

Effectiveness of various sorbents and biological oxidation in the removal of arsenic species from groundwater

Anna Corsini,^A Lucia Cavalca,^A Gerard Muyzer^{A,B} and Patrizia Zaccheo^{C,D}

^ADipartimento di Scienze per gli Alimenti, la Nutrizione e l'Ambiente (DeFENS), Università degli Studi di Milano, Via Celoria 2, I-20133 Milano, Italy.

^BInstitute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, 1090 GE Amsterdam, the Netherlands.

^CDipartimento di Scienze Agrarie e Ambientali – Produzione, Territorio, Agroenergia (DiSAA), Università degli Studi di Milano, Via Celoria 2, I-20133 Milano, Italy.

^DCorresponding author. Email: patrizia.zaccheo@unimi.it

Environmental context. Arsenic contamination of aquifers is a worldwide public health concern and several technologies have been developed to reduce the arsenic content of groundwater. We investigated the efficiency of various materials for arsenic removal from groundwater and found that iron-based sorbents have great affinity for arsenic even if groundwater composition can depress their ability to bind arsenic. Moreover, we showed that the use of microorganisms can enhance the removal of arsenic from groundwater.

Abstract. The As^{III} and As^V adsorption capacity of biochar, chabazite, ferritin-based material, goethite and nano zero-valent iron was evaluated in artificial systems at autoequilibrium pH (i.e. MilliQ water without adjusting the pH) and at approximately neutral pH (i.e. TRIS-HCl, pH 7.2). At autoequilibrium pH, iron-based sorbents removed 200 µg L⁻¹ As highly efficiently whereas biochar and chabazite were ineffective. At approximately neutral pH, sorbents were capable of removing between 17 and 100 % of As^{III} and between 3 and 100 % of As^V in the following order: biochar < chabazite < ferritin-based material < goethite < nano zero-valent iron. Chabazite, ferritin-based material and nano zero-valent iron oxidised As^{III} to As^V and ferritin-based material was able to reduce As^V to As^{III}. When tested in naturally As-contaminated groundwater, a marked decrease in the removal effectiveness occurred, due to possible competition with phosphate and manganese. A biological oxidation step was then introduced in a one-phase process (As^{III} bio-oxidation in conjunction with As^V adsorption) and in a two-phase process (As^{III} bio-oxidation followed by As^V adsorption). Arsenite oxidation was performed by resting cells of *Aliihoeflea* sp. strain 2WW, and arsenic adsorption by goethite. The one-phase process decreased As in groundwater to 85 %, whereas the two-phase process removed up to 95 % As, leaving in solution 6 µg L⁻¹ As, thus meeting the World Health Organization limit (10 µg L⁻¹). These results can be used in the scaling up of a two-phase treatment, with bacterial oxidation of As combined to goethite adsorption.

Received 19 November 2013, accepted 25 May 2014, published online 18 September 2014

Introduction

Extensive arsenic (As) pollution in groundwater affects highly populated areas in such a serious way that As became one of the major public health problems. Consequently a wide range of technologies has been tried for the removal of As from drinking water; the most common techniques utilise the processes of oxidation, co-precipitation, adsorption onto sorptive media, ion exchange and membrane techniques.^[1,2] Among these, the adsorption of As onto natural and synthetic materials have been broadly studied and it represents one of the most common treatment technologies practiced by the public drinking water systems in large municipal treatment plants and in small devices for small communities.

The adsorption of As onto natural and synthetic materials is a low cost, high efficiency process. A wide range of materials for aqueous As removal is available nowadays. Sorbent based on iron oxides and hydroxides and on activated alumina are the most common conventional materials; other metal oxide-based

sorbents, such as manganese dioxides, titanium dioxide and zirconium oxides, have been proposed, together with clays, natural zeolites and calcite.^[3]

A broad range of materials that are coming from agricultural or industrial processes, and that are easily accessible and low cost, have been evaluated in the screening of new sorbents. Materials derived from biological sources have also been studied as low cost sorbents, such as loaded orange waste gel,^[4] agricultural residue rice polish,^[5] iron-modified bamboo charcoal^[6] and bagasse fly ash.^[7] Some fresh and immobilised plant biomasses gained a significant interest for their ability to passively adsorb arsenite, thereby avoiding the pre-oxidation step.^[8,9] Mineral by-products such as magnesia-loaded fly ash cenospheres and manganese-loaded fly ash cenospheres^[10] and Zr^{IV} iron modified red mud^[11] have also been reported as promising sorbents for the removal of As.

Metallic iron as zero-valent iron nanoparticles has been used in the past for the treatment of As-contaminated groundwater

and also as a reactive medium in several field scale experiments.^[12] Similarly to inorganic iron nanoparticles, iron storage proteins (i.e. ferritin) are nanostructures that can encapsulate in the form of a nano-cage several compounds, such as phosphate.^[13] To the best of our knowledge, no evidence has been reported on the As removal capability of ferritin.

The main disadvantages of As adsorption onto solid materials are the direct competition for available adsorption sites between As and other oxyanions in the water^[14] and the general need of a pre-oxidation step to transform arsenite (As^{III}) to arsenate (As^{V}).^[12]

In fact, the two more common forms of As in water show completely different patterns of dissociation, as a consequence of the predominance of the neutral species H_3AsO_3 for As^{III} at pH 2–8 and of the single negatively charged H_2AsO_4^- for As^{V} at pH values 3–6.^[15] Arsenite is therefore more difficult to be removed by the positively charged surfaces of sorbents. This is a crucial point because the revised drinking water standard for As proposes to reduce As concentrations to less than $10 \mu\text{g L}^{-1}$ ^[16] and consequently there is a dramatic demand for oxidation technologies that effectively convert arsenite into arsenate before its removal.^[17] Biological oxidation of As^{III} by microorganisms has recently received a lot of attention as a sustainable alternative to the use of chemical oxidants.^[18–20]

In the present study natural minerals (goethite, chabazite), a pyrolysis by-product (biochar) and iron-based nanomaterials (ferritin-based material and zero-valent iron) were examined at their best effective dose for their ability and selectivity in removing As^{III} and As^{V} from water. The aim of the first part of the work was to explore the potential of conventional and novel materials as sorbents for As^{III} and As^{V} and their oxidising power with respect to As^{III} . We performed batch experiments under two conditions: (i) without controlling pH in order to evaluate the sorbents in the actual case of small devices with a high ratio of sorbent to water and (ii) at approximately neutral pH to simulate real groundwater conditions. Furthermore, in order to evaluate the interaction between chemical removal by sorbents and As^{III} biological oxidation, the effect of an As^{III} oxidiser selected bacterial strain on the sorption properties of a high effective As^{V} sorbent was evaluated in the artificial system and then assessed on a natural As-rich groundwater.

