of 500 pore volumes of 500 $\mu\text{g/L}$ As water. At values greater than 47 min, the empty bed contact time (EBCT) had only a weak influence on the removal capacity of pristine siderite–hematite filters. Due to the formation of fresh Fe(III)-oxide layer in the H_2O_2 -conditioned filter and the pristine hematite–siderite filter, both of them may be utilized as a cost-effective reactor for treating As water. A toxicity characteristic leaching procedure (TCLP) test showed that the spent minerals were not hazardous and could be safely landfilled.

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1. Introduction

There is an intensive research worldwide to improve established techniques and to develop novel treatment technologies for removing As from drinking water. The major technologies include precipitation-coagulation, membrane separation, ion exchange, lime softening and adsorption on iron oxides or activated alumina [1–5]. Among these techniques proposed in the literatures, techniques involving immobilization of As by adsorption have received much attention on natural geomaterials, including natural zeolite and volcanic stone [6], ferruginous manganese ore [7], oxisol [8], natural iron ores [9]. Although the use of hematite for As adsorption has been documented [10–12], investigations involving both natural siderite and natural hematite are less frequently reported [13,14]. There is a lack of information on the performance of siderite–hematite column filters for removing As species from water.

In As-affected regions the bulk of the population is poor, so that people urgently need appropriate technologies which are

cheap, simple to use, and easily adaptable to either a household or a village scale [15]. As relatively cheap materials, natural siderite and natural hematite could be valuable options to be used in those technologies. Actually, both materials are abundant in the nature, and readily available in As-affected regions. Our previous column experiments have shown that the siderite–hematite filter may efficiently remove aqueous As species [13]. However, prior to practical application, a more detailed characterization of the column filter is necessary, including effects of chemical conditioning, influences of empty bed contact time (EBCT) and As species on As adsorption. Hydrogen peroxide in the presence of Fe^{2+} catalyst is known to be Fenton's reagent, which is a powerful oxidising agent [16,17]. It would react with siderite and result in the formation of Fe(III) oxides which have a good affinity for As. The H_2O_2 also reacts with ferric ion (Fe^{3+}) to form weaker hydroperoxyl radical (OOH^\bullet) and restore ferrous ion (Fe^{2+}) [18], which would cause a surface alteration of hematite after reacted. It was observed that As(III) is oxidized in parallel to the oxidation of Fe(II) by H_2O_2 , which was believed as a reaction pathway for As removal [16]. Krishna et al. used the Fenton's reagent and zero valent iron for As removal and found As concentration of treated water was lower than 10 $\mu\text{g/L}$ [19]. In this study, H_2O_2 was utilized for chemical conditioning. Therefore,

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this study has the following objectives: (i) to evaluate As removal by H₂O₂-activated siderite and hematite in batch experiments; (ii) to investigate the As uptake by siderite–hematite filters as a function of H₂O₂-conditioning, EBCT, and inflow As species; (iii) to determine the leachability of the adsorbed As and the potential toxicity of the used adsorbents using the toxicity characteristic leaching procedure (TCLP).

2. Materials and methods

2.1. Materials

The natural Fe-minerals used in this study came from Mineral Collection Centre of Technische Universität Bergakademie Freiberg, Germany. The samples SIO3 (Fundorf, Germany) and SIO4 (Fuesseberg, Germany) contain considerable amounts of siderite (78 and 96%, respectively). The hematite-bearing samples HIO1 and HIO4 were from Fichtelberg, Germany and Great Britain, with hematite contents of 86 and 69%, respectively. Mineralogical and chemical compositions of these natural materials were described in more details by Guo et al. [13]. The mineral samples were ground and sieved to produce various particle size fractions. Particle size fraction of 0.25–0.50 mm used in this study was washed with deionised water to remove dust and fines before As adsorption tests. Specific surface area of the sample materials with the grain size of 0.25–0.50 mm was provided in Guo et al. [13].

All reagents used, including sodium chloride (NaCl), hydrogen peroxide (H₂O₂), sodium hydroxide (NaOH), and glacial acetic acid (CH₃COOH), were of analytical grade. Stock As solutions (100 mg/L) were prepared by dissolving sodium arsenite (NaAsO₂, Fluka Chemical, >99.0%), dimethylarsinic acid ((CH₃)₂As(O)OH, Sigma–Aldrich, >98.0%) or sodium arsenate (Na₂HAsO₄·7H₂O, Fluka Chemical, >98.5%), in Milli-Q water. All glassware and sample bottles were washed with a detergent solution, rinsed with tap water, soaked with 1% sub-boiled nitric acid for at least 12 h, and finally rinsed with Milli-Q water three times.

