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Arsenic mobilization from iron oxides in the presence of oxalic acid q under hydrodynamic conditions

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Abstract

Oxalic acid potentially enhances pump-and-treat for groundwater As remediation by accelerating mobilization. This study examines how oxalic acid mobilizes As from Fe(III)-oxide coated sand under hydrodynamic conditions. Four columns were packed with metal-substituted ferrihydrite or goethite to 1% Fe, presorbed to 50% As surface coverage, and reacted with pH = 2.2 artificial groundwater amended with 10 mM oxalic acid at 1 m day⁻¹. Arsenic elution was affected by both As and Fe speciation. Although the As(V) columns experienced faster substrate dissolution, As(V) elution was delayed by re-adsorption, whereas As(III) elution was rapid due to pH decrease that prevented re-adsorption. Cr-ferrihydrite and Ni-goethite dissolved both effectively initially but then diverged. The Cr-ferrihydrite columns experienced continuous stoichiometric Fe and Cr release, and As release could be sustained. The Ni-goethite columns initially experienced nonstoichiometric Fe and Ni release, and As release was extensive. Such release, however, was not sustained. We hypothesized that Ni-goethite contained sites with distinct reactivity, and oxalic acid targeted readily-dissolved, sorption-dense sites. Our data indicate that oxalic acid-enhanced pump-and-treat methods would be easier to apply to aquifers dominated by As(III), requiring less amendment to be injected; such oxalic acid-enhanced methods remove reactive sediment Fe and As, potentially preventing future groundwater contamination.

Graphical Abstract

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.08.058>.

Keywords

Arsenic contamination; Iron mineralogy; Oxalic acid; Groundwater remediation; Pump-and-treat

1. Introduction

Groundwater arsenic (As) contamination is a global concern (Fendorf et al., 2010; Ng et al., 2003; Smedley and Kinniburgh, 2002). In the U.S., as many as 20 million people may be exposed to excess As in their drinking water (Welch et al., 2000). Due to the combination of the frequency of occurrence, toxicity and potential for human exposure, As is also ranked the #1 priority hazardous substance at U.S. National Priorities List (also known as “Superfund”) sites (ATSDR, 2015). At these sites, As is enriched from anthropogenic inputs or naturally exists as adsorbed or precipitated species within sediments but releases into groundwater due to evolving biogeochemical conditions (Fendorf et al., 2010; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). No matter whether an anthropogenic or geogenic process is the primary culprit, As contamination at each site is a challenge to remediate. There is currently no active remediation strategy that targets As specifically. To date, as far as we are aware, no As-contaminated Superfund sites have been remediated to the extent where groundwater As concentrations can remain below $10 \mu\text{g L}^{-1}$.

Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is a low molecular weight, bio-degradable organic acid. It is produced naturally by plants, fungi and other organisms, and present in natural waters at concentrations up to 4mM (van Hees et al., 2000; Yu et al., 2013). Oxalic acid can effectively dissolve iron (Fe)-oxides, which are the key carriers for various metals in soils and aquifers, via ligand-promoted and reductive pathways (Bose and Sharma, 2002; Lee et al., 2007; Mohapatra et al., 2005; Panias et al., 1996). By affecting both adsorbent (host substrate) abundance and competing for surface binding sites, oxalic acid alters the environmental fate of As and many other elements (Bhattacharya et al., 2002; Kim and Baek, 2015; Kim et al., 2015; Shi et al., 2009; Tao et al., 2006). Nevertheless, most previous oxalate related studies explored processes within batch systems. *In situ* processes in aquifers can be distinct from batch studies in part because aquifer systems are open, and often have much higher solid-to-solution ratios. Oxalic acid and As may not interact in the same way in open systems because they react with minerals differently and travel at different rates. Understanding how oxalic acid accelerates As mobilization under realistic aquifer

conditions, and the impact(s) of As and Fe speciation on this process, is fundamental to predicting groundwater As concentrations.

Pump-and-treat (P&T) is the most widely used technology for remediating point-source groundwater contamination, which concurrently controls groundwater flow and removes contaminants. There are >700 P&T systems operating at Superfund sites (EPA, 2007). Unfortunately, due to slow desorption and aquifer heterogeneity, the effectiveness of conventional P&T for As remediation often progressively declines (EPA, 2003). Our previous work (Sun et al., 2016a; Wovkulich et al., 2010, 2012, 2014) has shown that *in situ* injection of oxalic acid-amended groundwater can accelerate As mobilization from aquifers at the Vineland Chemical Company and Dover Municipal Landfill Superfund sites, and thereby be beneficial for their currently-used P&T systems. These sites span a range of sediment compositions and redox conditions, between which the efficiency of oxalic acid on As mobilization differed considerably. It is clear that oxalic acid-amended ground water can mobilize significantly more As and Fe compared to acidified groundwater (by HCl) at equivalent pH or phosphate- amended groundwater at equivalent molar concentration (Sun et al., 2016a; Wovkulich et al., 2010). Yet, using complex sediments, it is difficult to isolate the individual factors that influence the rate and magnitude of As mobilization. However, the relative importance of these factors (i.e., substrate dissolution, competitive desorption, pH decrease, re-adsorption, and potential mineralogical transformations) need to be resolved to be able to optimize oxalic acid-enhanced P&T methods.

