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

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Environmental Context
Arsenic contamination of aquifers is a worldwide public health concern and several technologies have been developed to reduce arsenic concentrations below the limit imposed by World Health Organization. We investigated the efficiency of new and conventional 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 efficiency of adsorption in the removal of arsenic from groundwater.

Abstract
Batch experiments were conducted to evaluate As(III) and As(V) adsorption capacity of five sorbents (i.e., biochar, chabazite, ferritin-based material, goethite and nano zero-valent iron) in artificial systems at autoequilibrium pH (MilliQ water without adjusting the pH) and at circa neutral pH (i.e., Tris-HCl, pH 7.2). At autoequilibrium pH, the effects of sorbents on removal of 200 µg L⁻¹ As ranged from very high efficiency for iron-based sorbents to ineffectiveness for biochar and
chabazite. When tested at circa neutral pH, the sorbents were capable to remove between 17% and 100% of As(III) and between 3% and 100% of As(V) in the following order of sorbents: biochar < chabazite < ferritin-based material < goethite < nano zero-valent iron. The study also highlighted that chabazite, a ferritin-based material, and nano zero-valent iron oxidized As(III) to As(V) and that the ferritin-based material was also able to reduce As(V) to As(III). When tested in naturally arsenic-contaminated groundwater, a marked decrease in the removal effectiveness of nano zero-valent iron and goethite occurred (60% and 12%, respectively), due to possible competition with phosphates and manganese.

The usefulness of a biological oxidation step was evaluated in one-phase process (As(III) bio-oxidation in conjunction with As(V) adsorption) and in two-phase process (As(III) bio-oxidation followed by As(V) adsorption), both in As(III)-spiked Tris-HCl and in natural groundwater systems. As(III) oxidation was performed by resting cells of *Alihoeflea* sp. strain 2WW, and arsenic adsorption by goethite. In the one-phase process As removal in Tris-HCl was >95%, while in groundwater it decreased to 85%. More effective was the two-phase process that removed up to 95% As in groundwater leaving in solution 6 µg L\(^{-1}\) arsenic, thus meeting the limit of 10 µg L\(^{-1}\) imposed by World Health Organization.

These results can be used in the scaling up of a two-phase treatment, with bacterial oxidation of arsenic used in combination with goethite sorption.

Introduction

Extensive arsenic pollution in groundwater affects highly populated areas in such a serious way that arsenic became one of the major public health problems. Consequently a wide range of technologies has been tried for the removal of arsenic from drinking water; the most common techniques utilize the processes of oxidation, co-precipitation, adsorption onto sorptive media, ion exchange and membrane techniques.\(^{1,2}\) Among these, the adsorption of arsenic 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 arsenic onto natural and synthetic materials is a low cost, high efficiency process. A wide range of materials for aqueous arsenic removal is available nowadays. Sorbent based on iron oxides/hydroxides and on activated alumina are the most common conventional materials; other metal oxides-based sorbents, such as manganese dioxides, titanium dioxide, 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,\[6\] bagasse fly ash.\[7\] Some fresh and immobilized plant biomasses gained a significant interest for their ability to passively adsorb arsenite, thereby avoiding the pre-oxidation step.\[8,9\] Mineral byproducts such as magnesia-loaded fly ash cenospheres and manganese-loaded fly ash cenospheres,\[10\] Zr(IV) iron modified red mud \[11\] have also been reported as promising sorbents for the removal of arsenic.

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 a number of 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 have been reported on arsenic removal capability of ferritin.

The main disadvantages of As adsorption onto solid materials are the direct competition for available adsorption sites between arsenic and other oxyanions in the water,\[14\] and the general need of a pre-oxidation step to transform arsenite to arsenate.\[12\]

In fact, the two more common forms of arsenic in water show completely different patterns of dissociation, as a consequence of the predominance of the neutral species H$_3$AsO$_3$ for arsenite [As(III)] at pH 2-8 and of the single negatively charged H$_2$AsO$_4$ for arsenate [As(V)] at pH values
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 arsenic imposes to reduce arsenic concentrations to less than 10 µg L\(^{-1}\) and consequently there is a dramatic demand for oxidation technologies that effectively convert arsenite into arsenate prior to its removal. Biological oxidation of As(III) by microorganism has recently received lot of attention as a sustainable alternative to the use of chemical oxidants. In the present study natural minerals (goethite, chabazite), a pyrolysis byproduct (biochar) and iron-based nanomaterials (ferritin-based material and zerovalent 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 oxidizing power with respect to As(III). We performed batch experiments in two conditions: (i) without controlling pH in order to evaluate the sorbents in the actual case of small devices with a high ratio sorbent/water; (ii) at circa neutral pH simulating 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 oxidizer 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, ferritin-based material goethite (FeOOH), and nano zero-valent iron (Fe\(^0\)) NZVI. Biochar was from Agrindustria snc, and derived from pyrolysis of pinewood; the sample used in adsorption experiments was milled and successively prehydrated in Tris-HCl buffer (5 mM, pH 7.2) or MilliQ water for 24hrs.
The chabazite-rich tuff was obtained by 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 <200µm.