Materials and methods

Sorbents and chemicals

Sorption experiments were conducted with five materials: biochar, chabazite, a ferritin-based material, goethite (FeOOH) and nano zero-valent iron (Fe^0) (NZVI). Biochar was from Agrindustria snc (Cuneo, Italy), and derived from gasification of sprucewood; the sample used in adsorption experiments was milled and successively prehydrated in TRIS-HCl buffer (5 mM, pH 7.2) or MilliQ water for 24 h.

The chabazite-rich tuff was obtained from Verdi S.p.A. and contained 60 % (w/w) chabazite, 25 % (w/w) volcanic glass and traces of phillipsite, K-feldspar and biotite, with particles $<200 \mu\text{m}$. Biochar and chabazite were free from significant amounts of soluble As ($<0.5 \mu\text{g L}^{-1}$ for biochar and $4 \mu\text{g L}^{-1}$ for chabazite).

Ferritin-based material was provided by BiAqua B.V. (Badhoevedorp, the Netherlands) and the protein was stabilised onto sand, used as a carrier ($2.74 \text{ mg ferritin g}^{-1}$ dry sand).

The goethite used in this study was from Sigma–Aldrich (St Louis, MO, USA) and had a specific surface area of $11.6 \text{ m}^2 \text{ g}^{-1}$.

A commercial zero-valent iron (NANOIRON 25) was supplied by the NANOIRON s.r.o. (Rajhrad, Czech Republic) and consisted of an aqueous dispersion of Fe^0 nanoparticles stabilised by an inorganic modifier.

Arsenate and arsenite solutions were prepared by spiking MilliQ water and TRIS-HCl buffer (5 mM, pH 7.2) with $200 \mu\text{g L}^{-1} \text{As}^{\text{III}}$ or As^{V} from stock solutions of $1000 \mu\text{g L}^{-1} \text{NaAsO}_2$ or Na_2HAsO_4 (Sigma–Aldrich).

Groundwater sample

The groundwater sample used in the experiments was collected from an As-contaminated well in the Northern part of Italy (Cremona, Lombardy). Physico-chemical characterisation revealed that the groundwater sample was anoxic (with a redox potential (E_h) value of -113 mV , and no dissolved oxygen) and had the following physico-chemical characteristics: temperature of 15°C ; pH value of 7.6; CaCO_3 282 mg L^{-1} ; organic C $2.11 \mu\text{g L}^{-1}$; dissolved S- SO_4 $267 \mu\text{g L}^{-1}$; dissolved P- PO_4 $312 \mu\text{g L}^{-1}$; dissolved N- NO_3 $685 \mu\text{g L}^{-1}$; dissolved N- NH_4 $2680 \mu\text{g L}^{-1}$; dissolved Fe $760 \mu\text{g L}^{-1}$ and dissolved Mn $97 \mu\text{g L}^{-1}$. The As concentration in the sample was $171 \mu\text{g L}^{-1}$, with As^{III} as the main As species.

Resting cells preparation

The biological As^{III} oxidation step was carried out by addition of resting cells of *Aliihoeflea* sp. strain 2WW. Resting cells of the strain were able to oxidise As^{III} in TRIS-HCl.^[21]

The bacterial strain was grown for 48 h in mineral medium (BBWM) supplemented with sodium lactate (40 mmol L^{-1}) (BBWM-L) at 30°C under shaking conditions at 150 rpm. BBWM consisted of: solution A (g L^{-1}): KH_2PO_4 0.04; K_2HPO_4 0.04; NaCl 1.0; $(\text{NH}_4)_2\text{SO}_4$ 0.4; trace element solution 2 mL. The pH of solution A was 6.5. Solution B (g L^{-1}): CaCl_2 0.2; MgSO_4 0.2. Solutions A and B were sterilised separately by autoclaving. Equal volumes of solutions A and B were mixed after cooling and then supplemented with 1 % (v/v) vitamin solution. The vitamin solution was filter sterilised and contained (mg L^{-1}): *p*-aminobenzoic acid 5; biotin 5; folic acid 2; pyridoxine-HCl 1; riboflavin 5; thiamine 5; nicotinic acid 5; pantothenic acid 5; vitamin B12 0.1. The pH was adjusted to 8.0. After growth, cells were centrifuged at $12\,857 g$ at 10°C for 30 min. The cell pellet was washed three times with TRIS-HCl (5 mM, pH 7.2) and resuspended in the same medium. This cell suspension served as an inoculum in order to obtain a final cell density of $\sim 10^7 \text{ cell mL}^{-1}$.

Adsorption experiments in artificial and natural systems

Sorbents were tested at their most effective dose, identified in a preliminary screening carried out with different amounts of each sorbent. Based on these results, the following quantities of sorbents (g per 50 mL) were used: biochar 0.2, chabazite 1.0, goethite 0.2, ferritin-based material 11.4 and NZVI 0.05.

Adsorption experiments in artificial systems were performed in polypropylene tubes with the addition of 50 mL of TRIS-HCl (5 mM, pH 7.2) or MilliQ water, spiked with $200 \mu\text{g L}^{-1} \text{As}^{\text{III}}$ or As^{V} , chosen on the base of As content of the groundwater used in the present study. Batch experiments were prepared under aerobic conditions, with the exception of those with NZVI that were filled under anaerobic conditions in a Nitrogen Dry Box (Plas-Labs, Lansing, MI, USA) to prevent Fe^0 oxidation. The

tubes were closed with a cotton plug in order to allow gaseous exchange.

Adsorption experiments in natural systems were performed with 50 mL of natural As-contaminated groundwater in the presence of goethite (0.2 and 1.0 g) and of NZVI (0.05 g).

A preliminary check of a time course of the groundwater pH had shown a dramatic increase in pH values during 24 h of exposure to air (from 7.8 to 8.5), due to the evolution of dissolved CO₂. Consequently, batch experiments with natural As-contaminated water were prepared under anaerobic conditions in a Nitrogen Dry Box and tubes were closed with plastic plugs.

The effect of biological arsenite oxidation was evaluated in artificial and natural systems. Resting cells of *Aliihoeflea* sp. strain 2WW were added to 50 mL of TRIS-HCl or contaminated groundwater either in the absence or presence of goethite. A set of tubes with goethite only and one without addition of inoculum and goethite were used as controls.

