



## Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process

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### ABSTRACT

An electrochemical reactor was built and used to remove arsenite from water. In this reactor, arsenite can be oxidized into arsenate, which was removed by electro-coagulation process simultaneously. The reactor mainly included dimension stable anode (DSA) and iron plate electrode. Oxidation of arsenite will occur at the DSA electrode in the electrochemical process. Meantime, the iron ions can be generated by the electro-induced process and iron oxides will form. Thus, the arsenic was removed by coagulation process. Influencing factors on the removal of arsenite were investigated. It is found that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions promoted the removal of arsenite. However,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SiO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  ions inhibited the arsenic removal. And, it is observed that the inhibition effect was the largest in the presence of  $\text{PO}_4^{3-}$ . Furthermore, it is observed that the removal efficiency of arsenate is the largest in the pH value of 8. Increase or decrease of pH value did not benefit to the arsenite removal. Fourier transform infrared spectra were used to analyze the floc particles, it is suggested that the removal mechanism of As(III) in this system seems to be oxidative of As(III) to As(V) and to be removed by adsorption/complexation with metal hydroxides generated in the process.

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### 1. Introduction

Arsenic in drinking water is a worldwide concern. Arsenic is carcinogen and its ingestion may deleteriously affect the gastrointestinal tract, cardiac, vascular system and central nervous system [1]. Due to its high toxic effects on human health, recently USEPA has lowered the maximum contaminant level for arsenic in drinking water from 50 to 10  $\mu\text{g/L}$  [2]. Worldwide, up to several hundred million people consume water with arsenic above the WHO guideline of 10  $\mu\text{g/L}$  [3]. Inorganic arsenic is predominantly present in natural waters. Arsenate and arsenite are primary forms of arsenic in natural waters [4]. It is known that As(III) is more mobile in groundwater and 25–60 times more toxic than As(V) [5].

Removal of arsenic is one of the most important areas in water treatment [6]. Conventional treatment plants may employ several methods for removing arsenic from water. Commonly used processes include oxidation and sedimentation [7], coagulation and filtration [8], lime treatment, adsorption onto media [9–12], ion exchange [13], and membrane filtration. In the most affected regions large conventional treatment plants may not be appropriate. Factors of cost, acceptability, and performance must be considered. At the meantime, since As(III) is more mobile and more toxic than As(V), it is advantageous to convert As(III) to As(V). Also

due to poor As(III) removal from water by conventional processes, oxidation of As(III) to As(V) was generally performed [14–17].

Electro-coagulation (EC) is an emerging water treatment technology that has been applied successfully in treating various wastewaters [18]. In EC process, the electrodes are consumed and the coagulant is generated and precipitated. No liquid chemical is added; alkalinity is not consumed; and pH adjustment is not needed. Because EC systems typically use solid iron or aluminum anodes rather than corrosive iron or aluminum salt solution, EC units can be easily incorporated in “packaged” plants for use in remote areas or in emergency water supply treatment.

Removal of arsenic by EC process was also reported [19–22]. Gomes et al. adopted combination electrodes such as aluminum and iron in a single electrochemical cell to remove arsenate by an electro-coagulation method. The results indicated that arsenate can be partly oxidized into arsenite [21]. Kumar et al. conducted laboratory scale experiments with three electrode materials of iron, aluminum, and titanium to assess their efficiency for arsenite and arsenate removal from water. The iron electrode shows high removal efficiency for arsenic removal. And, their results indicated that the As(III) was more efficiently removed in EC than chemical coagulation, whereas, As(V) removal performance in both EC and chemical coagulation was nearly same.

