



Arsenic removal from groundwater using an aerated electrocoagulation reactor with 3D Al electrodes in the presence of anions

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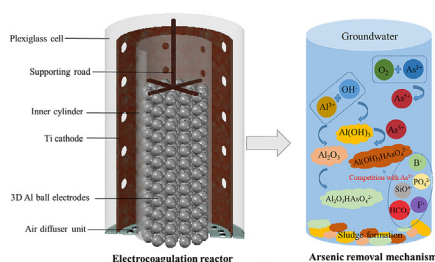
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HIGHLIGHTS

- Aerated EC reactor with 3D Al ball electrodes used for arsenic removal in presence of anions.
- The maximum arsenic removal efficiency was 98.6% was at optimized conditions.
- Silicate and phosphate ions affect performance more than boron, bicarbonate, and fluoride.
- Minimum operating cost of the process was found to be 0.098 \$ m⁻³ at optimum conditions.
- Aerated EC reactor exhibited a promising performance for arsenic and anions removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Co-occurrence of arsenic and anions in groundwater causes a severe health problems and combine effects of these pollutants significantly affect performance of treatment process. Thus, this study has been conducted to examine the combine effects of anions on arsenic removal using aerated electrocoagulation (EC) reactor with 3D Al electrodes in groundwater. A 3-level, six factors Box-Behnken experimental design (BBD) was applied to investigate the individual and combine effect of anions and operating time: phosphate (x_1 : 1–10 mg L⁻¹), silica (x_2 : 20–80 mg L⁻¹), bicarbonate (x_3 : 130–670 mg L⁻¹), fluoride (x_4 : 2–10 mg L⁻¹), boron (x_5 : 5–10 mg L⁻¹), and operating time (x_6 : 8–22 min) on desired responses. The specified responses were effluent arsenic concentration ($C_{f,As}$), removal efficiency of arsenic (R_e), consumptions of energy and electrode (ENC and ELC), operational cost (OC), and adsorption capacity (q_e). The optimum operating parameters predicted using BBD were found to be x_1 : 1.0 mg L⁻¹, x_2 : 26.0 mg L⁻¹, x_3 : 651.5 mg L⁻¹, x_4 : 2.0 mg L⁻¹, x_5 : 9.9 mg L⁻¹, and x_6 : 10.5 min considering highest removal efficiency of arsenic and lowest operational cost. Under these operating conditions, the experimental values of $C_{f,As}$, R_e , ENC, ELC, OC, and q_e were found to be 2.82 μg L⁻¹, 98.6%, 0.411 kWh m⁻³, 0.0124 kg m⁻³, 0.098 \$ m⁻³, and 17.65 μg As (mg Al)⁻¹, respectively. Furthermore, mathematical modelling was conducted using

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quadratic regression model and response surface analysis was performed to understand the relationship between independent parameters and responses.

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1. Introduction

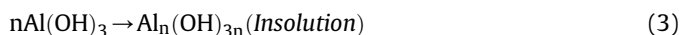
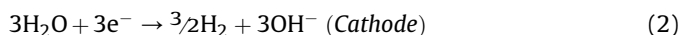
Water is essential for survival of all organisms, including humankind as a major component. Hence, availability and adequate accessibility to freshwater is a significant scientific and technological problems in worldwide. Recently, the increasing water demand in worldwide forced us to concentrate on reasonable use of sources, although the significant part of our planet is covered by water and is called as "Blue Planet". A common explanation regarding with lack of fresh water is that the most of water stored as either glaciers or deep ground water rendered not easily accessible. Globally, a serious number of people suffer from water scarcity. For instance, World Health Organization (WHO) reported that 748 million people do not have clean and adequate water resource, while almost 2 billion people expose to contaminated drinking water sources. On the other hand, roughly half of the entire population on world inhabit in water stressed areas (WHO/UNICEF (World Health Organization/United Nations International Children's Emergency Fund), 2014).

The sustainable management of natural resources is one of the targets of European Union Member States to fight against global warming. This objective should undeniably be compatible with environment. Groundwater sources are one of the most important field play an important role in this regard which offers significant resources that are widely available on a global scale. However, groundwater quality could be deteriorating potentially toxic trace elements and other ions present in groundwater which are commonly originate in water with the dissolution of mineral bearing rocks. The existence of hazardous pollutants in groundwater has been reported in different parts of world (Kumar and Puri, 2012). Among these hazardous pollutants, groundwater arsenic contamination has been widely investigated as a global problem because many people have to consume excessive amounts of arsenic containing drinking water (Ravenscroft et al., 2009). Turkey is one of the countries fight against groundwater arsenic contamination and arsenic contamination was reported as 0.5–10,700 $\mu\text{g L}^{-1}$ (Sik et al., 2017).

According to International Agency for Research on Cancer (IARC), arsenic is classified into Group I of human carcinogens and expose to arsenic containing drinking water leads to chronic health problems (IARC, 2019). Chronic health problems of arsenic include cancer in some organs (bladder, kidney, liver, lungs, and skin), nervous system defects such as loss of sensation in the limbs and hearing problems, digestive difficulties, diabetes, discoloration of the skin, and cardiovascular diseases (Sinha and Prasad, 2020). Therefore, the WHO set a highest permissible level of arsenic in drinking water at 10 $\mu\text{g L}^{-1}$ (WHO, 2011). The US-EPA reviewed potential Best Available Technologies (BATs) for removal of arsenic from aqueous solutions. These BATs are ion exchange, adsorption using activated alumina, enhanced coagulation and flocculation, enhanced lime softening, and reverse osmosis (US-EPA, 2001). Furthermore, alternative adsorption media such as iron, titanium, and zirconium based media, post of use treatment, and coagulation assisted microfiltration are classified as other available technologies for arsenic removal. The advantageous and drawbacks of above mentioned treatment processes have been reported in detail in literature (Jadhav et al., 2015; Litter et al., 2019). Most important

drawbacks of these technologies are summarized as follow: high operating and capital costs, excess sludge formation, needs for additional chemicals and further treatment, formation of toxic and carcinogenic by products, and high sensitivity to water physico-chemical properties. In conclusion, it is important to remark that the development of already available treatment technologies and/or invention of novel treatment technologies are urgent topics to overcome these drawbacks.

Recently, electrochemistry based technologies have gained much interest as an efficient arsenic removal technology (Syam-Babu and Nidheesh, 2020; Kobya et al., 2020). The electro-coagulation (EC) method is one of these methods owing to its significant benefits such as no need for extra chemical reagents, low cost, low sludge formation, easy operation, small space requirement, and possibility of automation (Thakur and Mondal, 2017). In simple EC reactor using Al anodes, Al^{3+} ions are produced by the dissolution of anode material and then these Al^{3+} species are transformed into aluminum hydroxides such as boehmite ($\text{AlOOH}_{(s)}$), gibbsite ($\alpha\text{-Al}(\text{OH})_{3(s)}$) and bayerite ($\gamma\text{-Al}(\text{OH})_{3(s)}$), and aluminum oxides ($\text{Al}_2\text{O}_{3(s)}$) depend on solution pH. The reactions in EC reactor using Al electrodes may be summarized as follows (Kobya et al., 2011):