A one- and two-phase process was compared by adding the bacterial cells either together with 0.2- and 1.0-g goethite (one-phase treatment) or by adding the bacterial cells 48 h before the addition of 0.2- and 1.0-g goethite followed by 48-h incubation (two-phase treatment).

All the experiments were incubated on a rotary shaker in the dark at 15 °C, chosen on the basis of the groundwater temperature measured on site. The pH was monitored at the beginning and at the end of the experiments using a Radiometer Copenhagen PHM210-pH meter. At the end of the experiments 20 mL of the suspensions were collected from each tube, centrifuged, filtered over nitrocellulose membranes (0.22-µm diameter) and acidified with HNO₃ to achieve a final concentration of 2% (v/v).

Analytical methods

Total As was determined in 5 mL of samples previously acidified with HNO₃. For speciation of As forms, As^{III} and As^V species were separated on the basis of their selective retention on a WATERS Sep-Pak Acell Plus QMA cartridge (Waters, Millford, MA, USA): As^V is retained in the cartridge, while allowing As^{III} to pass through and be collected. The procedure was performed according to Kim et al.^[22]: 5 mL of non-acidified samples was passed through the cartridge and the flow-through (containing As^{III}) was collected. The cartridge retaining As^V was then washed with 0.16 M HNO₃ to elute As^V from it.

Arsenic contents (total As, As^{III} and As^V) were determined by inductively coupled plasma–mass spectrometry (ICP-MS) (Agilent Technologies, Santa Clara, CA, USA). Standards of As for concentrations ranging from 0 to 1 mg L⁻¹ were prepared from NaAsO₂ (Sigma–Aldrich). For all the measures by ICP-MS an aliquot of a 2 mg L⁻¹ of an internal standard solution (⁴⁵Sc, ⁸⁹Y, ¹⁵⁹Tb, Agilent Technologies) was added both to samples and a calibration curve to give a final concentration of 20 µg L⁻¹. The instrument was tuned daily with a multi-element tuning solution for optimised signal-to-noise ratio.

Dissolved Mg, Ca, Mn, Fe and P content in the contaminated groundwater sample before and after the one-phase process were determined by ICP-MS; procedure was the same as that used for determining total As.

Statistical analysis

Data represent the mean values obtained from at least three replicates. The values were subjected to Student *t*-test

(*P* < 0.05) and to one-way analysis of variance (ANOVA) with Tukey-b test using *SPSS Statistics for Windows*, ver. 20.0 (IBM Corp., Armonk, NY).

Results

As^{III} and As^V removal by sorbents in artificial systems

Batch test studies with sorbents were conducted at auto-equilibrium pH (MilliQ water) and at neutral pH (TRIS-HCl solution).

Sorbents modified the pH of As-spiked MilliQ water at different values: pH 10.2 (biochar), pH 8.7 (chabazite), pH 6.4 (ferritin-based material), pH 5.8 (goethite) and pH 8.7 (NZVI). The effects of sorbents on As^{III} and As^V removal from MilliQ water are reported in Fig. 1a and 1b respectively. Removal of As from biochar and chabazite had no significant effect on As^{III} and As^V mobility; on the contrary ferritin-based material, goethite and NZVI were able to remove both As^{III} and As^V. Ferritin-based material and goethite showed a higher affinity for As^V than As^{III}; whereas no detectable As remained in both the As^{III}- and As^V-spiked solutions after 1 h of contact with NZVI. Checking a 50-fold concentrated As-spiked MilliQ solution added with 0.05 g of NZVI, a higher affinity of NZVI for As^{III} than As^V was found: the remaining As^{III} and As^V in solution accounted for 4.3 and 6.8 mg L⁻¹ respectively.

Results of As^{III} and As^V adsorption experiments conducted in TRIS-HCl buffered solutions are reported in Fig. 2a and 2b respectively.

Preliminary trials showed that As adsorption onto goethite was not significantly affected by the presence of TRIS-HCl (data not shown). At neutral pH all tested sorbents induced a statistically significant decrease of As^{III} concentration, the most drastic effect being exerted by ferritin-based material, goethite and NZVI. Similarly to As^{III}, ferritin-based material, goethite and NZVI efficiently immobilised As^V, whereas a slight removal of As^V by biochar and chabazite was observed. Goethite showed a greater affinity for As^V than for As^{III}.

When As^{III} was the initial As species in the buffer solution, As^V was detected at the end of the adsorption experiments in the presence of ferritin-based material, NZVI and, to a lesser extent, chabazite (Table 1), suggesting an abiotic oxidation of As^{III}. Conversely, As^V seemed not to be reduced by sorbents, with the exception of ferritin-based material, that induced a reduction of one third of the total soluble As recovered in the solution.

Adsorption of As^{III} and As^V from a natural system by goethite and NZVI

The As removal efficiency of NZVI and goethite was evaluated in a groundwater sample. The water pH in the control and in the treatments with sorbents were as follows: pH 7.5 (control), pH 7.1 (goethite) and pH 7.7 (NZVI).

A control without sorbents did not show changes in the amount and speciation of As (Fig. 3); this indicated that no apparent changes of As speciation due to biotic or abiotic reactions occurred during the experiments. The performance of both sorbents was worse in the natural than in the artificial system: As immobilisation by NZVI and by goethite were reduced by 60 and 12% respectively, as compared with those in MilliQ water. Speciation of the soluble As at the sampling time indicated that NZVI promoted a complete oxidation of remaining As^{III}, whereas no detectable As^V was recovered in the goethite treatment, thus confirming the absence of

