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Technical Note

# Simultaneous removal of arsenite and fluoride via an integrated electro-oxidation and electrocoagulation process

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ABSTRACT

An integrated electro-oxidation and electrocoagulation system was designed and used to remove As(III) and $F^-$ ions from water simultaneously. Dimensionally stable anodes (DSA), Fe electrodes, and Al electrodes were combined into an electrochemical system. Two pieces of DSA electrodes were assigned as the outside of the Fe and Al electrodes and were directly connected to the power supply as anode and cathode, respectively. The Fe and Al ions were generated by electro-induced process simultaneously. Subsequently, hydroxides of Fe and Al were formed. Arsenic ions are mainly removed by iron hydroxides and $F^-$ ions are mainly removed by the Al oxides. At the initial concentration of 1.0 mg $L^{-1}$, most of As(III) was transferred into As(V) within 40 min at current density of 4 mA $cm^{-2}$, whereas $F^-$ ions can be efficiently removed simultaneously. The effect of the ratio of Fe and Al plate electrodes and current density on the removal of As(III) and $F^-$ was investigated. With one piece of Fe plate electrode and three pieces of Al plate electrodes, it is observed that As(III) with concentration of 1 mg $L^{-1}$ and $F^-$ with concentration of 4.5 mg $L^{-1}$ can be removed and their final concentrations were below the values of 10 μg $L^{-1}$ and 1.0 mg $L^{-1}$, respectively within 40 min. Removal efficiency of As(III) increases with the increase of solution pH. However, in the pH range of 6–7, removal efficiency of $F^-$ is the largest.

## 1. Introduction

Groundwater contamination has been a major issue due to the presence of various pollutants such as fluoride, pesticides, and arsenic. Fluoride is essential to prevent dental caries but an excess intake is detrimental to human health. The suitable level of fluoride ions in drinking water specified by the World Health Organization is 1.5 mg $L^{-1}$ (Tripathy et al., 2006). However, the concentration of fluoride ion in groundwater is higher than 1.5 mg $L^{-1}$ in many areas throughout the world. Fluoride removal techniques mainly include chemical precipitation (He and Cao, 1996), membrane processes (Tahaikt et al., 2007), adsorption (Maliyekkal et al., 2006; Wu et al., 2007), and ion exchange (Meenakshi and Viswanathan, 2007). Adsorption is effective in defluoridation, but its operation is complex. Coagulation is simple in equipment and effective in defluoridation under proper conditions, but large amounts of contaminants such as $SO_4^{2-}$ are introduced to the water, especially when the fluoride ion concentration is high. The membrane processes are known to be effective for defluoridation. However, a common problem is their poor selectivity. It is suitable for treatment water containing high content of fluoride.

Arsenic, a toxic trace element present in groundwater, is a major unavoidable threat for the life of human beings and useful microorganisms (Ghiew et al., 2009). Arsenic exists in groundwater predominantly as As(III) and As(V). As(III) is the dominant form in anaerobic groundwater, and being more toxic than As(V). As(III) is more difficult to be removed from water than As(V) because of the lack of electrostatic attraction on the solid. Commonly used processes for arsenic removal include oxidation and sedimentation, coagulation and filtration, lime treatment, adsorption onto sorptive media, ion exchange and membrane filtration (Wang et al., 2003; Berg et al., 2006; Jang et al., 2006; Boddu et al., 2008). The major disadvantage of these techniques is that they are unable to removal As(III) efficiently. Thus, oxidation of arsenite is considered a prerequisite for the treatment method to be efficient.