According to literature studies, the main mechanisms in removal by EC process of anions with iron or aluminium electrodes are (i) the direct precipitation (charge neutralization) of anions and (ii) the adsorption or enmeshment of the inorganic anions within a growing iron or aluminium hydroxide precipitate (Lacasa et al., 2011, 2013). For example, removal of arsenic by aluminum or iron metal (oxy)hydroxylic flocs formed during the EC process most probably affected by the presence anions such as phosphate, silicate, fluoride, bicarbonate, and boron in groundwater, thus, these anions may compete with arsenic species for the possible adsorption surfaces as well as change the electrostatic charge of adsorption surfaces of these flocs (Lacasa et al., 2011, 2013). Several studies reported the arsenic, fluoride, silicate, and phosphate removal from aqueous solutions using EC process (Bandaru et al., 2020; Castañeda et al., 2020). However, most of these studies focused on individual pollutant removal, only a few study investigated the co-occurrence of the arsenic-fluoride, arsenic-phosphate, and arsenic-silicate on the EC process (Castañeda et al., 2019; López-Guzmán et al., 2019; Thakur et al., 2019), and there is no study on arsenic removal in the presence of more than three anions using EC reactor with Al electrodes, according to our literature survey. Furthermore, rod and plate type electrodes for the removal of arsenic from waters are commonly used in the conventional EC reactors (Kumar et al., 2004; Gomes et al., 2007). However, plate and rod types of electrodes have some disadvantages due to several difficulties in

operation and low surface areas. In conventional EC processes, the additional chemical reagents also used for pre-oxidation of As(III) to As(V). On the other hand, an aerated EC reactors no needs for chemical addition for oxidation owing to supplied oxygen as an oxidation reagent. The aeration in EC reactor can also reduce the passivation layer on the electrode surfaces and it can provide the well mixing in reactor. Therefore, an aerated EC reactor with Fe and Al sphere shape electrodes was designed and optimized in our previous studies to eliminate the above problems (Sik et al., 2015; Goren et al., 2020). Results showed that the aerated EC reactor with sphere shaped electrodes for removal of arsenic from groundwater were effective than conventional EC reactors. Moreover, simultaneous arsenic and anion removal using Al electrodes are better than Fe electrodes due to the high affinity of aluminum to anions (Flores et al., 2014). Kobya et al. (2011) demonstrated that aluminum was better than iron electrodes at removing arsenic from drinking water. Hernandez et al. (2010) obtained similar results. There is also limited study on simultaneous arsenic and anions removal using EC with Al electrodes in the literature. Consequently, the aerated EC reactor with 3D Al sphere electrodes was used in this study due to easy in operation, process compactness, high surface areas of electrodes, reduction of passivation layer, well mixing, and significant arsenic and anion removal efficiencies.

The novelty of this study lies in the removal of arsenic from groundwater in the presence of phosphate, silicate, bicarbonate, fluoride, and boron using aerated EC reactor with 3D Al ball electrodes and this study is the first and one of the most comprehensive study in this area. Furthermore, the arsenic removal efficiency was optimized by using BBD in order to achieve the desire qualities of groundwater for drinking purposes.

2. Materials and methods

2.1. Groundwater sample characterization

The groundwater sample were taken from the province of Kocaeli, Turkey. The quality of the groundwater sample are shown in Table 1. As, P, F, and B were not detected. Therefore, in this study, arsenic was added to real groundwater and it was fully simulated arsenic containing real groundwater thanks to the presence of other anions and cations in the groundwater. In this way, arsenic removal performance of the aerated EC process under the presence of anions and cations was investigated. Groundwater sample containing $200 \mu\text{g L}^{-1}$ of arsenic ($100 \mu\text{g L}^{-1}$ As(V) + $100 \mu\text{g L}^{-1}$ As(III)) was prepared daily from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and NaAsO_2 salts. Furthermore, stock solutions of bicarbonate, silicate, phosphate,

fluoride, and boron were prepared from NaHCO_3 , Na_2SiO_3 , Na_2HPO_4 , NaF , and HBO_3 salts, respectively. Required concentrations of these anions were prepared from the dilution of stock solution in real groundwater.

2.2. EC reactor and experimental method

Schematic diagram of the EC reactor with 3D Al electrodes were illustrated in Fig. 1. The detailed information about aerated EC reactor set up were reported in our previous study (Goren et al., 2020). Groundwater sample (0.80 L) containing $200 \mu\text{g L}^{-1}$ of arsenic and required concentrations of anions were filled into the reactor. The inner cylindrical anode compartment was filled with 7.5 mm of 3D Al electrodes to be 5 cm of electrode height. Application of current (0.15 A) to the system and the measurement of the voltage were accorded by DC power supply. Furthermore, the EC reactor was aerated (6 L min^{-1}) by air compressor. At the end of the specified operational time, groundwater samples were collected and filtered by $0.45 \mu\text{m}$ filter before to analysis. Furthermore, weight of the 3D Al ball electrodes were measured at start and end of the experiments to determine consumption of electrode.

2.3. Analytical methods

Electrical conductivity and pH measurements were carried out using a Mettler Toledo Seven Go conductivity meter and Mettler Toledo Seven Compact pH meter, respectively. The concentration of anions (bicarbonate, chloride, fluoride, nitrate, phosphate, and sulphate) was determined by ion chromatography (IC, Shimadzu HIC-20 A). The concentrations of aluminum, boron, calcium, iron, magnesium, manganese, and silicate were analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optime-7000DV). Furthermore, Scanning Electron Microscopy (SEM, Quanta 250FEG) with energy dispersive X-ray spectrometry (EDX) was used to obtain the surface morphology and elemental compositions of the sludge samples. Fourier Transform Infrared (FTIR) spectroscopy analyses were also performed (Shimadzu FTIR 8400 S) to determine functional groups of the sludge samples.

The hydride generation procedure coupled with ICP-OES spectrometer was used to analyze the total arsenic concentration ($\text{As}_{(\text{total})} = \text{As}(\text{III}) + \text{As}(\text{V})$). At first step, the sample containing arsenic was mixed with 1 mL of reducing agent mixture ($5\% \text{ C}_6\text{H}_8\text{O}_6$ and $5\% \text{ KI}$) and 1 mL of HCl , and allowed to reduction of As(V) to As(III) for 60 min at dark place. Furthermore, a reducing agent mixture ($2\% \text{ NaBH}_4$ and $0.5\% \text{ NaOH}$) and carrier solution ($5\% \text{ C}_6\text{H}_8\text{O}_7$) was used to detection of As(III) selectively in the analyze step with ICP-OES spectrometer (Chooto et al., 2016). Under these operating conditions, NaBH_4 instantaneously converted As(III) to arsine gas (AsH_3) at room temperature and detected, while the reduction of As(V) to AsH_3 occurred relatively slow. Finally, the As(V) concentration can be determined by deducting of As(III) to total arsenic. Detection limit of ICP-OES was found to be $0.10 \mu\text{g L}^{-1}$. All analysis was carried out threefold and results were averaged.

2.4. Process optimization design of Box-Behnken and data analysis

In present study, Box-Behnken Design (BBD) was chosen as a quadratic design instead of central design or full factorial design since BBD suggests some advantages. For instance, the BBD requires fewer experimental points, presents experimental points at the mid-points of the specified edges, prevents the extreme experimental points which led to more noticeable estimation of the coefficients, and reduces the update inaccuracies since it dissociates parametric extremes and have no corners (Majumder and Gupta,

Table 1
Quality of groundwater sample.

Parameters	Concentration
pH	7.6 ± 0.1
Electrical conductivity ($\mu\text{S cm}^{-1}$)	1055 ± 4
Alkalinity ($\text{mg CaCO}_3 \text{ L}^{-1}$)	260 ± 2
Total hardness ($\text{mg CaCO}_3 \text{ L}^{-1}$)	418 ± 1.6
TDS (mg L^{-1})	528 ± 5
TOC (mg L^{-1})	5 ± 0.01
Turbidity (NTU)	1 ± 0
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

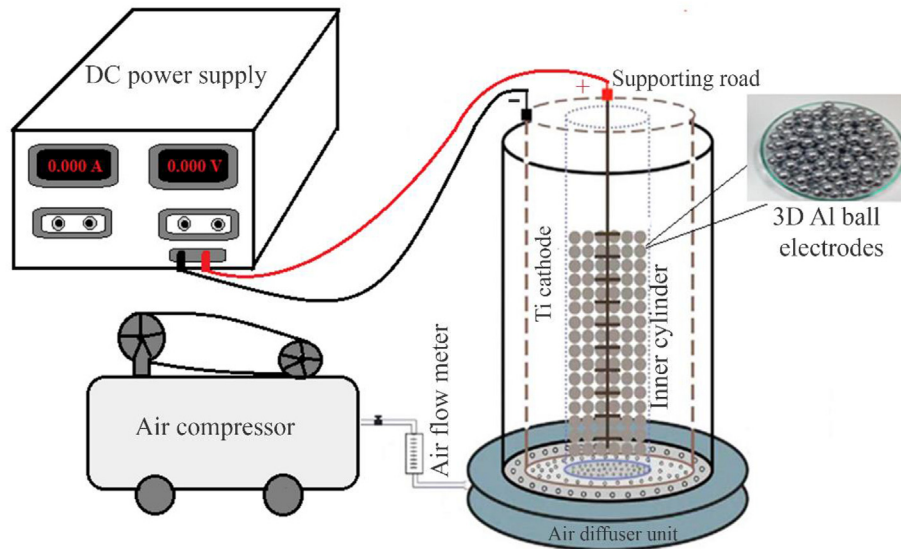


Fig. 1. Schematic diagram of EC reactor with 3D Al electrodes.