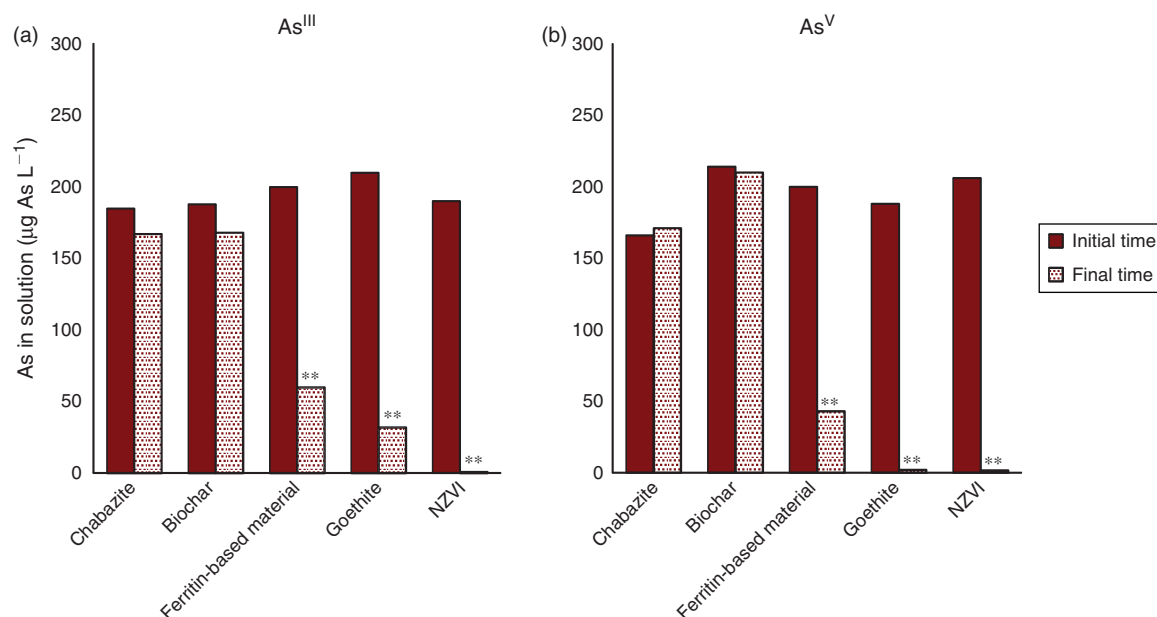


Fig. 1. Soluble As before and after contact of 50 mL of $200 \mu\text{g L}^{-1}$ (a) As^{III} - and (b) As^{V} -spiked MilliQ water with biochar (0.2 g), chabazite (1.0 g), ferritin-based material (11.4 g), goethite (0.2 g) and nano zero-valent iron (NZVI) (0.05 g). Experimental time: biochar, chabazite, ferritin-based material, goethite, 48 h; NZVI, 1 h. Asterisks indicate statistical significance at: *, $P=0.05$; **, $P=0.01$; as compared with time 0, determined by the Student's t test.

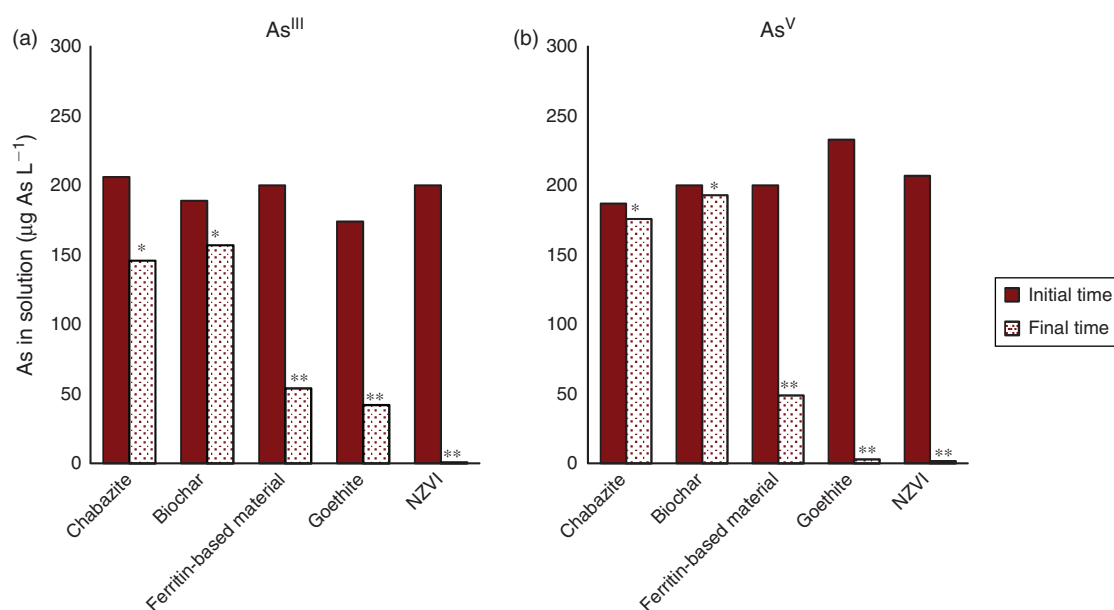


Fig. 2. Soluble As before and after contact of 50 mL of $200 \mu\text{g L}^{-1}$ (a) As^{III} - and (b) As^{V} -spiked TRIS-HCl with biochar (0.2 g), chabazite (1.0 g), ferritin-based material (11.4 g), goethite (0.2 g) and nano zero-valent iron (NZVI) (0.05 g). Experimental time: biochar, chabazite, ferritin-based material, goethite, 48 h; NZVI, 1 h. Asterisks indicate statistical significance at: *, $P=0.05$; **, $P=0.01$; (double asterisk) as compared with time 0, determined by the Student's t test.

Table 1. Speciation of soluble As ($\mu\text{g L}^{-1}$) retrieved after contact with sorbents (mean \pm standard deviation, $n = 3$)
nd, not determined

Sorbent	As^{III} -spiked TRIS-HCl			As^{V} -spiked TRIS-HCl		
	Total	As^{III}	As^{V}	Total	As^{III}	As^{V}
Chabazite	190 ± 1	180 ± 9	17 ± 6	nd	nd	nd
Ferritin-based material	54 ± 7	42 ± 3	23 ± 0.3	37 ± 10	30 ± 5	15 ± 7
Goethite	43 ± 4	40 ± 6	2.2 ± 0.7	5.0 ± 1.5	<0.1	4.5 ± 2.8
NZVI	4.4 ± 0.1	2.8 ± 0.3	1.1 ± 0.5	2.7 ± 0.4	0.4 ± 0.3	0.7 ± 0.0

chemical or biological activities towards As in the presence of goethite.

Effect of bio-oxidation of As^{III} on As removal in artificial and natural systems

Owing to the inability of goethite to oxidise As^{III} in the groundwater, thus leading to an As concentration higher than the WHO limit, a biological As^{III} oxidation step was considered in one- and two-phase experiments.

A preliminary one-phase experiment in As^{III}-spiked TRIS-HCl solution (Fig. 4a) indicated that the combination of As^{III} bio-oxidation and adsorption by goethite resulted in a high efficient removal of As (>95%), decreasing the soluble As concentration to 8 µg L⁻¹. At the end of the experiment, As^V was the only detectable As form in solution, indicating that the ability of the cells to oxidise As^{III} was not affected by

the presence of goethite. Resting cells of strain 2WW converted As^{III} into As^V completely, whereas goethite without cells removed ~85% of the initial As^{III}.