Biochar and chabazite were free from significant amount of soluble arsenic (<0.5 µg L⁻¹ and 4 µg L⁻¹ for biochar and chabazite, respectively).

Ferritin-based material was provided by BiAqua B.V. (The Netherlands) and the protein is stabilized onto sand, used as carrier (2.74 mg ferritin g⁻¹ dry sand).

The goethite used in this study was from Sigma Aldrich, and had a specific surface area of 11.6 m²g⁻¹.

A commercial zero-valent iron (NANOFER 25) was supplied by the NANOIRON s.r.o and consisted of aqueous dispersion of Fe⁰ nanoparticles stabilized by an inorganic modifier.

Arsenate and arsenite solution were prepared by spiking MilliQ water and Tris-HCl buffer (5 mM, pH 7.2) with 200 µg L⁻¹ As(III) or As(V) from stock solutions of 1000 µg L⁻¹ NaAsO₂ or Na₂HAsO₄ (Sigma).

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 characterization revealed that the groundwater sample was anoxic (with an Eₜ value of -113 mV, and no dissolved oxygen) and had the following physicochemical characteristics: temperature of 15 °C; pH value of 7.6; CaCO₃ 282 mg L⁻¹; organic C 2.11 µg L⁻¹; dissolved S-SO₄ 267 µg L⁻¹; dissolved P- PO₄ 312 µg L⁻¹; dissolved N-NO₃ 685 µg L⁻¹; dissolved N-NH₄ 2680 µg L⁻¹; dissolved Fe 760 µg L⁻¹; dissolved Mn 97 µg L⁻¹. The arsenic concentration in the sample was 171 µg L⁻¹, with As(III) as the main As species.

Resting cells preparation
The biological arsenite oxidation step was carried out by addition of resting cells of *Aliihoeflea* sp. strain 2WW. Resting cells of the strain were able to oxidize 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 in shaking condition at 150 rpm. BBWM consisted of:

- Solution A (g L\(^{-1}\)): KH\(_2\)PO\(_4\) 0.04; K\(_2\)HPO\(_4\) 0.04; NaCl 1.0; (NH\(_4\))\(_2\)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 sterilized separately by autoclaving. Equal volumes of solutions A and B were mixed after cooling and then supplemented with 1% (v/v) vitamin solution. Vitamin solution was filter sterilized and contained (mg L\(^{-1}\)): p-aminobenzoic acid 5; biotin 5; folic acid 2; pyridoxine-HCl 1; riboflavin 5; thiamine 5; nicotinic acid 5; panthotenic acid 5; vitamin B12 0.1. The pH was adjusted to 8.0. After growth, cells were centrifuged at 10,000 rpm, 10 °C for 30 min. Cell pellet was washed three times with Tris-HCl (5 mM, pH 7.2) and resuspended in Tris-HCl (5 mM, pH 7.2). This cell suspension served as inoculum in order to obtain a final cell density of about 10\(^7\) 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 50 mL\(^{-1}\)) were used: biochar 0.2, chabazite 1.0, goethite 0.2, ferritin-based material 11.4 and zero-valent iron (NZVI) 0.05.

Adsorption experiments in artificial systems were performed in polypropylene tubes with the addition of 50 mL Tris-HCl (5mM pH 7.2) or MilliQ water, spiked with 200 µg L\(^{-1}\) As(III) or As(V), chosen on the base of arsenic content of the groundwater used in the present study. Batch experiments were prepared in aerobic condition, with the exception of those with NZVI that were filled under anaerobic condition in Nitrogen Dry Box (Plas Labs, Inc.) to prevent Fe\(^0\) oxidation. The tubes were closed with cotton plug in order to allow gaseous exchange.
Adsorption experiments in natural systems were performed with 50 mL natural As-contaminated groundwater in the presence of goethite (0.2, 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 CO$_2$.