2.2. Analytical methods

Total As concentration was analyzed by standard method using graphite furnace atomic absorption spectrometry (GF-AAS, Model 4110ZL, Perkin-Elmer). Iron and Mn concentrations were determined by standard method using flame atomic absorption spectrometry (Model 1100B, Perkin-Elmer). Other trace elements were analyzed by means of high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Axiom, VG Elemental). A flow injection hydride generation system (FIAS 200, Perkin-Elmer) coupled with atomic absorption spectrometry (AAS 4001, Perkin-Elmer) was used for As speciation. The detailed analytical procedure was described by Rüdè and Puchelt [20] and Rüdè [21]. The solution pH was monitored by a WTW pH probe (pH-Electrode SenTix 43-1) and meter (Model # pH 330).

For the synchrotron-based methods, thin sections of 100 μm thickness mounted on Suprasil microscope slides were pre-

pared from siderite and hematite grains. Element mapping across grains were carried out at the FLUO beamline of the ANKA Synchrotron Facility (Karlsruhe, Germany) by confocal μ-synchrotron XRFA. The primary beam was focused to 2 μm × 4 μm, using refractory lenses. The characteristic X-rays were guided to the Si(Li) detector using a poly-capillary with a focal diameter of 20 μm. This results in a spatial resolution corresponding to an elliptical cylinder of 2 μm × 4 μm × 20 μm per voxel. Used siderite and hematite grains from the column experiments were mapped for Fe, Mn, and As distributions. Additionally, the pristine minerals and the used filling materials were examined under scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS) analysis capability.

2.3. Batch experiments

The activated material for batch adsorption was prepared by mixing 2 g of the material with 20 mL of H₂O₂ solution in a 100 mL polyethylene bottle. During reaction, the bottle was tightly closed and kept still. After a predetermined reaction time (usually 24 h, otherwise stated), the supernatant was decanted and filtered through 0.45 μm cellulose acetate filter. The filtered solution was analyzed for Fe and Mn, whereas the activated residue in the bottle was dried at 105 °C for 24 h. After cooling to room temperature in a desiccator, the activated material was weighed and stored in capped bottles for the batch adsorption experiments.

For the adsorption experiments, 50 mL of synthetic As solution of predetermined concentration (1000 μg/L As(V)) was added to 0.5 g of the activated material in a 100 mL polyethylene bottle. The dosage of adsorbent was kept a constant of 10 g/L. All experiments were conducted at room temperature (20 ± 2 °C). During the experiment, the samples were manually shaken every 8 h. After 24 h, the supernatant from each bottle was decanted and filtered through 0.45 μm cellulose acetate filter. The filtered solution was analyzed for total As. In order to maintain a relatively constant ionic strength, all As solutions were prepared in a 0.01 M NaCl matrix as a background electrolyte. It is presumable that in order to generate an activated material with optimal adsorption capacity, the concentration of H₂O₂ solution has to be optimised.

2.4. Column experiments

Plexiglass columns with an inner diameter of 30 mm and a height of 150 mm were used in the column study as fixed-bed up-flow reactor, which yielded a working volume of about 100 mL. In order to generate H₂O₂-conditioned filling materials, two column filters packed with pristine siderite (SIO4) in the lower half and pristine hematite (HIO1) in the upper half were in situ conditioned by 0.5 M H₂O₂ solution, the concentration of which was optimised by preliminary batch adsorption experiments, at an upward flow rate of 0.51 mL/min for 25 h (designated as C-A25) and 50 h (designated as C-A50), respectively. The purpose of the filter conditioning was to generate fresh Fe(III)-oxide coatings on the surface of grains. Prior to As adsorption, the conditioned columns were rinsed for 24 h with Milli-Q water