The one-phase treatment was tested in a natural system (i.e. As^{III}-contaminated groundwater) (Fig. 4b). Strain 2WW was able to completely oxidise 150 µg L⁻¹ As^{III} present in groundwater; in the absence of 2WW cells, goethite adsorbed As^{III} present in the groundwater at a comparable level to the artificial system (85% removal). The combined As^{III} bio-oxidation and adsorption process was not able to enhance As removal, as observed in the artificial system. This effect may be attributable to competition of other ions for goethite sorption sites. Changes in groundwater ion compositions during the time course of the experiment are reported in Table 2. A dramatic decrease of soluble iron concentration occurred in all tubes at the end of the incubation, whereas the manganese and phosphorous concentration decreased in the presence of goethite. Neither calcium nor magnesium were removed in any treatment and dissolved carbon concentrations were negligible (data not shown). When the amount of goethite was increased from 0.2 to 1.0 g per 50 mL, no dose effect on As removal was evidenced either in the presence or in the absence of 2WW cells.

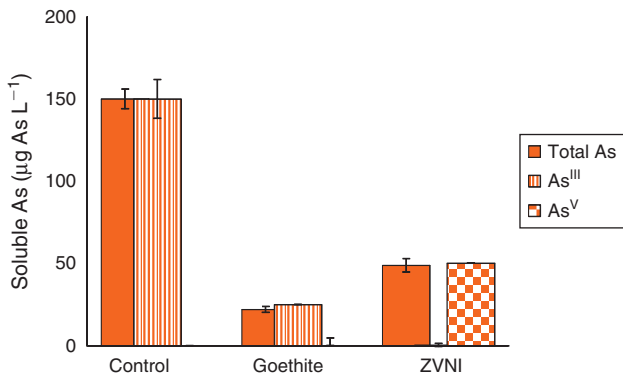


Fig. 3. Total As, As^{III} and As^V concentration in the As contaminated groundwater sample after contact with sorbents: nano zero-valent iron (NZVI) (0.05 g 50 mL⁻¹, experimental time: 1 h), goethite (0.2 g 50 mL⁻¹, experimental time: 48 h). Error bars represent the standard deviations of four replicates.

Table 2. Total As and main coexisting ions (µg L⁻¹) in natural groundwater sample before and after 48-h incubation

Values followed by the same superscript lower case letters denote those not significantly different within each column ($P < 0.05$). GW, As-contaminated groundwater

Sample	As	Mn	Fe	P
GW at initial time	171 ^c	97 ^b	760 ^b	312 ^b
GW at final time	150 ^b	84 ^b	151 ^a	373 ^b
GW + strain 2WW	154 ^b	97 ^b	186 ^a	269 ^b
GW + goethite	39 ^a	1.6	185 ^a	<10 ^a
GW + strain 2WW + goethite	26 ^a	1.4	179 ^a	<10 ^a

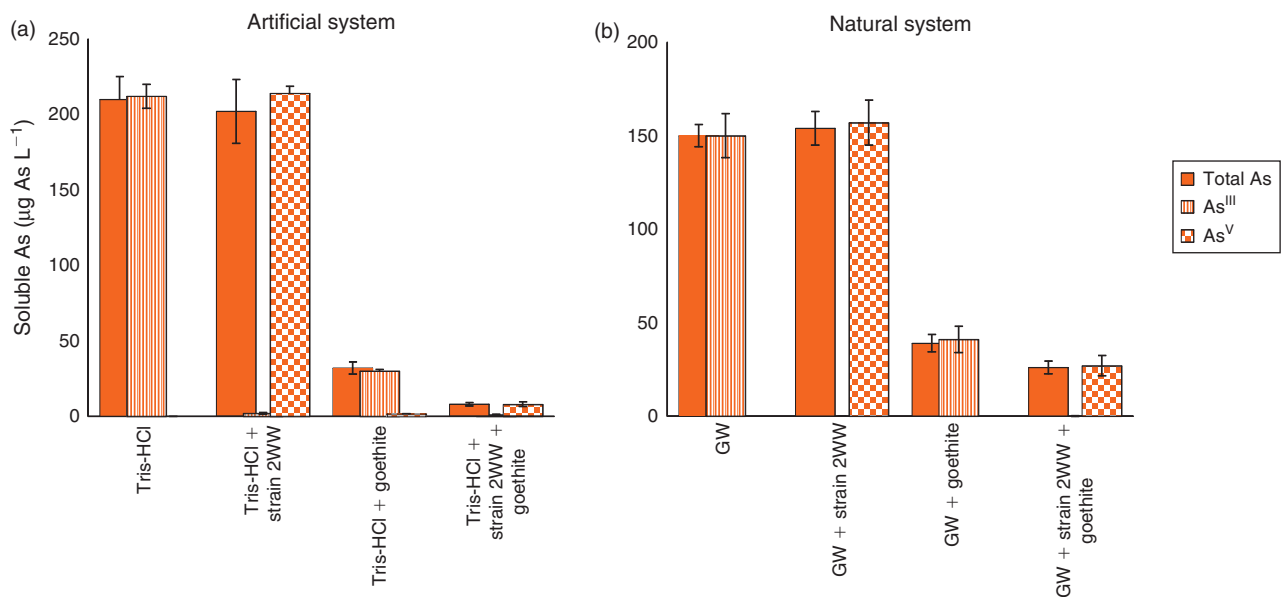


Fig. 4. Effect of As oxidizing strain 2WW on total As, As^{III} and As^V in 200 µg L⁻¹ As^{III}-spiked TRIS-HCl (artificial system) and in contaminated groundwater (natural system) after 48-h incubation. Error bars represent the standard deviations of quadruplicate experiments each with four replicates. GW, As-contaminated groundwater.

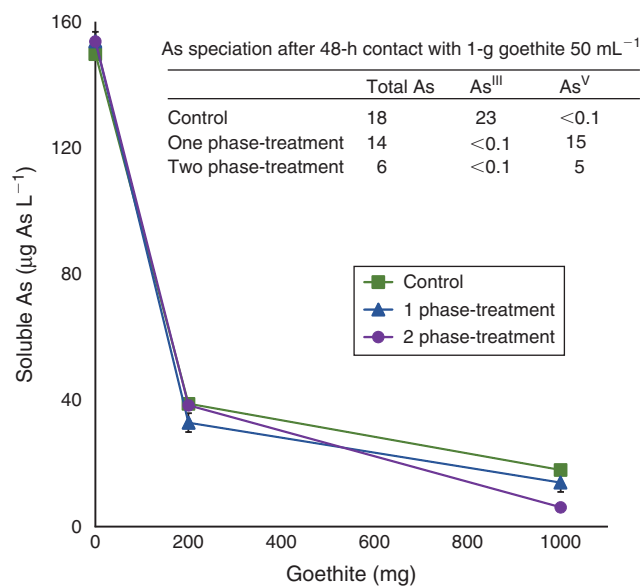


Fig. 5. Effect of biological As^{III} oxidation carried out in one- phase and two-phase process on total As concentration in contaminated groundwater after 48-h incubation. In the table is reported As speciation in 1.0-g goethite experiments.

