

Optimizing arsenic removal during iron removal: Theoretical and practical considerations

D. A. Lytle, T. J. Sorg and V. L. Snoeyink

ABSTRACT

New health effects research prompted the United States Environmental Protection Agency (USEPA) to reduce the drinking water standard for arsenic from 0.05 to 0.010 mg l⁻¹ (10 µg l⁻¹), and as a result many drinking water systems (particularly smaller ones) throughout the country will no longer be in compliance. In waters that contain natural iron, arsenic removal can be achieved during iron removal, but the effectiveness of iron to remove arsenic depends on many variables. The objective of this study was to identify the operational and water quality factors that impact arsenic removal during iron removal. Bench-scale ('batch' and standard jar) tests were used to evaluate the effects of pH, phosphate, other water chemistry variables, and the oxidant used to oxidize Fe(II) on the removal of arsenic. Treatment operation considerations, including sequence of oxidant addition and contact time, were also considered. Results showed that (1) arsenic removal improves with increasing iron concentration and particle surface area; (2) freshly precipitated iron particles had a much greater capacity to remove arsenic than preformed particles that were formed by oxidation of ferrous iron with either oxygen or chlorine; (3) chlorination, or application of a stronger oxidant, may be necessary to improve arsenic removal at many drinking water treatment plants; (4) the point of strong oxidant addition in the treatment train is important; and (5) the pH and other competing water quality variables such as phosphate play significant roles in the amount of arsenic removed.

Key words | arsenic, iron, optimizing removal, oxidant, water

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BACKGROUND

The US Environmental Protection Agency recently reduced the drinking water standard for arsenic from 0.05 to 0.010 mg l⁻¹ (10 µg l⁻¹) ('USEPA 2001a, 2002). This reduction was prompted by new health effects research, which concluded that extended human exposure to this element can cause severe illnesses (including various types of cancer) at much lower levels than previously believed. As a result of this reduced standard, arsenic levels in many drinking water systems (particularly smaller ones) throughout the country are no longer in compliance. In response, researchers are developing and evaluating new technologies and optimizing existing ones in order to help these systems meet the new arsenic standard by the compliance date set for January 2006.

General arsenic chemistry

Arsenic, which is found at varying levels in many groundwaters and some surface waters, can have both natural and anthropogenic sources. In natural environments, high levels of arsenic are generally caused by the leaching of arsenic from certain arsenic-containing minerals, such as arsenopyrite and other various arsenic sulfides and sulfosalts ('Kim *et al.* 2002; 'USEPA 2003a). In addition to arsenic-bearing host minerals, discharge from various industries (including mining, petroleum refining, and glass and ceramics manufacturing) can cause arsenic pollution. Pesticides, herbicides and fertilizers are also known sources of arsenic release ('Blakely 1984).

The valence state and species of inorganic arsenic in water depend upon the water's redox state and pH. As a general rule, the trivalent oxidation state form (arsenite), As(III), is normally found in groundwater and the pentavalent oxidation state (arsenate), As(V), is found in surface water. However, this rule does not always hold true in groundwater, where both forms have been found together in the same water source ('USEPA 2003b). In general, under anoxic conditions, As(III) is stable, with nonionic arsenous acid (H_3AsO_3) and anionic arsenite (H_2AsO_3^-) species dominant below and above pH 9.2, respectively (Figure 1a). As(V) is dominant in oxygenated

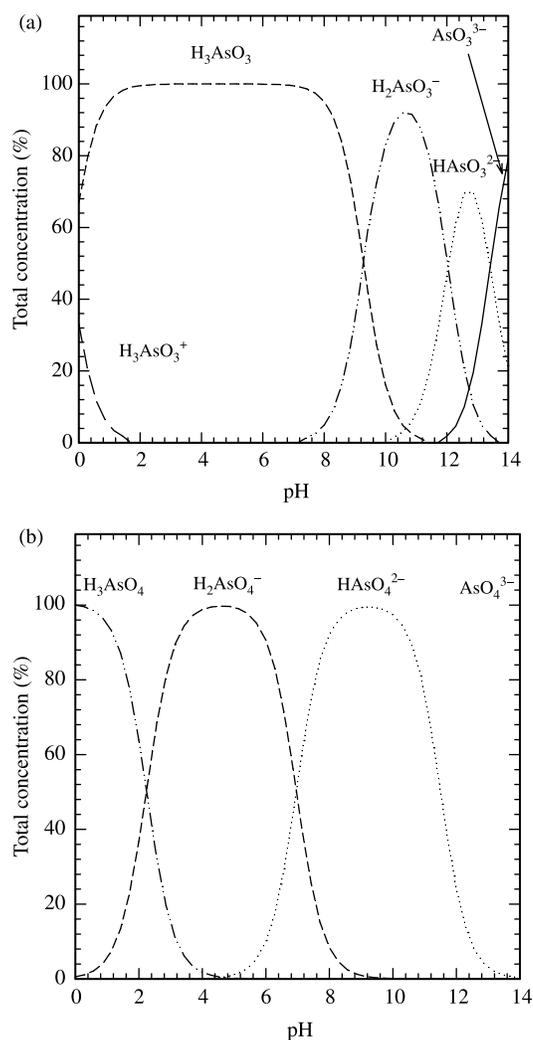


Figure 1 | Speciation of (a) arsenite, and (b) arsenate in water (25°C). Modelling was performed using MINEQL + : a chemical equilibrium modelling system version 4.0 ('Schecher & McAvoy 1998).

waters, existing in the anionic forms of H_2AsO_4^- , HAsO_4^{2-} or AsO_4^{3-} over the pH range typically encountered in drinking waters (pH 6 to 10) (Figure 1b). Generally, As(III) and As(V) acid-base reactions are assumed to occur instantaneously, whereas changes between oxidation states require indeterminate time periods in natural waters ('Schecher & McAvoy 1998). For example, while the conversion of As(III) to As(V) in oxygenated water is predicted, the rate of this transformation may take days or even months, depending on the specific conditions involved. Although organic arsenic species of arsenic exist, even when highly concentrated they are generally considered to be of less significance than inorganic species ('Edwards 1994).

Numerous studies ('Cheng *et al.* 1994; 'Scott *et al.* 1995; 'Hering *et al.* 1996; 'Tokunga *et al.* 1999) have concluded that As(III) is more toxic, soluble and mobile than As(V); therefore, investigating the oxidation of As(III) has been the subject of many studies ('Jain *et al.* 1999; 'USEPA 2001b). Chemical oxidants, including free chlorine, ozone and potassium permanganate have been found to successfully oxidize As(III) at rates that are much faster than those produced by dissolved oxygen alone ('Eary & Schramke 1990; 'Jekel 1994). Ghurye and Clifford ('USEPA 2001b) reported that chlorine and permanganate rapidly oxidize As(III) to As(V) in the pH range of 6.3 to 8.3. The authors found that dissolved manganese, dissolved iron, sulfide and total organic carbon (TOC) slowed the rate, but complete oxidation was still accomplished in less than one minute. Ozone rapidly oxidized As(III) in the absence of sulfide and TOC. When either sulfide or TOC was present, the oxidation rate was slowed and quenched, respectively. In addition, chlorine dioxide had only limited success in oxidizing As(III) and monochloramine was ineffective.

Treatment technologies for arsenic removal

Treatment methods for the removal of arsenic from water include coprecipitation processes using iron and aluminium salts, iron removal, anion exchange, lime softening, reverse osmosis, electrodialysis reversal (EDR), nanofiltration and adsorption media ('USEPA 2000a).