at an upward flow rate of 0.51 mL/min, in order to remove the residual H_2O_2 in the column. For sake of comparison, another column (C-0) packed with the pristine SIO4 in the lower half and the pristine HIO1 in the upper half was directly used to remove As. Feedwater containing 500 $\mu\text{g/L}$ total As (including 200 $\mu\text{g/L}$ As(V), 200 $\mu\text{g/L}$ As(III), and 100 $\mu\text{g/L}$ As-DMA), as well as 0.01 M NaCl, was pumped through the column filters at an upward flow rate of 0.51 mL/min with a peristaltic pump (Model # 205S, Watson Marlow Company, Germany). This flow rate yielded an empty bed contact time (EBCT) of about 200 min. In order to investigate the influence of flow rate and influent As species on As removal, two further columns with the same filling materials as C-0 were penetrated by As solution containing 250 $\mu\text{g/L}$ As(V) and 250 $\mu\text{g/L}$ As(III) at an upward flow rate of 1.48 mL/min (designated as C-1) and 2.15 mL/min (designated as C-2), corresponding to EBCT of 68 and 47 min, respectively. Effluent solutions from the column tests were collected at regular intervals and analyzed for residual As species.

2.5. The toxicity of characteristic leaching procedure (TCLP)

EPA SW846 Method 1311, the toxicity of characteristic leaching procedure (TCLP), developed by the United States Environmental Protection Agency [22], provides a means of classifying the solid material as inert or hazardous in respect of their potential to release chemical contaminants. The TCLP was applied to the filling adsorbents after completion of the adsorption experiment to evaluate the mobility of adsorbed As. In the TCLP, the used material was agitated for 18 h in the extraction solution at pH of 4.93, with a liquid/solid ratio of 20. This extraction solution was prepared by adding 64.3 mL of 1 M NaOH and 5.7 mL of glacial CH_3COOH to Milli-Q water, and diluting to a final volume of 1 L. After agitation, an aliquot was filtered through a 0.45 μm cellulose acetate filter and analyzed for total dissolved As by GF-AAS. If the As concentration exceeds 5 mg/L, the solid is classified as hazardous waste.

3. Results and discussion

3.1. Batch studies

3.1.1. Effect of H_2O_2 -activating time

Two grams of material was activated by 20 mL of 0.5 M H_2O_2 solution in a 100 mL polyethylene bottle for 0–125 h. After dried, the activated materials (activated SIO3, SIO4, HIO1, and HIO4) were nominated as ASIO3, ASIO4, AHIO1 and AHIO4, respectively) were used to remove As(V) from aqueous solution. Fig. 1 shows the As adsorption on the activated materials as affected by H_2O_2 activating time. In comparison with the pristine material, the As adsorption capacity of AHIO1 and ASIO3 (24 h of the activating time) increased by 13.0 and 16.2 $\mu\text{g/g}$, respectively. The As adsorption on both activated materials generally followed the same trend with the activating time, which decreased shortly after 24 h of the activating time, whereas reached a second slightly higher peak at 125 h. This trend possibly arose from the same activation mechanisms for both the siderite and the

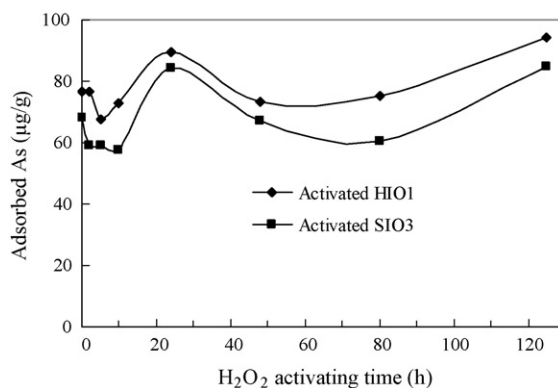


Fig. 1. Adsorption of As on activated materials as a function of H_2O_2 activating time (Activation conditions: concentration of H_2O_2 solution = 0.5 M; the ratio of solid to solution = 100 g/L. Arsenic removal conditions: ionic strength = 0.01 M NaCl; initial As(V) = 1000 $\mu\text{g/L}$; contact time = 24 h; dosage = 10 g/L; $T = 20 \pm 2^\circ\text{C}$).

hematite involving sequential reactions in the presence of Fenton's reagent, which is discussed later. Although an activating time of 125 h made the materials the highest adsorption efficiency, it took much time to prepare the adsorbents which would limit its application for As removal in practice. Hence, an activating time of 24 h was applied for the materials used in other batch experiments.

