



Arsenite removal from groundwater by aerated electrocoagulation reactor with Al ball electrodes: Human health risk assessment

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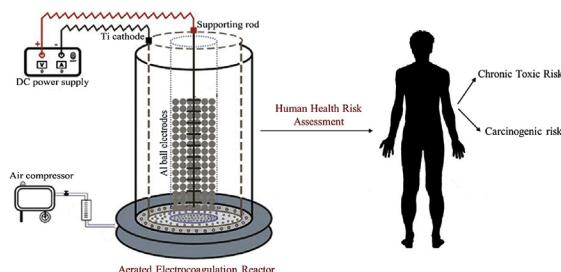
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HIGHLIGHTS

- Aerated EC reactor with Al ball electrodes used for As (III) removal from groundwater.
- The maximum As (III) removal efficiency was 95.65% was at optimized conditions.
- Air flow rate and electrode height affect performance more than initial pH.
- The carcinogenic risk (CR) and non-CR of arsenic was in the range of tolerable limits.
- Aerated EC reactor exhibited a promising performance for As (III) removal.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of conventional electrocoagulation (EC) process for removal of As(III) from groundwater suffers from the need of external oxidation agent for oxidation of As(III) to As(V). To tackle this limitation, an aerated EC reactor for the removal of As(III) from groundwater was evaluated in this study. The effect of initial pH_i, air flow rate, applied current, and electrode height in the EC reactor was examined. The experimental results showed that removal of arsenic mostly dependent on the applied current, electrode height in EC reactor, and air flow rate. The As(III) removal efficiency (99.2%) was maximum at pH_i of 7.5, air flow rate of 6 L min⁻¹, applied current of 0.30 A, and electrode height in EC reactor of 5 cm, with an total operating cost of 0.583 \$ m⁻³. Furthermore, the carcinogenic risk (CR) and non-carcinogenic risk of arsenic (As) was in the range of tolerable limits at all operating conditions except applied current of 0.075 A at the end of the aerated EC process to remove As from groundwater. The present EC reactor process is able to remove As(III) from groundwater to below 10 µg L⁻¹, which is maximum contaminant level of arsenic in drinking water according to the World Health Organization (WHO).

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1. Introduction

The surface water sources are becoming inadequate day by day with the growing population and industrialization on a world scale. The insufficient surface water sources led humans to find new water sources. Groundwater is an alternative fresh water source to

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supply the demand by humans as drinking water and for industrial purposes. Furthermore, a large population living in many parts of the world (Argentina, Bangladesh, Chile, India, Nepal, Japan, Mongolia, USA etc.) already use to groundwater as a drinking water source due to lack of surface water sources (Ng et al., 2003; Ravenscroft et al., 2009; Bundschuh et al., 2017; Maity et al., 2017). Unfortunately, the groundwater sources include undesirable compounds due to anthropogenic sources and/or geological composition of aquifers and that compounds restricts the usage of groundwater sources (Kumar et al., 2017). Among the common groundwater pollutants (fluoride, pesticides, fertilizers, lead etc.), the arsenic (As) contamination has attracted worldwide attention due to its serious danger to human health and ecological life (Fendorf et al., 2010). It has been published that about 140 million people in worldwide are expose to the excessive levels of As via groundwater consumption. Especially, in Bangladesh, the almost 125 million people are exposed to arsenic concentrations exceeding the maximum recommended arsenic level of $10 \mu\text{g L}^{-1}$ according to the WHO, (2004) (Smith et al., 2000).

In the long term, As containing drinking water consumption can cause cancer in humans. Exposed to As in drinking water can raise the risk of skin, bladder, lungs, prostate, and kidney cancer as well as depression and diabetes (Steinmaus et al., 2014; Mayer and Goldman, 2016; Sodhi et al., 2019). As in groundwater especially found as trivalent arsenite (As(III)) due to the anoxic conditions of water sources (Chammui et al., 2014). The As (III) has a lower affinity to minerals and 60 times toxic than arsenate (As(V)) (Jiang et al., 2015). The most of the technologies also requires pre-treatment steps for conversion of As (III) to As (V) for removal of As. Therefore, the direct removal of As(III) from groundwater is a challenging and critical topic to prevent the risk of As(III) and the drawbacks of conventional treatment processes. The commonly used conventional treatment processes include coagulation-flocculation, ion exchange resins, lime softening, adsorption, membrane processes, hybrid treatment processes, and electrocoagulation (Bora et al., 2016; Hering et al., 2017; Smith et al., 2017; Hao et al., 2018; Xu et al., 2019). However, as mentioned above, most of these technologies have a number of disadvantages including high amount of chemical consumption and sludge formation, high maintenances and operating cost, high energy consumption, requirement of additional pre-treatment process.

Electrocoagulation (EC) process is promising and moderately environmental friendly technology compared with conventional treatment processes for As removal, owing to its easy operation, compactness of process, no additional chemical requirement, relatively low maintenances and operating cost, low amount of sludge formation, high As removal efficiency, no needs for chemical addition for oxidation of As(III) to As(V) (Kobyta et al., 2006; Ulu et al., 2017). Nevertheless, commonly used plate and rod type electrodes present several handicaps due to its low surface area and difficulties in operation. Therefore, an air-injection EC reactor with Fe and Al ball electrodes for As(V) removal from groundwater was studied and optimized to eliminate problems related to electrode surface area (Şik et al., 2015; Goren et al., 2018). The results revealed that the ball electrodes in the EC reactor achieved as efficiently as the plate and rod type electrodes. Furthermore, the removal of As by EC at different operating conditions such as applied current, initial pH, electrode type, temperature and initial arsenic concentration etc. has been investigated. However, there is limited study about the effect of dissolved oxygen on As(III) removal efficiency by EC process. Therefore, a better understanding of aerated EC process for effective As(III) removal is necessary.

In this study, an aerated EC reactor with Al ball electrodes was investigated for As(III) removal. The effects of applied current, initial pH, air flow rate, Al ball electrode height in EC reactor, and

size of the Al ball electrodes were investigated. Furthermore, the human health risk assessment of As in treated water was determined. The human health risk assessment of As in treated water is necessary since the toxicity of As is an important topic in worldwide and it is a significant parameter to understand the performance of treatment processes. However, there are limited studies on determination of human health risk of As after treatment processes. Also, this paper is the first study, which is investigated the human health risk assessment of As in treated water using aerated EC process.

2. Materials and methods

2.1. Materials

Potassium iodide (KI, >99.5%) and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, >99%) were purchased from Sigma Aldrich and AppliChem, respectively. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, >99%), hydrochloric acid (HCl, 37%), sodium tetra borate (NaBH_4 , >98%), and sodium hydroxide (NaOH, >99%) were purchased from Merck, Turkey. All chemical reagents used in the removal tests were of analytical grade. Stock solutions of As(V) and As(III) were prepared from sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, Merck, >99%) and sodium arsenite (NaAsO_2 , Merck, >99%) powder, respectively. All solutions were also kept at refrigerator at under 4°C for inhibition of microorganism formation.

