**The effects of iron(II) on the kinetics of arsenic oxidation and sorption on
manganese oxides**

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ABSTRACT

In this study, As(III) oxidation kinetics by a poorly-crystalline phyllomanganate (δ -MnO₂) in the presence and absence of dissolved Fe(II) was investigated using stirred-flow and batch experiments. Chemically synthetic δ -MnO₂ was reacted with four influent solutions, containing the same As(III) concentration but different Fe(II) concentrations, at pH 6. The results show an initial rapid As(III) oxidation by δ -MnO₂, which is followed by an appreciably slow reaction after 8 hours. In the presence of Fe(II), As(III) oxidation is inhibited due to the competitive oxidation of Fe(II) as well as the formation of Fe(III)-(hydr)oxides on the δ -MnO₂ surface. However, the sorption of As(III), As(V) and Mn(II) are increased, for the newly formed Fe(III)-(hydr)oxides provide additional sorption sites. This study suggests that the competitive oxidation of Fe(II) and consequently the precipitation of Fe(III) compounds on the δ -MnO₂ surface play an important role in As(III) oxidation and As sequestration. Understanding these processes would be helpful in developing in situ strategies for remediation of As-contaminated waters and soils.

Keywords: arsenic; iron; stirred-flow; oxidation; sorption; kinetics; δ -MnO₂

1. Introduction

Arsenic (As) contamination in soils, sediments, and water from natural and anthropogenic sources pose environmental and human health risks. The predominate species of As in soil and aquatic environments are arsenite (As(III)) and arsenate (As(V)). As(V) is the most stable species under aerobic conditions and exists as deprotonated oxyanions of arsenic acid (H_2AsO_4^- and HAsO_4^{2-}), while As(III) is always electrically neutral, and primarily exists as the uncharged molecule H_3AsO_3 when the pH is below 9. As(III) is known to be more mobile in soil and sediment environments due to being weakly bound to mineral surfaces, and is more toxic than As(V), since it binds to sulfhydryl groups, impairing the function of many proteins [1]. Therefore, the transformation of As(III) to As(V) not only decreases the toxicity of As, but also enhances As removal from drinking water and sequestration to soils and sediments.

In environmental settings, manganese (Mn) oxide minerals commonly occur as coatings and fine-grained aggregates with large surface areas and exert chemical influences far out of proportion to their prevalence [2,3]. Manganese oxides minerals act as potent sorbents of heavy metals and nutrients, serving as natural sinks for environmental contaminants. More importantly, they are powerful oxidants and play a critical role in the transformation of As(III) to As(V) under natural conditions [4,5,6,7]. The oxidation process by Mn-oxides is quite rapid, compared to the direct oxidation of aqueous As(III) by molecular oxygen with a half-life around a year [8]. The reactivity of Mn-oxide minerals varies with their mineralogy. It has been found that layered Mn-oxide minerals, such as phyllomanganates, are more reactive than other types of Mn-oxides [9,10,11]. The most reactive Mn-oxides have a great potential in terms of As(III)

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4 69 oxidation even when present in small quantities. There is evidence that a large number of
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7 70 Mn-oxides found in surface environments are poorly crystalline and of biogenic origin
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9 71 [12,13]. Also, these poorly crystalline biogenic Mn-oxides may be among the most
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11 72 reactive Mn-oxides in the environment [1]. It is important to understand the reactivity of
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14 73 poorly crystalline Mn-oxides, as it relates to As speciation, not only because of their
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16 74 higher reactivity but also because of their abundance in the environment.
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19 75 Under natural conditions, various ions may coexist with As(III). However their
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21 76 impact on the As (III) oxidation process has attracted less attention. Power et al. [14]
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23 77 found that the competitive sorption of Zn(II) on the birnessite surface decreased the
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25 78 As(III) oxidation rates under all reaction conditions and this inhibition became more
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27 79 pronounced when Zn(II) was pre-sorbed onto the birnessite surface as opposed to when it
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29 80 was added simultaneously with As(III). Parikh et al. [15] reported that initial reaction
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31 81 rates of As(III) oxidation by hydrous Mn-oxides (δ -MnO₂) are reduced when high
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33 82 phosphate concentrations strongly passivate δ -MnO₂ and reduce As(III) interactions with
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35 83 the mineral surface. Naturally occurring As in soils and sediments is often associated
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37 84 with Fe-oxides and, hence, As can be mobilized by the reductive dissolution of the carrier
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39 85 phase [16,17]. Thus, co-occurrence of elevated concentrations of As(III) and Fe(II) are
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41 86 often observed under moderately reducing conditions [18,19]. There is a report that in
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43 87 Bangladesh, one of the most arsenic contaminated countries, some water wells contains
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45 88 0-30 mg/L Fe(II) and up to 1 mg/L As(III) [20]. As(III) and Fe(II) may also coexist in
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47 89 aerobic conditions. Acid mine drainage (AMD), which is caused by the biological
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49 90 oxidation of sulfidic materials, frequently contains sulfate, As(III) and/or As(V), along
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51 91 with much higher concentrations of dissolved Fe(II) and/or Fe(III) [21,22].
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Unlike other ions such as Zn(II) and phosphate, Fe(II) could also be oxidized by Mn-oxides, and thus can compete with As(III). The reaction of Fe(II) with Mn-oxides results in the formation of solid Fe(III)-(hydr)oxides on Mn-oxide surfaces [23], which may cause surface passivation and inhibit further oxidation of As(III) and Fe(II). Also, the newly formed Fe(III)-(hydr)oxides could adsorb both As(III) and As(V) in solution due to the high affinity of As(III) and As(V) to Fe-oxides [17,22, 24]. Therefore, the presence of Fe(II) could substantially alter As(III) oxidation on Mn-oxides, however, the effect of Fe(II) has not been elucidated to date. The aim of this study is to explore the extent to which dissolved Fe(II) could affect the oxidation of As(III) by Mn-oxides and the mechanism involved in this process. To achieve this goal, the following stirred-flow experiments were conducted: (1) oxidation of As(III) and Fe(II) individually by δ -MnO₂; (2) oxidation of As(III) and Fe(II) simultaneously by δ -MnO₂ under different Fe(II) concentrations; and (3) Oxidation of As(III) first by δ -MnO₂ and then addition of Fe(II) at different time periods. A unique benefit of the stirred-flow technique is that reaction products are removed from the reactor, thus limiting potential reactions between products and the mineral surface being studied.

