Interaction of arsenic with co-precipitated Fe(II,III) (hydr)oxides

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ABSTRACT: Iron electrocoagulation (EC) is a low-cost arsenic (As) treatment method that is able to produce Fe(II,III) phases that bind As effectively, such as green rust (GR) and magnetite (Mag). We compared the As removal performance of coprecipitated GR, Mag and lepidocrocite (Lp) produced by Fe(0) EC. The As(III) removal efficiency for these phases was >60%, increasing in order of GR < Mag ≤ Lp, and all three Fe phases removed >95% of the initial As(V) (0.5 to 11 mg L⁻¹). Spectroscopic data of EC samples revealed that As was able to substitute for tetrahedral Fe sites in Mag, associating with multiple Fe atoms, while As formed binuclear corner sharing geometries on GR and Lp surfaces. The formation of multinuclear As complexes during Mag production by Fe(0) EC can explain the low fraction of As remobilized from the solids during extractions with 2.5 mM PO₄³⁻ or 0.01 M NaOH. Taken together, our results show that Mag is the optimum phase for As removal in Fe(0) EC field treatment.

1 INTRODUCTION

Chronic exposure to arsenic (As) in groundwater used for drinking threatens the lives of millions of people worldwide. Iron electrocoagulation (Fe(0) EC) is a low cost As removal method based on the production of Fe(II) by Fe(0) electrolysis, followed by (partial) Fe(II) oxidation to form Fe precipitates that bind As. The mixed valent Fe(II,III) (hydr)oxide phases, green rust (GR) and magnetite (Mag), can be produced easily and at low cost by Fe(0) EC. The formation of these minerals can improve the performance of Fe(0) EC systems by improving particle separation and by binding As in highly stable multi-nuclear complexes (Wang et al., 2014). However, the As redox and sorption behavior during Fe(II,III) (hydr)oxide formation by Fe(0) EC must be understood before promoting these minerals in future EC systems.

In this work, we combined wet chemical measurements with X-ray absorption spectroscopy to determine the As removal efficiency and As speciation during GR, Mag and lepidocrocite (Lp) formation. These results can be used to optimize the design and operation of Fe(0) EC systems for As removal.

2 METHODS

2.1 Arsenic removal by Fe(0) EC

For the As removal experiments, we generated GR, Mag and Lp by EC following our previous approaches (Wang et al., 2014). Briefly, GR and Mag were produced by adding 3 mM Fe(II) by Fe(0) EC at 300 μM Fe(II) min⁻¹ to solutions open to the atmosphere that contained 10 mM dissolved inorganic carbon (to form

GR) or NaCl (to form Mag) at pH 7.5 and 9. Lepidocrocite was generated in a NaCl electrolyte by adding 3 mM Fe(II) by EC at 30 μM Fe(II) min⁻¹. In each experiment, the electrolyte solution initially contained either As(III) or As(V) at concentrations ranging from 0.5 to 11 mg L⁻¹. Immediately following the electrolysis stage, an aliquot of the suspension was passed through 0.2 μm filters and acidified with HNO₃. Arsenic in the filtrate was measured by GF-AAS (Perkin Elmer AAnalyst 800).

2.2 X-ray absorption spectroscopy

Samples for As K-edge X-ray absorption spectroscopy (XAS) were prepared by filtering particle suspensions in an anaerobic chamber and loading the solids into custom sample holders. Spectra were collected at 77°K in fluorescence mode at beam line BM-26A (DUBBLE) at ESRF (Grenoble, FR) and beam line 4-1 at SSRL (Menlo Park, USA). The As oxidation state in EC samples was quantified by linear combination fits using As reference minerals. The As uptake mode was determined with shell-by-shell fits of the Fourier transformed EXAFS spectra.

2.3 Extraction experiments

Extraction experiments were performed by filtering As(V)-bearing suspensions of GR, Mag and Lp and adding the solids to various solutions: 0.1 M NaCl, 0.01 M HCl (pH 2), 2.5 mM PO₄³⁻ and 0.01 M NaOH (pH 12). Aliquots of each extraction were filtered after 1 h and 1 d. The mobilization of As from the EC solids was measured by GF-AAS.

