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Electrochemically Induced Oxidative Precipitation of Fe(II) for As(III) Oxidation and Removal in Synthetic Groundwater

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Abstract

Mobilization of Arsenic in groundwater is primarily induced by reductive dissolution of As-rich Fe(III) oxyhydroxides under anoxic conditions. Creating a well-controlled artificial environment that favors oxidative precipitation of Fe(II) and subsequent oxidation and uptake of aqueous As can serve as a remediation strategy. We reported a proof of concept study of a novel iron-based dual anode system for As(III) oxidation and removal in synthetic groundwater. An iron anode was used to produce Fe(II) under iron-deficient conditions, and another inert anode was used to generate O₂ for oxidative precipitation of Fe(II). For 30 min's treatment, 6.67 μ M (500 μ g/L) of As(III) was completely oxidized and removed from the solution during the oxidative precipitation process when a total current of 60 mA was equally partitioned between the two anodes. The current on the inert anode determined the rate of O₂ generation and was linearly related to the rates of Fe(II) oxidation and of As oxidation and removal, suggesting that the process could be manipulated electrochemically. The composition of Fe precipitates transformed from carbonate green rust to amorphous iron oxyhydroxide as the inert anode current increased. A conceptual model was proposed for the in situ application of the electrochemically induced oxidative precipitation process for As(III) remediation.

INTRODUCTION

Millions of individuals worldwide are chronically exposed to toxic concentrations of arsenic (As) in groundwater drinking supplies.^{1,2} Arsenic in drinking water can cause skin and internal cancers, particularly in the lungs and urinary tract.^{3–5} A recent study estimates that 1 in 5 deaths in Bangladesh are due to As exposure.⁶ Many technologies, including oxidation and sedimentation,⁷ coagulation and filtration,⁸ adsorption,⁹ ion exchange,¹⁰ and membrane filtration,¹¹ have been proposed to remediate As-contaminated groundwater. Most of the processes are applied *ex situ* (pump and treat), generating As-containing hazardous wastes

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Notes

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which require regulated disposal.¹² In comparison, *in situ* treatments are more desirable as they essentially immobilize As, which in most cases originates from geological minerals in the subsurface, eliminating the need for waste disposal.

Although there is still some debate over the predominant source of As in groundwater in Southeast Asia,¹³ most researchers agree that As is derived from microbially reductive dissolution of As-rich Fe oxyhydroxides.^{14–18} When the redox environment of groundwater changes from oxidizing to reducing conditions, dissimilatory reduction of Fe(III) leads to the dissolution of Fe (hydr)oxides and the release of adsorbed As. Microbial reduction of As(V) to As(III) also increases the mobility of As because As(V) adsorbs to minerals more strongly than As(III) under circumneutral conditions.^{19,20} According to this mechanism, it is rational to hypothesize that As in anoxic zones can be immobilized again by increasing the redox potential of iron-rich groundwater. This hypothesis is supported by several previous investigations. A recent study revealed that injecting nitrate as an electron acceptor into Fe(II)-rich anoxic groundwater could immobilize As through microbial oxidation of Fe(II) and As(III).²¹ *In situ* oxidation of Fe(II) and As(III) was also obtained by injecting potassium permanganate directly into contaminated wells, yielding a reduction in As concentration from 13 600 to 60 $\mu\text{g/L}$.²² In a field survey, As was observed to accumulate remarkably in the interface between anoxic groundwater and oxic river water,²³ and *in situ* aeration was proposed as a method to remove As in Bangladesh groundwater.¹⁷