2.2. Quality of real groundwater

The natural groundwater sample was obtained from the province of Kocaeli, Turkey. The quality of the groundwater sample was measured with three time analyses and the results were shown in Table 1. Arsenic and phosphorus in the used natural water sample was not detected. Therefore, the stock arsenic solutions were prepared freshly before each experimental run by dissolving NaAsO_2 . The specified concentration of As(III) were made from the stock solution.

2.3. Aerated EC reactor construction and experimental methods

The aerated EC reactor were illustrated in Fig. 1. The size of cylindrical EC reactor was $254 \text{ mm} \times 100 \text{ mm} \times 5 \text{ mm}$. The reactor was made of a Plexiglas material and had a volume of 0.8 L. This consist of two parts including titanium cathode and anode compartment (holding the Al ball anodes), with the dimensions of each part being $250 \text{ mm} \times 70 \text{ mm} \times 1 \text{ mm}$ with 5 mm holes and $250 \text{ mm} \times 60 \text{ mm} \times 5 \text{ mm}$ with 2 mm holes, respectively. The air in EC reactor also supplied from round base unit (45 mm thick, 150 mm diameter, and 2 mm holes). The cathode and Al ball anodes contacted with the stainless steel road and connected to a DC power supply (Agilent 6675 A, 0–120 V/0–18 A). Before each

Table 1
Characterization of real groundwater.

Parameters	Concentration
pH	7.6 ± 0.1
Electrical conductivity ($\mu\text{S cm}^{-1}$)	1055 ± 4
Fe (mg L^{-1})	0.12 ± 0.02
NO_3^- (mg L^{-1})	24 ± 0.2
SO_4^{2-} (mg L^{-1})	94.2 ± 1
SiO_2 (mg L^{-1})	10.2 ± 0.3
Cl^- (mg L^{-1})	127 ± 2
Al (mg L^{-1})	0.006 ± 0.001
Na^+ (mg L^{-1})	22 ± 1
Ca^{2+} (mg L^{-1})	152 ± 5
Mg^{2+} (mg L^{-1})	15 ± 2

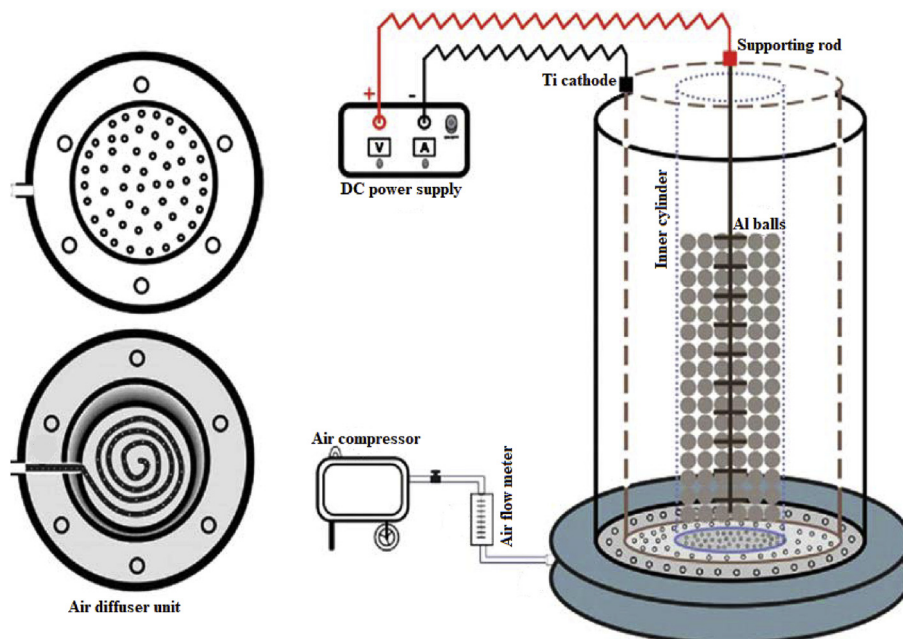


Fig. 1. Schematic diagram of aerated EC reactor set-up.

experimental run, the reactor filled with 0.8 L of groundwater sample. It was operated for different operating conditions and in batch mode. The supply of current to the system and the measurement of the voltage were also provided using a DC power supply. At specified time intervals, groundwater samples were collected and filtered by 0.45 μm filter before to analysis. Furthermore, the weight of the Al balls was measured at start and end of the experiments to calculate the electrode consumption.

The arsenic removal efficiency (R_e , %), electrode consumption (ELC, kg m^{-3}), energy consumption including energy consumption of DC power supply (ENC, kWh m^{-3}), and total operating cost (TOC, $\text{\$ m}^{-3}$) was calculated with following equations:

$$R_e(\%) = \frac{(C_i - C_f)100}{C_i} \quad (1)$$

$$ELC(\text{kg m}^{-3}) = \frac{it_{EC}M_{Al}}{z_{Al}Fv} \quad (2)$$

$$ENC(\text{kWh m}^{-3}) = \frac{Uit_{EC}}{v} \quad (3)$$

$$TOC(\text{\$ m}^{-3}) = \alpha ENC + \beta ELC \quad (4)$$

where C_i : initial arsenic concentration ($\mu\text{g L}^{-1}$), C_f : effluent arsenic concentration ($\mu\text{g L}^{-1}$), i : applied current (A), t_{EC} : operating time (s or h), M_{Al} : molecular weight of the Al anode (26.98 g mol^{-1}), z_{Al} : number of electrons, F : Faraday's constant ($96,487 \text{ C}$), U : cell voltage (V), v : volume of water in the reactor (m^3), α ($\text{\$ kWh}^{-1}$) and β ($\text{\$ kg}^{-1}$): electrical energy and Al ball electrodes prices according to Turkish market in November 2019, respectively.

2.4. Analytical methods

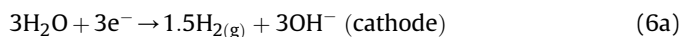
The all analyses in solutions was determined using American Public Health Association (APHA) standard methods (APHA, 1998). Total arsenic ($As_{(total)}$) and As(III) concentrations were analysed

using inductively coupled plasma optical emission spectrophotometer with hydrate generator (ICP-OES, PerkinElmer Optima 7000 DV, USA). Total arsenic ($As_{(total)} = As(III) + As(V)$) determination required reducing using KI and ascorbic acid to convert As(V) to As(III) prior to the arsine formation step (Chotoo et al., 2016). The water sample containing arsenic was first mixed with 1 mL HCl (10%) and 1 mL of reducing agent (5% KI and 5% ascorbic acid), and then allowed to react for about 60 min at dark place to reduce As(V) to As(III). To detect As(III) selectively, a mixture of 2% sodium borohydride (NaBH_4) and 0.5% NaOH was used as reducing solution, and 5% citric acid was used as carrier solution. Under this condition, only As(III) was converted to arsine gas (AsH_3) and detected on the ICP-OES. As(V) can be calculated by deducting of As(III) from $As_{(total)}$. The detection limit of $As_{(total)}$ and As(III) with solutions was $2 \mu\text{g L}^{-1}$ and the relative standard deviations ($n = 2-5$) in the range of $1-200 \mu\text{g L}^{-1}$ were $\pm 3\%$ or less. The detection limit of arsenic using ICP-OES was $0.1 \text{ L}^{-1} \mu\text{g}$. Chloride, nitrate, phosphate and sulphate ions in Table 1 were determined by ion chromatography (HIC-20 A Super, Shimadzu). Also, aqueous concentrations of total Ca, Mg, Si, Fe and Al were determined by the ICP-OES.

