



## Arsenite and arsenate removals from groundwater by electrocoagulation using iron ball anodes: Influence of operating parameters



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### ABSTRACT

Removals of arsenite (As(III)) and arsenate (As(V)) from groundwater by a cylindrical packed-bed electrocoagulation (EC) reactor using Fe ball anodes were investigated in this study. Effects of some operating parameters such as initial pH ( $pH_i$  of 6.5–8.5), applied current ( $i$  of 0.075–0.30 A), initial concentration ( $C_o$  of 30–200  $\mu\text{g/L}$ ), diameter of iron ball ( $d_p$  of 5.0–10.0 mm), height of anode balls in the reactor ( $h$  of 2–8 cm) and airflow rate ( $Q_{\text{air}}$  of 0.0–6.0 L/min) on the removal efficiency of arsenic were evaluated. The removal efficiency of arsenic decreased with increase in concentrations of arsenic from 30 to 200  $\mu\text{g/L}$  while its removal efficiency increased with increase in operating time, applied current, height of anode in the reactor, and airflow rate. The optimum operating conditions for effective As(III) and As(V) removals to meet the permissible level of arsenic effluent concentration of < 10  $\mu\text{g/L}$  were determined as 0.3 A, 14 min of EC time for As(III) and 12 min for As(V), a  $pH_i$  of 7.5,  $C_o$  of 200  $\mu\text{g/L}$ ,  $d_p$  of 7.5 mm,  $h$  of 7.5 cm and  $Q_{\text{air}}$  of 6 L/min, respectively. Arsenic removal efficiency, energy and electrode consumptions, operating cost, charge loading and arsenic removed capacity per amount of electrochemically generated Fe at the optimum conditions were also calculated as 96.0%, 1.442 kWh/ $\text{m}^3$ , 0.0752 kg/ $\text{m}^3$ , 0.612  $\$/\text{m}^3$ , 252 C and 2.55  $\mu\text{g}/\text{mg Fe}$  (0.762  $\mu\text{g}/\text{C}$ ) for As(III) removal and 95.8%, 1.386 kWh/ $\text{m}^3$ , 0.0628 kg/ $\text{m}^3$ , 0.546  $\$/\text{m}^3$ , 216 C and 3.05  $\mu\text{g}/\text{mg Fe}$  (0.887  $\mu\text{g}/\text{C}$ ) for As(V) removal, respectively.

### 1. Introduction

Elevated concentrations of arsenic in groundwater and other natural waters with geogenic sources occur in many areas around the world [1–3]. Processes of arsenic mobilization from sediments may vary depending on the hydro-geochemical characteristics of the aquifer, the presence of oxidized and/or reduced mineral phases and the cofactors associated with arsenic-rich solid phases [3]. Long term exposure to high levels of arsenic can cause a wide range of health effects including skin lesions such as hyperkeratosis and pigmentation changes, circulatory disorders, diabetes and cancers of bladder, lung, kidney and skin [4,5]. Thus, the World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) have revised the guideline for arsenic maximum contaminant level (MCL) in drinking water from 50 to 10  $\mu\text{g/L}$  [6,7]. The arsenic threat also affects many countries including Argentina, Bangladesh, Cambodia, Chile, China, Hungary, India, Japan, Laos, Mexico, Myanmar, Nepal, Turkey, USA, Vietnam, etc. [2,3,8].

Naturally elevated arsenic concentrations are common in the West-Anatolia of Turkey, particularly in geothermal waters and groundwaters in borate mines areas. Recently, numerous cases of natural arsenic pollution in these waters have been reported namely, Igdeköy (10–10,700  $\mu\text{g/L}$ ) and Dulkadir (300–500  $\mu\text{g/L}$ ) villages of Kütahya-Emet [9–11], Kütahya-Hisarçik (10–3000  $\mu\text{g/L}$ ) [12], Balıkesir-Bigadiç (33–911  $\mu\text{g/L}$ ) [13], Kütahya-Simav Plain (0.5–562  $\mu\text{g/L}$ ) [14], İzmir-Balçova Plain (1–182  $\mu\text{g/L}$ ) [15], and Eskisehir-Kırka (7–150  $\mu\text{g/L}$ ) [16,17].

The USEPA proposed the best available technologies (BAT) for arsenic removal to achieve compliance with MCL from small water facilities such as ion exchange (95%), activated alumina (95%), reverse osmosis (> 95%), modified coagulation/filtration (95%), modified lime softening (90%), and electrodialysis (85%). In addition, iron oxide-coated sand, manganese green sand filtration, iron filings, and granular ferric hydroxide were classified as emerging technologies by USEPA [18,19]. Drawbacks of these arsenic removal technologies forced municipalities and various industries to search for effective alternative

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treatment technologies for the arsenic removal, ideally by electrochemical methods [20]. Electrocoagulation (EC) is one of the most efficient technologies for removal of both As(III) and As(V) from contaminated water [21–23]. Recently, Amrose et al. [24] reported that real groundwater samples with arsenic concentrations of 80–760 µg/L from Bangladesh and Cambodia in 100 and 600 L of EC reactors (named as ECAR) were reduced to < 10 µg/L. The operating cost was varied in the range of 0.22–1.04 \$/m<sup>3</sup>. The EC is a very promising treatment process for the arsenic removal because of some advantages such as no addition of chemicals or regeneration, a shortened reactive retention time, higher removal efficiency, no pH adjustment, no chemical requirement for pre-oxidation of As(III) to As(V), simplicity in operation, compact treatment facility, and relatively cost-effectiveness [20,21,25].

The most important parameters affecting removal of arsenic from waters were current density, reaction time, arsenic species, type and shape of electrodes, geometry of electrodes and airflow rate in the EC process. Plate and rod types of Al or Fe anode electrodes were generally used in the EC reactors and these had some disadvantages namely, its being time consuming (changing and maintenance) and accommodating a limited number of plate and rod types of electrodes with low surface areas. Therefore, an air-injected EC reactor was used to eliminate the above problems. The new EC reactor using Fe ball electrodes was reported in earlier studies [21,26]. The new EC reactor had specifications of compactness, ease of use, accommodating more anode electrodes with higher surface areas, and providing better removal efficiency.

In this study, As(III) and As(V) removals from the groundwater by a cylindrical packed-bed EC reactor using iron ball anodes were performed to determine the optimum operating conditions. For that reason, effects of operating parameters such as initial pH, applied current, initial arsenic concentration, diameter of Fe ball anode, Fe ball anode height in the EC reactor, airflow rate and operating time on the arsenic removal efficiencies were evaluated. Energy, electrode consumptions, and operating cost for the removal were also calculated.

## 2. Material and methods

### 2.1. Characterization of groundwater

Real groundwater was obtained from a well situated in the province of Kocaeli in Turkey and stored in five tones high-density polyethylene container. All chemical species present in groundwater were determined with standard methods [27]. The concentrations of cations, Ca, Mg, Mn, Na, and Si by ICP optical emission spectrometry (Perkin-Elmer ICP-OES Optima 7000 DV) and anions such as nitrate, sulphate, and chloride by ion chromatography (Shimadzu HIC-20A) were measured in the groundwater. The groundwater was characterized as a pH of 7.6, conductivity of 1055 µS/cm, dissolved organic carbon of 5 mg/L, total alkalinity of 260 mg CaCO<sub>3</sub>/L, total hardness of 418 mg CaCO<sub>3</sub>/L, total Mn of 0.006 mg/L, total silica of 10.18 mg/L, total sulphate of 94.2 mg/L and total nitrate of 24.0 mg/L. Fe, Al, P, and F in the real groundwater were not detected. The groundwater containing arsenic concentration of 30–200 µg/L was prepared daily using sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub> × 7H<sub>2</sub>O) or sodium arsenite (NaAsO<sub>2</sub>) salts.

### 2.2. Experimental setup

A batch mode of the cylindrical packed-bed EC reactor (acrylic electrochemical cell with a total volume of 2041 cm<sup>3</sup>; 100 mm in diameter and 260 mm in height) was used for removal of the groundwater containing arsenic in Fig. 1. An iron (Fe) ball as anode and cylindrically porous titanium (Ti) as cathode (70 mm in diameter, 255 mm in height and 3 mm in thickness) were used in the EC reactor. The groundwater sample (0.95 L) containing As(III) or As(V) was placed in the EC reactor (Fig. 1). The anode and cathode were connected to a digital DC power supply (Agilent 6675A; 120 V and 18 A). An air-fed diffuser was

attached underneath the reactor and the air was fed continuously at different rates in the reactor to maintain uniform shaking. The electrical current was adjusted to a desired value by the DC power supply and the experimental operation was started. The samples were periodically taken from the reactor during the EC process and then analysed.