In addition, quantification of the initial rates of environmental reactions at the mineral/water interface is a fundamental prerequisite to determining reaction mechanisms and contaminant transport modeling and predicting environmental risk. Many important mineral surface processes (e.g., adsorption, oxidation-reduction, precipitation) are characterized by a rapid initial reaction on time scales of milliseconds to minutes in which a significant portion of the reaction process may occur [3,25]. In this study, we are also interested in knowing how Fe(II) could affect the initial As(III) oxidation rate by δ -

MnO₂. Therefore, batch kinetic experiments (up to 30min) were performed under different Fe(II) additions to quantify initial As(III) oxidation rates. Knowledge of these initial reaction rates is critical to determining chemical kinetic rate constants and reaction mechanisms, both of which are required to fully understand environmental chemical processes involving As.

2. Material and Methods

2.1. Chemicals

All chemicals used in this study met or exceeded American Chemical Society standards. The 18.2 MΩ deionized (DI) water was used for all solutions. NaAsO₂ and FeSO₄·7H₂O were used as sources of As(III) and Fe(II), respectively. As(III) stock solution (100 mmol/L) was stored at 4 °C and prepared every month. Fe(II) solution was freshly prepared every time in the glove box and the DI water used to make the Fe(II) solution was degased, using nitrogen gas, for 2 hours before use.

2.2. Synthesis of δ-MnO₂

δ-MnO₂, a poorly-crystalline, phyllomanganate, was used in the studies presented here because of its high reactivity as well as its similarities to biogenic Mn-oxides [26]. δ-MnO₂ is a form of hexagonal birnessite with a low degree of stacking of phyllomanganate sheets [27,28]. δ-MnO₂ was synthesized by drop wise addition of a 100 mL solution containing 11.29 g Mn(NO₃)₂·4H₂O to a 100 mL solution containing 2.4 g NaOH and 4.74 g KMnO₄, corresponding to a final Mn(II):Mn(VII):OH ratio of 3:2:4

[29]. After adding Mn(II) to the basic permanganate solution, the resulting suspension was stirred overnight (at least 12 hours) to allow complete conproportionation of Mn(II) and Mn(VII) to Mn(IV). Following synthesis, δ -MnO₂ was centrifuged at 10,000 RCF for 15 min, then the supernatant was removed and replaced with 18.2 M Ω deionized (DI) water. This wash step was repeated 6 times. Following washing, δ -MnO₂ was transferred to a polypropylene bottle, resuspended in DI water, and stored at 4 °C prior to use in experiments. Experiments were conducted using δ -MnO₂ within a month of synthesis. Characterization of synthetic δ -MnO₂ is provided in Appendix A.

2.3. Stirred-flow Kinetics Experiments

The stirred-flow system is shown in Figure 1. The reactor is a modified version of the stirred-flow reactor described by Wielinga et al. [30] and Strawn and Sparks [31]. The chamber volume is 12.0 mL. All stirred-flow reactions were conducted by pumping a solution of As(III) or Fe(II) or both in a 0.01 M NaNO₃ background electrolyte buffered at a certain pH at a rate of 1.0 mL/min into a stirred-flow chamber containing 2.0 g/L δ -MnO₂. For reactions involving Fe(II), nitrogen gas was pumped into the solution to maintain anoxic conditions. All suspensions in the reaction chamber were mixed at 100 rpm via a magnetic stir bar. Effluent solutions were filtered with a 0.22 μ m pore size filter and then collected by a fraction collector. Effluent solutions which contained Fe(II) were immediately transferred into a glove box until analysis, and all other solutions were stored at 4 °C in the dark until analysis. All stirred-flow experiments were conducted at least in duplicate.

2.4. Batch kinetics Experiments

Batch studies were conducted using 500 mL of reaction solution, which was prepared in 0.01 mol/L NaNO₃ (or NaF) background electrolyte buffered at a particular pH. The reaction was then initiated by adding a certain amount of HMO stock solution to achieve a HMO concentration of 0.1 g/L. All reaction mixtures were stirred at 200 rpm via a magnetic stir bar and for those containing Fe(II), nitrogen gas was pumped during reaction to maintain anoxic conditions. The reaction was sampled every 15 seconds for the first 2 minutes, every 1 minute from 2 to 10 minutes and then every 5 minutes until 30 minutes by removal of 2 mL of the reaction mixture using a syringe. Within 2 second of removal, the reaction mixture was filtered through a 0.2 µm polypropylene syringe filter to quench the reaction. The filtered solutions which contained Fe(II) were immediately transferred into a glove box until analysis, and all other solutions were stored at 4 ° C in the dark until analysis. All kinetic experiments were conducted at least in triplicate.