As noted above, many arsenic removal processes are iron-based treatment technologies, such as chemical

coagulation with iron salts, natural iron removal from source waters by oxidation and filtration, and iron-based adsorptive media ('Gupta & Chen 1978; 'Edwards 1994; 'McNeill & Edwards 1995, 1997; 'Scott *et al.* 1995b; 'Holm 1996; 'Hering *et al.* 1996). These processes are particularly effective at removing arsenic from aqueous systems because iron surfaces have a strong affinity to adsorb arsenic. As a result, the adsorption and coprecipitation of arsenate and arsenite on iron oxide surfaces have been investigated extensively ('Manceau 1995; 'Waychunas *et al.* 1996; 'Sun & Doner 1998; 'Jain *et al.* 1999). Table 1 provides a list of studies that examined the adsorption of arsenic onto various iron solids. Studies have shown that the sorption of arsenic is affected by many factors, including pH, water quality, amount and form of iron present, and the existence of competing ions such as phosphate, silicate and natural organic matter (NOM) ('Andreae 1979; 'Azcue & Nriagu 1993; 'Edwards 1994; 'Al-Juaid *et al.* 1994; 'Borho & Wilderer 1996). Research has also shown that arsenic is more effectively removed by these methods when present in the arsenate form, although the success of each removal process varies ('Edwards 1994; 'Hering *et al.* 1996; 'Leist *et al.* 2000).

Arsenic removal by iron removal and iron precipitation

Due to geochemistry, many arsenic-containing groundwaters also contain significant levels of iron, which is typically in the reduced (i.e. dissolved) Fe(II) state. In these cases, conventional iron removal processes can be used to reduce arsenic by taking advantage of the surface adsorptive capacity of natural iron particles that are produced following the oxidation of Fe(II). The capacity to remove arsenic during iron removal depends largely on the amount of arsenic and natural iron present in the source water. Sorg (2002) proposed an arsenic treatment strategy screening guide (Figure 2), which is based on iron to arsenic concentrations in the source water relative to a 20:1 ratio ('USEPA 2001a, 2002). This ratio equates to 1 mg l⁻¹ iron to remove 50 µg l⁻¹ arsenic. Section A of Figure 2 represents waters with high iron levels of > 0.3 mg l⁻¹ at an iron to arsenic ratio that is greater than 20:1. Source waters with these qualities are potentially strong candidates for arsenic removal by iron removal. Section B represents waters that have significant levels of

iron but it is likely that they do not have enough iron to remove the relatively high levels of arsenic (i.e. iron concentrations > 0.3 mg l⁻¹ with an iron to arsenic ratio that is less than 20:1). 'Modified' iron removal, such as adding more iron to the iron removal process can be used to optimize removal under these source water conditions. Section C illustrates source water conditions that have little natural iron (< 0.3 mg l⁻¹) in which case arsenic removal would most likely be approached by other techniques such as adsorptive media, coagulation/filtration and ion exchange technologies. The treatment strategy screening guide presented in Figure 2 is very basic, and the removal capacities depicted are based on optimum adsorptive processes and operational conditions for As(V). Despite the fact that removal of natural iron can be an effective means of removing arsenic from water, little information is available on this subject.

'McNeill & Edwards (1995) conducted a survey of arsenic removal in five Fe-Mn removal plants. Two of the plants reported only 0.01 mg Fe l⁻¹ in the source water (i.e. manganese removal systems). Three of the plants reported between 1.5 and 3.6 mg Fe(II) l⁻¹ and 20.5, 5.2 and 3.2 µg As l⁻¹, respectively, in the source water. Arsenic removal efficiencies of 8 to 95% were obtained in the plants with greater than 1.5 mg Fe(II) l⁻¹ in their source water. Significant levels of arsenic removal were not achieved in the two systems that had very low levels of iron (Mn removal plants). Using adsorptive modelling alone (a conservative approach), 'Edwards (1994) predicted that by removing 2 mg Fe l⁻¹ (initially as Fe(II)) from a water with an initial As(V) concentration of 10 µg l⁻¹, a 0.75 µg l⁻¹ soluble effluent arsenic concentration can be achieved. The model also predicts that 1 mg l⁻¹ of Fe(II) is capable of adsorbing 83% of a 22 µg l⁻¹ As(V), producing soluble arsenic concentrations of about 3.5 µg l⁻¹. In similar work, 'Clifford and Lin (1991) reported that 60% removal of As(V) was removed by oxidation and coprecipitation of 2 mg Fe(II) l⁻¹.

The US EPA evaluated the long-term removal of arsenic from two full-scale iron removal plants, Plant A and Plant B ('USEPA 2000b). Plant A had a treatment capacity of 6.1 million litres per day and a treatment train consisting of aeration, chlorination, sedimentation, filtration, softening and postchlorination. Total arsenic concentrations at Plant A were reduced from an average of 20.3 µg l⁻¹ to 3.0 µg l⁻¹ during the removal of 2.28 mg l⁻¹ iron.

Table 1 | Adsorption of arsenic onto iron-based solids

Artenic species	Sorbent	Source of sorbent	Reference
As	Goethite, (α -FeOOH)	Mother Lode District, Tuolumne County, California	Savage <i>et al.</i> (2000)
As(V)	Goethite, (α -FeOOH)	Cerro del Hierro, Sevilla, Spain	García-Sánchez <i>et al.</i> (1999)
As(V)	Goethite, (α -FeOOH)	Sierra de la Culebra, Zamora, Spain	García-Sánchez <i>et al.</i> (1999)
As(III) and As(V)	Goethite, (α -FeOOH)	Synthetic	Sun and Doner (1998)
As(V)	Goethite, (α -FeOOH)	Synthetic	Fendorf <i>et al.</i> (1997)
As(V)	Goethite, (α -FeOOH)	Synthetic	Grossl <i>et al.</i> (1997)
As(V)	Granular ferric hydroxide (β -FeOOH)	Synthetic	Driehaus <i>et al.</i> (1998)
As	Jarosite, ($\text{KFe}_3^+(\text{SO}_4)_2(\text{OH})_6$)	Mother Lode District, Tuolumne County, California	Savage <i>et al.</i> (2000)
As(III) and As(V)	Ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)		Swedlund and Webster (1999)
As(III) and As(V)	Ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)		Jain <i>et al.</i> (1999)
As(V)	Limonite, ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)	Rio Tinto, Huelva, Spain	García-Sánchez <i>et al.</i> (1999)
As	Corroding iron and sulfate reducing bacteria (SRB)	Acid rock drainage	Shokes and Möller (1999)
As	Ferrihydrite, ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)	Synthetic	Paige <i>et al.</i> (1997)
As(V)	Iron-oxide coated sand	Synthetic	Vagliasindi <i>et al.</i> (1996)
As(III) and As(V)	Hydrous ferric oxide (coagulant FeCl_3)		Hering <i>et al.</i> (1996)
As(III)	$\text{Fe}(\text{OH})_3$		Edwards (1994)
As(V)	Ferrihydrite, ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)	Synthetic	Fuller <i>et al.</i> (1993)
As	Hydrous ferric oxides		Smith <i>et al.</i> (1992)
As(V) and As(III)	$\text{Fe}^{\text{III}}(\text{OH})_3$	Solution of FeCl_3 and HCl (Fisher Scientific)	Meng & Korfiatis (2000)
As(V) and As(III)	$\text{Fe}^{\text{III}}(\text{OH})_3$	Solution of FeCl_3 and HCl (Fisher Scientific)	Meng & Korfiatis (2000)
As(V)	Fe(III)/Cr(III) hydroxide		Namasivayam & Senthilkumar (1998); Peng & Di (1994)
As	Ferric hydroxide and sodium dodecyl sulfate		