3.1.2. Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the adsorption property was investigated by treating the materials for 24 h with H_2O_2 solutions of different concentrations and afterwards using the treated material for As adsorption. The results are shown in Fig. 2. After activated, the materials increased their adsorption capacity to different extent. Although the greatest relative improvement was observed for HIO4, As adsorption was less

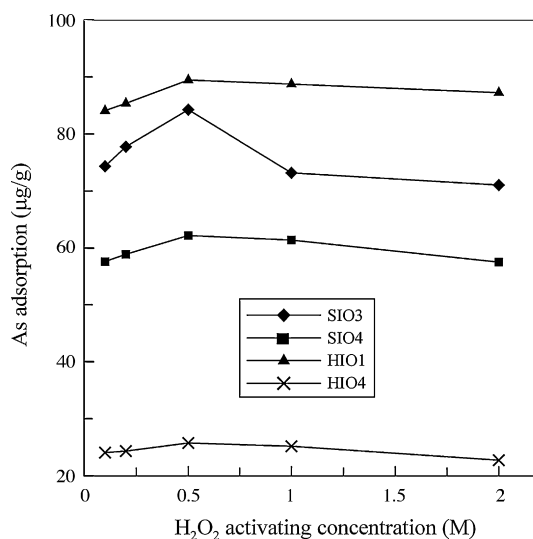
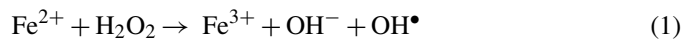
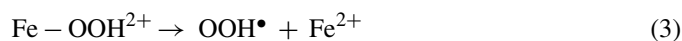
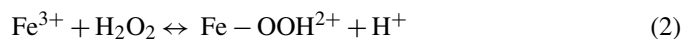


Fig. 2. Effect of H_2O_2 concentration on As removal by the activated materials (Activation conditions: concentration range of H_2O_2 solution = 0.1–2.0 M; the ratio of solid to solution = 100 g/L; reaction time = 24 h. Arsenic removal conditions: ionic strength = 0.01 M NaCl; initial As(V) = 1000 $\mu\text{g/L}$; contact time = 24 h; dosage = 10 g/L; $T = 20 \pm 2^\circ\text{C}$).

than 26.0 µg/g. The highest As adsorption occurred at a H₂O₂ concentration of 0.5 M, with an increase relative to the pristine material by 23.6 and 24.7% for SIO3 and SIO4, respectively. HIO1 and SIO4 were to be used in the column tests to investigate effects of in situ H₂O₂ activation on As adsorption. The improved adsorption of the activated materials was possibly due to the dissolution of the mineral surfaces and the formation of a fresh Fe(III)-oxide layer, as suggested by variable quantities of solution Fe (Supporting Material, Table A). The H₂O₂ in the presence of Fe²⁺ catalyst is known to be Fenton's reagent, which is a powerful oxidising agent because of the generation of OH• during the reaction [13]



Near pH 7.0, this reaction produces the precipitation of Fe(OH)₃, which lowers the concentration of Fe species available for reacting with H₂O₂, consequently promoting the dissolution of Fe minerals, especially of siderite. The freshly formed Fe(OH)₃ has a very high affinity for As [23,24]. This is the possible reason for the increase in As adsorption on the H₂O₂-activated siderite. The excess H₂O₂ reacts with ferric ion (Fe³⁺) to form weaker hydroperoxyl radical (OOH•) and restore ferrous ion (Fe²⁺) according to the following reaction scheme:



For example, in the SIO3–H₂O₂ batches, Fe concentration reached a minimum around a H₂O₂ concentration of 0.5 M, but generally increased at higher and lower H₂O₂ concentrations (Supporting Material, Table A). This suggests that up to a H₂O₂ concentration of 0.5 M, Fe(OH)₃ was continuously forming on the surface of the SIO3 grains, which however was re-dissolved at higher H₂O₂ concentrations due to the presence of excess H₂O₂. Consequently, the greatest amount of As(V) was adsorbed by the H₂O₂-activated siderites at a H₂O₂ concentration of 0.5 M (Fig. 2). Similar to the siderite-dominated material, the Fenton's reaction may also have been involved in the formation of fresh Fe oxides/oxyhydroxides on H₂O₂-activated hematites, contributing to the increase in their As adsorption capacity.