Consequently, batch experiments with natural As-contaminated water were prepared under anaerobic condition in Nitrogen Dry Box (Plas Labs, Inc.) 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 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 base of 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 (Ø 0.22 µm) and acidified with HNO$_3$ to achieve a final concentration of 2% (v/v).

**Analytical methods**

Total arsenic was determined in 5 mL of samples previously acidified with HNO$_3$. For speciation of arsenic forms, As(V) and As(III) species were separated on the basis of their selective retention on a WATERS Sep-Pak® Plus Acell Plus QMA cartridge (Waters, MA, USA): As(V) is retained in the cartridge, while allowing As(III) to pass through and to be collected. The procedure was performed according to Kim et al. [22] 5 mL of non-acidified samples were passed through the cartridge and
the flow-through (containing As(III)) was collected. The cartridge retaining As(V) was then washed with 0.16M 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, USA). Standards of As for concentrations ranging from 0 to 1 mg L⁻¹ were prepared from sodium arsenite NaAsO₂ (Sigma Aldrich, USA). For all the measures by ICP–MS an aliquot of a 2 mg/L of an internal standard solution (⁴⁵Sc, ⁸⁹Y, ¹⁵⁹Tb, Agilent technologies, USA) was added both to samples and calibration curve to give a final concentration of 20 mg 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 arsenic.

Statistical analysis

Data represent the mean values obtained from at least three replicates of each experiments. The values were subjected to Student t-test (p<0.05) and to one-way ANOVA with Tukey-b test using the SPSS version 20.0.

Results

As(III) and As(V) removal by sorbents in artificial systems

Batch test studies with sorbents were conducted at autoequilibrium 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 Figures 1a and 1b,
respectively. Removal of arsenic 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); while no detectable As remained in both the As(III) and As(V)-spiked solutions after 1h contact with NZVI. Checking a 50-fold concentrated As-spiked MilliQ solutions 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 mg L$^{-1}$ 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 Figure 2a and 2b, respectively.

Preliminary trials showed that arsenic 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 immobilized As(V), while 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 arsenic 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 arsenic recovered in the solution.
Adsorption of As(III) and As(V) from natural system by goethite and NZVI

Arsenic removal efficiency of NZVI and goethite was evaluated in 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).

Control without sorbents did not show changes in the amount and speciation of arsenic (Fig. 3); these indicated that no apparent changes of arsenic speciation due to biotic or abiotic reactions occurred in the time of the experiments. The performance of both sorbents was worse in the natural than in the artificial system: As immobilization by NZVI and by goethite were reduced by 60% and 12%, respectively, as compared with those in MilliQ water. Speciation of the soluble arsenic at the sampling time indicated that NZVI promoted a complete oxidation of remaining As(III), while no detectable As(V) was recovered in the goethite treatment, thus confirming the absence of chemical or biological activities towards arsenic in the presence of goethite.

Effect of bio-oxidation of As(III) on As removal in artificial and natural systems

Due to the inability of goethite to oxidize As(III) in the groundwater, thus leading to arsenic concentration higher than the WHO limit, a biological As(III) oxidation step was considered in one- and two-phase experiments.

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 soluble As concentration to 8 µg L⁻¹. At the end of the experiment, As(V) was the only detectable arsenic form in solution, indicating that the ability of the cells to oxidize As(III) was not affected by the presence of goethite. Resting cells of strain 2WW converted As(III) to As(V) completely, whereas goethite without cells removed approximately 85% of initial As(III).

One-phase treatment was tested in natural system (i.e., As(III) contaminated groundwater) (Fig. 4b). Strain 2WW was able to completely oxidize 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.
of artificial system (85% removal). The combined As(III) bio-oxidation and adsorption process was not able to enhance arsenic removal, as observed in 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, while manganese and phosphorous concentration decreased in the presence of goethite. Neither calcium nor magnesium was removed in any treatment and dissolved carbon concentrations were negligible (data not shown). When the amount of goethite was increased from 0.2 g 50 mL$^{-1}$ to 1.0 g 50 mL$^{-1}$, no dose effect on As removal was evidenced either in the presence and in the absence of 2WW cells.

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 50 mL$^{-1}$ (Figure 5). In the presence of goethite 0.2 g 50 mL$^{-1}$ the two-phase system led to 38.5 µg L$^{-1}$ soluble arsenic, comparable with data obtained in the one-phase system (26 µg L$^{-1}$ soluble arsenic). When goethite dose was increased to 1.0 g 50 mL$^{-1}$, As removal was >95%, thus lowering As concentration at 6 µg L$^{-1}$, evidencing a dose effect on As removal. When in the presence of 2WW cells, As(V) was the only arsenic species in solution in all the systems (Figure 5).