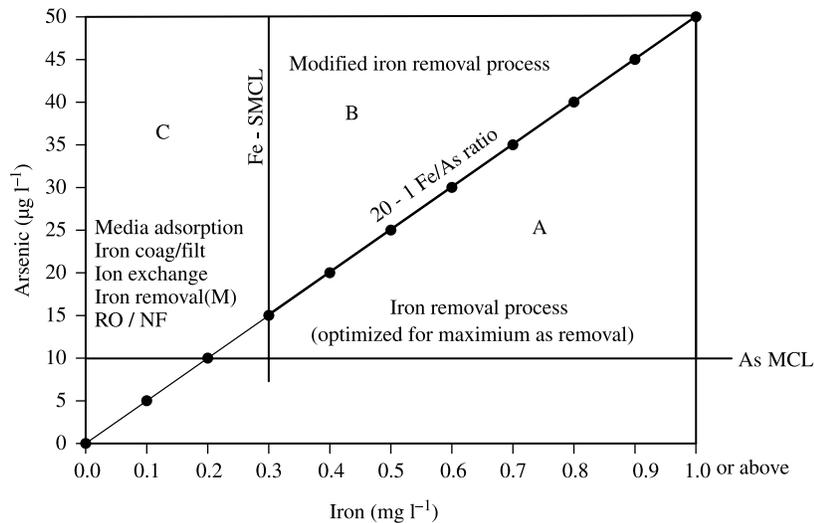


Figure 2 | Arsenic treatment strategy selection guide as a function of initial arsenic and iron content of water. Based on optimized arsenic removal of As(V) (Sorg 2002).

Plant B treated 5.3 million litres and the treatment train consisted of chlorination, reaction vessels, filtration vessel and blending. By removing 1.14 mg l^{-1} of iron, Plant B decreased the arsenic from an average of $48.5 \text{ } \mu\text{g l}^{-1}$ to $11.9 \text{ } \mu\text{g l}^{-1}$. Differences in arsenic removal levels between the two plants were attributed to the amount of iron in the source waters. Consequently, it was suggested that increasing the amount of iron at Plant B (using a coagulant such as ferric chloride) would have improved arsenic removal.

Although natural iron removal processes and iron coagulation/filtration processes are not identical water treatment processes, arsenic removal during each is mechanistically similar in that dissolved Fe(II) oxidation leads to the formation of iron hydroxide solids that coprecipitate or adsorb with arsenic. Bench and full-scale studies have investigated these processes of arsenic removal.

The removal of As(V) by iron coagulation/filtration is more effective than As(III) removal (‘Sorg & Logsdon 1978; ‘Sorg 1993; ‘Edwards 1994; ‘Hering *et al.* 1996). For both forms of arsenic, removal has been shown to be dependent upon iron concentration; removal increased as concentration increased (‘Gulledge & O’Conner 1973; ‘Sorg & Logsdon 1978; ‘Hering *et al.* 1996). Arsenic removal of As(III) or As(V) has also been shown to be independent of initial arsenic concentration at levels important in drinking water (‘Edwards 1994; ‘Chen *et al.* 1994; ‘Hering *et al.* 1996). Investigators have reported that As(III) removal during iron

coagulation is relatively unaffected by pH (‘Sorg & Logsdon 1978; ‘Hering *et al.* 1996). As(V) removal during iron coagulation has been shown to be less affected by pH at or below 8; however, pH levels above 8 result in decreases in removal efficiencies (‘Sorg & Logsdon 1978; ‘Edwards 1994).

Optimizing arsenic removal during iron removal

Iron removal in its simplest form involves the oxidation (typically aeration) of soluble iron, Fe(II), to the relatively insoluble Fe(III) form. If manganese is also present, a stronger oxidant, such as potassium permanganate or chlorine, is necessary to oxidize the manganese. Arsenic removal by iron removal processes is achieved through two primary mechanisms: adsorption and coprecipitation (‘Benefield & Morgan 1990). Adsorption involves the attachment of arsenic to the surface of Fe(III) particles, whereas coprecipitation involves adsorption and entrapment of arsenic within growing Fe(III) particles by inclusion, occlusion or adsorption. The capacity to remove arsenic during iron removal is dependent on a number of factors, including water quality, operating conditions and treatment flow processes. Redox relationships between arsenic, iron and oxidants are particularly important for optimizing the removal of arsenic during iron removal.

Oxidation of Fe(II) by oxygen (aeration) is well understood and is strongly dependent on the pH of the water

(‘Stumm & Lee 1961). In the proper pH range and with sufficient contact times, Fe(II) oxidation can be achieved by aeration. When followed by filtration, aeration is an effective approach to remove iron from groundwater. Aeration, however, does not effectively oxidize either Mn(II) or As(III). Although some As(III) will adsorb onto iron surfaces, the amount is low compared with As(V) (‘Sorg 1993; ‘Edwards 1994; ‘Hering *et al.* 1996). Therefore, the use of a strong oxidant, such as potassium permanganate or free chlorine, will oxidize As(III) to As(V), thereby improving arsenic removal.

Research has shown that pre-formed Fe(III) particles have less capacity to remove As(V) than iron particles formed in the presence of As(V). ‘Edwards (1994) reported that preformed iron hydroxides only reached a maximum adsorption density of 0.1 M As(V) per M iron hydroxide solid in comparison with a maximum adsorption density of 0.5 to 0.6 for iron hydroxides achieved in the presence of As(V). Edwards attributed such differences to mechanisms that were in place: strictly surface adsorption versus adsorption/coprecipitation.

‘Hering *et al.* (1996) examined the water quality factors that affect arsenic removal during iron coagulation and adsorption to preformed hydrous ferric oxides (HFO). Based on experimental results and surface complexation modelling, the author demonstrated that, although adsorption is an important mechanism, it is not the only mechanism controlling arsenic removal during coagulation. Such a case is analogous to the condition in a natural iron removal aeration/filtration plant that applies aeration to oxidize iron, followed by chlorination or permanganate to oxidize As(III); that is, iron particles are formed prior to As(III) oxidation.

The point of strong oxidant addition is, therefore, important with respect to optimizing arsenic removal. Arsenic removal has been observed to increase during this sequence of treatment steps, as opposed to air oxidation followed by chemical oxidation of both Fe(II) and As(III) at the same time. Consequently, oxidation of dissolved Fe(II) and arsenic, As(III), should occur at the same time to maximize arsenic removal.

The need for contact time (contact basin) following oxidant addition is debatable. Strong oxidants oxidize As(III) and Fe(II) very rapidly (‘AWWARF 1990; ‘USEPA

2001b), so time is not critical in the oxidation step process. Based on the experience of the authors, the majority of arsenic is incorporated into the Fe(III) particle during the first several minutes following oxidation. Relatively small amounts of additional arsenic adsorption/removal take place with extended contact time. Particle development, however, may benefit from extended contact times and may improve filterability. Although there are many systems that operate without contactors, contact time should be examined when anticipated arsenic removals are not achieved. Obviously, water utilities would reduce cost and space requirements by avoiding contactors.

Chemical oxidation

The stoichiometric amount of oxidant necessary to oxidize As(III), Fe(II) and Mn(II) is important when approximating chemical feed dosage in iron/arsenic removal systems. Avoiding oxidant under-dosing is particularly important in achieving optimal arsenic removal, because under-dosing can result in the incomplete oxidation of As(III), Fe(II) and Mn(II). Table 2 presents the stoichiometric relationships between relevant oxidants and constituents of interest to this research. Given the fact that Fe(II) and Mn(II) typically occur in mg l^{-1} concentrations, their oxidant demand dominates relative to arsenic, which occurs in $\mu\text{g l}^{-1}$ concentrations.