In the current work, an EC reactor which consists of DSA electrodes and iron plate electrodes was built. The DSA electrodes were connected to anode and cathode by cable line to direct powder, respectively. The iron electrodes were put in the middle of the two

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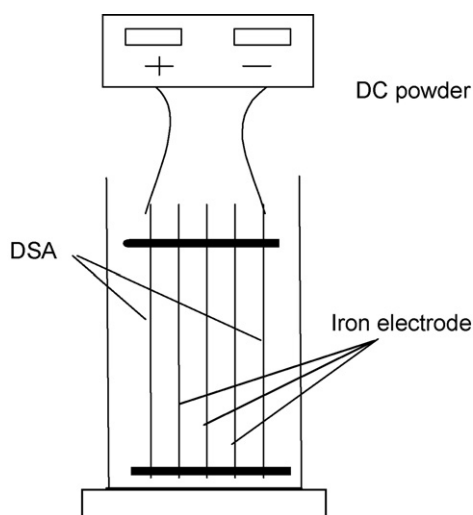


Fig. 1. Schematic of the experimental setup.

DSA electrodes. The built reactor was used to remove the arsenite. The main objective of the present study was to investigate the possible oxidation of As(III) to As(V) during DSA anode oxidation and electro-coagulation. Evaluation of the removal efficacy and mechanism of arsenate removal was also performed.

## 2. Experimental

### 2.1. Materials

All chemicals with analytical grade were purchased from Beijing Chemical Co. (Beijing, China). The stock solutions of As(III) and As(V) were prepared with deionized water using  $\text{NaAsO}_2$  and  $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$ , respectively. Arsenic working solutions were freshly prepared by diluting arsenic solutions with deionized water. The concentrations of arsenic species were given as elemental arsenic concentration.

### 2.2. Reactor and experimental procedure

Two DSA electrodes and three iron plate electrodes with the active areas of  $71.5 \text{ cm}^2$  were used to build the electro-coagulation reactor. A schematic of the experimental setup was shown in Fig. 1. The two DSA electrodes were connected to the positive and negative of the direct power by cable lines. The three iron plate electrodes were placed between the two DSA electrodes with a constant distance of 2 cm. The volume of the reactor was 1.5 and 1.0 L of arsenic containing water was added. Before each experiment, the electrodes were abraded with sand paper and then cleaned with successive rinses of water and 1N  $\text{H}_2\text{SO}_4$ . A direct current by stabilized power supply was applied by electrochemical equipment. The current was reversed each 30 min to inhibit anode passivation. At given time, a sample was taken from the effluent and the arsenic concentration was measured. Duplicate runs were carried out for each experiment. A red-orange precipitate formed during the experiments was collected in the sedimentation part of the reactor cell.

### 2.3. Analysis and characterization methods

As(III) analysis was performed using spectroscopy equipment (AF-610, Beijing Ruili Analytical Instrument Co., Ltd., China) on the basis of hybrid generation-atomic fluorescence spectrometry. Total arsenic concentrations of (As(III) + As(V)) were determined using an

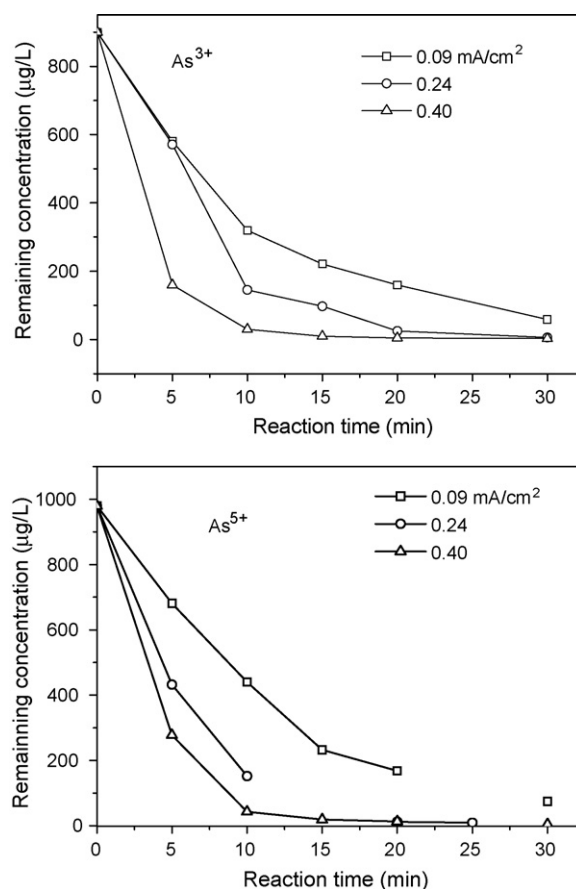


Fig. 2. Removal of As(III) and As(V) with various current densities (the initial arsenic concentration of 899 and 980  $\mu\text{g/L}$ ).