2.5. Determination of Metal Concentrations

As(III) and As(V) were quantified by liquid chromatography inductively coupled plasma mass spectrometry (LC-ICP-MS). As(III) and As(V) were separated using a Phenomenex Prodigy 5 µm ODS-3 100 Å (150 x 4.6) column with a flow rate of 1 mL/min, using a 10 µm sample injection before quantification by LC-ICP-MS. The mobile phase consisted of 5% methanol in 5 mM tetra-butyl ammonium hydroxide, and the pH was adjusted to 5.9 using malonic acid (final concentration of about 3 mM). Arsenic species separated by LC were directly introduced via a nebulizer into an Agilent

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4 183 7500ce inductively coupled plasma mass spectrometer operated in helium mode. Fe(II)
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6 184 concentration was determined by the ferrozine method [32]. In order to eliminate the
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9 185 interference of Fe(III) in Fe(II) measurements, 0.05 mol/L NaF was added to mask Fe(III)
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11 186 in Fe(II) determination. Total Fe was determined by reducing total Fe(III) to Fe(II) and
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14 187 then Fe(II) was measured by the ferrozine method without addition of NaF solution. The
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16 188 Fe(III) content in the liquid solution was obtained by difference. Mn(II) concentration
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19 189 was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES),
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21 190 where 5 mL of sample were acidified using 1% (w/v) nitric acid mixed with 0.5% (w/v)
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24 191 hydrochloric acid. The amount of As sorbed during the reaction was determined by
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26 192 calculating the difference between the mass of As (μmol) introduced into the reactor and
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29 193 the mass of As (μmol) removed from the reactor over time (more details please see
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197 3. Results and Discussion

198 3.1. Oxidation of As(III) and Fe(II) Individually by $\delta\text{-MnO}_2$

199 3.1.1. As(III) Oxidation by $\delta\text{-MnO}_2$. The reaction shows a similar pattern at
200 both pH 3 (Fig 2a) and 6 (Fig 2b). As(V) appears immediately in the effluent solution and
201 reaches a maximum within 2 hours, indicating a fast initial oxidation rate of As(III) by $\delta\text{-MnO}_2$.
202 After that the As(V) concentration starts to decrease and gradually reaches
203 equilibrium. The decrease of As(V) in the effluent is due to both the decreased As(III)
204 oxidation rate, producing less As(V), and the sorption of As(V) onto $\delta\text{-MnO}_2$ surface.
205 Changes in Mn(II) concentration in the effluent resembles As(V). It reaches a maximum

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4 206 in a few hours and then decreases. However, Mn(II) appears relatively late in the effluent,
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6 207 compared to As(V). This late appearance could be attributed to either the complete
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9 208 retention of Mn(II) by δ -MnO₂, or the formation of a Mn(III) intermediate early in the
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11 209 reaction process [5,33], since no Mn(II) is produced when Mn(IV) is reduced to Mn(III).
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14 210 At both pHs, there are two clear As(III) oxidation phases, a fast oxidation phase in the
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16 211 first few hours followed by a gradual decrease in the oxidation process. During the fast
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18 212 oxidation phase, no As(III) is detected in the effluent. After that, As(III) starts to appear
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20 213 as the oxidation rate decreases and finally reaches equilibrium. As(III) appears at 3.6 h at
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23 214 pH 3, which is about 5 hours earlier than what occurs at pH 6, indicating a higher As(III)
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25 215 oxidation rate by δ -MnO₂ at the higher pH.

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28 216 The two-phase As(III) oxidation by Mn-oxides has been observed previously
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30 217 [3,4,6,11,15,33,34] and was attributed to surface passivation of Mn-oxides [6,11,15,33].
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33 218 Three possible causes could contribute to the passivation of the Mn-oxides surface. First
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35 219 is the sorption of Mn(II) and As(V). The reaction of As(III) with Mn-oxides produces
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37 220 Mn(II) and As(V). Typically, Mn(II) and As(V) are not released into solution in
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39 221 stoichiometric amounts during the reaction, indicating that some of the Mn(II) and As(V)
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41 222 are re-adsorbed onto the Mn-oxide surface [4,33]. The sorption is thought to occur at the
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43 223 reactive sites where As(III) is oxidized, thus blocking the potential sites for further
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45 224 As(III) oxidation. A possible second reason could be the formation of a Mn-As
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47 225 precipitate. Under certain reaction conditions, a Mn(II)-As(V) precipitate that
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49 226 compositionally resembles the mineral krautite ($\text{Mn}^{\text{II}}\text{HAs}^{\text{V}}\text{O}_4 \cdot \text{H}_2\text{O}$) has been observed
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51 227 during As(III) oxidation by birnessite. This precipitate could also block the reactive site
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53 228 for As(III) oxidation [6]. Third is the formation of a Mn(III) intermediate. Studies have
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shown that As(III) oxidation by birnessite proceeds in two discrete electron transfers, where one electron was transferred from Mn(IV) at first, involving the reduction of Mn(IV) to Mn(III), and then another one electron was transferred from either Mn(IV) or Mn(III)⁵. The formation of a Mn(III) intermediate could contribute to Mn-oxide passivation because Mn(III) sites are thought to be less reactive than Mn(IV) sites on the Mn-oxide surface [10,33,35].