Recently, electrocoagulation (EC) has a more prominent role in the drinking treatment because it provides some significant advantages such as quite compact and easy operation and automation, no chemical additives, high velocities and reduced amount of sludge (Holt et al., 2002). Generally, the Fe and Al plates are used as anode materials and stainless steel is used as cathode material (Holt et al., 2002; Mollah et al., 2004). EC has been employed to perform defluoridation (Mameri et al., 1998; Hu et al., 2003). In the EC cell using Al as anode, sacrificial dissolution of aluminum gives $Al^{3+}$, which precipitates as $Al(OH)_3$ in solutions of near neutral pH (Canizares et al., 2007). $Al(OH)_3$ is further polymerized to $Al_n(OH)_{3n}$. The $Al(OH)_3$ floc is believed to adsorb $F^-$ strongly (Emamjomeh and Sivakumar, 2009). When Fe plate was used as anode in the EC process, As(V) can be efficiently removed from

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contaminated water via the co-operation between Fe and As ions (Ratna Kumar et al., 2006). However, removal of As(III) was limited by EC method.

It is known that the anode oxidation is an efficient method in removing contaminants in aqueous solution. The contaminants can be destroyed by the direct electrochemical oxidation or indirect electrochemical oxidation induced by the electrogenerated active species (Chen, 2004). The electrocatalytic oxidation and detection of As(III) has been largely investigated at platinum wire (Lown and Johnson, 1980), and platinum disc (Williams and Johnson, 1992) electrodes and more recently at platinum nanoparticles modified carbon electrodes (Dai and Compton, 2006). The oxidation reaction is likely electrocatalyzed by the formation of platinum hydroxide on the electrode surface. Recently, three kinds of electrode materials of Fe, Al, and Ti were used to remove arsenic via electrocoagulation process (Ratna Kumar et al., 2006). It is observed that arsenic removal was the highest with iron electrodes. Dimensionally stable anode (DSA) electrode is widely used due to its high stability and high efficiency. DSA electrodes prepared by the deposition of a thin layer of metal oxides onto a base metal, usually titanium, are found to have various degrees of success in the application of environmental electrochemistry.

Herein, the combination of Fe, Al and DSA electrodes in an electrochemical reactor was studied in order to remove As(III) and $F^-$ ions simultaneously. The DSA electrode was connected to the direct current (DC) power and used as anode and cathode with frequent change of their polarity. The oxidation of As(III) can be achieved on the DSA anode. Meanwhile, the dissolution of Fe and Al anodes is produced by the electro-induced process.

## 2. Experimental

An EC unit was designed and built. It consisted of a 1.0 L active-volume, electrode chamber with $4.5 \times 7.5$ cm long sheet-shaped Fe, Al and DSA electrodes. The distance between the adjacent electrodes was 2 mm. The effective surface area of each electrode was ca. 24 $cm^2$. Two DSA electrodes were put outside and connected to the power and used as anode and cathode, respectively. The diagram of the experimental equipment is given in Fig. 1. With different amount ratio, Fe and Al plate electrodes were put in the middle of the DSA electrodes. The Fe and Al electrodes had no connection to the DC source. In such condition, induced polarization took place when voltage was applied to the DSA electrodes, leading to the dissolution of Fe and Al plate electrodes. The polarity of DSA electrodes is reversed each 15 min to avoid anode passivation of Fe and Al plate electrodes. A constant current was maintained using a potentiostat in galvanostatic mode. Magnetic stirring maintained a homogeneous solution in the batch reactor. All the experiments were performed in batch mode at a temperature of 25 ± 2 °C.