This study uses flow-through columns to examine the mechanism(s) by which oxalic acid mobilizes As(III) and As(V) from metal-substituted ferrihydrite- and goethite-coated quartz sand under continuous advective flow. The use of chromium (Cr) and nickel (Ni)-substituted ferrihydrite and goethite, instead of pure minerals, improves our ability to quantify substrate dissolution and thereby to isolate the effect of dissolution from other As mobilization mechanisms. The evolution of solution and solid composition, and As and Fe mineralogical transformations were measured. These data illustrate the fate and transport of the mobilized As, Fe and substituted metal ions (Cr and Ni), and inform the prospects for remediating groundwater As contamination using oxalic acid- enhanced P&T methods.

2. Experimental

2.1. Synthesis of metal substituted iron oxides

Ferrihydrite and goethite with minor percentages of Cr and Ni substitution were synthesized following the procedures of Frommer et al. and Frierdich et al., respectively (Frierdich et al., 2011; Frommer et al., 2010). To ensure the goethite was free of any amorphous fraction, a diluted (pH ~2) HCl wash step was conducted on the Ni-goethite. The distribution of substituted metal was found to be nearly uniform throughout the minerals (Frierdich et al., 2011; Frommer et al., 2010). X-ray diffraction (XRD) verified mineral identities on random dried powder mounts (Supplementary Data Fig. S1). Based on digestion, the extent of substitution was Cr:Fe = 1:46 (2.2 mol% Cr) in Cr-ferrihydrite and Ni:Fe = 1:93 (1.1 mol% Ni) in Ni-goethite. Such minor substitution ensured that the structural stability of the Fe-oxides was unaltered. Based on nitrogen BET isotherm, the surface areas of Cr-ferrihydrite and Ni- goethite were 237 and 57 m² g⁻¹, respectively.

2.2. Arsenic adsorption on the synthesized minerals

Similar to commonly used procedures (e.g., Kocar et al., 2010), As adsorption maxima on the synthesized Fe-oxides were determined based on isotherms before column experiments. To perform isotherm experiment, “artificial groundwater” (A-GW) containing 0–64 mM As was prepared. The A-GW composition was consistent with previous experiments and buffered with 10 mM PIPES (Sun et al., 2016a, 2016b). Arsenic(V) and As(III) were added from freshly prepared arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and arsenite (NaAsO_2) stock solutions, respectively. The As-containing solutions were adjusted to pH 7.0 with NaOH or HCl. Then, 2 g L^{-1} Cr-ferrihydrite or Ni-goethite was added. The suspensions were equilibrated for 48 h, centrifuged and filtered through $0.2 \mu\text{m}$ filters. Dissolved As concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). Based on Langmuir models (Fig. S2), for Cr-ferrihydrite, As(V) and As(III) adsorption maxima corresponded to As:Fe = 1:11 and 1:5, respectively; for Ni-goethite, As(V) and As(III) adsorption maxima corresponded to As:Fe = 1:49 and 1:26, respectively.

2.3. Column set-up and sampling

To conduct column experiments, As(III) or As(V) were presorbed on Cr-ferrihydrite and Ni-goethite as performed for the isotherms to ~50% of the adsorption maxima, and mixed with autoclaved high-purity silica sand (Acros Organics, 40–100 mesh) to ~1 wt% Fe. Based on digestion, initial As content was $133\text{--}1359 \text{ mg kg}^{-1}$ ($1.77\text{--}18.1 \mu\text{mol g}^{-1}$, Table 1), similar to the condition at the Vineland Superfund site prior to the remediation activities (~100 and > 500 mg kg^{-1} in contaminated aquifer and “hot” zone, respectively) (Sun et al., 2016a; Wovkulich et al., 2010). Results from X-ray fluorescence (XRF) analysis were consistent with digestion, and XRF on random dried sub-samples confirmed the homogeneity of the mineral-sand mixtures. The four mineral-sand mixtures were wet-packed into four clear polycarbonate columns (McMaster-Carr), referred to hereafter as As(V)-Cr-ferrihydrite, As(V)-Ni-goethite, As(III)-Cr-ferrihydrite and As(III)-Ni-goethite columns, respectively. The columns had 1 cm ID and 0.3 cm walls, and column lengths packed with solids were 16.5–17.5 cm. Glass wool was packed into each end of the column to help distribute solution over the full cross sectional area. Before use, all the column parts were washed with acid, 70% ethanol, and then autoclaved A-GW. The columns were oriented vertically with upward flow (Fig. S3). Based on bromide tracer tests, effective porosity of the columns was 0.28–0.34. The influent flow was controlled by a peristaltic pump (ISMATEC) at 1 m day^{-1} , equal to ~6 pore volumes (PVs) day^{-1} . This velocity was in the range of groundwater velocity during active P&T cycles.