3.1.2. Fe(II) Oxidation by δ -MnO₂. Fe(II) can be readily oxidized by δ -MnO₂ at both pH 3 (Fig. 3a) and 6 (Fig. 3b), however, the reaction rate varies at different pHs. At pH 3, Fe(II) appears in the effluent after 0.5 h of the reaction, while at pH 6 Fe(II) appears after 8 h. The delayed appearance of Fe(II) indicates a faster oxidation rate at higher pH. Similar to As(III) oxidation, the oxidation of Fe(II) by δ -MnO₂ shows a two-phase trend, a fast initial oxidation followed by a decrease in oxidation rate, indicating passivation of δ -MnO₂ surface also exists during Fe(II) oxidation. The reaction of Fe(II) with Mn-oxides can result in the formation of solid Fe(OH)₃ and FeOOH [23], and also release Mn(II) to solution. Therefore, the sorption of Mn(II) and the formation of Fe(III)-(hydr)oxides can both cause the surface passivation of δ -MnO₂ by blocking reactive sites on the δ -MnO₂ surface.

3.2. Oxidation of As(III) and Fe(II) Simultaneously by δ -MnO₂

In order to investigate the effects of Fe(II) on As(III) oxidation by δ -MnO₂, stirred-flow experiments were conducted using influent solutions containing 100 μ mol/L As(III) and simultaneously adding 100, 200, or 1000 μ mol/L Fe(II) to react with 2 g/L δ -

MnO₂ at both pH 3 and 6. Due to the similarity of reactions at both pHs, results are shown only at pH 6.

3.2.1. Effects of Fe(II) on As(III) Oxidation. As(III) oxidation by δ -MnO₂ was strongly influenced by the addition of Fe(II) (Fig. 4 and Fig. 5a). In the absence of Fe(II) (Fig. 4a), no As(III) appears in the effluent during the initial 8 hours, indicating that all As(III) introduced into the reactor is oxidized to either solution As(V) or As(V) adsorbed onto the δ -MnO₂ surface. In the presence of Fe(II), As(III) appears earlier in the effluent. Compared to 8 hours with no Fe(II) addition, As(III) appears after 2.3 hours with 100 μ mol/L of Fe(II) addition (Fig 4b), 0.8 hours with 200 μ mol/L of Fe(II) addition (Fig. 4c), and As(III) appears almost immediately with 1000 μ mol/L of Fe(II) addition (Fig. 4d). The higher the concentration of added Fe(II), the earlier the As(III) appears in the effluent, which suggests that the As(III) oxidation rate is lowered in the presence of Fe(II). This decreased As(III) oxidation rate could be explained by two reasons: (1) since δ -MnO₂ can also effectively oxidize Fe(II) (Fig. 3), Fe(II) may compete with As(III) for oxidation by sorbing on some of the reactive sites on δ -MnO₂ surface, thus lowering the As(III) oxidation rate; (2) the reaction of Fe(II) and δ -MnO₂ could result in the formation of solid Fe(III)-(hydr)oxides [23] on the δ -MnO₂ surface, blocking some of the reactive sites, therefore decreasing the As(III) oxidation rate. Furthermore, the finding that the final As(III) concentration in the effluent increases with increasing Fe(II) addition (Fig 2.5 a), except for the 1000 μ mol/L Fe(II) addition, shows that less As(III) is oxidized by δ -MnO₂ in the presence of Fe(II). This also indicates the inhibitive impact that Fe(II) has on As(III) oxidation, either through competing with As(III) or the formation of sorbed Fe(III)-(hydr)oxides. Some previous studies also observed a decrease in As(III) oxidation

rate by Mn-oxides when other ions were present. Power et al. [14] confirmed competitive sorption of Zn(II) on birnessite decreased the oxidation rate of As(III). Choi et al. [36] assumed competition between Fe(II) and As(III) for sorption sites on manganese oxides further blocked the oxidation rate of As(III). Parikh et al. [15] showed a reduced As(III) oxidation in the presence of phosphate (PO_4^{3-}) caused by competitive adsorption between As(III) and PO_4^{3-} . He also reported a decrease in As(III) oxidation when goethite (α -FeOOH) was present, resulting from the competition between δ -MnO₂ and α -FeOOH for As(III). Han et al. [22] found that the removal rate of As(III) significantly decreased with an increasing ratio of Fe(II):As(III) from 1/64:1 to 1:1. He also pointed out that the presence of As(III) significantly inhibited the oxidation of Fe(II) by MnO₂ significantly as well.

3.2.2 Effects of Fe(II) on As Sequestration. The concentration of As(V) in the effluent decreases with increasing Fe(II) addition (Fig. 5b). This decreased As(V) concentration could be attributed to two reasons: (1) less As(V) is produced with Fe(II) addition; (2) more As(V) is sorbed with Fe(II) addition. The first reason is confirmed in the last section since less As(III) is oxidized as more Fe(II) added. The second reason can be proved by noting that the decrease in As(V) concentration in the effluent is more pronounced than the increase of As(III) concentration in the effluent (Fig. 5a). Also, we calculated the total As (both As(III) and As(V)) sorption amounts at different Fe(II) addition (Fig. 6). The results show that as more Fe(II) is added, more As is sorbed on the solid phase due to more Fe(III)-(hydr)oxides being formed, providing additional sorption sites for both As(III) and As(V). He and Hering [17] confirmed that As(III) and As(V) predominantly adsorbed on the freshly formed Fe(III) precipitates when Fe(II) is added in

the presence of birnessite. Chio et al. [36] also showed that in the presence of dissolved Fe(II), the precipitation of Fe(III) hydrous oxides was an effective mechanism for As scavenging from groundwater if there exists sufficient oxidants to oxidize Fe(II). In some environments, oxygen is available as the oxidant for Fe(II) and microbial mediation can be important in catalyzing this reaction [37,38]. Native manganese oxides in soils and sediments can also serve as the oxidants for Fe(II). This enhancement in Fe(II) oxidation could be an effective strategy for augmenting the natural attenuation of As.