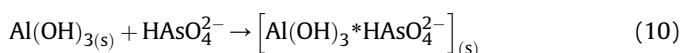
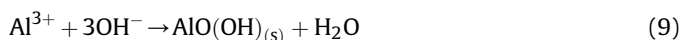
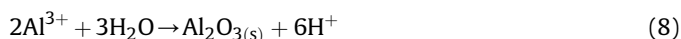
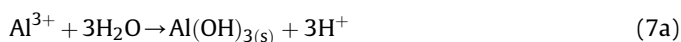
The pH and electrical conductivity of solutions were measured using a pH meter (Mettler Toledo Seven Compact) and electrical conductivity meter (Mettler Toledo Seven Go), respectively. Each individual analysis was executed thrice, and then, the results were averaged.

2.5. Arsenic removal mechanism with EC

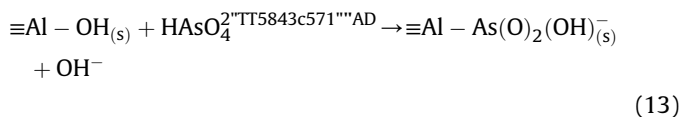
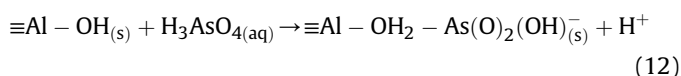
Electrochemically dissolution of anode in EC process generates aluminium ions (Al^{3+}) and hydrogen gas (H_2) is evolved at the cathode. By hydrolyse reactions of Al^{3+} ions in the bulk generate monomeric and polymeric Al species. At result, these species is transformed to aluminium hydroxide and aluminium oxide. The electrode and chemical reactions in solution are shown below:



During EC process with Al electrodes, various monomeric species such as $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^-$, and polymeric Al species e.g., $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ are formed (Holt et al., 2002; Kobya et al., 2011). All these Al species have strong affinity against counter ions like arsenate to cause coagulation. These monomeric and polymeric species transform into amorphous $\text{Al}(\text{OH})_3$ (minimum solubility near pH 6) at between pH 5.2 and 8.8, and then polymerized to $\text{Al}_n(\text{OH})_{3n}$ with high surface area for adsorption of arsenic. $\text{Al}(\text{OH})_3$ and $\text{Al}_n(\text{OH})_{3n}$ flocs at pH 6–9 in the EC process are believed to adsorb arsenic species such as HAsO_4^{2-} , H_2AsO_4^- and H_2AsO_3^- (Vasudevan et al., 2010; Mohora et al., 2012; Alcacio et al., 2014), since these flocs have a positive zeta potential (Alcacio et al., 2014). The sorbent surfaces such as amorphous $\text{Al}(\text{OH})_3$ and Al_2O_3 are positively charged up to pH 7 and at this pH, As(III) species (H_3AsO_3 below pH 9.2, but H_2AsO_3^- above pH 9.2) are uncharged and therefore cannot be bounded to the surface by electrostatic reaction. Sweep coagulation, in which interaction occurs between arsenic species and aluminium oxyhydroxide flocs such as $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$ and Al_2O_3 (Kuan et al., 2009; Hernandez, 2010).



As(III) in EC process can weakly adsorb to the Al-oxyhydroxide surfaces with forming outer-sphere species. As(III) is attached to the Al-hydroxide via outer-sphere complex and released H^+ ion in the reaction (Kuan et al., 2009):



where the surface symbols (\equiv); is used to denote the bonds of the cations with the surface of the solid such as $\text{Al}-\text{OH}_{(s)}$ and $\text{AlO}(\text{OH})$ represents the surface of $\text{Al}(\text{OH})_{3(s)}$, because $\text{Al}(\text{OH})_3$ is an octahedron, with three O atoms bonded to each Al atom. The $\text{Al}-\text{OH}$ surface groups can accept a proton, resulting in a positive surface charge, or donate a proton, resulting in a negative surface charge. Aluminium oxyhydroxide has a positive surface charge of pH 7.4, and the isoelectric point of aluminium oxyhydroxide and $\text{Al}(\text{OH})_3$ are 11.4 and 9.6, respectively (Johnston et al., 2002).

On the other hand, at the above pH 9 in the EC process, $\text{Al}(\text{OH})_4^-$ is dominant, which is soluble and useless for arsenic removal. The reason behind the low arsenic removal efficiencies at pH > 7 could

be explained insight of the above information. As pH of the solution rises to 7, concentration of negative charge of As(III) species, $\text{Al}(\text{OH})_3$, and $\text{Al}_n(\text{OH})_{3n}$ increases. Besides, the concentration of negatively charged $\text{Al}(\text{OH})_4^-$ species increases. Consequently, As(III) removal efficiency decreases due to charge repulsive force between As(III) species and aluminum hydroxide (Thakur and Mondal, 2017).

Previous literature indicated that As(III) removal by Al electrodes was 80% at operating conditions (current density 2 A m^{-2} , EC time 40 min, initial As(III) concentration 75 mg L^{-1} and initial pH 3–11). As(III) was expressed weakly adsorb to the Al-oxyhydroxide surfaces with forming outer-sphere species. Also, As(III) attached to the Al-hydroxide via outer-sphere complex in which reaction H^+ ion (Eq. (12)) was released (Kuan et al., 2009). Danilenko et al. (2005) indicated that As(III) in EC process is partially oxidized to As(V) in the case of using Al anodes. As(III) and As(V) removals in model solutions after an EC process were 95% and 86.3% for Al electrode and 100% and 100% for Fe electrode at electrolysis time of 30 s and current of 400 A. Therefore, arsenic removal rate in the process by Al electrode is lower than Fe electrode, and necessity for a permanent stirring of the solution to oxidize As(III) to As(V) by hydrogen peroxide or by air bubbling. Gomes et al. (2007) reported that As(III) removal by EC process using Al anodes could be >97.5% at operating conditions (300 A m^{-2} , 60 min, initial pH_i 4–6 and initial As(III) concentration of 13.4 mg L^{-1}). Kumar et al. (2004) pointed out that As(III) is oxidized to As(V) during EC using Al electrode, and it is subsequent removal by adsorption/complexation with metal hydroxides generated in the process. As(III) removal efficiency and operating cost of synthetic solution were obtained as 95.7% and $0.019 \text{ \$ m}^{-3}$ at operating conditions (initial As(III) concentration $150 \text{ }\mu\text{g L}^{-1}$ As, initial pH 7, current density 2.5 A m^{-2} , EC time 15 min) (Kobya et al., 2011). By comparison, it is obvious that EC by Al electrodes is more effective for arsenic (III) removal than chemical coagulation by potassium aluminium sulphate. In chemical coagulation residual arsenic concentration decreased by 30–40% at experimental conditions, while As(III) by EC at conditions: initial As concentration $100 \text{ L}^{-1}\mu\text{g}$, initial pH 6–8, current density 100 A m^{-2} and EC time 60 min) is almost entirely removed (Ihos et al., 2005). Arsenic removal by EC using Al plate anodes was performed in a 1.4 L batch reactor for real groundwater (initial As concentration of $512 \text{ }\mu\text{g L}^{-1}$) from Kaudikasa village in India, and obtained 98.41% removal efficiency at optimum conditions (current density of 10 A m^{-2} , initial pH of 7, EC time of 95 min). The estimated operating cost of the study was $0.357 \text{ US \$ m}^{-3}$ (Thakur and Mondal, 2017). Alcacio et al., (2014) investigated As removal from a deep well (initial As concentration of $134 \text{ }\mu\text{g L}^{-1}$ and initial pH of 6.8) in Central Mexico by electrocoagulation using sacrificial Al anode and the respective As removal efficiency and energy consumption were reported as 89.6% and 0.89 kW h m^{-3} at the optimums (mean linear flow rate of 0.91 cm s^{-1} and current density of 60 A m^{-2}). A Similar study by Sandoval et al., (2018) involving simultaneous removal of fluoride and arsenic from contaminated groundwater containing initial arsenic and fluoride concentrations of $50.4 \text{ }\mu\text{g L}^{-1}$ and 5.5 mg L^{-1} using sacrificial aluminium anode in a continuous filter-press reactor, achieved WHO standards (fluoride < 1.5 mg L^{-1} , arsenic < $10 \text{ }\mu\text{g L}^{-1}$) at mean linear flow rate of 0.23 cm s^{-1} and current densities of 60 and 70 A m^{-2} . Another research by Mohora et al. (2018) on As removal from raw groundwater without pH modifications, obtained 96% (effluent concentration of $1.52 \text{ }\mu\text{g L}^{-1}$) As removal within 4 h of experimental runs at optimums; charge loading of 54 C L^{-1} , current density of 1.98 A m^{-2} and flow rate of 12 L h^{-1} .

