# ARSENIC REMEDIATION IN DRINKING WATERS USING FERRATE AND FERROUS IONS

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# ABSTRACT

As groundwaters used for municipalities become increasingly contaminated with arsenic and as Environmental Protection Agency, EPA, acceptable threshold limits decrease (currently 50 ppb) (Pontius 1993), new methods for inexpensive arsenic removal are needed since existing methodologies are inadequate to meet such requirements. The objective of this study was to determine the ability of ferrate to remediate arsenic and arsenic containing compounds in water.

The basic approach is to produce soluble ion pairs between dissolved arsenic and ferrous ions. Oxidation of these moieties using ferrate produces the extremely insoluble ferric arsenate which precipitates and settles from solution.

$$Fe^{2+} + AsO_4^{3-} \rightleftharpoons FeAsO_4^- \xrightarrow{FeO_4^{2-}} FeAsO_{4(s)} + Fe(OH)_3$$
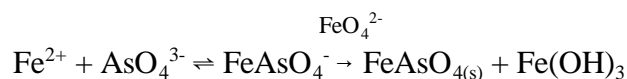
The ferrate and ferrous dose, pH, and ferrous ion source were all optimized. Optimal ferric arsenate removal (to below 5 ppb) was found at pH 5 and a total iron/arsenate ration approaching 8:1.

Removal efficiencies for monomethylarsenate ($CH_3AsO_3^{2-}$) and dimethylarsenate ($(CH_3)_2AsO_2^-$) were also determined using this approach. Due to their decreased charges, these latter two species were less efficiently removed. There is, however, some evidence for oxidation of methylarsenate with resultant increases in arsenic removal. Arsenic removal using ferrate alone also was studied. The potential for nitrate and phosphate ion to interfere with this process was studied. While nitrate was found to be innocuous, the addition of phosphate does lead to decreased removal efficiencies.

**Keywords:** arsenic, drinking waters, remediation, methylarsenate, dimethylarsenate, treatment

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**Research Objectives**

This study's primary objective was to develop an efficient and inexpensive method for arsenic remediation from drinking waters using ferrate and ferrous ions. This method represents a new variation on an old approach, that is, precipitation of ferric arsenate. Unlike previous studies using ferric salts, this method approaches the theoretical 1:1 iron/arsenic ratio and does so under mildly acidic conditions. Arsenate, arsenite, monomethylarsenate (MMA), and dimethylarsenate (DMA) were used as substrates and removal to below 5 ppb was achieved for the first three compounds. DMA however was found to be intractable to this removal method. The potential interference from nitrate and phosphate ions were also studied. Plots of removal versus total iron dose were constructed over a range of pHs. Studies in spiked tap water were also undertaken.

In addition to removal, the oxidation kinetics for arsenite, MMA and DMA with ferrate were studied. Arsenite and MMA were found to react rapidly with ferrate whereas DMA was unaffected by ferrate. Rate laws were determined for each system.

**Introduction**

Current Approaches to Arsenic Removal

Four physical/chemical treatment processes are commonly used to remove inorganic contaminants such as As(V) from water. These include chemical precipitation, reverse osmosis, anion exchange, and electrodialysis (Harper and Kingham 1992). Clifford (1990) reports that both anion exchange and activated alumina adsorption for arsenic removal have been successful and are in use for treating drinking water where the initial arsenic concentration is not much greater than the maximum contaminant level (MCL) of 0.05 ppb. Anion exchange is normally not economically attractive for waters with high total dissolved solids (TDS) (>500 ppb) or sulfate (>25 ppb) levels because of background competition for exchange sites (Clifford 1990). Alumina adsorption is specific for arsenate and it is not greatly affected by these variables. However, this process has the disadvantage in that only 50 to 70 percent of the adsorbed arsenic is recovered. Also, the arsenic capacity tends to deteriorate by about 15 percent after each regeneration cycle (Clifford 1990). Huang and Vane (1989) and Huang and Fu (1984) explored the chemistry of arsenic adsorption onto activated carbon. Before arsenic

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addition, the activated carbon was tailored (washed) with an iron salt solution. When performed under optimal conditions, a ten-fold increase in arsenic removal over untreated activated carbon was reported. One of their optimal conditions requires a pH between 3 and 4. These researchers state that the enhancement in removal by pretreatment occurs by adsorption of arsenate complexes onto the ferrous-activated carbon matrix. Membrane processes (i.e., reverse osmosis and electrodialyses) are very effective for arsenic removal from solution. However, these processes generate large volumes of waste (in the form of reject) due to the presence of dissolved minerals. The problem of high levels of dissolved silica and carbonate hardness is particularly common in water supplies that report elevated arsenic levels. Thus, even though effective, the use of membrane processes is inefficient in water production because it generates a large volume of unusable wastewater. Activated alumina and strong-base anion exchangers have been investigated extensively. The shortcomings of these methods to remove arsenic from water include: (1) severe capacity reduction and chromatographic elution of dissolved arsenic during fixed-bed column runs in the presence of competing sulfate ions for synthetic anion exchangers, (2) dissolution and loss of activated alumina during regeneration with caustic soda and (3) the need to adjust the pH of the contaminated water below 6.0 for activated alumina (Ramana and Sengupta 1992). Again, because of the competition by background ions for exchange sites, anion exchange is not economically attractive at high total dissolved solids (TDS >500 ppb) or sulfate (>25 ppb) levels (Clifford 1990). Recent experimental work (Kirk 1993; Cadena and Kirk 1995; Wilkie and Hering 1996) showed that it is possible to coprecipitate arsenic with ferric iron under acidic conditions. This method shows good removal of arsenic but has some disadvantages. First, significantly low pH values are required to obtain adequate arsenic removal. The optimal iron concentration range at pH 3 is narrow and higher iron concentrations than the optimal amount hinder arsenic removal. At pH 4 more than twice the amount of iron is required than at pH 3. Due to the relative insolubility of ferric compounds, the amount of chemicals needed and sludge produced are much greater than the method of precipitation proposed in this document.