To condition the columns and establish the baseline, the columns started with ~10 PVs of pH = 7.0 A-GW influent. Then the columns were treated with unbuffered pH = 2.2 A-GW amended with 10 mM oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). The concentration and pH were consistent with previous experiments (Sun et al., 2016a; Wovkulich et al., 2012). ~45 PVs of oxalic acid were injected into the As(V) columns, and ~55 PVs for the As(III) columns. More PVs were used for the As(III) system because effluent metal concentrations from the As(V)-Ni-goethite column decreased markedly during injection, and sufficient PVs of oxalic acid were injected to the As(III)-Ni-goethite column to examine the reproducibility of the concentration decrease. The columns were finally treated with a minimum of 10 PVs of A-

GW before termination of flow. Bromide tracer tests were conducted before and after oxalic acid injection, to estimate effective porosity and examine potential physical changes caused by oxalic acid if any.

A fraction collector (LKB Bromma) was used to collect column effluents. Trace metal samples were acidified to 1% HCl and analyzed by ICP-MS. Bromide samples were unacidified and analyzed by ion chromatography (IC). Reported data were from unfiltered effluent samples, which were consistent with filtered (0.2 μm) samples collected occasionally. Immediately after flow termination, each column was divided into the inlet, middle and outlet sections, and the solids were retrieved from the sections. Aliquots of the solids were coated in glycerol to prevent exposure to oxygen and frozen at $-20\text{ }^{\circ}\text{C}$ for X-ray absorption spectroscopy (XAS) analysis. The rest of the solids were freeze-dried and used in other analyses. Unamended solids were also sampled, preserved and subject to the same analyses for comparison.

2.4. Analytical procedures

XAS analysis was used to speciate As and Fe in the solid samples. XAS analysis was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 11-2. The beamline was configured with a Si(220) monochromator and a ϕ angle of 90° . Sample fluorescence was measured with a 100-element Ge detector, in combination with a 6 μx Ge filter for As or a 6 μx Mn filter for Fe, respectively. The spectra were processed in SIXpack (Webb, 2005) using standard procedures (Sun et al., 2016a, 2016b). Least-squares linear combination fitting was used to quantify As and Fe speciation. Normalized As X-ray absorption near edge structure (XANES) were fitted over 11860–11890 eV using Na-arsenate and Na-arsenite as references. Normalized Fe XANES spectra were fitted over 7110–7150 eV using ferrihydrite and goethite as references. Fitting with Fe extended X-ray absorption fine structure (EXAFS) over 2–13 $\text{\AA}^{-1}$ produced similar results. No additional references were necessary in fitting.

The freeze-dried solid samples were ground into powders with an agate mortar-and-pestle. The elemental composition of the powder was determined using (1) microwave-assisted digestion with HNO_3 and HF (EPA, 1995), followed by ICP-MS, and (2) an Innov-X Delta Premium handheld XRF. The digestion and XRF methods reported consistent compositions, and reported data were from digestion. Color and diffuse reflectance of the powder were recorded using a Konica Minolta CM-700d spectrophotometer (Fig. S4).

Dissolved metal concentrations were determined by Element XR ICP-MS (Thermo Fisher Scientific) using previously published procedure (Sun et al., 2016a, 2016b). Detection limits for Fe, As, Cr and Ni on the instrument were 5.4, 2.7, 0.8 and 0.2 nM, respectively. The dilution factors for A-GW and oxalic acid effluents were $\times 10$ and $\times 200$, respectively, which need to be accounted for to calculate the effective detection limits. Dissolved bromide concentrations were determined by a Dionex ICS-2000 IC system (Sunnyvale) using previously published procedure (Sun et al., 2016b).