2011; Morya et al., 2018). In view of these advantages, BBD with six independent variables at 3-level was used to optimize arsenic removal and investigate the correlation between the independent variables and the responses using the Design Expert Software (version 8.0.4.1).

The specific independent variables were the concentrations of phosphate (x_1), silica (x_2), bicarbonate (x_3), fluoride (x_4), and boron

$$\text{Consumption of electrode (ELC, kg m}^{-3}\text{)} = \frac{it_{EC}M_{Me}}{zMeFv} \quad (6)$$

$$\text{Consumption of energy (ENC, kWh m}^{-3}\text{)} = \frac{Uit_{EC}}{v} \quad (7)$$

$$\text{Adsorption capacity (} q_e, \mu\text{g As mg Al}^{-1}\text{)} = \frac{(C_i - C_e)}{(it_{EC}M_{Al}/zF)} \text{ or } q_e (\mu\text{g As C}^{-1}\text{)} = \frac{(C_i - C_e)}{it_{EC}} \quad (8)$$

(x_5), as well as the operating time (x_6) which had considerable effect on arsenic removal. The independent variables and 3-levels of each variable; low, mid-point, and high were coded as -1 , 0 , and $+1$ (Table 2). Tables S1–3 shows the design matrix consist of 62 sets of experimental runs from the design procedure and responses from the experimental procedure. Moreover, Re , ELC , ENC , q_e , and OC were selected as responses of the process and the determination of variables were shown in Eq. (5)–(9), respectively.

$$\text{Arsenic removal (} Re, \% \text{)} = \frac{(C_i - C_e)100}{C_i} \quad (5)$$

$$\text{Operating cost (} OC, \$ m^{-3}\text{)} = (xENC) + (yELC) \quad (9)$$

where C_i and C_e are initial and final concentrations of arsenic ($\mu\text{g L}^{-1}$), t_{EC} is operating time (min), i is applied current (A), M_{Al} is the molecular weight of Al (26.98 g mol^{-1}), z is the number of electrons ($z = 3$), F is Faraday's constant ($96,487 \text{ C mol}^{-1}$), v is volume of groundwater (m^3), U is voltage (V), and x ($0.092 \text{ \$ kWh}^{-1}$) and y ($5.1 \text{ \$ kg}^{-1}$) is unit electrical energy and 3D Al ball electrode prices in December 2019, respectively.

3. Results and discussion

3.1. Statistical analysis and mathematical model

Box-Behnken experimental design was carried out to investigate the effect of anions on arsenic removal efficiency of EC process. The analysis of variance (ANOVA) was performed to get adequacy of mathematical model. Sum of square (R^2), adjusted sum of square (Adj- R^2), standard deviation (SD), coefficient of variance (CV), predicted residual error sum of squares (PRESS), Fisher's variance ratio (F-value), probability of obtaining results (p-value), and adequate precision (AP) values of responses are presented in

Table 2
The actual and coded levels of variables studied in BBD.

Independent variables	Variable levels		
	(-1)	(0)	(+1)
x_1 : $\text{C}_{\text{PO}_4\text{-P}}$ (mg L^{-1})	1	5.5	10
x_2 : $\text{C}_{\text{SiO}_3\text{-Si}}$ (mg L^{-1})	20	50	80
x_3 : C_{HCO_3} (mg L^{-1})	130	400	670
x_4 : C_F (mg L^{-1})	2	6	10
x_5 : C_B (mg L^{-1})	5	7.5	10
x_6 : t_{EC} (min)	8	15	22

Table 3
Statistical analysis of responses using ANOVA.

Responses	R ²	Adj R ²	S.D.	CV	PRESS	F-value	p-value	AP
C _f (μg L ⁻¹)	0.962	0.911	8.51	22.9	12,622	18.8	<0.0001	16.9
R _e (%)	0.962	0.911	4.26	5.23	3156	18.8	<0.0001	16.9
ENC (kWh m ⁻³)	0.987	0.969	0.035	5.57	0.21	54.7	<0.0001	30.8
ELC (kg m ⁻³)	0.944	0.868	0.002	11.9	0.0004	12.4	<0.0001	13.3
OC (\$ m ⁻³)	0.883	0.726	0.029	17.3	0.15	5.61	<0.0001	9.50
q _e (μg As mg Al ⁻¹)	0.951	0.885	0.73	6.72	95.5	14.4	<0.0001	17.7
q _e (μg As C ⁻¹)	0.951	0.885	0.068	6.72	0.83	14.4	<0.0001	17.7

Table 3.

The R² value was defined as the proportion of the variance in the dependent variable that was predictable from independent variables and R² values that were higher than 0.7 indicated a well model of fit (Burton and Kurien, 1959; Moore et al., 2013). Hence, it was concluded that the responses fitted good with R² values in the range of 0.883–0.987. Furthermore, Adj-R² values were found in the range of 0.885–0.969. In addition, F-value and p-value of 123.7 and < 0.0001 indicate that the model was statistically significant (Binnal and Babu, 2017). The F-values and p-values of responses were in the range of 5.61–54.7 and < 0.0001. CV values of Re (5.2%), ENC (5.6%), and q_e (6.7%) terms suggested that they could be considered to be reproducible due to the CV value is not greater than 10%. On the other hand, the C_f (22.9%), ELC (11.9%), and OC (17.3%) terms had a CV value greater than 10%, proving it's not reproducible. AP values used to compare the predicted values range at the specified design points to the average prediction error. In this study, AP values of all responses were greater than 4 which indicated an adequate signal. Consequently, these results showed that the relationship between independent and dependent variables was determined well with the mathematical model.

The quadratic regression mathematical model for Re (%) and OC (\$ m⁻³) in terms of independent variables was presented in Eqs. (10) and (11).

$$\begin{aligned} \text{Re}(\%) = & +39.43 - 5.33x_1 - 0.176x_2 + 0.06x_3 - 5.58x_4 + 0.47x_5 + 7.47x_6 - 5.13 \times 10^{-3}x_1x_2 - 1.8 \times 10^{-3}x_1x_3 \\ & + 0.36x_1x_4 - 0.044x_1x_5 + 0.061x_1x_6 - 1.3 \times 10^{-4}x_2x_3 + 8.16 \times 10^{-3}x_2x_4 - 8.16 \times 10^{-3}x_2x_5 - 2.41 \\ & \times 10^{-4}x_2x_6 - 6.12 \times 10^{-4}x_3x_4 + 1.23 \times 10^{-3}x_3x_5 - 1.2 \times 10^{-3}x_3x_6 + 0.106x_4x_5 + 0.067x_4x_6 + 0.012 \\ & x_5x_6 - 0.051(x_1)^2 - 6.14 \times 10^{-3}(x_2)^2 - 2.59 \times 10^{-5}(x_3)^2 + 0.019(x_4)^2 + 0.1182(x_5)^2 - 0.23(x_6)^2 \end{aligned} \quad (10)$$