Proposed Removal Technology

The proposed technology (oxidation of ferrous iron in slightly acidic conditions), takes

advantage of the high solubility of Fe(II) to target dissolved arsenates. Sudden oxidation with free chlorine (or other strong oxidizer) converts the ferrous into ferric iron, thus decreasing the inter-ionic distance between available iron and the pollutant. Therefore lower iron doses than those required when using ferric iron are needed to obtain similar performance. Precipitation of innocuous substances, in particular calcium and magnesium hardness, is eliminated by working under slightly acidic conditions. Additional waste volume minimization may be accomplished by several dewatering/drying techniques of the waste sludge using conventional processes. The primary benefits of this simple technology are characterized by minimization of both chemical requirements and sludge production.

**Methods**

Materials

All chemicals used were of analytical-reagent grade with the exception of the potassium ferrate and the monomethylarsenate (MMA). Potassium ferrate was prepared using the method of Thompson et al. (1951 ). Ferrate purity was determined spectrophotometrically to be above 90 percent. MMA was generously donated by ISK Biosciences.

Standard arsenic solutions of 2, 5, 10, 15, 25, 40 and 50 ppb were prepared each day in nanopure water from a SPEX Plasma Standard of 1,000 ppm. Ferrous ammonium sulfate and ferrous sulfate were of analytical grade. Sodium hydroxide and perchloric acid were used to adjust the pH of the solutions. Perchloric acid was used to circumvent any complexation problems.

Procedure

All initial arsenic concentrations were at 50 ppb. This level was selected because of the present EPA MCL for drinking waters. A typical treatment procedure involved addition of a known aliquot of iron(II) salt to the arsenic solution. The mixture was stirred to disperse the iron(II) salt. At this point, potassium ferrate was added and the solution was further stirred until the purple color of the ferrate disappeared. The time involved for this varied from a few seconds to several minutes. Iron doses are reported typically as total iron, iron(II) plus iron(VI). When dealing with the two oxidation states, the oxidation number is specified. The pH was adjusted and the final step involved filtering off the solid

ferric arsenate using 0.45µm nylon membrane filters. Each 25 mL sample was stored in a borosilicate glass sample vial containing two drops of dilute nitric acid to prevent adsorption of the arsenic.

To test interferences, the inhibitors were added following the addition of iron(II) and prior to the addition of potassium ferrate. The nitrate was introduced as potassium nitrate, $KNO_3$, and the phosphate was added as monobasic potassium phosphate, $KH_2PO_4$.

All arsenic samples were analyzed using a Perkin-Elmer 5000 graphite furnace atomic absorption spectrophotometer. Samples were deposited using a Perkin-Elmer AS40 auto-sampler. A nickel chloride, ($NiCl_2 \cdot 6H_2O$), matrix modifier was added to enhance sensitivity.

<u>Treatment of Spiked Tap Water</u>

To provide some idea of how well this procedure will work with "real life" samples, tap water from New Mexico State University was spiked with 50 ppb sodium arsenate (analysis of this water source showed no naturally occurring arsenate). Treatment was at pH 5, the optimal pH as determined in the earlier studies, and 400 ppb ferrate dose.

An alternate source of iron(II) also was used to check whether the ammonium ion played any role in arsenic removal. Ferrous sulfate was used in place of ferrous ammonium sulfate under the same conditions as described in Results Section.

**Results and Discussion**

<u>Adsorption Studies</u>

Before treatment studies were carried out, the effect of storing arsenic samples in borosilicate glass containers was determined. These studies show that storage overnight of an acidified sample of ppb range arsenic solutions does not significantly lower the determined arsenic levels due to adsorption onto glass, see Table 1. Longer periods of time (days); however, do show significant reduction in determined arsenic. For this reason, arsenic samples used in this study were never allowed to age for more than an overnight period.

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**Table 1**. Time study of arsenic adsorption onto glass vials.

| Concentration of arsenate added, ppb | Concentration of arsenate determined, ppb | Time of setting in glass container, hrs. |
|---|---|---|
| 5 | 4.8 | 15 |
| 10 | 7.8 | 88 |
| 15 | 8.4 | 66 |
| 20 | 11.2 | 66 |

Treatment Studies

Initial experiments in distilled water were carried out to find the "useful" range of total iron doses needed to decrease arsenic levels to detection limits of the graphite furnace AAS (approximately 2 ppb). Potassium ferrate, $K_2FeO_4$ , (iron in the +6 oxidation state) was used as the oxidant and ferrous ammonium sulfate was used as a pure source of iron(II). The iron dose is a sum of the amount of iron(II) as well as iron(VI) added to the solution. As the iron concentration increases, the amount of arsenic removed increases. Optimization of the pH, and increase removal, studies were performed between pH 4 and 10. As is clearly shown in Figure 1, optimal removal (to detection limits) occurs around pH 5. It is interesting to note that this corresponds to the minimum solubility of naturally occurring arsenic containing minerals such as scorodite, $FeAsO_4^.2H_2O$ (Virčíková et al. 1995).