The two-phase system approach applied to natural system was tested in the presence of two different goethite doses: 0.2 and 1.0 g per 50 mL (Fig. 5). In the presence of goethite at 0.2 g per 50 mL the two-phase system led to 38.5 µg L⁻¹ soluble As, comparable with data obtained in the one-phase system (26 µg L⁻¹ soluble As). When the goethite dose was increased to 1.0 g per 50 mL, As removal was >95 %, thus lowering the As concentration to 6 µg L⁻¹, evidencing a dose effect on As removal. When in the presence of 2WW cells, As^V was the only As species in solution in all the systems (Fig. 5).

Discussion

Groundwater contamination by As may occur under both reducing and oxidising conditions, and the ratio of As^{III} to As^V can vary significantly, depending on the condition of the in situ oxidation state of water.^[23] Moreover, groundwater treatment plants for drinking water can treat groundwater as it is or after an oxygenation step. Therefore, the choice of the best sorbent for As removal from water must take into consideration its affinity for the species of As to be removed. Low cost and high availability materials could be good candidates as point-of-use sorbents to mitigate As polluted groundwater.

In our study we tested low cost sorbents such as biochar, chabazite and goethite, and compared them with highly efficient, but highly operational complex materials (i.e. NZVI and ferritin-based material). Batch experiments without controlling pH allow evaluation of the sorbents in the actual case of small devices, with a high ratio of sorbent to water. Autoequilibrium pH values gave rise to systems that varied from mildly acid to highly alkaline and the effects of sorbents on As removal by water ranged from very high efficiency to ineffectiveness. When tested at approximately neutral pH, simulating real groundwater conditions, almost all the tested materials were shown to remove both species of As from As-spiked buffer solutions, from 4 to 100 %, depending on the sorbent and on the As species. Biochar was recently proposed as a low cost adsorbent in water

treatment^[24]; nevertheless no studies have been reported on As retention by biochar in natural water. At pH 7.2 a significant but small removal of As by biochar was detected, with a more favourable adsorption of As^{III} v. As^V, in agreement with the ability of biochar to adsorb heavy metals.^[25] A rise in pH seemed to have an adverse effect on biochar efficiency. Arsenate retention to biochar can be attributed to the same mechanism that allows phosphorus adsorption, as postulated by Beesley and Marmiroli^[26]; the greater ability of biochar to remove As^{III} than As^V could be due to outer surfaces and inner porous microstructures that explain retention.^[27]

The zeolite used in this study was mainly chabazite, which is reported to be more effective than other zeolitic rocks in removing As from waters.^[28] At autoequilibrium pH chabazite induced a 10 % reduction of As^{III} concentration and showed no effect on As^V. At neutral pH the removal percentages of As^{III} and As^V were 30 and 6 % respectively. In our study a small amount of As^V was retrieved in the solution at the end of the experiment, although Lièvrement et al. suggested that the high As^{III} sorption capacity of chabazite was due to abiotic oxidation of As^{III}.^[29]

As expected, iron-based sorbents showed the highest adsorption capacity in the artificial system. A ferritin-based material was recently proposed as a new bionanotechnological system for phosphate removal from waters.^[13] To the best of our knowledge, no studies have been reported on As removal by ferritin-based materials in natural systems. At autoequilibrium pH and at approximately neutral pH, the ferritin-based material was able to adsorb As^{III} and As^V in a range from 70 to 78 %. In particular, As^V retention to the ferritin-based material can be due to the same mechanisms involved in phosphates adsorption.

The As adsorption rate onto NZVI reaches 100 % both for As^{III} and As^V after 1-h contact of As-spiked solutions with a 20-fold lower amount of sorbent than goethite. The adsorption process using NZVI can remove both As^V and As^{III} simultaneously, without a pre-oxidation step, and such a process does not require the use of additional chemical reagents.^[30] A removal ability of NZVI was determined by Kanel et al. on a minute time scale, explained by As adsorption onto corrosion products formed by heterogeneous reactions onto a NZVI surface.^[31]

In our artificial system goethite removed 72 % of 200 µg L⁻¹ As^{III} and 98 % of 200 µg L⁻¹ As^V, bringing down the As^V level below the threshold limit of 10 µg L⁻¹. The higher affinity of goethite for As^V suggests that oxidation of As^{III} to As^V is required in the treatment of anoxic-suboxic groundwaters where As^{III} can be the most abundant species. In line with this, As adsorption onto goethite was deeply enhanced (>95 % of As removal) when the biological oxidation step was introduced in a one-phase treatment. For the As^{III} oxidation in groundwater the findings from this study reveal that a biological process performed with resting cells of strain 2WW can be utilised as an alternative to chemical oxidants.

Our findings were in agreement with Lièvrement et al. who studied the As removal process by using a TRIS-HCl solution in order to exclude competition between oxyanions (organic or inorganic ligands such as phosphate) and As^V for sorption sites.^[29] In accordance with this hypothesis, a decrease in the efficiency of As removal from groundwater was observed in the natural system during the one-phase process.

Among the coexisting ions, present in similar or much higher concentrations than As, Fe^{II} oxidation followed by precipitation

is known to promote As removal from water by adsorption and co-precipitation. Moreover the formation of ternary goethite–Fe–As complexes can increase the adsorption of As^{III} by goethite.^[32] In our experiments without goethite addition the decrease of soluble Fe concentration in the groundwater sample at the end of the experiment suggests that Fe^{II} was chemically or biotically oxidised by O₂ or by O₂-respiring bacteria, with a consequent precipitation as (oxy)hydroxides; at the same time only a slight decrease in As concentration of the groundwater was detected. Among other ions, manganese and phosphate showed a high affinity for goethite, being strongly removed from water. As for arsenic, manganese, which is naturally present in water in reduced form, can be retained on goethite by selective adsorption. The authors evidenced that Mn adsorption on hematite followed by Mn oxides production took up the potential sorption sites for As^V and resulted in a decrease of As^V removal.^[33] Moreover, phosphate and arsenate compete primarily for a similar set of surface sites on goethite.^[34] Meng et al. demonstrated that at high phosphate concentrations (i.e. >400 µg L⁻¹), As removal is not efficient, at least for an initial As concentration of 50 µg L⁻¹.^[35] In our study, after strain 2WW completely oxidised As^{III}, a PO₄/AsO₄ molar ratio of 6.0 was detected in the water sample indicating a competitive effect of phosphate on arsenate adsorption. Phosphate naturally present in the studied groundwater could first be adsorbed to goethite and saturated the sorption site of goethite, hindering biologically formed As^V to be adsorbed to sites pre-occupied.