3.2.3. Effects of Fe(II) on Mn(II) Sequestration. Apart from As(III) and As(V), we are also interested in the changes of Mn(II) concentration in the effluent. The Mn(II) concentration reaches a maximum after a few hours of reaction, and this maximum value increases as more Fe(II) is added to the system (Fig 2.4). After 24 hours, the concentration of Mn(II) remains stable, and the final concentration of Mn(II) in the effluent decreases with increasing Fe(II) addition. This suggests more Mn(II) is re-sorbed onto the newly formed Fe(III)-(hydr)oxides.

3.3. Oxidation of As(III) by δ -MnO₂ with Fe(II) Added at Different Times

In order to fully investigate the effects of Fe(II) on the As(III) oxidation by δ -MnO₂ over time, since the oxidation rate is decreasing as δ -MnO₂ becomes passivated, 100 μ mol/L Fe(II) was introduced into the reaction of 100 μ mol/L As(III) with 2 g/L δ -MnO₂ at different times (4, 10 and 24 hours) at pH 6. The reason why 4, 10 and 24 hours were chosen is that during the As(III) oxidation by δ -MnO₂ (Fig 2.2 b), maximum As(V) appeared at 4 hours, As(III) starts to appear in solution at about 10 hours, which is the changing point from rapid As(III) oxidation to a slower oxidation rate, and after 24 hours,

the whole system reaches a steady state, where the change in concentration of that immediately after Fe(II) is introduced to the system at each time point, there is a dramatic increase in Mn(II) as well as a marked drop in As(V) in the effluent (Fig 2.7 b, c and d). The boost in Mn(II) can be attributed to the readily oxidation of Fe(II) by δ -MnO₂, releasing a large amount of additional Mn(II) to the solution. The concentration jump in Mn(II) is about the same value (~ 40 μ mol/L), regardless of when Fe(II) is added to the system. This is different from our expectation that as δ -MnO₂ becomes passivated with time, the oxidation rate of Fe(II) by δ -MnO₂ should decrease from 4 hours to 24 hours. Thus, the concentration jump of Mn(II) would be less pronounced at 24 hour compared to 10 or 4 hours. We have shown that the very initial oxidation rate of Fe(II) by δ -MnO₂ is independent of the surface passivation of δ -MnO₂ during As(III) oxidation, which suggests that the initial rapid Fe(II) oxidation might occur at certain reactive sites that are not blocked by the oxidation of As(III). The large drop in As(V) right after Fe(II) is added could be the result of the formation of Fe(III)-(hydr)oxides, which provides extra sorption sites for As(V). This result also confirms that the sorption of As(V) on the newly formed Fe(III)-(hydr)oxides takes place as soon as As(III) is oxidized to As(V). Interestingly, when Fe(II) is involved in the reaction, the concentration of As(III) in the effluent doesn't increase as expected, but rather As(III) decreases (not that obvious in Fig. 7b) and then increases. Once Fe(II) is added to the system, there are two contradictory effects on As(III). One is the competitive oxidation of Fe(II), which causes As(III) to increase; the other one is the sorption of As(III) on the newly formed Fe(III)-(hydr)oxides, resulting in a decrease in As(III). The decrease in As(III) concentration

after Fe(II) is added could be the result of the sorption effect, which outcompetes the competitive effect.

3.4. Initial As(III) Oxidation Rate by δ -MnO₂ in the Presence of Fe(II)

In order to investigate how the initial As(III) oxidation rate changes when Fe(II) is present, batch kinetic experiments were conducted under different Fe(II) additions and the As(III) depletion rates were quantified (Fig. 8). The oxidation of As(III) by δ -MnO₂ proceeds very rapidly and follows first-order kinetics nicely (Fig. 8). When no Fe(II) is present (Fig. 8a), As(III) concentration decreases to 60% of the initial value within 15 seconds and As(V) appears immediately in the solution after reaction starts. As(III) concentration continues to decrease while As(V) increases over the course of 30 minutes reaction. Similar to many environmental redox reactions, this reaction exhibits biphasic kinetics. The depletion of As(III) is fast in the first couple of minutes and then slows down after 5 minutes. Therefore, two sets of apparent first-order rate constants were calculated using data from either the initial (0 to 60 second, shown in Fig. 8) or final (10 to 30 minute) portion of the reaction. Under all reaction conditions, the rate constants after 10 minutes are approximately 1/10 of the rate constants within 1 minute as a result of surface passivation of δ -MnO₂ (Table 1).