### 2.3. Analytical methods

The arsenic concentration in the groundwater samples was determined by an atomic absorption spectrometer (Perkin-Elmer SIMAA 6000 AAS) equipped with a manual hydride generator (MSH-10, PerkinElmer) at 188.9 nm wavelength. The detection limit of this study was 0.10 µg/L and analysis of the duplicates was within 2% of errors. pH of the solutions was adjusted by 0.10 N NaOH or 0.10 N H<sub>2</sub>SO<sub>4</sub>. pH and conductivity of solutions before and after the EC process were measured by a pH meter (Mettler Toledo Seven Compact) and a conductivity meter (Mettler Toledo Seven Go), respectively.

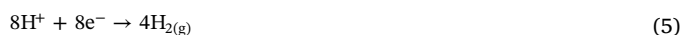
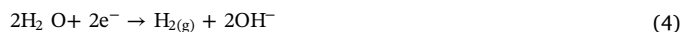
## 3. Mechanism of arsenic removal in the EC process

When a charge is applied through an external power source, the electrolytic dissolution of sacrificial anode produces the cationic monomeric species according to the following Eqs. ((1)–(3)):

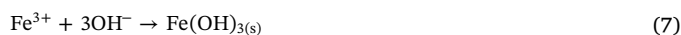
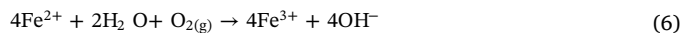


Fe(II) forms highly reactive oxidizing species [Fe(IV)] during oxidation which can oxidize As(III) to As(IV) [28]. This affects oxidation of Fe(II) and effective Fe(IV) utilization such as pH, dissolved oxygen for removal of arsenic.

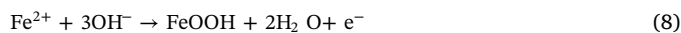
The increase in pH during the EC is primarily attributed to the increase in hydroxyl ion concentration in solution resulting from reduction of water at the cathode (Eqs. (4) and (5)).



The rate of the oxidation depends on the availability of dissolved oxygen (Eq. (6)). Typically at the cathode, the solution becomes alkaline with time. The applied current forced hydroxyl ion migration towards the anode favors ferric hydroxide formation (Eq. (7)). Fe<sup>2+</sup> ions released from anode are gradually hydrolyzed and form Fe(OH)<sub>3(s)</sub>. Thus, the removal of arsenic species from solution is sorption onto the freshly precipitated Fe(OH)<sub>3(s)</sub> particles or flocs



Iron is dissolved giving rise to ferrous ions and its oxidation occurs in the following reaction.



Ferric ions generated by electrochemical oxidation of iron electrode may form monomeric species with respect to pH of the medium, Fe(OH), and polymeric hydroxyl complexes such as Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Fe(OH)<sub>4</sub><sup>-</sup>, Fe(H<sub>2</sub>O)<sub>2</sub><sup>+</sup>, Fe(H<sub>2</sub>O)<sub>5</sub>(OH)<sup>2+</sup>, Fe(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub><sup>+</sup>, Fe(H<sub>2</sub>O)<sub>8</sub>(OH)<sub>2</sub><sup>4+</sup>, and Fe<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>(OH)<sub>4</sub><sup>2+</sup>. These iron hydroxides/polyhydroxides compounds (HFO) have strong affinity for arsenic species. Generally FeOOH produced in the EC has an isoelectric pH of about 7.0. Above the isoelectric point, both arsenic species and FeOOH surface are negatively charged and adsorption is less favorable [21,26]. Hydrous ferric oxides such as amorphous ferric hydroxide, ferrihydrite, lepidocrocite, and goethite strongly sorb both As(V) and As(III) [29–31]. Iron(III) oxyhydroxides can also participate in the

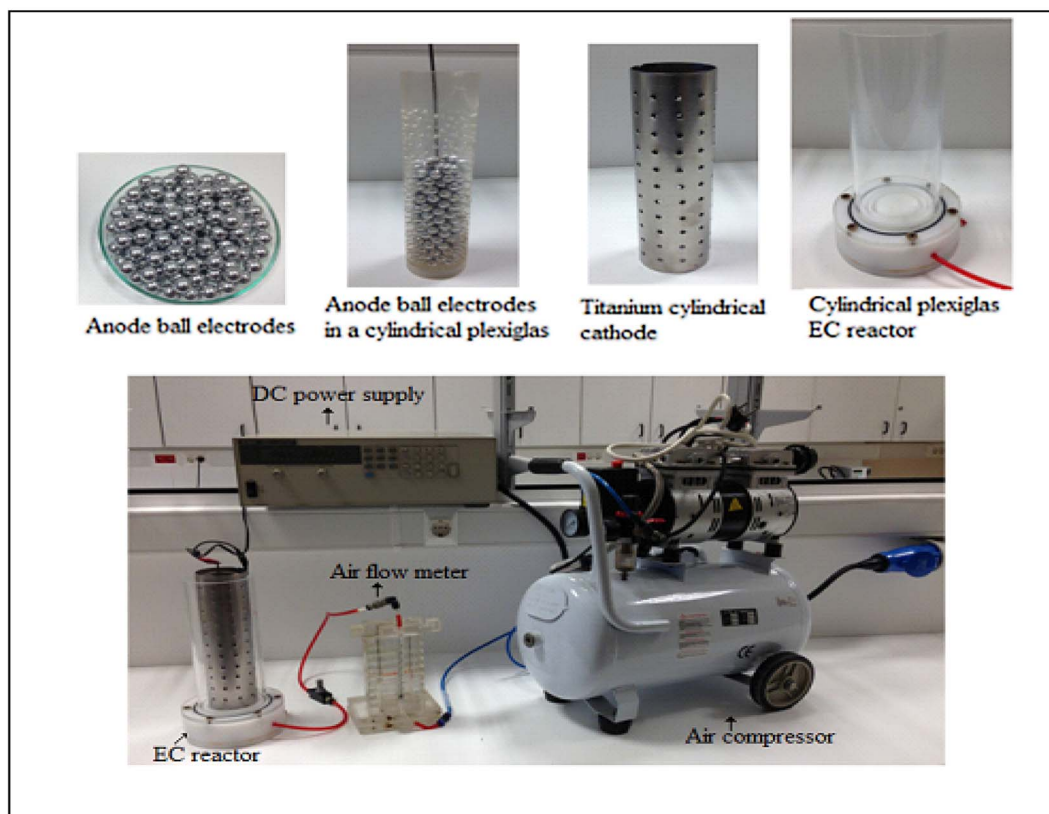
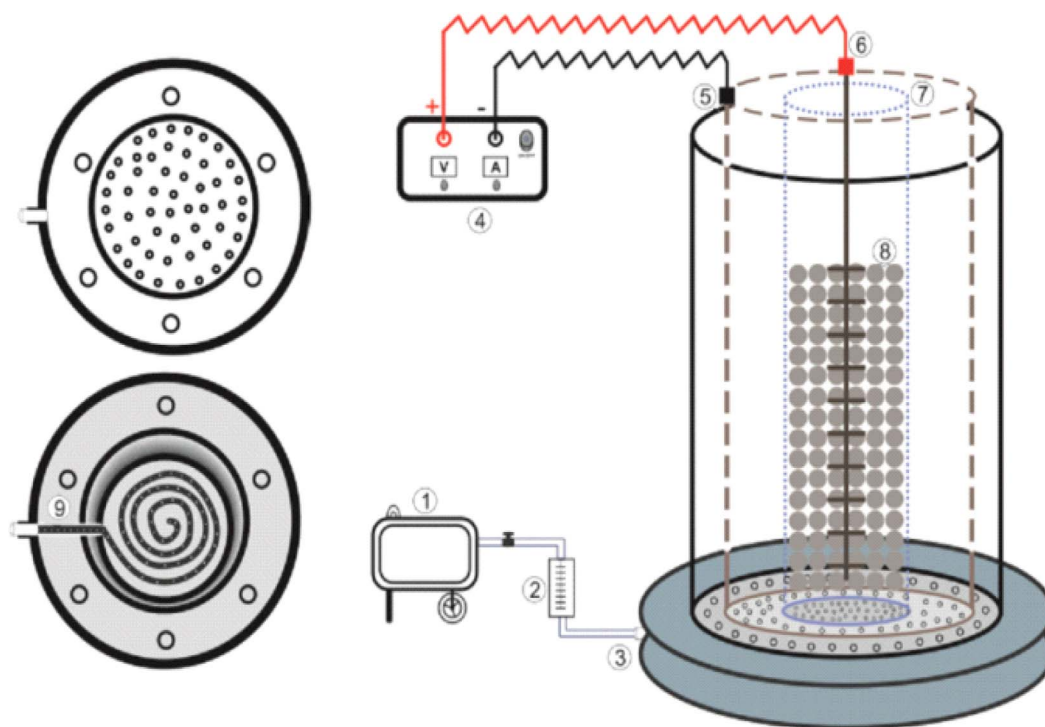
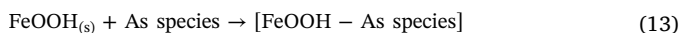
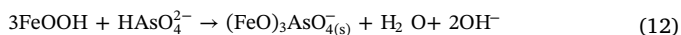
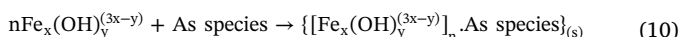
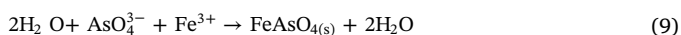