A series of experiments were also performed in order to optimize the ferrate dose, Figure 2 shows the results of these studies. At 300 ppb ferrate, the arsenic is removed to detection limits with a total iron dose of 400 ppb. Although a 200 ppb ferrate dose will achieve similar results, a 700 ppb total iron dose is required. The cost of ferrate versus the cost of increased sludge production must be kept in mind when evaluating cost efficiencies of this process.
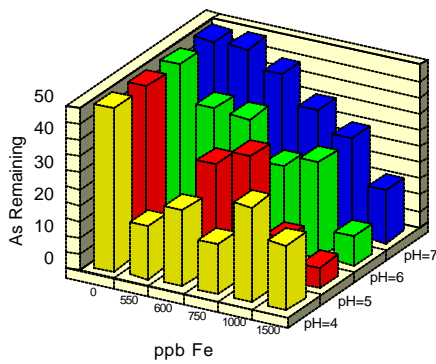
To determine whether ferrate alone is capable of removing arsenic from water, a study using ferrate alone was conducted. The results are shown in Figure 3. At pH 5 and a 750 ppb
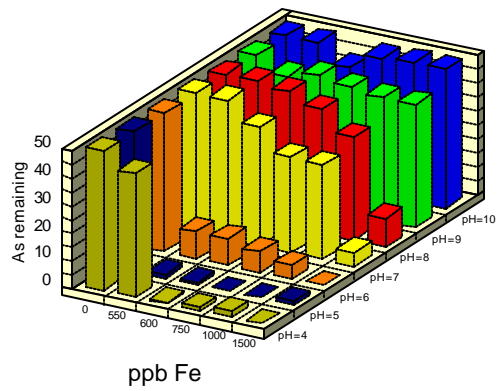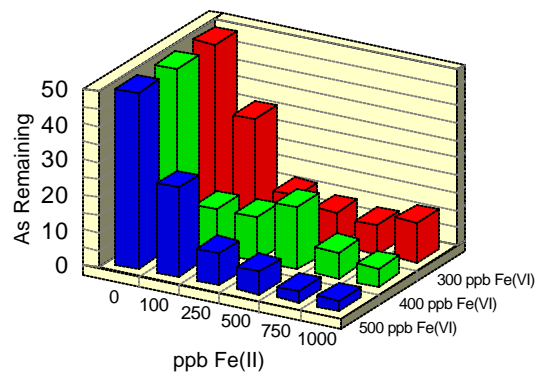
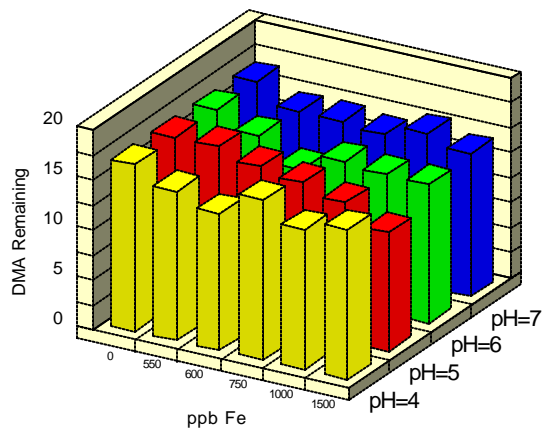**Figure 1.** pH optimization of arsenic removal
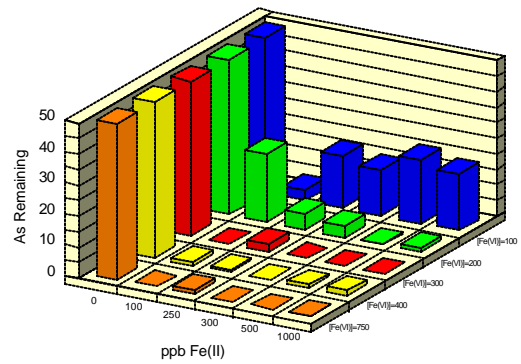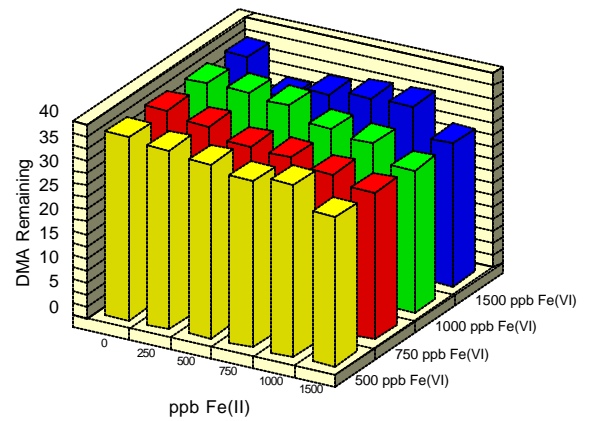


**Figure 2.** Optimization of ferrate dose



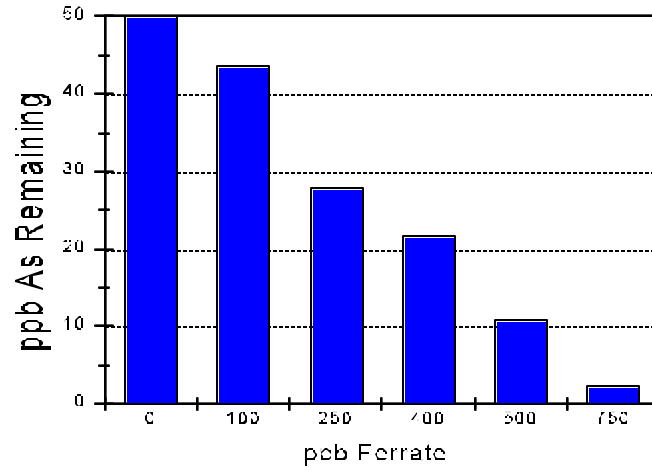**Figure 6.** Monomethylarsenate removal using ferrous/ferrate