inductively coupled plasma optical emission spectrometer (SCIEX Perkin Elmer Elan mode 5000). The analytical method has been described in details in our previous work [17]. Solid-state Fourier transform infrared (FTIR) spectra were recorded by a FTIR spectrometer (Thermo Nicolet NEXUS 670 FTIR).

## 3. Results and discussions

### 3.1. Arsenite and arsenate removal

It can be seen from Fig. 2 that As(III) and As(V) can be efficiently removed within 30 min with the initial concentration of about 1 mg/L. Fig. 2 also show the arsenic concentration of aqueous phase as a function of current densities. It is shown that the removal efficiency of arsenate increase with the current densities. It is well-known that current densities not only determine the coagulant dosage rate but also the bubble production rate, size and the flocs growth, which can influence the treatment efficiency and the cost of the EC. According to the Faraday's law, since the current density increases, the efficiency of ion production on the anode increases. Therefore, there is an increase in flocs production in the solution and hence an improvement in the efficiency of arsenate removals. It is also advisable to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effects, like heat generation. Therefore, 0.24 mA/cm<sup>2</sup> is selected in the subsequent experiments. During the course of the experiment, the current with a constant value was reversed each 30 min to avoid anode passivation. Thus, the voltage value nearly remains constant.

In the removal of As(III) process, the concentration of As(V) and total arsenic was also detected. It is seen from Fig. 3 that the As(V)

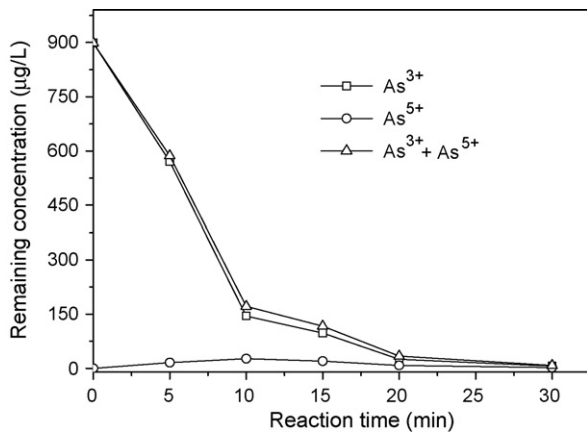


Fig. 3. The concentration variation of As(III), As(V), and As(III) + As(V) in the As(III) removal process with the initial As(III) concentration of 899 µg/L.

was produced and the concentration of As(V) increased with the reaction time and subsequently decreased with the time evolution. A possible reason for the behavior may be that at the beginning of the EC process, the rate of As(III) oxidation to As(V) is quicker than the rate of adsorption of As(V) onto hydrous ferric oxides, as initially hydrous ferric oxides would be quite less. However, as the time proceeds sufficient hydrous ferric oxides are generated and arsenic adsorbs on it. The concentrations of Fe(II), Fe(III), and total Fe were detected in the reaction process. As shown in Fig. 4, the amount of Fe(II) nearly remained constant; the amount of Fe(III) and total Fe increases with the reaction time, which were largely increased after 20 min. These results indicated that part of As(III) was oxidized into As(V) in the electrochemical reaction process. As(III) can also be removed by the EC process directly. As(V) generated via As(III) oxidation process will be removed by coagulation immediately and cannot be detected in the aqueous solution.

### 3.2. Influencing factors

Generally, groundwater contains high concentrations of coexisting ions. It is necessary to quantify the effects of the coexisting ions on the arsenate removal in the combined electro-oxidation and electro-coagulation process. Effect of ions on arsenic removal was performed by the addition of ions, respectively.