On the other hand, Goldberg and Johnston (2001) stated that arsenate forms inner-sphere surface complexes on both amorphous Al and Fe oxide while As(III) forms both inner- and outer-sphere

surface complexes on amorphous Fe oxide and outer sphere surface complexes on amorphous Al oxide. In this case, the adsorption capacity for As(III) and As(V) were calculated as 15.7 mg g⁻¹ at pH 6.5–9.5 and 75.7 mg g⁻¹ at pH 2–5 for amorphous Al oxide and 63.7–89.9 mg g⁻¹ at pH 7.9 and 63.7–30.5 mg g⁻¹ at pH 4–9 for amorphous Fe oxide, respectively (Goldberg and Johnston, 2001). At the specific surface area of the forming iron oxides equal to 105 m² g⁻¹, the adsorption values for As(III) and As(V) were 96.1 and 156.7 mg g⁻¹, respectively (Danilenko et al., 2005). Adsorption capacity of Al₂O₃ was 0.40–38.8 mg g⁻¹ for As(III) and 0.5–121.4 mg g⁻¹ at pH 7 (Maiti, 2012).

3. Results and discussion

3.1. Effect of initial pH

The initial pH has significant impact on As(III) removal in aqueous solution and feasibility of EC treatment process. The arsenic speciations mainly depend on initial pH and redox potential of aqueous solution. At low pH values and moderate reducing conditions (>0.10 V), As(III) is thermodynamically stable and found as arsenic acid (H₃AsO₃⁰, H₂AsO₃⁻, HAsO₃²⁻ and AsO₃³⁻) (Smedley and Kinniburgh, 2002). The negative and neutral As(III) species that dominate in relation to pH are H₃AsO₃⁰ at pH < 9.2 and H₂AsO₃⁻ at 9.2 < pH < 12 (Can et al., 2014). In the meantime, HAsO₃²⁻ and AsO₃³⁻ species are formed and become dominant with increasing pHs. The effect of initial pH in the range of 5.5–8.5 on As(III) removal was investigated at the constant operational parameters (i = 0.30 A, d_p = 7.5 mm, h = 5 cm, and Q_{air} = 6 L min⁻¹) which are determined based on our previous studies (Şık et al., 2015; Şık et al., 2017). Fig. 2 illustrates the effect of initial pH on the effluent As(III)

concentration and As(V) concentration formed by oxidation of As(III) to As(V) during EC process. Basically, the As(V) concentration increased with decreasing As(III) concentration as a results of oxidation reaction, while the total arsenic (As_(total)) concentration decreased with increasing operating time at all initial pH_i values. For instance, the initial As(III) concentration of 200 µg L⁻¹ reduced to 149.10 µg L⁻¹ (As_(total)) at operating time of 2 min and initial pH_i of 5.5, while the final As(III) and As(V) concentrations found to be 76.58 µg L⁻¹ and 72.52 µg L⁻¹, respectively. The results distinctly revealed that the As(III) concentration of 72.52 µg L⁻¹ was oxidized to As(V). Namely, the As(III) removal mechanism in aerated EC reactor with Al ball electrodes occurs by oxidation of As(III) to As(V) and then surface complexation and co-precipitation of As(V) with aluminum hydroxides. At operating time of 12 min, the arsenic removal efficiencies were found to be 97.2% (C_{f, As(total)} = 5.62 µg L⁻¹) for pH_i = 5.5, 96.2% (C_{f, As(total)} = 7.56 µg L⁻¹) for pH_i = 6.5, 95.7% (C_{f, As(total)} = 8.7 µg L⁻¹) for pH_i = 7.5, and 92.0% (C_{f, As(total)} = 15.98 µg L⁻¹) for pH_i = 8.5. The effluent arsenic concentrations also reduced to under 10 µg L⁻¹ of permissible WHO arsenic limit value at all pH values except pH_i 8.5. At the end of the EC process, a minor increase in the initial pH_i of 5.5, 6.5, 7.5, and 8.5 resulted in effluent pHs of 6.0, 7.57, 8.12, and 8.55, respectively. The increased effluent pH values could be explained with the pH neutralization in EC process by formation of OH⁻ ions to make solution alkaline.

Based on the above result, it was concluded that the aerated EC reactor was capable to remove As(III) efficiently at pH of 5.5–7.5. The similar trend was observed by Thakur and Mondal (2017) and they found effluent As(III) concentration as 8.19 µg L⁻¹ at operating conditions of pH: 7, current density: 10 A m⁻², operating time: 95 min, inter electrode distance: 1 cm, NaCl concentration:

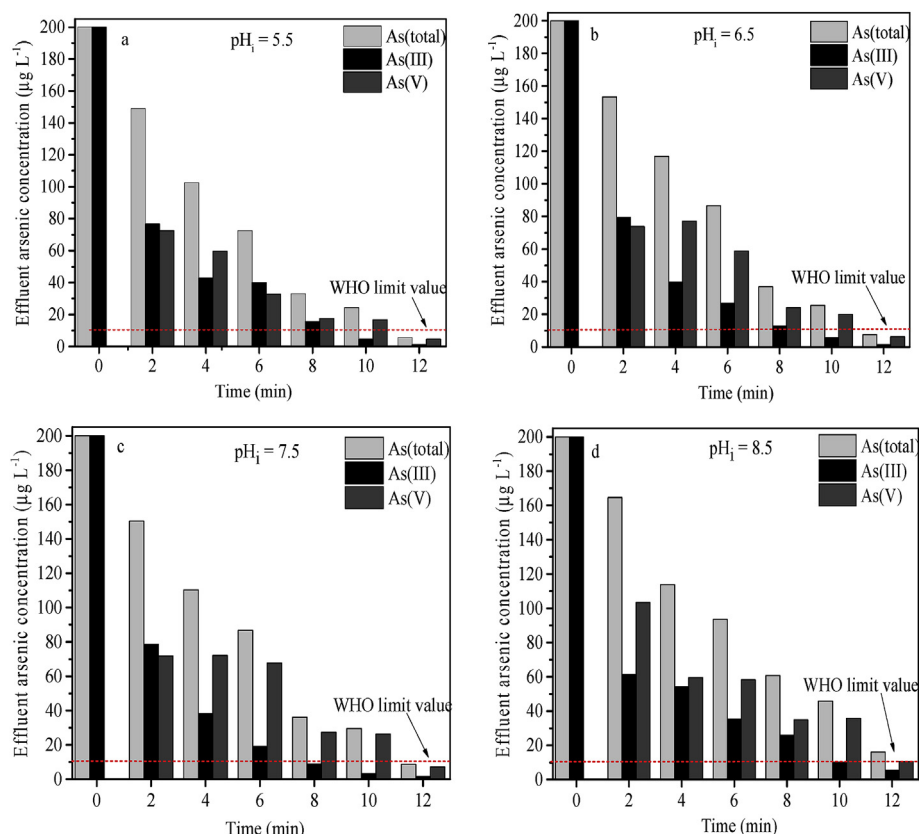


Fig. 2. Effluent arsenic concentrations at different initial pH_i values: (a) pH_i = 5.5, (b) pH_i = 6.5, (c) pH_i = 7.5 and (d) pH_i = 8.5.

0.71 g L⁻¹, and initial arsenic concentration 550 mg L⁻¹. In a separate study, Kumar et al. (2004) studied As (III) removal using EC with iron electrodes and they had removal efficiency of As(III) up to 97–99% at pH_i 6–8. Therefore, the initial pH of the solution was kept constant at pH_i 7.5 when the effect of other operating parameters on As(III) removal was investigated in this study.

The ELC (kg m⁻³), ENC (kWh m⁻³), and TOC (\$ m⁻³) of the EC system were calculated from equations of 2, 3, and 4 to predict or get insight the applicability of aerated EC reactor in treatment plants. The ELC and ENC for As(III) removal was calculated as 0.022 kg m⁻³ and 2.624 kW h m⁻³ for pH_i of 5.5, 0.019 kg m⁻³ and 2.726 kW h m⁻³ for pH_i of 6.5, 0.026 kg m⁻³ and 2.921 kW h m⁻³ for pH_i of 7.5, 0.034 kg m⁻³ and 2.925 kW h m⁻³ for pH_i of 8.5, respectively. TOC of aerated EC process was found to be 0.615 \$ m⁻³ for pH_i of 5.5, 0.620 \$ m⁻³ for pH_i of 6.5, 0.693 \$ m⁻³ for pH_i of 7.5, and 0.735 \$ m⁻³ for pH_i of 8.5.

3.2. Effect of applied current

The applied current is one of the most important operating parameter in electrochemical treatment processes since it controls the reaction rate in reactor (Adjeroud et al., 2018; Chen et al., 2018). The applied current affects the amount of coagulant produced in reactor, size and growth of the flocs, and bubble formation (Yilmaz et al., 2008). In this study, the effect of applied current in the range of 0.075–0.30 A on As(III) removal efficiency was investigated at the constant operational parameters (pH_i = 7.5, d_p = 7.5 mm, h = 5 cm, and Q_{air} = 6 L min⁻¹). The results are presented in Fig. 3.

The arsenic removal efficiency increased with the increasing

current density from 0.075 A to 0.30 A. The amount of dissolved Al³⁺ increased with increment of applied current and then the constant amount of arsenic interact to more Al(OH)₃ and thus the arsenic removal efficiencies were increased. The arsenic removal efficiencies were found to be 85.9% (C_{f, As(total)}: 28.10 μg L⁻¹) for applied current of 0.075 A, 90.7% (C_{f, As(total)}: 18.71 μg L⁻¹) for applied current of 0.15 A, and 95.7% (C_{f, As(total)}: 8.70 μg L⁻¹) for applied current of 0.3 A (Fig. 3). The effluent arsenic concentration reduced to under 10 μg L⁻¹ of permissible WHO arsenic limit value only at applied current of 0.30 A. On the other hand, the applied current was increased from 0.075 to 0.30 A increased from 85.9% to 95.7% of arsenic removal efficiency at the end of the operating time of 18 min, electrode and energy consumption reached from 0.031 kg m⁻³ to 0.311 kW h m⁻³ to 0.051 kg m⁻³ and 2.921 kW h m⁻³, respectively. The high energy and electrode consumption with increasing applied current values was observed due to energy and electrode consumption affected linearly applied current as seen in Eqs. (2) and (3). Although the applied current significantly promote to dissolution of electrode material and remove high amount of arsenic, the higher applied current was not desirable in terms of overall EC process performance considering overall operating cost. TOC of EC process was found to be 0.583 \$ m⁻³ at applied current of 0.30 A. In comparison with the studies in the literature, it was observed that the 0.30 A of applied current was acceptable considering the maximum arsenic removal efficiency and minimum operating cost. For instance, Kobya et al. (2015) studied on arsenic removal from groundwater using electrocoagulation with iron ball electrodes and the operating cost was found to be 1.55 \$ m⁻³. In our previous study, the As(V) removal from groundwater