However, microbial oxidation by injecting nitrate requires a substantial amount of time and there is a risk of As being remobilized once nitrate is depleted; potassium permanganate gives water an unattractive color which needs further treatment. Compared with other chemical oxidants, O_2 is a more easily available and environmentally friendly agent to increase groundwater redox potential. Oxidative precipitation of Fe(II) has been enabled by injecting aerated water through tube-wells to the subsurface for As(III) remediation.^{24–28} Fe(II) solution was also injected into groundwater to produce additional As scavenger when its background concentration is less than the threshold concentration for As removal under oxidizing conditions.²⁹ However, there are several problems associated with $\text{O}_2/\text{Fe(II)}$ injection process: (1) O_2 has limited aqueous solubility and may be significantly consumed by organic matter, sulfide, and other reducing compounds before it reaches the contaminated plume. Fe(II) oxidation and hydrolysis causes a drop in groundwater pH, which needs further adjustment.³⁰ (2) It is difficult to supply an appropriate concentration of Fe(II) and ratio of $[\text{DO}]/[\text{Fe(II)}]$ for As(III) remediation. A low concentration of Fe(II) is not sufficient for As immobilization, while a high concentration increases precipitates. A low ratio of $[\text{DO}]/[\text{Fe(II)}]$ leads to a low efficiency because the excess Fe(II) competes with As(III) for the intermediate oxidant.³¹ (3) The long-term performance is questionable because of the risk of As release when groundwater redox potential decreases to anoxic conditions with depletion of oxidants.

In this study, a new electrochemically induced oxidative precipitation process is tested for As(III) oxidation and removal in contaminated groundwater. The conceptual model is presented in Figure 1. An Fe anode and a mixed metal oxide (MMO) anode are used to simultaneously produce Fe(II) (eq 1) and O_2 (eq 2), respectively, and an MMO cathode is used to produce OH^- (eq 3). When As(III)-contaminated groundwater is electrolyzed in the

dual anode system, As(III) can be oxidized to As(V) by the oxidizing species produced from the reaction of Fe(II) with O₂.⁷ Both As(III) and As(V) can be adsorbed and/ or coprecipitated by the produced Fe(III) precipitates. In this new process, both O₂ and Fe(II) can be produced *in situ* by installing electrodes in the contaminated aquifer. The production rate of O₂ and Fe(II) can be quantitatively regulated by the current applied to the two anodes according to Faraday's Law. Moreover, O₂ production from electrolysis can be initiated to suppress the reductive dissolution of iron oxides at the time when the groundwater redox environment tends to shift to reducing conditions.

The effectiveness of this new electrochemical process for As(III) oxidation and removal is tested. In particular, the ratio of the production rate of O₂ and Fe(II), which is quantitatively controlled by the currents partitioned in the two anodes, is evaluated for its influence on the production and transformation of Fe-precipitates as well as the oxidation and removal of As(III). The Fe-precipitates produced at different ratios of [O₂]/[Fe(II)] are characterized. The mechanisms of As(III) oxidation and removal are discussed. It is aimed to justify the concept of electrochemically induced oxidative precipitation of Fe(II) for As(III) remediation in groundwater.

EXPERIMENTAL METHODS

Chemicals.

As₂O₃ (99.8%, Shanghai General Reagent Factory) and Na₂HAsO₄·7H₂O (99.99%, Sigma-Aldrich) were used to prepare As(III) and As(V) solutions. All other chemicals used in experiments were of reagent grade or higher. Fe plate (S45C type, Wuhan Steel Processing Co., Ltd., China) and MMO (IrO₂ and Ta₂O₅ coated on titanium diamond mesh, Shanxi Kaida Chemical Ltd., China) with dimensions of 58 mm length, 50 mm width, and 1.7 mm thickness were used as the electrodes. Among the two main types of titanium-based dimensionally stable electrodes, Ir instead of Ru oxides coatings were chosen mainly because of the low overpotential for oxygen evolution.^{32,33} The materials have been used as inert anodes for oxygen production in laboratory studies and field applications.^{34–36} The evolution of Cl₂ can be prevented by controlling the anode potential higher than that for O₂ evolution but lower than that for Cl₂ evolution. Sixteen holes (4.1 mm in diameter) were evenly distributed through the Fe plate electrode. Prior to the experiments, the Fe electrode was polished with a coarse emery cloth, etched by diluted HCl solution (5% by weight), and

washed with deionized water. Deionized water (18.2 M Ω -cm) from a Heal Force NW ultrapure water system was used in all of the experiments.

Synthetic Groundwater.