3. Results

3.1. Arsenic(V) columns

3.1.1. Effluent composition—During A-GW injection, effluent metal concentrations were low in both columns (Fig. 1). When oxalic acid was introduced, Fe, Cr and Ni were immediately released whereas As release was initially limited. The rates of Fe and Cr release from Cr-ferrihydrite were stable, at 32.3 ± 3.0 and $0.7 \pm 0.1 \mu\text{mol PV}^{-1}$, respectively (Fig. S5). Effluent Fe and Cr concentrations were 9.3 ± 1.0 and $0.20 \pm 0.03 \text{ mM}$, respectively, producing Cr:Fe of $1:48 \pm 3$, consistent with initial mineral stoichiometry (Cr:Fe = 1:46). The rate of As release was low until the As(V)-Cr-ferrihydrite column received 10 PVs of oxalic acid, subsequently steadily increasing to $2.0 \mu\text{mol PV}^{-1}$ by the end of oxalic acid injection, translating to 0.67 mM effluent As. Upon oxalic acid injection, the rates of Fe and Ni release from Ni-goethite reached the maxima of 45.1 and $2.0 \mu\text{mol PV}^{-1}$, respectively; their effluent concentrations reached maxima of 13.3 and 0.72 mM, respectively (Figs. 1 and S5). Over the next 13 PVs (c.a. PV = 11–24), the rates of Fe and Ni release decreased to 22.6 and 0.5 mmol PV^{-1} , respectively; their concentrations declined to 6.1 and 0.13 mM, respectively. Effluent Ni:Fe was consistently greater than initial mineral stoichiometry (Ni:Fe = 1:93), with 1:56 the lowest ratio measured. Arsenic release was limited until the As(V)-Ni-goethite column received 8 PVs of oxalic acid, and then rapidly reached a maximum release rate of $2.5 \mu\text{mol PV}^{-1}$ and maximum As concentration of 0.71 mM. Around the 25th PV, the metal release suddenly stopped in the As(V)-Ni-goethite column (Fig. 1). Re-injection of A-GW then produced low or undetectable metal concentrations in both columns. Bromide breakthrough curves before and after oxalic acid injection were identical (Fig. S6).

3.1.2. Solid composition and mineralogy—In the As(V)-Cr-ferrihydrite column, the dark-red ferrihydrite coating dissolved during oxalic acid injection, exposing white quartz, producing a color contrast along the flow path (Figs. S3 and S4); by the time flow was terminated, Fe mineralogy was dominated by ferrihydrite at the outlet, and by goethite at the inlet, but the amount of goethite (bulk Fe content $\times$ goethite mol%) was very low (Table 1 and Fig. S7). Contrastingly, the As(V)-Ni-goethite column had no measurable changes in color or Fe mineralogy (yellowish goethite). Based on effluent data, cumulative amounts of Fe, Cr and As released from As(V)-Cr-ferrihydrite were 1330, 28 and 51 μmol , respectively, accounting for 34%, 32% and 25% of initial contents; Fe, Ni and As released from As(V)-Ni-goethite were 440, 10 and 17 μmol , respectively, accounting for 12%, 25% and 43% of initial contents (Figs. 2 and 3). These numbers agreed with digestion of the solids from sectioned columns (Table 1). Digestion also indicated that Cr-ferrihydrite dissolved much more extensively at the inlet than the outlet, whereas Ni-goethite dissolved relatively evenly along the flow path. Solid Cr:Fe remained uniform within the As(V)-Cr-ferrihydrite column at $1:47 \pm 3$, consistent with initial stoichiometry (1:46, Fig. 4). Solid Ni:Fe remained uniform in the As(V)-Ni-goethite column at $1:156 \pm 6$, an appreciable deviation from initial stoichiometry (1:93). Arsenic was mobilized disproportionately. Solid As:Fe in the As(V)-Cr-ferrihydrite column decreased from 1:19 initially to 1:207 at the inlet, but increased to 1:17 and 1:16 at the middle and outlet, respectively. Solid As:Fe in the As(V)-Ni-goethite

column decreased from 1:95 initially to 1:496, 1:263 and 1:162 at the inlet, middle and outlet, respectively.

3.2. Arsenic(III) columns

3.2.1. Effluent composition—During A-GW injection, effluent Fe, Cr and Ni concentrations were low or undetectable, whereas As concentration was ~0.5 mM in the As(III)-Cr-ferrihydrite column and ~0.3 mM in the As(III)-Ni-goethite column (Fig. 1). When oxalic acid was injected, steady, commensurate Fe and Cr release from Cr-ferrihydrite was observed. The rates of Fe and Cr release were 23.7 ± 1.8 and 0.5 ± 0.1 mmol PV⁻¹, respectively, a factor of ~2 lower than rates in the As(V)-Cr-ferrihydrite column (Fig. S5). Accordingly, Fe and Cr concentrations were also a factor of ~2 lower, but effluent Cr:Fe remained at $1:53 \pm 6$, similar to initial mineral stoichiometry (1:46). The rates of Fe and Ni release from Ni-goethite reached maxima of 20.0 and 0.7 $\mu\text{mol PV}^{-1}$, respectively, upon injection of oxalic acid, and then decreased to 16.9 and 0.3 mmol PV⁻¹, respectively, over the next 35 PVs (c.a. PV = 14–49). While Fe and Ni release from the As(III)-Ni-goethite column was a factor of ~2 slower than the As(V)-Ni-goethite column, effluent Ni:Fe remained similar, consistently greater than initial mineral stoichiometry (1:93), with 1:54 the lowest ratio measured. Counter to the release of As(V) which was limited initially, oxalic acid rapidly initiated release of As(III) (Figs. 1 and S5). In the As(III)-Cr-ferrihydrite column, the rate of As release was at its maximum of 10.7 $\mu\text{mol PV}^{-1}$ at the onset of oxalic acid flow and declined to 1.6 $\mu\text{mol PV}^{-1}$ by the end of oxalic acid injection, which translated to 2.76 mM and 0.39 mM effluent As, respectively. In the As(III)-Ni-goethite column, oxalic acid injection initiated a maximum As release rate of 5.1 $\mu\text{mol PV}^{-1}$, translating to a maximum As concentration of 2.18 mM. This was followed by a rapid decrease in rate to 0.4 $\mu\text{mol PV}^{-1}$, equivalent to ~0.10 mM As, where it stabilized. Around the 50th PV, the cessation of metal release occurred in the As(III)-Ni-goethite column. Re-injection of A-GW produced low or undetectable metal concentrations. Bromide breakthrough curves before and after oxalic acid injection were identical (Fig. S6).