3.2. Column studies

3.2.1. Effect of H₂O₂ conditioning on As removal by the filters

Column experiments were carried out to evaluate the possibility of using H₂O₂ solution to in situ improve the As removal efficiency of the siderite–hematite filter. Based on the results of the batch experiments, the optimal H₂O₂ concentration, producing the best ASIO4 and AHIO1, was considered to be around 0.5 M. Consequently, a 0.5 M H₂O₂ solution was used as reactant for conditioning the natural materials in columns C-A25 and C-A50. The results presented in Fig. 3 show that there was no significant difference in the As removal between the conditioned columns and the original column packed with the pristine SIO4 and the pristine HIO1. After around 1000 pore volumes (PV) of As water were filtered, total As concentrations in the

effluents from C-0, C-A25 and C-A50 were still below 10 µg/L. A mass balance calculation indicates that total As load in C-0, C-A25 and C-A50 was about 185, 177 and 170 µg/g, respectively, before 50 µg/L of As breakthrough was observed. About 90% of total As in the effluents of all three columns was in form of organic As (DMA). Furthermore, As(III) was observed to be the major inorganic As species, the concentration of which was 2–4 times higher than that of As(V). During the entire operation, concentrations of total inorganic As were always below 10 µg/L. This result suggests that the SIO4–HIO1 column filter is a promising facility to be used for the removal of As, especially of inorganic species.

Up to a throughput of 500 PV, total As was much lower in the effluents from columns C-A25 and C-A50 than in those from C-0, indicating that at an early stage the conditioned columns adsorbed more As than the pristine column did. For example, at a throughput of 280 PV, total As concentration of the effluent from C-0, C-A25 and C-A50 was 3.43, 1.15 and 1.24 µg/L, respectively. However, the adsorption efficiencies of the conditioned columns and the pristine column did not significantly differ, after about 500 PV of As water were filtered. Guo et al. [13] observed Fe(III)-oxide coatings gradually developed on the SIO4 particles as the As solution flowed through the column packed with SIO4 and HIO1. It was found that, during aeration and filtration, a coating of Fe(III)-dominated precipitates formed on the surface of the filter sand in many centralized water treatment facilities. Such products constituted a significant part of the sand filter and contributed the high capacity for contaminant removal [25,26]. It can be speculated that the spontaneously formed Fe(III) oxides in C-0 may have played an important role in removing As after filter operation proceeded for about 20 days, closely approaching the As removal capacity of columns C-A25 and C-A50 previously catalytically conditioned by upward percolating 0.5 M H₂O₂ solution. Besides, the conditioning time greater than 25 h had no significant impact on As removal.

3.2.2. Effect of empty bed contact time (EBCT)

Empty bed contact time is a critical parameter, which determines residence time during which the solution being treated is in contact with the adsorbent. Hence, EBCT may strongly affect adsorption, especially if the adsorption mainly depends on the contact time between the adsorbent and adsorbate [27]. The flow rate ranged between 1.48 and 2.15 mL/min, corresponding to EBCT between 68 and 47 min. As shown in Fig. 4, the adsorption in SIO4–HIO1 filter was slightly influenced by the flow rate. It can be seen that the higher the flow rate, the lower the adsorptive efficiency due to the resulting lower contact time [28]. For example, at the flow rate of 1.48 mL/min a total As concentration of 10 µg/L was attained in the effluent after 8160 PV of As water were filtered through the column, while at the flow rate of 2.15 mL/min the same concentration was attained after a throughput of 7950 PV. At 50 µg/L of As breakthrough, total As load in C-1 and C-2 was about 780 and 753 µg/g, respectively. The weak response of As adsorption to the flow rate indicates that the adsorption slightly depended on diffusion.