Simulated Bangladesh ground-water (SBGW) was used as the background media in this study because Bangladesh has been intensively studied as a region with a high prevalence of waterborne As poisoning in the world.^{2,4–6} According to British Geological Survey,^{37,38} the Bangladesh groundwater typically contains 6.67 μ M (500 μ g/L) As(III), 8.2 mM NaHCO₃, 2.5 mM CaCl₂, 1.6 mM MgCl₂, 0.025 mM NaH₂PO₄, and 0.246 mM Na₂SiO₃. SBGW was prepared based on these compositions by adding the specific mass of NaHCO₃, MgCl₂, Na₂HPO₄, CaCl₂, and Na₂SiO₃ to deionized water under vigorously stirring conditions. The initial solution pH obtained was 8. As the final As(III) removal efficiency was reported to be independent of pH in the range of 6 to 8,^{39,40} no attempt was made to condition the pH in our experiments.

Batch Experiments.

An undivided acrylic electrolytic cell (Figure S1 in the Supporting Information (SI)) was used to investigate the oxidative precipitation of Fe(II) for oxidation and removal of As(III) under ambient conditions. Three electrodes were placed in the cell. An Fe plate was used as the first anode to produce Fe(II), an MMO was used as the second anode to produce O₂, and another MMO was used as the cathode to produce OH[−]. The cathode was placed in the center of the two anodes with 40 mm spacing. For each test, 750 mL of SBGW was transferred into the cell. The concentration of dissolved oxygen (DO) in the solution was reduced to about 1 mg/L (determined by a DO meter) by purging the solution with N₂ (99.999%). The reactor was sealed and stirred at 300 rpm with a magnetic stir bar. A constant current of 30 mA was maintained on the Fe anode by a direct current (DC) power supply (GPC-3060D, Taiwan Goodwill Instrument, Taiwan), thus producing a constant rate of total Fe release. A series of different currents (0, 5, 10, 15, 30, 45, and 60 mA) were applied to the MMO anode, corresponding to different ratios of production rate of O₂/Fe(II). The initial solution pH was 8 and was not adjusted during the treatment. The variation of solution pH was less than 1 for all treatments.

For electrocoagulation (EC) experiments, only one iron anode and one MMO cathode were employed and a constant current of 30 mA was applied. The cell was exposed to air to sustain an oxic environment, but was closed to maintain an anoxic environment. For O₂/Fe(II) addition experiments, no electrodes were installed, 0.73 mM Fe²⁺ (the maximum concentration produced at 30 mA) was added to SBGW initially, and the system was exposed to air. The SBGW in the cell were deoxygenated before electrolysis for the above experiments. All the experiments were carried out in duplicate.

At predetermined time intervals, about 8 mL of solution were taken out for analysis. Three mM 2, 2'-bipyridine was immediately added to quench the further reaction between Fe²⁺ and O₂ in solution samples.⁴¹ The first set of samples were filtered through a 0.45- μ m filtration membrane for determination of As and Fe species in the aqueous phase. The second set of unfiltered samples were digested by 1 M HCl for analysis of total As and Fe

species. The adsorbed fractions of As and Fe species were calculated from the difference of the two measurements.

Anodic Oxidation, Cathodic Reduction, and Free Chlorine Oxidation.

To evaluate the contribution of different mechanisms to As(III) transformation, a series of batch experiments were conducted. The anodic oxidation of As(III) and cathodic reduction of As were tested in a divided electrolytic cell. Two MMO electrodes were used as the anode and cathode. The anodic and cathodic compartments were connected by a salt bridge, which was filled with saturated K_2SO_4 with 2% agar. For each test, 500 mL of 6.67 μM As(III) in 20 mM Na_2SO_4 solution was transferred into the anodic cell, and another 500 mL of 6.67 μM As(III) or As(V) in SBGW was transferred into the cathodic cell. Sulfate was used in the anodic cell because it has negligible influence on the removal of As.^{39,42} To evaluate the contribution of free chlorine produced on the MMO anode to As(III) oxidation, MMO anode and cathode in the dual anode system were retained while the Fe anode was removed. For a comparison, 6.67 μM As(III) in 20 mM Na_2SO_4 solution and in SBGW (containing 8.2 mM Cl^-) was treated independently. The current was always maintained at 30 mA.

