High concentration of arsenate removal by electrocoagulation with calcium

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ABSTRACT

The effect of calcium on arsenate removal by electrocoagulation with aluminum electrode was investigated in this study. The addition of calcium salt dramatically improved the removal efficiency of As(V). The residual arsenate decreased from more than 0.5 mM to less than 0.05 mM after the addition of stoichiometrically equivalent amounts of calcium salt (γ = 1). The arsenate cannot be completely removed if the γ is under 1. If the γ is over 1, the calcium concentration rose and lead to the increase of hardness. The calcium ions can neutralize the negative surface charges of the precipitate and increase the binding energy of As–O. The addition of calcium also prevented the formation of deposit layer on anode surface which caused an increase of applied potential and decrease the concentration of dissolve aluminum.

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1. Introduction

Epidemiological studies have shown the association between the intake of inorganic arsenic and the increase of risk of various diseases [1–5]. The World Health Organization (WHO), therefore, established a regulation for arsenic in drinking water of 10 ppb in 1993 due to its high toxicity. The United States and the European Union also lowered their standard of arsenic in drinking water from 50 ppb to this level.

Both natural processes (volcanic eruption and weathering) and anthropogenic activities (mining, agricultural and hydrometallurgical and other industrial processes) may liberate arsenic to the environment. High arsenic concentration may be found in the wastewater from the copper smelting [6], the gallium arsenide polishing process [7], the manufacture of light emitting diodes (LEDs) [8] and the processing of arsenic-bearing ores [9]. Because of the high toxicity of arsenic, how to treat these kinds of wastewater is an important issue for environmental engineers. Many technologies such as coagulation [10–12], ion exchange [13], adsorption of active alumina [14] or other absorbents [6], electro-dialysis [15] and reverse osmosis [16] can be used to remove arsenic

[17]. However, the arsenic concentration in these kinds of wastewater is extremely high (may be over 500 mg/L). Therefore, conventional methods for arsenic removal are not practical and economical for treating this kind of wastewater.

To avoid the generation of high toxic H_3As gas, all the arsenic in wastewater should be pre-oxidized to As(V) species. Currently, the main way to treat the high As(V) contaminated wastewater is through calcium precipitation. Calcium arsenate, arsenate-hydroxy-apatite or other calcium–arsenate-hydroxide precipitates form when calcium salt is added to an alkaline solution as shown in the following reaction [18–20]:

$$3Ca^{2+}_{(aq)} + 2AsO_4^{3-}{}_{(aq)} \rightarrow Ca_3(AsO_4)_{2(s)} \qquad K_{sp} = 1.1 \times 10^{-21} \qquad (1)$$
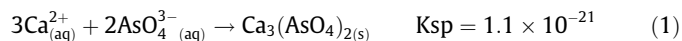
The precipitate ($Ca_3(AsO_4)_{2(s)}$), however, is soluble at near neutral pH because the major As(V) species is $HAsO_4^{2-}$ or $H_2AsO_4^-$ rather than AsO_4^{3-} if pH is under 11 [21]. Thus, large amounts of acid and base are consumed to adjust the pH of wastewater before and after calcium precipitation. Moreover, the particle size of $Ca_3(AsO_4)_{2(s)}$ without aging ranges from 0.4 to 4 μm and is very difficult to settle [8].

An electrochemical method (Electrocoagulation, EC) has been used to remove arsenic from water [12,15,22–33]. It can effectively remove arsenic in solution and reduce arsenic concentration to 10 μg/L which is the level recommended by World Health Organization (WHO) [12,30–33]. The electrocoagulation can keep the pH of solution at neutral or alkaline condition and prevent the increase

of solubility of the arsenate compounds from the reduction of pH caused by the hydrolysis of metal salts during the coagulation process [12,33].

Metal ions such as Fe^{3+} or Al^{3+} are released from anodes when sacrificial electrodes (iron or aluminum) are used (Eq. (2)):

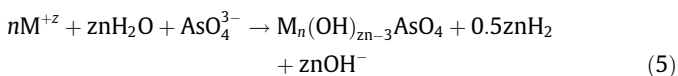$$M \rightarrow M^{+z} + ze^- \tag{2}$$

The cations than coprecipitate with arsenate and hydroxide ions as shown in reaction 3:

$$nM^{+z} + (zn - 3)OH^- + AsO_4^{3-} \rightarrow M_n(OH)_{zn-3}AsO_4 \tag{3}$$
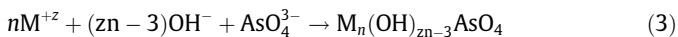
Hydrogen gas generates simultaneously from cathode during the EC process and causes the liberation of hydroxide ions (Eq. (4)):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4}$$

Combining reactions 2–4 derives reaction 5:

$$nM^{+z} + znH_2O + AsO_4^{3-} \rightarrow M_n(OH)_{zn-3}AsO_4 + 0.5znH_2 \\ + znOH^- \tag{5}$$

According to reaction 5, the more arsenate ions are removed, the more OH^- ions are released. If the initial arsenate concentration is not too high the increase of pH is acceptable and can prevent the increase of solubility of the coprecipitates. If the initial arsenate concentration is high, the released OH^- ions may lead to the dissolution of the coprecipitates. The arsenic removal efficiency, therefore, decreases with the increase of initial arsenic concentration [15,33].