$$\begin{aligned} \text{OC}(\$m^{-3}) = & +0.38 - 0.0124x_1 - 4.02 \times 10^{-3}x_2 - 3.6 \times 10^{-4}x_3 - 0.02x_4 - 0.013x_5 + 6.13 \times 10^{-3}x_6 + 2.23 \times 10^{-5}x_1x_2 \\ & + 8.85 \times 10^{-6}x_1x_3 - 9.02 \times 10^{-4}x_1x_4 + 2.14 \times 10^{-4}x_1x_5 - 1.27 \times 10^{-4}x_1x_6 + 1.73 \times 10^{-6}x_2x_3 - 9.16 \times \\ & 10^{-5}x_2x_4 + 5.31 \times 10^{-6}x_2x_5 + 3.04 \times 10^{-5}x_2x_6 - 6.33 \times 10^{-6}x_3x_4 + 1.28 \times 10^{-5}x_3x_5 + 5.66 \times 10^{-6}x_3 \\ & x_6 + 9.67 \times 10^{-4}x_4x_5 + 6.6 \times 10^{-4}x_4x_6 + 1.06 \times 10^{-5} - x_5x_6 + 1.19 \times 10^{-4}(x_1)^2 + 2.81 \times 10^{-6}(x_2)^2 \\ & + 1.02 \times 10^{-7}(x_3)^2 + 8.63 \times 10^{-4}(x_4)^2 + 1.65 \times 10^{-3}(x_5)^2 + 7.13 \times 10^{-5}(x_6)^2 \end{aligned} \quad (11)$$

The positive and negative signs in front of the independent variables indicates that there is positive and negative effect, respectively. As seen from Eq. (6), the negative sign of x₁:C_{PO4-P}, x₂:C_{SiO3-Si}, x₃:C_{HCO3}, x₄:C_F and x₅: C_B linear terms shows that the arsenic removal efficiency could be decrease with increasing phosphate, silicate, bicarbonate, fluoride, and boron concentrations. The most negative effect was observed with x₁: C_{PO4-P}. On the other hand, the positive sign of x₆: t_{EC} indicates the arsenic removal efficiency increase with an increase in the operational

time. Furthermore, the combine effect of independent variables on removal efficiency can be predicted. For instance, the increase in the concentration of phosphate and silicate in the mathematical formula could have a negative effect on the arsenic removal efficiency, as shown by the negative sign of x₁:C_{PO4-P} and x₂:C_{SiO3-Si} interaction terms, respectively. Similar results observed for the operating cost. As seen from Eq. (7), the operational cost of the EC process increases with an increasing anion concentrations. Consequently, the mathematical models in this study make an important contribution to the literature by allowing the performance of EC process to be determined without experiment.

3.2. Effect of phosphate and silicate

The main source of phosphate in groundwater resources is anthropogenic processes such as leaching of phosphate containing fertilizers from agricultural areas to groundwater sources, human, animal, and industrial wastes, and leaching from septic system (Carlyle and Hill, 2001; Funk et al., 2019). On the other hand, natural activities are the main source of silicate in groundwater resources. Phosphate and silicate in groundwater resources are the important inhibitory ions due to the tendency to form polymeric species and then sorption to aquifer rock surfaces, mineral surfaces, sediments and solution (Meng et al., 2000; Su and Puls, 2001; Holm, 2002; Holman et al., 2008). Furthermore, phosphate, silicate, bicarbonate,

and nitrate ions decreases arsenic removal efficiency due to the increasing electrical double layer thickness and negative charges on the flocs which cause low aggregation. Therefore, the effect of phosphate and silicate on arsenic removal was investigated in this study.

Competition between the phosphate and arsenic species for the adsorption surfaces on the Al(OH)₃ flocs at pH > 6.5 is one of the most important problems during the electrocoagulation process. Furthermore, phosphate species can be reacting with Al³⁺ ions and then forms AlPO₄ species at pH < 6.5 (İrdemez et al., 2006).

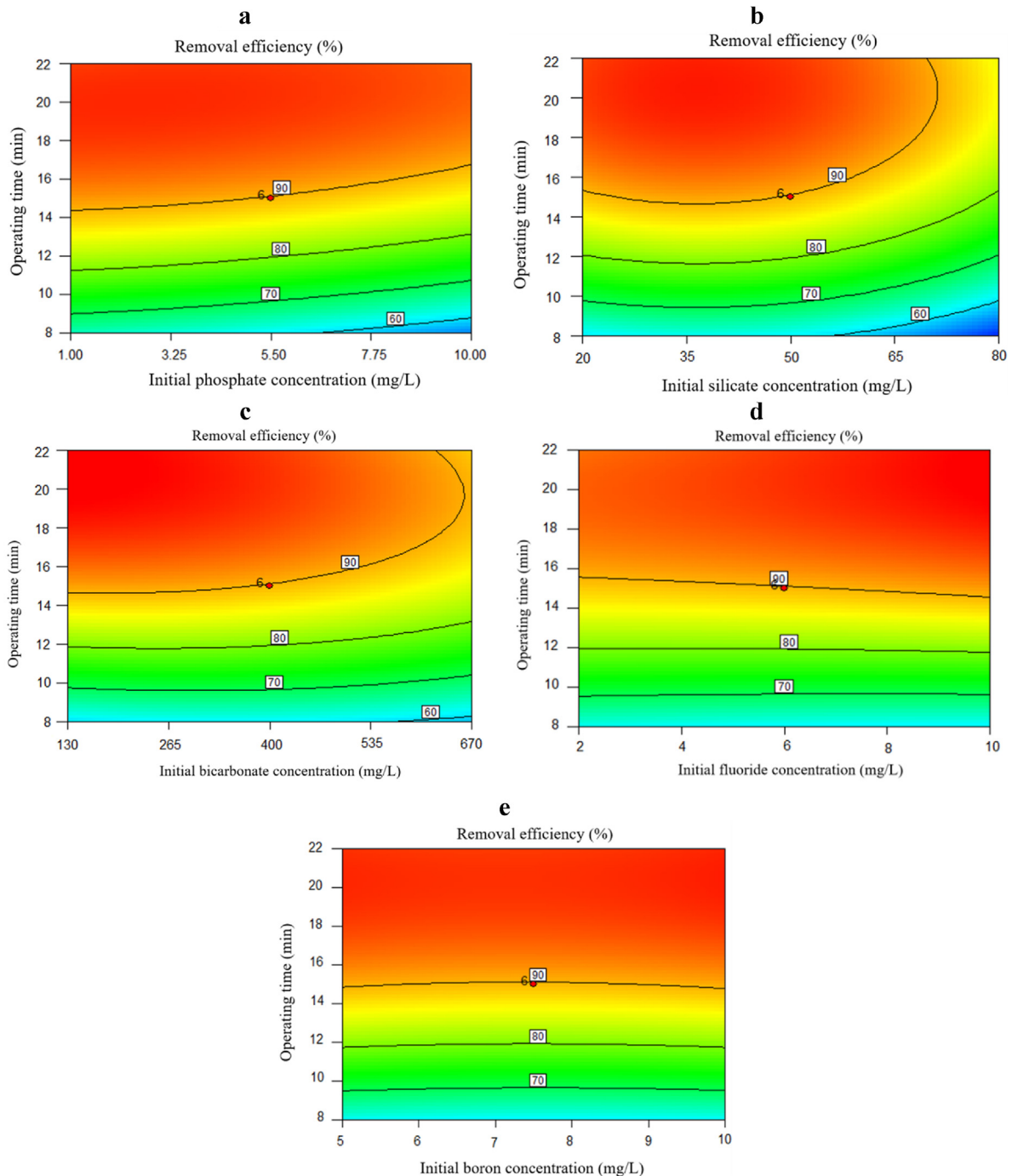
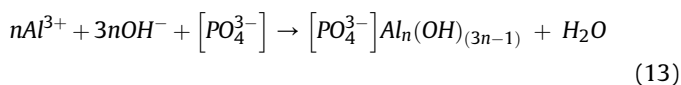
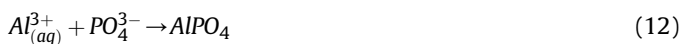


Fig. 2. Effect of phosphate (a), silicate (b), bicarbonate (c), fluoride (d), and boron (e) on arsenic removal efficiency.