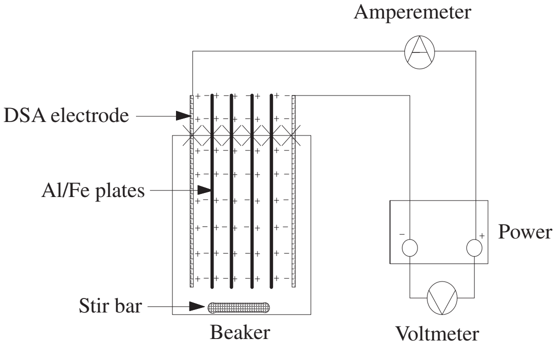

**Fig. 1.** The diagram of the experimental equipment.

A 1000 mg $L^{-1}$ fluoride stock solution was prepared by dissolving 1.1030 g NaF (analytical grade) in 500 mL distilled water. $F^-$ ions bearing solutions were prepared by diluting the stock solution to different concentrations with deionized water. Concentration of $F^-$ ions was analyzed with a $F^-$ selective electrode connected to an ion meter (IM-40S, TOA, Japan). Stock As(III) solutions of 1000 mg $L^{-1}$ were prepared according to the method described in our previous work (Zhang et al., 2007). And, analysis methods of As(III) and As(V) ions are also given in the above literature. Samples were taken for a given time from the effluent and the concentration of As(III) and $F^-$ ions was measured after filtration (0.45 μm).

The filtrate samples were analyzed in order to determine the amount of residual arsenic and $F^-$ ions. In order to examine the conversion of As(III) to As(V), the sample including water and coagulant were treated by strong $HNO_3$ and the coagulant was dissolved completely. Thus, the total As was measured.

## 3. Results and discussion

### 3.1. Removal efficiency of arsenic and fluoride ions

It can be seen from Fig. 2 that the As(III) and $F^-$ ions can be efficiently removed in the electrochemical process in the integrated reactor with three Fe plate and one Al plate electrodes under a current density of 4 mA $cm^{-2}$. The As(III) ion with initial concentration of 1 mg $L^{-1}$ was efficiently removed within 40 min. $F^-$ ion was also efficiently removed. In contrast, removal of As(III) and $F^-$ ions by individual Fe electrode or Al electrode was also performed. In these experiments, the same amount of Fe or Al plate with same area and thickness was used. Within 40 min, in the reaction system of four Fe electrodes, four Al electrodes, and three Al and one Fe electrodes, the removal efficiencies of $F^-$ ions are 8.1%, 89.0%, and 81%, respectively. Conversely, the removal efficiencies of As(III) are 100%, 7.5%, and 98%, respectively. It is concluded that As is removed by sorption on generated iron hydroxide, whereas $F^-$ is adsorbed on produced aluminum hydroxide, which further precipitate. Both processes are different.. Al metal dissolves as $Al^{3+}$ which precipitates as "$Al(OH)_3$" with minimum solubility near pH 6. Fe metal dissolves as $Fe^{2+}$, which must be oxidized to $Fe^{3+}$, but is then highly insoluble throughout the pH range of typical waste or drinking water sources. These results indicate the advantage of the combined electrodes for the removal of As(III) and $F^-$ ions.

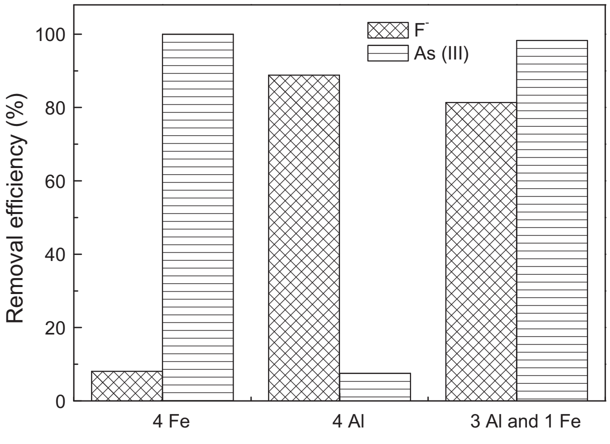

**Fig. 2.** Removal of As(III) and $F^-$ ions in electrochemical process with different electrodes (initial concentration of As(III) and $F^-$ ions: 1.0 and 4.5 mg $L^{-1}$ respectively; current density of 4 mA $cm^{-2}$; 40 min).