Analysis.

A high performance liquid chromatography (HPLC) system consisting of a ternary pump, an injector and a 100- μL sampling loop coupled to an atomic fluorescence spectrometer (AFS 9600, Beijing Kechuang Haiguang Instrument Co., Ltd., Beijing, China) was used for the analysis of As(III) and As(V) in the solutions. Separation of As(III) and As(V) was performed on a Hamilton PRP-X100 anion-exchange column (10 μm , 4.1 $\times$ 250 mm). Hydride generation of volatile arsines was conducted by adding online solutions of HCl and KBH_4 using a peristaltic pump. Fe(II) and total Fe were measured at 510 nm using the 1,10-o-phenanthroline analytical method,⁴³ and the concentration of Fe(III) was calculated as the difference in concentration between total Fe and Fe(II).

The Fe-precipitates generated in the dual anode system were characterized by X-ray diffraction (XRD). The precipitates were obtained by filtering the solution through a 0.45 μm filtration membrane. All the operations including filtration, washing and drying were conducted under an N_2 atmosphere. XRD was operated on a D8-FOCUS X-ray diffractometer with Cu K radiation (Bruker AXS., Germany). The analysis was carried out at 40 kV and 40 mA at the scanning step size of 0.01° and step time of 0.05 s.

RESULTS AND DISCUSSION

Oxidation and Removal of As(III) by the Dual Anode System.

Figure 2 shows that the total As in SBGW with 6.67 μM As(III) was completely oxidized and removed within 30 min by dual anode system when a total current of 60 mA was equally partitioned between the two anodes. The fraction of As(V) in solution increased by 29.5% within 5 min but decreased afterward; while in solid phase, the fraction of As(V) increased to 100% within 30 min. This feature appears to suggest the production of As(V) in solution and the subsequent uptake by precipitates. Iron-based electrocoagulation process has been widely investigated for treating As(III)-contaminated groundwater in the presence

of O₂.^{31,39,40,44} For example, total As was almost completely removed within 2 h when 1 L of 13.3 μ M As(III) was treated by applying a current of 22 mA to an iron anode and an aeration rate of 60 mL/min,³⁹ above 99% removal of total As was obtained within 30 min when 1 L of 26.6 μ M As(III) was treated at a current of 55 mA in an open reactor.⁴⁰ The similar trends of As(V) production and partition were observed in literature.^{39,40} For comparison, electro-coagulation experiments in oxic environment using two electrodes (an iron anode and an MMO cathode) were also carried out in this study. Results demonstrate that As(III) was completely oxidized within 5 min, and total As was completely removed within 30 min (SI Figures S2a, S3a, and S3b). The rate of As(III) oxidation was higher than that with 30 mA applied to MMO anode in the dual anode system (SI Figure S3a), which was attributed to the increased O₂ supply in the open cell. However, electrocoagulation in anoxic environment led to much slower rates of As(III) oxidation and removal (SI Figures S2b, S3a, and S3b), and the oxidation was also slower regardless the similar removal when 0.73 mM Fe²⁺ (the maximum concentration produced at 30 mA) was added at one time at the beginning of experiments without electrolysis (SI Figures S2c, S3a, and S3b). As a consequence, O₂ is prerequisite for As(III) oxidation and removal in anoxic environment, and an increased [DO]/[Fe(II)] ratio can improve the oxidation efficiency. Therefore, the dual anode system could serve as an *in situ* strategy under anoxic conditions to provide the required amount of O₂ and Fe(II) for As(III) oxidation and removal.

Effect of Current Partition on Iron Species Production.

