



## Technical Note

# Rapid oxidation and immobilization of arsenic by contact glow discharge plasma in acidic solution



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## HIGHLIGHTS

- Preferable oxidation of As(III) was achieved in glow plasma system.
- Adding Fe(II) led to enhanced As(III) oxidation and immobilization of arsenic.
- The precipitation was amorphous ferric arsenate-bearing ferric oxyhydroxides.
- The presence of organics retarded the immobilization of arsenic.

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## ABSTRACT

Arsenic is a priority pollutant in aquatic ecosystem and therefore the remediation of arsenic-bearing wastewater is an important environmental issue. This study unprecedentedly reported simultaneous oxidation of As(III) and immobilization of arsenic can be achieved using contact glow discharge process (CGDP). CGDP with thinner anodic wire and higher energy input were beneficial for higher As(V) production efficiency. Adding Fe(II) in CGDP system significantly enhanced the oxidation rate of As(III) due to the generations of additional ·OH and Fe(IV) species, accompanied with which arsenic can be simultaneously immobilized in one process. Arsenic immobilization can be favorably obtained at solution pH in the range of 4.0–6.0 and Fe(II) concentration from 250 to 1000 μM. The presence of organics (i.e., oxalic acid, ethanol and phenol) retarded the arsenic immobilization by scavenging ·OH or complexing Fe(III) in aqueous solution. On the basis of these results, a mechanism was proposed that the formed ionic As(V) rapidly coprecipitated with Fe(III) ions or was adsorbed on the ferric oxyhydroxides with the formation of amorphous ferric arsenate-bearing ferric oxyhydroxides. This CGDP-Fenton system was of great interest for engineered systems concerned with the remediation of arsenic containing wastewater.

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## 1. Introduction

Arsenic, existing mainly as As(III) and As(V), is a toxic metalloid introduced into terrestrial and aquatic environments through natural sources and anthropogenic activities (Mohan and Pittman, 2007). In these arsenic-contaminated waters, the concentration of arsenic varies from micromolar (up to 70 μM in natural waters) to millimolar levels (Gräfe et al., 2004). Till now, to remedy arsenic containing wastewaters, a great deal of effort has been made on the widely used methods, such as coprecipitation, adsorption to different solids, ion exchange and membrane processes (Bissen and Frimmel, 2003). However, compared with As(V), As(III) is more toxic and mobile in aquatic ecosystem resulting in inferior

immobilization efficiency using above methods (Jiang et al., 2014a). Thus, pre-oxidation of As(III) to As(V) is considered highly desirable and beneficial for arsenic immobilization.

Up to now, a variety of advanced oxidation processes (AOPs) using ozone (Khuntia et al., 2014), H<sub>2</sub>O<sub>2</sub>/UVC (λ = 253.7 nm) (Lescano et al., 2011), photo catalyst (Choi et al., 2010), electro-oxidation system (Zhao et al., 2010) and sonochemical method (Neppolian et al., 2010) have been applied for As(III) oxidation. However, most of the above established technologies do not only lead to a hazard for secondary contamination with the use of chemical reagents or nano-catalysts, but need subsequent processes for the final removal of arsenic from wastewater. Thus, it is required to find more effective and environmental benign AOPs for simultaneous oxidation and immobilization detoxification of arsenic.

Electrical discharge plasma processes become outstanding for wastewater treatment owing to reagent free and environmental

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compatibility (Zhang et al., 2008; Jiang et al., 2014b). Contact glow discharge process (CGDP), as one of electrical discharge plasma processes is an unconventional electrolysis process with generating  $\cdot\text{OH}$ , which has a higher oxidation potential up to  $2.8 V_{\text{NHE}}$  ( $E^0(\cdot\text{OH}/\text{H}_2\text{O})$ ) (Chen et al., 2013). Thus it has been extensively applied for organic contaminants abatement such as pesticides, dyestuffs, pharmaceuticals and phenolic compounds (Jiang et al., 2014b). However, to the best of our knowledge, the application of CGDP for aqueous hypertoxic inorganic arsenic detoxication has not been reported.

This study unprecedentedly sought to examine the applicability of CGDP for arsenic oxidation and simultaneous immobilization of arsenic species in one process. The effects of electrical discharge and solution properties on As(III) oxidation and arsenic immobilization were investigated. Besides, the experiments of quenching active radicals and adding complexing agents were also conducted to confirm the reaction mechanism in CGDP-Fenton system.

## 2. Materials and methods

### 2.1. Materials

Sodium arsenite ( $\text{NaAsO}_2$ , 97%) was supplied by Xiya Reagent. Ammonium molybdate tetrahydrate, ethanol, antimony potassium tartrate, oxalic acid, phenol, ferrous sulfate, coumarin,  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ , NaF and  $\text{H}_2\text{O}_2$  were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents were of analytical grade and used without further purification. UltraPure water (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ) was used for all experiments. Fe(II) stock solution (50 mM) was prepared by dissolving  $\text{FeSO}_4$  in 1 mM  $\text{H}_2\text{SO}_4$  with the presence of reduced iron powder. As(III) stock solution (50 mM) were prepared by dissolving appropriate amounts of  $\text{NaAsO}_2$  in 10 mM  $\text{H}_2\text{SO}_4$ .