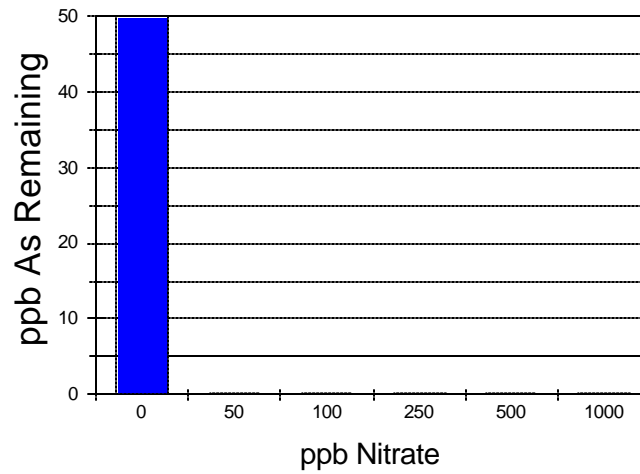**Figure 7.** Iron dose optimization for MMA removal



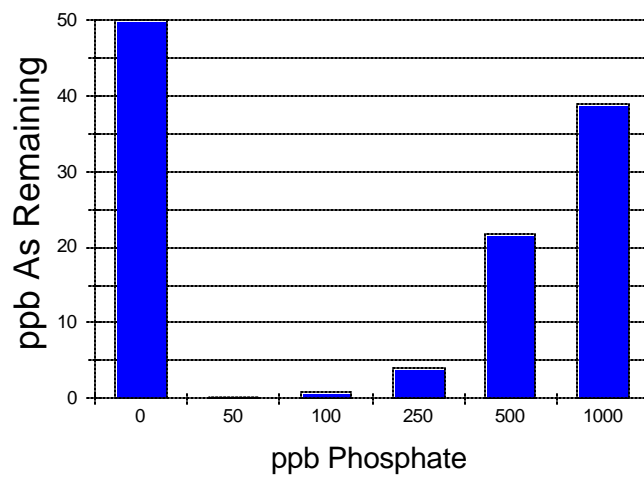**Figure 9.** pH optimization for DMA removal



**Figure 10.** Iron dose optimization for DMA removal

**Figure 3.** Arsenic removal using ferrate alone



**Figure 4.** Nitrate inhibition of arsenic removal



**Figure 5.** Phosphate inhibition of arsenic removal

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iron dose, the arsenic concentrations are decreased to 2.4 ppb. Clearly ferrate alone is not as efficient in decreasing arsenic concentrations.

Proposed Mechanism for Removal

The mechanism by which arsenic is removed by this procedure probably involves initial formation of a soluble ion pair between the ferrous ion and arsenate. Subsequent oxidation of the iron(II) arsenate complex by ferrate forms ferric arsenate ($pK_{sp} = 20.24$), which would precipitate from solution along with ferric oxyhydroxides, which are formed from excess iron.

$$Fe^{2+} + AsO_4^{3-} \rightleftharpoons FeAsO_4^- \xrightarrow{FeO_4^{2-}} FeAsO_{4(s)} + FeO(OH)_{(s)}$$
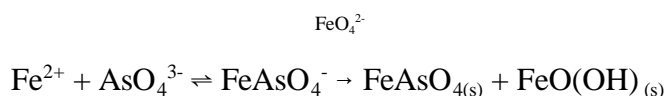
The effectiveness of this method results from the strong interactions between the ferrous and arsenate ion. Based on coulombic interactions alone, a $K_{IP}$ may be calculated, using a Debye-Huckel approach, to be approximately $10^4$ (Miralles et al. 1977). This calculation assumes that the arsenate is fully deprotonated and the ferrous ion is unhydrolyzed. These assumptions are pH dependent so the precise values for ion-pairing will vary but this calculation does show that significant ion pairing can take place. In addition, complexation (formation of As-O-Fe bonds) may also take place which would increase the association constant.

Potential Interferants

Clearly this mechanism would be susceptible to breakdown if ions were present that strongly compete with arsenate for complexation to the iron(II). To test this, we have studied the effects of nitrate and phosphate on the removal efficiencies. Optimal treatment conditions, determined in the previous studies, were employed and increasing amounts of the interfering ions were added to solution prior to treatment. From Figure 4 (page 7) it is immediately apparent that nitrate has little or no effect on the removal efficiencies. The first column represents the starting amount of arsenic, i.e., before remediation. The insensitivity of the method with respect to nitrate is not surprising since the association of the -1 charged ion would provide little competition with arsenate for ion pairing. Phosphate however, with its -3 charge should compete very effectively with arsenate and inhibit removal. This is clearly shown in Figure 5 (page 7) where phosphate concentrations of 1,000 ppb essentially eliminate arsenic

removal. Again, zero phosphate represents the starting arsenic concentration, before treatment.

**Methylated Arsenicals**

Monomethylarsenate ($CH_3AsO_3^{2-}$, MMA) and dimethylarsenate (($CH_3$)$_2AsO_2^-$, DMA) removal were also studied. These compounds were selected for two reasons. First, organoarsenicals, such as MMA are used as herbicides in agricultural regions and represent a potential source for water contamination for surface waters. Secondly, the decreased charges of these compounds provide a further test for our ion-pairing mechanism in the removal process.

Monomethylarsenate

pH Optimization

The initial study performed with MMA was to determine the optimum pH for removal of this arsenical. A pH range between pH 4 and 7 was used since a brief preliminary study carried out by this lab showed that higher pHs were ineffective, essentially 0 percent removal. The ferrous ammonium sulfate concentrations ranged from 50 to 1,000 ppb. The ferrate dose was set at 500 ppb and all solutions were prepared in nanopure water to eliminate any competition from foreign ions. Figure 6 (page 6) shows best removal of MMA occurs at pH of 5.

Iron Dose Optimization

The next set of experiments was carried out to determine the minimum total iron dose required for optimal MMA removal at pH 5. A constant range of ferrous ammonium sulfate concentrations, between 100 and 1,000 ppb, was used, while the potassium ferrate doses used were 300, 400 and 500 ppb. The results from these MMA remediation experiments were used to formulate the iron dose profile presented in Figure 7 (page 6). The lowest amount of remaining MMA following remediation was 3 ppb, achieved upon the addition of 1,000 ppb ferrous ion and 500 ppb ferrate ion. The ratio of total iron to MMA removed is roughly 32:1, considerably higher than the 4:1 ratio achieved for arsenate removal. It should also be noted that in no MMA removal experiment did the amount of arsenic remaining in solution ever drop below the detection limits of the GF-AAS. These studies indicate that the methyl group present in monomethylarsonic acid somehow impairs the removal efficiency of this technique.