In order to limit the effects of competing ions on As removal and thus meeting the threshold limit of 10 µg L⁻¹ As for drinking water, biological As^{III} oxidation and goethite adsorption were performed separately (two-phase process). Differently from the one-phase process, As^{III} removal increased up to 96 %, suggesting that the oxidation and adsorption steps must be performed separately. Our results are in agreement with previous findings on similar treatments that incorporate a biological transformation of As and subsequent adsorption by different materials such as zero-valent iron,^[36] kutnahorite mineral sorbent^[29] and activated alumina.^[37]

Conclusions

Experimental results showed that many materials can be used for the treatment of As-polluted water, even if only iron-based sorbents are able to remove As from water to levels below 10 µg L⁻¹, to assure the water quality as recommended by government health agencies. Among them, NZVI and goethite have the highest As removal efficiency. Along with the excitement over the prospects of nanotechnology, there have been increasing concerns regarding risks to public health that exposure to nanomaterials poses especially after disposal.^[38] In this perspective and considering the high efficiency of iron-based materials, the use of non-nanoscale sorbents (i.e. zero-valent iron filings, natural iron oxide goethite) for drinking water treatment plants might be advantageous.

This study showed that ferritin-based material could be considered an interesting iron-based sorbent, because it has the advantage to be regenerable, allowing a cost-effective solution for the end-user.

Among the other tested sorbents, the use of biochar requires further investigation to evaluate the role of raw materials, process conditions and feasible treatments to improve its ability to remove As^{III}, as biochar is highly available, of wide geographical distribution and a low cost material.

The study also highlights that some of the studied sorbents can modify soluble As speciation (i.e. chabazite, ferritin-based material, NZVI). Consequently the choice of the adsorption technique must take into account not only the main As species in the water, but also changes in the As chemical form that could occur during treatments, due to oxygenation of water, contact with highly reactive sorbents and microbial processes.

Moreover this study highlights that the effectiveness of sorbents decrease in natural systems, particularly that of NZVI. Because removal of As^V by goethite is more efficient than As^{III} adsorption, there is a need for a pre-oxidation step that can enhance operational costs. In this sense, biological oxidation methods are considered to be a suitable approach to overcome these problems.

These results pointed out that two main factors affected the As removal from groundwater and should be considered in the scaling up of a treatment system: (i) the quantity of sorbent in relation to As and competing ion concentration and (ii) the separation of As^{III} oxidation and As^V adsorption steps.

Acknowledgements

The research was supported by the CARIPLO Foundation, project 2010-2221. The authors are grateful to BiAqua B.V. for kindly providing ferritin-based material.

References

- [1] P. Mondal, C. B. Majumder, B. Mohanty, Laboratory based approaches for arsenic remediation from contaminated water: recent developments. *J. Hazard. Mater.* **2006**, *137*, 464. doi:10.1016/J.JHAZMAT.2006.02.023
- [2] W. Höll, Mechanisms of arsenic removal from water. *Environ. Geochem. Health* **2010**, *32*, 287. doi:10.1007/S10653-010-9307-9
- [3] D. Mohan, C. U. Pittman Jr, Arsenic removal from water/wastewater using adsorbents – a critical review. *J. Hazard. Mater.* **2007**, *142*, 1. doi:10.1016/J.JHAZMAT.2007.01.006
- [4] B. K. Biswas, K. Inoue, H. Harada, K. Ohto, K. Kawakita, Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. *J. Environ. Sci. (China)* **2009**, *21*, 1753. doi:10.1016/S1001-0742(08)62484-5
- [5] D. Ranjan, M. Talat, S. H. Hasan, Biosorption of arsenic from aqueous solution using agricultural residue ‘rice polish’. *J. Hazard. Mater.* **2009**, *166*, 1050. doi:10.1016/J.JHAZMAT.2008.12.013
- [6] X. Liu, H. Ao, X. Xiong, J. Xiao, J. Liu, Arsenic removal from water by iron-modified bamboo charcoal. *Water Air Soil Pollut.* **2012**, *223*, 1033. doi:10.1007/S11270-011-0921-7
- [7] I. Ali, Z. A. Al-Othman, A. Alwarthan, M. Asim, T. A. Khan, Removal of arsenic species from water by batch and column operations on bagasse fly ash. *Environ. Sci. Pollut. Res.* **2014**, *21*, 3218. doi:10.1007/S11356-013-2235-3
- [8] C. T. Kamala, K. H. Chu, N. S. Chary, P. K. Pandey, S. L. Ramesh, A. R. K. Sastry, K. Chandra Sekhar, Removal of arsenic(III) from aqueous solutions using fresh and immobilized plant biomass. *Water Res.* **2005**, *39*, 2815. doi:10.1016/J.WATRES.2005.04.059
- [9] P. K. Pandey, S. Choubey, Y. Verma, M. Pandey, K. Chandrashekhar, Biosorptive removal of arsenic from drinking water. *Bioresour. Technol.* **2009**, *100*, 634. doi:10.1016/J.BIORTECH.2008.07.063
- [10] Q. Li, X. Xu, H. Cui, J. Pang, Z. Wei, Z. Sun, J. Zhai, Comparison of two adsorbents for the removal of pentavalent arsenic from aqueous solutions. *J. Environ. Manage.* **2012**, *98*, 98. doi:10.1016/J.JENV MAN.2011.12.018
- [11] S. Zhang, C. Liu, Z. Luan, X. Peng, H. Ren, J. Wang, Arsenate removal from aqueous solutions using modified red mud. *J. Hazard. Mater.* **2008**, *152*, 486. doi:10.1016/J.JHAZMAT.2007.07.031
- [12] P. Mondal, S. Bhowmick, D. Chatterjee, A. Figoli, B. Van der Bruggen, Remediation of inorganic arsenic in groundwater for safe