Fig. 1. The cylindrical packed-bed EC reactor 1. Air compressor, 2. Air flow meter, 3. Line for air diffuser, 4. DC power supply, 5. Cylindrical shaped Ti cathode, 6. Supporting steel rod contact with Fe ball anodes, 7. Fe ball anodes put into inner cylindrical shaped Plexiglas, 8. Fe ball anodes.

oxidation of As(III) to As(V), which changes adsorption behavior and arsenic's toxicity [30]. The HFO has strong affinity for arsenic species as well as counter ions to cause chemical precipitation (Eq. (9)).

Therefore, arsenic is removed by mechanisms such as co-precipitation of iron arsenate (Eqs. (10)–(12)) and adsorption (Eqs. (13) and (14)).



## 4. Results and discussion

### 4.1. Effect of initial pH

The initial pH has a considerable influence on the performance of an electrocoagulation process [32]. Removal of arsenic from contaminated water is affected by its composition and chemistry. The speciation of As(V) in aqueous solution as a function of pH is  $\text{AsO}_4^{3-}$  at  $\text{pH} > 12.4$ ;  $\text{HAsO}_4^{2-}$  at  $7.2 < \text{pH} < 12.4$ ;  $\text{H}_2\text{AsO}_4^-$  at  $3.6 < \text{pH} < 7.2$ . The effect of the initial pH of groundwater in the range of 6.5–8.5 on As(III) and As(V) removals at different EC times ( $t_{\text{EC}}$ ) was explored at the constant operating conditions because most of groundwaters containing arsenic have the pH in the range of 6–9 [32] (Fig. 2). As seen in Fig. 2(a), As(III) removal efficiencies and effluent concentrations ( $C_f < 10 \mu\text{g/L}$ ) were

obtained as 99.8% and  $0.40 \mu\text{g/L}$  at 20 min, 96.30% and  $7.40 \mu\text{g/L}$  at 16 min for a  $\text{pH}_i$  of 6.5, 99.9% and  $0.10 \mu\text{g/L}$  at 20 min, 96.0% and  $8.01 \mu\text{g/L}$  at 14 min for a  $\text{pH}_i$  of 7.5, and 99.6% and  $0.80 \mu\text{g/L}$  at 20 min, 95.6% and  $8.9 \mu\text{g/L}$  at 16 min for a  $\text{pH}_i$  of 8.5, respectively. On the other hand, As(V) removal efficiencies along with the effluent concentrations in Fig. 2(b) were 99.9% and  $0.20 \mu\text{g/L}$  at 20 min, 96.1% and  $7.9 \mu\text{g/L}$  at 12 min for a  $\text{pH}_i$  of 6.5, 99.9% and  $0.30 \mu\text{g/L}$  at 20 min, 95.8% and  $8.50 \mu\text{g/L}$  at 12 min for a  $\text{pH}_i$  of 7.5, and 99.7% and  $0.60 \mu\text{g/L}$  at 20 min, 96.9% and  $6.3 \mu\text{g/L}$  at 14 min for a  $\text{pH}_i$  of 8.5.

According to the above results, the new EC reactor was able to remove arsenic species efficiently at  $\text{pH}_i$  of 6.5–8.5, no significant effect was observed on the removal efficiency. The similar trend was observed by Kumar et al. [32] and they had removal efficiencies of As(III) and As(V) up to 97–99% in the  $\text{pH}_i$  range 6–8. The removal efficiencies of arsenic in the studied pH range were  $> 96\%$  at 14–16 min for As(III) and 12–14 min for As(V), which were consistent with the results reported earlier [21,25]. Therefore, the rest of experiments were carried out at its natural pH value (7.5). A slight increase in the  $\text{pH}_i$  of 6.5, 7.5 and 8.5 resulted in final  $\text{pH}_s$  ( $\text{pH}_f$ ) of 7.2, 8.0 and 9.1 for As(III) removal and 7.2, 7.9 and 9.1 for As(V) removal after the EC process. Some researchers observed similar effect during the EC process and also reported that the EC can act as pH neutralization step [21,32]. The pH increase in the EC process was attributed to the formation of hydrogen gas and hydroxyl ions at the cathode according to Eqs. (4) and (5). Thus, the electrolytic cell was capable of producing enough hydroxides ions to compensate the acid-buffer and make the solution alkaline. In addition, a slight pH increase in the EC process may be expected because of sorption reactions of As(V) and As(III), which release hydroxyl ion groups from HFO surfaces as a result of ligand exchange [29–31,33]. The amount of electro-generated iron species increased with the increase in the operating time resulted in increase in the amount of flocs which was made up of insoluble monomeric and polymeric species, depending on redox conditions and pH of the aqueous medium. The species of metallic iron, depended on the final pH of the EC process, in turn precipitated as  $\text{Fe}(\text{OH})_2$ , a variety of Fe(II/III) (oxy)(hydro)oxides and  $\text{Fe}(\text{OH})_3$  [34]. These HFO have strong affinity for arsenic species as well as counter ions to cause adsorption, precipitation and co-precipitation reactions (Eqs. (9)–(14)).

Amount of Fe dissolved at the anode in the EC process is expressed with the Faraday's law (Eq. (15)), which depends on the EC time ( $t_{\text{EC}}$ ) and applied current ( $i$ ). In this case, the increasing current and EC time in the EC process caused an increase in the amount of dissolved coagulant from the anode ( $C_{\text{electrode}}$ ):

$$C_{\text{electrode}} = (i \times t_{\text{EC}} \times M_{\text{Fe}}) / (z \times F) \quad (15)$$

where  $M_{\text{Fe}}$  (55.85 g/mol) is the molecular weight,  $i$  is applied current (A),  $t_{\text{EC}}$  is required the EC time (min),  $z$  is the number of electrons involved in the oxidation/reduction reaction ( $z_{\text{Fe}} = 2$ ) and  $F$  is the Faraday's constant (96,487 C). Amounts of the dissolved Fe in the  $\text{pH}_i$  range of 6.5, 7.5 and 8.5 at the optimum conditions were 0.0909, 0.0752 and 0.0875 g for As(III) removal, and 0.0650, 0.0628, and 0.0751 g for As(V) removal, respectively. The current efficiency ( $CE$  (%) =  $(C_{\text{exp}}/C_{\text{theo}}) \times 100$ ) is defined as the ratio of the actual electrode consumption to the theoretical value. It is also an important parameter for the EC process because it affects the lifetime of the electrodes. Because of the electrochemical side-reactions, the experimental (or actual) electrode consumption may be reduced or increased from this theoretical value depending upon the groundwater characteristics in the EC reactor and operational conditions [33]. Current efficiencies at  $\text{pH}_i$  6.5, 7.5 and 8.5 in the EC process were calculated as 109.0%, 103.1% and 105.0% for As(III) removal, and 104.0%, 100.4% and 103.1% for As(V) removal.