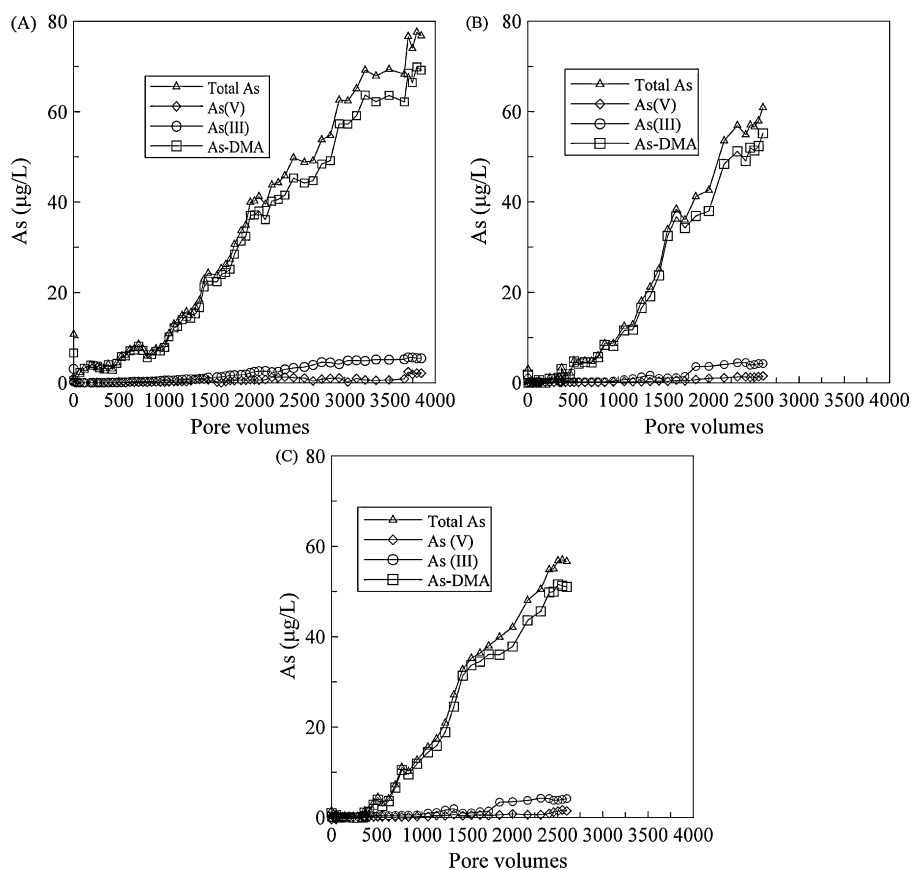


Fig. 3. Arsenic species in the effluents from pristine and H_2O_2 -conditioned $\text{SIO}_4\text{-HIO}_1$ filters. Experimental conditions: initial total As concentration = $500 \mu\text{g/L}$ (including $200 \mu\text{g/L}$ As(V), $200 \mu\text{g/L}$ As(III) and $100 \mu\text{g/L}$ As-DMA); ionic strength = 0.01 M NaCl ; EBCT = 200 min; flow rate = 0.51 mL/min . (A) The pristine filter (C-0), (B) the filter conditioned with $0.5 \text{ M H}_2\text{O}_2$ for 25 h at an upward flow rate of 0.51 mL/min (C-A25), and (C) the filter conditioned with $0.5 \text{ M H}_2\text{O}_2$ for 50 h at an upward flow rate of 0.51 mL/min (C-A50).

3.2.3. Effect of As species

As mentioned above, a higher flow rate caused a relatively lower adsorptive efficiency. However, the bed capacity of C-0 at the flow rate of 0.51 mL/min was much lower than that of C-1 at the flow rate of 1.48 mL/min . This suggests that, besides the flow rate, the As species in the influent was another important factor controlling the adsorption capacity of the column filter.

For instance, with the presence of $100 \mu\text{g/L}$ As-DMA, C-0 filter treated 1040 PV of As solution with $500 \mu\text{g/L}$ total As meeting the WHO guideline value of $10 \mu\text{g/L}$, while C-1 treated 8160 PV of $500 \mu\text{g/L}$ As solution with the absence of organic As (DMA). It seems that DMA possibly blocked the adsorption sites on the surface of the hematite–siderite grains in the filter, and consequently lowered the adsorptive efficiency. Cheng et al.