As discussed in the previous sections, when Fe(II) is present, the depletion of As(III) in solution could be ascribed to two factors. First, As(III) is oxidized by δ -MnO₂ to As(V). Second, As(III) is sorbed on the produced Fe(III)-(hydr)oxide products as Fe(II) is oxidized by δ -MnO₂. In order to differentiate the two effects, batch kinetic experiments were performed in two background electrolyte solutions, NaNO₃ and NaF. For reactions

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4 365 in the NaNO₃ solutions, the As(III) depletion rate can be considered as the summation of
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6 366 As(III) oxidation by δ -MnO₂ and As(III) sorption by the Fe(III)-(hydr)oxides products.
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9 367 For reactions in NaF solutions, the As(III) depletion is due only to As(III) oxidation by δ -
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11 368 MnO₂, since F⁻ would complex with the produced Fe³⁺ to form soluble FeF₆³⁻ in solution,
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14 369 and thus prevent the formation of Fe(III)-(hydr)oxides. The initial As(III) oxidation rate
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16 370 by δ -MnO₂ decreases when Fe(II) is added to the system and the more Fe(II) that is added,
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19 371 the slower the As(III) oxidation rate (Table 1, reaction a, e, f and g). This result proves
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21 372 the competitive oxidation between As(III) and Fe(II), which also agrees with the results
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24 373 from the stirred-flow experiments. The As(III) depletion rates of reactions in NaNO₃
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26 374 solutions are higher than those of reactions in NaF solutions (Table 1, reaction b vs. e, c
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29 375 vs. f and d vs. g), indicating that some amount of As(III) is sorbed by the produced
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31 376 Fe(III)-(hydr)oxides. This effect is even more obvious at the highest Fe(II) concentration
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34 377 (Table 1, reaction d vs. g) and is also shown in Fig. 8d, where both As(III) and As(V)
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36 378 concentrations are much lower than those in Fig. 8g.

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38 379 Total As concentration is also observed during the reaction (Fig. 9). When Fe(II)
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41 380 is absent (Fig. 9, set a), total As concentration is quite constant over the course of the
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43 381 reaction, however, total As concentration (about 85 μ mol/L) is lower than the initial value
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46 382 of 100 μ mol/L. This might be the reason that some As is sorbed on δ -MnO₂. For reactions
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48 383 in NaF solutions (Fig. 9, set e, f and g), since there is no formation of Fe(III)-
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51 384 (hydr)oxides, total As concentration doesn't change with Fe(II) addition. For reactions in
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53 385 NaNO₃ solutions (Fig. 9, set b, c and d), total As concentration decreases over the course
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55 386 of reaction as more Fe(III)-(hydr)oxides are formed. Also, the more Fe(II) that is added,
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58 387 the lower the total As concentration in solution, suggesting that the newly formed Fe(III)-

(hydr)oxides provide additional sorption sites for both As(III) and As(V). The results are consistent with our stirred-flow experiments as well as some previous studies [17,36,39] .

4. Conclusions

The oxidation of As(III) via Mn-oxides is an important process for natural As cycling and for developing in situ strategies for remediation of As-contaminated waters and soils. The present study shows that both As(III) and Fe(II) can be efficiently oxidized by δ -MnO₂. Both oxidation reactions are rapid initially, followed by a decrease in oxidation rates as a result of the surface passivation of δ -MnO₂. As(III) oxidation is inhibited in the presence of Fe(II), due to both the competitive oxidation of Fe(II) and the formation of Fe(III)-(hydr)oxides on the δ -MnO₂ surface. The Fe(III) precipitate products also play an important role in the sorption of As(III) and As(V). As the amount of added Fe(II) (simultaneously) increased, less As(III) is oxidized, but the total sorption of both As(III) and As(V) increases as well as more sorption of Mn(II). These results demonstrate a possible remediation strategy for increasing As removal through addition of Mn-oxides and Fe(II) (or Fe-oxides) to As contaminated waters and soils.

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14 415 HPLC ICP-MS analyses on arsenic speciation.
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20 21 418 **References**

- 22
23
24 419 [1]. J. Jiang, I. Bauer, A. Kappler, Environ. Sci. Technol. 43 (2009) 3639.
25
26
27 420 [2]. J.E.Post, Proc. Natl. Acad. Sci. 96 (1999) 3447.
28
29
30 421 [3]. M. Ginder-Vogel, G. Landrot, J. S. Fischel, D. L. Sparks, PNAS .106 (2009) 16124.
31
32
33 422 [4]. M.J. Scott, J.J. Morgan, Environm ental Science & Technology .29 (1995) 1898.
34
35
36 423 [5]. H.W.Nesbitt, , G.W. Canning, G.M, Geochim. Cosmochim. Ac. 62 (1998) 2097.
37
38
39 424 [6]. C.Tournassat, L.Charle, D.Bosbach, A.Manceau, Environ. Sci. Technol. 36 (2002)
40
41 425 493.
42
43
44 426 [7]. J. Yang, M. O.Barnett, J.Zhuang, S. E.Fendorf, P. M .Jardine, Environmental Science
45
46
47 427 & Technology.39 (2005) 7102.
48
49
50 428 [8]. L. E.Eary , J. A. Schramke, ACS Symposium Series, American Chemical Society,
51
52 429 Washington, DC, pp. (1990) 379.
53
54
55 430 [9]. D. W.Oscarson, P. M.Huang , W. K.Liaw , U. T .Hammer, Soil Sci. Soc. Am. J. 47
56
57 431 (1983) 644.
58
59
60
61
62
63
64
65