In conventional chemical coagulation, the arsenic removal efficiency improved with an increase of dosages of coagulants such as  $\text{FeCl}_3$  and alum. Similarly, the arsenic removal in the EC process depended on the amount of coagulant generated or the applied charge as the applied

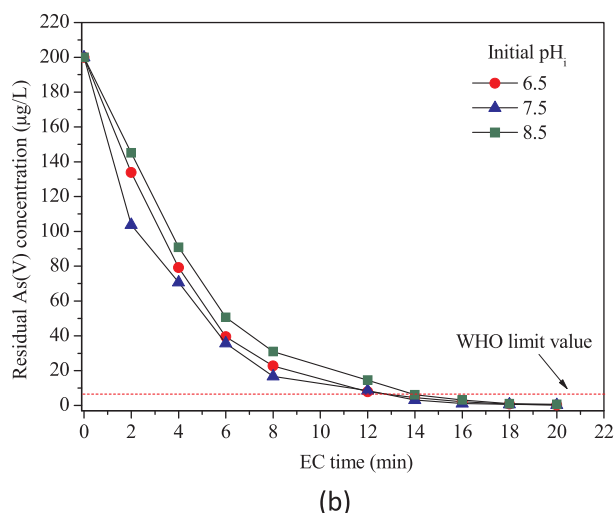
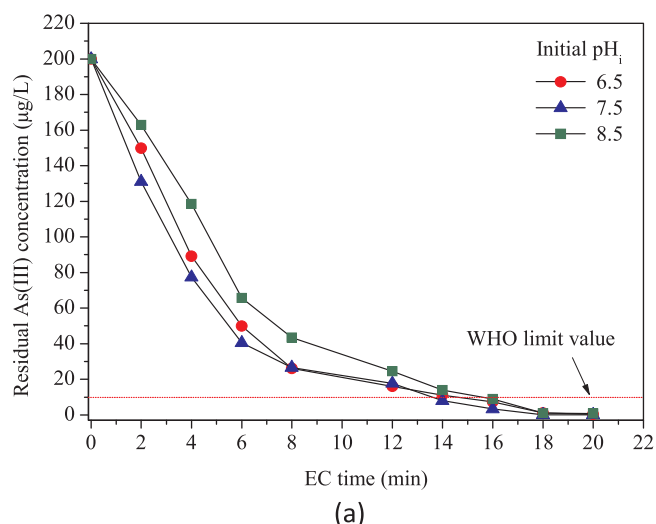


Fig. 2. Effect of initial pH on (a) As(III) and (b) As(V) removal efficiencies (Operating conditions:  $C_0 = 200 \mu\text{g/L}$ ,  $i = 0.3 \text{ A}$ ,  $d_p = 7.5 \text{ mm}$ ,  $h = 5 \text{ cm}$ ,  $Q_{\text{air}} = 6 \text{ L/min}$ ).

charge is directly proportional to the amount of coagulant generated. Actually, the charge loading ( $q = i \times t_{EC}$ ) rather than current density affects the treatment efficiency. The required charge loadings for  $C_f < 10 \mu\text{g/L}$  at  $\text{pH}_i$  6.5, 7.5 and 8.5 were determined to be 288, 252 and 288C for As(III) removal and 216, 216 and 252C for As(V) removal, respectively. In this case, the arsenic removal capacity (RC) as removed  $\mu\text{g As per C}$  or  $\text{mg Fe}$  is calculated from the following equation (Eq. (16))

$$RC = [(C_o - C_t) \times v]/q \text{ or } RC = [(C_o - C_t) \times v]/C_{Fe} \quad (16)$$

where  $v$  is solution volume in the EC reactor,  $q$  is charge loading (Coulomb), and  $C_o$  and  $C_t$  are initial and at time  $t$  arsenic concentrations ( $\mu\text{g/L}$ ) in solution. RC values for  $\text{pH}_i$  of 6.5, 7.5 and 8.5 were  $2.12 \mu\text{g/mg}$  ( $0.671 \mu\text{g/C}$ ),  $2.55 \mu\text{g/mg}$  ( $0.762 \mu\text{g/C}$ ) and  $2.18 \mu\text{g/mg}$  ( $0.664 \mu\text{g/C}$ ) for As(III) removal, and  $2.96 \mu\text{g/mg}$  ( $0.891 \mu\text{g/C}$ ),  $3.05 \mu\text{g/mg}$  ( $0.889 \mu\text{g/C}$ ) and  $2.58 \mu\text{g/mg}$  ( $0.769 \mu\text{g/C}$ ) for As(V) removal, respectively. Amounts of sludge at the optimum the EC times for  $\text{pH}_i$  of 6.5, 7.5 and 8.5 were calculated as  $0.133$ ,  $0.139$  and  $0.129 \text{ kg/m}^3$  for As(III) removal and  $0.126$ ,  $0.144$  and  $0.1351 \text{ kg/m}^3$  for As(V) removal.

#### 4.2. Effect of applied current

In electrochemical processes, current and EC time are the most important parameters for controlling the reaction rate in the reactor. Current determines not only the coagulant dosage but also the mixing rate within the EC process [21,26,34–37]. The EC time determines the rate of dissolution of iron ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), as it strongly depends on the applied current value. Fig. 3 illustrates effect of the applied current on the residual arsenic concentration as a function of  $t_{EC}$ . As seen in Fig. 3, the  $t_{EC}$  required to meet effluent arsenic concentration of  $< 10 \mu\text{g/L}$  reduced with increase in the applied current. The obtained effluent As concentrations and operating times for As(III) removal were  $11.5 \mu\text{g/L}$  and  $> 20$  min at  $0.075 \text{ A}$ ,  $9.02 \mu\text{g/L}$  and  $16$  min at  $0.15 \text{ A}$ , and  $8.01 \mu\text{g/L}$  and  $14$  min at  $0.30 \text{ A}$ , respectively. Values of  $C_f$  and  $t_{EC}$  for As(V) removal were  $9.09 \mu\text{g/L}$  and  $18$  min at  $0.075 \text{ A}$ ,  $7.70 \mu\text{g/L}$  and  $16$  min at  $0.15 \text{ A}$ , and  $8.50 \mu\text{g/L}$  and  $12$  min at  $0.30 \text{ A}$ , respectively.

According to the Faraday's law, whenever 1 Faraday of charge passes through the circuit,  $28 \text{ g}$  of iron are dissolved at Fe anode in the EC process. When the charge loading of the EC was low, the coagulant dosages were not sufficient to remove arsenic ions, and thus the arsenic removal efficiency was not high [33]. The minimum required charge loadings for effluent arsenic concentration of  $< 10 \mu\text{g/L}$  in the EC using Fe ball anodes were obtained as  $90$ ,  $144$  and  $252\text{C}$  for As(III) removal,  $81$ ,  $144$  and  $216\text{C}$  for As(V) removal. Amount of iron dosages both theoretically ( $C_{theo}$ ) and experimentally ( $C_{exp}$ ) along with current efficiency (Eq. (15)) were calculated as  $0.0261 \text{ g}$ ,  $0.0281 \text{ g}$  and  $108.0\%$  at  $0.075 \text{ A}$ ;  $0.0417 \text{ g}$ ,  $0.0433 \text{ g}$  and  $104.0\%$  at  $0.15 \text{ A}$ ; and  $0.0729 \text{ g}$ ,  $0.0752 \text{ g}$  and  $103.1\%$  at  $0.30 \text{ A}$  for As(III) removal, and  $0.0234 \text{ g}$ ,  $0.0244 \text{ g}$  and  $104.0\%$  at  $0.075 \text{ A}$ ;  $0.0421 \text{ g}$ ,  $0.0417 \text{ g}$  and  $101.0\%$  at  $0.15 \text{ A}$ ; and  $0.0625 \text{ g}$ ,  $0.0628 \text{ g}$  and  $100.4\%$  at  $0.30 \text{ A}$  for As(V) removal. It can be concluded from the results that the coagulant dosage increased with respect to increase in current to achieve the required effluent concentration of arsenic during the removal. Amount of removed As per  $\text{mg Fe}$  or  $\text{C}$  for As(III) and As(V) were also determined to be  $6.70 \mu\text{g/mg}$  ( $2.10 \mu\text{g/C}$ ) and  $7.83 \mu\text{g/mg}$  ( $2.36 \mu\text{g/C}$ ) at  $0.075 \text{ A}$ ,  $4.40 \mu\text{g/mg}$  ( $1.33 \mu\text{g/C}$ ) and  $4.57 \mu\text{g/mg}$  ( $1.34 \mu\text{g/C}$ ) at  $0.15 \text{ A}$ , and  $2.55 \mu\text{g/mg}$  ( $0.762 \mu\text{g/C}$ ) and  $3.05 \mu\text{g/mg}$  ( $0.889 \mu\text{g/C}$ ) at  $0.30 \text{ A}$ , respectively.