### *3.2. Effect of ratio of Fe to Al plate electrode on the removal of arsenic and fluoride ions*

Following, the effect of ratio of Fe to Al plate electrodes on the removal of As(III) and $F^-$ ions was investigated. As shown in Fig. 3, with the ratio of Fe plate to Al plate electrodes decreases, the removal efficiency of $F^-$ ions increases. The effect of ratio of Al plate to Fe plate electrodes on the As(III) removal is not obvious. It is suggested that the generated iron hydroxides were enough for the removal As(III) with one iron plate in the electrochemical process. In the case of the ratio of Fe to Al of 1:3, the As(III) and $F^-$ ions can be simultaneously removed within 40 min. Thus, the ratio of Fe to Al was selected as 1:3 in the subsequent experiment.

### *3.3. Effect of current density on the removal of arsenic and fluoride ions*

The effect of current density on the removal of As(III) and $F^-$ ions were investigated. The initial concentration of As(III) and $F^-$ ions was 1 mg $L^{-1}$ and 4.5 mg $L^{-1}$, respectively. It can be seen from Fig. 4 that removal rate of As(III) and $F^-$ ions increase with the increase of current density in the electrochemical process. The effect on $F^-$ ions removal is larger than that on As(III) removal. It is suggested that the amount of produced iron hydroxides was enough for As(III) removal with initial concentration of 1 mg $L^{-1}$. The removal efficiency of $F^-$ ions increased with the increase of current density, which can be induced by the increased amount of Al coagulants and Al hydroxides.

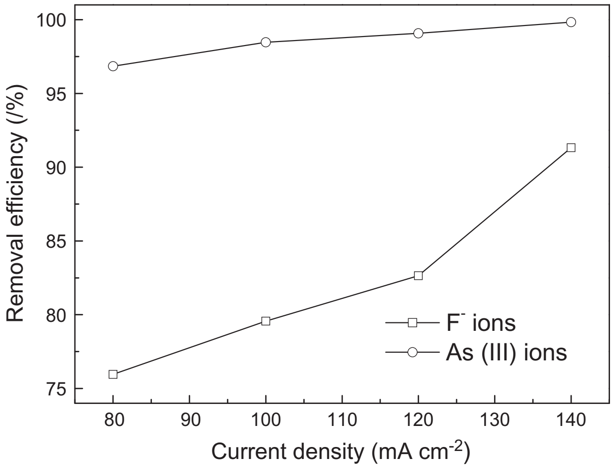

**Fig. 4.** Effect of current density on the removal of As(III) and $F^-$ ions in electrochemical process (initial concentration of As(III) and $F^-$ ions: 1.0 and 4.5 mg $L^{-1}$ respectively; 40 min).

### *3.4. Effect of pH on the removal of arsenic and fluoride ions*

It is observed from Fig. 5 that there is nearly no significant effect of pH on arsenic removal. In the examined pH range, all the removal efficiency was over 95%, which is consistent with the results reported by Ratna Kumar et al. (2006). It is also noticed that the removal efficiency of $F^-$ ions increases with increasing pH. The hydrolysis of $Fe^{3+}$ will speed up and more Fe coagulant will be produced at high pH, which will be responsible for the higher efficiency of As(III) removal.

A different variation trend was observed for the $F^-$ ions removal with the variation of solution pH. When the initial pH value increased from 5 to 6, the $F^-$ ions removal rate increased. By increasing the initial pH from 6 to 7, the $F^-$ ion removal rate decreased slightly. Furthermore, the removal rate largely decreased when the pH is larger than 7. $F^-$ ion removal can be taken as the ion exchange of $F^-$ with $OH^-$ in $Al(OH)_3$. When $OH^-$ concentration decreases, the ion exchange equilibrium shifts.