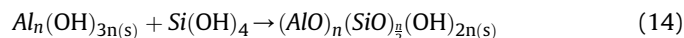
Therefore, the arsenic removal efficiencies may decrease with the formation of $AlPO_4$ species and/or $Al(OH)_3$ flocs at the present of phosphate ions in EC process. The possible reactions in the present of phosphate and Al^{3+} in aqueous solution may be expressed in Eqs. (12) and (13):



The effect of phosphate and silicate concentrations on arsenic removal efficiencies depending on EC operating time are presented in Fig. 2a and b. As we expected, the results showed that the removal efficiencies decreased with increasing phosphate concentration. On the other hand, the arsenic removal efficiencies increased with increasing EC operating time at all phosphate concentrations. Removal efficiencies were found to be almost 70.0% for phosphate concentration of 1, 3.25, and 5.5 $mg\ L^{-1}$ at EC operating time of 8 min, while the removal efficiencies were almost 60.0% for phosphate concentration of 7.75 and 10 $mg\ L^{-1}$. Similarly, at EC operating time of 12 min, the arsenic removal efficiency decreased from 80.0% to 70.0% by increasing the phosphate concentration

from 5.5 to 10 mg L⁻¹. This is because arsenic ion has similar pK_a values (pK_{a1} = 2.19; pK_{a2} = 6.94; pK_{a3} = 11.5) and chemical structure as that of orthophosphoric acid (pK_{a1} = 2.1; pK_{a2} = 7.2; pK_{a3} = 12.3), which clarifies the low removal efficiency of arsenic at the present of phosphate ions in aqueous solution (Vasudevan et al., 2009). Phosphate and arsenic exists as H₂PO₄⁻ and HPO₄²⁻ and H₂AsO₄⁻ and HAsO₄²⁻ at pH 6.5–8.5, respectively. Mono and divalent phosphates can have mainly precipitation as AlPO_{4(s)} and ligand-exchange reactions with the Al-hydroxides formed and compete for adsorption sites with the arsenates. Consequently, the arsenic removal efficiency decreases with the occurrence of phosphate in aqueous solution due to the competition between phosphate and arsenic for possible adsorption surfaces of Al(OH)₃ particles (Lakshmanan et al., 2010). As expected, arsenic removal efficiencies were found to be 95.0% (C_{f,As}: 9.92 μg L⁻¹) and 87.6% (C_{f,As}: 24.89 μg L⁻¹) at phosphate concentration of 5.5 and 10 mg L⁻¹, respectively, when the other anions and operating time were constant (runs of 6 and 21 in Table S1). Furthermore, removal of other ions were found to be 79.5 (C_{f,B}: 1.536 mg L⁻¹) and 78.1% (C_{f,B}: 1.643 mg L⁻¹) for boron, 93.3 (C_{f,F}: 0.40 mg L⁻¹) and 93.5% (C_{f,F}: 0.39 mg L⁻¹) for fluoride, 2.75 (C_{f,HCO3}: 389 mg L⁻¹) and 15% (C_{f,HCO3}: 340 mg L⁻¹), 86.5 (C_{f,SiO3-Si}: 6.742 mg L⁻¹) and 66.3% (C_{f,SiO3-Si}: 16.83 mg L⁻¹), 96.9 (C_{f,PO4-P}: 0.166 mg L⁻¹) and 80.4% (C_{f,PO4-P}: 1.960 mg L⁻¹) at 5.5 and 10 mg L⁻¹ phosphate concentration, respectively. Similar results observed for the experimental runs of 21 and 44. The pH values of treated water for the runs 6 and 21 were measured as 7.75 and 8.13, respectively (Table S2). The results showed that high amount of silicate removal was observed at low phosphate concentration and 1.2 times silicate removal was observed at maximum silicate concentration. The arsenic removal efficiency probably decrease due to low removal efficiencies of other ions at 5.5–10 mg L⁻¹ phosphate concentration. The results also showed that the residual Al concentration in treated water was satisfied the WHO standard (0.1–0.2 mg L⁻¹) (WHO, 2011). Arsenic adsorption capacity per mg Al and arsenic removal per charge loading were calculated as 12.08 μg As (mg Al)⁻¹ (or 1.13 μg As (C)⁻¹) and 1.408 μg As (LC)⁻¹ for 5.5 mg L⁻¹ phosphate and 11.12 μg As (mg Al)⁻¹ (or 1.04 μg As (C)⁻¹) and 1.297 μg As (LC)⁻¹ for 10 mg L⁻¹ phosphate concentration, respectively. EC process using Al electrodes had arsenate (As(V)) adsorption capacity of 46.6 μg As (mg Al)⁻¹ at pH 6.03 (Goren et al., 2018). Kobya et al. (2011) studied on arsenic removal from drinking water using EC process with Al and Fe electrodes and they found that the arsenic adsorption capacities were 17.5 μg As (mg Al)⁻¹ and 5.2 μg As (mg Fe)⁻¹ at initial arsenic concentration of 75 μg L⁻¹ and applied current of 2.5 Am². In a separate study, the arsenic adsorption capacities were found in the range of 37.89 to 0.62 μg As (mg Al)⁻¹ at applied current of 0.01–0.1 A (Omwene et al., 2019).

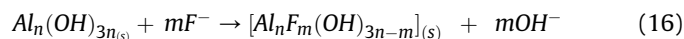
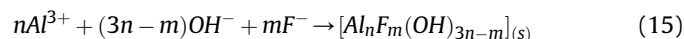
On the other hand, the results also revealed that the arsenic removal efficiency significantly affected by silicate concentration. As clearly seen in Fig. 2b, the arsenic removal efficiency decreased with increasing silicate concentration. This trend shows that the highest silica concentration inhibits the substitution reaction between the arsenic and the hydroxyl group from aluminum hydroxide flocs. This shows that there is a competition between arsenic and silica for active sites in aluminum hydroxide flocs; similar results observed by López et al. (2020). The formation of fresh aluminium hydroxides and oxides in the EC process in the presence of silica cause to formation of AlOOH_(s), Al(OH)_{3(s)} and Al₂O_{3(s)} precipitates and silicates adsorption onto these precipitates (Sheikholeslami et al., 2001). The insoluble Al-hydroxides react with the suspended and/or colloidal solids and precipitate. Later, the Al-hydroxides react with silicates as Eq. (14) (Deng and Wang, 2008):



The arsenic removal efficiency decreased from 95.7% at 20 mg L⁻¹ silicate concentration to 77.2% at 80 mg L⁻¹ silicate concentration (runs of 10 and 39 in Table S1). Similarly, the arsenic removal efficiencies were found to be 90.5% and 81.6% at silicate concentration of 20 and 80 mg L⁻¹, respectively (runs of 37 and 40 in Table S1). Furthermore, the combined effect of silicate and phosphate on arsenic removal showed that the removal efficiency of arsenic varied from 90.5% to 95.7% at low silicate concentration of 20 mg L⁻¹ and 1–10 mg L⁻¹ phosphate concentrations, and the arsenic removal decreased as concentration of silicate and phosphate increased together (runs of 37 and 39 in Table S1). Similar trend observed at experimental runs 10 and 40, the removal efficiency of arsenic decreased from 81.6% to 77.2% at high silicate concentration of 80 mg L⁻¹ and phosphate concentration of 1 and 10 mg L⁻¹ phosphate concentration, respectively and effluent arsenic concentration was found to be above 10 μg L⁻¹. These results showed that during the EC operating time, the production of polymeric and monomeric aluminum species wasn't enough to remove arsenic efficiently. The silicate species reacts with aluminum hydroxides to produce aluminum-silicates and reduced potential adsorption sites on aluminum hydroxide species for arsenic (Guzman et al., 2016; Sandoval et al., 2019). Rosales et al. (2018) studied on arsenic, fluoride, and silicate removal using electrocoagulation and found that the aluminum flocs were predominantly composed of aluminum silicates. Consequently, the increase in silicate and phosphate concentrations decreased the arsenic removal efficiency, but the higher arsenic removal could be achieved with lowering phosphate and silicate concentrations.