As shown in Fig. 5, phosphate caused the greatest percentage decrease in arsenic adsorption among the anions at each concentration level. The adsorption follows the selectivity pattern of

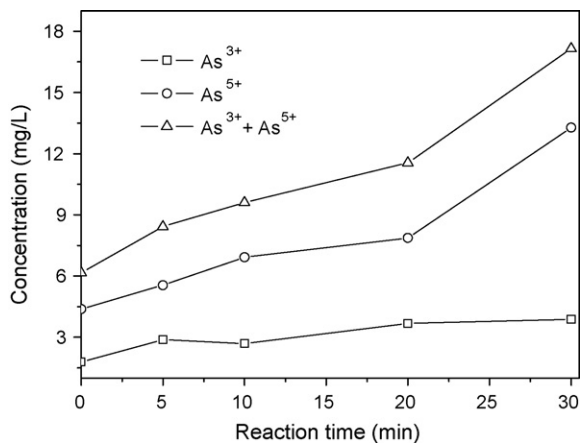


Fig. 4. Concentration variations of Fe(II), Fe(III), and total Fe (current density of 0.40 mA/cm<sup>2</sup>, pH 7.1 ± 0.1, 1 mg/L, applied bias potential of 10V).

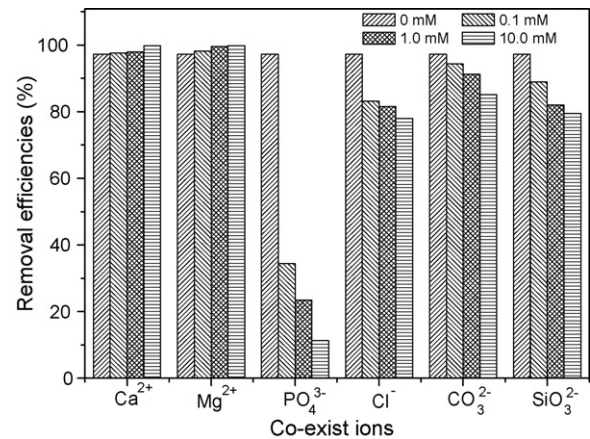


Fig. 5. Effects of coexisting ions on the removal of As(III) with the applied bias potential of 10 V (current density of 0.40 mA/cm<sup>2</sup> and reaction time of 20 min, pH 7.1 ± 0.1, 1 mg/L, applied bias potential of 10 V).

phosphate > chloride > silicate > bicarbonate. The molecular structure of phosphate ions is very similar to that of arsenic ion. Thus, the phosphate ion will compete with arsenic ion for adsorptive sites on the surface of iron oxides. By contrast, a slight increase in arsenic removal was observed in the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup>. These results were consistent with that reported by Kumar and Goel [23].

Fig. 6 shows the effects of pH on the removal efficiency of As(III) in the electro-coagulation process. The pH 8 was found to be the optimum pH for a maximum arsenic removal. When the pH value was lower or higher, the formation rate of metal-arsenate/arsenite complexes may be lower due to solubility effects than that at pH 8. Under various pH conditions, the concentrations of Fe(II), Fe(III), and total Fe in the reaction process were furthermore investigated. As shown in Fig. 7, the amount of Fe(II) increase with the decrease of pH. And, the amount of Fe(III) and total Fe increase with the solution pH up to 7.5. When the pH is furthermore increased, the concentration of Fe(III) and total Fe decrease. The concentration variation of Fe(III) and total Fe is similar with the effect of pH on As(III) removal, which indicated that the amount of iron oxides largely influence the As(III) removal. Meantime, the pH increased with the reaction evolution in the electrochemical experiments.

