Separation and Purification Technology 122 (2014) 225–230

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Arsenic removal in synthetic ground water using iron electrolysis

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ARTICLE INFO

Article history:
Received 23 June 2013
Received in revised form 6 November 2013
Accepted 7 November 2013
Available online 15 November 2013

Keywords:
Iron scrap
Electrocoagulation
Arsenic removal
Sustainable water treatment
Groundwater

ABSTRACT

Electrocoagulation (EC) using electrodes made from iron scrap is a novel and promising strategy for arsenic (As) contaminated ground water remediation. In synthetic groundwater, amorphous hydrous ferric oxide (HFO) precipitates formed by the rapid dissolution of a sacrificial iron scrap anode adsorbed As very effectively. A competitive adsorption model developed in this study with parameters fitted for As and other coexisting anions (phosphate and silicate) was in good agreement with the observed results. It is indicated that the maximum adsorption capacity of HFO generated in the EC system was ~0.70 mol/mol. Reducing the As concentration in water from 500 μg/L As(V) and As(III) to below 50 μg/L (local drinking water standard in Bangladesh) required ~8 mg/L and ~32 mg/L iron respectively (pH = 7.1 ± 0.1, charge dosage rate = 3 coulomb/L/min). It was found that coexisting cations (Ca^{2+} and Mg^{2+}) neutralized the HFO surface charge, promoted aggregation and resulted in greater As removal. The presence of humic acid exhibited a negligible effect on As removal and HFO precipitate settling. Jar tests showed that the turbidity of the solution could be reduced to <1 NTU with the addition of 2 mg/L Al^{3+}.

1. Introduction

Tens of millions of people worldwide are exposed to toxic concentrations of naturally occurred arsenic (As) in groundwater drinking supplies [1,2]. In Bangladesh, an estimated one third of tube wells deliver groundwater with As concentrations higher than Bangladesh's standard of 50 μg/L [3], and As accounts for one fifth of adult deaths [4]. The United States Environmental Protection Agency (EPA), the World Health Organization (WHO) and some developing countries such as China have decreased the maximum contaminant level of arsenic in drinking water from 50 to 10 μg/L [5–7].

Among the several proven technical approaches [8–10] for removing arsenic from municipal water supplies, iron-based strategy (i.e. chemical coagulation (CC) by Fe(III)) is widely accepted because of its high capacity for arsenate (As(V)) adsorption and low cost [11,12]. However, arsenite (As(III)), which is much more mobile and toxic than As(V) and accounts for up to 67–99% of the total As in groundwater [13], has orders of magnitude less affinity with Fe(III) precipitate than As(V) and other coexisting competitors such as Phosphate (P) [12,14]. Therefore, As(III) is usually pre-oxidized to As(V) using an oxidant (e.g. ferrate , chlorine, UV radiation, permanganate) to improve the removal efficiency [9,15]. Much of recent research has focused on Fenton and Fenton-like reagents such as Fe(II)/H_2O_2, ZVI/O_2, and Fe(II)/O_2 [14,16–18], since the intermediate production could oxidize As(III) to As(V), which could be easily absorbed by amorphous hydrous ferric oxide (HFO) precipitates formed afterwards. As a result, less iron is required as compared to direct adsorption [14].

Electrocoagulation (EC), based on the generation of Fe(II) through the rapid dissolution of a sacrificial Fe(0) anode, is a promising As removal strategy for drinking water as, (1) it is efficient, low cost and easy to maintain and operate with locally available materials [19,20], (2) EC introduces Fe(II)/Fe(III) [21] without introducing undesirable anions into the solution, (3) the release of H_2 (g) from the cathode [22] neutralizes the consumption of hydroxide by the Fe(III) hydrolysis and therefore likely to buffer the system better than CC, and (4) the gradual release of Fe(II)/Fe(III) in EC may produce intermediate oxidants that enhance the efficiency of As(III) oxidation as compared to CC [14,23]. In addition, using electrodes made of iron scrap, an abundant byproduct from iron planing machines, would further reduce the material cost of EC compared with using iron plates.

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http://dx.doi.org/10.1016/j.seppur.2013.11.012

Previous EC researchers have mostly focused on the effect of design and operation parameters (current density (current per electrode area, amps/cm^2), electrode distance and conductivity, pH) or water matrix (different initial As, P and Si concentrations) on As removal, and proposed some qualitative conclusions [11,12,19,22,24], which were mainly applicable only under the particular conditions in which the data were taken. In addition, the effect of typical co-existing substances such as Ca^{2+}, Mg^{2+} and natural organic matter (NOM) on HFO precipitate formation and As removal in EC systems has not been previously reported, despite the fact that these substances exhibited great effects on HFO particle size and As removal efficiency in other similar As removal methods [15,25–27]. Moreover, the separation of HFO precipitates from EC system, one of the most significant steps for drinking water treatment, has rarely been explored in the literature.

This paper reports the successful application of iron scrap electrolysis on arsenic remediation, discusses the redox reactions in the EC system, quantifies the effects of P and Si on As(V) and As(III) adsorption based on a competitive adsorption model and X-ray diffraction patterns, evaluates the effect of other co-existing substances (Ca^{2+}, Mg^{2+} and humic acid) in groundwater on As oxidation and adsorption, and finally optimizes Al^{3+} concentration and other parameters for better HFO sludge separation.