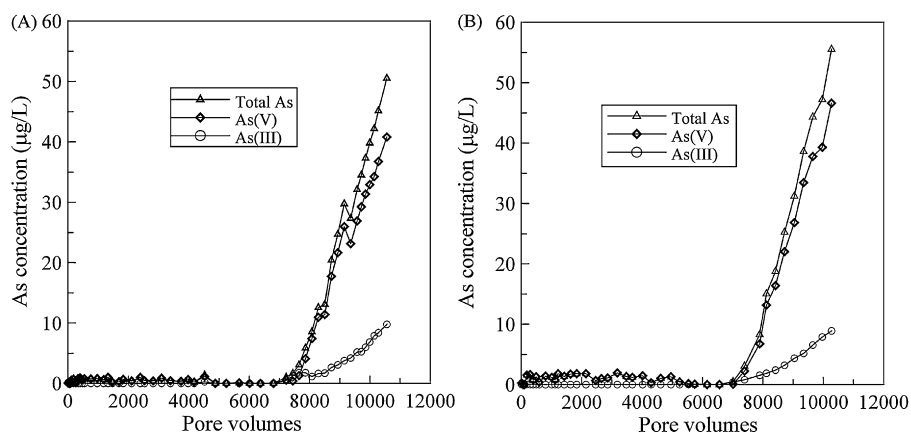


Fig. 4. Arsenic species in the effluents from pristine $\text{SIO}_4\text{-HIO}_1$ filters (Experimental conditions: initial total As concentration = $500 \mu\text{g/L}$ (including $250 \mu\text{g/L}$ As(V) and $250 \mu\text{g/L}$ As(III)); ionic strength = 0.01 M NaCl ; upward flow rate = 1.48 mL/min (A, C-1) and 2.15 mL/min (B, C-2), respectively).

also observed that the amount of DMA adsorbed on Fe fillings was much less than that of inorganic As(V) and As(III) [29]. They speculated that the two methyl groups of DMA molecule did not form bidentate inner-sphere complexes with adsorbents, whereas inorganic As(V) and As(III) did. However, it was found that the amount of DMA adsorbed on hematite or siderite was slightly greater than that of As(III) in the static batch study [13]. The difference in adsorption behavior between the static batch and the column filter was likely due to freshly formed Fe(III) hydroxides in the column filter during operation, as discussed later.

The results also show that there was a significant difference in As speciation of effluents between C-0 and C-1 (or C-2). For C-0, As(III) accounted for about 75% of inorganic As, and about 90% of total As was found to be in form of organic As (DMA). In comparison, As(V) was the dominant As species in the effluents of C-1 or C-2, which was generally equal to 80% of total As. This implies that organic As adversely affected the adsorption of As(III), possibly due to competitive adsorption between DMA and As(III) in the filter.

The pH of all effluents ranged between 6.80 and 7.20. ICP-MS analysis of few effluents shows that concentrations of trace elements were below EPA drinking water guideline. Therefore, the pristine siderite–hematite filter and the activated filter may be utilized to treat As-affected groundwater, which mainly contained inorganic As [30–32]. Guo et al. has investigated effect of other anions on As adsorption by SIO4 and HIO1 and found the presence of phosphate had a negative effect on As(V) adsorption, whereas the nitrate up to 10 mg N/L had no significant effect on As(V) uptake [13]. The phosphate would suppress As removal from real groundwater samples by the materials studied.

3.3. Leachability of adsorbed As

The TCLP was used to evaluate the leachability of the trapped As and to estimate the toxicity of the used SIO4 and HIO1 to the environment. Results show that the As released did not exceed 300 µg/L, which is well below the EPA regulatory limit of 5 mg/L for As. This suggests that the used SIO4 and

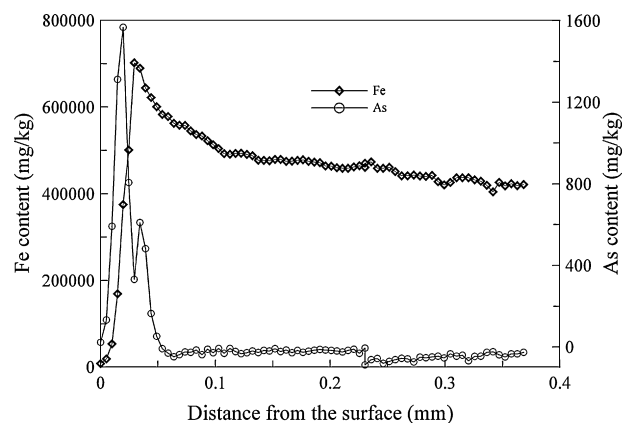


Fig. 5. Arsenic and Fe contents along a sectioned grain from the used SIO4 of column C-0. High-resolution element analysis was carried out by means of μ -synchrotron XRF with a resolution of 5 μ m.

HIO1 were not hazardous, and could be discharged in landfill deposits.