Objective

The objective of this research was to examine the impact of water quality and treatment operation factors on the effectiveness of conventional iron removal processes to remove arsenic from water. The study results provide practical scientific-based guidance on how to optimize arsenic removal efficiency during the iron removal process.

MATERIALS AND METHODS

Arsenic bench-scale studies were conducted in a series of controlled single ‘batch’ reactor experiments and standard jar tests. Batch reactor experiments were conducted in a 1.2 litre glass reaction vessel. The top of the cell contained ports for a pH electrode, dissolved oxygen/temperature probe,

Table 2 | Chemical oxidant stoichiometry

	As(III)	Fe(II)	Mn(II)
Chlorine	0.95 mg Cl ₂ per ug As(III)	0.64 mg Cl ₂ per mg Fe(II)	1.29 mg Cl ₂ per mg Mn(II)
Permanganate	1.06 mg MnO ₄ ⁻ per ug As(III)	0.71 mg MnO ₄ ⁻ per mg Fe(II)	1.44 mg MnO ₄ ⁻ per mg Mn(II)
Ozone	0.64 mg O ₃ per ug As(III)	0.45 mg O ₃ per mg Fe(II)	0.88 mg O ₃ per mg Mn(II)
Chlorine Dioxide	1.80 mg ClO ₂ per ug As(III), 1-electron transfer	0.24 mg ClO ₂ per mg Fe(II), 5-electron transfer	2.45 mg ClO ₂ per mg Mn(II), 1-electron transfer
Monochloramine	0.56 mg ClO ₂ per ug As(III), 5-electron transfer	0.46 mg NH ₂ Cl per mg Fe(II)	0.94 mg NH ₂ Cl per mg Mn(II)

Note: Table created from calculations presented in United States Environmental Protection Agency 2001b.

plexi-glass mechanical stirrer, acid and base feed lines, and a water sampling port. A computer software-controlled dual titrator system (Schott Geräte, Germany) maintained a constant pH by rapidly adding small increments of acid or base to compensate for pH changes caused by the addition of iron and chemical reactions. The computer software (Jensen Systems, Hamburg, Germany) recorded and maintained pH values and titrant volumes in a data file.

Experiments were initiated by adding 1 litre of oxygen saturated double deionized (DDI) water to the reaction cell. The water was mixed using a mechanical stirrer and plexiglass paddle (with a 19.05 mm radius blade) at 20 rpm ($G = 3.5 \text{ s}^{-1}$). Appropriate amounts of sodium bicarbonate (to provide buffering), chlorine and arsenic were then added to the water. The titration system was programmed to the desired pH and started after several minutes of mixing. When the pH stabilized, an initial water sample was drawn from the cell for total arsenic analysis. Ferrous sulfate (FeSO₄) was then added to give the desired initial iron concentration (typically 1 mg Fe l^{-1} [$1.79 \times 10^{-5} \text{ M}$] or 5 mg Fe l^{-1} [$8.95 \times 10^{-5} \text{ M}$]), depending on the experiment goal. Reduced ferrous iron was used to simulate the natural iron, Fe(II), found in source waters. Modifications to chemical addition sequence and chemical forms (e.g. ferrous or ferric iron, arsenite or arsenate) were made to meet experimental objectives. The titration system maintained the pH through changes brought about by iron addition, oxidation and precipitation, and CO₂ transfer at the water:air interface. At the end of the jar test, two 60 ml samples were collected for ICP analysis: a non-filtered sample and a 0.02 μm filtered sample. Water samples were drawn out of the cell with a syringe, approximately 20 minutes after complete oxidation of Fe(II) had taken place (time determined in an independent study).

Jar tests were performed using a six jar (six 1.5-litre plexiglass jars) test apparatus (Phipps and Bird, PB-700 Jar Tester, Richmond, Virginia) with synthetic or field-site-test water, when tight water quality control (e.g. pH) was not critical (primarily at field sites using natural waters). Global mixing conditions and experimental protocol of jar testing were identified in experiments using a reaction vessel. Synthetic water was prepared by adjusting 7 litres of oxygen saturated DDI with appropriate amounts of sodium bicarbonate. The pH of each sample was adjusted by adding

either 0.6 M HCl or 0.5 N NaOH to achieve the pH test goal. Chlorine or potassium permanganate (if needed) were added at this point as well. The water was mixed using a mechanical stirrer at 20 rpm. Arsenic and iron were then added to the jars. The levels, forms and sequence of iron and arsenic added were defined by the test objectives (e.g. iron first (either ferrous or ferric) for preformed experiments, or arsenic first (arsenate or arsenite) for fresh particle experiments). Initial arsenic and iron levels were measured. After both chemicals were added, samples were collected and tested by the Hach Benchtop spectrophotometer for total iron. The pH of each sample was also determined and adjusted to the appropriate value. At the end of the jar test, two 60 ml samples were collected for ICP analysis: a non-filtered sample and a 0.02 μm filtered sample. Both samples from each jar were collected approximately 20 minutes after complete oxidation of Fe(II) had taken place for pH 7 and approximately 1 hour afterwards for all other pH values.

Water and chemicals

Unless otherwise specified, all chemicals used in this study were Analytical Reagent (AR) grade. The amount of ultrapure nitric acid, HNO_3 (Ultrex, J.T. Baker Chemical Company, Phillipsburg, New Jersey), used to preserve samples for metals analysis was 1.5 ml l^{-1} per sample. Dilute 0.6 M HCl (Malinckrodt, Inc., Paris, Kentucky) and 0.5 N NaOH (Fischer Scientific, Fairlawn, New Jersey) were used to adjust the pH, and sodium bicarbonate (NaHCO_3) (Fischer Scientific, Fairlawn, New Jersey) was used to adjust water quality. Sodium hypochlorite (4 to 6% NaOCl, purified grade) (Fischer Scientific, Fairlawn, New Jersey) was used to oxidize iron (II), which was added as ferrous sulfate ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$)¹ (Fisher Scientific, Fairlawn, New Jersey). Ferric iron was added as $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ (Ultrex, J.T. Baker Chemical Company, Phillipsburg, New Jersey), arsenite as NaAsO_2 (Malinckrodt, Inc., Paris, Kentucky) and arsenate as $\text{NaHAsO}_4 \cdot n\text{H}_2\text{O}$ (Malinckrodt, Inc., Paris, Kentucky).

¹The purchased material was listed as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fisher Scientific); however, X-ray diffraction (XRD) analysis and titrimetric standardization of stock solution indicated that the original chemical dehydrated over time. Analysis showed that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ were present and that the chemical dehydration accounted for about 10% error in the final stock solution concentration.

Analytical methods

The pH was measured with a Hach Company (Loveland, Colorado) EC40 benchtop pH/ISE meter (Model 50125) and a Hach Company (Loveland, Colorado) combination pH electrode (Model 48600) with temperature corrections. A two-point calibration with pH 7 and 10 standard solutions standardized the instrument daily (Whatman Hillsboro, Oregon). Dissolved oxygen (DO) was measured with a Hach Company (Loveland, Colorado) Model DO175 dissolved oxygen meter and a Model 50180 dissolved oxygen probe. Free and total chlorine were measured with a Hach DR/2000 spectrophotometer (Loveland, Colorado), using the DPD method (Standard Method, 4500-Cl G) (‘Hach Company 1990). Arsenic was analysed with a Thermo Jarrel Ash (Franklin, MA) Model SH-4000 graphite furnace atom adsorption spectrophotometer (USEPA Method 7060A). A Thermo Jarrel Ash (Franklin, MA) 61E[®] purged inductively coupled argon plasma atomic emission spectrophotometer (ICP-AES) was used to analyse total iron (USEPA Method 200.7). Ferrous iron was measured using the 1,10 phenanthroline method (‘Hach Company 1990; ‘*Standard Methods* 1995). Total iron was also measured by the same method except that a reducing reagent was also included in the reagent powder pillow provided by the Hach Company to convert Fe(III) to Fe(II). Dissolved inorganic carbon (DIC) was analysed by a coulometric procedure on a UIC Model 5011 CO_2 coulometer (Joliet, Illinois) with Model 50 acidification module, operated under computer control. Syringe filters (0.02 μm) (Anotop 25[®], Whatman, Inc., Clifton New Jersey) were used to separate colloidal iron-arsenic from soluble arsenic. Filtration studies were conducted in advance to ensure that soluble arsenic adsorption onto the filter media during filtration was not an issue.