3.3. Effect of bicarbonate and fluoride

The fluoride, bicarbonate, and arsenic are the three main pollutants found naturally in groundwater sources. Fluoride ions compete with arsenic ions for the possible binding sites of aluminum hydroxides when fluoride and arsenic ions simultaneously present in groundwater. The possible reaction between fluoride and Al³⁺ or/and aluminum hydroxide may be expressed in Eqs. (15) and (16) (Hu et al., 2003; Mohammad and Muttucumar, 2011; Sandoval et al., 2019):



The effect of fluoride concentrations on arsenic removal efficiencies depending on EC operating time are presented in Fig. 2d. For instance, the removal efficiency decreased from almost 80.0% to 70.0% at fluoride concentration of 2 and 10 mg L⁻¹, respectively. Results showed that the arsenic removal efficiencies slightly decreased with the increasing fluoride concentration, which compete with arsenic for possible adsorption sites of aluminum hydroxides; similar results observed by López-Guzmán et al. (2019) and Silva et al. (2018). Furthermore, the combined effect of fluoride and other anions on arsenic removal efficiency were evaluated and results showed that the arsenic removal efficiency decreased with both boron and fluoride concentration increased from 7.5 to 10 mg L⁻¹ and 6–10 mg L⁻¹ 95.0%–89.8% at experimental runs 6 and 13, 96.1%–88.9% at experimental runs 36 and 44), respectively. Similarly, the arsenic removal efficiency decreased from 87.56 (C_{f,As}: 24.89 μg L⁻¹) to 83.51% (C_{f,As}: 32.98 μg L⁻¹) with increase in both silicate (50–80 mg L⁻¹) and fluoride (6–10 mg L⁻¹) concentrations (Table SM1, experimental runs 21 and 25). Removal

efficiency of arsenic decreased due to the increase in silicate concentration despite the decrease in fluoride concentrations in experimental runs 13 and 26 (89.8% ($C_{f,As}$: 20.44 $\mu\text{g L}^{-1}$) to 82.2% ($C_{f,As}$: 35.55 $\mu\text{g L}^{-1}$). As seen in experimental runs 10–31 and 10–21, the arsenic removal efficiency increased with the decreasing silicate concentration even if fluoride concentration increased. These results showed that silicate ions have significant effect on arsenic removal efficiency than fluoride ions. Namely, the removal of arsenic and fluoride most probably related to silicate removal since silicate interact with aluminum hydroxides to form aluminosilicate complexes (Guzman et al., 2016). Similar results observed by Thakur et al. (2017), they reported that arsenic removal efficiency decreased from 99.1, 98.7, 95.4 and 94.2% with the increase in fluoride concentration from 5, 10, 15 and 20 mg L^{-1} , respectively.

Considering the combined effect of all anions, at constant initial bicarbonate concentration, the increase in concentrations of phosphate, silicate, fluoride, and boron were significantly decreased arsenic removal efficiency 92.3% ($C_{f,As}$: 15.5 $\mu\text{g L}^{-1}$) to 83.5% ($C_{f,As}$: 32.98 $\mu\text{g L}^{-1}$) at experimental runs 18 and 25). Similar trend observed at experimental runs 13 and 27, the arsenic removal efficiency were increased from 89.8% ($C_{f,As}$: 20.44 $\mu\text{g L}^{-1}$) to 94.0% ($C_{f,As}$: 11.97 $\mu\text{g L}^{-1}$) with the increasing silicate, bicarbonate, fluoride, and boron concentrations. This trend shows that the high anion concentrations inhibited the substitution reaction between the arsenic and aluminum hydroxide flocs, but the low anion concentrations favors the arsenic removal. These results clearly shows that there is a competition between silicate, bicarbonate, fluoride, boron, and arsenic for possible adsorption sites of flocs. Moreover, removal of other ions were found to be 97.0% ($C_{f,PO_4^{3-}}$: 0.166 mg L^{-1}) for phosphate, 93.3% ($C_{f,F}$: 0.40 mg L^{-1}) for fluoride, 86.5% (C_{f,SiO_3-Si} : 6.742 mg L^{-1}) for silicate, 79.5% ($C_{f,B}$: 1.536 mg L^{-1}) for boron, and 2.75% (C_{f,HCO_3} : 389 mg L^{-1}) for bicarbonate at experimental run 6 in Table S1.

Fig. 2c shows the effect of bicarbonate concentration on arsenic removal efficiency as a function of operating time. The arsenic removal efficiencies were slightly decreased with increasing bicarbonate concentrations at operating time of 15 min. Removal efficiency decreased from 88.8% ($C_{f,As}$: 22.48 $\mu\text{g L}^{-1}$) to 87.0% ($C_{f,As}$: 25.96 $\mu\text{g L}^{-1}$) at 5.5 mg L^{-1} of phosphate concentration as bicarbonate concentration were increased from 130 to 670 mg L^{-1} in experimental runs 2 and 17. However, the significant decreased in arsenic removal efficiency were observed when both bicarbonate and silicate concentrations increased. For instance, removal efficiency decreased from 95.0% ($C_{f,As}$: 9.92 $\mu\text{g L}^{-1}$) to 87.0% ($C_{f,As}$: 25.96 $\mu\text{g L}^{-1}$) with the increase in both silicate (50–80 mg L^{-1}) and bicarbonate (400–670 mg L^{-1}) concentrations (experimental runs 6 and 17). This reduction in arsenic removal was caused by silicate ions. Namely, the arsenic removal efficiency increased from 88.8% ($C_{f,As}$: 22.48 $\mu\text{g L}^{-1}$) to 95.0% ($C_{f,As}$: 9.92 $\mu\text{g L}^{-1}$) with the decreasing silicate concentration, while bicarbonate concentration increased from 130 to 400 mg L^{-1} (experimental runs 2 and 6). The similar trend by combined effect of bicarbonate (130–400 mg L^{-1}) and boron (7.5–10 mg L^{-1}) on the arsenic removal efficiency was observed and arsenic removal efficiencies were found in the range of 82.2–93.0% (experimental runs 17 and 29, 2 and 26). Consequently, our results showed that bicarbonate ions had a slight effect on the arsenic removal efficiency unlike silicate, phosphate, and boron ions.

3.4. Effect of boron

Boron contamination in groundwater sources mainly occurs due to leaching from rocks. Numerous cases of natural arsenic and boron contamination have been reported in groundwater sources around mining deposits in Turkey. Kütahya-Simav (0.21–3.6 mgB L^{-1} and 0.5–562 $\mu\text{gAs L}^{-1}$) and Kütahya-Emet-Hisarçik (0.2–4.4 mgB L^{-1} and 70–7754 $\mu\text{gAs L}^{-1}$) are affected by boron and arsenic dissolved from minerals like realgar and orpiment (Colak et al., 2003). Therefore, the effect of boron content on arsenic removal efficiency should be taken into account while treating arsenic containing groundwater by EC reactor. In this study, the effects of boron ions on arsenic removal were evaluated (Fig. 2e).

Removal efficiency decreased from 93.0% ($C_{f,As}$: 14.02 $\mu\text{g L}^{-1}$) to 82.2% ($C_{f,As}$: 35.55 $\mu\text{g L}^{-1}$) (experimental runs 26 and 29) and 96.1% ($C_{f,As}$: 7.74 $\mu\text{g L}^{-1}$) to 64.9% ($C_{f,As}$: 64.13 $\mu\text{g L}^{-1}$) (experimental runs 36 and 53) when initial boron concentration increased from 5 to 10 mg L^{-1} . As expected, high boron concentration was negatively affected arsenic removal efficiency as the competition between boron and arsenic for possible adsorption surfaces of aluminum hydroxides.