In this preliminary investigation, the operating cost of the treated arsenic removal can be calculated by considering two parameters as major cost items namely, the amounts of energy ( $C_{energy}$ ) and electrode consumptions in the EC process [21]. According to the Turkish market in December 2016, prices for electrical energy ( $\alpha$ ) and Fe ball electrode ( $\beta$ ) were  $0.190 \text{ \$/kWh}$  and  $4.50 \text{ \$/kg}$ , respectively. The operating cost

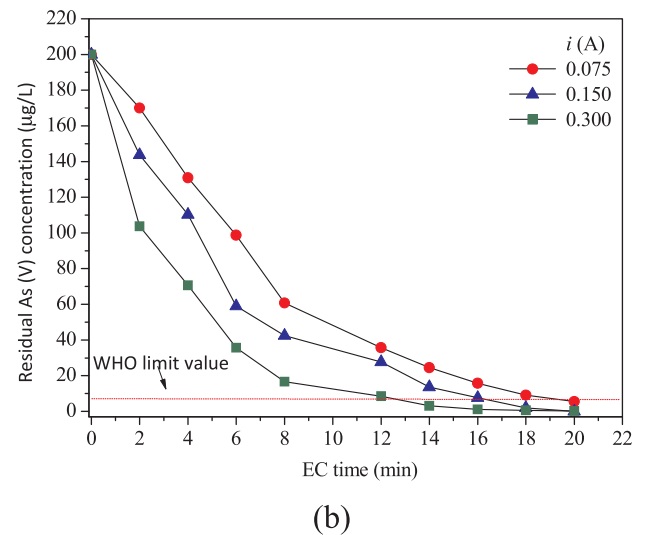
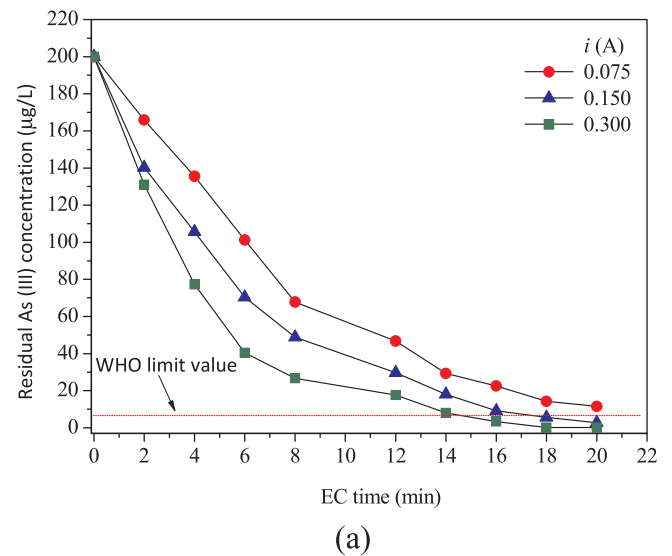


Fig. 3. Effect of applied current on (a) As(III) (b) As(V) removal efficiencies (Operating conditions:  $C_o$  of  $200$ , a  $\text{pH}_i$  of  $7.5$ ,  $d_p$  of  $7.5 \text{ mm}$ ,  $h$  of  $5 \text{ cm}$ ,  $Q_{air}$  of  $6 \text{ L/min}$ ).

for the EC process was calculated with the following equation

$$OC = \alpha \times C_{energy} + \beta \times C_{electrode} \quad (17)$$

The following equation was used to calculate  $C_{energy}$

$$C_{energy} = \frac{i \times t_{EC} \times U}{v} \quad (18)$$

where  $U$  is cell voltage (V) and  $v$  is the volume ( $\text{m}^3$ ) of wastewater ( $1 \text{ L}$ ). The operating cost (OC) for As(III) and As(V) removals were also calculated as  $0.737$  and  $0.530 \text{ \$/m}^3$  for a  $\text{pH}_i$  of  $6.5$ ,  $0.612$  and  $0.546 \text{ \$/m}^3$  for a  $\text{pH}_i$  of  $7.5$ , and  $0.734$  and  $0.632 \text{ \$/m}^3$  for a  $\text{pH}_i$  of  $8.5$ , respectively. From Equations of (15), (17) and (18), energy and electrode consumptions and operating cost at  $0.075$ – $0.3 \text{ A}$  for As(III) removal were calculated as  $0.530 \text{ kWh/m}^3$ ,  $0.0281 \text{ kg/m}^3$  and  $0.227 \text{ \$/m}^3$  for  $0.075 \text{ A}$ ,  $0.904 \text{ kWh/m}^3$ ,  $0.0433 \text{ kg/m}^3$  and  $0.367 \text{ \$/m}^3$  for  $0.15 \text{ A}$ , and  $1.442 \text{ kWh/m}^3$ ,  $0.0752 \text{ kg/m}^3$  and  $0.612 \text{ \$/m}^3$  for  $0.30 \text{ A}$ , respectively. On the other hand,  $C_{energy}$ ,  $C_{electrode}$  and OC for As(V) removal at  $0.075$ – $0.3 \text{ A}$  were  $0.502 \text{ kWh/m}^3$ ,  $0.0244 \text{ kg/m}^3$  and  $0.205 \text{ \$/m}^3$  for  $0.075 \text{ A}$ ,  $0.872 \text{ kWh/m}^3$ ,  $0.0421 \text{ kg/m}^3$  and  $0.355 \text{ \$/m}^3$  for  $0.15 \text{ A}$ , and  $1.386 \text{ kWh/m}^3$ ,  $0.0628 \text{ kg/m}^3$  and  $0.546 \text{ \$/m}^3$  for  $0.30 \text{ A}$ , respectively. The amounts of sludge were calculated for the currents of  $0.075$ ,  $0.15$  and  $0.30 \text{ A}$  as  $0.112$ ,  $0.139$  and  $0.124 \text{ kg/m}^3$  for As(III) removal and  $0.126$ ,  $0.144$  and  $0.128 \text{ kg/m}^3$  for As(V) removal. According to the

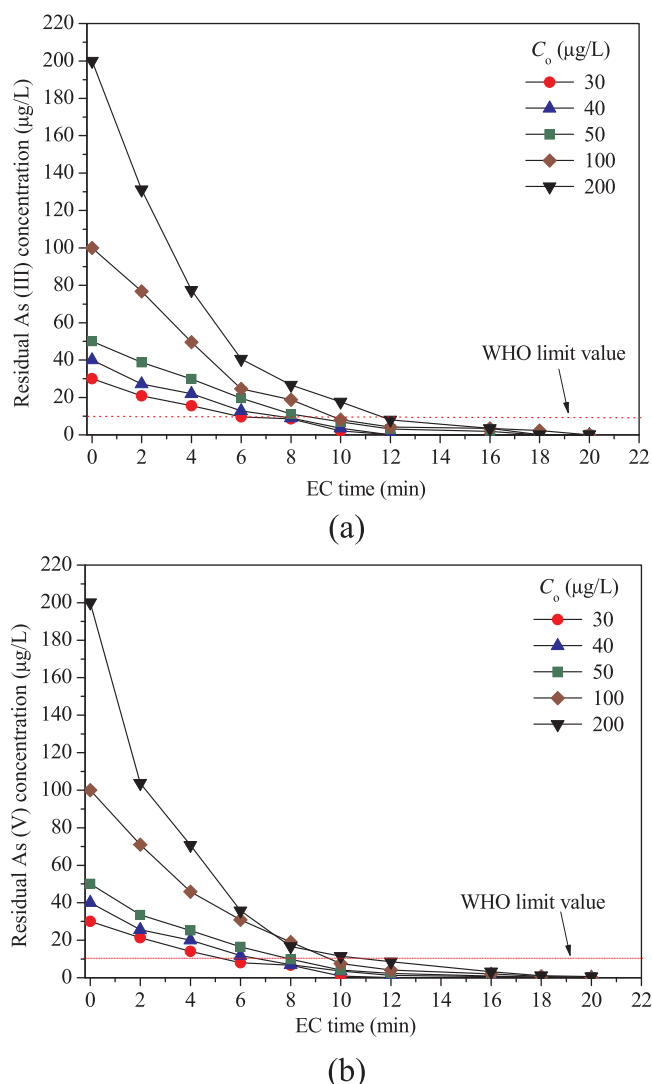


Fig. 4. Effect of arsenic concentration on (a) As(III) and (b) As(V) removal efficiencies (Operating conditions: a pH<sub>i</sub> of 7.5, 0.10 A,  $d_p$  of 5 mm,  $h$  of 5 cm,  $Q_{air}$  of 6 L/min).

results, as  $i$  and  $t_{EC}$  time increased, energy and electrode consumptions increased.  $OC$  of As(III) removal was less than that of As(V) removal. The retention time of groundwater containing arsenic in the EC reactor was also important since the increase in the applied current decreased the groundwater retention time which could reduce the EC reactor volume. Therefore, 0.30 A was chosen as the optimum current value for the rest of experiments.