3 RESULTS AND DISCUSSION

3.1 Arsenic removal

The formation of Mag and Lp (3 mM Fe) resulted in >90% removal of initial As(III) ranging from 0.5 to 11 mg L⁻¹ at pH 7.5 and 9 (Fig. 1). By contrast, GR was less effective at removing As(III), with ≈82% removal of 0.5 mg L⁻¹ As(III) at pH 7.5 and 9. While As(III) removal varied with Fe(II,III) mineral and pH, As(V) removal was >95% for GR, Mag and Lp regardless of pH.

3.2 As K-edge XANES and EXAFS spectroscopy

Comparing the As K-edge XANES spectra across EC samples (Fig. 2) shows that the extent of As(III) oxidation increases during GR and Mag coprecipitation when pH increases from 7.5 to 9. In addition, decreasing the rate of Fe(II) production, which produced Fe(III) phases instead of Fe(II,III) (hydroxides, increased As(III) oxidation significantly. For example, at pH 7.5 and an As/Fe ratio of 5 mol%, producing GR (300 μM Fe(II) min⁻¹) oxidized only 17% As(III), whereas generating Lp (30 μM Fe(II) min⁻¹) oxidized 60% As(III). No evidence for As(V) reduction during coprecipitation with GR and Mag (data not shown), nor during adsorption to presynthesized GR and Mag (Fig. 2A) was observed. Although we found little difference between the extent of As(III) oxidation when generating GR and Mag, the EC Mag samples showed distinct post edge features (arrows in Fig. 2B) that were absent in the XANES spectra for all other EC samples and adsorption references, which indicates a unique As coordination environment.

Consistent with the XANES spectra, the EXAFS spectra and corresponding Fourier transforms (data not shown) of the coprecipitated EC Mag samples were unique among the data set. The second shell peak of the Fourier transformed EC Mag samples had considerably larger amplitude relative to those of the adsorption standards and GR and Lp EC samples. The second shell peak amplitude and position of the EC Mag samples matched that of a synthetic Mag reference with incorporated As(V), which suggests at least partial incorporation of As into EC-generated Mag. Shell-by-shell fits of the EC Mag samples confirmed the existence of multinuclear As coordination geometries, with fit-derived As-Fe coordination numbers ($N_{As-Fe1} = 5.3$, $N_{As-Fe2} = 3.1$) and interatomic distances ($R_{As-Fe1} = 3.44$ Å, $R_{As-Fe2} = 3.65$ Å) consistent with partial As substitution for tetrahedral Fe in Mag.

3.3 Arsenic remobilization

No As(V) was mobilized from any EC generated sample in the 0.1 M NaCl and pH 2 extractions, but different As(V) fractions were extracted from the PO₄³⁻ and pH 12 solutions, depending on the Fe phase (data not shown). We found that 2.5 mM PO₄³⁻ mobilized 22 to 25% of As(V) bound to GR and Lp, while only 12%

Figure 1. Removal of As(III) and As(V) during the formation of GR (green symbols), Mag (black symbols) and Lp (orange symbols) by Fe(0) EC. The squares and circles represent experiments at pH 7.5 and 9.

Figure 2. As K-edge XANES spectra of (A) adsorption references and (B-C) EC samples containing As(III) concentrations of 1.1 and 11 mg L⁻¹ (As/Fe = 0.5 to 5 mol%). GR samples are shown in green, Mag in black and Lp in orange.

was extracted from Mag. Furthermore, only 20% of As(V) initially bound to Mag was extracted at pH 12 compared to nearly 50% for Lp. The lower fraction of As(V) mobilized from Mag relative to GR and Lp in the PO₄³⁻ and pH 12 extractions can be explained by the partial incorporation of As(V) into EC generated Mag, which was detected by EXAFS spectroscopy.

4 CONCLUSIONS

Combining the As(III) and As(V) removal experiments with the EXAFS results and chemical extractions suggests that As treatment performance in the field can be optimized by generating Mag rather than GR or Lp. The benefits of producing Mag are further supported by the ease of separating Mag particle suspensions using low strength magnetic fields.

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REFERENCE

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