3.2.2. Solid composition and mineralogy—Similar to the As(V) columns, a color contrast developed along the flow path during oxalic acid injection in the As(III)-Cr-ferrihydrite column, whereas the change in the As(III)-Ni-goethite column was subtle (Figs. S3 and S4). Arsenic remained as As(III) on Cr-ferrihydrite, but partially oxidized to As(V) on Ni-goethite (Table 1 and Fig. S8). Based on effluent data, cumulative amounts of Fe, Cr and As released from As(III)-Cr-ferrihydrite were 1305, 25 and 205 μmmol , respectively, accounting for 36%, 33% and 55% of initial contents; Fe, Ni and As released from As(III)-Ni-goethite were 757, 16 and 43 μmol , respectively, accounting for 20%, 38% and 64% relative to initial contents (Figs. 2 and 3). These numbers agreed with digestion of the solids from sectioned columns (Table 1). Again, Cr-ferrihydrite dissolved more extensively at the inlet, whereas Ni-goethite dissolved evenly for each interval. In the As(III)-Cr-ferrihydrite column, solid Cr:Fe remained uniform at $1:50 \pm 3$, similar to initial stoichiometry (1:46); As:Fe decreased from 1:10 initially to 1:181, 1:30 and 1:17 at the inlet, middle and outlet, respectively (Fig. 4). In the As(III)-Ni-goethite column, solid Ni:Fe remained uniform at $1:141 \pm 3$, again deviating appreciably from initial stoichiometry (1:93); As:Fe decreased from 1:58 initially to 1:485, 1:288 and 1:182 at the inlet, middle and outlet, respectively.

4. Discussion

The environmental fate of trace metals is regulated by many confounding variables, including their own redox cycles, sediment mineralogy, pH change, and the presence of competing ions and complexing ligands, etc (Fendorf et al., 2010; Ng et al., 2003; Smedley and Kinniburgh, 2002). To predict groundwater metal concentrations and formulate remedial strategies at distinct sites, the differences in individual variables and in their combinations require careful consideration. Our previous studies have demonstrated that, compared to the lowering of pH and competitive desorption from phosphate, oxalic acid can mobilize As from contaminated sediments much more extensively (Sun et al., 2016a; Wovkulich et al., 2010). This study allows us to further distinguish between the mechanisms of metal mobilization by oxalic acid, and to evaluate how the differences in environmental variables would impact the effectiveness and efficiency of oxalic acid-enhanced P&T methods.

4.1. Oxalic acid promoted substrate dissolution

Metal-substituted minerals were used to unambiguously assess the contribution of substrate dissolution versus other mobilization mechanisms. The structurally bound Cr and Ni can only be mobilized in conjunction with mineral dissolution, and the amount of Fe dissolved should supposedly follow the stoichiometric Cr:Fe and Ni:Fe ratios. Although the general trends of Fe release from the columns were always analogous to Cr and Ni release (Fig. 1), oxalic acid affected Ni-goethite above that for simple dissolution (Fig. 2B). In contrast to Cr-ferrihydrite from which Fe and Cr were mobilized equally efficiently, Fe was mobilized from Ni-goethite much slower than Ni in the first few PVs of oxalic acid and subsequently remained twice as slow as Ni (Figs. 3A and S9). Since Ni should be fairly homogeneously distributed throughout goethite (Friedrich et al., 2011; Gadol et al., 2017) and no new (other than goethite) mineral was detected (Table 1 and Fig. S6), we attribute the slower-than-expected release of Fe to coupled Ni-goethite dissolution and (pure) goethite re-precipitation. This dynamic goethite recrystallization process was hypothesized in a recent oxalate-involved hydrostatic study from Gadol et al., who also discovered that Ni was released from Ni-goethite in substantial excess over Fe (Gadol et al., 2017). Due to the limited amount of uncomplexed Fe^{2+} and its limited adsorption under the experimental conditions, such goethite recrystallization was probably oxalate-catalyzed instead of Fe(II)-catalyzed (Gadol et al., 2017). The differences between Fe and Ni elution indicate that half of the dissolved Fe re-precipitated in the Ni-goethite columns while Ni was eluted freely (Fig. 3A). The nonstoichiometric release of structurally bound metals from Fe minerals by oxalic acid has profound implication concerning contaminant mobility and micronutrient accessibility, worthy of future study. Due to dynamic goethite recrystallization, substrate dissolution in the following sections is discussed based on the elution of substituted metals instead of Fe (Figs. 2 and 3, gray lines).