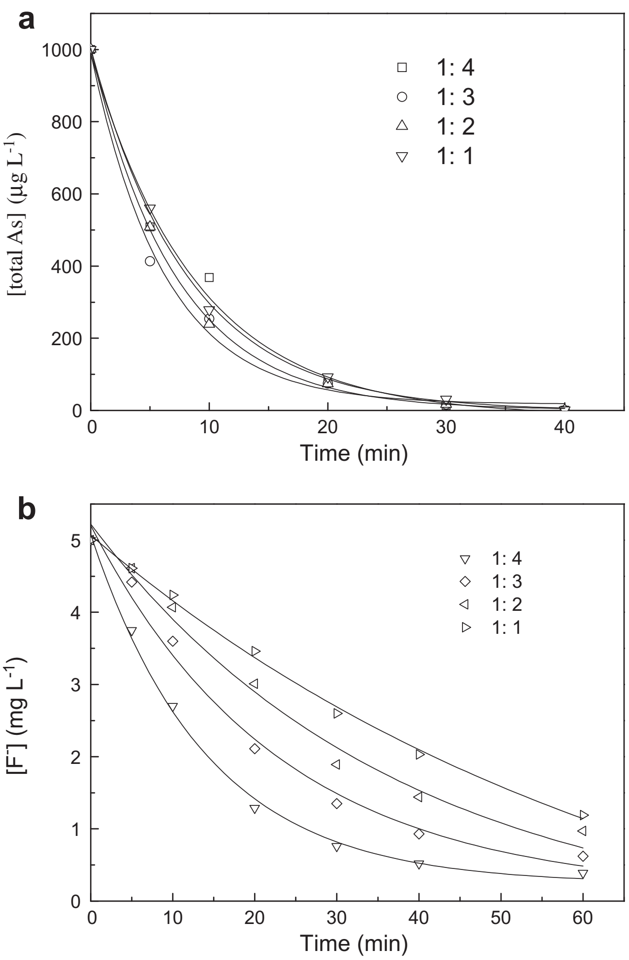

**Fig. 3.** Effect of the ratio of Fe to Al electrodes on the removal of As(III) (a) and $F^-$ ions (b) in electrochemical process (initial concentration of As(III) and $F^-$ ions: 1.0 and 4.5 mg $L^{-1}$ respectively; current density of 4 mA $cm^{-2}$; 40 min).

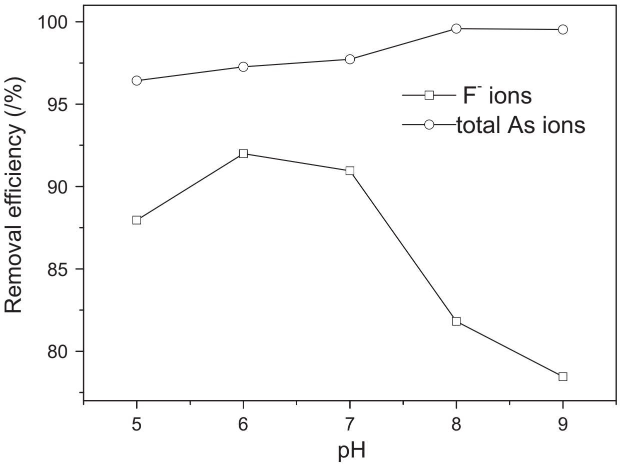

**Fig. 5.** Effect of solution pH on the removal of As(III) and $F^-$ ions in electrochemical process (initial concentration of As(III) and $F^-$ ions: 1.0 and 4.5 mg $L^{-1}$ respectively; current density of 4 mA $cm^{-2}$; 40 min).

Additionally, the solubility of total Al increases as pH increases. This explains why low pH value is beneficial to $F^-$ removal (Zhu et al., 2007).

## 4. Conclusions

It has been demonstrated that As(III) and $F^-$ ions can be efficiently removed in the integrated electro-oxidation and EC reactor simultaneously with the ratio of Fe to Al plate electrode of 3:1 and optional current density of 4 mA $cm^{-2}$. Most As(III) was oxidized to As(V) in the reaction process. The oxidation is induced by electro-oxidation at the DSA electrode. The optimal pH range is 5–7 for the efficient removal of As(III) and $F^-$ ions. The experimental results indicated that the electro-oxidation and EC process using combined Fe, Al and DSA electrodes can be used to efficiently remove As(III) and $F^-$ ions simultaneously.

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