Since the oxidation of As(III) and the removal of total As are both closely related to the speciation of iron,^{7,30,31} it is essential to describe the compositions of Fe species in the dual anode system at different current partitions. When the current applied to the MMO anode was increased from 5 to 60 mA, the rate of O₂ production increased from 1.04 to 12.44 mM/min (SI Figure S4). Since a constant rate of Fe(II) production (12.4 mM/min) was maintained at a fixed current of 30 mA applied to the Fe anode (SI Figure S5), different ratios of production rates of O₂/Fe(II) were attained. Figure 3a shows the accumulation of Fe(II) in the dual anode system. Only the concentrations of Fe(II) in the solid phase are presented because the fractions of Fe in solution were extremely low (SI Figure S6). Both the accumulation of Fe(II) and production of Fe(III) fitted pseudo zero-order kinetics (Figures 3a and 3b, SI Table S1). The kinetic analysis of Fe(II) accumulation and Fe(III) production is provided in SI Section S1. When the current applied to the MMO anode was increased from 0 to 60 mA, the rate constants of Fe(II) accumulation ($k_{0, \text{Fe(II)}}$) decreased significantly from 11.39 to 3.19 mM/min, while the production of Fe(III) ($k_{0, \text{Fe(III)}}$) increased from 4.03 to 9.25 mM/min. Interestingly, Figure 3c reveals that the rate constants of Fe(II) accumulation negatively correlated with the currents applied to the MMO anode (eqs 4 and 5), while the rate constants of Fe(III) production positively correlated (eqs 6 and 7). The high correlation coefficients ($R^2 > 0.985$) suggest that the transformation of Fe(II) to Fe(III) can be quantitatively regulated by the currents applied to the MMO anode.

$$k_{0, \text{Fe(II)}} = -0.190 \cdot I_{\text{MMO}} + 9.4 (5\text{mA} \leq I_{\text{MMO}} \leq 15\text{mA}) \quad (4)$$

$$R^2 = 0.988$$

$$k_{0, \text{Fe(II)}} = -0.053 \cdot I_{\text{MMO}} + 6.4 (30\text{mA} \leq I_{\text{MMO}} \leq 60\text{mA}) \quad (5)$$

$$R^2 = 0.988$$

$$k_{0, \text{Fe(III)}} = 0.183 \cdot I_{\text{MMO}} + 3.1 (5\text{mA} \leq I_{\text{MMO}} \leq 15\text{mA}) \quad (6)$$

$$R^2 = 0.986$$

$$k_{0, \text{Fe(III)}} = 0.053 \cdot I_{\text{MMO}} + 6.1 (30\text{mA} \leq I_{\text{MMO}} \leq 60\text{mA}) \quad (7)$$

$$R^2 = 0.988$$

However, the correlation shows the characteristic of two stages of less than 15 mA and higher than 30 mA (Figure 3c). Under neutral pH conditions, the stoichiometric ratio of O₂ to Fe(II) for Fe(II) oxidation was reported to be between 1:4 and 1:3.^{31,45} SI Figure S7 shows that the theoretical ratios of [DO]/[Fe(II)] in the dual anode system at the currents of 15 and 20 mA equal the stoichiometric ratios of 1:4 and 1:3, respectively. As a result, an appropriate current applied to the MMO anode ranged from 15 to 20 mA in theory. O₂ production was a rate-limiting step for Fe(II) oxidation at the currents less than 15 mA but was sufficient at the currents higher than 20 mA. This deduction is consistent with the two-stage correlation in Figure 3c. The slower variation of the slope at the currents above 30 mA compared with below 20 mA is ascribed to the mass transfer limitation of O₂ dissolving. Appearance of Fe(II) at the currents higher than 20 mA (Figure 3a) was attributable to the limitations of O₂ dissolving and incomplete oxidation of the newly formed mixed Fe(II)/Fe(III) phases.

Compositions of Fe-Precipitates at Different Current Partitions.