#### 4.3. Effect of arsenic concentration

The arsenic removal in the EC process at initial concentrations of 30–200 µg/L with respect to residual arsenic concentrations vs EC time is shown in Fig. 4. As seen in Fig. 4, As(III) and As(V) removal efficiencies decreased with increase in arsenic concentrations from 30 to 200 µg/L while its removal efficiency increased with increase in the EC time. The obtained effluent arsenic concentrations and EC times for As(III) and As(V) removals from the groundwater were 9.62 and 8.03 µg/L at 6 min for 30 µg/L, 8.99 and 6.90 µg/L at 8 min for 40 µg/L, 6.87 µg/L at 10 min and 9.87 µg/L at 8 min for 50 µg/L, 8.20 and 7.50 µg/L at 10 min for 100 µg/L, 8.01 µg/L at 14 min and 8.50 µg/L at 12 min for 200 µg/L, respectively. The results from these experiments showed that the effluent As(III) and As(V) concentrations decreased significantly with increase in initial concentration of arsenic from 30 to 200 µg/L. In addition, it was clear that the rate of removal was sharp at the

beginning of the EC process (between 0 and 6 min), and afterwards the slope of the curve decreased. At the beginning (i.e., lag stage) of the EC process, the amount of iron produced electrochemically at especially high As(III) and As(V) concentrations would be quite less to cause decrease in concentration in the groundwater. However, amount of coagulant (hydrrous ferric oxides) produced in the EC process was increased with the increase in the EC time which led to decrease in the effluent arsenic concentration and arsenic was adsorbed on it. The curves were nearly the same at the end of experiment since abundance of hydrrous ferric oxides occurred at the end of the process (Fig. 4). Higher removal efficiency at low  $C_0$ ,  $t_{EC}$  (2–8 min) and constant applied current observed as compared to high  $C_0$ .

Values of electrode consumption and  $CE$  for 30, 40, 50, 100 and 200 µg/L at the permissible effluent concentration of < 10 µg/L in the EC process were calculated as 0.0331 g and 106%, 0.0433 g and 104%, 0.0533 g and 102%, 0.0531 g and 102.0%, and 0.0752 g and 103.1% for As(III) removal, 0.0322 g and 103.0%, 0.0417 g and 104.0%, 0.0417 g and 101.0%, 0.0521 g and 104.0%, and 0.0625 g and 100.4% for As(V) removal, respectively. The required minimum charge loadings for 30, 50, 100 and 200 µg/L were determined as 108, 144, 180, 180, and 252C for As(III) removal, and 108, 144, 144, 180 and 216C for As(V) removal. The amounts of removed As per mg Fe or C for As(III) and As(V) removals were calculated as 5.746 µg/mg (1.763 µg/C) and 5.963 µg/mg (1.778 µg/C) for 30 µg/L, 4.407 µg/mg (1.327 µg/C) and 4.409 µg/mg (1.327 µg/C) for 40 µg/L, 3.635 µg/mg (1.073 µg/C) and 4.517 µg/mg (1.320 µg/C) for 50 µg/L, 3.610 µg/mg (1.066 µg/C) and 3.553 µg/mg (1.069 µg/C) for 100 µg/L, and 2.553 µg/mg (0.762 µg/C) and 3.051 µg/mg (0.887 µg/C) for 200 µg/L, respectively. These results indicated that as the initial concentration of arsenic increased, the EC time increased. The amount of sludge at the optimum EC times for 30, 40, 50, 100 and 200 µg/L were calculated as 0.062, 0.084, 0.0981, 0.1052, and 0.124 kg/m<sup>3</sup> for As(III) removal and 0.065, 0.088, 0.1002, 0.115, and 0.128 kg/m<sup>3</sup> for As(V) removal, respectively.

#### 4.4. Effect of airflow rate

Introduction of air or oxygen in the EC process was necessary to assure oxidation of electrochemically dissolved  $Fe^{2+}$  from the anodes [38]. Moreover, the effect of air bubbling not only oxidizes  $Fe^{2+}$  to  $Fe^{3+}$  but also promotes the coagulation/flocculation process due to the movement in the solution in the EC reactor. Then, removals of As(III) and As(V) ions were governed by adsorption/complexation with iron hydroxides generated in the process. At same time, formation and growth of passivation layer (like metal (oxy)hydroxides precipitates) on the anode surfaces didn't occur due to the turbulent (or mixing) behavior of the airflow in EC reactor. Some researches [26,32,34,39] reported that As(III) removal mechanism in the EC with iron electrodes was oxidation of As(III) to As(V) and surface complexation with iron hydroxides. The standard potential of the oxidation of As(III) to As(V) is + 0.56 V, which is lower than the oxidation potential of Fe(II) to Fe(III) and other species typically found in groundwater. Although Fe(II) oxidation occurred rapidly in the presence of air, the oxidation rate of As(III) is extremely slow. It was reported that As(III) was only slowly oxidized by dissolved  $O_2$  at pH 7.6–8.5 although As(V) was thermodynamically favored under oxidizing conditions [40].

The effect of air flow rate ( $Q_{air}$ ) at 0–6 L/min was investigated with respect to the effluent arsenic concentration and EC time in the EC process using Fe ball anodes (Figs. 5 and 6). The effluent arsenic concentrations for As(III) and As(V) removals decreased with the increase in both air flow rate and shorter EC time. As seen in Fig. 5, the effluent arsenic concentration with no airflow present for As(III) and As(V) removals reduced to 7.80 µg/L at 20 min and 9.03 µg/L at 18 min. When the air was present in the EC reactor, the residual arsenic concentration for As(III) and As(V) removals were 9.02 µg/L and 4.90 µg/L at 16 min for 2 L/min, and 8.01 µg/L at 14 min and 8.5 µg/L at 12 min for 6 L/min, respectively. In this case, the required charge loadings for  $Q_{air}$  of 0,

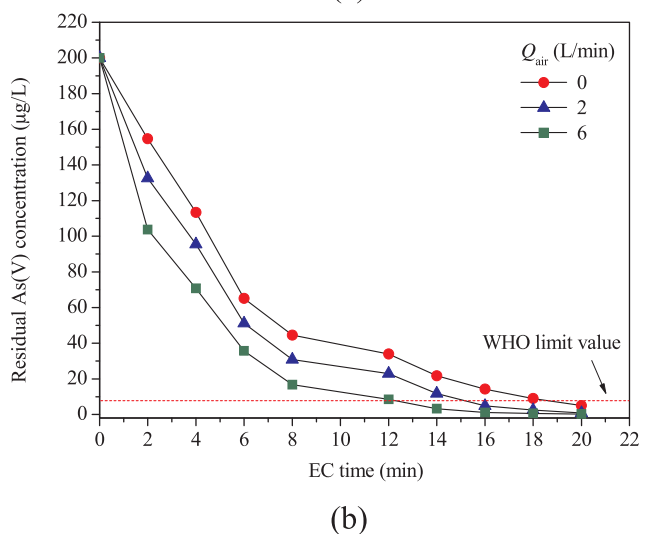
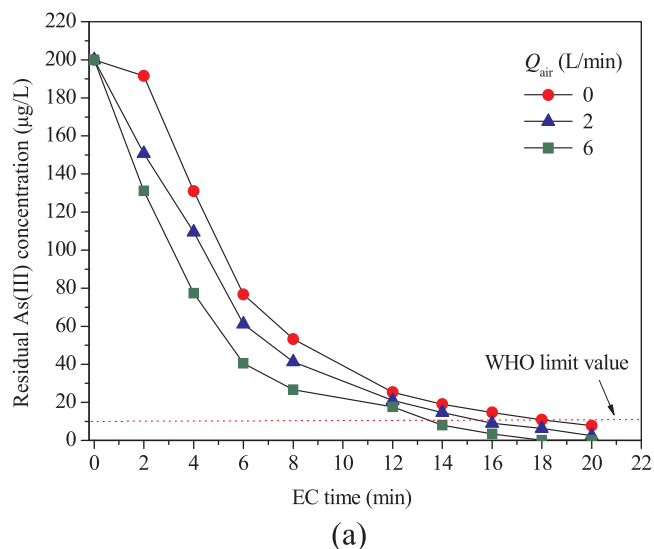


Fig. 5. Effect of airflow on (a) As(III) and (b) As(V) removal efficiencies (Operating conditions:  $pH_i = 7.5$ ,  $i = 0.30$  A,  $C_o = 200$  µg/L,  $d_p = 7.5$  mm,  $h = 5$  mm).