Other

Glassware (excluding pipettes) used for the preparation of standards and solutions was cleaned using a 5% solution of Contrad 70[®]. The glassware was thoroughly rinsed with deionized water. Reused glassware was immediately cleaned by soaking in 10% (v/v) concentrated HNO_3 and rinsed with DDI H_2O . Air displacement micropipettes with

disposable tips were used for handling and transferring solutions.

RESULTS

The removal of arsenic during iron removal was evaluated using bench-scale tests conducted in the laboratory and at field sites. Unless otherwise noted, experiments were obtained from batch reactor experiments. Fe(II) was oxidized to Fe(III) particles (referred to as ‘fresh’ iron particles), either in the presence of arsenic or by adding arsenic approximately 5 minutes following iron particle formation (referred to as ‘pre-formed’ particles). The following results identify several operational and water quality factors that affect arsenic removal during iron removal.

pH dependency

A series of tests were conducted in chlorinated and nonchlorinated (saturated dissolved oxygen) synthetic water that initially contained $100\ \mu\text{g l}^{-1}$ As (V), $10\ \text{mg Cl}^{-1}$ of dissolved inorganic carbon (DIC) and $1\ \text{mg l}^{-1}$ of Fe(II) at 24°C . Fe(II) was added following arsenic addition, which resulted in the formation of ‘fresh’ iron particles. The removal of As(V) in both oxygen alone and chlorinated waters was strongly dependent on pH (Figure 3). Arsenic removal decreased in a near linear fashion from approximately 65% to 15% between pH 7 and 10 in the iron particle system that originated from the oxidation of Fe(II) by oxygen. As(V) removal decreased from nearly 100% at pH 7 and 8 to 30% at pH 10 in the iron particle system that originated from the oxidation of Fe(II) by free chlorine.

Freshly precipitated iron particles

Particles formed from the oxidation of Fe(II) by chlorine had a greater capacity (by more than 40%) to remove As(V) than particles formed from oxygen alone at pH values less than 9 (Figure 3). The improved arsenic removal capacity is analogous to the earlier observations of ‘Lytle & Snoeyink (2002), who reported that the removal of phosphate (a

chemically similar anion) by iron particles formed under identical conditions was greater when chlorine was used to oxidize Fe(II). The findings were attributed to differences in particle properties, particularly density and surface area, which they explained in a particle growth model that considered oxidation kinetics and Fe(II)–Fe(III) particle interactions.

As(V) removal efficiency during coprecipitation with a Fe(III) salt, ferrous sulfate, in the pH range 7 to 10 was compared with As(V) removal efficiencies achieved when iron particles were initially formed from Fe(II) (Figure 3). Removal efficiencies were nearly identical to the removal of As(V) achieved when chlorine was used to oxidize Fe(II) over the evaluated pH range. ‘Lytle & Snoeyink (2004) showed that the iron properties of the particles formed with chlorine and from hydrolysis of Fe(III) were similar. Their results are consistent with similarities in arsenic removal results brought about by the two different iron particles. The similarities in As(V) removal suggest similarities in iron particle properties (surface area, mineralogy, etc.).

Iron concentration

As(V) removal during iron removal can be improved by increasing iron concentration to increase the number of surface adsorption sites. For example, increasing the initial Fe(II) concentration from 0.1 to $2\ \text{mg l}^{-1}$ (pH 7, saturated dissolved oxygen alone, 23°C) linearly increased the removal of $100\ \mu\text{g As (V) l}^{-1}$ from 20% to over 80% (Figure 4). Improvement in As(V) removal efficiency can be achieved at all pH values by increasing Fe(II) concentration. Figure 5 illustrates that increasing the initial Fe(II) from 1 to $5\ \text{mg l}^{-1}$ (no chlorine, $100\ \mu\text{g As(V) l}^{-1}$, 23°C) increased arsenic removal by approximately 40% between pH 7 and 10.

Increasing arsenic concentration while holding iron Fe(II) dose constant had a different impact on arsenic removal and the capacity of iron particles to adsorb arsenic. Increasing the initial arsenic concentration from 60 to $240\ \mu\text{g l}^{-1}$ while holding the initial iron concentration at $1\ \text{mg l}^{-1}$ ($10\ \text{mg Cl}^{-1}$, pH 7.6 to 8.2, 23°C) increased the capacity to remove arsenic linearly ($r^2 = 0.987$) from 73 to $195\ \mu\text{g As per mg Fe}$ (92 to 82% arsenic removal) in chlorinated water (Figure 6). Because the capacity of iron to

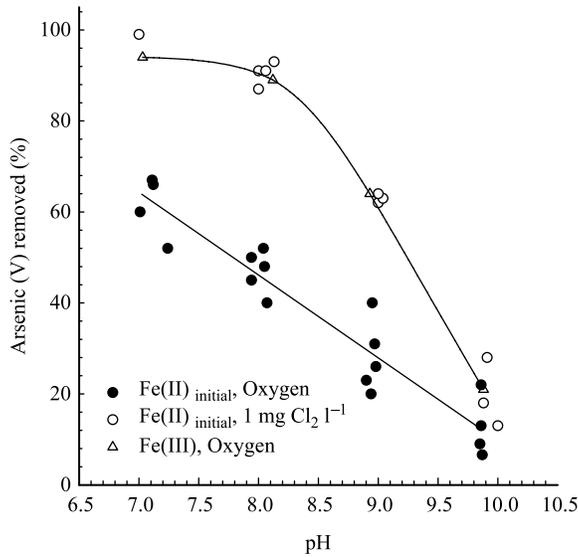


Figure 3 | Effect of pH, iron and chlorine on arsenic(V) removal with iron(II) and (III) (1 mg Fe l^{-1} , $100 \mu\text{g As(V) l}^{-1}$, $10 \text{ mg Cl}^{-1} \text{ DIC}$, $\text{O}_2 = \text{saturated}$, 24°C).

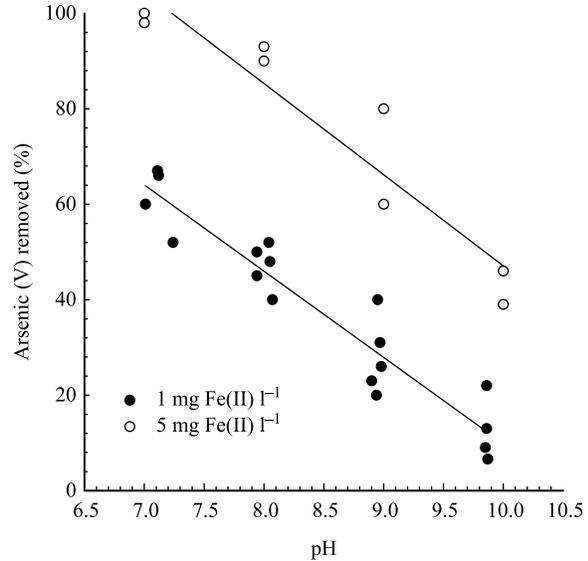


Figure 5 | Effect of pH and iron(II) dose on arsenic(V) removal ($100 \mu\text{g As(V) l}^{-1}$, $10 \text{ mg Cl}^{-1} \text{ DIC}$, $\text{O}_2 = \text{saturated}$, 24°C).

remove arsenic changes with initial arsenic concentration, predicting arsenic removal is site specific and subject to local variability in arsenic water levels.