Both the adsorption with metal oxide and the coprecipitation with EC process involve the ligand exchange reaction of metal hydroxides [34]. Addition of calcium salts enhances the arsenate adsorption onto aluminum or ferric hydroxides [35–37]. The addition of calcium, therefore, may increase the arsenate removal in the EC process.

This study tried to enhance the As(V) removal of high arsenic contaminated semiconductor wastewater using the EC process by the addition of calcium (EC/CA process). To avoid the variation of the water quality of wastewater, synthetic arsenic solution was used. The effect of calcium dosage and initial As(V) concentration on the arsenic removal was investigated. Although the As(V) removal efficiency with iron electrode is higher than that with aluminum electrode, aluminum electrodes were employed because iron is more corrodible and the iron-arsenic precipitants may cause oxidative hepatic damage and lead to the increase of toxicity for human [38].

2. Material and method

2.1. EC experiments

Experiments were conducted in a bipolar batch reactor with seven aluminum electrodes connected in parallel, as shown in the authors' pervious work [39–41]. In bipolar EC system, only the outer electrodes are connected to the power source and no interconnections between the sacrificial electrodes. This cell arrangement has the maximum ratio of the electrode area to volume of the treated water and is easy for maintenance during operation [42]. The continuous EC process, therefore, usually use this arrangement. Aluminum electrodes were used because the iron electrode may produce the ferrous ions (Fe^{2+}) and need to add hypochlorite to oxidize them [31].

A constant current ($I = 0.6$ A) was maintained using a potentiostat in intensiostat mode. The volume (V) of the solution in each batch was 1 l. Magnetic stirring at 400 rpm maintained a homogeneous solution in the batch reactor.

Charge loading (Q_e), which can be calculated by Eq. (6), has been considered an important design parameter for the EC process [30,41,43]:

$$Q_e = \frac{nIt}{V} \tag{6}$$

where n is the number of cells, I is the current (A), t is the reaction time and V is the volume of reactor (L).

According to Faraday's Law, the aluminum dosage of the EC process can be calculated by the following equation:

$$[Al^{3+}] = \varepsilon_c \frac{Q_e}{ZF}, \qquad Z = 3 \text{ for Al(III)} \tag{7}$$

where ε_c is the current efficiency (%), F is Faraday's constant ($F = 96,487$ C mol^{-1}) and Z is the valence of metal ions ($Z = 3$ for aluminum ions). Whereas the As(V) is removed by aluminum ion. The amount of As(V) removal should be proportional to the charge loading. The relation of As(V) removal and charge loading was also evaluated in this study. The As(V) removal in EC and EC/CA systems was compared based on the same Q_e.

All chemicals used in this study were reagent grade. Synthetic arsenic solutions were prepared by mixing various amounts of sodium-hydro-arsenate (NaH_2AsO_4) in 1 l D.I. water to simulate the semiconductor wastewater after oxidation with various initial arsenic concentrations. Various amounts of calcium chloride salts were added to the synthetic solutions to investigate the effects of calcium addition. The chloride concentrations in all experiments were kept at 20.0 mM by adding different amounts of sodium chloride. The conductivity in the synthetic arsenic solution of every experiment was about 3500 μS/cm.

2.2. Sample preparation and analysis

Samples were extracted every 5 min and then immediately filtrated through a 0.2 μm mixed cellulose ester membrane. The arsenic, calcium and aluminum concentrations were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 2000DV, Perkin Elmer). After each reaction the total concentrations of the three elements in the sludge obtained from a digested sample (Standard method, Section3030E) were measured by the same instrument. All analyses were conducted in duplicate for reproducibility of data, and all of the data in figures and tables were the average one.

The sludge was separated by centrifugation after EC reaction and then dried by lyophilization. FTIR analysis were carried out by the monicolate FT-IR spectrometer with OMNIC software using potassium bromide pellets (sample:KBr = 1:50) to investigate the variation of binding energy. The spectra were recorded in the range of 4000–400 cm^{-1} with 2 cm^{-1} resolution. Each specimen was scanned 64 times. An Orion-2101 pH meter was used to measure pH. The zeta potential of particles in different solutions was analyzed by an electroacoustic spectrometer (Dispersion Technology, DT-1200).

3. Results and discussion

3.1. Effect of the molar ratio of arsenic and calcium

To examine the effects of the amount of calcium addition on arsenic removal by the EC process, the molar ratio of calcium to arsenic (γ) was defined by the following equation:

$$\gamma = \frac{[Ca^{2+}]_0}{[As(V)]_0} \tag{8}$$

where $[Ca^{2+}]_0$ is the initial calcium concentration and $[As(V)]_0$ is the initial arcenate concentration.