With the increase in the current applied to the MMO anode in the dual anode system, that is, an increase in O₂/Fe(II) ratio, the color of Fe-precipitates changed from dark green at 0 mA to light orange at 30 mA applied to the MMO anode (SI Figure S8). The mineral compositions of Fe-precipitates were characterized by XRD analysis. The dark green precipitates generated at 0 mA applied to the MMO anode were identified to be carbonate green rust (Fe^{II}₄Fe^{III}₂(OH)₁₂CO₃) in a crystalline form (Figure 4), which is known as an intermediate phase for Fe(II) oxidation under neutral and alkaline conditions.^{46–49} The partial oxidation of Fe(II) is attributed to low concentrations of DO initially in SBGW. The diagnostic peaks in XRD patterns decreased dramatically at 10 mA applied to the MMO anode and completely disappeared at 30 mA. This indicates the transformation of crystalline carbonate green rust to amorphous iron minerals which cannot give identifiable peaks in XRD patterns. The observation of amorphous iron minerals is consistent with that obtained by Wan et al.,³⁹ who observed only amorphous iron oxide in iron-based electrocoagulation process with excess O₂ in the presence of high concentrations of dissolved silica. The

presence of silica likely influenced the structure of electrocoagulation precipitates by preventing FeO_6 corner-sharing linkages, leading to poorly crystalline materials that cannot be adequately characterized by XRD.^{50,51} A recent X-ray absorption spectroscopy (XAS) study revealed that the electrocoagulation precipitates generated in SBGW primarily consisted of edge-sharing FeO_6 octahedra, and As formed binuclear, corner-sharing As(V) surface complexes on the iron precipitates.⁵¹ As a conclusion, Fe-precipitates produced in the dual anode system transformed from iron oxyhydroxide as the ratios of production rates of $\text{O}_2/\text{Fe(II)}$ increased.

Electrochemical Regulation of As Oxidation and Removal.

Figure 5a illustrates the effect of current applied to the MMO anode on the oxidation of As(III). The pseudo first-order rate constant of As(III) oxidation ($k_{1, \text{As(III)}, \text{ox}}$) increased from 0.083 to 0.273 min^{-1} as the current increased from 5 to 60 mA (SI Table S1). A positive correlation was observed between the rate constants and the currents applied to the MMO anode (Figure 5b, eqs 8 and 9). Further, the rate constants of As(III) oxidation ($k_{1, \text{As(III)}, \text{ox}}$) positively correlated with the rate constants of Fe(III) production ($R^2 = 0.972$, SI Figure S9), indicating that oxidation of As(III) was mainly attributed to the reaction of Fe(II) with O_2 . This observation is in agreement with the results of many other investigations.³¹ A comparison of As(III) oxidation and Fe(II) oxidation at different current partitions (SI Table S2) reveals that the reaction stoichiometry of As(III)/Fe(II) ranged from 1:30– 1:11, which is lower than the theoretical value of 1:3.

$$k_{1, \text{As(III)}, \text{ox}} = 8.5 \cdot 10^{-3} \cdot I_{\text{MMO}} + 0.044 (5\text{mA} \leq I_{\text{MMO}} \leq 15\text{mA}) \quad (8)$$

$$R^2 = 0.968$$

$$k_{1, \text{As(III)}, \text{ox}} = 1.5 \cdot 10^{-4} \cdot I_{\text{MMO}} + 0.180 (30\text{mA} \leq I_{\text{MMO}} \leq 60\text{mA}) \quad (9)$$

$$R^2 = 0.938$$

$$k_{1, \text{As(III)}, \text{re}} = 3.3 \cdot 10^{-3} \cdot I_{\text{MMO}} + 0.029 (5\text{mA} \leq I_{\text{MMO}} \leq 15\text{mA}) \quad (10)$$

$$R^2 = 0.976$$

$$k_{1, \text{As(III)}, \text{re}} = 7.1 \cdot 10^{-4} \cdot I_{\text{MMO}} + 0.078 (30\text{mA} \leq I_{\text{MMO}} \leq 60\text{mA}) \quad (11)$$

$$R^2 = 0.977$$

Figure 5c demonstrates that the removal of As(III) also increased as the current applied to the MMO anode increased. The pseudo first-order rate constant of As(III) removal ($k_{1, \text{As(III)}, \text{re}}$) increased from 0.046 to 0.120 min^{-1} when the current applied to the MMO