2 and 6 L/min were calculated as 360, 288 and 252C for As(III) removal and 324, 288 and 216C for As(V) removal. Experimentally dissolved Fe dosage for As(III) and As(V) removals were obtained as 0.110 g (CE of 106.0%) and 0.0966 g (CE of 103.0%) for  $Q_{air}$  of 0 L/min, 0.0859 g (CE of 103.0%) and 0.0875 g (CE of 105.0%) for  $Q_{air}$  of 2 L/min, and 0.0752 g (CE of 100.4%) and 0.0628 (CE of 100.3%) for  $Q_{air}$  of 6 L/min, respectively. In addition, removed arsenic per mg Fe for As(III) and As(V) removals were calculated as 1.740 µg/mg and 1.977 µg/mg for  $Q_{air}$  of 0 L/min, 2.225 µg/mg and 2.229 µg/mg for  $Q_{air}$  of 2 L/min, and 2.553 µg/mg and 3.051 µg/mg for  $Q_{air}$  of 6 L/min, respectively.

In general, oxygen concentration in natural groundwaters is low, but value of dissolved oxygen (DO) in surface water is high. In the case of As(III) removal from the groundwater, values of DO increased from 7.2 to 8.1 mg/L with the increase in values of  $Q_{air}$  from 0 to 6 L/min at 20 min whereas the value of DO without air decreased from 7.2 to 3.1 mg/L at the same operating time. However, the arsenic removal efficiency increased with increase in oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  and homogeneous mixture within the EC reactor. Concentrations of DO increased with increase in flow rate as compared to no  $Q_{air}$ . The results indicated that the operating time needed for the permissible WHO limit value reduced as the  $Q_{air}$  increased in the range of 0–6 L/min.

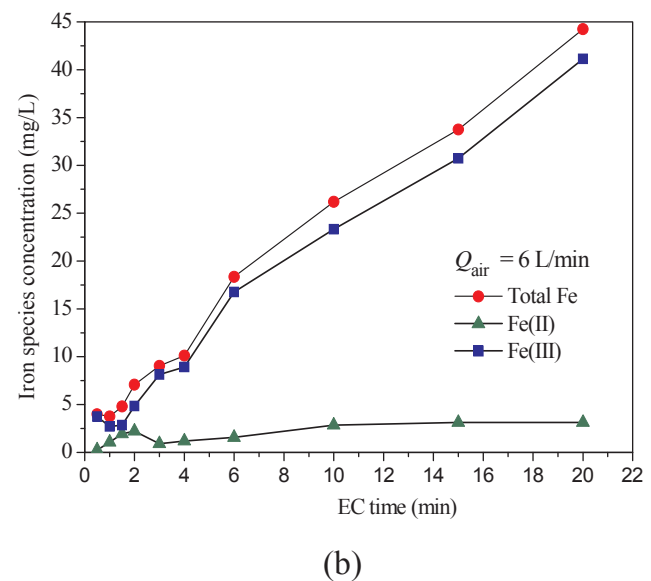
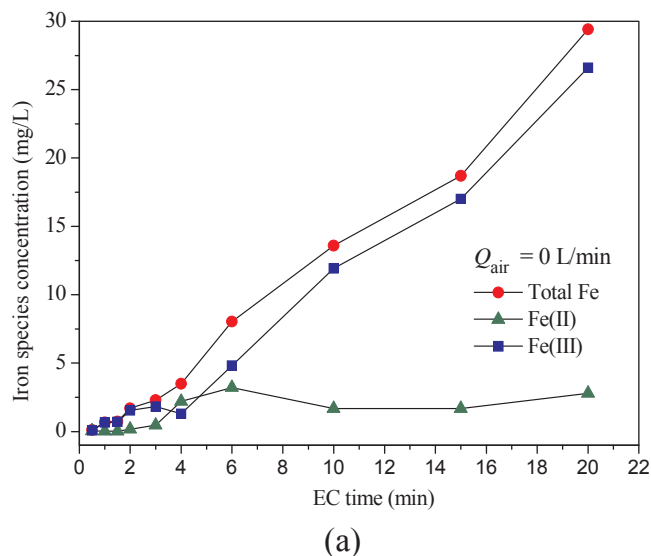


Fig. 6. The effect of air flow rate on iron species generated during EC process (Operating conditions:  $C_o = 200$  µg/L,  $i = 0.30$  A,  $d_p = 7.5$  mm,  $h = 5$  cm).

#### 4.5. Effect of diameter of Fe ball anode

Diameter of Fe ball anode ( $d_p$ ) in the EC process is an important operating parameter which influences the arsenic removal efficiency. As diameter of Fe ball anode in the reactor increases at a constant anode height in the reactor, the total surface area of anodes used in the reactor decreases. The experiments were conducted at varying diameters of iron ball anodes from 5 to 10 mm in the fixed-bed EC reactor at the constant operating conditions. Fig. 7 shows the influence of diameter of Fe ball anodes on the As(III) and As(V) removals. As seen in Fig. 7, the effluent arsenic concentrations at 5.0, 7.5 and 10 mm of Fe ball anodes were 7.10 µg/L and 14 min, 8.01 µg/L and 14 min, 6.60 µg/L and 16 min for As(III) removal, and 7.50 µg/L and 12 min, 8.50 µg/L and 12 min, 7.90 µg/L and 14 min for As(V) removal, respectively.

The charge loading values for effluent concentration of  $< 10$  µg/L at 5.0, 7.5 and 10 mm were calculated as 252, 252, and 288C for As(III) removal and 216, 216, and 252C for As(V) removal, respectively. The charge loadings for both As(III) and As(V) increased with increasing diameter of Fe ball anodes. Total surface area of Fe ball anodes at constant height of 5 cm and 0.3 A in the EC reactor were obtained as

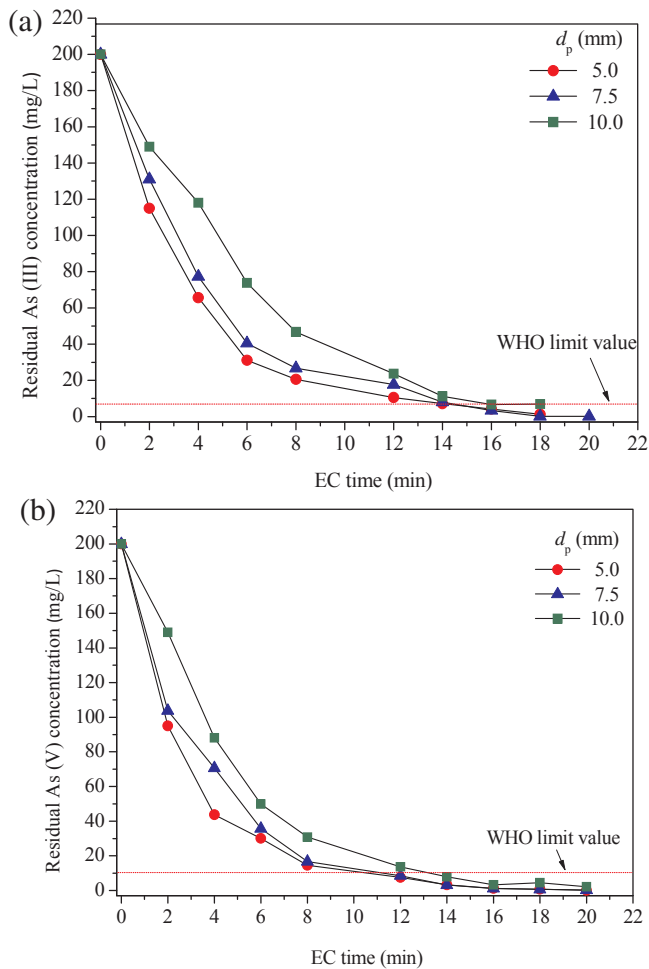


Fig. 7. Effect of diameter of Fe ball anode on (a) As(III) and (b) As(V) removal efficiencies (Operating conditions:  $C_o = 200 \mu\text{g/L}$ ,  $\text{pH}_i = 7.5$ ,  $i = 0.30 \text{ A}$ ,  $h = 5 \text{ mm}$ ,  $Q_{\text{air}} = 6 \text{ L/min}$ ).