In order to test how MMA remediation would work in a "real" situation, removal tests at pH 5, 500 ppb ferrate and doses of ferrous ion ranging from 100 to 1,000 ppb were performed in tap water. The results are shown in Figure 8 and demonstrate that removal of MMA in tap water is hindered, as removal efficiency is roughly 50 percent at the highest iron dose, 1500 ppb, compared to about 95 percent% when the identical experiment is performed in nanopure water. The reduced arsenic removal efficiency is tentatively attributed to foreign ion competition for ferric ion or for adsorption sites on the surface of the insoluble ferric hydroxide.
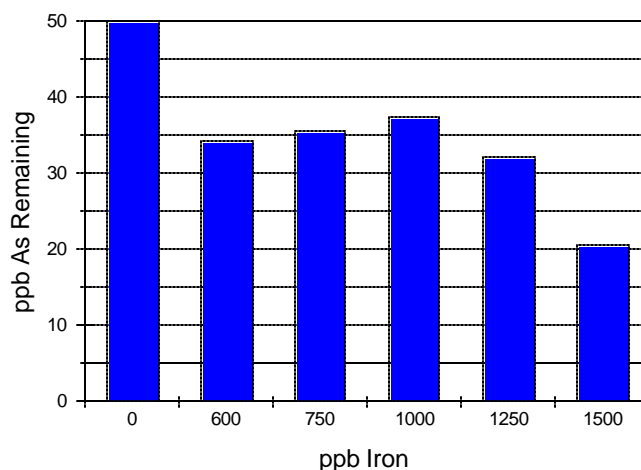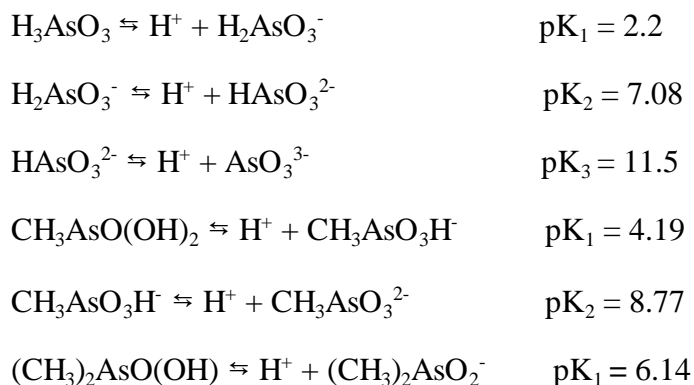


**Figure 8.** MMA removal in tap water

To follow up on these observations, a pH study was performed to ascertain the optimal pH for removal of cacodylic acid (DMA). Identical ferrous and ferrate ion doses and pH range used for the MMA pH profile were repeated for DMA. Figure 9 (page 6) shows that DMA remediation is extremely poor, a maximum removal efficiency of only 28 percent is observed at pH 5 and the highest iron dose, 1500 ppb. In an attempt to improve removal of DMA, the range of ferrous ion concentration was increased as well as the amount of ferrate applied. The new doses of ferrous ion ranged between 250 to 1500 ppb and concentrations of ferrate used were 500, 750, 1,000 and 1500 ppb. DMA removal using these combinations is presented in Figure 10 (page 6). Even when a total iron dose of 3,000 ppb is used, poor removal of DMA is still observed. Removal of the dimethylated arsenate species is negligible using this remediation technique due to the additional methyl groups.

The arsenic remediation efficiency of all the arsenic compounds studied follows the trend: $AsO_4^{3-} > MMA >> DMA$. The acid dissociation reactions and constants for these three species are presented can be used to discuss the remediation trend.

$$H_3AsO_3 \leftrightarrows H^+ + H_2AsO_3^- \qquad\qquad pK_1 = 2.2$$

$$H_2AsO_3^- \leftrightarrows H^+ + HAsO_3^{2-} \qquad\qquad pK_2 = 7.08$$

$$HAsO_3^{2-} \leftrightarrows H^+ + AsO_3^{3-} \qquad\qquad pK_3 = 11.5$$

$$CH_3AsO(OH)_2 \leftrightarrows H^+ + CH_3AsO_3H^- \qquad pK_1 = 4.19$$

$$CH_3AsO_3H^- \leftrightarrows H^+ + CH_3AsO_3^{2-} \qquad pK_2 = 8.77$$

$$(CH_3)_2AsO(OH) \leftrightarrows H^+ + (CH_3)_2AsO_2^- \qquad pK_1 = 6.14$$

The arsenical that showed poorest removal is DMA and it can be seen that at pH 5 this species exists predominantly as a neutral species, $(CH_3)_2AsO(OH)$. Due to the fact that DMA is uncharged it will not be able to form insoluble salts with ferric ion or with the positively charged surface of the ferric hydroxide floc. At pH 5, both MMA and arsenate exist as negatively charged oxyions and are capable of ionic interactions with ferric ion and ferric hydroxide. However, the ratio of deprotonated MMA to the neutral species at pH 5 is still relatively low (6.5:1); therefore, not all the MMA is present in ionic form which could account for the decreased removal efficiency. The possibility that ferric monomethylarsenate is more soluble than ferric arsenate may also explain the lower removal efficiency of MMA.