The impact of As(V) concentration on the removal capacity is illustrated in the following case study at site A. The source water at site A contained 1.3 mg Fe l^{-1} and $129 \mu\text{g As l}^{-1}$ (complete average water chemistry shown in

Table 3). The treatment process consists of aeration, chlorination, addition of KMnO_4 , and the addition of a polymer coagulant aid, a contact basin and filtration. The system is able to achieve a final As level of $18 \mu\text{g l}^{-1}$ or an As(V) removal capacity of $80 \mu\text{g As}$ per mg Fe on average, although the capacity can reach as high as $100 \mu\text{g As}$ per mg Fe . One approach to meet the new arsenic

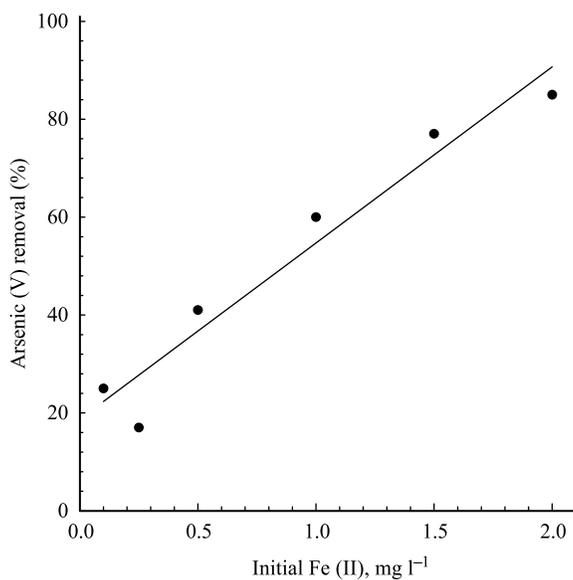


Figure 4 | Effect of iron(II) dose on arsenic(V) removal ($\text{As(V)}_{\text{initial}} = 100 \mu\text{g l}^{-1}$, $10 \text{ mg Cl}^{-1} \text{ DIC}$, $\text{pH} = 7.33\text{--}7.50$, $\text{O}_2 = \text{saturated}$, 23°C).

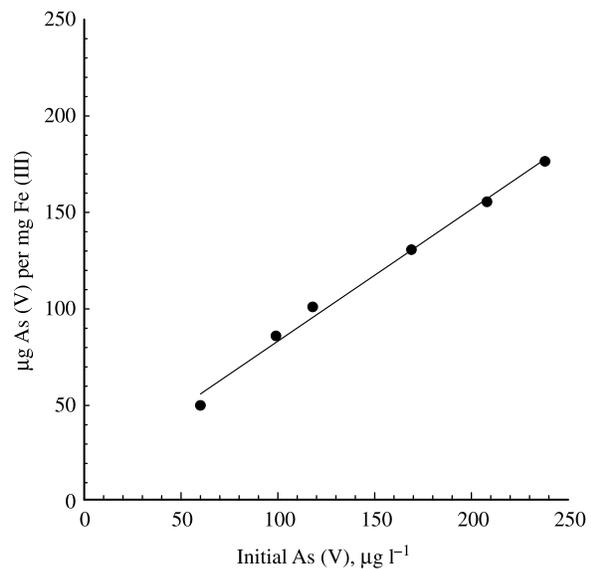


Figure 6 | Effect of chlorine and arsenic(V) concentration on the capacity of iron to adsorb arsenic(V) ($1 \text{ mg Fe(II)}_{\text{initial}} \text{ l}^{-1}$, $1 \text{ mg Cl}_2 \text{ l}^{-1}$, $10 \text{ mg Cl}^{-1} \text{ DIC}$, $\text{pH} = 7.55$, 24°C).

Table 3 | Water chemistry data for arsenic sites

Site	Location	Sample location description	As $\mu\text{g l}^{-1}$	Ca mg l^{-1}	Cl mg l^{-1}	Fe mg l^{-1}	Mg mg l^{-1}	Mn mg l^{-1}	Na mg l^{-1}	Total $\text{PO}_4 \text{mg l}^{-1}$	$\text{SiO}_2 \text{mg l}^{-1}$	$\text{SO}_4 \text{mg l}^{-1}$	Total alkalinity $\text{mg l}^{-1} \text{CaCO}_3$	pH
A	North Dakota	Raw	129	133	na	1.39	32	0.64	159	na	31	376	na	7.88
		Finished water	18	132	2.2	0.05	31	0.03	159	na	30	374	na	na
B	Ohio	Raw	69	115	nd	1.38	59	0.163	11	na	na	10	210	7.9
		Finished water	8	48	na	0.01	14	0.363	10	na	11	na	na	na
		Distribution	5	111	na	0.07	57	0.292	11	na	na	1	213	7.7

na = not available.
nd = non detected.

standard is to add more iron. If one assumes that the capacity of $80 \mu\text{g As per mg Fe}$ is independent of initial arsenic concentration, roughly only 0.1 mg l^{-1} of additional iron should be needed to reduce $18 \mu\text{g As l}^{-1}$ to below the $10 \mu\text{g l}^{-1}$ MCL. However, jar tests showed that it takes at least 1 mg l^{-1} of additional iron, Fe(II) or Fe(III), to achieve the arsenic MCL. Therefore, the removal ability of 1 mg l^{-1} of additional iron at lower initial As(V) concentrations was reduced from $100 \mu\text{g As per mg Fe}$ to $8 \mu\text{g As per mg Fe}$, which indicates that low initial As(V) concentrations require a greater amount of iron to optimize As(V) removal.

Other competing water quality variables

Anions such as phosphate and silicate are known to compete with arsenic for adsorption sites on iron hydroxides and subsequently will reduce arsenic removal. Figure 7 shows the impact of phosphate concentration on As(V) removal during iron removal by oxidation of Fe(II) with oxygen alone and chlorine at pH 8. Arsenic removal efficiency dropped rapidly from approximately 50% to 15% with the addition of $0.5 \text{ mg PO}_4 \text{ l}^{-1}$ for oxygen-formed Fe(III) particle systems. Orthophosphate concentrations above 0.5 mg had little additional effect. Phosphate also caused a reduction in As(V) removal when iron particles formed from chlorine oxidation. As(V) removal decreased

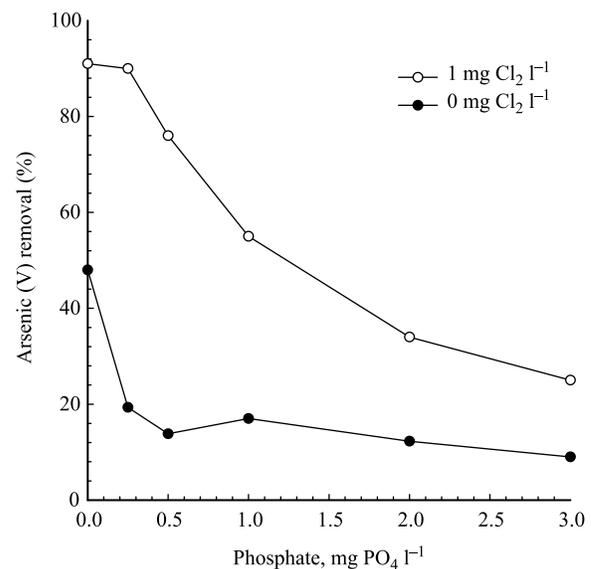


Figure 7 | Effect of chlorine and phosphate on arsenic(V) removal with iron(III) ($10 \text{ mg Cl}^{-1} \text{ DIC}$, $1 \text{ mg Fe(II)}_{\text{initial}} \text{ l}^{-1}$, pH = 8, $100 \mu\text{g As(V)} \text{ l}^{-1}$).

in an exponential manner from approximately 90% to 20% as phosphate concentration was increased from 0.25 to 3 mg PO₄I⁻¹ (see Figure 7).