**Discussion**

Groundwater contamination by arsenic may occur under both reducing and oxidizing conditions, and the ratio of As(III) to As(V) can vary significantly, depending on the condition of *in situ* oxidation state of water. 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 arsenic to be removed. Low cost and high available materials could be good candidate 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 high efficient, but highly operational complex materials (*i.e.*, nano zero-valent iron and ferritin-based material). Batch experiments without controlling pH allow evaluating the sorbents in the actual case of small devices, with a high ratio sorbent/water. Autoequilibrium pH values led systems 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 circa neutral pH simulating real groundwater conditions, almost all the tested materials showed to remove both species of arsenic 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 are reported on As retention by biochar in natural water. At pH 7.2 a significant but small removal of arsenic by biochar was detected, with a more favorable adsorption of As(III) versus As(V), in agreement with the ability of biochar in the adsorption of heavy metals.[25] 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] biochar higher ability to remove arsenite than arsenate could be due to outer surfaces and inner porous micro-structures 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 arsenic 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 Lièvremont 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 artificial system. 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 are reported on As removal by
ferritin-based material in natural systems. At autoequilibrium pH and at circa neutral pH, ferritin-based material was capable to adsorb As(III) and As(V) in range from 70% to 78%. Particularly, arsenate retention to ferritin-based material can be due to the same mechanisms involved in phosphates adsorption.

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

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 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 groundwater where As(III) can be the most abundant species. In line with this, arsenic 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 utilized as an alternative to a chemical oxidants.

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

Among the coexisting ions, present in similar or much higher concentrations than arsenic, Fe(II) oxidation followed by precipitation is known to promote As removal from water via adsorption and co-precipitation. Moreover the formation of ternary goethite-Fe-As complexes can increase
adsorption of As(III) by goethite.\cite{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 and/or biotically oxidized by O$_2$ or by O$_2$-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. Moreover, phosphate and arsenate compete primarily for a similar set of surface sites on goethite.\cite{34} Meng et al. demonstrated that at high phosphate concentrations (i.e. > 400 µg L$^{-1}$), arsenic removal is not efficient, at least for an initial arsenic concentration 50 µg L$^{-1}$.\cite{35} In our study, after strain 2WW completely oxidized As(III), a PO$_4$/AsO$_4$ molar ratio of 6.0 was detected in the water sample indicating a competitive effect of phosphate on As(V) adsorption. Phosphate naturally present in the studied groundwater can firstly 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 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 arsenic and subsequent adsorption by different materials such as zero valent iron,\cite{36} kutnahorite mineral sorbent,\cite{29} and activated alumina.\cite{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 arsenic from water to levels below 10 µg L\(^{-1}\), to assure the water quality as recommended by government health agencies. Among them, nano zero-valent iron 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 nano-scale 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 require further investigations to evaluate the role of raw materials, process conditions and feasible treatments to improve its ability to remove As(III), as biochar is a highly available, of wide geographically distribution and low cost material. The study also highlights that some of the studied sorbents can modify soluble As speciation (i.e., chabazite, ferritin-based material, nano zero-valent iron). 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, microbial processes.

Moreover this study highlights that the effectiveness of sorbents decrease in natural system, particularly that of nano zerovalent iron. 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 arsenic removal from groundwater and should be considered in the scaling up of a treatment system: i) the quantity of sorbent in relation to arsenic and competing ion concentration; ii) the separation of As(III) oxidation and As(V) adsorption steps.

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References


Figures Legend
Fig. 1 Soluble As before and after contact of 50 mL of 200 µg L⁻¹ As(III)- (a) and As(V)- (b) spiked MilliQ water with biochar (0.2 g), chabazite (1.0 g), ferritin-based material (11.4 g), goethite (0.2 g) and NZVI (0.05 g). Experimental time: biochar, chabazite, ferritin-based material, goethite: 48 h; NZVI: 1 h. The asterisk indicates statistical significance at p=0.05 (single asterisk) and p=0.01 (double asterisk) 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 µg L⁻¹ As(III)- (a) and As(V)- (b) spiked Tris-HCl with biochar (0.2 g), chabazite (1.0 g), ferritin-based material (11.4 g), goethite (0.2 g) and NZVI (0.05 g) Experimental time: biochar, chabazite, ferritin-based material, goethite: 48 h; NZVI: 1 h. The asterisk indicates statistical significance at p=0.05 (single asterisk) and p=0.01 (double asterisk) as compared with time 0, determined by the Student’s t test.