anode increased from 5 to 60 mA. A positive correlation is also found between k_1 , As(III), re and the current (Figure 5b, eqs 10 and 11). There are two reasons for the removal enhancement with increasing the MMO current. Transformation of As(III) to As(V) increased with the increase in the current. In the pH range of 4–10, the negatively charged As(V) are more likely to adsorb on the positively charged Fe-precipitates than the neutrally charged As-(III),^{39,52–54} which coincides with the finding that the rate constants of As(V) removal were always higher than those of As(III) removal under identical conditions (Figure 5b). It suggests that the enhanced oxidation of As(III) with the increase in the current facilitated the removal of As. (2) Transformation of Fe(II) to Fe(III) was enhanced by increasing the MMO current. The adsorption capacity of Fe(III)-containing minerals for As is much higher than that of Fe(II)-containing minerals,^{30,45} and the amorphous Fe (hydr)-oxides are more effective in adsorbing As than the crystalline forms.⁵⁵ Evidence for this reason is the enhanced removal of As(V) with an increase in the current for O₂ production (Figure 5d). The correlations obtained above suggest that the oxidation and removal rates of As(III) can be regulated by the current in the Fe-based dual anode system.

Mechanisms of As(III) Oxidation and Removal.

A quick oxidation and removal of As(III) has been obtained in the Fe-based dual anode system. There are three possible mechanisms for the oxidation of As(III): direct oxidation by the MMO anode,⁵⁶ indirect oxidation by free chlorine produced on the MMO anode in the presence of Cl[−],³⁰ and indirect oxidation by the reactive species (•OH or Fe(IV)) generated in the reaction of Fe(II) with O₂.^{7,57,58} A series of comparison experiments were thus conducted to evaluate the relative contributions of these three oxidation pathways. The direct oxidation by the MMO anode was tested by the single anode system (MMO anode) using the Na₂SO₄ electrolyte. Results show that As(III) can be oxidized by the MMO anode, but the efficiency was lower than in the dual anode system (Figure 6). This small portion of As(III) oxidation is in part responsible for the appearance of As(V) in solution in the dual anode system. The contribution of oxidation by free chlorine was evaluated using SBGW (contains 8.2 mM Cl[−]) and Na₂SO₄ solution in the single anode system (MMO anode). The percentage of As(III) oxidation was almost the same as that using the Na₂SO₄ electrolyte, precluding the contribution of free chlorine. The negligible contribution of free chlorine to As(III) oxidation can be ascribed to the lower overpotential of oxygen evolution than chlorine evolution on the MMO anode.^{32–34}

The contribution of reactive species generated in the reaction of Fe(II) with O₂ was investigated by a set of control experiments in which specific reactions were suppressed. When excess 2,2'-bipyridine was added to protect Fe²⁺ from oxidation,^{41,59} As(III) oxidation was remarkably suppressed, approaching the direct oxidation by the anode. Therefore, a large portion of As(III) oxidation was induced by the reaction of Fe(II) with O₂. Previous work has shown that 2-propanol and As(III) react similarly with •OH (the rate constants for As(III) and 2-propanol oxidation by •OH are 8×10^9 and 1.9×10^9 M^{−1} s^{−1}, respectively).^{31,60} To examine the identity of the As(III) oxidant, 2-propanol in excess (100 mM) was added to scavenge •OH in the dual anode system, showing negligible influence on As(III) oxidation (Figure 6). This indicates that this portion of As(III) was oxidized in solution by the reactive intermediates (likely Fe(IV))^{7,31} rather than •OH, or was oxidized on

the surface of solid phase.⁵⁷ However, the partitions of As(III) and As(V) in our study support that the oxidation happened in solution. The oxidation percentages of As(III) induced by Fe(II) and O₂ were about 24% higher than the removal percentage of total As within the initial 10 min (SI Table S3). As only As(V) was observed in the solid phase (Figure 2) and the precipitates produced initially were minimal, the higher oxidation percentage validated the solution oxidation mechanism. In sum, As(III) was mainly oxidized to As(V) by the reactive intermediates, rather than [•]OH in solution phase, and was partly oxidized by the anode.