<u>Removal of MMA Using Ferrate as the Only Iron Source</u>

An interesting observation for the removal of MMA was made when remediation was attempted using ferrate as the sole iron source. Treatment at pH 5 and a ferrate dose ranging between 100 and 750 ppb showed improved MMA removal, see Figure 11. MMA removal to 3.5 ppb are achieved at a ferrate dose of only 750 ppb. This gives a ratio of about 15:1 for iron to arsenic removal which is roughly half that required for removal using the $FeO_4^{2-}/Fe^{2+}$ technique. In the following experiment, ferrate was added prior to the ferrous ion to explore the effect of the oxidant upon MMA removal when no reductant, Fe(II), is present. A 500 ppb ferrate dose was administered prior to the addition of ferrous ion which ranged from 100 ppb to 1,000 ppb followed by adjustment to pH 5. The results were compared with a previous study that used identical concentrations of iron, the sole difference being that the ferrate dose followed the ferrous ion application, see Figure 12. Slightly improved removals were observed for MMA; however, removal to below detection limits was still not achieved. It appears that addition of the ferrous ion following the ferrate dose does aid in MMA removal, albeit by a small amount. When 500 ppb ferrate was added on its own, Figure 11, the amount of remaining MMA after treatment was 5.2 ppb. The ability of ferrate to remove such a large amount of MMA on its own may be due to the oxidation of the methyl group on the MMA to a carboxyl group thereby creating a more negatively charged species.
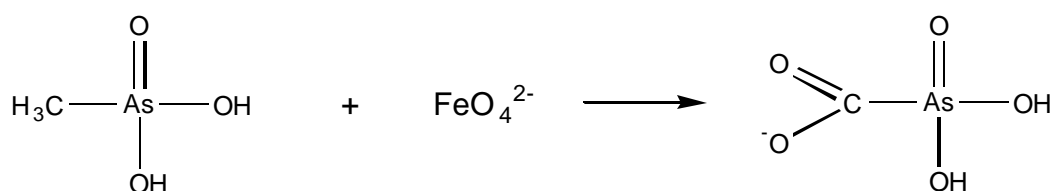


This would render the species more susceptible to adsorption on any floc that may be formed following reduction of the potassium ferrate or ionic attraction to any ferric ion present.
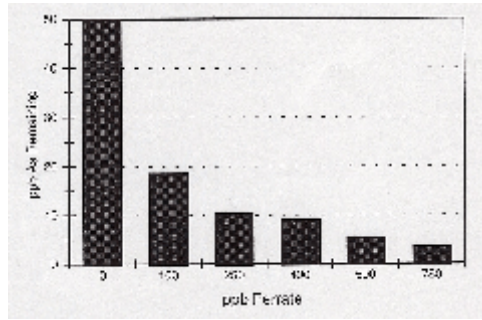
**Figure 11**. MMA removal with ferrate as the sole iron source
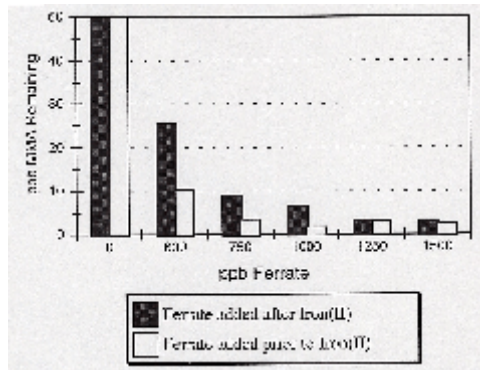


**Figure 12.** MMA removal in two steps: initial iron(II) dose followed by ferrate compared to MMA removal with the iron(II) Dose following the addition of ferrate
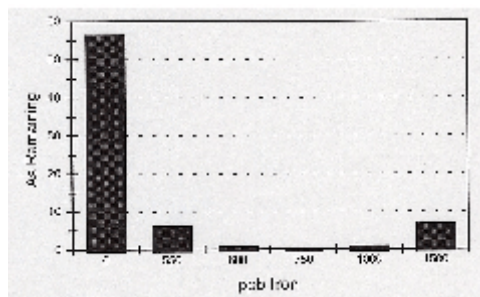


Figure 13. Arsenite removal at pH 5

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**Arsenite**

Since arsenite exists as a neutral species, $H_3AsO_3$, below pH 9, arsenic remediation techniques that rely upon ionic interactions for removal will show poor removal. In order to improve arsenic remediation, the majority of these techniques include an oxidation step to form arsenic(V), which is present as an ionic species above pH 2. The addition of ferrate is necessary in the use of ferrous salts for arsenic remediation. Since ferrate is a strong oxidant, it should oxidize any arsenic(III) to arsenic(V) and improve removal efficiencies.

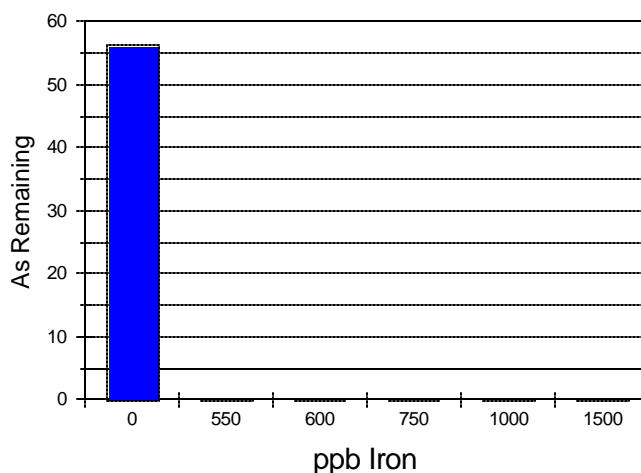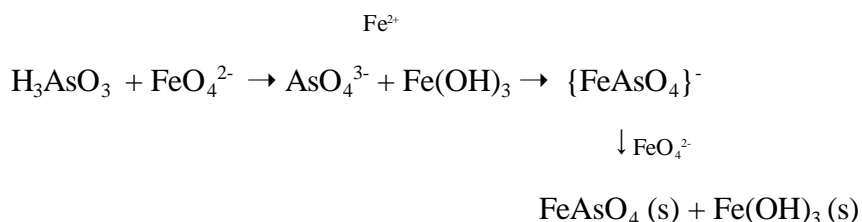$$2\ FeO_4^{2-} + 3\ AsO_3^{3-} \leftrightarrows 2\ Fe^{3+} + 3\ AsO_4^{3-}$$
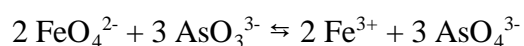
Arsenite remediation was studied at pH 5 and an initial arsenic(III) concentration of 50 ppb was used. Doses of ferrous ammonium sulfate ranged between 50 and 1,000 ppb and a concentration of 500 ppb potassium ferrate was administered in all trials. The results for arsenite are presented in Figure 13 (page 13). Arsenic concentrations are dropped to below the detection limit of the GF-AAS at a total iron dose of 600 ppb, this gives an iron to arsenic ratio of 12:1 which is higher than the ratio observed for the optimal arsenate removal experiment (4:1). A higher iron dose is required for efficient removal of arsenite because two oxidations by ferrate are required, arsenic(III) to arsenic(V) and iron(II) to iron(III).