2. Experimental procedures

2.1. Chemicals and experimental set up

All chemicals were reagent grade or higher. Experiments were conducted in synthetic Bangladesh ground water (SBGW) containing 8.2 mM $NaHCO_3$, 2.5 mM $CaCl_2$, 1.6 mM $MgCl_2$, 500 μg/L As(III)/(V), 3 mg/L P and 30 mg/L Si according to British Geological Survey (BGS) [28] and previous study [14] for better comparison unless otherwise noted. Batches of SBGW were prepared by adding $NaHCO_3$, $MgCl_2$, Na_2HPO_4, and Na_2SiO_3 as solids to ultrapure 18 MΩ water in sequence under vigorous stirring. The pH was then reduced to ~8 by bubbling CO_2(g). $CaCl_2$ stock solution (5% w/v) was added subsequently [14]. As(III) or As(V) was added before adjusting pH to 7.0 by bubbling CO_2(g). All batches were aged at least 1 h after all components had been added and then sampled to verify the initial concentrations of P, Si, As(III), and As(tot) [23].

All experiments were conducted in a 1-L glass beaker. The spring-shaped iron scrap (origin steel type: 41CrAlMo74) were twist together to form solid electrodes before submerged in the SBGW and connected with the power supply by copper wires. Prior to experiments, electrodes were chemically cleaned with 1% HCl and rinsed by ultrapure water 3 times to remove the iron oxides and any passive film that may have formed. Samples taken from the reactor under various electrolysis duration were mixed for 2 h allowing complete Fe(II) oxidation and maximum As adsorption. Then, unfiltered samples were taken to determine total (dissolved and adsorbed) As (As(tot)). A second set of samples was filtered through 0.45-μm nylon filters to determine dissolved/aqueous As, P and Si.

2.2. Chemical analysis

As(III) and As(tot) concentrations were determined using a hydride generation atomic fluorescence spectrometer (AFS-230E). To selectively detect As(III), procedures were adopted from Roberts et al. [14]. P, Si and Fe(III) were determined with ICP-OES or ICP-MS for low concentrations. All the detection procedures were done right after the experiment and the relative standard deviations (RSD) for all the determinations were <10% (normally <4%). A ferrozine method was used to determine the concentrations of dissolved and total Fe(II) [29]. The suspension under various electrolysis duration in EC system were subjected to particle size detection at a 90 degree scattering angle using Dynamic Light Scattering, as well as zeta potential detection using Laser Doppler Microelectrophoresis (Zetasizer Nano ZS90, Malvern) within 10 min after sampling. The deviations between repeated experiments were <10% if error bars are not shown.

2.3. X-ray diffraction

Powder diffraction data were collected at beamline 11-ID-B of the Advanced Photon Source located at Argonne National Laboratory (Argonne, IL). Air-dried samples were packed into 3 mm diameter polyimide tubes and diffraction data were obtained with 58 keV (0.2128 Å) X-rays. Radiation scattered from the sample was collected on an amorphous silicon MAR-345 image plate detector and processed using the Fit2-D program [30]. Diffraction data from a CeO_2 standard were used to calibrate the sample-to-detector distance and tilt angle of the detector. Diffraction data were also collected for 2-line ferrihydrite prepared following the Schwertmann and Cornell recipe [31].

2.4. Jar test procedure

$Al_2(SO_4)_3$ was newly made and added to the post-electrolysis solution prior to coagulation/flocculation in a 1 L jar tester run at 200RPM for 2 min, 90RPM for 6 min and 30RPM for 9 min. The supernatant was then sampled after different settling times for As and turbidity tests.

3. Results and discussion

3.1. Role of the electrodes

Which redox reactions (e.g. the mechanism of Fe(0) dissolution and As(III) oxidation) occur on the electrodes in the EC system has been debated [21,32]. Reactions that could potentially be occurring on the electrodes are discussed in this section.

As electrodes were exposed to the water and oxygen, Fe(0) would be sacrificed through electrolysis (Eqs. (1), (2)) and natural corrosion (Eq. (3)). Fig. SI1 shows that Fe(II) (total bivalent Fe) generated in the system accounted for over 90% of the total Fe (Fe(II) + Fe(III)) while the solution was sealed and purged with N_2 during the electrolysis (DO was kept below 1 mg/L), implying that Fe(II) instead of Fe(III) was generated through the sacrifice of the anode. This conclusion is consistent with previous research with a similar ground water recipe in an EC system [21]. In addition, Fig. SI2 shows that the total iron concentration matched well (error <15%) with the value calculated using Faraday's law (Eq. (4), where m is mass (g) of iron oxidized at a specific current, I is current (A), t is the time (s), M is the molecular weight of iron, Z is the number of electrons involved, and F is the Faraday constant (96,485.3 coulomb/mole)) under both high and low charge dosage rates (24 and 3 coulomb/L/min, the corresponding currents and voltages were 0.4 A, ~24 V and 0.05 A, ~3 V). This finding is consistent with the report from Lakshmanan et al. [21]. When the electrode was submerged in the SBGW without current, ~1.1 mg/L iron was detected after 30 min exposure, indicating that natural corrosion of the electrode contributed negligibly to HFO generation.

$$Fe - 2e \rightarrow Fe(II) \quad (1)$$

$$Fe - 3e \rightarrow Fe(III) \quad (2)$$

$$Fe + O_2 \rightarrow Fe(II)/Fe(III) \quad (3)$$

$$m = \frac{I \times t \times M}{Z \times F} \quad (4)$$