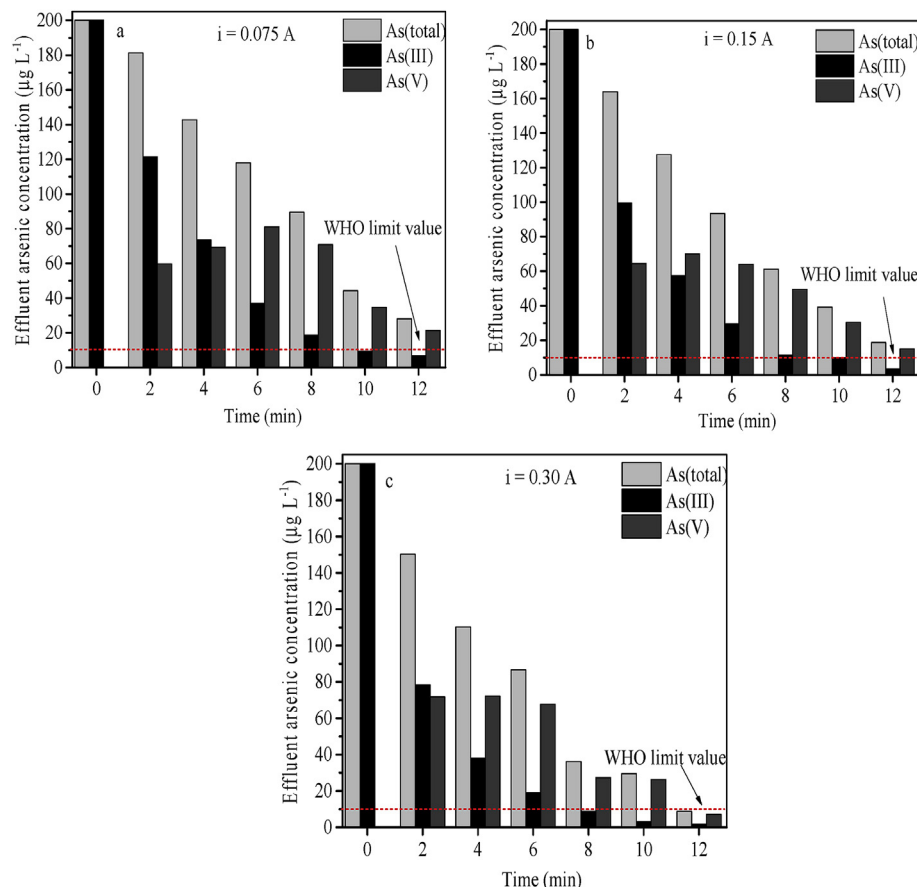


Fig. 3. Effluent arsenic concentrations at different applied current values: (a) $i = 0.075$ A, (b) $i = 0.15$ A and (c) $i = 0.30$ A.

using EC reactor with Al ball electrodes was studied and the maximum arsenate removal efficiency and minimum operating cost were 99.0% and $0.442 \text{ \$ m}^{-3}$ (Goren et al., 2018). Besides, the operating costs of granulated ferric hydroxide, activated alumina, coagulation-filtration, air oxidation-filtration, and reverse osmosis processes were 1.20, 3.20, 1.21, 0.054, and $3.72 \text{ \$ m}^{-3}$ for obtain maximum permissible arsenic concentration according to WHO, respectively.

The sludge formation were also calculated under different applied currents and operating time of 12 min. The amount of sludge as expected increased with increasing applied current. As expected, the amount of sludge increased from 0.081 kg m^{-3} to 0.255 kg m^{-3} at applied current of 0.075 and 0.30 A, respectively. At the end of the EC process, an increase in the initial pH_i of 7.5 resulted in effluent pH s of 7.75, 7.77, and 8.15 at applied current of 0.075, 0.15, and 0.30 A, respectively. The increased effluent pH value especially at applied current of 0.30 A could be explained with the high amount of OH^- ions formation which make solution alkaline. Based on the above results, the optimum applied current was determined as 0.30 A when the effect of air flow rate, electrode height in EC reactor, and size of Al ball electrodes were investigated.

3.3. Effect of airflow rate

To enhance the performance of EC process, we evaluated the effect of the air flow rate on As(III) removal efficiency. The effects of air flow rate on As(III) removal efficiency of the EC system were investigated by varying air flow rate ($Q_{\text{air}} = 0, 2, \text{ and } 6 \text{ L min}^{-1}$), while keeping the other operating parameters (i.e., $\text{pH}_i = 7.5$, $d_p = 7.5 \text{ mm}$, $h = 5 \text{ cm}$, and $i = 0.30 \text{ A}$) constant. As seen in Fig. 4, an increase in air flow rate significantly favored As(III) removal efficiency. The arsenic removal efficiencies were found to be 88.4% ($C_f, \text{As}(\text{total}) = 23.3 \text{ }\mu\text{g L}^{-1}$) without oxygen ($Q_{\text{air}} = 0 \text{ L min}^{-1}$), 92.3% ($C_f, \text{As}(\text{total}) = 15.5 \text{ }\mu\text{g L}^{-1}$) with air flow rate of $Q_{\text{air}} = 2 \text{ L min}^{-1}$, and

95.7% ($C_f, \text{As}(\text{total}) = 8.70 \text{ }\mu\text{g L}^{-1}$) with air flow rate of $Q_{\text{air}} = 6 \text{ L min}^{-1}$ at operating time of 12 min. At air flow rate of $Q_{\text{air}} = 6 \text{ L min}^{-1}$, the effluent arsenic concentration was $8.70 \text{ }\mu\text{g L}^{-1}$, which satisfied for the safe drinking according to the WHO.

The air flow rate in EC reactor probably increased the As(III) removal efficiency in two ways. Firstly, at an EC process, mixing of solution in EC reactor is supplied by generated hydrogen gas at the cathode. In aerated EC process, mixing of solution in EC reactor is supplied by air flow in reactor. At low applied current or current density are deposits on electrode surfaces of colloidal and polymeric matters in the solution. For this problem, position (as anode or cathode) of electrodes from DC power supply in an EC reactor using plate and rod is generally reversed with certain time intervals during process. At an EC process using ball anodes, the air flow is providing the coagulation/flocculation process by mixing in the solution in EC reactor. Therefore, deposits of Al-hydroxide flocs formation at surfaces on and between Al ball anodes in the reactor is prevents with the air flow rate (Kobyta et al., 2011). Secondly, the As(III) probably oxidized to As(V) by $\text{O}_{2(\text{g})}$ as an oxidizing agent. In this study, the effluent As(III) concentration decreased from $12.1 \text{ }\mu\text{g L}^{-1}$ at without oxygen to $1.6 \text{ }\mu\text{g L}^{-1}$ at air flow rate of $Q_{\text{air}} = 6 \text{ L min}^{-1}$ at the end of the operating time of 18 min. These results showed that in EC process As(III) firstly oxidized to As(V) and then As(V) species removed from water with $\text{Al}(\text{OH})_3$ hydroxide. In furtherance, Kumar et al. (2004) reported that the As(III) removal mechanism in EC process was mainly oxidation of As(III) to As(V) and then surface complexation of As(V) species with metal (Al or Fe) hydroxides.

Consequently, it can be concluded that the aerated EC reactor significantly increased the removal efficiency of As(III). Since, the homogenous mixing in solution increased, the passivation layer on the surfaces of Al ball anodes prevented, and the As(III) oxidized to As(V) with the increment of air flow rate. Nevertheless, the surface investigation of formed flocs and electrodes after EC process are