0.13188  $\text{m}^2$  (2.28  $\text{A/m}^2$ ) for 5.0 mm, 0.07592  $\text{m}^2$  (3.95  $\text{A/m}^2$ ) for 7.50 mm, and 0.03454  $\text{m}^2$  (8.69  $\text{A/m}^2$ ) for 10 mm. From these results, increased  $d_p$  at constant Fe anode height in the EC reactor increased current density because of decreased total Fe anode surface area. Fe electrode consumptions and removed As per mg Fe of generated electrochemically at 5.0, 7.5 and 10 mm of Fe ball anodes were calculated as 75.12 mg and 2.57  $\mu\text{g/mg}$  (CE of 103%,  $C_{\text{theo}}$  of 72.93 mg), 75.19 mg and 2.55  $\mu\text{g/mg}$  (CE of 103.1%,  $C_{\text{theo}}$  of 72.93 mg) and 84.19 mg and 2.30  $\mu\text{g/mg}$  (CE of 101%,  $C_{\text{theo}}$  of 83.35 mg) for As(III) removal, and 66.27 mg and 2.91  $\mu\text{g/mg}$  (CE of 105.8%,  $C_{\text{theo}}$  of 62.51 mg), 62.76 mg and 3.05  $\mu\text{g/mg}$  (CE of 100.4%,  $C_{\text{theo}}$  of 62.51 mg), and 76.20 mg and 2.52  $\mu\text{g/mg}$  (CE of 104.5%,  $C_{\text{theo}}$  of 72.93 mg) for As(V) removal, respectively. Amounts of sludge at 5.0, 7.5 and 10 mm were determined as 0.148, 0.139 and 0.143  $\text{kg/m}^3$  for As(III) removal and 0.135, 0.144 and 0.138  $\text{kg/m}^3$  for As(V) removal, respectively. Average voltages between anode and cathode electrodes in the EC reactor at 5.0, 7.5 and 10 mm were measured as 19.3, 20.6 and 22.4 V for As(III) removal and 19.8, 23.1 and 22.9 V for As(V) removal.

#### 4.6. Effect of Fe ball anode height

Another important parameter with regard to electrode life time and arsenic removal efficiency is Fe ball anode height in the EC reactor. The effect of the ball height was studied with the experimental conditions at 6 L/min, 7.5 cm, 0.30 A, a  $\text{pH}_i$  of 7.5 for the groundwater sample containing 200  $\mu\text{g/L}$  of arsenic. The results are shown in Fig. 8. When value of  $h$  in the EC reactor increased, the arsenic removal efficiency

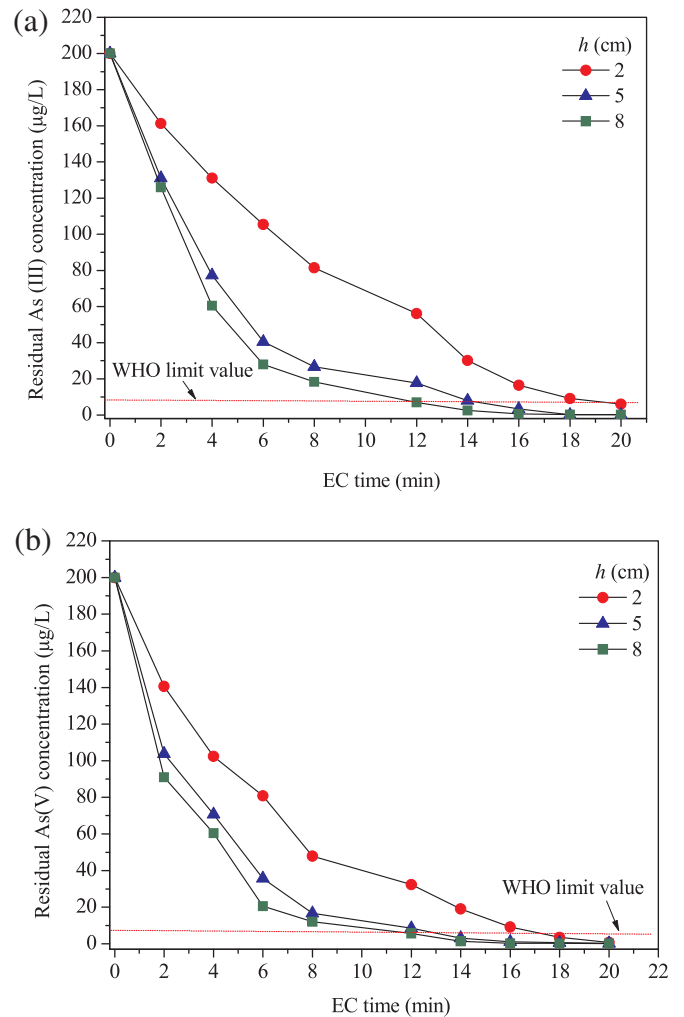


Fig. 8. Effect of anode height in the EC reactor on (a) As(III) and (b) As(V) removal efficiencies.

increased because of increase in amount of iron ball anodes or total iron anode surface area. Total anode surface area for anode heights of 2, 5 and 8 cm in the EC reactor were calculated as 0.03179  $\text{m}^2$ , 0.07595  $\text{m}^2$ , and 0.11657  $\text{m}^2$ , respectively. According to the Faraday law, increasing  $h$  value meant increasing both surface area of anode and dissolved amount of metal ions. Consequently, there was an increase for both As(III) and As(V) removal efficiencies related to  $h$  value. Minimum EC times and effluent arsenic concentrations for electrode heights of 2, 5, and 8 cm in the EC reactor were 18 min and 9.12  $\mu\text{g/L}$ , 14 min and 8.01  $\mu\text{g/L}$ , 12 min and 6.99  $\mu\text{g/L}$  for As(III) removal and 16 min and 9.10  $\mu\text{g/L}$ , 12 min and 8.50  $\mu\text{g/L}$ , 12 min and 5.71  $\mu\text{g/L}$  for As(V) removal.

On the other hand, the minimum charge loadings required for the arsenic removal efficiency above 95% (or  $C_f < 10 \mu\text{g/L}$ ) at anode height of 2, 5, and 8 cm in the EC reactor were calculated as 324, 252, and 216C for As(III) removal and 288, 216, and 216C for As(V), respectively. According to the above results, the charge loading decreased with an increase of anode height. In this case, amounts of electrochemically generated iron and current efficiency at minimum EC times (or coagulant dosage) were found to be 95.928 mg Fe and 102.3% for  $h$  of 2 cm, 75.194 mg Fe and 103.1% for  $h$  of 5 cm, and 65.265 mg Fe and 104.4% for  $h$  of 8 cm for As(III) removal and 86.103 mg Fe and 103.3% for  $h$  of 2 cm, 62.764 mg Fe and 100.4% for  $h$  of 5 cm, and 66.453 mg Fe and 106.3% for  $h$  of 8 cm for As(V) removal, respectively. Amount of removed arsenic per mg Fe for anode height of 2, 5 and 8 cm in EC reactor at minimum EC times were calculated as 1.99  $\mu\text{g/mg}$ , 2.55  $\mu\text{g/}$



mg, and 2.96 µg/mg for As(III) removal, and 2.22 µg/mg, 3.05 µg/mg, and 2.92 µg/mg for As(V) removal, respectively. Amounts of sludge at the optimum EC times for *h* of 2, 5 and 8 cm were calculated as 0.183, 0.139 and 0.118 kg/m<sup>3</sup> for As(III) removal and 0.176, 0.144 and 0.121 kg/m<sup>3</sup> for As(V) removal, respectively. Average voltages between anode and cathode electrodes in the EC reactor at *h* of 2, 5 and 8 cm were measured as 20.4, 20.6 and 20.3 V for As(III) removal and 23.8, 23.1 and 23.4 V for As(V) removal. As height of Fe ball anodes (amount of iron ball anodes) in the EC reactor for both arsenic species was increased, the required operating time decreased to obtain the recommended effluent arsenic concentration. This was important for changing of electrodes and maintenance of the process. Therefore, it would be an advantage to run the EC process at low cost.

## 5. Conclusions

In the present study, electrocoagulation was evaluated as a treatment technology for removals of As(III) and As(V) from the groundwater. The results indicated that the arsenic removal efficiency increased with increase in current, air flow rate, anode height in the reactor and operating time, but it decreased with the increase in both initial concentration and diameter of iron ball anode. Effect of pH on arsenic removal was not significant in the pH range of 6.5–8.5. The highest effects on the removal of efficiencies of As(III) and As(V) from the groundwater were observed with column height in the reactor and current. The maximum removal efficiency and minimum operating cost at a pH<sub>i</sub> of 7.5, 0.3 A, 200 µg/L, ball diameter of 7.5 mm, *h* of 5 cm and Q<sub>air</sub> of 6 L/min were 96.0% and 0.612 \$/m<sup>3</sup> at 14 min for As(III), and 95.8% and 0.546 \$/m<sup>3</sup> at 12 min for As(V), respectively. It can be concluded from this study that the electrocoagulation with iron ball anodes is a promising technique for the removal of arsenic.

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