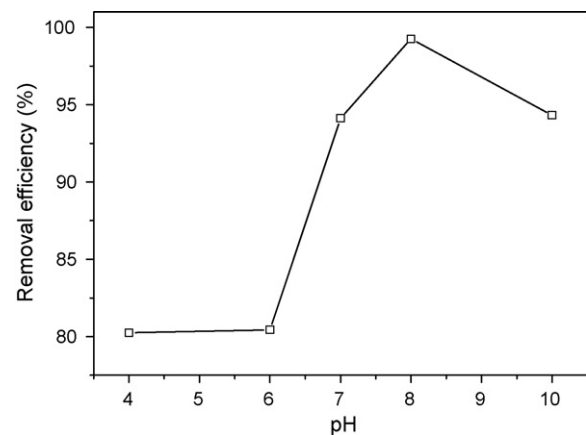


Fig. 6. Effect of pH on As(III) removal with the current densities of 0.24 mA/cm<sup>2</sup> and reaction time of 30 min (initial concentration of As(III), 1 mg/L).

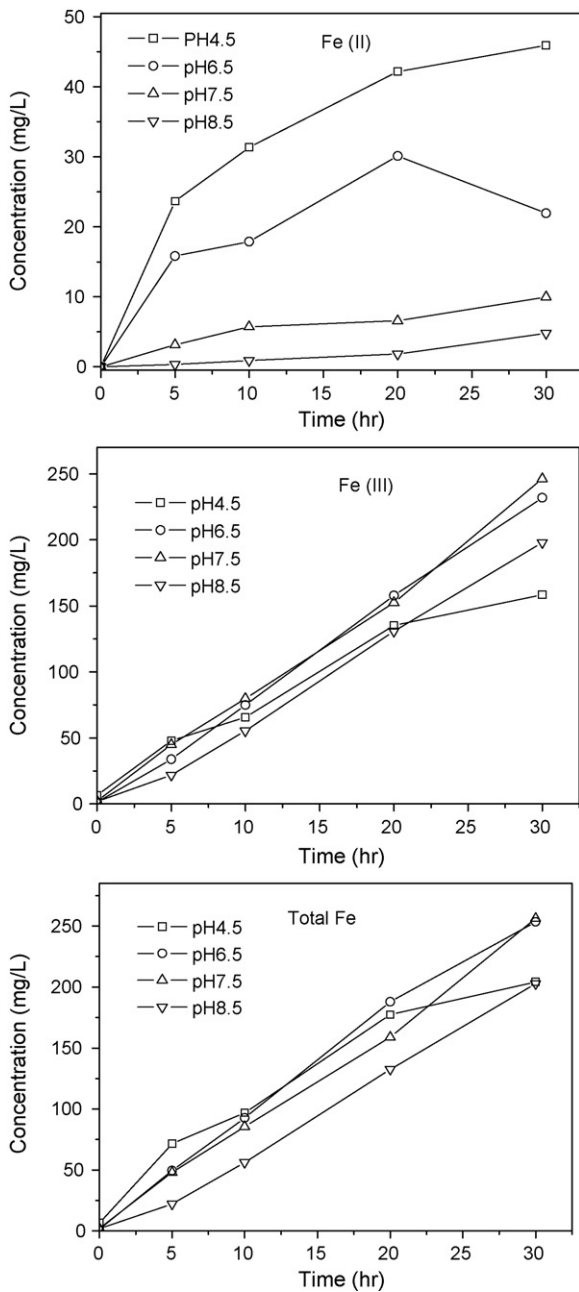


Fig. 7. Concentration variations of Fe(II), Fe(III), and total Fe with various pH (current 120 mA, current density of 2.85 mA/cm<sup>2</sup>).

### 3.3. Characterization of coagulation particles

As shown in Fig. 8, hydroxyl groups corresponding to the iron oxyhydroxides were seen at 3463, 3439, and 3424 cm<sup>-1</sup>. Hydroxyl bending and  $\gamma'(\text{OH})$  water bending vibration or overtones of hydroxyl bending were identified around 1637 cm<sup>-1</sup> and lepidocrocite bands phase was showed up at 1120 and 1023 cm<sup>-1</sup>, respectively. It is reported that the vibration of As(III)-O and As(V)-O was at 795 and 874 cm<sup>-1</sup>, respectively [24]. In our case, the vibration of As(III)-O was not observed. Instead, the vibration of As(V)-O at 874 cm<sup>-1</sup> was observed. These results furthermore confirmed the oxidation of As(III).