Ferrihydrite and goethite were used in this study because both of them are environmentally important minerals in aquifers (Gimenez et al., 2007; Stahl et al., 2016; Sun et al., 2016d, 2018), which supposedly effectively dissolve in the presence of oxalate (Gadol et al., 2017; Lee et al., 2007; Sun et al., 2016c). In our columns, initially, the amount of substrate dissolution was linearly correlated to the amount of oxalic acid that was injected (Fig. 2A);

Ni-goethite dissolved at equal rates with (Fig. 2B, red and blue lines) or even faster than (Fig. 2B, gray lines) Cr-ferrihydrite in either As(V) or As(III) systems. Yet, while Cr-ferrihydrite dissolution sustained at a constant rate during oxalic acid injection, Ni-goethite dissolution experienced a reproducible, sharp termination (Fig. 1). Bromide tracer tests verified that no preferential flow channels were developed during injection (Fig. S6). Owing to the HCl washing step used in Ni-goethite synthesis, it is unlikely this goethite contained an appreciable amorphous fraction. XAS and XRD analyses also confirmed goethite (Figs. S1 and S7). Surface passivation by As adsorption is also unlikely, as surface coverage of As on Ni-goethite decreased during oxalic acid injection (Fig. 4B, As:Fe ratio). It is possible that the neoformed (re-precipitated) goethite was more crystalline and less reactive, which covered residual Ni-goethite and prohibited further dissolution. The phenomena of dissolution termination is also consistent with what was found in oxalic acid-involved hematite systems (Echigo et al., 2012; Yu et al., 2013): The dissolution of hematite by oxalic acid was initially fast on structural defects and sharp edges before significantly slowing afterwards. The Ni-goethite synthesized in this study might contain defects due to the acid washing step and also sharp edges, with high reactivity; when these defect and sharp edge sites were exhausted, the reactivity dramatically decreased. Cr-ferrihydrite, on the other hand, should not contain morphologically distinct components (Yu et al., 2013), consistent with no change in reactivity.

Another notable difference between columns is the dissolution of Fe(III)-oxides in the As(V) systems was twice as fast as in the As(III) systems (Figs. 2A and S5). Iron(III)-oxides can dissolve by oxalate through reductive and ligand-promoted processes, both of which require the complex $[\text{Fe(III)}-\text{C}_2\text{O}_4]^-$ to form on mineral surface before any dissolution can occur (Yu et al., 2013). The dissolution rate, therefore, depends more on oxalate surface coverage than influent oxalate concentration (Gadol et al., 2017). Consequently, any species that persists on the sorption sites would decrease oxalate surface coverage and suppress dissolution (Shi et al., 2009). Arsenic(III) had a larger inhibitory effect on the dissolution process, consistent with As(III) being presorbed more extensively compared to As(V) (Table 1). Additionally, as the surface was partially pre-occupied with As, the surface complex $[\text{Fe(III)}-\text{C}_2\text{O}_4]^-$ may form through an associative pathway (Dou et al., 2012):

(1)

(2)

Detachment of As (Reaction 2) is possibly slower in As(III) system than in As(V) system, which might have also inhibited the formation of $[\text{Fe(III)}-\text{C}_2\text{O}_4]^-$. Yet the As(III) system eventually experienced a higher amount of Ni-goethite dissolution than the As(V) system (Fig. 2B). This higher amount of dissolution might result from less As(III) re-adsorption, which will be discussed further in the following sections.

4.2. Oxalic acid promoted arsenic mobilization

Reactive Fe(III)-oxides readily dissolve during oxalic acid injection (Sun et al., 2016a; Wovkulich et al., 2012). The successive destruction of adsorbent should proportionately liberate presorbed As at the point of reaction, obviously important for As mobilization. If substrate dissolution solely regulated As, then the proportion of As released would equal to the proportion of Cr or Ni released. Arsenic elution, however, was never proportional to substrate dissolution (Fig. 3B), indicating that the fate of As was affected by other processes. One process is available sorption sites along the flow path retarded As transport (Figs. 1 and 4). For example, the As(V)-Cr-ferrihydrite column had 32% and 25% of Cr and As released, respectively, indicating that 7% of As(V) mobilized by ferrihydrite dissolution was re-adsorbed. Therefore, oxalic acid-enhanced P&T methods can be useful in aquifers dominated by As(V), but oxalic acid may need to be injected in sufficient quantities to destruct sorption sites along the flow path before As(V) can be advected to the pumping well(s), consistent with our previous experience with a forced-gradient injection at the As(V)-rich Vineland Superfund site (Wovkulich et al., 2014).