The removal mechanism of arsenic(III) is slightly more complex than that of arsenate. Formation of a ferrous arsenite soluble ion pair, $\{FeAsO_3\}^-$ is unlikely since arsenic(III) remains a neutral species until about pH 9, pKa around 8.5. The addition of ferrous ammonium sulfate and subsequent oxidation by potassium ferrate generates ferric ions and oxidizes arsenic(III) to arsenic(V) simultaneously. From this point, removal is similar to that of arsenate in that precipitation of ferric arsenate and adsorption to ferric hydroxide are the likely removal mechanisms of arsenic.

The only difference, and the reason for the decreased removal efficiency, is that no pre-oxidation iron to arsenic interactions are present between arsenite and ferrous ion.

To determine whether the pre-oxidation, ferrous-arsenate interaction can be exploited in arsenite removal, a second study was attempted. Ferrate was applied in two 250 ppb doses, the first added to the arsenite solution prior to ferrous ion application and the second following the iron(II) dose, which varied from 50 ppb to 1,000 ppb. The results of this experiment are presented in Figure 14. Removal of arsenic to below GF-AAS detection limits was observed at all total iron doses.

The first ferrate dose oxidizes arsenite since there is no ferrous ion present. Since ferrate is unstable at pH 5; no oxidant will be present when the ferrous ion is added and iron(II) will not be oxidized to iron(III) at this point. The soluble ferrous arsenate can then be formed and oxidized to the insoluble ferric arsenate upon addition of the second 250 ppb dose of ferrate. This combination of ferrous and ferrate ion allows for the formation of a soluble ferrous arsenate ion pair and accounts for improved remediation of arsenite. A schematic is shown below.

$$\overset{Fe^{2+}}{H_3AsO_3 + FeO_4^{2-} \rightarrow AsO_4^{3-} + Fe(OH)_3 \rightarrow \{FeAsO_4\}^-}$$

$$\downarrow FeO_4^{2-}$$

$$FeAsO_4\ (s) + Fe(OH)_3\ (s)$$



**Figure 14.** Arsenite removal with two doses of ferrate

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## Treatment of Spiked Tap Water

In order to provide some idea of how well this procedure will work with "real life" samples, tap water from New Mexico State University was spiked with 50 ppb sodium arsenate (analysis of this water source showed no naturally occurring arsenate). Treatment was at pH 5, the optimal pH as determined in the earlier studies, and 400 ppb ferrate dose. Figure 15 shows the results of this study along with a comparison with earlier studies in nanopure water. The removal in tap water required slightly higher total iron doses to achieve similar removal. This is probably due to small amounts of ions in the tap water which can compete with arsenate for the ferrous ion.
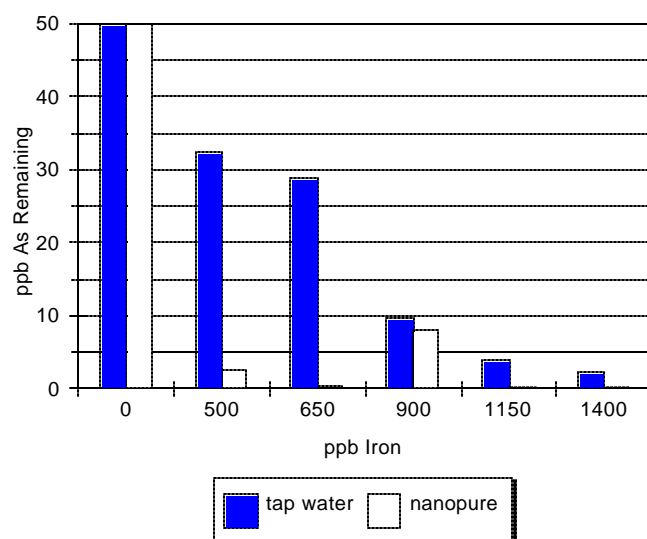