- 1
2
3
4 432 [10]. V. Q.Chiu, J. G Hering , Environ. Sci. Technol. 34 (2000) 2029.
5
6
7 433 [11]. B.A. Manning, S.E. Fendorf, B. Bostick, D.L. Suarez, Environ. Sci. Technol. 36
8
9 434 (2002) 976.
10
11
12 435 [12]. B.M. Tebo, J.R. Bargar, B.G. Clement, G.J. Dick, K.J. Murray, D. Parker, R. Verity,
13
14 436 S.M. Webb, Ann. Rev. Earth and Plan. Sci. 32 (2004) 287.
15
16
17 437 [13]. A.M. Shiller, T.H. Stephens, Geomicrobiol. J. 22 (2005) 117.
18
19
20 438 [14]. L. E. Power, Y. Arai, D. L. Sparks, Environ. Sci. Technol. 39 (2005) 181.
21
22
23 439 [15]. S.J. Parikh, B. J. Lafferty, T. G. Meade, D. L. Sparks, Environ. Sci. Technol. 44
24
25 440 (2010) 3772.
26
27
28 441 [16]. M. Herbel, S. Fendorf , Chem. Geol. 228 (2006) 16.
29
30
31 442 [17]. Y. T. He, J. G. Hering, Water, Air, Soil Pollut. 203 (2009) 359.
32
33
34 443 [18]. R. T. Nickson, J. M. McArthur, P. Ravenscroft, W. G. Burgess, K. M. Ahmed,
35
36 444 Applied Geochemistry. 15 (2000) 403.
37
38
39 445 [19]. C. H . Swartz, N. K. Blute, B. Badruzzman, A. Ali, D.Brabander, J. B. Jay,
40
41 446 Geochemical et Cosmochimica Acta. 68 (2004) 4539.
42
43
44 447 [20]. R. Nickson, J. McArthur, W. Burgess, K. M. Ahmed, P. Ravenscroft, M. Rahman,
45
46 448 Nature. 395 (1998) 338.
47
48
49 449 [21]. J. W. Wang, D. Bejan, N. J. Bunce, Environ. Sci. Technol. 37 (2003) 4500.
50
51
52 450 [22]. X. Han, Y. L. Li, J. D. Gu, Geochimica et Cosmochimica Acta. 75(2011) 368.
53
54
55 451 [23]. D. Postma, C. A. J. Appelo, Geochim. Cosmochim. Acta 64 (2000) 1237.
56
57
58
59
60
61
62
63
64
65

- 1
- 2
- 3
- 4 452 [24]. S. Dixit, J.G. Hering, Environ. Sci. Technol. 37 (2003) 4182.
- 5
- 6
- 7 453 [25].A.M. Scheidegger, D.L. Sparks, Soil Sci. 161(1996) 813.
- 8
- 9
- 10 454 [26]. M. Villalobos, B. Toner, J. Bargar, G. Sposito, Geochim. Cosmochim. Acta 67
- 11
- 12 455 (2003) 2649.
- 13
- 14
- 15 456 [27]. V.A. Drits, E. Silvester, A.I. Gorshkov, A. Manceau, Am. Mineral. 82(1997) 946.
- 16
- 17
- 18 457 [28]. E. Silvester, A. Manceau, V.A. Drits, Am. Mineral. 82 (1997) 962.
- 19
- 20
- 21 458 [29]. J.J. Morgan, W. Stumm, J. Colloid Sci. 19 (1964) 347.
- 22
- 23
- 24 459 [30]. B. Wielinga, M.M. Mizuba, C.M. Hansel, S. Fendorf, Environ. Sci. Technol. 35
- 25
- 26 460 (2001) 522.
- 27
- 28
- 29
- 30 461 [31]. D. G. Strawn, D. L. Sparks. Soil Sci. Soc. Am. J. 64, (2000) 144.
- 31
- 32
- 33 462 [32]. L.L. Stookey, Anal. Chem. 42 (1970) 779.
- 34
- 35
- 36 463 [33]. B. Lafferty, M. Ginder-Vogel, D.L.Sparks, Environ. Sci. Technol. 44 (2010 a) 8460.
- 37
- 38
- 39 464 [34]. S.J. Parikh, B.J. Lafferty, D.L. Sparks, J. Colloid Interface Sci. 320 (2008) 177.
- 40
- 41
- 42 465 [35]. M.Zhu, K. W. Paul, J. D. Kubicki , D.L. Sparks, Environ. Sci. Technol. 43 (2009)
- 43
- 44 466 6655.
- 45
- 46
- 47 467 [36]. S.Choi, P. A.Day, J. G. Hering, Environ. Sci. Technol. 43, (2009) 4253.
- 48
- 49
- 50 468 [37]. L. C.Roberts, S. J.Hug, T.Ruettimann, M. M.Billah , A.W.Khan, M. T.Rahman,
- 51
- 52 469 Environ. Sci. Technol. 38 (2004) 307.
- 53
- 54
- 55 470 [38]. M. M.Berg, S.Luzi, P. T. K.Trang, P. H.Viet , W.Giger, D. Stuben, Environ. Sci.
- 56
- 57 471 Technol. 40 (2006) 5567.
- 58
- 59
- 60
- 61
- 62
- 63
- 64
- 65

1
2
3
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8
9
10
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46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

472 [39] S. Ying, S.C., B.D. Kocar, S. Fendorf. Oxidation and competitive retention of
473 arsenic between iron- and manganese oxides. *Geochimi. Cosmochim. Acta.* 96 (2012)
474 294-303.
475

Table and Figures

Table 1

Apparent first-order rate constants of As(III) depletion, determined by linear regression analysis of data from batch kinetic experiments. All reactions were conducted at pH 6 with 0.1 g/L δ -MnO₂ and 0.01 mol/L NaNO₃ or NaF.