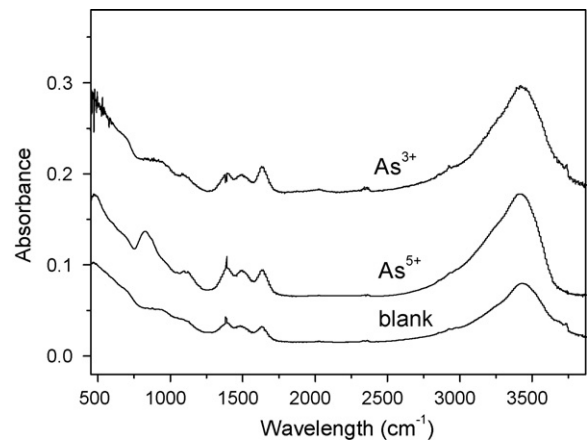


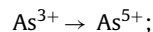
Fig. 8. FTIR spectrum analysis of the dried coagulation particles in the blank, As<sup>3+</sup> solution, and As<sup>5+</sup> solution in the electro-coagulation experiment.

### 3.4. Removal process modeling

In the current electro-oxidation and electro-coagulation system, DSA anode and cathode were stable and used to induce the electrolysis of iron plate anode. And the anode and cathode were inverted for 30 min in turn to prevent the passivation. The anode and cathode reactions can be described as follows:

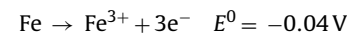
Anode reaction:

DSA anode:

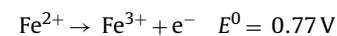
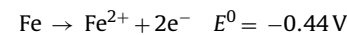


Iron plate anode:

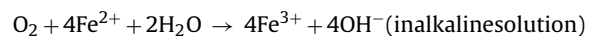
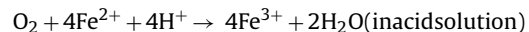
(a) Single step oxidation of Fe into ferric ion:



A two-step process where iron is firstly oxidized to ferrous ion which, depending on anode potential, then oxidizes to ferric ion:

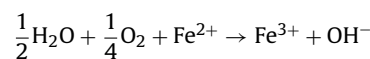


The second step would take place at the anode; however, it can also be promoted by the presence of other oxidants in aqueous phase:

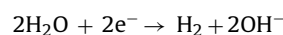


The actual occurrence of these couplings depends on the availability of dissolved oxygen.

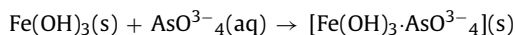
Ferrous ions are oxidized to ferric ions by oxygen in the aqueous phase:



Cathodic reaction:



Following, coprecipitation of As(V) with iron oxides occur as described by the following equation.



In the pH range of 4–10 the predominating species of As(V) present a net negative charge. On the other hand, the species of As(III) generally has no net charge. Based on this, it is expected that the As(V) removal efficiency of As(V) would be higher than that of As(III), since  $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$  or  $\text{H}_2\text{AsO}_4^-$  are adsorbed by the  $\text{Fe}(\text{OH})_3$  colloids. In order to enhance the removal rate, it would be necessary to oxidize As(III) to As(V). Arsenate anion bound to hydrous ferric oxide can form common naturally occurring arsenate minerals  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  (scorodite) and  $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  (symplectite) as the dominant solid phase. Therefore, arsenic is removed by iron species either by compound formation or by surface complex adsorption or both. Although electrochemical reduction of As(III) and As(V) may occur, it was nearly inefficient.

#### 4. Conclusions

Nearly complete oxidation of As(III) to As(V) was achieved by using DSA electrode at a constant current density. As(V) were removed by electro-coagulation processes. As(III) removal by the hydrous ferric oxides occur slightly, which further supports that oxidation in the reaction system have significant role in As(III) removal. It is noteworthy that the arsenic removal efficiency of arsenic is directly linked to the oxidation of As(III) to As(V). Combined with the FIIR results, it is confirmed that most of As(III) ions are converted to As(V).

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