**Figure 15.** Arsenic removal at pH 5 in tap water

## Alternate Iron(II) Sources

An alternate source of iron(II) was also used to check whether the ammonium ion played any role in the arsenic removal process. Ferrous sulfate was used in place of ferrous ammonium sulfate under the same conditions as described for the previous study. Figure 16 shows that there is essentially no difference between the two iron sources.
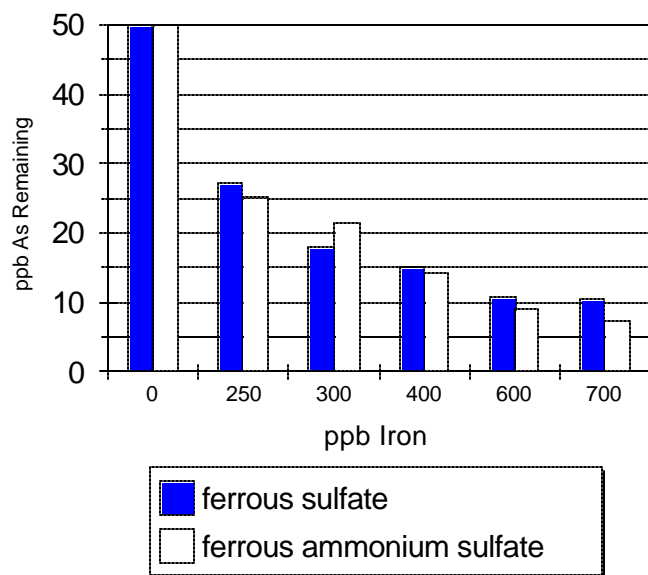
**Figure 16.** Ferrous sulfate versus ferrous ammonium sulfate
for arsenic removal

Oxidation Kinetics

Although arsenic is usually present as As(V) in surface waters, groundwaters may contain

appreciable amounts of As(III), which must be oxidized to the +5 state to ensure removal. Since our

procedure offers a good method for oxidation, the reaction kinetics between arsenite ($AsO_3^{3-}$) and

ferrate was studied. The stoichiometry was determined in this lab.

$$2\ FeO_4^{2-} + 3\ AsO_3^{3-} \rightarrow 2\ Fe^{3+} + 3\ AsO_4^{3-}$$
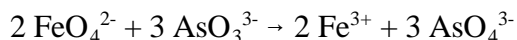
The reaction rates were monitored spectrophotometrically at 505 nm (absorption maximum for

ferrate) with arsenite in excess, pseudo-first order conditions, and at a constant pH. The disappearance

of ferrate fit nicely to a single exponential decrease to provide first order rate constants, $k_{obs}$. A plot of

$k_{obs}$ versus [arsenite] is shown in Figure 17 at pH 10 . The linearity of the plot shows that it is first order

with respect to arsenite. The slope of this line provides the second order rate constant. This reaction

was studied at several pHs, see Figure 18. The hydrogen ion dependence was fitted using the following

equation and shown as a line in Figure 18. The rate law for this reaction may be written as follows:

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where $k_a = 3.09 \times 104 M^{-1}s^{-1}$ , $k_{ah} = 2.32 \times 10^7$ $M^{-1}s^{-1}$ , $k_b = 1.03 \times 10^5$ $M^{-1}s^{-1}$, $k_{bh} = 5.24 \times 10^5$ $M^{-1}s^{-1}$

Where $k_a$ is the reaction between the deprotonated forms of each species, $k_{ah}$ is for the protonated ferrate/deprotonated arsenite, $k_b$ is between protonated arsenite and deprotonated ferrate and $k_{bh}$ is between the two protonated reactants. $K_{ah}$ and $K_{bh}$ are the dissociation constants for $HFeO_4^-$ and $HAsO_3^{2-}$, respectively. From this study it is clear that the reaction between arsenite and ferrate is extremely rapid (within milliseconds) for all forms of each species and reaction times will not pose a problem for arsenic remediation.
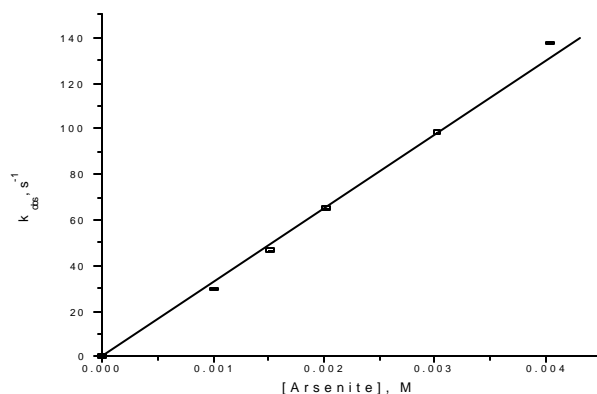


**Figure 17.** Plot of k $_{obs}$ vs [arsenite] at pH 10
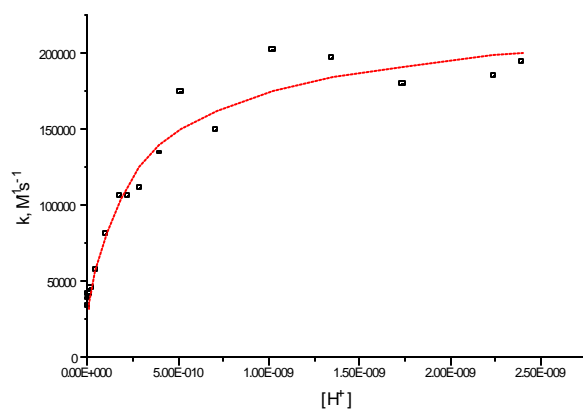


**Figure 18.** Plot of k versus [H$^+$]

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The reaction between MMA and ferrate also was examined cursorily. The reaction was complete within the time of mixing in a Durrum stopped-flow spectrophotometer (2 ms) and could not be studied kinetically. Since the reaction is very fast for this system, it again will not pose a problem for wastewater treatment. As of yet, no product analysis has been performed.

**Conclusions**

The ability of ferrate or the ferrate/ferrous combination provides an efficient method for remediation of arsenic from water under mildly acidic conditions. Both As(III) and As(V) forms of arsenic are amenable to treatment since ferrate rapidly oxidized the former to the +5 oxidation state. This procedure could decrease the amount of sludge produced during treatment since it uses a soluble form(s) of iron to treat the waters. More importantly, this method provides an inexpensive approach to meet new drinking waters regulation where acceptable levels of arsenic may reach as low as 2 ppb.

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