Reaction Conditions	≤ 1 min		≥ 10 min	
	k (s ⁻¹)	R ²	k (s ⁻¹)	R ²
a. 100 μ mol/L As(III), NaNO ₃	1.3 x 10 ⁻²	1.00	1.3 x 10 ⁻³	1.00
b. 100 μ mol/L As(III) + 100 μ mol/L Fe(II), NaNO ₃	6.5 x 10 ⁻³	0.94	9.0 x 10 ⁻⁴	0.99
c. 100 μ mol/L As(III) + 200 μ mol/L Fe(II), NaNO ₃	3.0 x 10 ⁻³	0.99	3.0 x 10 ⁻⁴	0.99
d. 100 μ mol/L As(III) + 1000 μ mol/L Fe(II), NaNO ₃	7.5 x 10 ⁻³	0.87	5.0 x 10 ⁻⁵	0.83
e. 100 μ mol/L As(III) + 100 μ mol/L Fe(II), NaF	4.2 x 10 ⁻³	0.99	5.0 x 10 ⁻⁴	0.98
f. 100 μ mol/L As(III) + 200 μ mol/L Fe(II), NaF	1.4 x 10 ⁻³	0.99	2.0 x 10 ⁻⁴	0.99
g. 100 μ mol/L As(III) + 1000 μ mol/L Fe(II), NaF	1.1 x 10 ⁻³	0.92	2.0 x 10 ⁻⁵	1.00

Fig. 1. Schematic illustration of the stirred-flow experiments. (Reprinted with permission from Strawn and Sparks, 2000 [31]).

Fig. 2. Concentrations (μmol/L) of As(III), As(V) and Mn(II) in the effluent of a stirred-flow experiment where 100 μmol/L As(III) was reacted with 2 g/L δ-MnO₂ for 48 hours at (a) pH 3 and (b) pH 6.

Fig. 3. Concentrations (μmol/L) of Fe(II) and Mn(II) in the effluent from a stirred-flow experiment reacting 100 μmol/L Fe(II) with 2 g/L δ-MnO₂ for 48 hours at (a) pH 3 and (b) pH 6.

Fig. 4. Concentrations (μmol/L) of As(III), As(V), Mn(II) and Fe(II) in the effluent of a stirred-flow experiment reacting 2g/L δ-MnO₂ with simultaneously (a) 100 μmol/L As(III) and no Fe(II); (b) 100 μmol/L As(III) and 100 μmol/L Fe(II); (c) 100 μmol/L As(III) and 200 μmol/L Fe(II) and (d) 100 μmol/L As(III) and 1000 μmol/L Fe(II), at pH 6 for 48 hours.

Fig. 5. (a) As(III) and (b) As(V) concentrations in effluents of stirred-flow experiments reacting 2g/L $\delta\text{-MnO}_2$ with 100 $\mu\text{mol/L}$ As(III) and 0, 100, 200, or 1000 $\mu\text{mol/L}$ Fe(II) simultaneously at pH 6 for 48 hours.

Fig. 6. (a) Calculated amount of As sorption (nmol) in stirred-flow experiments where 2 g/L δ -MnO₂ was reacted with 100 μ mol/L As(III) and 0, 100, 200, or 1000 μ mol/L Fe(II) simultaneously at pH 6 for 48 hours; (b) Plot of (a) for the first 4 hours.

Fig. 7. Concentrations ($\mu\text{mol/L}$) of As(III), As(V), Mn(II) and Fe(II) in the effluent from a stirred-flow experiment where $2\text{g/L } \delta\text{-MnO}_2$ reacts with $100\text{ }\mu\text{mol/L}$ As(III) first and then $100\text{ }\mu\text{mol/L}$ Fe(II) is added to the influent solution at (a) 0 hour (simultaneously); (b) 4 hours; (c) 10 hours and (d) 24 hours, at pH 6.

Fig. 8. Concentrations (μmol/L) of As(III) and As(V) determined from batch kinetic experiments, reacting 0.1 g/L δ-MnO₂ with (a) 100 μmol/L As(III); (b) 100 μmol/L As(III) and 100 μmol/L Fe(II); (c) 100 μmol/L As(III) and 200 μmol/L Fe(II); (d) 100 μmol/L As(III) and 1000 μmol/L Fe(II); (e) 100 μmol/L As(III) and 100 μmol/L Fe(II); (f) 100 μmol/L As(III) and 200 μmol/L Fe(II); (g) 100 μmol/L As(III) and 1000 μmol/L Fe(II), at pH 6. Reactions (a), (b), (c) and (d) were conducted in 0.01 mol/L NaNO₃ background electrolyte, while reactions (e), (f) and (g) were conducted in 0.01 mol/L NaF background electrolyte. Plots to the right are the corresponding first-order As(III) depletion rates within 60 seconds.

Fig. 9. Concentrations ($\mu\text{mol/L}$) of total As, As(III) plus As(V), determined from batch kinetic experiments, reacting $0.1 \text{ g/L } \delta\text{-MnO}_2$ with (a) $100 \mu\text{mol/L As(III)}$; (b) $100 \mu\text{mol/L As(III)}$ and $100 \mu\text{mol/L Fe(II)}$; (c) $100 \mu\text{mol/L As(III)}$ and $200 \mu\text{mol/L Fe(II)}$; (d) $100 \mu\text{mol/L As(III)}$ and $1000 \mu\text{mol/L Fe(II)}$; (e) $100 \mu\text{mol/L As(III)}$ and $100 \mu\text{mol/L Fe(II)}$; (f) $100 \mu\text{mol/L As(III)}$ and $200 \mu\text{mol/L Fe(II)}$; (g) $100 \mu\text{mol/L As(III)}$ and $1000 \mu\text{mol/L Fe(II)}$, at pH 6. Reactions (a), (b), (c) and (d) were conducted in $0.01 \text{ mol/L NaNO}_3$ background electrolyte, while reactions (e), (f) and (g) were conducted in 0.01 mol/L NaF background electrolyte.