Cations can also affect arsenic removal effectiveness during iron removal although their importance is far less than phosphate. Calcium (80 mg l⁻¹) improved As(V) removal by nearly 30% at pH 7, 8 and 9 (in oxygenated system) (Figure 8). These improvements are thought to be associated with changes in the electrophoretic mobility (zeta-potential) as a result of cation addition. Cations tend to decrease the zeta potential and shift the pH of the zero point of charge (ZPC) to a higher pH. This effect is more favourable for arsenic anions to reach adsorption sites, thus increasing effectiveness of arsenic removal.

Oxidant strength and point of application

Test results showed that As(V) removal by iron removal is optimized when oxidized with both chlorine and oxygen as apposed to being treated with only oxygen (Figure 3). In natural systems containing iron, however, arsenic is typically in the reduced As(III) form. A common method to remove iron is air oxidation of the iron followed by filtration. In such systems, As(III) will not be oxidized by oxygen by the time Fe(II) is oxidized completely or partially in the time-frame of the treatment process. Even though

some As(III) will be removed by coprecipitation/adsorption with Fe(III) particles, removal efficiency will be substantially lower than As(V) removal. The removal of As(III) and As(V) over a pH range of 7–10 (Fe(II) = 1 mg l⁻¹, As_{init} = 100 µg l⁻¹, DIC = 10 mg Cl⁻¹, 23° C) was compared (Figure 9). The removal of As(III) was much less efficient than As(V) removal at pH values below 9 in oxygenated systems. Less than 25% of As(III) removal was achieved at pH 7 and 8 in comparison with approximately 65% and 50% removal of As(V) at the same pH values. There was no difference at pH 9 and, actually, As(III) was more easily removed at pH 10 than As(V): 45% and 20% removal respectively. The shift in As removal was probably due to Fe(III) particle and As chemical charge considerations. When chlorine was used as the primary oxidant, As(III) removal was identical to when arsenic was initially added as As(V) (Figures 3 and 9). Consequently, chlorination (or other strong oxidant) in lieu of oxygen can improve arsenic removal at existing iron removal plants using oxygen for Fe(II) oxidation.

The point where chlorination is applied relative to the point of aeration (and/or Fe[II] oxidation by background oxygen) is extremely important. When the natural ferric iron, Fe(II), is oxidized by oxygen prior to chlorine feed, ‘preformed’ iron particles (which may contain some As[III],

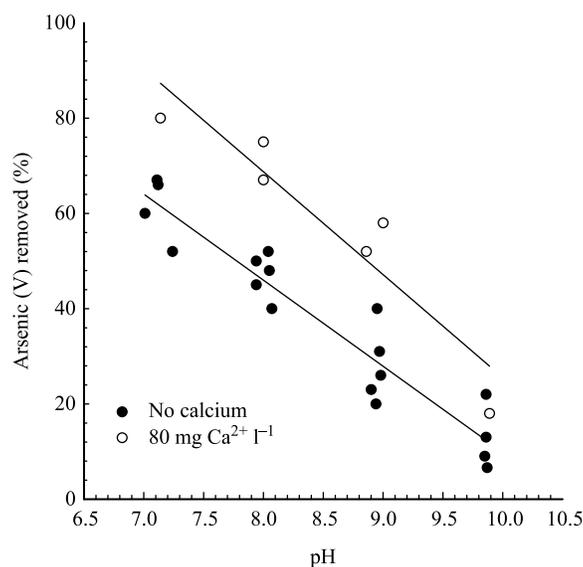


Figure 8 | Effect of pH and calcium on arsenic(V) removal with iron(III) (1 mg Fe(II)_{initial} l⁻¹, 100 µg As(V) l⁻¹, 10 mg Cl⁻¹ DIC, O₂ = saturated, 24°C).

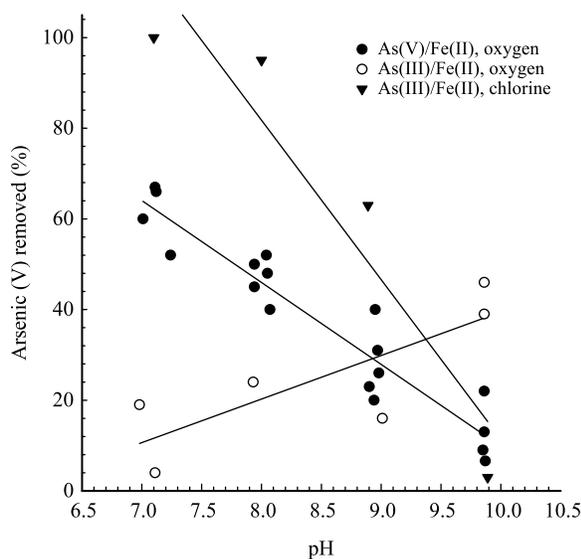


Figure 9 | Effect of the oxidant, chlorine and oxygen, on arsenic(III) and (V) removal with iron (III) (1 mg Fe(II)_{initial} l⁻¹, 100 µg As l⁻¹, 10 mg Cl⁻¹ DIC, O₂ = saturated, 24°C).

Figure 9) are present when As(III) is oxidized to As(V) by chlorine. In this case, arsenic removal is solely controlled by surface adsorption onto the preformed iron particles rather than a coprecipitation/adsorption mechanism. Jar test results performed at site B with natural water containing $75 \mu\text{g As(III) l}^{-1}$ and 1.4 mg Fe l^{-1} provide a good illustration (complete water chemistry in Table 3). The tests were conducted to investigate the impact of oxidant dose (chlorine and potassium permanganate) on arsenic removal. The test data show that when only oxygen was present ($1.0 \text{ mg O}_2 \text{ l}^{-1}$ at test start to $4.2 \text{ mg O}_2 \text{ l}^{-1}$ at test completion), approximately $15 \mu\text{g l}^{-1}$ of arsenic was removed after 20 minutes of contact time. Arsenic removal dramatically improved when chlorine and permanganate concentrations were used to oxidize the ferric iron and As(III) (Figure 10). Data also shows removal increases as oxidant dose was increased from 0.5 to 2 mg l^{-1} . Arsenic levels reached the same low level of nearly $10 \mu\text{g l}^{-1}$ with both oxidants at a dose of 2 mg l^{-1} . The test shows that oxidant concentration must be greater than the stoichiometric amount necessary to oxidize major oxidizable species (As, Mn, Fe, etc.) to maximize arsenic removal. However, when a strong oxidant is added after the iron is oxidized by oxygen, little additional arsenic removal is realized. In this work, $4 \text{ mg Cl}_2 \text{ l}^{-1}$ was added to the jar that initially did not contain chlorine (i.e. iron particles were

preformed). Only an additional $20 \mu\text{g As l}^{-1}$ was removed by adding chlorine. Point A on Figure 10 represents this situation.