The phenomenon of decrease in arsenic removal with increase in boron concentration can be explained thus; at high boron concentration, the Al^{3+} concentration generated in solution is not sufficient and only form a low amount of aluminum hydroxide flocs which could not efficiently adsorb arsenic; at low boron concentration, aluminum hydroxide flocs in solution could be sufficient to efficiently adsorb arsenic and boron. The adsorbed total arsenic was found to be 192.0 and 135.8 μg at initial boron concentration of 5 and 10 mg L^{-1} , respectively, at 12.58 mg of Al^{3+} ions released in solution (experimental runs 36 and 53). Furthermore, the arsenic adsorption capacity per mg Al was found to be 8.63 $\mu\text{gAs (mgAl)}^{-1}$ (or 1.14 $\mu\text{gAs C}^{-1}$) and 12.21 $\mu\text{gAs (mgAl)}^{-1}$ (or 0.81 $\mu\text{gAs C}^{-1}$) at initial boron concentration of 10 and 5 mg L^{-1} , respectively. Consequently, under the same operating conditions, low boron concentrations can accommodate more adsorbed arsenic on aluminum hydroxide flocs due to the sufficiency of flocs in solution. In other words, when treating the boron and arsenic simultaneously, the arsenic removal efficiency of EC is diminished due to the change in net available aluminum hydroxide flocs used. Furthermore, boron concentration can be effective on amount of sludge formation. The sludge formation significantly increased from 0.0738 to 0.119 kg m^{-3} with the increase in boron concentration from 5 to 10 mg L^{-1} . On the other hand, the energy consumption and operating cost of EC decreased with the increasing boron concentration owing to increasing solution conductivity. In other words, applied potential and consumption of energy decreased with increase in ionized species in solution. The energy consumption and operating cost were calculated as 0.6042 kWh m^{-3} and 0.175 $\text{\$ m}^{-3}$ at 5 mg L^{-1} of boron concentration and 0.5372 kWh m^{-3} and 0.129 $\text{\$ m}^{-3}$ at 10 mg L^{-1} .

The combined effect of boron and bicarbonate on arsenic removal efficiency was found to be 94.0% ($C_{f,As}$: 11.97 $\mu\text{g L}^{-1}$) at 10 mg L^{-1} of boron and 400 mg L^{-1} of bicarbonate and 86.4% ($C_{f,As}$: 27.16 $\mu\text{g L}^{-1}$) at 7.5 mg L^{-1} of boron and 130 mg L^{-1} of bicarbonate (experimental runs 11 and 27). Similarly, the combined effect of boron, phosphate, and fluoride on arsenic removal efficiency was found as 83.5% ($C_{f,As}$: 32.98 $\mu\text{g L}^{-1}$) at 7.5 mg L^{-1} of boron, 10 mg L^{-1} of phosphate, and 10 mg L^{-1} of fluoride concentrations and 93.0%

($C_{f,As}$: 14.02 $\mu\text{g L}^{-1}$) at 5 mg L^{-1} of boron, 5.5 mg L^{-1} of phosphate, and 6 mg L^{-1} of fluoride concentrations (experimental runs 25 and 29). Results showed that simultaneous increase in anion concentrations decreased arsenic removal efficiency. Furthermore, the amount of adsorbed arsenic decreased from 185.80 to 166.86 μg with the increase in boron, phosphate, and fluoride concentrations from 7.5 to 10 mg L^{-1} , 5.5–10 mg L^{-1} , and 6–10 mg L^{-1} , respectively. Arsenic adsorption capacity decreased from 811.82 $\mu\text{g As (mg Al)}^{-1}$ (or 1.10 $\mu\text{g As C}^{-1}$) and 10.61 $\mu\text{g As (mg Al)}^{-1}$ (or 0.99 $\mu\text{g As C}^{-1}$) with increasing anion concentrations. As expected, amount of sludge formation and operating cost also decreased from 0.0786 to 0.0501 kg m^{-3} and 0.202 to 0.149 $\text{\$ m}^{-3}$ with decrease in anion concentrations.

3.5. Effect of operating time

In EC process operating time is one of the most important parameter, which directly effects arsenic removal. Furthermore, consumption of energy and electrode, sludge formation, and operating cost are mainly depending on operating time. Results showed that the removal of anions and arsenic increased with increasing operating time. At similar operating conditions, the arsenic removals were found to be 57.3% ($C_{f,As}$: 85.35 $\mu\text{g L}^{-1}$), 83.4% ($C_{f,As}$: 33.16 $\mu\text{g L}^{-1}$), and 94.1% ($C_{f,As}$: 11.74 $\mu\text{g L}^{-1}$) at operating time of 8, 15, and 22 min, respectively (experimental runs 1, 5, and 45). Furthermore, the silicate and phosphate removal efficiencies were found to be 62.2% (C_{f,SiO_3-Si} : 18.91 mg L^{-1}) and 60.7% (C_{f,PO_4-P} : 2.16 mg L^{-1}), 77.0% (C_{f,SiO_3-Si} : 11.51 mg L^{-1}) and 77.2% (C_{f,PO_4-P} : 1.254 mg L^{-1}), and 85.7% (C_{f,SiO_3-Si} : 7.157 mg L^{-1}) and 91.4% (C_{f,PO_4-P} : 0.472 mg L^{-1}) at operating time of 8, 15, and 22 min, respectively. The results showed that high amount of dissolved Al^{3+} concentration was achieved at high operating time and 2.7 times more Al^{3+} ion was observed in solution. The reason for increasing arsenic removal efficiency at high operating time was related to high Al^{3+} release in solution. For instance, the Al^{3+} concentrations were calculated as 18.45 and 6.71 mg at operating time of 8 and 22 min, respectively (experimental runs 1 and 45). As expected, the adsorbed total arsenic amount also increased from 113.9 to 188.0 μg with the increasing operating time and amount of dissolved Al^{3+} in solution. On the other hand, increased operating time had negative effect on energy and electrode consumption, sludge formation, and operating cost of EC reactor. The sludge formation and electrode consumption was increased from 0.049 to 0.128 kg m^{-3} and from 0.0084 to 0.0231 kg m^{-3} at operating time of 8 and 22 min, respectively (experimental runs 1 and 45). Furthermore, the energy consumption and operating cost was found to be 0.2923 kWh m^{-3} and 0.063 $\text{\$ m}^{-3}$ and 0.8601 kWh m^{-3} and 0.309 $\text{\$ m}^{-3}$ at operating time of 8 and 22 min, respectively.

3.6. Optimization of EC performance using model

The optimization of the EC process is one of the most important objective of this study. In the optimization process, two desired target qualified. In the first target, the BBD was carried out to optimize the levels of operational variables within the specified ranges that result in maximization of arsenic removal and minimization of operational cost. The optimum values of independent operating parameters were as follows: C_{PO_4-P} : 1.0 mg L^{-1} , C_{SiO_3-Si} : 26.0 mg L^{-1} , C_{HCO_3} : 651.5 mg L^{-1} , C_F : 2.0 mg L^{-1} , C_B : 9.9 mg L^{-1} , pH_i : 5.8, and t_{EC} : 10.5 min. The experimental values of the $C_{f,As}$, R_e , ENC, ELC, OC, and q_e were found to be 2.819 $\mu\text{g L}^{-1}$, 98.6%, 0.411 kWh m^{-3} , 0.0124 kg m^{-3} , 0.098 $\text{\$ m}^{-3}$, and 17.65 $\mu\text{g As/mg Al}$, respectively. In addition, the second desired goal for the effluent arsenic concentration was chosen to a target value of 9.9 $\mu\text{g L}^{-1}$ and independent variables were set to in ranges. The recommended

independent operating parameters were found to be C_{PO_4-P} : 5.9 mg L^{-1} , C_{SiO_3-Si} : 45.0 mg L^{-1} , C_{HCO_3} : 616 mg L^{-1} , C_F : 9.5 mg L^{-1} , C_B : 7.5 mg L^{-1} , pH_i : 6.5, and t_{EC} : 20 min. Under these operating conditions, the R_e , ENC, ELC, OC, and q_e were found to be 95.1%, 0.790 kWh m^{-3} , 0.0225 kg m^{-3} , 0.23 $\text{\$ m}^{-3}$, and 8.93 $\mu\text{g As (mg Al)}^{-1}$ respectively.