Fig. 3 Total As, As(III) and As(V) concentration in the As contaminated groundwater sample after contact with sorbents: 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.

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 4 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.
Arsenic in solution (µg As L\(^{-1}\))

**a)**

**b)**

http://www.publish.csiro.au/nid/188.htm
Arsenic in solution (µg As L\(^{-1}\))

**a)**

<table>
<thead>
<tr>
<th></th>
<th>Chabazite</th>
<th>Biochar</th>
<th>Ferritin-based material</th>
<th>Goethite</th>
<th>NZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>initial</td>
<td>*</td>
<td></td>
<td></td>
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<tr>
<td>final</td>
<td>**</td>
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</table>

**b)**

<table>
<thead>
<tr>
<th></th>
<th>Chabazite</th>
<th>Biochar</th>
<th>Ferritin-based material</th>
<th>Goethite</th>
<th>NZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>initial</td>
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<tr>
<td>final</td>
<td>**</td>
<td></td>
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</tr>
</tbody>
</table>

* initial time
** final time
For Review Only

Control Goethite ZVNI

soluble As (µg As L⁻¹)

- total As
- As(III)
- As(V)

http://www.publish.csiro.au/nid/188.htm
a) artificial system

b) natural system

soluble As (µg As L⁻¹)

- Tris-HCl
- Tris-HCl + strain2WW
- Tris-HCl + goethite
- Tris-HCl + strain2WW + goethite

soluble As (µg As L⁻¹)

- GW
- GW + strain2WW
- GW + goethite
- GW + strain2WW + goethite

- total As
- As(III)
- As(V)
As speciation after 48h contact with 1 g goethite 50 mL⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Total As</th>
<th>As(III)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>18</td>
<td>23</td>
<td>&lt;0.1</td>
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<tr>
<td>One phase-treatment</td>
<td>14</td>
<td>&lt;0.1</td>
<td>15</td>
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<tr>
<td>Two phase-treatment</td>
<td>6</td>
<td>&lt;0.1</td>
<td>5</td>
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</tbody>
</table>

Goethite (mg) vs. soluble As (µg As L⁻¹)
Table 1. Speciation of soluble arsenic (µg L\(^{-1}\)) retrieved after contact with sorbents (mean ± standard deviation, n =3).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>As(III) spiked Tris-HCl</th>
<th></th>
<th></th>
<th>As(V) spiked Tris-HCl</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>As(III)</td>
<td>As(V)</td>
<td>Total</td>
<td>As(III)</td>
<td>As(V)</td>
</tr>
<tr>
<td>Chabazite</td>
<td>190±1</td>
<td>180±9</td>
<td>17±6</td>
<td>nd^A</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Ferritin-based material</td>
<td>54±7</td>
<td>42±3</td>
<td>23±0.3</td>
<td>37±10</td>
<td>30±5</td>
<td>15±7</td>
</tr>
<tr>
<td>Goethite</td>
<td>43±4</td>
<td>40±6</td>
<td>2.2±0.7</td>
<td>5.0±1.5</td>
<td>&lt;0.1</td>
<td>4.5±2.8</td>
</tr>
<tr>
<td>NZVI</td>
<td>4.4±0.1</td>
<td>2.8±0.3</td>
<td>1.1±0.5</td>
<td>2.7±0.4</td>
<td>0.4±0.3</td>
<td>0.7±0.0</td>
</tr>
</tbody>
</table>

^A not determined

Table 2. Total arsenic and main coexisting ions (µg L\(^{-1}\)) in natural groundwater sample before and after 48 h incubation

<table>
<thead>
<tr>
<th>Condition</th>
<th>As</th>
<th>Mn</th>
<th>Fe</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW^A at initial time</td>
<td>171</td>
<td>c</td>
<td>97</td>
<td>b</td>
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<tr>
<td>GW at final time</td>
<td>150</td>
<td>b</td>
<td>84</td>
<td>b</td>
</tr>
<tr>
<td>GW + strain 2WW</td>
<td>154</td>
<td>b</td>
<td>97</td>
<td>b</td>
</tr>
<tr>
<td>GW + goethite</td>
<td>39</td>
<td>a</td>
<td>1.6</td>
<td>a</td>
</tr>
<tr>
<td>GW + strain 2WW + goethite</td>
<td>26</td>
<td>a</td>
<td>1.4</td>
<td>a</td>
</tr>
</tbody>
</table>

Values followed by the same lower case letters denote those not significantly different in each column (P < 0.05); ^A GW= As-contaminated groundwater