- water supply: a critical assessment of technological solutions. *Chemosphere* **2013**, *92*, 157. doi:10.1016/J.CHEMOSPHERE.2013.01.097
- [13] J. F. Jacobs, M. H. Hasan, K. H. Paik, W. R. Hagen, M. C. M. van Loosdrecht, Development of a bionanotechnological phosphate removal system with thermostable ferritin. *Biotechnol. Bioeng.* **2010**, *105*, 918.
- [14] H. Guo, D. Stüben, Z. Berner, Removal of arsenic from aqueous solution by natural siderite and hematite. *Appl. Geochem.* **2007**, *22*, 1039. doi:10.1016/J.APGEOCHEM.2007.01.004
- [15] M. Vaclavikova, G. P. Gallios, S. Hredzak, S. Jakabsky, Removal of arsenic from water streams: an overview of available techniques. *Clean Techn. Environ. Policy* **2008**, *10*, 89. doi:10.1007/S10098-007-0098-3
- [16] WHO, *Arsenic in drinking water. Fact sheet number 210* **2001**. Available at <http://www.who.int/inf-fs/en/fact210.html> [Verified October 2013].
- [17] M. Bissen, F. H. Frimmel, Arsenic – a review. Part II: oxidation of arsenic and its removal in water treatment. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 97. doi:10.1002/AHEH.200300485
- [18] J. Michon, C. Dagot, V. Deluchat, M.-C. Dictor, F. Battaglia-Brunet, M. Baudu, As(III) biological oxidation by CAsO1 consortium in fixed-bed reactors. *Process Biochem.* **2010**, *45*, 171. doi:10.1016/J.PROCBIO.2009.09.003
- [19] A. Dastidar, Y. T. Wang, Modeling arsenite oxidation by chemoautotrophic *Thiomonas arsenivorans* strain b6 in a packed-bed bioreactor. *Sci. Total Environ.* **2012**, *432*, 113. doi:10.1016/J.SCITOTENV.2012.05.051
- [20] A. Ito, J. I. Miura, N. Ishikawa, T. Umita, Biological oxidation of arsenite in synthetic groundwater using immobilised bacteria. *Water Res.* **2012**, *46*, 4825. doi:10.1016/J.WATRES.2012.06.013
- [21] A. Corsini, P. Zaccheo, G. Muyzer, V. Andreoni, L. Cavalca, Arsenic transforming abilities of groundwater bacteria and the combined use of *Aliihoeflea* sp. strain 2WW and goethite in metalloid removal. *J. Hazard. Mater.* **2014**, *269*, 89. doi:10.1016/J.JHAZMAT.2013.12.037
- [22] Y. T. Kim, C. Yoon, N. C. Woo, An assessment of sampling preservation and analytical procedures for arsenic speciation in potentially contaminated waters. *Environ. Geochem. Health* **2007**, *29*, 337. doi:10.1007/S10653-007-9091-3
- [23] K. Sasaki, H. Nakano, W. Wilopo, Y. Miura, T. Hirajima, Sorption and speciation of arsenic by zero-valent iron. *Colloid. Surface A* **2009**, *347*, 8. doi:10.1016/J.COLSURFA.2008.10.033
- [24] EPA, *Progress report: sustainable sorbents and monitoring technologies for small groundwater systems* **2013**. Available at <http://cfpub.epa.gov/ncer/abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/9607/report/2012> [Verified 15 November 2013].
- [25] X. Han, C.-F. Liang, T.-Q. Li, K. Wan, H.-G. Huang, X. Yang, Simultaneous removal of cadmium and sulfamethoxazole from aqueous solution by rice straw biochar. *J. Zhejiang Univ. Sci. B* **2013**, *14*, 640. doi:10.1631/JZUS.B1200353
- [26] L. Beesley, M. Marmiroli, The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environ. Pollut.* **2011**, *159*, 474. doi:10.1016/J.ENVPOL.2010.10.016
- [27] J. Major, M. Rondon, D. Molina, S. J. Riha, J. Lehmann, Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil* **2012**, *357*, 369.
- [28] F. Ruggieri, V. Marín, D. Gimeno, J. L. Fernandez-Turiela, M. García-Valles, L. Gutierrez, Application of zeolitic volcanic rocks for arsenic removal from water. *Eng. Geol.* **2008**, *101*, 245. doi:10.1016/J.ENGGEOL.2008.06.006
- [29] D. Lièvremon, M. A. N'negue, P. H. Behra, M. C. Lett, Biological oxidation of arsenite: batch reactor experiments in presence of kutnahorite and chabazite. *Chemosphere* **2003**, *51*, 419. doi:10.1016/S0045-6535(02)00869-X
- [30] V. Tanboonchuy, J.-C. Hsu, N. Grisdanurak, C.-H. Liao, Impact of selected solution factors on arsenate and arsenite removal by nanoiron particles. *Environ. Sci. Pollut. Res.* **2011**, *18*, 857. doi:10.1007/S11356-011-0442-3
- [31] S. R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environ. Sci. Technol.* **2005**, *39*, 1291. doi:10.1021/ES048991U
- [32] K. Amstaetter, T. Borch, P. Larese-Casanova, A. Kappler, Redox transformation of arsenic by Fe^{II}-activated goethite (α -FeOOH). *Environ. Sci. Technol.* **2010**, *44*, 102. doi:10.1021/ES901274S
- [33] H. T. Ren, S. Y. Jia, Y. Liu, S. H. Wu, X. Han, Effects of Mn(II) on the sorption and mobilization of As^V in the presence of hematite. *J. Hazard. Mater.* **2012**, *217–218*, 301. doi:10.1016/J.JHAZMAT.2012.03.032
- [34] F. Liu, A. De Cristofaro, A. Violante, Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci.* **2001**, *166*, 197. doi:10.1097/00010694-200103000-00005
- [35] X. Meng, G. P. Korfiatis, S. Bang, K. W. Bang, Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol. Lett.* **2002**, *133*, 103. doi:10.1016/S0378-4274(02)00080-2
- [36] S. A. Mokashi, K. M. Paknikar, Arsenic(III) oxidizing *Microbacterium lacticum* and its use in the treatment of arsenic contaminated groundwater. *Letts. Appl. Microbiol.* **2002**, *34*, 258. doi:10.1046/J.1472-765X.2002.01083.X
- [37] M. Ike, T. Miyazaki, N. Yamamoto, K. Sei, S. Soda, Removal of arsenic from groundwater by arsenite-oxidizing bacteria. *Water Sci. Technol.* **2008**, *58*, 1095. doi:10.2166/WST.2008.462
- [38] S. T. Stern, S. E. McNeil, Nanotechnology safety concerns revisited. *Toxicol. Sci.* **2008**, *101*, 4. [Published online early 30 June 2007]. doi:10.1093/TOXSCI/KFM169