3.4. Characterization of As-loaded adsorbents

High-resolution element analysis by means of μ -synchrotron XRF on a thin section prepared from the spent SIO4 from column C-0 yielded information on the distribution of As and Fe contents in the used filling material. The line scans were carried out near to the surface of a particle using a resolution of 5 μ m. Due to the lack of adequate standards, only relative concentrations could be determined. The semi-quantitative As and Fe contents along the scan line are presented in Fig. 5. It can be seen that, the contents of As and Fe near to the surface were much higher than those in its inner part. Scavenged As was mainly presented within the surfacial reaction rim of the particles, which possibly indicates that As was removed as a result of both co-precipitation with Fe(III), and subsequently adsorption on fresh Fe(III) oxides/oxyhydroxides. Iron concentrations in the center roughly corresponded to the stoichiometric Fe content of siderite (\sim 48% Fe), whereas at the rim to that of goethite (\sim 70% Fe) (Fig. 5). This change in Fe content was accompanied by a strong increase in As content of up to 1600 mg/kg.

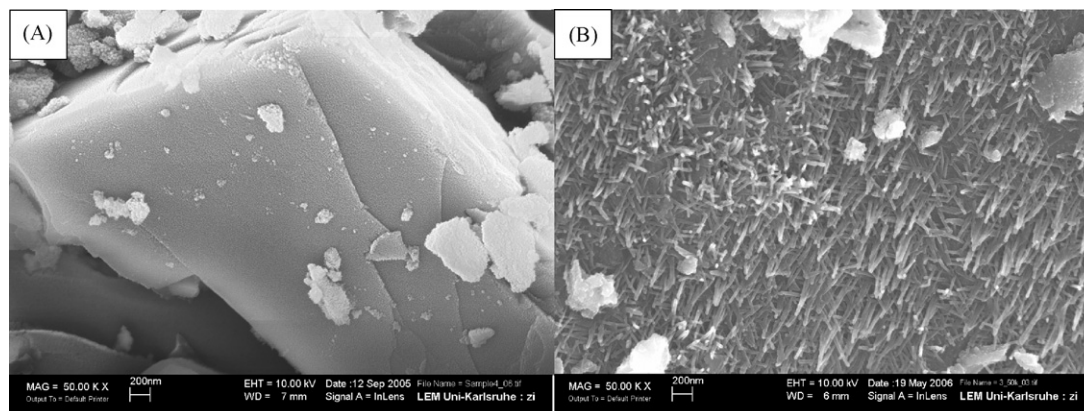


Fig. 6. SEM images of the pristine SIO4 (A) and the used SIO4 from column C-0 (B).

The high contents of Fe and As near the surface suggests that surficial FeCO_3 and/or solution Fe(II) were oxidized, leading to the co-precipitation of As with Fe(III)-oxides subsequently coating on the siderite matrix (SIO4 particles). This implication is supported by the SEM images of the pristine SIO4 and the used SIO4 (Fig. 6). In comparison with the original material (Fig. 6A), the used SIO4 (Fig. 6B) was found to be covered by needle-like goethite (or ferrihydrite) developed during filter operation. These freshly formed Fe-oxides have a very high affinity for As [24], contributing to the high adsorption capacity of the filling material.

4. Conclusions

A siderite–hematite filter was studied for its As retention capacity in dynamic experiments using artificial As solutions. The experiments allowed the identification of fundamental information in terms of the effects of H_2O_2 conditioning, empty bed contact time, and As species on As adsorption. Both H_2O_2 -activated hematites and H_2O_2 -activated siderites adsorbed a little more As(V) than the originals in batch experiments. The H_2O_2 -conditioning increased the adsorption efficiency of the activated siderite–hematite filter up to a throughput of 500 PV of As water. The conditioning time greater than 25 h did not significantly enhance the retention capacity of the column filter. An EBCT greater than 47 min had a slight impact on the removal capacity of the siderite–hematite filter. The combination of the μ -synchrotron XRFA and the SEM test proves that the freshly formed Fe(III)-oxides were developed on the surface of siderite grains, which contributed to the high adsorption capacity of the filling material in the columns. The spontaneously formed Fe oxides in the pristine mineral-packed column may have played an important role in removing As after filter operation proceeded for about 20 days, closely approaching the As removal capacity of the H_2O_2 -activated columns where the Fe(III) oxides were previously formed during conditioning. The TCLP test indicates the used adsorbents can be safely discharged in landfill sites. Results show that both the pristine hematite–siderite filter and the H_2O_2 -conditioned filter may be successfully employed to remediate As water meeting the WHO guideline.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.06.035.

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