Contact time

Contact time (time for particle and soluble arsenic to interact prior to filtration) is a factor that can potentially influence adsorption and oxidation kinetics (As and Fe), and filterability of resulting iron particles. Batch experiments were conducted to evaluate the role of contact time on As(V) removal with fresh iron particles formed in the presence of As(V) and preformed iron particles (pH 8, 10 mg Cl^{-1} DIC, 1 mg Fe l^{-1} , $100 \mu\text{g As l}^{-1}$, pH = 25°C). Interestingly, no arsenic removal was observed with preformed iron particles produced by the oxidation of Fe(II) by oxygen (Figure 11). Furthermore, contact time (up to 120 minutes) had no impact on arsenic removal. Preformed iron particles created by the oxidation of Fe(II) by chlorine did have some capacity to remove arsenic from water. Removal was time dependent, improving rapidly throughout the first 24 minutes of contact to a maximum removal efficiency of approximately 40%. Additional contact time (up to 120 minutes) did not improve arsenic removal. The removal of arsenic with fresh iron

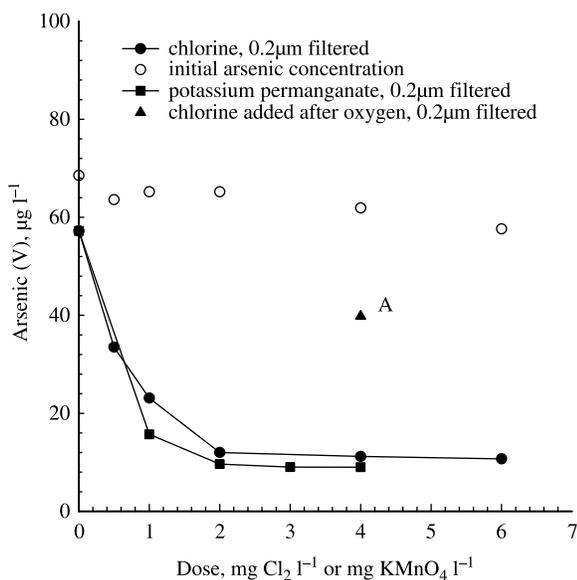


Figure 10 | Effect of oxidant type and concentration on the removal of arsenic(V) with iron(II) ($60\text{--}64 \mu\text{g As(III) initial l}^{-1}$, pH = 7.9).

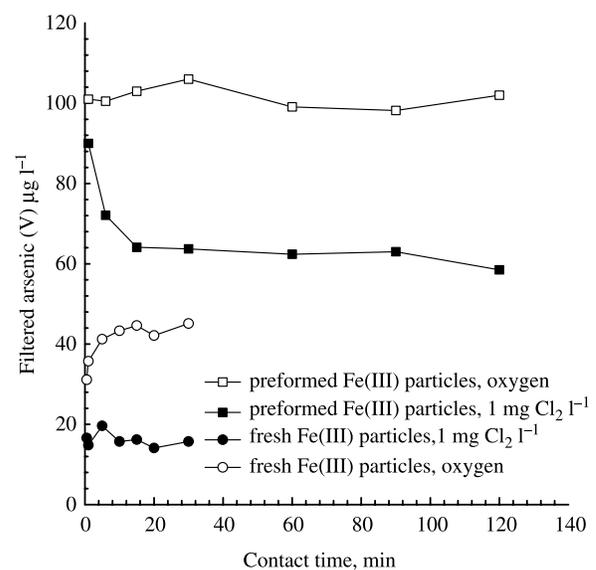


Figure 11 | Effect of contact time and iron(III) particle formation conditions on arsenic(V) removal with iron ($1 \text{ mg Fe(II) initial l}^{-1}$, $100 \mu\text{g As(V) initial l}^{-1}$, 10 mg Cl^{-1} DIC, pH = 8, 24°C).

particles increased to approximately 60% and 80% when oxygen and chlorine, respectively, were used to oxidize Fe(II). Contact time did not improve arsenic removal in either case. The importance of oxidant type and chlorine addition sequence is re-emphasized.

CONCLUSIONS AND RECOMMENDATIONS

When an arsenic-containing source water contains natural iron, removing the natural iron can reduce the arsenic concentration, with the reduction dependent on the iron to arsenic ratio and water quality. This study demonstrated the effects of water quality and operational factors on arsenic removal during iron removal using bench-scale experiments. This study reinforced the following previous findings: (1) arsenic removal decreases during iron removal with increasing pH and phosphate concentration, and (2) arsenic removal capacity was improved by adding iron under all conditions evaluated. The work also introduced the following newer findings: (1) calcium improved the removal of arsenic although the mechanism was not clear, (2) initial increases in arsenic concentration increased arsenic removal capacity ($\mu\text{g As per mg Fe}$), and (3) the point of iron particle formation relative to the point of As(III) oxidation to As(V) was very important.

Source waters containing both natural iron and arsenic can be treated for arsenic reduction by conventional iron removal processes. Recommendations to optimize arsenic removal when designing new iron removal/arsenic removal plants or modifying existing iron removal plants to increase removal are as follows:

- **Strong oxidant addition.** The form of arsenic – As(III) or As(V) – is very important when designing arsenic removal approaches; therefore, arsenic speciation analysis should always be conducted. When the source water arsenic is in the As(III) form, it will almost always be necessary to convert it to As(V) during treatment by the addition of a strong oxidant such as free chlorine or potassium permanganate. Oxygen (aeration) will not complete the conversion of As(III) to As(V) even though it will oxidize iron. Existing aeration systems that have an arsenic problem will probably need to add chlorine before their aerators, as location in the treatment chain is

critical (see oxidation protocol modification, below). Naturally, chemical costs and handling issues will need to be considered, particularly when strong oxidants have not been used. In addition, some groundwaters may have significant levels of organic carbon that might limit the use of chlorine addition out of concern for creating elevated levels of disinfection by-products.

- **Oxidation protocol modification.** This work clearly supported the conclusion that preformed iron particles have little capacity for As(V) removal. Fresh iron particles formed from chlorine in the presence of As(V) are less dense and have a greater capacity to adsorb arsenic. Thus, arsenic removal capacity is optimized when (1) As(III) and Fe(II) are oxidized at the same time, and (2) a strong chemical oxidant (e.g. free chlorine) is used. In cases where aeration is already in place, the strong oxidant must be added before aeration to achieve optimum results; that is, fresh iron particles lend to more immediate removal of arsenic than preformed iron particles.
- **pH adjustment.** Decreasing the pH should improve arsenic removal in most cases. However, pH adjustment involves the addition of an acid such as sulfuric acid or carbon dioxide, which raises handling and safety issues, and introduces up front storage costs and long-term chemical costs. In addition, post treatment pH readjustment may be necessary to meet corrosion control objectives.
- **Iron addition.** When the amount of natural iron is insufficient to reduce arsenic below the revised MCL, the addition of iron (ferrous or ferric) will improve arsenic removal. Adding iron provides additional surfaces for arsenic to interact with and improved arsenic removal under all conditions evaluated in this study. Like pH adjustment, however, iron addition involves the addition of an acidic chemical and therefore requires safety, handling and storage considerations. Supplemental natural iron levels will improve arsenic removal during iron removal; however, several considerations must be made. First, the chemicals are acidic and many of the same issues as observed from adjusting pH may exist depending on the buffer capacity of the water. Second, increasing the mass of iron will result in additional solids in the waste stream.

This research has provided a scientific basis for optimizing iron removal processes as well as iron coagulation for the

removal of arsenic from water. Many of these points have been effectively employed at a number of full-scale treatment plants and will be the subject of a separate paper. Finally, jar testing is a simple approach for evaluating these treatment approaches at the site based on the extensive experience of the researchers. Jar testing is a common bench-scale test designed to represent full-scale processes and provide treatment performance predictions, chemical dosing levels, operational protocols and physical-chemical characterization of the aqueous system.

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Any opinions expressed in this paper are those of the author(s) and do not, necessarily, reflect the official positions and policies of the USEPA. Any mention of products or trade names does not constitute recommendation for use by the USEPA.

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