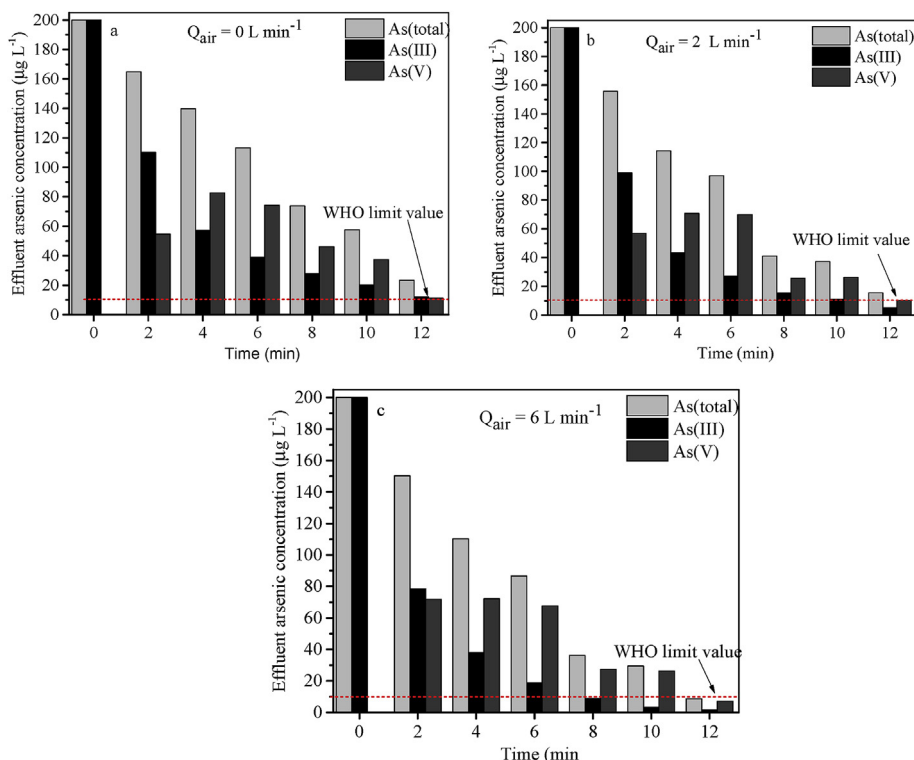


Fig. 4. Effluent arsenic concentrations at different air flow rates: (a) $Q_{\text{air}} = 0 \text{ L min}^{-1}$; (b) $Q_{\text{air}} = 2 \text{ L min}^{-1}$ and (c) $Q_{\text{air}} = 6 \text{ L min}^{-1}$.

important to approve these results.

3.4. Effect of Al ball height in EC reactor

The Al ball height in EC reactor is significant operating parameter which effects the electrode life time and As(III) removal efficiency. The effect of electrode height in EC reactor on As(III) removal efficiency was investigated by varying electrode level ($h = 2, 5,$ and 8 cm) at pH of 7.5, size of Al ball electrodes of 7.5 mm, air flow rate of 6 L min^{-1} , and applied current of 0.30 A (Fig. 5). As expected, the As(III) removal efficiency increased with increasing electrode level as the increase in Al ball electrode surface area. Thus, the dissolved Al^{3+} concentration increased with increasing electrode height and formed high amount of $\text{Al}(\text{OH})_3$ to remove arsenic.

As seen in Fig. 5, the arsenic removal efficiencies were 89.9% ($C_f, \text{As}(\text{total}) = 20.17 \mu\text{g L}^{-1}$), 95.7% ($C_f, \text{As}(\text{total}) = 8.70 \mu\text{g L}^{-1}$), and 98.8% ($C_f, \text{As}(\text{total}) = 2.40 \mu\text{g L}^{-1}$) at electrode height (h) of 2, 5, and 8 cm, respectively. The effluent arsenic concentrations also reduced to under $10 \mu\text{g L}^{-1}$ of permissible the WHO arsenic limit value at electrode height of 5 and 8 cm. Furthermore, the effluent arsenic concentrations decreased to under $10 \mu\text{g L}^{-1}$ limit value at electrode height of 8 cm after operating time of 8 min. The results showed that the operating time of EC process could be reduce by increasing electrode height. Total surface areas for Al ball anode size of 7.5 mm with column heights of 2, 5, and 8 cm were found to be 0.03179, 0.07595, and 0.18214 m^2 , respectively. These results showed that the surface area of the total Al ball electrodes increased with the increasing electrode height at constant Al ball electrode size. On the other hand, at the end of the EC process, the

amount of sludge was found to be 0.1381, 0.2134, and 0.3241 kg m^{-3} for height of 2, 5, and 8 cm, respectively. Based on the above results, it can be concluded that the optimum electrode height was determined as $h = 5$ cm considering maximum As(III) removal efficiency and minimum sludge formation.

3.5. Health risk assessment

The effluent arsenic concentrations after EC treatment process were evaluated in terms of health risk to understand the quality of treated water. The chronic daily intake (CDI) of contaminants in water sources are calculated for dermal, inhalation, or oral (ingestion) exposures (Muhammad et al., 2010; USEPA, 1998). In this study, exposure assessment for arsenic was conducted depending on oral exposure. CDI for oral exposure to arsenic with drinking water was calculated using Eq. (5). The hazard quotient (HQ) for non-carcinogenic risk and carcinogenic risk (CR) of arsenic in drinking water also calculated using Eq. (6) and (7), respectively.

$$CDI_{\text{oral}} = \frac{(C_{\text{As}}CRFCDF)}{(BWTime)} \quad (5b)$$

where, CDI_{oral} : chronic daily intake ($\text{mg kg}^{-1} \text{ day}^{-1}$), C_{As} : effluent arsenic concentration in groundwater ($\mu\text{g L}^{-1}$), F : conversion factor from μg to mg (0.001), CR : consumption of water (2 L day^{-1}) (USEPA, 2018), CF : water consumption frequency ($365 \text{ day year}^{-1}$), CD : water consumption duration (70 year), BW : body weight (70 kg), and $Time$ (25,550 days) (USEPA, 2009).

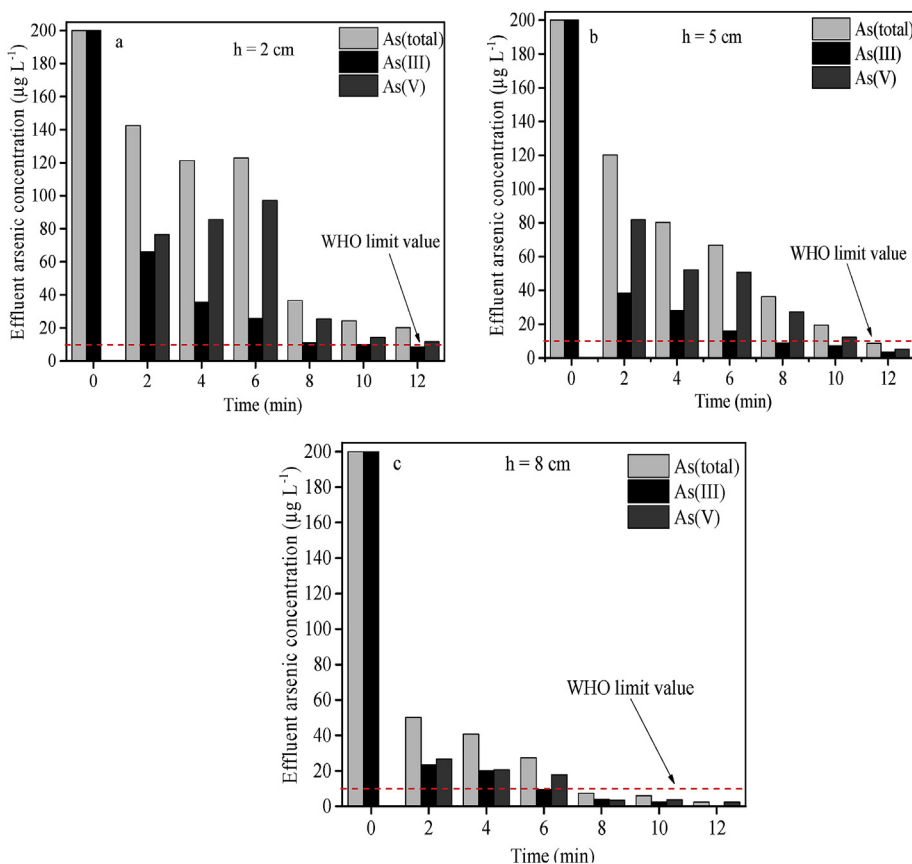


Fig. 5. Effluent arsenic concentrations at different electrode height in EC reactor: (a) $h = 2$ cm, (b) $h = 5$ cm and $h = 8$ cm.

$$HQ_{\text{oral}} = CDI_{\text{oral}}/RfD_{\text{oral}} \quad (6b)$$

$$CR_{\text{oral}} = CDI_{\text{oral}}SF \quad (7b)$$

where, RfD_{oral} : oral reference dose value of arsenic ($0.0003 \text{ mg kg}^{-1} \text{ day}^{-1}$) and SF : slope factor for oral arsenic exposure ($1.5 \text{ mg kg}^{-1} \text{ day}^{-1}$) (USEPA, 2018; USEPA, 2009).