Although As(III) removal by Fe(II)/O₂ system has been widely investigated, the mechanisms of As(III) oxidation and removal at circumneutral pH is still a controversial issue. Most researchers claimed that As(III) was first oxidized in aqueous solution by Fenton reagent produced, and was then removed by sorption onto newly formed Fe (hydr)oxides (solution-oxidation/adsorption mechanism).^{7,40,41,58,61} In contrast, some others stated that the oxidation of As(III) occurred on the surface of Fe precipitates (adsorption/surface-oxidation mechanism).⁵⁷ Evidences in this study suggest that solution-oxidation/adsorption mechanism was applicable in the dual anode system.

Implications for *In-Situ* Remediation of As(III)-Contaminated Groundwater.

In this study, a novel electro-chemical process using Fe-based dual anodes is tested for As(III) oxidation and removal in synthetic groundwater. The production of Fe and O₂ can be controlled by the currents applied to the Fe and MMO anode, respectively. By varying the current partition between the two anodes, the transformation of Fe(II) to Fe(III) can be regulated, thereby controlling the transformation of As(III) to As(V) as well as the removal of total As in groundwater. The composition of Fe precipitates transformed from carbonate green rust to lepidocrocite as the inert anode current increased. These results shed light on the importance of applying an appropriate ratio of O₂/Fe(II) through *in situ* treatments to As(III)-contaminated ground-water. A conceptual model of the *in situ* application of the electrochemically induced oxidative precipitation process for As remediation is illustrated in SI Figure S10. The dual anode system is installed in the flow path of As(III)-contaminated groundwater, producing a redox increase zone for As(III) oxidation and adsorption/coprecipitation. According to the background concentration of Fe and DO in the groundwater, appropriate currents are applied to the iron and MMO anodes. The feasibility of introducing electrodes to the aquifer has been tested by many researchers in pilot, field and full scale.^{36,62} The risk of As release because of redox potential decrease can be mitigated or even eliminated by periodically performing electrolysis to produce O₂.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Conceptual model of electrochemically induced oxidative precipitation of Fe(II) by an iron-based dual anode system for the remediation of As(III) in groundwater.

Figure 2.

Arsenic transformation and partitioning in dual anode system (iron and MMO anodes). The initial concentration of As(III) was $6.67 \mu\text{M}$, the cell was closed to avoid the influence of air and a constant current of 30 mA was applied to each anode. The pH change during the reaction was less than 0.2 (SI Figure S3c).

Figure 3.

Effect of current partition on the production of (a) Fe(II) and (b) Fe(III) in the solid phase in the dual anode system, (c) correlation between pseudo zero-order rate constants of production of Fe(II)/Fe(III) and the current applied to the MMO anode for O_2 production. In (a) and (b), dots are experimental data, and solid lines represent the pseudo zero-order fitting. The current applied to the iron anode was kept at 30 mA and the initial concentration of As(III) was $6.67 \mu\text{M}$.

Figure 4. XRD patterns of Fe-precipitates generated at different currents applied to the MMO anode. The samples were taken at 60 min with different currents applied to the MMO anode and a constant current of 30 mA on the iron anode.

Figure 5.

The effect of current partition on (a) oxidation of As(III), (c) removal of total As, and (d) removal of As(V) in SBGW in the dual anode system, (b) correlation between the pseudo first-order rate constants of As(III) oxidation, total As removal, and As(V) removal and the current applied to the MMO anode. The oxidation and removal percentages are the fractions of total As occurring as As(V) and adsorbed As, respectively. A constant current of 30 mA was applied to the iron anode. The contaminant in (a) and (c) was As(III) ($6.67 \mu\text{M}$), and in (d) was As(V) ($6.67 \mu\text{M}$).

Figure 6.

Comparison of As(III) oxidation under different conditions. Unless otherwise specified, the reaction conditions were based on a 30 mA current applied to each anode and an initial As(III) concentration in SBGW of 6.67 μM .