Under hydrostatic conditions, As(III) often adsorbs more extensively to Fe-oxides than does As(V) at circumneutral pH (Fig. S2) (Banerjee et al., 2008; Dixit and Hering, 2003). However, the As(III)-Cr-ferrihydrite column had 33% and 55% of Cr and As released, respectively, indicating that this column had no observable re-adsorption and, instead, had 22% additional As mobilization due to mechanism(s) other than substrate dissolution. Although both As(III) and As(V) can form bidentate, binuclear complexes on Fe-oxides (Ona-Nguema et al., 2005), a large proportion of As(III) is often an outer-sphere complex (Sverjensky and Fukushima, 2006). The rapid desorption of weaker outer-sphere As(III) complexes under hydrodynamic conditions explains partially why the As(III) columns had an order of magnitude higher As elution than the As(V) columns during A-GW injection (Fig. 1). Nevertheless, compared to A-GW, As(III) elution was much more substantial in the presence of oxalic acid. The extensive desorption and fast transport of As(III) (Figs. 2C and 3B) largely resulted from pH changing from neutral to acidic conditions: While As(V) adsorption on Fe-oxides increases with this pH decrease, As(III) adsorption behavior is the opposite (Dixit and Hering, 2003). Therefore, compared to As(V), when applying enhanced P&T methods in aquifers dominated by As(III), As elution will potentially be efficient and substantial upon initiation of oxalic acid-amended flow. pH buffering capacity of the aquifer will then be a critical parameter to determine before planning such remediation.

Oxalic acid not only caused nonstoichiometric Ni and Fe release from Ni-goethite, but also regulated presorbed As in a complicated manner (Figs. 2 and 3). In both Ni-goethite columns, As elution stopped simultaneously with termination of substrate dissolution (Fig. 1). As discussed above, this Ni-goethite appeared to contain structural defects and sharp edges. These reactive sites which readily dissolve by oxalic acid should also have been sites with high sorption density. Consequently, the full consumption of these sites not only dramatically slowed down dissolution, but also terminated As release. Alternatively, the termination of As elution could be explained by neoformed goethite being recalcitrant, which protected the mineral surface and the As on the surface sites. Nevertheless, the interpretation that the majority of As was associated with the readily-dissolved, sorption-

dense sites of Ni-goethite also explains why, on a proportional basis, both As(V) and As(III) were mobilized more extensively from Ni-goethite than from Cr-ferrihydrite (Fig. 3B). Therefore, to apply oxalic acid-enhanced P&T methods in aquifers that contain crystalline Fe-minerals, complete substrate dissolution and As extraction will be difficult to achieve, but also that it may not be required for such remediation methods to be successful. Additionally, the fact that As elution stopped when As adsorbent could no longer be “destroyed” implies that competition between oxalate and As oxyanions for binding sites might have played a minor role in As elution from these columns.

Furthermore, as indicated by As XANES on the amended solids, As(III) oxidation occurred in the As(III)-Ni-goethite column (Table 1 and Fig. S8), which must have influenced As elution. Unfortunately, effluent As speciation was not monitored, which makes it difficult to conclude the exact extent of oxidation, because As(V) might have been preferentially retained in the solids owing to (re)adsorption. Since no As(III) oxidation was observed in the ferrihydrite column that was simultaneously conducted and analyzed, As(III) oxidation on goethite is unlikely a result of photochemical oxidation, X-ray beam (during XANES analysis) induced change, or the presence of dissolved oxygen or Fe(III) (Bhandari et al., 2011). Amstaetter et al. found that goethite activated by Fe(II) has high redox activity capable of oxidizing As(III) (Amstaetter et al., 2009). In our experiment, an oxalate-activated process is also possible, which requires further investigation but is beyond the scope of this study.

5. Conclusions

This study was motivated by the potential of *in situ* oxalic acid injection to enhance P&T for groundwater As remediation, and sought to decipher the role of oxalic acid on the fate and transport of As within Fe(III)-oxide coated sand. The destruction of adsorbent and pH decrease were identified as the dominant mechanisms promoting As elution. The importance of these processes on controlling the mass flux of As, however, can be locally overtaken by readsorption or other processes. Of course, continued efforts are warranted for this remediation strategy to be used in practice, which needs be refined according to varying geochemical and hydrogeologic framework. For example, to best utilize such oxalic acid-enhanced methods, detailed characterization on the type and distribution of As-bearing Fe-minerals in aquifers, pH buffering capacity, preferential flow paths, etc, is necessary. Additional laboratory experiments and *in situ* trials, which can combine different Fe-minerals and take other common solid and solution species such as manganese oxides and dissolved phosphate into account (Nagar et al., 2010; Tao et al., 2006), also would be valuable. Nevertheless, based on the findings from this study, it is reasonable to expect that as long as oxalic acid is injected in sufficient quantities, this enhanced P&T approach can effectively remove As from typical aquifer matrix in which As is bound to Fe(III)-oxides and reduce the cumulative operation time and cost required for remediation. It is challenging to achieve 100% As removal where As is associated with crystalline minerals. Fortunately, residual As, in such a scenario, will be less likely to be a source for future contamination of the groundwater (Rawson et al., 2017; Stahl et al., 2016; Sun et al., 2016a), because oxalic acid would have removed the “vulnerable” fraction of the As in the sediments.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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HIGHLIGHTS

- We study oxalic acid promoted metal release from As presorbed Fe oxide coated sand.
- Cr and Ni substituted ferrihydrite and goethite were used.
- The effect of substrate dissolution was isolated from other As release mechanisms.
- As(V) elution was retarded, whereas As(III) elution was rapid due to pH decrease.
- Unlike Cr-ferrihydrite, metal release from Ni-goethite could not be sustained.