The CDI values, non-carcinogenic risk, and carcinogenic risk values of groundwater after treatment of arsenic by EC process under different operating conditions were presented in Table 2. In the health risk assessment, if CR value for arsenic is in the range of the 10^{-6} – 10^{-4} , it is tolerable according to USEPA and if HQ value is found to be > 1 , it is concluded that there is adverse health effects of arsenic on human health (USEPA, 2004).

The HQ value of treated water ranged from 0.23 to 2.68. For instance, the HQ values were found to be 0.53, 0.72, 0.83, and 1.52 at initial pH values of 5.5, 6.5, 7.5, and 8.5, respectively. Based on the HQ higher than 1, it can be concluded that the harmful effects of As in treated water on humans increased with the increasing initial pH. On the other hand, the harmful effect of As decreased with increasing applied current, air flow rate, and height of electrode in EC reactor. For instance, the HQ decreased from 2.22 to 0.83 at air flow rate of 0 and 6 L min^{-1} , respectively. The highest HQ was found as 2.68 in treated water with the applied current of 0.075 A. Considering the electrode height in EC treatment process, the HQ values were found in the order of $2 \text{ cm} > 5 \text{ cm} > 8 \text{ cm}$ of electrode height. The HQ were acceptable at the optimum operating conditions of initial pH_i of 7.5, applied current of 0.30 A, air flow rate of 6 L min^{-1} , and electrode height of 5 cm. As seen in Table 2, the CR of As in treated water under different operating conditions ranged from $1.029\text{E-}04$ to $1.204\text{E-}03$. As expected, the CR of As increased with increasing initial pH value, while it decreased with increasing applied current, air flow rate and electrode height. The maximum CR of As in treated water was found to be $1.204\text{E-}03$ at applied current of 0.075 A, which exceed the tolerable CR value of As in drinking water according to USEPA. On the other hand, the minimum CR of As was found to be $1.029\text{E-}04$ at electrode height of $h = 8 \text{ cm}$. Consequently, the CR of As was in the range of tolerable limit at all operating conditions except applied current of 0.075 A at the end of the aerated EC process to remove As from groundwater. Nguyen et al. (2009) studied on risk assessment of As in water treated with sand filtration system in Ha Nam province, Vietnam and they found that the almost 40% of the people, who consuming treated groundwater, were at chronic toxic risk for arsenic exposure. Consequently, our results showed that the aerated EC reactor is sustainable treatment technology for As(III) removal from

groundwater with the low HQ and CR values.

3.6. Comparison of present process with relevant processes

The removal of arsenic by EC process was studied by many authors. The treated water type, electrode type, operating parameters including initial pH, applied current, initial As (III) concentration, and operating time, operating cost, and As (III) removal efficiencies of the relevant articles reviewed and summarized in Table SM-1. A number of electrode materials were used in EC reactor: Fe and Al plate, Fe rod, Fe and Al scrap, Al–Fe hybrid plate, Mild-steel plate, and Fe ball. In these electrode materials, the most commonly used electrode material was Fe plate. In 24 articles that reported arsenic removal using EC process, Fe plate electrodes were used in 45% ($n = 11$). The percentages of the other electrode materials were as follows: 8.3% ($n = 2$) Mild-steel electrode and Fe rod electrode, 4.2% ($n = 1$) Fe and Al scrap electrode, 12.5% ($n = 3$) Al plate and Al–Fe hybrid electrode.

The arsenic removal efficiencies of EC processes were in the range of 85.0–99.9%. Furthermore, the operating cost of the EC processes were in the range of 0.002 – $0.84 \text{ \$ m}^{-3}$. The removal efficiency and operating cost of aerated EC process using Al ball electrodes was calculated as 99.2% and $0.583 \text{ \$ m}^{-3}$, which was higher compared to the most of the literature values. Consequently, aerated EC process compared with the other studies considering other advantages which are mentioned in introduction, aerated EC process turns out to be an effective and environmental friendly method for the removal of arsenic from groundwater.

4. Conclusions

In this study, aerated EC process using Al ball electrodes for As(III) removal from groundwater was evaluated. The results showed that the aerated EC process is able to oxidized As (III) to As (V) and this oxidation is mainly dependent on the amount of air flow rate. If the air flow rate is high, as in the case of optimum pH_i 7.5, then the oxidation of As(III) is increased. Moreover, As(III) removal efficiency increased with the increasing applied current and electrode height in the EC reactor. The optimum applied current and electrode height was found to be 0.30 A and 5 cm, respectively. The results were also revealed that the effluent arsenic concentration at optimum operating conditions ($pH_i = 7.5$, $Q_{\text{air}} = 6 \text{ L min}^{-1}$, $i = 0.30 \text{ A}$, and $h = 5 \text{ cm}$) was met the WHO standard for arsenic in drinking water. Furthermore, the human health risk assessment of treated groundwater presented that aerated EC reactor is promising treatment technology for As(III) removal from groundwater with the acceptable HQ and CR values.

Table 2
Arsenic health risk assessments in treated groundwater using EC process under different operating parameters.

Operating parameter		CDI_{oral} ($\text{mg kg}^{-1} \text{ day}^{-1}$)	HQ_{oral} (non-carcinogenic risk)	CR_{oral} (Carcinogenic risk)
Initial pH_i (–)	5.5	1.606E-04	0.53	2.409E-04
	6.5	2.160E-04	0.72	3.240E-04
	7.5	2.486E-04	0.83	3.729E-04
	8.5	4.566E-04	1.52	6.849E-04
i (A)	0.075	8.029E-04	2.68	1.204E-03
	0.15	5.346E-04	1.78	8.019E-04
	0.3	2.486E-04	0.83	3.729E-04
Q_{air} (L min^{-1})	0	6.657E-04	2.22	9.986E-04
	2	4.429E-04	1.48	6.643E-04
	6	2.486E-04	0.83	3.729E-04
	8	5.762E-04	1.92	8.644E-04
h (cm)	2	2.486E-04	0.83	3.729E-04
	5	2.486E-04	0.83	3.729E-04
	8	6.857E-05	0.23	1.029E-04

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

A.Y. Goren: Data curation, Writing - original draft. **M. Kobya:** Conceptualization, Methodology, Supervision. **M.S. Oncel:** Validation, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126363>.

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