### 2.2. Experimental procedure

The experimental apparatus consisted of a DC high voltage power supply and a reactor, as described in Fig. S1. All working solutions were freshly prepared before use by diluting the stock solution with  $\text{Na}_2\text{SO}_4$  solution, and the pH was adjusted to the desired values with concentrated solution of NaOH (5.0 M) or  $\text{H}_2\text{SO}_4$  (5.0 M). Typically, 150 mL of solution with conductivity:  $3 \text{ mS cm}^{-1}$  was treated in the plasma reactor at 550 V/100 mA. During the reaction, the solution temperature in the reactor was controlled at  $298 \pm 5 \text{ K}$  by running tap water in the outer jacket. A magnetic stirrer was used to stir the reactor. The depth of the electrode immersed in the solution was carefully adjusted to stabilize the current and input voltage with deviation less than  $\pm 3\%$ .

At the given specific time intervals, the reaction samples were withdrawn and immediately filtrated through a  $0.45 \mu\text{m}$  membrane filter, and then the concentrations of different chemical species in the filtrate were analyzed. To determine the constituent of the precipitation in this system, the precipitation was separated from solution via vacuum filtration and then redissolved in  $\text{H}_2\text{SO}_4$  solution (pH 2.0, 100 mL) for the measurements of arsenic and iron species (Paktunc and Bruggeman, 2010). All experiments were conducted in duplicate, and the relative error was less than 3%.

### 2.3. Analysis

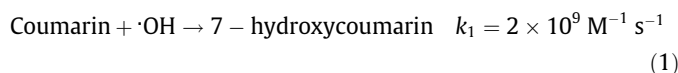
The solution conductivity and pH were measured by conductivity meter (DDS-307A) and pH meter (PHS-3C), respectively. X-ray diffraction (XRD) pattern was obtained using a Holland X'pert PRO MRD diffractometer with Cu K $\alpha$  radiation. As(V) concentration was determined using modified molybdenum-blue method (Dhar

et al., 2004), with a detection limit of  $0.03 \mu\text{M}$ . Briefly, for each 2.3 mL quenched aliquot (0.3 mL of sample + 1 mL of methanol + 1 mL of UltraPure water), 0.3 mL of the 2% HCl acidifying solution and 0.3 mL of the coloring reagent were added orderly. For total arsenic determination, 0.3 mL of the 2% HCl containing  $2 \text{ mmol L}^{-1} \text{ KIO}_3$  was used instead of 2% HCl solution. The absorbance at 880 nm was determined within 30 min using an UV–vis spectrophotometer (UV-3000, MAPADA).

$\text{H}_2\text{O}_2$  formed in the solution was determined by a spectrophotometrical method using titanyl reagent (Eisenberg, 1943). 0.3 mL of the reaction mixture and 6 mL of titanium potassium oxalate (4 mM in 0.25 M sulfuric acid) were mixed together. Then the absorbance of the resulting solution was measured at 400 nm on the UV–vis spectrophotometer.

The concentration of Fe(II) ion was spectrophotometrically determined at the wavelength of 510 nm using a modified phenanthroline method (Liu et al., 2014). The premix was prepared by adding 2 mL of sodium acetate/acetic acid buffer, 2 mL of 1,10-phenanthroline solution (5.0%), and 2 mL of water (or 2 mL of ammonium fluoride solution (10%) for total iron ion concentration determination), then followed by addition of 0.5 mL of sample solution.

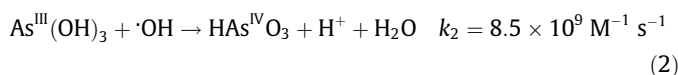
Based on Eq. (1), 1 mM coumarin was employed for probing and estimating  $\cdot\text{OH}$  in plasma system (Ishibashi et al., 2000). The fluorescence emission spectrum (excited at 332 nm) of the product 7-hydroxycoumarin (1 mL sample and 4 mL deionized water) was measured by a fluorescence spectrophotometer (F97PRO, Lengguang Tech).



## 3. Results and discussion

### 3.1. As(III) oxidation to As(V) in CGDP

In most cases, platinum is more suitable as the working anode due to its properties of corrosion resistance, high melting points and service life. However, platinum utilization greatly limits economical feasibility of CGDP for industrial applications (Jiang et al., 2014b). In present study, stainless steel wire was utilized for As(III) oxidation instead of platinum wire owing to its lower cost. Fig. 1(a) shows As(III) oxidation efficiencies using stainless steelwires with different diameters as anode and a relatively preferable As(III) oxidation rate can be obtained for 0.4 mm diameter of stainless steel wire. In this process, aqueous As(III) exists almost entirely as the nonionic  $\text{H}_3\text{AsO}_3$  at pH 4.0 (Fig. S2) and can be rapidly oxidized by OH radicals with rate constant of  $8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Eq. (2)) (Wang et al., 2014). One-electron oxidation of As(III) would involve the formation of the unstable As(IV) intermediate, which was further transformed to ionic As(V) (Fig. S2). Consequently, as electrical plasma discharge proceeded the solution conductivity rised from  $3.0$  to  $3.87 \text{ mS cm}^{-1}$  after 24 min in Fig. S3.



Energy input is a determinant factor for active species generation and plasma treatment performance. As shown in Fig. S4, fluorescence intensity of 7-hydroxycoumarin produced from coumarin reacting with  $\cdot\text{OH}$  increased as a function of treatment time and energy input. This indicates larger amount of  $\cdot\text{OH}$  were produced at higher energy input. As a consequence, As(III) oxidation efficiency was enhanced by increasing the applied energy. For

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