3.7. Characterization of sludge sample

To determine the characteristics of the sludge samples after the electrocoagulation process, SEM-EDX, and FTIR analyses were conducted. The SEM image, EDX spectrum, and elemental mapping of sludge sample are shown in Fig. 3. From SEM analyses, it was observed that the Al(OH)_3 products appeared to be aggregated particles. Furthermore, EDX was used to analyze the elemental composition of sludge. As seen in Fig. 3b, the elemental analysis showed elements in the following order as per mass %: $\text{O} > \text{Al} > \text{P} > \text{As} > \text{Mg} > \text{Si} > \text{Ca} > \text{Fe}$ in the sludge sample. High contents of oxygen (33.6%), aluminum (24.2%), arsenic (12.9%), and phosphate (9.8%) in the sludge provides direct evidence that the presence of expected products such as aluminum hydroxide, aluminum phosphate, and aluminum hydroxide-arsenic complexes. In addition, results indicate that the aluminum ball anodes were oxidized to form metal oxide species such as Al(OH)_3 , Al_2O_3 , and AlO(OH) . Consequently, elemental analysis of sludge sample mainly revealed presence of other anions and cations as well as arsenic, which were the pollutants to be removed from the real groundwater.

Finally, the FTIR spectra of the Al ball electrode sludge sample generated after arsenic treatment under optimum operating conditions are shown in Fig. 3d. FTIR spectra exhibited peak at 3311.8 cm^{-1} , indicating OH stretching vibration in the Al(OH)_3 structures (Vasudevan et al., 2010). The peak that is observed at 1832.6 cm^{-1} corresponds to O–H bond belonging to the hydrogen phosphate group. The peaks at 1623.8 and 1383.0 cm^{-1} indicate bent vibration of H–O–H and Al–H stretching, respectively. Furthermore, the peaks observed around 1189.2 and 1136.8 cm^{-1} is possibly due to symmetric stretching mode of phosphate in the crystalline structure of AlPO_4 (Inan and Alaydin, 2014). The peaks at 858.1 and 702.6 is also possibly suggests the presence of metal oxides. From these results, it was concluded that aluminum forms complexes with pollutants and precipitated at the bottom of the reactor.

4. Conclusions

The results of present study revealed that the aerated EC process with 3D Al electrodes is able to remove the arsenic from groundwater in the presence of anions. The arsenic removal efficiency increased with increasing operating time. On the other hand, there was a negative effect on the arsenic removal efficiency as especially phosphate, silicate, boron, and bicarbonate concentrations decreased the arsenic removal efficiency. The competitive effects of silicate and phosphate on arsenic removal efficiency ($C_{f,As} > 10 \mu\text{g L}^{-1}$) was observed when silicate and phosphate concentrations were higher than 50 and 7.5 mg L^{-1} , respectively. The effect of fluoride on the arsenic removal efficiency did not have a significant effect. Quadratic regression model equations also indicated that the anions have significant influence on arsenic removal. Furthermore, the results showed that our treatment process is able to remove simultaneously arsenic and other anions from groundwater. According to BBD, the optimal operating conditions were 1.0 mg L^{-1} , 26.0 mg L^{-1} , 651.5 mg L^{-1} , 2.0 mg L^{-1} , 9.9 mg L^{-1} , and 10.5 min for phosphate, silicate, bicarbonate, fluoride, boron, and operating time, respectively. Under these

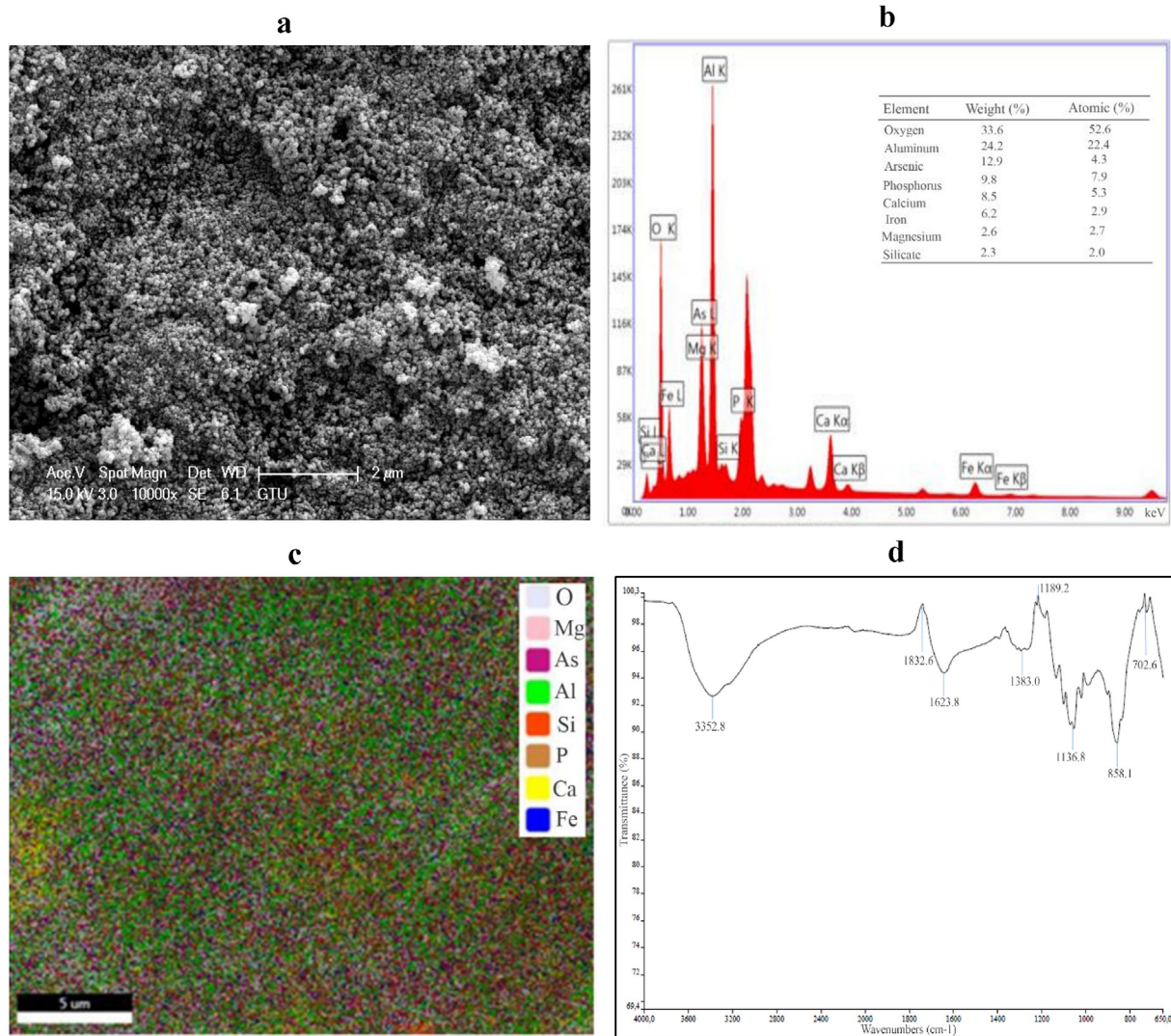


Fig. 3. SEM image (a), EDAX spectrum (b), elemental mapping (c), and FTIR spectrum (d) of sludge sample.

optimal conditions, the experimental values of $C_{f,As}$, R_e , ENC, ELC, OC, and q_e were found to be $2.819 \mu\text{g L}^{-1}$, 98.6%, 0.411 kWh m^{-3} , 0.0124 kg m^{-3} , $0.098 \text{ \$ m}^{-3}$, and $17.65 \mu\text{g As (mg Al)}^{-1}$, respectively. In conclusion, this study offers significant benefits as one of the limited number of studies investigated the combine effect of anions on arsenic removal efficiency using EC process.

Credit author statement

Ayşegül Yagmur Goren: Data curation, Writing - original draft, Reviewing and Editing.; Mehmet Koby: Conceptualization, Methodology, Supervision, Validation, Writing- and Reviewing.

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.

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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.2020.128253>.

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