Fig. 1.

Effluent As, Fe and Cr or Ni concentrations as a function of pore volumes. This figure is organized as the Cr-ferrihydrite columns on the left and Ni-goethite columns on the right, and as As(V) columns on the top and As(III) columns on the bottom. Hatched lines represent the switches between pH = 7.0 A-GW and pH = 2.210 mM oxalic acid-amended influent.

Fig. 2.

Amounts of (A) Cr or Ni, (B) Fe and (C) As released versus amount of oxalic acid injected. In (B) (C), red and blue symbols represent apparent amounts, whereas gray symbols represent the calculated amounts if the release of Fe and As is proportional to the release of substituted metal based on initial stoichiometry. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3.

Proportions of (A) Cr or Ni and (B) As release versus Fe release. In (B), red and blue symbols represent apparent proportions, whereas gray symbols represent the calculated proportions if the release of Fe is proportional to the release of substituted metal based on initial stoichiometry. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4.

Ratios of As over Fe and substituted metal (Cr or Ni) over Fe in the amended solids. Red and blue symbols represent apparent proportions, whereas gray symbols, when shown, represent the calculated proportions if the release of Fe is proportional to the release of substituted metal based on initial stoichiometry. Dash lines represent initial ratios. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Elemental contents and As and Fe speciation of the solids from four columns before and after the experiment. The elemental contents were based on digestion and expressed on dry weight basis. The numbers in parentheses are % change of initial content, with + meaning increase and - meaning decrease. Solid As and Fe speciation were based on XAS analysis (Figs. S7 and S8).

D	As $\mu\text{mol g}^{-1}$ (% change)	As(V) %	As(III) %	Fe $\mu\text{mol g}^{-1}$ (% change)	Ferrihydrite %	Goethite %	Cr or Ni $\mu\text{mol g}^{-1}$ (% change)
As(V)-Cr-ferrihydrite column							
Initial	8.69	-	-	165	100 $\pm$ 2	0 $\pm$ 2	3.62
Outlet	10.4 (+19)	-	-	162 (-2)	100 $\pm$ 2	0 $\pm$ 2	3.48 (-4)
Middle	8.31 (-4)	-	-	143 (-13)	-	-	2.87 (-21)
Inlet	0.01 (-100)	-	-	1.93 (-99)	16 ^A $\pm$ 3	84 ^A $\pm$ 3	0.04 (-99)
As(V)-Ni-goethite column							
Initial	1.77	-	-	168	0 $\pm$ 2	100 $\pm$ 2	1.78
Outlet	0.98 (-45)	-	-	159 (-6)	0 $\pm$ 3	100 $\pm$ 3	0.98 (-45)
Middle	0.57 (-68)	-	-	150 (-11)	-	-	0.96 (-46)
Inlet	0.27 (-85)	-	-	135 (-20)	0 $\pm$ 4	100 $\pm$ 4	0.90 (-49)
As(III)-Cr-ferrihydrite column							
Initial	18.1	0 $\pm$ 1	100 $\pm$ 1	174	-	-	3.75
Outlet	9.45 (-48)	0 $\pm$ 1	100 $\pm$ 1	159 (-9)	-	-	3.44 (-8)
Middle	5.31 (-71)	3 $\pm$ 1	97 $\pm$ 1	157 (-10)	-	-	2.96 (-21)
Inlet	0.02 (-100)	ND ^B	ND ^B	3.63 (-98)	-	-	0.07 (-98)
As(III)-Ni-goethite column							
Initial	3.08	0 $\pm$ 1	100 $\pm$ 1	179	-	-	1.97
Outlet	0.78 (-75)	35 $\pm$ 1	65 $\pm$ 1	141 (-21)	-	-	0.98 (-50)
Middle	0.52 (-83)	74 $\pm$ 1	26 $\pm$ 1	151 (-15)	-	-	1.07 (-46)
Inlet	0.29 (-90)	56 $\pm$ 1	44 $\pm$ 1	143 (-20)	-	-	1.03 (-47)

Note:

^AThis sample had noisy XAS spectra due to low Fe concentration, which might affect the accuracy of fitting result.

^BThis sample was analyzed for As XANES, but no As edge could be detected due to low As concentration.